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## IV.A.1q Li-Mg-N System Hydrogen Storage Materials and Metal Hydride System Engineering Analysis

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### Objectives

- Verify reversibility conditions of 4 wt%  $\text{TiCl}_3$  doped LiMgN material.
- Quantify the sorption kinetics for the LiMgN system as a function of composition, temperature and pressure to aid in system design.
- Optimize the sorption kinetics in the LiMgN through modification of the Li:Mg ratio and transition metal catalyst content.
- Minimize  $\text{NH}_3$  byproduct production through understanding of its temperature dependence.
- Lead the Metal Hydride Center of Excellence Task E, Engineering, Analysis, Design and Test.
- Quantify the system mass penalty associated with various advanced heat exchange methodologies.
- Quantify the hydrogen fueling station requirements necessary for metal hydrogen storage systems.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (F) Codes and Standards
- (H) Balance of Plant Components

- (J) Thermal Management

### Technical Targets

This project is both conducting fundamental studies of the sorption kinetics in the LiMgN system as well as engineering studies of the in situ rechargeable hydrogen storage systems. Insights gained from these studies will be applied toward the design of storage systems that meet the following DOE 2010 and 2015 hydrogen storage targets:

- System Gravimetric Capacity and Volumetric Density
- Charging/Discharging Rates
- Fuel Purity
- System Fill Time
- Minimum Hydrogen Delivery Rate

### Accomplishments

- Corroborated recharging rates for LiMgN system (University of Utah).
- Measured hydrogen charge and discharge kinetic rates for LiMgN + 4 wt%  $\text{TiCl}_3$ .
- Conducted cycling studies for the initial charge/discharge behavior.
- Performed X-ray diffraction (XRD) analyses to help identify charge and discharge compositions and possible formation and decomposition mechanisms.
- Performed analysis on a fuel station design based on an onboard hydride-based storage system to determine the hydrogen cooling load and estimated space and other siting requirements.

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## Task 1: Li-Mg-N System Hydrogen Storage Materials

### Introduction

In the effort to identify or synthesize a reversible metal hydride material capable of meeting the 2010 and 2015 DOE FreedomCar technical targets, researchers are investigating various metal hydrides/catalyst combinations. One general chemical group which has been considered as a practical material on which to base a hydrogen storage system is the Li-Mg-N-H system, which has been initially explored [1-6]. Under certain

conditions, it has been found that the predominant hydrogen absorbing material is LiMgN, which has been reported to be reversible under fairly moderate conditions (160°C–220°C for dehydriding, 160°C and 2,000 psi for rehydriding) [1]. Furthermore, the material has been reported to have a hydrogen storage capacity of 8.0–8.1 wt% [6] where the starting materials are LiNH<sub>2</sub> and MgH<sub>2</sub> combined in a 1:1 molar ratio with a small amount of TiCl<sub>3</sub> dopant. This study of the LiMgN hydrogen storage material primarily used autoclave-type high pressure charging apparatus and transient thermogravimetric analysis measurements to confirm hydrogen storage capacities. The work reported here was designed to compliment the work of Lu *et al.* [6], by thoroughly measuring the isothermal kinetic hydrogen charge and discharge rates and further optimizing the kinetics through compositional adjustments.

## Approach

The previously identified LiMgN material was studied by ball milling the precursor LiNH<sub>2</sub> and MgH<sub>2</sub> materials with the TiCl<sub>3</sub> catalyst to ensure a well-mixed and controlled initial state in terms of particle size. The present studies are intended to provide a detailed understanding of the isothermal kinetics of charging and discharging of the material, in addition to tabulations of the weight percent of hydrogen stored under specified conditions. The basic parameters that are explored in the current study are charge and discharge temperature, charge and discharge pressure, and the catalyst loading used to activate the material. The charge and discharge are proposed to occur via the following reactions.

