

# The effects of titanium precursors on hydriding properties of alanates

K.J. Gross\*, E.H. Majzoub, S.W. Spangler

Sandia National Laboratories, Analytical Material Science Department, P.O. Box 969, Livermore, CA 94550, USA

Received 3 September 2002; accepted 6 December 2002

## Abstract

An overview is presented of recent advances in the development of new and improved alanates for applications and in the fundamental understanding of how Ti-doping enhances hydrogen absorption. Sample materials were produced using approaches based on direct-synthesis and dry Ti-doping methods. It is desirable to introduce Ti through non-reactive processes to avoid the hydrogen capacity loss that occurs through the formation of inactive byproducts (for example Na-halide from the decomposition of Ti-halides and Na-oxides from the decomposition of Ti-alkoxides). We show, for the first time, that alanates can be Ti-doped using  $\text{TiH}_2$  or through indirect-doping by pre-reacting  $\text{TiCl}_2$  with LiH. Both methods result in enhanced kinetics. However, improved rates were achieved only after a prolonged activation period of about a 10 cycles, suggesting that cycling leads to Ti diffusion and substitution into the alanate lattice which provides the mechanism through which Ti-doping enhances kinetics. Thus, the reactive decomposition of Ti-halide and alkoxide precursors in the doping process serves an important but not necessarily required function.

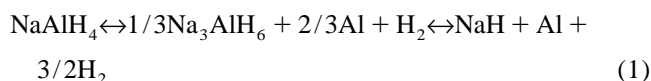
Published by Elsevier B.V.

**Keywords:** Alanates; Titanium precursors; Hydrogen absorption

## 1. Introduction

Ti-doped alanates offer an entirely new prospect for lightweight hydrogen storage [1]. These materials have nearly ideal equilibrium thermodynamics [2,3]. However, there is much room for improving both absorption and desorption kinetics, and the less than theoretical reversible capacities.

Unlike the interstitial intermetallic hydrides, the alanates release hydrogen through a series of decomposition–recombination reactions:



The two combined reactions give a theoretical reversible hydrogen storage capacity of 5.6 wt.%. However, the current state-of-the-art at reasonable charge and discharge rates is closer to 4 wt.%  $\text{H}_2$ . The pursuit of materials development for practical hydrogen storage applications has raised many questions about the fundamental mechanisms involved in hydrogen–alanate interactions. The

following is a brief look at both improvements in material performance and hints of the mechanisms underlying the enhanced reversibility.

The break-through discovery that doping  $\text{NaAlH}_4$  with Ti-compounds enhanced reversibility was reported by Bogdanovic' and Schwickardi in 1996 [1]. These studies were performed using a wet-synthesis method where  $\text{NaAlH}_4$  was doped with either  $\beta\text{-TiCl}_3$  or  $\text{Ti}(\text{Obu})_4$  in ether. This was followed by measurements on samples prepared by a doping method in which solid  $\text{NaAlH}_4$  was mechanically doped with  $\text{Ti}(\text{Obu}^n)_4$  and/or  $\text{Zr}(\text{OPr})_4$  (70 wt.% propanol solution) [4,5].

Our initial studies [2,6,7] were performed on Ti/Zr-alkoxide doped  $\text{NaAlH}_4$  (precipitated from THF) materials using the previously described preparation method [5]. We refer to this as *Generation I* materials. Since those initial studies, we have developed several new generations of materials with improved hydrogen storage properties. These include a dry-doping process of milling solid  $\text{NaAlH}_4$  (precipitated from THF) together with varying amounts of solid  $\text{TiCl}_3$ . The first measurements on these materials were reported by Sandrock and co-workers [8,9]. Dry-doping methods have also been suggested [3,10] and tested [11] by other researchers. Most recently we have developed solvent-free direct-synthesis methods in which Ti-dopants are milled directly together with NaH or Na

\*Corresponding author. Tel.: +1-925-294-4639; fax: +1-925-294-3410.

E-mail address: [kjgross@sandia.gov](mailto:kjgross@sandia.gov) (K.J. Gross).

and Al [12–14]. Such direct synthesis techniques have also been developed in parallel efforts by other research groups [15,16].

The following is a description of the various Ti-doped alanate materials that we have developed and for which some results will be presented in this paper:

*Generation II:* Solid  $\text{TiCl}_3$  doped  $\text{NaAlH}_4$  (precipitated from THF).

