

Synopsis of the thesis entitled

**ON SOME CHALLENGING AVENUES IN HYDROGEN
STORAGE**

to be submitted by

L. HIMA KUMAR

for the award of the degree

of

DOCTOR OF PHILOSOPHY



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY MADRAS
CHENNAI – 600 036, INDIA**

FEBRUARY 2008

1. INTRODUCTION

Efficient onboard hydrogen storage is a critical issue in utility of hydrogen as an energy carrier for any mode of modern transportation. Solid state hydrogen storage is the viable means of storing hydrogen and it has two challenging issues; one is to achieve the desirable levels of hydrogen storage (greater than 6.5 wt % as postulated by DOE) and the other is to be able to release the stored hydrogen near ambient conditions. Considerable research has been focused on employing the carbon materials as storage materials. In literature the substantial storage capacities for carbon in various forms (carbon nanotubes, graphite nanofibers, SWNT, MWNT) have been reported (Dillon and Heben, 2001). Another possibility is the use of metal hydrides. Many metals have the property of combining chemically with hydrogen to form a class of compounds called metal hydrides. Intermetallics, which can be formed by alloying two or more metals, can store hydrogen reversibly at ambient conditions with faster kinetics (Sandrock, 1999). But the main disadvantage with intermetallic compounds is that they can store hydrogen only up to 3 wt% due to the high gravimetric density of metals. The most logical approach to develop a high storage material would be, to decrease the weight of metals. This can be done by considering the light metals like Li, Be, B, Na, Mg and Al and their alloys. These metals form a large class of compounds called as complex metal hydrides

Motivation and scope

Magnesium based hydrogen storage systems and complex metal hydrides based on alanates and borohydrides are potential candidates for hydrogen storage because of their high storage capacity (> 6 wt %). But these systems do not release hydrogen near ambient conditions (Stioui *et al.*, 1986; Bogdanovic and Schwickardi, 1997). Various attempts have been made to facilitate (or even enhance the kinetic parameters or decrease the activation parameters) desorption process by addition of suitable materials that are conventionally termed as “catalysts” (Bagdonavic *et al.*, 2000; Zaluska *et al.*, 2000; Gross *et al.*, 2002). However, the role of these additions has to be carefully understood, since they not only function as catalysts but also have to facilitate the transport of the species to the surface before desorption. A catalyst only functions in the surface transformations but the diffusion of hydrogen from the solid bulk has to be achieved by some affinity parameters and the kinetics of this transport process is related to the ad-

lineation that can take place between the species and the added component. Mg₂Ni alloy is an interesting material for metal hydride battery applications because of its high energy density (Rongeat *et al.*, 2006). Attempts have been made to improve sorption kinetics and discharge capacity of Mg-Ni alloy by preparing in nano/amorphous form through mechanical milling (Liu *et al.*, 1997) which is an energy expensive process. The effect of graphite on hydriding properties of Mg (Imamura *et al.*, 2002) and the effect of graphite as co-dopant on dehydrogenation properties of Ti catalyzed sodium alanates (Dehouche *et al.*, 2005; Wang *et al.*, 2005) have been reported. Carbon can act as a catalyst to improve kinetics by facilitating transport of hydrogen atoms from bulk to surface or vice versa. Moreover, there is no clear understanding about the effect of carbon on the hydrogenation and dehydrogenation properties of alanates.

In the light of the above, the present study aims to show how the addition of carbon materials and hetero atom substituted carbon materials affect the hydrogen storage properties of Magnesium and alanates. Since borohydride decomposes at high temperatures (>573 K), another possibility i.e. generating hydrogen by hydrolysis of borohydride has been studied by using cobalt based catalysts. The thesis focuses on the following aspects:

- To synthesize Mg₂Ni alloy by polyol reduction method and to study its sorption kinetics and the electrochemical characteristics
- To study the desorption kinetics of carbon admixed alanates and to find out the role of carbon additives
- To synthesize nitrogen containing carbon nanotubes (NCNT) and test the reversibility of NCNT admixed alanates
- To synthesize boron and nitrogen containing carbon materials and to study their effect on the sorption properties of Mg
- To study the catalytic effect of cobalt based catalysts on the hydrogen generation from alkali stabilized sodium borohydride.

2. MATERIALS AND METHODS

Volumetric high pressure hydrogen sorption measurements have been carried out using custom built volumetric apparatus (Fig. 1). The amount of hydrogen uptake/release for the material is calculated from the pressure changes in a known volume using the ideal

gas law (modified with compressibility factor). For dehydrogenation measurements the reactor is loaded with material and it is evacuated. Then the reactor is heated slowly to the desired temperature and the released hydrogen is allowed to expand into vacuum. Similarly, for hydrogenation measurements the calibrated cylinder is filled with hydrogen to desired pressure then hydrogen is allowed to flow into the reactor and the pressure change is monitored with time.