First discharge from precursor materials:



Charging of the LiMgN material:



Subsequent discharge of the Mg(NH<sub>2</sub>)<sub>2</sub>, MgH<sub>2</sub>, and LiH material is proposed to cycle back and forth to LiMgN via Reaction 2.

A Seivert's apparatus was used to measure the isothermal kinetic rates of hydrogen charge and discharge for the identified samples. An experimental matrix was devised for the first set of isothermal kinetic measurements. The previous work by Lu [6] on the LiMgN system found that the system could be discharged in the range of 160°C–220°C, and recharged at pressures in excess of 135 bar (~2,000 psi). Therefore, experiments were planned to determine the isothermal discharge rates at temperatures of 200°C–280°C, and the isothermal recharge kinetic rates at temperatures between 140°C–170°C under 150 bar. In some cases, lower charging pressures were used due to limitations on the available H<sub>2</sub> pressure with the newly-installed equipment. Additionally, two cycling profiles were

designed to probe the materials early-stage charge/discharge behavior. Material for this study was Frisch milled with a ball mass to material mass ratio of 35:1, following the work of Lu [6].

## Results

Figure 1 shows the discharge profiles of the as-milled precursor material as a function of temperature. It can be seen from the calculated weight percent profiles that the majority of hydrogen stored in the material is discharged in the first 30 minutes, although the material is clearly still undergoing a reduced rate of hydrogen discharge after the 2 hour period selected for presentation. The general profiles of the discharge curves are consistent with those expected from kinetic and thermodynamic considerations; namely that a greater amount of H<sub>2</sub> was discharged at higher temperature, with an increase in the rate of hydrogen release with increasing temperature.

The results from isothermal charging measurements are shown below in Figure 2. It can be seen in Figure 2 that the temperature of recharging only has a small effect on the overall weight percent of hydrogen charged to the sample, and a moderate effect on the rate of charging between the temperatures of 140°C and 160°C. At 170°C, it can be seen that a shift has occurred in the thermodynamics of hydrogen charging, and a lower equilibrium charging position has been achieved.

In addition to the kinetic measurements of the hydrogen which is charged and discharged, samples were collected and sent for XRD using analytical facilities at Savannah River National Laboratory. The results of this preliminary analysis indicate that two Li-Mg-N products were formed during the experiments that were performed, (Li<sub>0.51</sub>Mg<sub>2.49</sub>)N<sub>1.83</sub> and Mg<sub>3</sub>N<sub>2</sub>. It is very difficult to make a definitive conclusion concerning the phase behavior of the potential phases based on

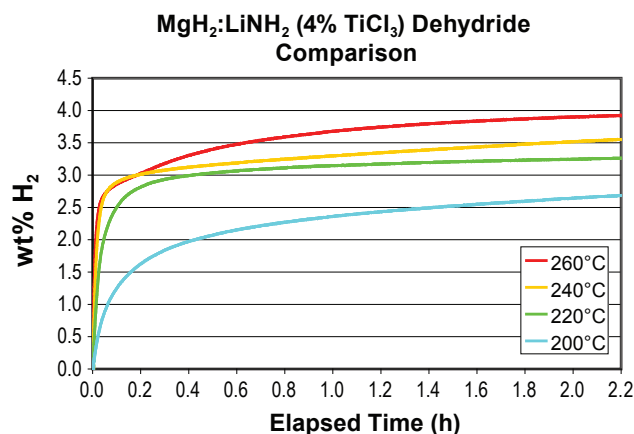
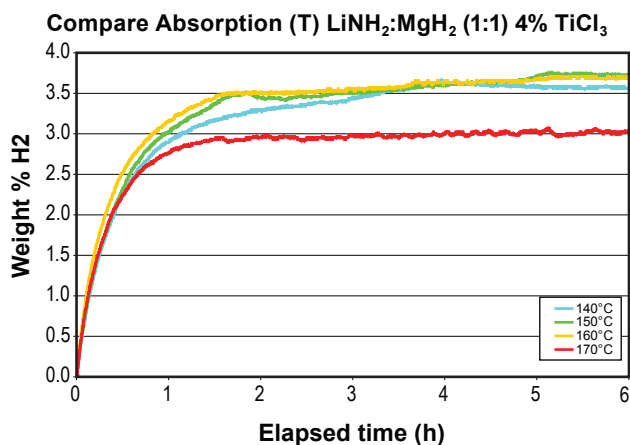