*Generation III-A:* Solid  $\text{TiCl}_3$  doped sodium alanates synthesized directly from NaH and Al by mechanical milling followed by hydrogen absorption at about 100 bar and 125 °C.

*Generation III-B:* Solid  $\text{TiCl}_3$  doped sodium aluminum hydrides and deuterides synthesized directly from Na metal and Al by mechanical milling followed by hydrogen absorption at about 100 bar and 125 °C.

*Generation III-C:* Solid Ti–halide ( $\text{TiCl}_2$ ,  $\text{TiF}_3$ , and  $\text{TiBr}_4$ ) doped sodium alanates synthesized directly from NaH and Al by mechanical milling followed by hydrogen absorption at about 100 bar and 125 °C.

*Generation III-D:* Indirectly Ti-doped sodium alanates synthesized by mechanical milling NaH, Al and solid  $\text{TiCl}_2$  that has been pre-reacted with LiH (by milling), followed by hydrogen absorption at about 100 bar and 125 °C.

*Generation III-E:* Sodium alanates synthesized directly from NaH and Al doped with  $\text{TiH}_2$  all mechanically-milled together followed by hydrogen absorption at about 100 bar and 125 °C.

These materials have demonstrated better hydrogen storage and delivery properties than materials produced using earlier methods. The direct synthesis method also

has the added advantage of producing materials without the use of solvents. The result is a hydrogen storage material that should be less expensive to produce and deliver hydrogen free of hydrocarbon impurities (Fig. 1).

## 2. Improved kinetics vs. capacity loss with increasing catalyst content

X-ray diffraction analysis has shown that  $\text{NaAlH}_4$  and  $\text{TiCl}_3$  react during the milling process to form NaCl (*Generation II*) [17]. Na-halides were also formed when using  $\text{TiF}_3$  and  $\text{TiCl}_2$  precursors (*Generation III-C*) [13]. The amount of  $\text{NaAlH}_4$  that is rendered inactive by decomposition into NaCl and Al increases with higher Ti-halide doping levels. Thus, the total reversible hydrogen capacity decreases as the Ti-halide doping level is increased [18]. The use of some Ti-halides other than  $\text{TiCl}_3$  results in an incremental increase in hydrogen capacity [12]. In the case of  $\text{TiCl}_2$ , this is due to a lowering of the relative content of the inactive NaCl component since only 2 moles of  $\text{NaAlH}_4$  are lost to form NaCl per mole of  $\text{TiCl}_2$  vs. 3 moles for  $\text{TiCl}_3$ . For  $\text{TiF}_3$ , on the other hand, the total capacity is slightly improved because NaF is lighter than NaCl. However, the use of these other halides solely to improve capacity will only have a significant benefit at higher doping levels (>4 mol.%).

The rates of hydrogen absorption and desorption are also strongly dependent on the level of catalyst doping [3,18]. It was found that the addition of even a minor amount (1 mol.%) of  $\text{TiCl}_3$  significantly reduced the activation energy of decomposition for both  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  [18]. The addition of more  $\text{TiCl}_3$  had no further effect on the activation energy. However, the rates of decomposition did continue to increase as the level of  $\text{TiCl}_3$  was increased. This was due to an increase in the pre-exponential factor  $k$  in the rate equation (Eq. (2))

$$\text{Rate} = k \exp(-Q/RT) \quad (2)$$

The desorption rates at 125° for  $\text{NaAlH}_4$  doped with 0.9, 2, 4, 6 and 9 mol.%  $\text{TiCl}_3$  (*Generation II*) are shown in Fig. 2 for both  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$ . Other Ti-halides show similar behavior [13], with the possible exception of  $\text{TiCl}_2$  which appears to nominally improve the desorption kinetics when compared to  $\text{TiCl}_3$ .

