ON THE ROLE OF CARBON ADDITIVE IN THE HYDROGENATION AND DEHYDROGENATION OF LiAlH$_4$

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The addition of carbon material has been shown to increase the hydrogenation and dehydrogenation kinetics of LiAlH$_4$. The enhancement of kinetics of these processes have been shown to be due facilitating of the transporting species by the transporting agent namely carbon.
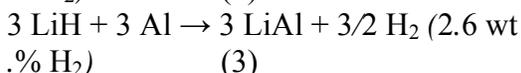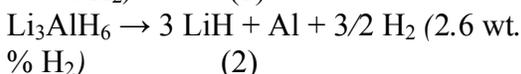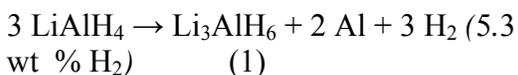
Introduction

In the pursuit of alternative energy sources, hydrogen was identified as one of the possible energy carriers. Hydrogen appears to be the choice, because of its uniqueness in terms of renewability, high energy density and environmental benignity. The technical challenges ahead of achieving hydrogen driven society include cost effective hydrogen production, storage and distribution. Hydrogen storage is a key enabling technology for the introduction of hydrogen economy and the extensive use of hydrogen as the energy carrier. Unfortunately this particular aspect of hydrogen economy has not yet reached maturity for adoption and exploitation by the society. So far the available methods for hydrogen storage have not yet become economical. Conventional methods of storage such as, high-pressure or cryogenic systems are impractical for vehicular applications due to safety concerns and volumetric constraints. This has prompted an extensive effort to develop solid hydrogen-storage systems for vehicular applications. Chemical storage of hydrogen in the form of metal hydrides is an attractive alternative; this has been the subject of a large number of investigations. The group I, II and III light elements, e.g. Li, Na, Mg, B, and Al build a large variety of metal hydrogen complexes. Aluminum-based complex metal hydrides, such as sodium and lithium aluminum hydrides (NaAlH$_4$ and LiAlH$_4$) attract considerable attention as potential high-capacity hydrogen storage media because of their hydrogen content reaches 7.4 and 10.5% by weight, respectively.

Bogdanovic and Schwickardi [1] reported the adsorption and desorption pressure-concentration isotherms for catalyzed NaAlH$_4$ at temperatures of 180 °C and 210 °C. The isotherms exhibit no hysterisis and a nearly horizontal plateau pressure region. Furthermore the catalyzed system reversibly absorbed and desorbed hydrogen up to 4.2 wt % and the mechanism of the two-step desorption reaction was delineated.. Following this, there have been efforts aimed at the utilization of NaAlH$_4$ and related hydrides with high gravimetric hydrogen storage capacity as practical hydrogen storage materials. Advancements have been made in accelerating the kinetics of solid state NaAlH$_4$ dehydrogenation and hydrogenation through modification by dopant compositions and processing conditions [1-8]. To date the main focus has been on NaAlH$_4$ although it does not

fully meet the DOE targets for gravimetric hydrogen storage density and thermodynamics. LiAlH$_4$, on the other hand, has a higher gravimetric hydrogen storage capacity. Thermodynamics allows hydrogen desorption at 1 bar pressure and at a temperature 100 ^{o}C. But LiAlH$_4$ has not yet been investigated as thoroughly as NaAlH$_4$. Its total hydrogen storage capacity is approximately 10.6 wt. % desorbed in a three-step decomposition reaction, as given in the reaction scheme:

3 LiAlH$_4$ → Li$_3$AlH$_6$ + 2 Al + 3 H$_2$ *(5.3 wt % H$_2$)*   (1)

Li$_3$AlH$_6$ → 3 LiH + Al + 3/2 H$_2$ *(2.6 wt. % H$_2$)*   (2)

3 LiH + 3 Al → 3 LiAl + 3/2 H$_2$ *(2.6 wt .% H$_2$)*   (3)

Both ball milling and doping with transition metals like V and Ti result in a lowering of the decomposition temperature of reactions (1) and (2). In the present study, the focus is on LiAlH$_4$ with carbon additives. Recent studies have demonstrated that co-milling metal hydrides with carbon improves the hydrogen sorption kinetics [9-13], suggesting that carbon plays a catalytic role. The purpose of this study is to improve the understanding on how additives, in particular carbon, affect the dehydrogenation kinetics of alanates.