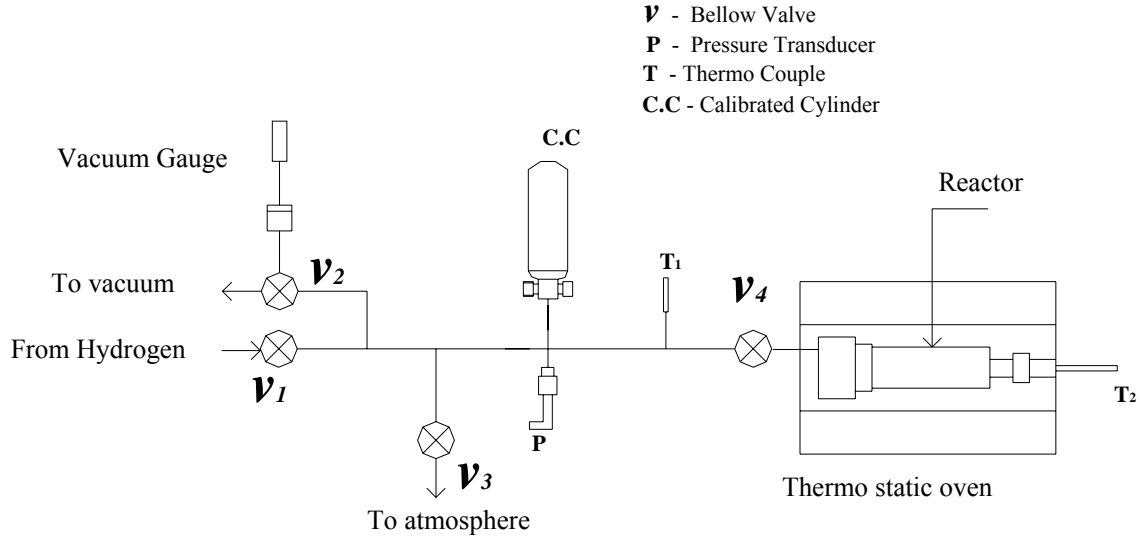


Fig. 1 Experimental set up for hydrogenation/dehydrogenation measurements

3. SORPTION PROPERTIES OF Mg_2Ni PREPARED BY POLYOL REDUCTION

Nanosized Mg_2Ni alloy particles have been synthesized by polyol reduction method followed by annealing (Chen and Jehng, 2004). The presence of unreacted Ni is detected in XRD studies. The average particle size of the nanocrystalline Mg_2Ni alloy is in the range of 50 ± 20 nm. The kinetic curves of hydrogen absorption at different temperatures and at an initial pressure of 2.5 MPa and hydrogen desorption at 10 kPa for the nanosized Mg_2Ni are shown in Fig. 2. At a temperature as low as 473 K, the nanocrystalline Mg_2Ni is able to absorb and desorb hydrogen. The Mg_2Ni compound absorbs hydrogen quickly and reaches a maximum value within 1 min at 573 K. After 5 min the maximum hydrogen storage capacity of the Mg_2Ni compound is about 3.0, 3.12 and 3.23 wt% at temperatures of 473, 523 and 573 K respectively. The rate of desorption is low at lower temperatures and increases with increasing temperature. The maximum amount of

hydrogen desorbed is found to be 0.75, 1.61 and 2.5 wt% at 473, 523 and 573 K respectively in 30 min.

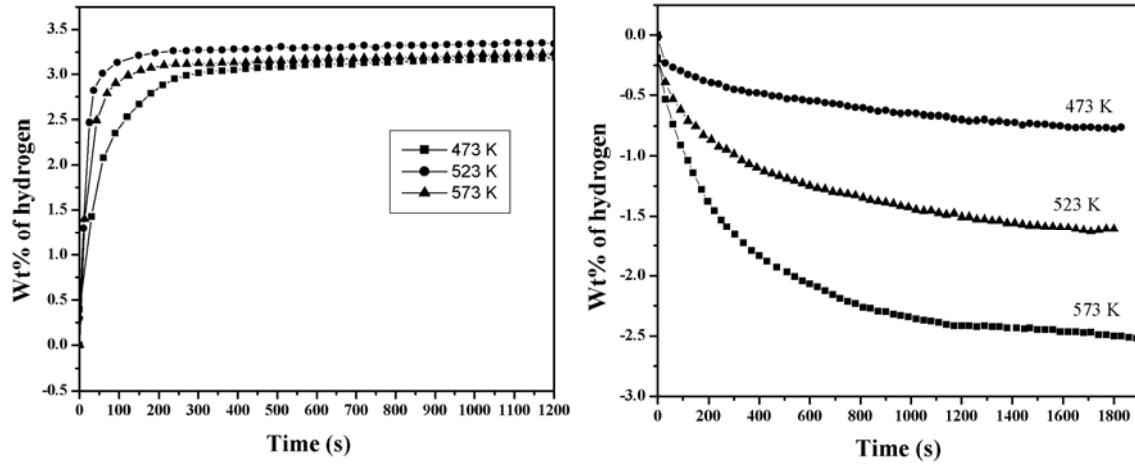


Fig. 2 Hydrogen absorption and desorption kinetics for nano-Mg₂Ni at 2.5 MPa and 10 kPa and 473, 573 and 573 K respectively.

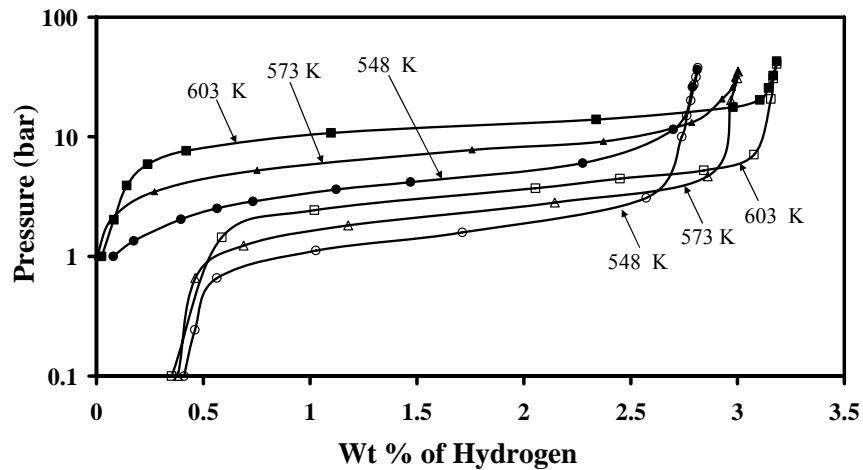


Fig. 3 Pressure-composition isotherms of nano-Mg₂Ni at temperatures of 548, 573 and 603 K