Thus, using Ti-halide precursors, presents a strong trade-off between improved kinetic performance and the reversible capacity loss as the level of Ti-doping is increased. Such considerations will impact the selection of material composition for any given hydrogen storage application. To overcome this penalty, we have begun to investigate Ti-dopants that reduce or avoid the creation of inactive reaction byproducts. These include  $\text{TiAl}_3$  [13], pre-reacted

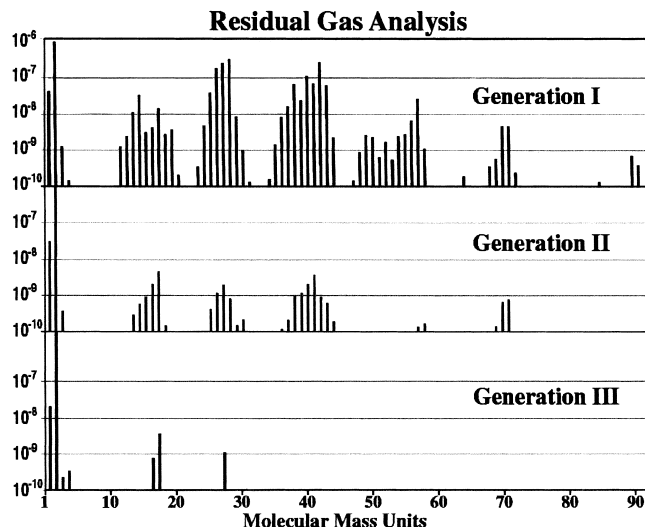


Fig. 1. Residual gas spectra from samples of Generation I, II and III materials (reproduced from Ref. [5]).

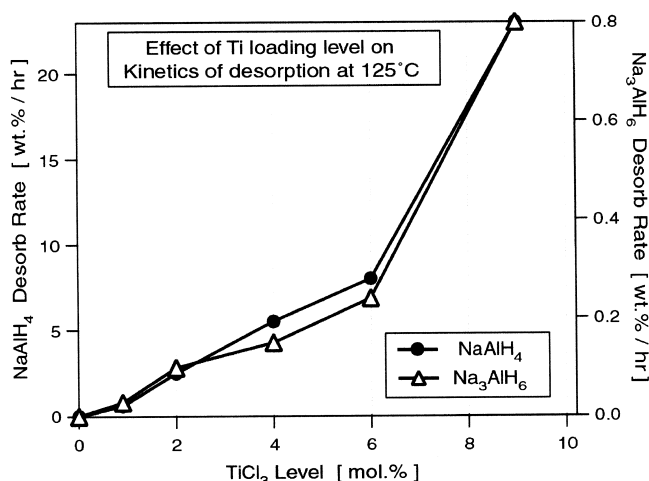


Fig. 2. Rates of hydrogen desorption as a function of  $\text{TiCl}_3$  content for the decompositions of  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$ .

$\text{TiCl}_2$ , and  $\text{TiH}_2$ . The present paper discusses some initial results obtained using these Ti-dopants.

### 3. Mechanisms of Ti-enhanced kinetics

It has been shown that many types of reactive-dopant-precursors including non-halide and non-titanium based compounds result in enhanced sorption kinetics [3]. However, the mechanism of the enhanced kinetics and, in particular, the advantage of Ti-based dopants has remained a mystery. Speculation has led many to question whether the valence state of the Ti in the catalyst-precursor plays any role. Reported X-ray measurements on lattice parameters of Ti-doped  $\text{NaAlH}_4$  seem to indicate that Ti is substituting in the lattice [19]. This model appears to be supported by electron spin resonance (ESR) studies conducted in collaboration with Denver University and the University of Hawaii [20]. These studies revealed the presence of  $\text{Ti}^{3+}$  in samples of  $\text{NaAlH}_4$  that were doped with both  $\text{TiCl}_3$  as well as the Ti(IV) precursor,  $\text{Ti}(\text{O}i\text{Bu})_4$ . While this hypothesis should be confirmed using a number of different experimental techniques, further insight has been gained into the mechanism by doping sodium alanate with Ti-halide catalyst-precursors of varying Ti valency such as  $\text{TiCl}_2$ ,  $\text{TiF}_3$ , and  $\text{TiBr}_4$  [13]. Arrhenius analysis of desorption rate data indicate that the kinetics of doped alanate are enhanced by all the Ti-halide catalyst-precursors tested (*Generation III-C*). Together, these results indicate that the halide component is important insofar as the large exothermic reaction of Ti-halide with NaH or  $\text{NaAlH}_4$ , forming Na-halide, is responsible for leaving Ti in a highly active state. The titanium resulting from these reactions may substitute into the alanate lattice and/or form other Ti-compounds. Favorable stoichiometry suggests that  $\text{TiAl}_3$  may form. This compound has been

observed in mechanical decomposition of both  $\text{LiAlH}_4$  [21] and  $\text{NaAlH}_4$  [13]. However, attempts to improve sorption kinetics of  $\text{NaAlH}_4$  by doping with  $\text{TiAl}_3$  demonstrated desorption rates that are significantly below those doped with Ti-halide [13]. Ti-alloys may simply provide a source of Ti for substitution, or the enhanced rates may be a combination of mechanisms involving Ti-alloys such as  $\text{TiAl}_3$  and Ti-substitution into the  $\text{NaAlH}_4$  structure.