FIGURE 1. Discharge profiles of the as-milled precursor materials LiNH<sub>2</sub> and MgH<sub>2</sub> + 4 wt% TiCl<sub>3</sub> as a function of temperature over 2 hours.



**FIGURE 2.** Charge profiles of material discharged from the as-milled precursor materials LiNH<sub>2</sub> and MgH<sub>2</sub> + 4 wt% TiCl<sub>3</sub> at 220°C as a function of temperature over 2 hours.

temperature and pressure of experimental conditions, as the XRD spectra of the  $(\text{Li}_{0.51}\text{Mg}_{2.49})\text{N}_{1.83}$  and  $\text{Mg}_3\text{N}_2$  phases are very similar, presumably because of structural similarities. However, some general conclusions can be drawn from the current results. As expected, the higher temperatures result in a larger relative concentration of the (Mg/Li)N phase as a result of more complete discharge, while the lower temperature discharges result in predominant presence of the LiNH<sub>2</sub> and MgH<sub>2</sub> materials. Comparing materials that were recharged from the discharged material at 280°C, it can be seen that more of the material was recharged by the relative decrease in the (Mg/Li)N phase, although there is no evidence of cycling back to Mg(NH<sub>2</sub>)<sub>2</sub>. There is some evidence of very small amounts of LiH in some of the charged materials. In no samples was the presence of LiMgN detected. Current analysis is consistent with the concept that there may be multiple reaction pathways possible with these material phases. Identification of the reaction intermediates for different cycling conditions is an active area of research.

## Conclusions and Future Directions

### Conclusions

- The Li-Mg-N material is chargeable through a limited number of initial cycles.
- A maximum of 3.6 wt% hydrogen absorption was observed at 120-160°C under 150 bar.
- A maximum of 4.0 wt% hydrogen desorption was observed at 260°C at 1 bar back pressure.
- A pre-discharge pressure of 150 bar is insufficient to prevent partial discharge of sample prior to discharge experiments leading to low discharge wt% results.

- The current analysis indicates the charged material to be LiNH<sub>2</sub> + MgH<sub>2</sub> with no XRD evidence for Mg(NH<sub>2</sub>)<sub>2</sub> thus far identified.
- Current analysis indicates that discharge of LiNH<sub>2</sub> and MgH<sub>2</sub> favors the formation of a Mg<sub>3</sub>N<sub>2</sub> [(Li<sub>0.51</sub>Mg<sub>2.49</sub>)N<sub>1.83</sub>] phase, not LiMgN as previously reported.

### Future Directions

- Explore in greater detail, the sorption path ways and products.
- Expand temperature and pressure values explored to determine optimum conditions for cycling.
- Explore addition catalyst types and compositions.
- Determine identity of solid and gaseous reaction products.

## Task 2: Metal Hydride System Engineering Analysis

### Introduction

The Metal Hydride System Engineering Analysis Task involves two separate subtasks:

- 1.1 Hydrogen Storage Scoping and Integrated Modeling
- 1.2 Fueling Station System Modeling

### Approach

#### Hydrogen Storage Scoping and Integrated Modeling

Hydrogen storage is recognized as a key technical hurdle that must be overcome for the realization of hydrogen-powered vehicles. Metal hydrides and their doped variants have shown great promise as a storage material and significant advances have been made with this technology. A full understanding of the complex interplay of physical processes that occur during the charging and discharging of a practical storage system requires models that integrate the salient phenomena. In any practical storage system the rate of H<sub>2</sub> uptake will be governed by all processes that affect the rate of mass transport through the bed and into the particles. These coupled processes include heat and mass transfer as well as chemical kinetics and equilibrium. However, with few exceptions, studies of metal hydrides have focused primarily on fundamental properties associated with hydrogen storage capacity and kinetics.