Single sloping plateau is observed for absorption / desorption process indicating the presence of nanocrystalline / amorphous nature of the alloy (Orimo and Fujii, 2001). The slope of plateau decreases with increasing temperature (Fig. 3). The hydrogen absorption capacities are 2.8, 3.03 and 3.20 wt% at temperatures of 548, 573 and 603 K respectively. Changes in enthalpy and entropy for the hydrogen sorption of the nanosize Mg₂Ni obtained are -50.0 kJ/mol, -103.6 J/(mol K) for absorption and 56.3 kJ/mol,

105.3 J/(mol K) for desorption, respectively. The Mg_2Ni electrode is charged/ discharged galvanostatically in 6 M KOH aqueous solution at room temperature. The typical discharge curves at the 1st cycle measured at different discharge current densities are shown in Fig. 4. The maximum discharge capacity obtained is 408 mAh/g at a discharge current density of 20 mA/g in the first cycle.

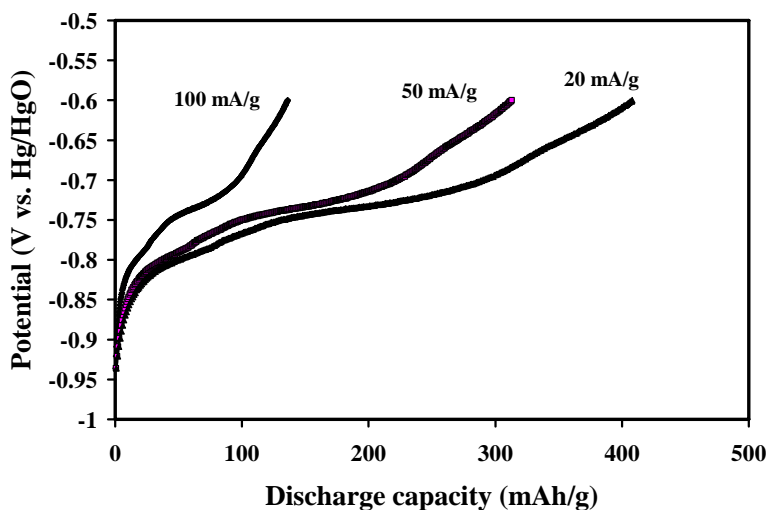


Fig. 4 Galvanostatic discharge curves of nano- Mg_2Ni at different current densities

4. DEHYDRIDING BEHAVIOR OF CARBON ADMIXED LiAlH_4

Effect of carbon additives

To understand how carbon additives affect the dehydrogenation kinetics of alanates direct dehydrogenation of solid LiAlH_4 by isothermal experiments are carried out. The isothermal dehydrogenation kinetic behaviour of five different composite materials, all based on LiAlH_4 which is mixed with different carbons (Vulcan XC72R, Black Pearls 2000, CDX 975 and Mesoporous carbon) are given in Fig 5. It is observed that the dehydrogenation kinetics improved considerably by the addition of various carbon materials. The enhancement is 5 times for the Black Pearls BP 2000, CDX 975, Mesoporous carbon and 2.5 times for the Vulcan XC-72R in comparison to pure LiAlH_4 (at 45 min). Dehydrogenation kinetics of LiAlH_4 with different amounts of carbon (3, 5, 7 and 9 wt %) is studied. With an increase in the carbon content the rate increases, further increase in carbon amount may lead to a decrease in the total hydrogen capacity.

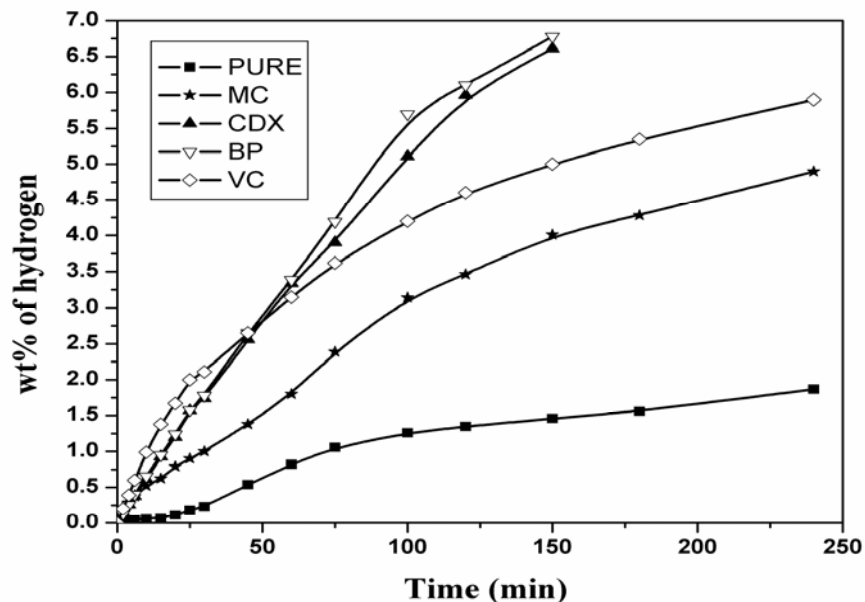


Fig. 5 Dehydrogenation profiles for the pure LiAlH_4 , 5 wt% Vulcan XC 72R, 5 wt% Mesoporous carbon, 5 wt% CDX 975 and 5 wt% Black pearls admixed LiAlH_4