Experimental methods

Lithium aluminum hydride, LiAlH$_4$ (purity 95% minimum, typically 97%), in powder form was purchased from Sigma-Aldrich. All material handling (including weighing and loading) was performed in a glove box with a carefully controlled atmosphere, with low oxygen and water vapour content.

Four different types of carbons, Vulcan XC72R (250 m^2 g^{-1}), Black Pearls 2000 (1500 m^2 g^{-1}), CDX 975 (240 m^2 g^{-1}) and Mesoporous carbon (1400 m^2 g^{-1}) were used as received.

2 g of LiAlH$_4$ was admixed with x wt% of carbon (x = 5, 7 and 9) by milling for 45 min in argon atmosphere. For X-ray diffraction (XRD) studies samples were prepared in the glove box. To avoid exposure to air, the samples were covered with Parafilm. The powder samples were characterized by X-ray diffractometry (Rigaku D/max 2400) with Cu Kα radiation. Isothermal dehydrogenation of LiAlH$_4$ was followed by volumetric measurement of the hydrogen evolved. In the glove box, typically 500 mg of sample was loaded in a stainless-steel reactor with suitable valves. The sample was heated to the desired isothermal operating temperature at a heating rate of 10 °C/min.

Results and Discussion:

For comparison, pure LiAlH$_4$ without any additive was milled for 45 min and the decomposition kinetics was followed at 130°C. XRD patterns obtained from the carbon (Black pearls 2000) admixed samples before and after complete dehydrogenation with that of pure LiAlH$_4$ are shown in Fig 1. All observed peaks in the diffraction pattern of the as-received LiAlH$_4$ could be indexed as belonging to a monoclinic unit cell (*P2$_1$/c*) with unit cell parameters a = 4.84, b= 7.82, c = 7.917. The diffraction pattern of the LiAlH$_4$ after milling with carbon for 45 min closely resembles that of the pure LAlH$_4$ as seen from Fig. 1. After complete dehydrogenation the diffraction pattern showed only peaks corresponding to Al. LiH may be present in amorphous form as a result of which

the peaks were not observed. This implies that complete desorption took place within three hours at 130 °C.

Dehydrogenation measurements:

Zaluska et al [14] reported the improvement in the absorption and desorption kinetics by the addition of carbon. The isothermal dehydrogenation kinetics of five different
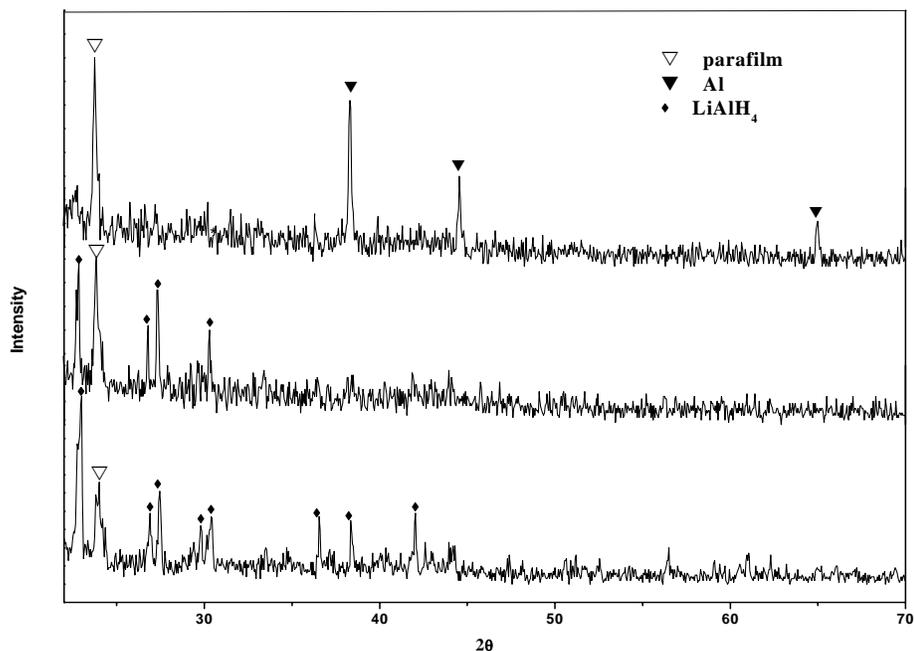