The full document [7] describes a detailed numerical model for general metal hydride beds that couples reaction kinetics with heat and mass transfer, for both hydrating and dehydrating of the bed. The detailed

model is part of a comprehensive methodology for the design, evaluation and modification of hydrogen storage systems. In [8], scoping models for reaction kinetics, bed geometry and heat removal parameters are discussed. The scoping models are used to perform a quick assessment of storage systems and identify those which have the potential to meet DOE performance targets. The operational characteristics of successful candidate systems are then evaluated with the more detailed models.

## Results

### Hydrogen Storage Scoping and Integrated Modeling

The detailed analysis for hydrogen storage systems is modeled in either 2 or 3-dimensions, via the general purpose finite element solver COMSOL Multiphysics®. The 2-dimensional model serves to provide rapid evaluation of bed configurations and physical processes, while the 3-dimensional model, which requires a much longer run time, is used to investigate detailed effects that do not readily lend themselves to 2-dimensional representations. The model is general and can be adapted to any geometry or storage media. In this study, the model is applied to a modified cylindrical shell and tube geometry with radial fins perpendicular to the axis, see Figures 3. Sodium alanate,  $\text{NaAlH}_4$ , is used as the hydrogen storage medium. The model can be run on any DOS, LINUX or Unix-based system.

The detailed finite element models indicated that the modified shell and tube heat exchanger, with fins normal to the axis, was very effective from the perspective of heat removal and temperature control. For identical

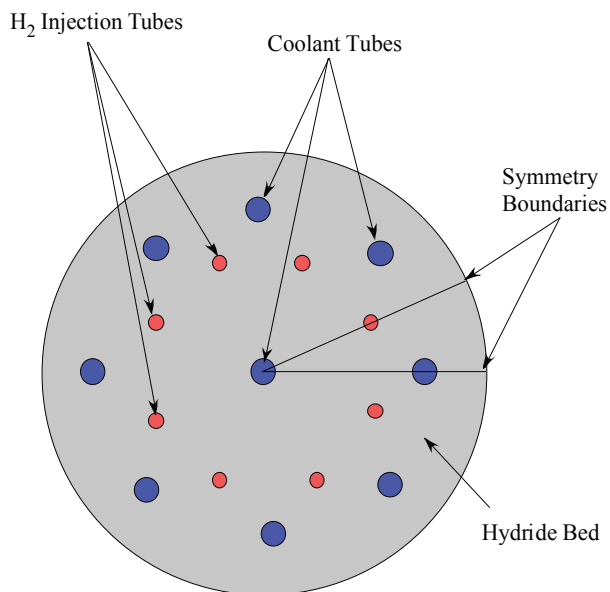


FIGURE 3. Schematic of Cross-Section for Hydride Bed

states of the coolant and feed hydrogen, the modified shell and tube system permits far better control of the bed temperature than the system without fins. This was clearly demonstrated by comparing the temperatures predicted by the 3-dimensional and 2-dimensional models, which represented storage systems with and without fins, respectively. Because the bed temperatures were maintained below  $120^\circ\text{C}$ , the hydrogen charging rate was significantly improved for the modified shell and tube system. The more uniform spatial temperatures in the modified storage system yielded smaller concentration gradients for the hexa- and tetra-hydrides formed from NaH. This resulted in more efficient utilization of the bed. Figure 4 shows that the charging rate for the modified system is essentially the same as predicted by the 0-dimensional kinetics scoping model. This means that charging in the modified system is limited by kinetics alone, which represents an upper bound to the charging rate at a given temperature and pressure.