Effect of carbon nanofibers

Carbon nanofibers (CNFs) are prepared by catalytic decomposition of gaseous ethylene on NiCu/H-ZSM-5. They are characterized by XRD and TEM techniques. Typically 2 g of LiAlH_4 is admixed with 5 wt% of carbon by mechanical milling under argon atmosphere for 45 min. The dehydrogenation kinetics improved remarkably by the addition of carbon nanofibers (Fig. 6). In the XRD pattern after complete dehydrogenation, only peaks corresponding to Al are observed. Maximum observed release of hydrogen from $\text{LiAlH}_4 + \text{CDX 975}$ composite is 6.8 wt%, the decrease in the maximum capacity (theoretical capacity 7.8 wt%) may be due to partial decomposition of LiAlH_4 during mechanical milling with carbon nanofibers. As the temperature increases the rate of dehydrogenation also increases which is the case for many solid state thermal decomposition reactions. When John-Mehl-Avrami model is applied for the dehydrogenation of $\text{LiAlH}_4 + \text{CNFs}$ composite, a good agreement between the fit and the experimental data is observed (Fig 7a). Fig. 7b shows Avrami plot ($\ln(-\ln(1-\alpha))$ vs. $\ln t$) for dehydrogenation of $\text{LiAlH}_4 + \text{CNFs}$ at temperatures of 398, 408, 418 and 428 K. In k values are determined from the intercept of $\ln(-\ln)$ plot. From Arrhenius plot, activation energy E_a , obtained is 46 ± 0.2 kJ/ mol. In order to improve the kinetics further CNF

admixed LiAlH_4 is co-doped with VCl_3 . As expected LiAlH_4 with CNF and 3 mol% VCl_3 shows better desorption kinetics than LiAlH_4 with CNF.

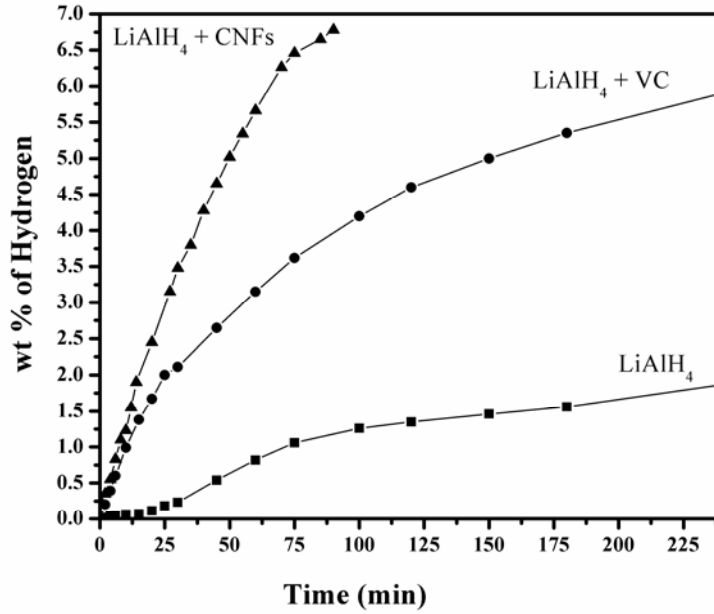


Fig. 6 Dehydrogenation kinetics of LiAlH_4 admixed with CNFs, LiAlH_4 admixed with Vulcan carbon and LiAlH_4 at 403 K

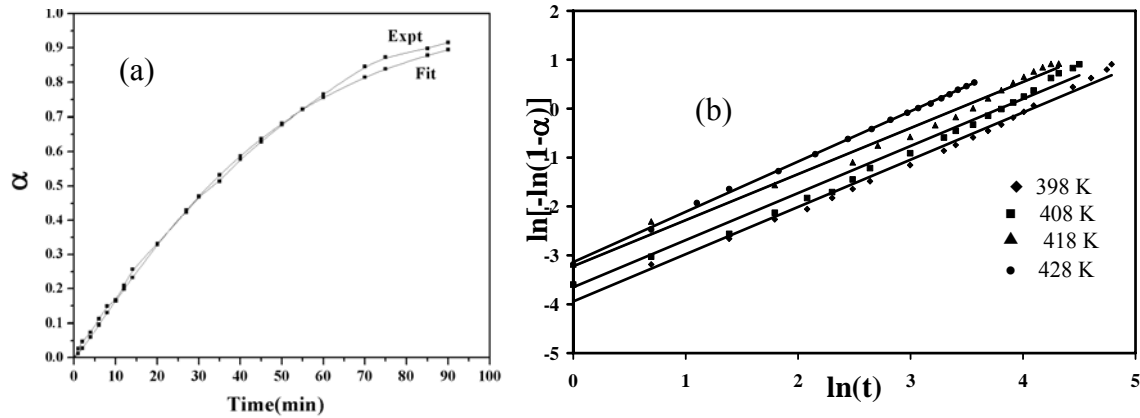


Fig. 7 (a) Fit of the John-Mehl Avrami model to experimental hydrogenation data (b) Plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln(t)$ of CNFs + LiAlH_4 at (♦) 398 K (■) 408 K (▲) 418 K (●) 428 K