Fig. 1. X-ray diffraction patterns recorded on (a) as received LiAlH$_4$ (b) Black pearls 2000 admixed LiAlH$_4$ (before dehydrogenation) (c) Black pearls 2000 admixed LiAlH$_4$ (after dehydrogenation at 135 °C)

composite materials, all based on Lithium aluminum hydride which was mixed with different carbons (Vulcan XC72R, Black Pearls 2000, CDX 975 and Mesoporous carbon) are shown Fig 2. The curves were obtained by dehydrogenating the composites at 130 °C. For comparison the dehydrogenation kinetics of pure LiAlH$_4$ milled for 45 min, decomposed at the same temperature, 130 °C was included. It was observed that dehydrogenation kinetics improved considerably by addition of various carbon materials. The

enhancement is nearly 4-5 times for the Black Pearls BP 2000, CDX 975, Mesoporous carbon and ~2 times for the Vulcan XC-72R in comparison to pure LiAlH$_4$ (at 45 min). The profile of the Vulcan XC-72R/LiAlH$_4$ resembles the as received LiAlH$_4$ curve. On the other hand, the Black Pearls BP 2000, CDX 900, Mesoporous carbon containing composites give higher rates significantly altering the curve profile. It suggests that the reaction does not follow the same mechanism in all the cases. It follows
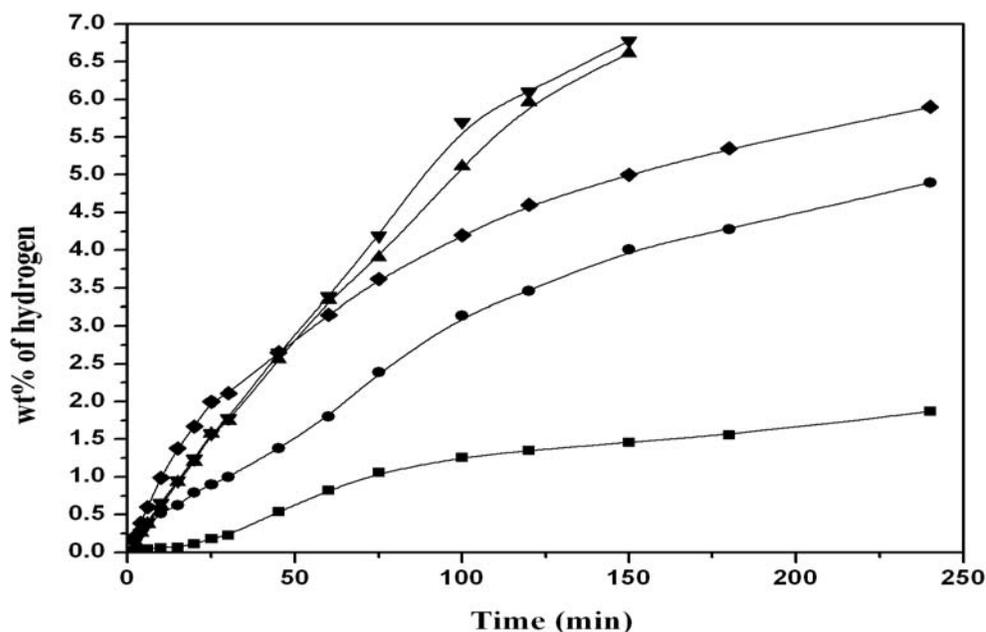
Fig 2 Dehydrogenation profiles for the (■) pure LiAlH$_4$ (●) 5 wt% Vulcan XC 72R admixed LiAlH$_4$ (♦) 5 wt% Mesoporous carbon admixed LiAlH$_4$ (▲) 5 wt% CDX 975 admixed LiAlH$_4$ (▼) Black pearls 2000 admixed LiAlH$_4$