## 4. Experimental details

### 4.1. Generation II materials

Crystalline  $\text{NaAlH}_4$  was made by cryopumping THF from a 1.0 M solution of  $\text{NaAlH}_4$  in THF (Sigma-Aldrich), followed by vacuum drying with a mechanical and/or turbomolecular pump. Mixtures of  $\text{NaAlH}_4$  and solid  $\text{TiCl}_3$  (99.999% Sigma-Aldrich) were weighed in a purified argon glovebox in the levels of 0.9, 2, 4, 6 and 9 mol.%  $\text{TiCl}_3$ . These mixtures were then ball-milled in argon for 3 h, using a high-energy SPEX mill and WC balls and milling vial. Samples were transferred from the milling pot to the reactor vessel in the Ar glovebox.

### 4.2. Generation III-A to III-E materials

Aluminum powder (~20 micron, 99+% Sigma-Aldrich), NaH 95% Sigma-Aldrich), and solid Ti-halides (Sigma-Aldrich) were weighed into appropriate proportions in a purified argon glovebox. These were then mixed and sealed under argon into a tungsten-carbide milling vial. These mixtures were then ball-milled in argon for 30 min–2 h, using a high-energy SPEX mill. The powder to ball weight ratio was approximately 10:1. After milling, about 1.5 g of the mixture was transferred (under argon) to a stainless steel reactor vessel with an internal volume of about 16 cm<sup>3</sup> and exposed to high purity (Matheson Trigas research purity 99.999%) hydrogen gas pressurized to between 80 and 100 atm while the steel reactor and its contents are heated externally to about 125 °C.

Dehydrogenating and hydriding rates and capacities were obtained volumetrically using a Sieverts' apparatus and a cylindrical 316 SS reactor containing 1.5–3 g of material. A thermocouple well in the center of the vessel allows for accurate temperature measurements during cycling. Desorption pressure changes were quantified with a 1000 Torr (1.3 atm) Baratron capacitance manometer. During absorption, the applied  $\text{H}_2$  pressure was generally in the 80–90 atm range, well above the 30–40 atm plateau pressure for  $\text{NaAlH}_4$  at 125 °C. For the desorption experiments, the back-pressure during  $\text{NaAlH}_4$  decomposition was kept below 0.5 atma, well below the  $\text{Na}_3\text{AlH}_6$  plateau pressure

of about 2 atma. Hydrogen capacity data are presented as wt.% with respect to the total sample weight, including the catalyst.

## 5. Results and discussion

### 5.1. Indirect Ti-doping

Our previous work raised questions about the importance of the Ti-halide to Na-halide decomposition reaction on the overall Ti-induced enhanced kinetics. For this reason, a sample was tested in which  $\text{TiCl}_2$  was pre-reacted with LiH by mechanical milling. The resulting powder was then milled in a 6 mol.% ratio with NaH and Al to form a pre-alanate mixture in which the Ti-halide had not been directly reacted with NaH (Generation III-D). From a mechanistic point-of-view, this method should indicate whether-or-not the Ti-halide and Na reaction is necessary for Ti-enhanced kinetics. From a practical perspective, this method may also provide an incremental improvement in capacity at higher doping levels due to the formation of the lighter LiCl byproduct rather than NaCl. The mixture was subjected to a series of hydriding/dehydriding cycles (Fig. 3). The measurements clearly show an activation process that is much more profound than in the direct Ti-halide doped materials. Thus, directly reacting Ti-halides with sodium (hydride or metal) is beneficial for initially rapid kinetics, but not necessary for long cycle-life materials.