5. HYDROGEN STORAGE PROPERTIES OF ALANATES ADMIXED NITROGEN CONTAINING CARBON NANOTUBES (NCNT)

Even though addition of carbon or carbon nanomaterials improve desorption kinetics considerably, the rehydrogenation in these composites is difficult. In order to facilitate rehydrogenation activators are needed. Hetero atoms like nitrogen or boron in carbon

framework can act as activation centers (Sankaran and Viswanathan, 2006). Nitrogen containing carbon nanotubes are prepared by pyrolyzing poly (N-vinyl pyrrolidine) (carbon precursor) in alumina membrane template at 1173 K (Maiyalagan and Viswanathan, 2005). The obtained nanotubes are characterized by SEM and XRD techniques. The tube diameter is found to be 200 nm. $\text{LiAlH}_4 + 5\text{wt}\%$ NCNT and $\text{NaAlH}_4 + 5\text{wt}\%$ NCNT composites are prepared by grinding sodium or lithium alanate and 5 wt% of NCNT manually in argon filled glove box for 30 min. The composites are studied by XRD, DSC, isothermal decomposition and in-situ FT-IR techniques. The dehydrogenation kinetics of $\text{LiAlH}_4 + 5\text{wt}\%$ NCNT and $\text{NaAlH}_4 + 5\text{wt}\%$ NCNT composites are obtained at 423 K and 473 K respectively. The DSC curves reveal that upon adding NCNT the decomposition temperatures of NaAlH_4 lowered by 30 K (Fig. 8a).

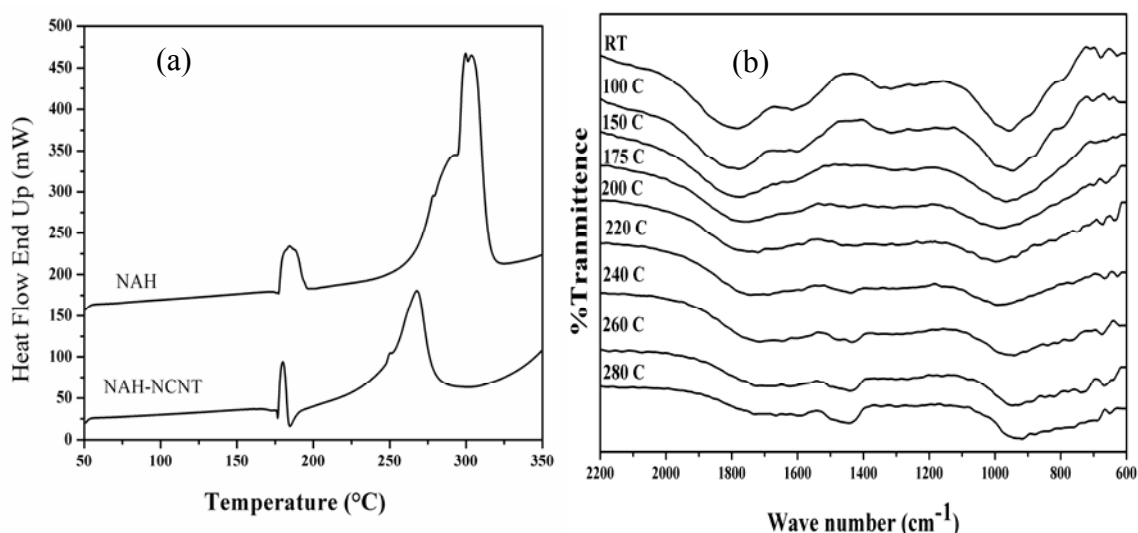


Fig. 8 (a) DSC curves at the scan rate of 20 °C/min NAH and NAH-NCNT composites (b) In-situ FT-IR spectra from room temperature to 553 K for NAH-NCNT composite

The apparent activation energies, E_a , of the two steps in the decomposition processes are obtained by Kissinger method. The activation energies for NaAlH_4 -NCNT composite are lower compared to pure NaAlH_4 (86.3 ± 0.3 , 115.3 ± 1.5 and 93.8 ± 1 , 160.6 ± 0.9 kJ/mol for first and second step decompositions respectively). Activation energies for NaAlH_4 -NCNT composite calculated from isothermal decomposition kinetic data are found to be 88 ± 1.2 and 118 ± 1.5 kJ/mol respectively. Shifting of Al-H stretching frequency to higher value (1635 to 1655 cm^{-1}) is observed in the IR spectra. This indicates that Al-H bond is

altered by the addition of nitrogen containing carbon nanotubes to the sodium aluminum hydride. Two step decomposition of NaAlH₄-NCNT composite is confirmed by both DSC and in-situ IR studies which are shown in Fig. 8a and 8b. In-situ DRIFT IR experiments have been carried out to verify the dehydrogenation pathway of NaAlH₄-NCNT composite. After complete dehydrogenation NaAlH₄-NCNT composite is subjected to rehydrogenation at 473 K and 8 MPa pressure. This composite is able to take 4 wt% of hydrogen reversibly which infers the necessity of activation centers in carbon nanomaterials.

6. HYDROGEN STORAGE PROPERTIES OF Mg – N and B SUBSTITUTED CARBON COMPOSITES

Mg-C composites are prepared by ball milling of Mg and 10 wt% carbon materials (C= graphite, boron containing carbon and nitrogen containing carbon) for 3 h in argon atmosphere.