different path in the case of Black Pearls BP 2000, CDX 975 and Mesoporous carbon admixed LiAlH$_4$. Among the four carbons, Black Pearls and CDX 975 shows high desorption kinetics. The rate is higher for the mesoporous carbon in the initial stages and drops down slowly. The surface area and dehydrogenation rates for the corresponding four carbons used are given in Table 1. The rate is not directly proportional to surface area of the carbon. The order of dehydriding reaction rate is Black Pearls ~ CDX > Mesoporous carbon > Vulcan XC72R. Hence the change in the rate cannot be solely attributed to the surface area of the carbon.

Table 1. Surface area and dehrogenation rate for various carbons

Carbon additive	Specific surface area (m^2 g^{-1})	Dehydrogenation rate (wt % min^{-1})
Black Pearls 2000	1500	0.053
Mesoporous carbon	1400	0.036
Vulcan XC72R	250	0.03
CDX 975	240	0.051

Differential thermal analysis revealed significant changes in the thermodynamic behavior of the carbon admixed Lithium aluminum hydride as compared to pure $LiAlH_4$. The thermochemical behavior of $LiAlH_4$ [14-16] was studied extensively and it is well known that the thermal decomposition of $LiAlH_4$ into Li_3AlH_6, H_2 and Al is exothermic, while the decomposition of Li_3AlH_6 into LiH and Al is endothermic. As shown in Fig. 3, the number of thermal events in the DSC trace of the carbon admixed $LiAlH_4$ between 50 and 250 °C is reduced to only one. An exothermic effect with a peak maximum at 150 °C which is considerably lower than that of pure $LiAlH_4$ was observed.
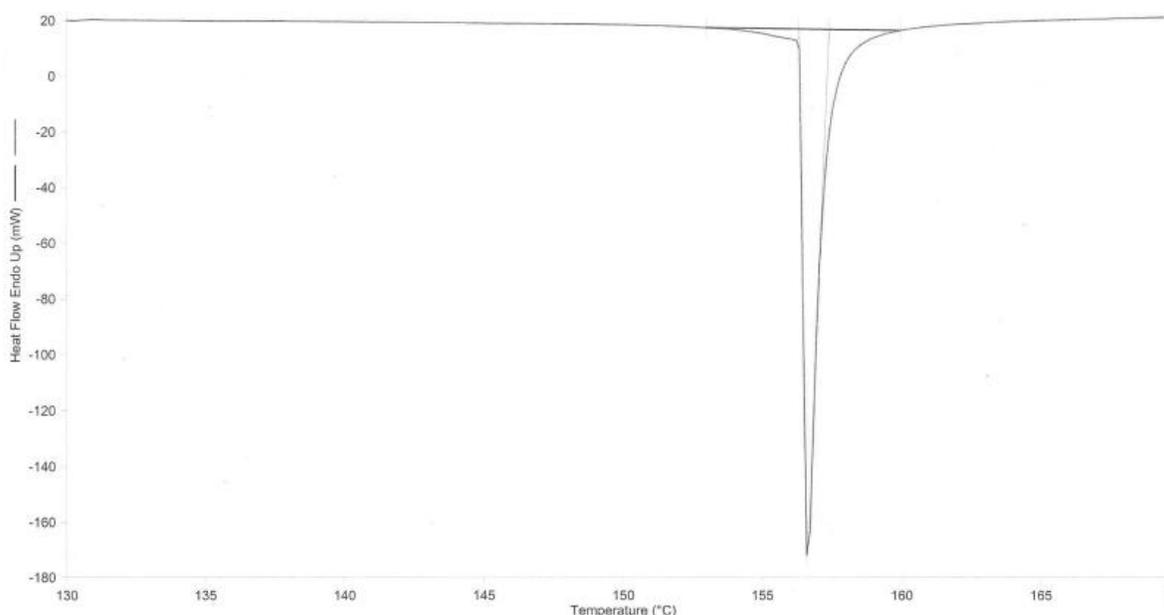

Fig. 3 DSC analysis of the 5 wt% Black pearls admixed $LiAlH_4$ at the heating rate of 5 °C/min.