Desorption rates for the decomposition of  $\text{NaAlH}_4$  were measured during the 14th cycle at different temperatures. This data is compared, on an Arrhenius plot (Fig. 4), with desorption data for  $\text{NaAlH}_4$  samples directly doped with

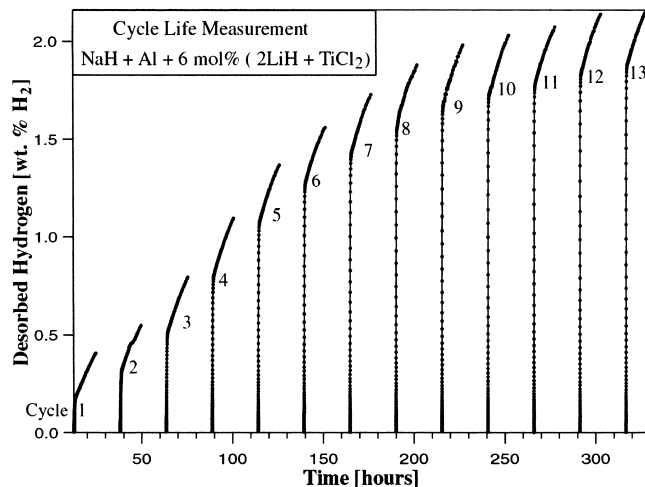


Fig. 3. Initial desorption cycles for a sample of Generation III-D alanates. Desorbed hydrogen given as wt.% with respect to the total sample mass.

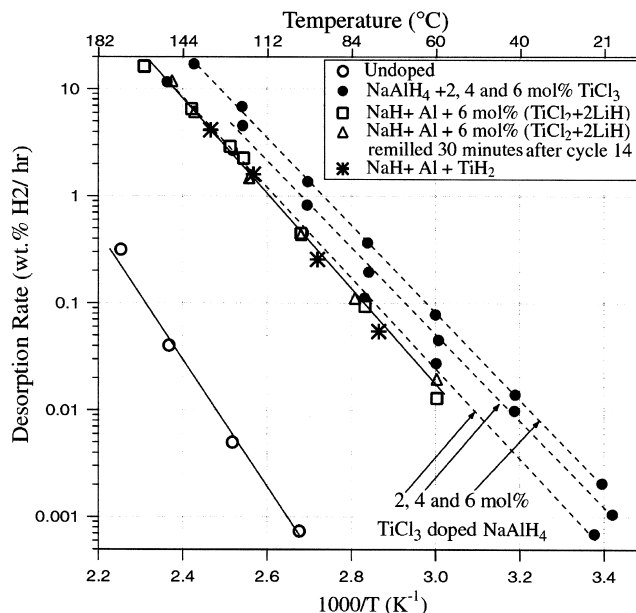


Fig. 4. Arrhenius plot comparing  $\text{NaAlH}_4$  desorption rates of Generation II, III-D, and III-E alanates (rates: II on a total weight basis, III-D and III-E on a NaH + Al weight basis).

varying levels of  $\text{TiCl}_3$  (generation II materials). In addition rate data is shown for the 18th cycle after the sample had been removed from the sample holder and re-milled following cycle 14. The slope of these plots indicates similar activation energies for both the direct and the indirect doping methods. The desorption rates are much greater than the undoped  $\text{NaAlH}_4$ . In fact, they are only just slightly lower than the 2 mol.%  $\text{TiCl}_3$  doped generation II alanates.  $\text{TiCl}_2$  was pre-reacted with LiH, not with NaH, suggesting that the free-Ti that is formed, diffuses and substitutes into the  $\text{NaAlH}_4$  lattice during the initial hydrogen absorption/desorption cycles. This could explain the enhanced activity that occurs with cycling (observed as an activation period in Fig. 3).

Such a doping mechanism would be expected to reach a level of Ti saturation in the host lattice. The kinetics appear to be stabilized by the 14th cycle at which point the Arrhenius data was taken. The rate data is very similar to the 1–2 mol.%  $\text{TiCl}_3$  generation II alanates even though the total Ti-loading of this sample was much higher (6 mol.%). In a previous study, it was also found that the activation energy of desorption was constant for  $\text{TiCl}_3$  levels  $>1$  mol.% [18]. The combination of these two observations points to the possibility that Ti reaches saturation in the host lattice at the 1–2 mol.% level.

A question that arises from the data of Fig. 4 is: why are the rates of this 6 mol.% indirect-Ti-doped sample not equivalent to the 6 mol.% direct-reaction  $\text{TiCl}_3$ -doped sample? Perhaps, Ti–Al phases are responsible for enhanced kinetics above the 1–2 mol.% Ti doping level.

Other measurements have shown that Ti–Al phases do provide a small increase performance [13]. One difference between this sample and the direct  $\text{TiCl}_3$ -doped sample, is that no Al was present during the  $\text{TiCl}_2$ –LiH reaction step of the preparation process. Thus, Ti–Al phases could only form during the non-reactive second step of the process when the pre-reacted  $\text{TiCl}_3$ –LiH mixture is milled together with NaH and Al, or possibly later during hydrogen cycling. However, these particular conditions may not be adequate for forming Ti–Al phases, and ultimately limit the kinetic enhancement to a Ti-saturation level of 1–2 mol.%. In addition, re-milling the sample (after cycle 14) also had no significant effect on the desorption rates. This is an indication that particle size and/or redistribution of the component phases are not responsible for the lower desorption rates, and probably not rate limiting factors. The less than desirable capacities are due to incomplete hydriding reactions.

An overall picture is emerging that leads to the hypothesis that a limited level (<2 mol.%) of Ti substitution into the  $\text{NaAlH}_4$  host lattice is responsible for the observed dramatic increase in desorption rates and the reduction in the desorption activation energy in the alanates. Further increases in kinetics are mainly due to changes in the pre-exponential factor which may be a secondary mechanism associated with the presence of Ti-compounds or Ti–Al alloys. Indeed, Ti–Al alloys acting as dehydrogenation catalysts were suggested early on [22]. Experiments using mixed Ti-halide/ $\text{TiAl}_3$  alloy catalysts are under way to test this hypothesis.

### 5.2. Doping with $\text{TiH}_2$

Extending the above notion that Ti-diffusion/substitution may be possible without using a Ti-halide or organic precursor, a sample was tested using only  $\text{TiH}_2$ . In this case, a mixture of NaH, Al, and  $\text{TiH}_2$  in a 1:1:1 composition was mechanically milled and tested for hydrogen absorption and desorption. This composition did absorb hydrogen (130 °C and 82 atm  $\text{H}_2$ ) to form  $\text{NaAlH}_4$ . Desorption rate measurements were then taken for the first cycle decomposition of  $\text{NaAlH}_4$ . This data is also shown on the Arrhenius plot of Fig. 4. Once again, the rates are nearly identical to those of the indirect doped material and the 2 mol.%  $\text{TiCl}_3$  doped alanates. This provides additional evidence that a strong Ti-precursor+alanate (or NaH) reaction is not required for the large initial improvement in kinetics. The consistent rates regardless of the total Ti content of the sample also supports the notion that this initial improvement is driven by Ti-substitution into the alanate lattice. It is reasonable then to assume that lower  $\text{TiH}_2$  contents will provide the same improvement in kinetics after some activation period. From an applications perspective,  $\text{TiH}_2$  as a dopant precursor should overcome

the problem of capacity loss associated with the use of Ti-halides.

## 6. Conclusion

The development of advanced sodium alanates with the goal achieving a viable hydrogen storage material has shown steady progress [23]. Several new generations of materials with modified approaches to synthesis and doping have produced significant improvements in: (1) the purity of the delivered hydrogen gas; (2) the relative ease and the cost of synthesis; (3) the kinetics of hydrogen absorption and desorption; and (4) the reversible hydrogen storage capacity. Currently  $\text{TiCl}_3$  doped materials store over 4 wt.%  $\text{H}_2$  and initially deliver a desorption rate in excess of 10 wt.%/h at 125 °C. For Ti–halide precursors, the kinetics improve as the doping level is increased, but at the expense of the total hydrogen capacity due to Na–halide formation. The enhanced kinetics are relatively independent of which Ti–halide precursor is used, with the possible exception of  $\text{TiCl}_2$ , which shows a nominal improvement in both capacity and kinetics.

These advances have helped to stimulate a number of fundamental questions concerning the mechanisms by which Ti-doping enhances both absorption and desorption kinetics. In particular, we have examined the importance of reactive-doping (reacting Ti–halide or alkoxide precursors with  $\text{NaAlH}_4$ , NaH, or Na) on the performance of the alanates. Indirect doping with  $\text{TiCl}_2$  pre-reacted with LiH demonstrated enhanced kinetics only after a prolonged activation period. However, the desorption rates were equivalent to those of samples direct reactively-doped with 1–2 mol.%  $\text{TiCl}_3$ . Doping with large amounts of the non-halide precursors,  $\text{TiH}_2$ , also demonstrated identical kinetics. These results support the suggestion that Ti-substitution in the  $\text{NaAlH}_4$  lattice [19] is responsible for enhanced kinetics and implies a Ti-substitution limit at the 1–2 mol.% level.