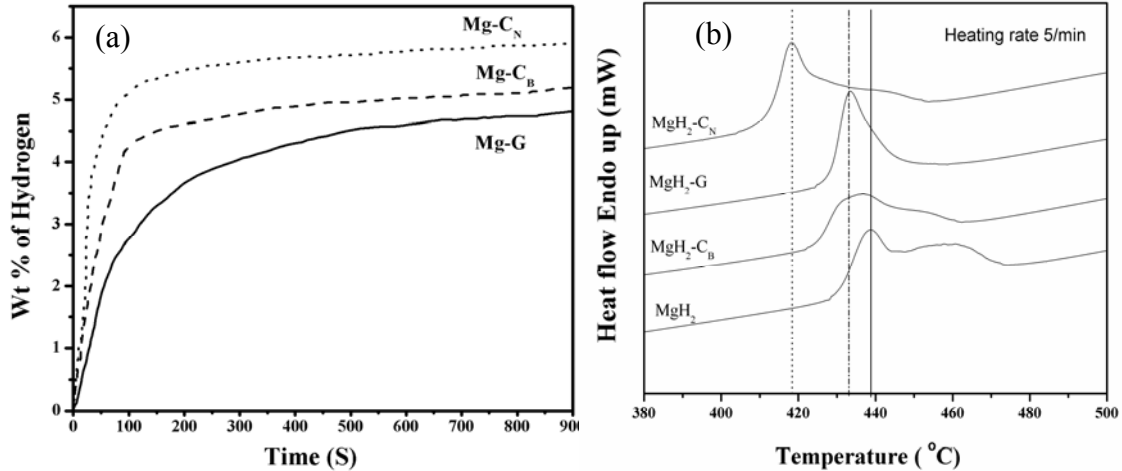


Fig. 9 (a) Hydrogen absorption by Mg-C composites at 573 K and 2 MPa (b) DSC profiles for hydrogenated Mg-C composites with the scan rate of 5 °C/min

Boron containing carbon is prepared by thermal decomposition of boron containing phenyl formaldehyde resin at 1173 K (Xiang *et al.*, 2002). Nitrogen containing carbon is prepared by thermal decomposition of poly (N-vinyl pyrrolidone) in presence of Fe nanoparticles at 973 K. The synthesized materials are characterized by XRD and SEM techniques. Mg-nitrogen containing carbon (C_N) composite showed better sorption properties compared to either Mg-boron containing carbon (C_B) or pure Mg (Fig 9a). The

composite Mg -10 wt. % CN milled for 3 h can absorb 6 wt. % hydrogen within 15 min at 573 K and 2 MPa, and desorb 6 wt. % hydrogen in 25 min at 573 K and 0.1 MPa. Addition of carbon materials results in lowering of decomposition temperature of MgH_2 ; for Mg-CN the decomposition temperature is lowered by 20 K compared to pure MgH_2 (Fig 9b).

7. CATALYTIC EFFECTS IN GENERATION OF HYDROGEN FROM $NaBH_4$

Sodium borohydride in alkali medium is stable under ordinary conditions and liberates hydrogen in presence of catalyst in a safe and controlled manner (Schlesigner *et al.*, 1953; Kaufman and Sen, 1985). Hydrolysis reaction occurs at different rates depending on the catalyst used and its preparation method. Cobalt based catalysts are prepared by the chemical reaction of cobalt chloride and metal precursor ($NiCl_2$ for Ni, $CrCl_3$ for Cr, $SnCl_2$ for Sn and Na_2MoO_4 for Mo) with the sodium borohydride in methanol followed by annealing in hydrogen atmosphere for 3 hrs at 623 K.

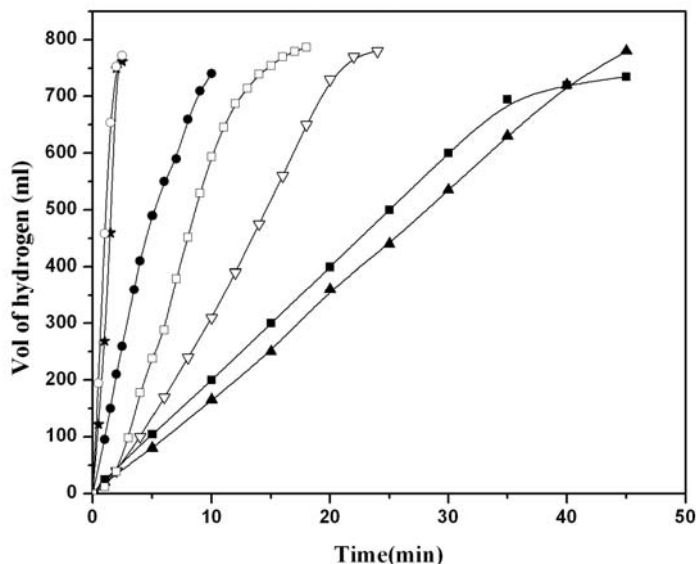


Fig. 10 Catalytic performance of cobalt based catalysts (■) Co- commercial (▲) NiCo-commercial (▽) Co (●) NiCo (□) CoSn (★) CoCrO₃ (○) CoMo₃ and (20 ml of 1.5 wt% $NaBH_4$ + 4 wt% NaOH).

In all the measurements, 0.1g of catalyst is taken in the reaction vessel then the reactor is introduced in the thermostatic bath for about 15 min, after that 20 ml of 1.5 wt% $NaBH_4$ + 4 wt% NaOH solution is rapidly injected with 20 ml syringe. Among the examined catalysts Co-Mo has shown higher catalytic activity compared to other catalysts (Fig. 10).