The effect of temperature on the dehydrogenation kinetics of carbon admixed $LiAlH_4$ is shown in Fig 4. McCarthy et al. [17] reported apparent activation energy of ~100 kJ/mol for the reaction 1. For Black pearls 2000 admixed $LiAlH_4$ system the activation energy is found to be 56 kJ/mol. Chen et al. [18] investigated the dehydrogenation kinetics of $TiCl_3.1/3AlCl_3$ doped $LiAlH_4$. They found for the first step decomposition, the apparent activation energy to be 43 kJ/mol.

In order to find out the optimum level of mixing, dehydrogenation kinetics of $LiAlH_4$ with different amounts of carbon (3, 5, 7 and 9 wt %) was studied. With an increase in the carbon content the rate increases as shown in Fig. 5. 7 to 9 wt % of carbon is sufficient to produce the enhancement in the dehydrogenation kinetics of $LiAlH_4$; further increase in carbon amount may lead to decrease in the total hydrogen capacity by adding weight to material.
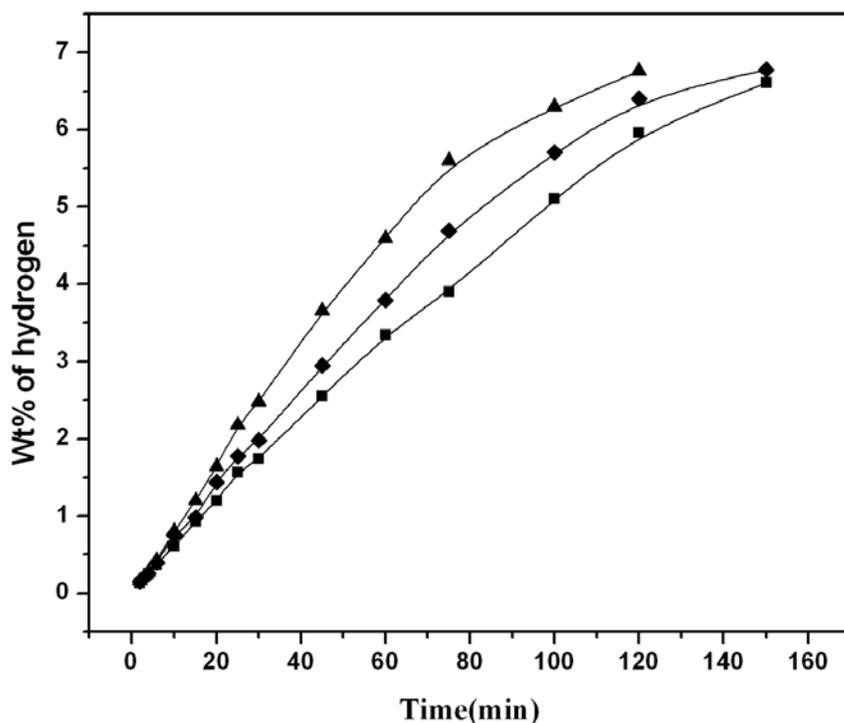
Fig. 4. Dehydrogenation kinetics of LiAlH₄ admixed with 5 wt% of Black Pearls 2000 admixed LiAlH₄ at (■) 135 °C (♦) 140 °C (▲) 145 °C

Role of carbon in the dehydrogenation kinetics of alanates:

The nature of the active catalyst species in transition metal doped alanates has been a subject of interest. There is speculation and controversy in this aspect. It was initially suggested that the remarkable enhancement of the hydrogen cycling kinetics in Ti-doped NaAlH₄ was due to surface-localized catalytic species consisting of titanium metal or a Ti–Al alloy [1- 3]. Alternatively, Sun et al reported the possibility of substitution of titanium into the hydride lattice [4]. Evidence for both the presence of a Ti–Al alloy in the doped hydride [5] and substitution of Ti into the bulk hydride lattice [4 and 6] was reported. However, neither a catalytically active Ti–Al alloy nor evidence for well characterized sites of lattice substitution have yet been obtained.

The results presented suggest that the grain/particle size and specific surface area of carbon are not the key factors that are responsible for the improved hydrogen storage properties of carbon admixed alanates. Pukazhselvan et al [11] investigated the effect of carbon nanotubes on the cycling behavior of NaAlH₄. But the reason for the enhancement in the kinetics was not clearly understood.
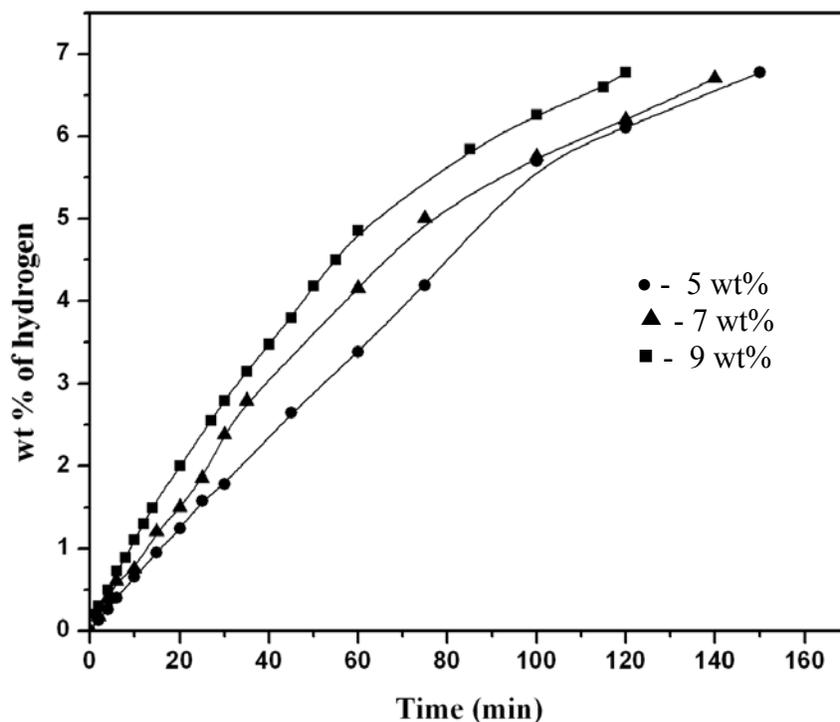
Fig.5. Dehydrogenation kinetics of LiAlH$_4$ admixed with different (5, 7 and 9) wt% of Black Pearls 2000

It is appropriate at this stage to summarize the observations and the postulates reported in literature on the effect of addition of carbon on the kinetics of hydrogenation and dehydrogenation of alanates.

The anxiety to modulate the adsorption and desorption process in alanate materials has led to a spate of studies involving additives especially carbon materials. These studies have thrown out a number of seemingly contradicting observations and postulates. These can be summarized as follows:

(i)   Imamura et al [19] observed that the active composites as hydrogen absorber are formed only when ground with benzene or THF or cyclohexane. The role of these organic additives as envisaged by them is to facilitate the fracture along the graphite layers thus enhancing the particle size reduction in magnesium with charge transfer. It is to be remarked the essentiality of the organic substrates has not been unambiguously re-established in subsequent studies.