## Approach

### Fueling Station System Modeling

A typical hydrogen refueling station was designed based on DOE targets and existing gasoline filling station operations (Figure 5). The purpose of this design was to determine typical heat loads, how these heat loads will be handled, and approximate equipment sizes.

For the station model, two DOE targets that had the most impact on the design were vehicle driving range and refueling time. The target that hydrogen-fueled vehicles should have the equivalent driving range as present automobiles requires five kg hydrogen storage. Assuming refueling occurs when the tank is 80% empty yields a refueling quantity of four kg. The DOE target for 2010 of a refueling time of three minutes was used in this design. There is additional time needed for payment of the fuel, and connecting and disconnecting

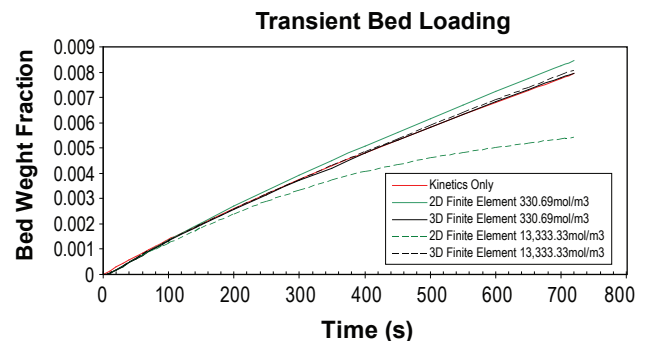


FIGURE 4. Comparison of the weight fraction of stored hydrogen for the kinetics scoping model and the 2 and 3-dimensional finite element bed models.



hoses and grounds. It was assumed that this could be accomplished in five minutes. Using eight minutes for each vehicle refueling gives a maximum hourly refueling rate of 7.5 cars per hour per fueling point.

The number of pumps at a gasoline filling station varies greatly. Small stations may have two to four pumps. A typical neighborhood gasoline station may have eight pumps. A large station as on an interstate or major highway, may have as many as 24 pumps. This first design is based on a hydrogen station with eight pumps.

For the purposes of this design, it was assumed that there would be at least one hour per day when all the fueling points (two cars per pump) would be in use. The size of the cooling equipment was based on this one-hour maximum loading. An estimate of daily demand was calculated from the one-hour peak demand being equal to 7% of daily fuel needed. For the aforementioned design system, this gives a maximum hourly fuel demand of 480 kg of hydrogen and a daily demand of 6,900 kg of hydrogen.

When refueling a hydride storage tank, significant energy is released in the form of heat. The amount of heat released is based on the heat of formation for the particular hydride being used. Rather than considering a specific hydride, the energy balances investigated used a generic hydride with a heat of formation of  $-27.5$  kJ/mol.

## Results

### Fueling Station System Modeling

The design presented here assumes the hydride in both units operate at the same temperature and all heat generated must be dissipated to the environment. The dissipation facility must be sized to handle the maximum heat generated, which would be during the hours of maximum refueling. Refueling the bulk storage tank would require the same amount of cooling but would not require a separate heat dissipation facility. The bulk storage tank would be regenerated and consequently cooled during off hours when there is excess cooling capacity in the dissipation facility. During times of vehicle refueling the bulk storage tank may require heat input. Waste heat from the compressor can be used but may not be enough. Additional heat from burning a side stream of hydrogen may be necessary. This portion of the design is not included in the model.