An overall picture is emerging which may involve heterogeneous mechanisms for enhanced kinetics involving both Ti lattice substitution and the presence of Ti–Al phases. Finally, these results show that halide or alkoxide-based reactive precursors are not required for Ti-doping. This opens up the possibility of new alanate hydrogen storage materials that do not suffer the capacity loss associated with Na–halide or oxide formation.

## Acknowledgements

This work was funded by the US Department of Energy, Office of Power Technologies, Hydrogen Program Office under contract No. DE-AC36-83Ch10093. The authors thank Scott Spangler for in situ XRD measurements,

Andres Orozco for sample preparation, and Ken Stewart for help in developing experimental equipment.

## References

- [1] B. Bogdanovic', M. Schwickardi, *J. Alloys Comp.* 253 (1997) 1.
- [2] K.J. Gross, G.J. Thomas, G. Sandrock, Hydride development for hydrogen storage, Proceedings of the US DOE Hydrogen Program Review, NREL/CP-570-26938,452, Baltimore, MD, 2000.
- [3] B. Bogdanovic', R.A. Brand, A. Marjanovic', M. Schwickardi, J. Tölle, *J. Alloys Comp.* 302 (2000) 36.
- [4] C.M. Jensen, R.A. Zidan, N. Mariels, A.G. Hee, C. Hagen, *Int. J. Hydrogen Energy* 24 (1999) 461.
- [5] R.A. Zidan, S. Takara, A.G. Hee, C.M. Jensen, *J. Alloys Comp.* 285 (1999) 119.
- [6] G.J. Thomas, S.E. Guthrie, K. Gross, Hydride development for hydrogen storage, Proceedings of the US DOE Hydrogen Program Review NREL/CP-570-26938, San Ramon, CA, 1999.
- [7] K.J. Gross, S. Guthrie, S. Takara, G.J. Thomas, *J. Alloys Comp.* 297 (2000) 270.
- [8] G. Sandrock, K. Gross, G. Thomas, C. Jensen, D. Meeker, S. Takara, *J. Alloys Comp.* 330–332 (2002) 696.
- [9] K.J. Gross, G.J. Thomas, E. Majzoub, G. Sandrock, Light-weight Hydride Development, Proceedings of the US DOE Hydrogen Program Review, NREL/CP-570-30535, San Ramon, CA, 2001.
- [10] B. Bogdanovic' et al., 2000 US Patent 6,106,801.
- [11] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, *J. Alloys Comp.* 298 (2000) 125.
- [12] K.J. Gross, E. Majzoub, G.J. Thomas, G. Sandrock, Hydride development for hydrogen storage, Proceedings of the US DOE Hydrogen Program Review, NREL/CP-610-32405, Golden, CO, 2002.
- [13] E.H. Majzoub, K.J. Gross, in: A. Percheron-Guégan (Ed.), Titanium–Halide Catalyst-Precursors in Sodium Aluminum Hydrides, Proceedings of the International Symposium on Metal Hydrogen Systems, Annecy, France, September 2–6, 2002.
- [14] US Patent Application, S.N. 10/066,375, (January 29, 2002).
- [15] B. Bogdanovic', M. Schwickardi, *Appl. Phys. A* 72 (2001) 221.
- [16] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, *Appl. Phys. A* 72 (2001) 157.
- [17] K.J. Gross, G. Sandrock, G.J. Thomas, *J. Alloys Comp.* 330–332 (2002) 691.
- [18] G. Sandrock, K. Gross, G. Thomas, *J. Alloys Comp.* 339 (2002) 299.
- [19] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, C.M. Jensen, *J. Alloys Comp.* 337 (2002) 8.
- [20] S. Eaton, K.J. Gross, E.H. Majzoub, K. Murphy, C.M. Jensen, *Chem. Commun.* (submitted).
- [21] V.P. Balema, J.W. Wiench, K.W. Dennis, M. Pruski, V. Pecharsky, *J. Alloys Comp.* 329 (2001) 108.
- [22] A.J. Maeland, B.C. Hauback, H. Fjellvag, M. Sørby, *Int. J. Hydrogen Energy* 24 (1999) 163.
- [23] B. Bogdanovic', G. Sandrock, *MRS Bull.* 27 (9) (2002) 712.