(ii) Zaluska et al. [9] reported that NaAlH$_4$ or Na$_3$AlH$_6$ milled with carbon exhibited enhancement of kinetics of adsorption and desorption in terms of hydrogenation/dehydrogenation at lower pressures and temperatures (80°C) and faster kinetics. However, Shang and Guo [20] observed that addition of graphite

shows little influence on the desorption properties of MgH_2. However, according to them, addition of graphite favoured rapid rehydrogenation which is attributed to the interaction between the crystalline graphite with hydrogen dissociation close to the MgH_2 or Mg surface. They also postulated that the presence of graphite can inhibit the formation of oxide layer on the metallic particles.

(iii) Wang et al.[12] reported that co-doping of $NaAlH_4$ with Ti-graphite improved the kinetics of both the first and second reactions of the decomposition of alanates by decreasing the temperature of reaction as much as 15^oC compared to the system without the addition of graphite. The kinetics of the dehydrogenation reaction also increased by 3-6 times depending on the temperature of the reaction. The role of graphite has been postulated to be both a mixing agent manifested through lubrication (grapheme layer slippage and breakage) as well as a micro-grinding agent.

(iv) Dehouche et al [13]have examined the effect of addition of SWNT with Ti/Zr doped $NaAlH_4$ and observed fast adsorption/desorption kinetics. They postulated that the creation of new hydrogen transition sites might be the factor responsible for the observed increase of the kinetics of absorption/desorption process.

(v) Pukazhselvan et al.[11] showed that CNT admixed $NaAlH_4$ exhibited good rehydrogenation characteristics and also stated that 8 mol% CNT is the optimum material composition. The observed effects have been attributed to increased solid-gas surface area resulting from the presence of CNT.

(vi) Darok et al. [21] showed that the Mg thin film generated in presence of carbon contained lesser surface oxygen as compared to the thin film obtained from pure metal based targets. The presence of carbon (in other words lower oxygen content) facilitates the ex-situ hydrogenation of Mg based thin films. This observation agrees with the earlier observation of Shang and guo.

(vii) Huang et al. [22] reported that there is no significant difference in the hydrogen storage capacity, the composite containing graphite displayed remarkable decrease in the desorption temperature. This observation is in agreement with those of Wang et al. [12]

(viii) Recently Balde et al. [23] have stated that nano sized $NaAlH_4$ displayed improved hydrogen absorption and desorption characteristics compared to the bulk alanates.

Against this background let us evaluate the hydrogentiaon and dehysdrogenation behaviour of Li AlH_4 based on the results reported in this paper.

During the mechanical milling, the carbon materials may get incorporated into the hydride matrix resulting in an increase in the phase boundary. Also the nature of carbon fragments generated various sp hybridised valence forces. These hybridized orbitals can interact with hydrogen. In this sense these additives can be considered to provide a transition site for the hydrogen. More over the additives can have greater affinity for hydrogen compared to aluminum, thus destabilizing the Al-H bond. However, with transition metal additives, the tendency to form metal hydrides with hydrogen is probable, and hence the kinetics and storage capacity can be affected. The possibility of formation of TiH_2 while doping $NaAlH_4$ with Ti has been reported [6 and 7]. Further, the loss of catalytic activity of Ti species upon cycling [8] can be due to the formation of Titanium hydride. Theoretical studies [24] suggest that under the experimental conditions employed carbon cannot dissociate hydrogen while can bind with dissociated hydrogen and this facilitates the hydrogen sorption and desorption.. Since carbon is anisotropic with only weak van der Waals forces accounting the bonding interaction between the individual graphene layers, the layers tend to slide past one over other quite easily during the milling process. Therefore lithium aluminum hydride can be well dispersed with in the layers of carbon. Hence, the oxidation of hydride

surface and the agglomeration of Al during the dehydrogenation process can be prevented. This is another advantage of using carbon as catalyst. Similarly during the rehydrogenation process hydrogen molecule was adsorbed on the carbon surface and dissociated into active hydrogen atoms which will react with the LiH and Al to form alanates. Wang et al [12] studied the effect of graphite as a co dopant. Recently, Dehouche et al. [13] reported the effect of single walled nanotubes on cycling behavior of $NaAlH_4$. In both the cases it is observed that hydriding and dehydriding kinetics improved significantly by the addition of carbon in addition to Ti and Zr. The increase in the catalytic activity of transition metals upon co-doping with carbon is due to the formation of bridged species for the transport of active species between the alanate and the additive particles. The exact nature of this carbon layer which facilitates the transfer of hydrogen from the activating site to the storage site is not yet known. This is similar to hydrogen spill over promoted by water molecules. The model proposed in this communication needs further experimental support and it will be taken up in subsequent publication.