Co-M systems (M=Mo, Cr and Ni) are more active than Co alone. The hydrolysis reaction rate depends on NaOH concentration as given in the Fig. 11. The reaction rate is enhanced by increase of NaOH concentration. The reaction rate increases with increasing NaOH concentration up to 12 wt% and then decreases. The catalysts are active even at lower temperature (283 K). The reaction rate increases with increase in temperature.

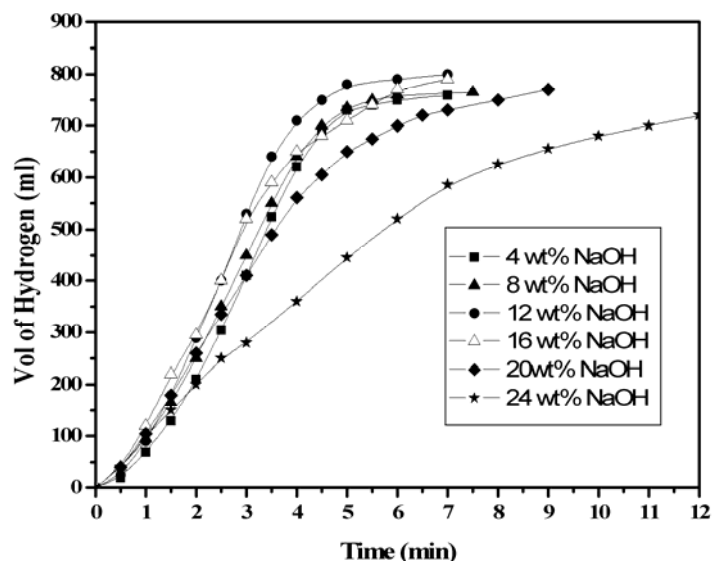


Fig. 11 Effects of NaOH concentration on the hydrogen generation rate measured using 20 ml of x wt% NaOH + 1.5 wt% NaBH₄ solutions ($x = 4, 8, 12, 16, 20, 24$) at room temperature using 0.1 g of Co-Ni catalyst.

Table 1 Activation energies and borohydride hydrolysis rate for Cobalt based catalysts.

Catalyst	Activation energy (kJ/mol)	Hydrogen evolution rate at 301 K (ml/min)
Co	60	100
Co-Ni	36.4	205
Co-Cr	61.19	370.6
Co-Mo	74.2	458.2
Co-Sn	57.68	72.6

Activation energies for the sodium borohydride hydrolysis are comparatively low for Co-Ni and Co-Sn catalysts than for Co-Cr and Co-Mo and Co but the hydrogen generation rates for Co-Mo and Co-Cr catalysts are higher compared to Co-Ni and Co-Sn catalysts (Table 1). The Co-Mo catalyst can be recovered and reused, although the catalytic

activity is gradually diminished, a conversion of over 90% is still achieved even after 100 h.

8. SUMMARY AND CONCLUSIONS

- Among the various options for solid state hydrogen storage, Mg based systems and complex metal hydrides appear to be viable options.
- Polyol reduction method is an alternative route to synthesize nanocrystalline / amorphous alloys. Nanosize Mg₂Ni alloy, synthesized by polyol reduction has shown promising hydrogen absorption as well as electrochemical hydrogen absorption characteristics. The maximum hydrogen storage capacity and discharge capacity observed are 3.23 wt % (573 K) and 408 mAh/g (at discharge current density of 20 mA/g) respectively.
- Carbon materials have been observed to increase dehydrogenation kinetics of LiAlH₄ by facilitating the diffusion and spill over of hydrogen from storage systems and also subsequent desorption of hydrogen to the gas phase.
- Al-H stretching frequency of NaAlH₄ altered by admixing with NCNT and results in the lowering of decomposition temperature. After complete dehydrogenation it can be rehydrogenated to give 4 wt% of hydrogen reversibly.
- Hydrogen sorption properties of magnesium can be improved by the addition of boron and nitrogen atom containing carbon materials. The dissociation temperature of MgH₂ can be lowered by adding nitrogen containing carbon.
- In the case of borohydrides alternate route for hydrogen generation based on hydrolysis promoted by catalysts is a viable option.

REFERENCES

1. **Bogdanovic, B. and M. Schwickardi**, Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials, *J. Alloys Comp.* **253–254** (1997) 1-9.
2. **Bogdanovic, B., R.A. Brand, A. Marjanovic, M. Schwickardi and J. Tölle**, Metal-doped sodium aluminum hydrides as potential new hydrogen storage materials, *J. Alloys Comp.* **302** (2000) 36–58.
3. **Chen, C.-M. and J.-M. Jehng**, Amination application over nano-Mg–Ni hydrogen storage alloy catalysts, *Appl. Catal. A: General* **267** (2004) 103-110.

4. **Dehouche1, Z., L. Lafi, N. Grimard, J. Goyette and R. Chahine**, The catalytic effect of single-wall carbon nanotubes on the hydrogen sorption properties of sodium alanates, *Nanotechnology* **16** (2005) 402-409.
5. **Dillon, A.C., and M.J. Heben**, Hydrogen storage using carbon adsorbents: past, present and future, *Appl. Phys. A: Materials Science & Processing*, **72** (2001) 133-142.
6. **Gross, K.J., G.J. Thomas and C.M. Jensen**, Catalyzed alanates for hydrogen storage, *J. Alloys Comp.* **330–332** (2002) 683-690.
7. **Imamura, H., S. Tabata, N. Shigetomi, Y. Takesue and Y. Sakata**, Composites for hydrogen storage by mechanical grinding of graphite carbon and magnesium, *J. Alloys Comp.* **330–332** (2002) 579-583.
8. **Kaufman, C.M. and B. Sen**, Hydrogen generation by hydrolysis of sodium tetrahydroborate: effects of acids and transition metals and their salts, *J. Chem. Soc. Dalton Trans.* (1985) 307-313.
9. **Liu, W., H. Wu, Y. Lei, Q. Wang and J. Wu**, Amorphization and electrochemical hydrogen storage properties of mechanically alloyed Mg–Ni, *J. Alloys Comp.* **252** (1997) 234-237.
10. **Maiyalagan, T. and B. Viswanathan**, Template synthesis and characterization of nitrogen containing carbon nanotubes, *Mater. Chem. Phys* **93** (2005) 291.
11. **Orimo, S. and H. Fujii**, Effects of nanometer-scale structure on hydriding properties of Mg–Ni alloys: a review, *Appl. Phys. A* **72** (2001) 167–186.
12. **Rongeat, C., M.-H. Grosjean, S. Ruggeri, M. Dehmas, S. Bourlot, S. Marcotte and L. Roue**, Evaluation of different approaches for improving the cycle life of MgNi-based electrodes for Ni-MH batteries, *J. Power Sources* **158** (2006) 747-753.
13. **Sandrock, G.**, A panoramic overview of hydrogen storage alloys from a gas reaction point of view, *J. Alloys Comp.* **293–295** (1999) 877–888
14. **Sankaran, M. and B. Viswanathan**, The role of heteroatoms in carbon nanotubes for hydrogen storage, *Carbon* **44** (2006) 2816-2821
15. **Schlesinger, H.I., H.C. Brown, A.E. Finholt, I.R. Gilbreath, H.R. Hoekstra and E.K. Hyde**, Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen, *J. Amer. Chem. Soc.* **75** (1953) 215-219.

16. **Stioui, M., A. Ggayevsky, A. Resnik, D. Shaltiel, and N. Kaplan**, Macroscopic and microscopic kinetics of hydrogen in magnesium-rich compounds, *J. Less-Common Met.* **123** (1986) 9-24.
17. **Wang, J., A. D. Ebner, T. Prozorov, R. Zidan and J. A. Ritter**, Effect of graphite as a co-dopant on the dehydrogenation and hydrogenation kinetics of Ti-doped sodium aluminum hydride, *J. Alloys Comp.* **395** (2005) 252-262.
18. **Xiang, H-Qi, S.-Bi Fang and Y.-Yan Jiang**, Carbons prepared from boron-containing polymers as host materials for lithium insertion, *Solid State Ionics* **148** (2002) 35– 43.
19. **Zaluska, A., L. Zaluski, and J.O. Stroëm-Olsen**, Sodium alanates for reversible hydrogen storage, *J. Alloys Comp.* **298** (2000) 125-134.

PROPOSED CONTENTS OF THE THESIS

- Chapter 1** Introduction
- Chapter 2** Materials and Methods
- Chapter 3** Sorption properties of Mg₂Ni prepared by polyol reduction
- Chapter 4** Dehydrating behavior of carbon admixed LiAlH₄
- Chapter 5** Hydrogen storage properties of alanates admixed nitrogen containing carbon nanotubes
- Chapter 6** Hydrogen storage properties of Mg–N and B containing carbon composites
- Chapter 7** Catalytic effects in generation of hydrogen from NaBH₄
- Chapter 8** Summary and Conclusions

LIST OF PUBLICATIONS BASED ON RESEARCH WORK

Refereed Journals

1. **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, Alanates – Are they the appropriate hydrogen storage material? *Photo/Electro chemistry and photobiology in the environmental Energy and Fuel* **4** (2005) 13-42.
2. **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, On the role of carbon additive in the hydrogenation and dehydrogenation of LiAlH₄, *Bulletin of the Catalysis Society of India* **5** (2006) 45-54.

3. **M. Helen, B. Viswanathan, L. Hima Kumar and S. Srinivasa Murthy**, Strategies for the design of membranes for fuel cells, *Photo/Electro chemistry and photobiology in the environmental Energy and Fuel* **5** (2006) 1-42.
4. **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, Catalytic effects in the generation of hydrogen from NaBH₄, *Bulletin of the Catalysis Society of India* **5** (2006) 94-100.
5. **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, Hydrogen absorption by Mg₂Ni prepared by polyol reduction, *Journal of alloys and compounds* (2007), doi:10.1016/j.jallcom.2007.07.028
6. **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, Dehydriding behaviour of LiAlH₄—the catalytic role of carbon nanofibers, *International Journal of Hydrogen Energy* **33** (2007) 366-373.

In National/International Conference

1. Alanates as hydrogen storage materials, **B. Viswanathan, L. Hima Kumar and S. Srinivasa Murthy**, Indo-Belarus workshop on ‘Advances in sorption based thermal devices’ held at Minsk, Belarus, Nov 2nd - 3rd, 2004.
2. Hydrogen generation from alkaline solution of sodium borohydride using cobalt based catalysts, **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, National workshop on ‘Catalysis for Energy’ held at Banaras Hindu University, Varanasi, India, Feb 23rd - 25th, 2006.
3. Dehydriding behaviour of LiAlH₄ – The catalytic role of carbon nanofibers, **L. Hima Kumar, B. Viswanathan and S. Srinivasa Murthy**, International Workshop on ‘Hydrogen Energy (Production, Storage and Application)’ held at Jaipur, India, Nov 5th - 9th, 2006.