



# Advanced materials for solid state hydrogen storage: “Thermal engineering issues”



S. Srinivasa Murthy<sup>a,\*</sup>, E. Anil Kumar<sup>b</sup>

<sup>a</sup>Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

<sup>b</sup>Discipline of Mechanical Engineering, Indian Institute of Technology Indore, Indore 453446, India

## HIGHLIGHTS

- Advanced materials suitable for solid state hydrogen storage are discussed.
- Issues related to thermodynamic and thermo-physical properties of hydriding materials are brought out.
- Hydriding and dehydriding behavior including sorption kinetics of complex hydrides with emphasis on alanates are explained.

## ARTICLE INFO

### Article history:

Received 20 December 2013

Received in revised form

26 March 2014

Accepted 10 April 2014

Available online 2 May 2014

### Keywords:

Solid state hydrogen storage

Physisorption

Chemisorption

Alanates

Complex hydrides

Thermo-physical properties

## ABSTRACT

Hydrogen has been widely recognized as the “Energy Carrier” of the future. Efficient, reliable, economical and safe storage and delivery of hydrogen form important aspects in achieving success of the “Hydrogen Economy”. Gravimetric and volumetric storage capacities become important when one considers portable and mobile applications of hydrogen. In the case of solid state hydrogen storage, the gas is reversibly embedded (by physisorption and/or chemisorption) in a solid matrix. A wide variety of materials such as intermetallics, physisorbents, complex hydrides/alanates, metal organic frameworks, etc. have been investigated as possible storage media. This paper discusses the feasibility of lithium– and sodium–aluminum hydrides with emphasis on their thermodynamic and thermo-physical properties. Drawbacks such as poor heat transfer characteristics and poor kinetics demand special attention to the thermal design of solid state storage devices.

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## 1. Introduction

Depletion of fossil fuels and the increased awareness of their negative ecological impacts have necessitated the need for environmentally benign alternatives. Characterized by its high gravimetric energy content and clean conversion, hydrogen is considered as a very promising alternative. Cost effective, efficient and safe means of storage and delivery of hydrogen is essential to make this a reality.

Hydrogen in compressed, liquefied or solid state is the possible means of storage. Compressing hydrogen to very high pressures (about 700 bar) or liquefaction at cryogenic temperatures (20 K) present several safety and design challenges [1,2]. Hence, solid state

hydrogen storage emerged as a safe and viable alternative, especially for mobile and portable applications.

Hydrogen can be physisorbed by sorbents such as porous carbon and zeolite, whereas metal hydrides and complex hydrides can store hydrogen through chemisorption and chemical reaction respectively. Important requirements for potential applications include high storage capacity, low cost, favorable operating temperatures and pressures, low hysteresis, easy activation, high cyclability, low density and low specific heat. Intermetallics and complex hydrides can be used to store hydrogen reversibly at their respective operating conditions, with suitable techniques for heat transfer enhancement. The DoE (USA) targets for on-board hydrogen storage in automobiles is given in Table 1 [3].

Intermetallics like LaNi<sub>5</sub> are easily reversible at moderate temperatures and pressures and exhibit fast sorption kinetics. However, they are characterized by poor gravimetric storage capacity (1.5–2.5 wt.%). Table 2 shows the comparison of the gravimetric storage capacity of some intermetallic hydrides [4]. High capacity hydrides like MgH<sub>2</sub>, are reversible only at temperatures above

\* Corresponding author. Fax: +91 44 2257 0545/4652.

E-mail addresses: [ssmurthy@iitm.ac.in](mailto:ssmurthy@iitm.ac.in), [ssmurthy.iitm@gmail.com](mailto:ssmurthy.iitm@gmail.com) (S. Srinivasa Murthy).

**Table 1**  
DOE targets for on-board hydrogen storage for automobiles [3].

Storage parameter	Units	2017 goals	Ultimate
System gravimetric capacity	%	5.5	7.5
System volumetric capacity	kg H <sub>2</sub> /L system	0.04	0.07
Operating temperature	°C	40/60	40/60
Operational cycle life	Cycles	1500	1500
System fill time (5 kg)	Min	3.3	2.5

250 °C [5] i.e., beyond the optimum temperature range of operation for PEM fuel cells (~80 °C) [6]. High density and cost of the reversible low temperature hydrides also limit their practical usability. The volume change associated with these hydrides during absorption and desorption cycles are also higher than complex hydrides [7]. With inherent low thermal conductivity of hydrogen storage materials, heat transfer is often the major rate limiting parameter [8–10]. Temperature of the storage bed has a significant impact on the reaction rate. Minimizing of refueling time is an important objective in the development of mobile hydrogen storage devices. Appropriate temperature levels need to be maintained in the storage bed so as to get maximum sorption performance. Excess cooling and overheating of the bed lead to poor sorption performance [11,12]. The initial reaction rate is a characteristic of the material used while the later reaction is controlled by heat transfer [13]. It has been observed that absorption reaction commences from cooler regions of the storage bed, normally near to heat exchanger surfaces [9]. A metal hydride reactor embedded with multi tubular heat exchanger previously reported by the author, improved sorption kinetics by enhancing heat transfer within the bed [11]. Major developments in metal hydride based hydrogen storage were recently reviewed by this author [14].

## 2. Complex hydrides

Complex hydrides, mostly alانات or borates of lithium, sodium and potassium have hydrogen retaining capacity up to 18 wt.%. These hydrides based on sodium and lithium store 7.4 wt.% and 10.5 wt.% respectively [15] while borates like sodium borohydride and lithium borohydride have higher theoretical storage capacities of 10.4 wt.% [16] and 18 wt.% [17] respectively. Their high hydrogen content, lower weight and lesser costs make them attractive for portable and mobile applications. However, their low thermal conductivity and high heat of reaction limits their application in practical systems. They also decompose in a multi-step reaction at high temperatures and pressures, exhibiting slow kinetics and poor reversibility. LiAlH<sub>4</sub> can be easily dehydrogenated in a three step reaction similar to NaAlH<sub>4</sub>, but its hydrogenation occurs at very high pressures [15]. The third dissociation step of sodium and lithium alانات occurs at temperatures 425 °C and 680 °C respectively [15,18,19], which is beyond the desired temperature range for practical hydrogen storage applications. LiBH<sub>4</sub> can reversibly store over 8 wt.% hydrogen at temperatures above 325 °C with magnesium additives and Titanium based catalysts [20].

**Table 2**  
Hydrogen storage capacity of some metal hydrides [4].

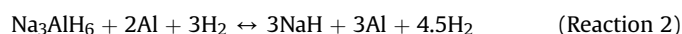
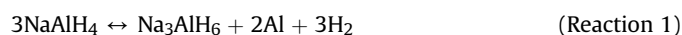
Material	Capacity in wt. % of H <sub>2</sub>	Material	Capacity in wt. % of H <sub>2</sub>
LaNi <sub>5</sub>	1.49	ZrCr <sub>2</sub>	1.82
MmNi <sub>5</sub>	1.46	Ca	4.8
Ti	4.0	CaNi <sub>5</sub>	1.87
TiFe	1.86	CeNi <sub>5</sub>	1.5
TiCr <sub>1.8</sub>	2.43	Mg	7.66
Zr	2.2	MgNi	3.6
ZrMn <sub>2</sub>	1.77	Mg + 2 wt.% Ni	7.48

Desorption of the compound at low temperature is negligible (0.3 wt.%). Another complex hydride, Lithium nitride (Li<sub>3</sub>N) releases most part of its capacity only above 230 °C [19]. Mixtures of such hydrides have been tried by different investigators to improve the overall sorption characteristics [21–24]. Among different mixtures of LiAlH<sub>4</sub> and LiBH<sub>4</sub>, 2:1 ratio specimen exhibited a maximum desorption of 6.6 wt.% H<sub>2</sub> in the presence of TiCl<sub>3</sub> catalyst precursor at temperatures below 220 °C [25].

In this paper thermodynamic properties, modeling of kinetics, measurement of thermophysical properties of Alانات are reviewed. Heat and mass transfer characteristics, Numerical Simulation, Design optimization of hydrogen storage devices (with NaAlH<sub>4</sub>) are discussed.

### 2.1. Sodium aluminum hydride

Asby et al. [26,27], were one of the earliest to synthesize sodium aluminum hydride and study its sorption characteristics. Sodium aluminum hydride, NaAlH<sub>4</sub> decomposes into sodium hexahydride (Na<sub>3</sub>AlH<sub>6</sub>) and aluminum, accompanied with evolution of hydrogen in the first step. In the second step Na<sub>3</sub>AlH<sub>6</sub> decomposes into sodium hydride (NaH), aluminum metal and hydrogen at elevated temperatures and pressures [28]. Dehydrogenation returns the crystalline alانات [29]. These are shown in the following reactions:



The first and second reactions release 3.70 wt.% and 1.85 wt.% of H<sub>2</sub> respectively. Sodium alانات, in its pure form takes nearly 22 h to attain saturation at 200 °C and much slower at lower temperatures. The rate of reaction is almost negligible at 160 °C. The studies also revealed the effect of Titanium doping in sodium alانات. Ti doping was found to increase the sorption kinetics drastically, simultaneously improving cyclability and storage capacity. Addition of catalysts in small amounts remarkably improved its sorption performance [30]. These results generated greater interest in the development of complex hydrides for portable applications. Jensen et al. [31] reported that significant decomposition of neat alانات occurs only above the melting point of the material at 183 °C, while melting of the material doesn't affect the reaction kinetics [7]. Several studies were conducted subsequently to understand modified kinetics and dopant action in the lattice. Considering the favorable operating conditions and available thermodynamic data, sodium alانات can be used for practical hydrogen storage applications. Moreover, alانات can be produced in laboratory scale from NaH and aluminum powder with aluminum reduced TiCl<sub>3</sub> [32].

#### 2.1.1. Role of catalyst

It is well established that catalysts improve the sorption kinetics drastically. The above mentioned reactions of the sodium alانات at 200 °C were completed within an hour when doped with 2 mol% of Ti(OBu)<sub>4</sub> precursors [30]. Characteristic fast and slow kinetic regimes were observed in the desorption curve indicates the two step reaction [33]. It has been confirmed by different studies that the addition of Titanium as catalyst enhances the sorption capacity and improves reversibility under moderate conditions while maintaining important thermodynamic properties [6,15,30,31,33–37]. Zidan et al. [35] confirmed superior decomposition of Ti/Zr doped Sodium alانات below 100 °C. Addition of catalysts into pure alانات in any manner decreases dehydrogenation temperature and enhances kinetics [38].

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