References:

1. B. Bogdanovic and M. Schwickardi, *J. Alloys Comp.* **253–254** (1997) 1

2. B. Bogdanovic, R.A. Brand, A. Marjanovic, M. Schwickardi and J. Tölle, *J. Alloys Comp.* **302** (2000) 36

3. K.J. Gross, G.J. Thomas and C.M. Jensen, *J. Alloys Comp.* **330–332** (2002) 683.

4. D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama and C.M. Jensen, *J. Alloys Comp.* **337** (2002) L8

5. B. Bogdanovic, M. Felderhoff, M. Germann, M. Härtel, A. Pommerin, F. Schüth, C. Weidenthaler and B. Zibrowius, *J. Alloys Comp.* **350** (2003) 246.

6. G. Sandrock, K. Gross and G. Thomas, *J. Alloys Comp.* **339** (2002) 299.

7. E. H. Majzoub and K. J. Gross, *J. Alloys Comp.* **356-357** (2003) 363.

8. Miesner G P, Tibbetts G G, Pinkerton F E, Olk C H and BaloghM P, *J. Alloys Compounds* **337** (2002) 254.

9. A. Zaluska, L. Zaluski, and J. O. Stro¨m-Olsen, *J. Alloys Compd.* **298** (2000) 125.

10. Imamura H, Tabata S, Shigetomi N, Takesue Y and Sakata Y, *J. Alloys Compd.* **330–332** (2002) 579.

11. D. Pukazhselvan, Bipin Kumar Gupta, Anchal Srivastava, O.N. Srivastava, *J. Alloys Compod. 403* (2005) 312

12. J. Wang, A. D. Ebner, T. Prozorov, R. Zidan and J. A. Ritter, *J. Alloys Compounds* 395 (2005) 252.

13. Z. Dehouche1, L. Lafi, N. Grimard, J. Goyette and R. Chahine, *Nanotechnology* **16** (2005) 402.

14. V.P. Balema, V.K. Pecharsky and K.W. Dennis, *J. Alloys Compd.* **313** (2000) 69.

15. J.A. Dilts and E.C. Ashby, *Inorg. Chem.* **11** (1972) (6) 1230.

16. T.N. Dymova, D.P. Aleksandrov, V.N. Konoplev, T.A. Silina and A.S. Sizareva, *Russ. J. Coord. Chem.* **20** (1994) (4) 279.

17. M. McCarthy, J.N. Maycook and V.R.P. Verneker Jr., *J. Phys. Chem.* **72** (1968) 4009

18. J. Chen, N. Kuriyama, Q. Xu, H.T. Takeshita and T. Sakai, *J. Phys. Chem. B* **105** (2001) 11214.

19. H.Imamura, Y.Takesue, T.Akimoto and S.Tabata, J.Alloys Compd., 293-295(1999)564.

20. C.X.Shang and Z.X.Guo, J.Power Sources, 129(2004)73.

21. X.Darok, A.Rougier, V.Bhat, L.Aymard, L.DuPont, L.Laffont and J.M.Tarascon, Thisn Solid films (2006)

22. Z.G.Huang, Z.P.Guo, A.Calka, D.Wexler and H.K.Liu, J.Alloys Compd., (2006)

23. C.P.Balde, B.P.C. Hereijgers, J.H.Bitter and K.P.Dejong, Angew.Chem.Int.Edn., 45 (2006)3501.

24. M.Sankaran and B.Viswanathan, Bull.Catal Soc India, 2 (2003) 9.