Using the above design parameters, 6.5 gigajoules (GJ) of heat must be dissipated or stored during each hour of maximum fueling. Since the generated heat during refueling is produced at a low temperature, there are no normal reuse or storage options. In some combined power-heat systems, hot water is piped to buildings or houses for comfort heating. This would only be practical in colder weather if the demand was

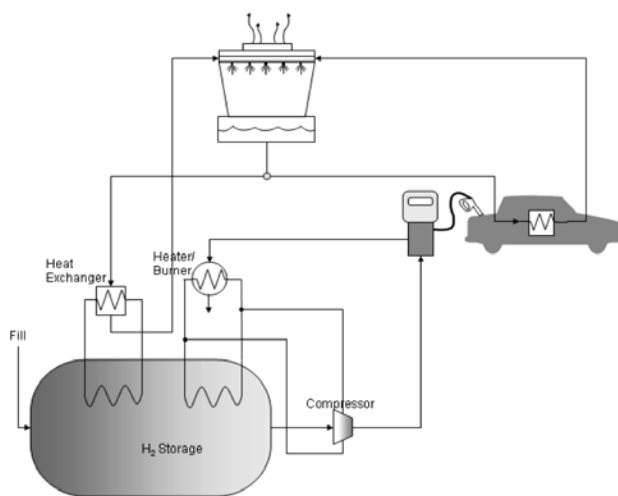


FIGURE 5. Simplified Hydrogen Fueling Station

present. Determining uses for this low quality heat is outside the boundary of this model.

The two most common methods of dissipating this type of heat are cooling towers and air coil units. A cooling tower operates on the principle of using evaporation to cool water which can be used as the primary coolant or as the secondary coolant in a heat exchanger to cool the primary cooling fluid. The 6.5 GJ/hr of heat to be dissipated corresponds to a cooling load of 517 tons.

As cooling loads increase, a cooling tower is the preferred method for heat dissipation primarily due to cost. There are no standard dimensions for cooling towers. Sizes are unique to each manufacturer. Based on experience and standard rules of thumb, a 500-ton cooling tower will be approximately 20 feet long, 12 feet wide and 18 feet tall and be composed of two, four or six cells. A cooling tower this size is small by industrial standards but may be significant when added to a fueling station.

### Fueling Station Design Summary

- Large quantities of heat are generated during hydrogen refueling.
- Heat removal structures (i.e. cooling towers) will need a sizeable area but are commercially available today.
- For storage materials having  $\Delta H=5$  kJ/mole, fueling station cooling requirements are  $\sim 100$  tons while materials having  $\Delta H=40$  kJ/mole would require 700 ton cooling.
- Bulk fuel storage tanks utilizing metal hydrides would need to be approximately four times as large as those in existing gasoline filling stations to match capacity.

- Significant water and waste water resources are needed for cooling tower operation.

## Conclusions and Future Directions

### Task 2. Metal Hydride System Engineering Analysis

- A combination of both scoping and integrated 2 and 3-dimensional models were developed and found to be effective in modeling hydride hydrogen storage systems.
- The detailed finite element model showed the effectiveness of a modified shell and tube design versus a system without heat transfer fins.
- A kinetic scoping model of the hydrogen charging rate showed good agreement with the integrated model showing the value of using scoping models to save computation time and to gain preliminary information and insight into some complex processes.
- A preliminary design on a fueling station based on an onboard hydride-based storage system indicated that a 6.5 GJ/hr of heat would need to be dissipated corresponding to a cooling load of 517 tons.
- While the cooling load required is large, the size of a cooling tower to handle the load is small by industrial standards but may be significant when added to a fueling station.

## FY 2008 Publications/Presentations

1. “Design, Fabrication and Testing of NaAlH<sub>4</sub> Based Hydrogen Storage Systems”, *Journal of Alloy and Compounds*, Mosher, Arsenault & Tang, 12/2007.
2. Integrated Model for Hydrogen Storage Systems, International Conference on Metal Hydrides, Reykjavik, Iceland June, 2008.

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8. *Geometry, Heat Removal and Kinetics Scoping Models for Hydrogen Storage Systems* (PDF 6.2 MB), Bruce J. Hardy of Savannah River National Laboratory, November 16, 2007. [http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen\\_publications.html#h2\\_storage](http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage)