Thermal conductivity and specific heat measurements of metal hydrides

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ABSTRACT

There are extensive efforts underway worldwide to develop inexpensive and practical hydrogen storage materials for the implementation of a hydrogen-based energy economy. Metal hydrides are leading candidates for hydrogen storage applications because they are solid at room temperature and release hydrogen on demand when heated. HSM systems Inc. has developed a practical hydrogen storage system in which the metal hydride is housed in a sealed stainless-steel vessel. Hydrogen is generated by simply heating the enclosed metal hydride. It is important to understand the thermal response of the metal hydride as it is heated to determine when and at what rate the hydrogen will be released. Heat transfer can be modeled with the appropriate knowledge of the vessel's geometry, composition and intrinsic thermal characteristics (i.e. thermal conductivity and specific heat). Although the thermal properties of stainless steel are well known, those of metal hydrides are poorly characterized. This paper presents a simple and efficient measurement technique for determining the thermal conductivity and the specific heat of metal hydrides. Since practical hydrogen storage applications will likely involve the use of compacted powders, the thermal conductivity of both powdered and pressed pellets of select metal hydrides have been determined; namely:

- $NaAlH_4$ powder/compressed pellet
- $NaAlH_4$ + 2% $TiCl_3$ powder/compressed pellet
- $LiAlH_4$ powder/compressed pellet
- $LiNH_2$+2LiH powder/compressed pellet
- 7:1 MgH_2:$LiBH_4$ + 1 % $TiCl_3$ powder/compressed pellet

The thermal conductivity of each sample has been measured via the modified transient plane source technique. Specific heat measurements have been made using differential scanning calorimetry (DSC).

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INTRODUCTION

There are extensive efforts underway worldwide to develop inexpensive and practical hydrogen storage materials for the implementation of a hydrogen-based energy economy. Metal hydrides are leading candidates for hydrogen storage applications and offer many advantages compared to compressed hydrogen; for example, metal hydrides are solid are room temperature, can be stored at low pressure, and release high purity hydrogen simply by heating. A suitable hydrogen storage material must satisfy many requirements, including high gravimetric hydrogen content (>5%); fast hydrogen adsorption/desorption kinetics; practical adsorption/desorption conditions (i.e. low pressure/temperature); and economic feasibility. Several metal hydride-based systems, such as $NaAlH_4$, $NaAlH_4$ + 2 % $TiCl_3$, $LiAlH_4$, $LiNH_2$ + 2LIH and 7:1 MgH_2:$LiBH_4$ + 1 % $TiCl_3$ (i.e. those presented here) satisfy these requirements, and have been studied extensively in the literature [1-9]. Once a suitable metal hydride has been identified, an appropriate vessel must be designed so the material can be used in a real-world application. The vessel must isolate the highly reactive hydride from environmental contaminations (i.e. moisture and atmosphere), while being able to withstand the temperatures and pressures associated with the release and buildup of hydrogen gas. Sodium alanate ($NaAlH_4$) has been identified as a hydrogen storage material that satisfies all of the requirements outlined above, and HSM systems Inc. (Fredericton, New Brunswick, Canada) has pioneered efforts to commercialize $NaAlH_4$-based metal hydrides for portable hydrogen storage applications. The prototype design consists of catalyzed $NaAlH_4$ powder, which is compressed into rods and contained in a stainless steel vessel. The vessel can operate at pressures in excess of 100 bar and temperatures up to 400 ^{o}C.

The vessel is designed for multiple hydrogen release and uptake cycles. To release hydrogen, the unit is heated by an onboard heating element and forced hot air convection. The heating rate and temperature can be varied to release hydrogen at a controlled rate, which is determined by the operating temperature and the thermal characteristics of the vessel and metal hydride. Although the thermal characteristics of stainless steel are well known, those of $NaAlH_4$ and the other hydrides listed above are poorly defined. It is crucial to know the thermal response of these metal hydrides in order to understand and control how they behave in real-world applications. This paper outlines the measurement of the specific heat and thermal conductivity of several leading metal hydride systems for hydrogen storage applications. The values obtained are useful for modeling the thermal response of the metal hydrides in applications such as that described above.

EXPERIMENTAL

Thermal conductivity measurements were performed using the modified transient plane source technique employed by the C-Therm TCi Thermal Conductivity Analyzer. The TCi system is comprised of an external sensor, control electronics and computer software. The sensor includes a central heater/sensor element in the shape of a spiral surrounded by a guard ring. The guard ring generates heat in addition to the spiral heater, approximating a one-dimensional heat flow from the sensor into the sample under test in contact with the sensor [10]. The difference between this configuration and the traditional hot-wire or transient plane source method is that the central heater and guard ring are supported on a backing material, which provides mechanical support, electrical insulation, and thermal insulation which enable a one-sided interfacial measurement and greatly enhance flexibility. The external sensor is rated from -50 to +200 deg C and is sealed so that it can test solid, liquids, powders and pastes – making it ideal for testing of metal hydride materials in various forms and environments.

The sample is tested by placing it in intimate contact with the heating element of the sensor for a specific length of time (typically 0.8 seconds). A known current is applied to the sensor's heating element, providing a small amount of heat. This results in a rise in temperature at the interface between the sensor and the sample – typically less than 2 ºC. This temperature rise at the interface induces a change in the voltage drop of the sensor element. A typical voltage data chart is displayed in Figure 1 [11]. The slope of the voltage time chart is inversely proportional to the thermal conductivity of the sample material. The TCi is factory-calibrated with known standards across a thermal conductivity range of 0 to 100 W/mK for powders, liquids, foams, polymers, ceramics and metals.

Due to the reactive nature of metal hydrides with environmental contaminants (e.g. H_2 and H_2O), thermal conductivity measurements were made within an inert atmosphere glove box (MBraun Labmaster 130 with automatic regenerable oxygen and moisture purifier units). The thermal conductivity sensor and accessories were introduced into the glove box via an evacuable antechamber. One of the glove ports was then capped and the glove removed. A small hole was cut in the finger of a sacrificial glove, and the cable connecting the sensor to the control box was fed through the finger hole. A hose clamp was installed around the cable/finger to seal the breakthrough. The glove was then placed on the vacant glove port and the cable connected to the sensor. This setup allows air-sensitive materials - such as metal hydrides - to be measured in an inert atmosphere. Refer to Figure 2 for an image of the instrument - in use - in the glovebox.

Disc shaped metal hydride pellets were compressed to 6 Tons using a hydraulic press and die. Specific heat measurements were recorded in the temperature range 10-50 °C using a Setaram MicroDSC III Evo (a Calvet calorimeter). Samples were sealed in a standard stainless steel cell in the nitrogen-filled glovebox environment. Data were collected using a two run method (sample and blank runs), with a heating rate of 0.5 °C/min. Calisto software (AKTS) was used to analyze the data and determine specific heat values. Thermal conductivity and specific heat measurements were confirmed using independent instruments at Dalhousie University.

RESULTS

Thermal conductivity measurements of $NaAlH_4$, $NaAlH_4$ + 2% $TiCl_3$, $LiAlH_4$, $LiNH_2$+2LiH, 7:1 MgH_2:$LiBH_4$ + 1 % $TiCl_3$ (powder and compressed pellets) are presented in Table 1, along with specific heat (C_p) measurements of $NaAlH_4$ (powder), $LiAlH_4$ (powder) and $LiNH_2$+2LiH (powder). The $NaAlH_4$ and $LiAlH_4$ C_p values measured in this study agree well with previous results. The specific heat of $NaAlH_4$ was measure by Bonnetot et. al. [12]. They report a C_p value of 85.51 J/K·mole, compared to 86.24 J/K·mole as reported in Table 1. The CRC [13] reports a C_p value for a $LiAlH_4$ as 83.2 J/K·mole compared to 84.2 J/K·mole as reported in Table 1. To the authors' knowledge there are no published values for the other systems studied here. A graph of the thermal conductivity of pressed vs. powdered metal hydride samples is given in Figure 3. The pressed samples have much higher thermal conductivities, as expected. Pressed metal hydrides may be better suited for certain hydrogen storage applications due to their higher thermally conductive.

MODELLING

The specific details of the techniques used to model heat transfer in real-world applications are beyond the scope of this dissertation. It is sufficient to say that thermal conductivity and specific heat values are integral components of the heat transfer modeling process. As an example, HSM Systems used finite-element heat transfer software in conjunction with Cosmos and SolidWorks (3D mechanical engineering computer assisted design (CAD) software) to model heat flow through the metal hydride hydrogen storage vessel. An example of the vessel design schematic (created using SolidWorks) is presented in Figure 4.

CONCLUSIONS

The thermal conductivity of $NaAlH_4$, $NaAlH_4$ + 2 % $TiCl_3$, $LiAlH_4$, $LiNH_2$ + 2LIH and 7:1 MgH_2:$LiBH_4$ + 1 % $TiCl_3$ (pressed pellet and powder forms) have been measured using the modified transient plane source technique. Specific heat measurements for powdered $NaAlH_4$, $LiAlH_4$ and $LiNH_2$ + 2LIH were carried out using a Calvet calorimeter. The results obtained agree well with values available in the literature. It is important to know the thermal characteristics of metal hydrides when designing and engineering storage vessels in order to understand and control heat transfer to and from these important hydrogen storage materials in a wide range of potential real-world applications.

FIGURE CAPTIONS

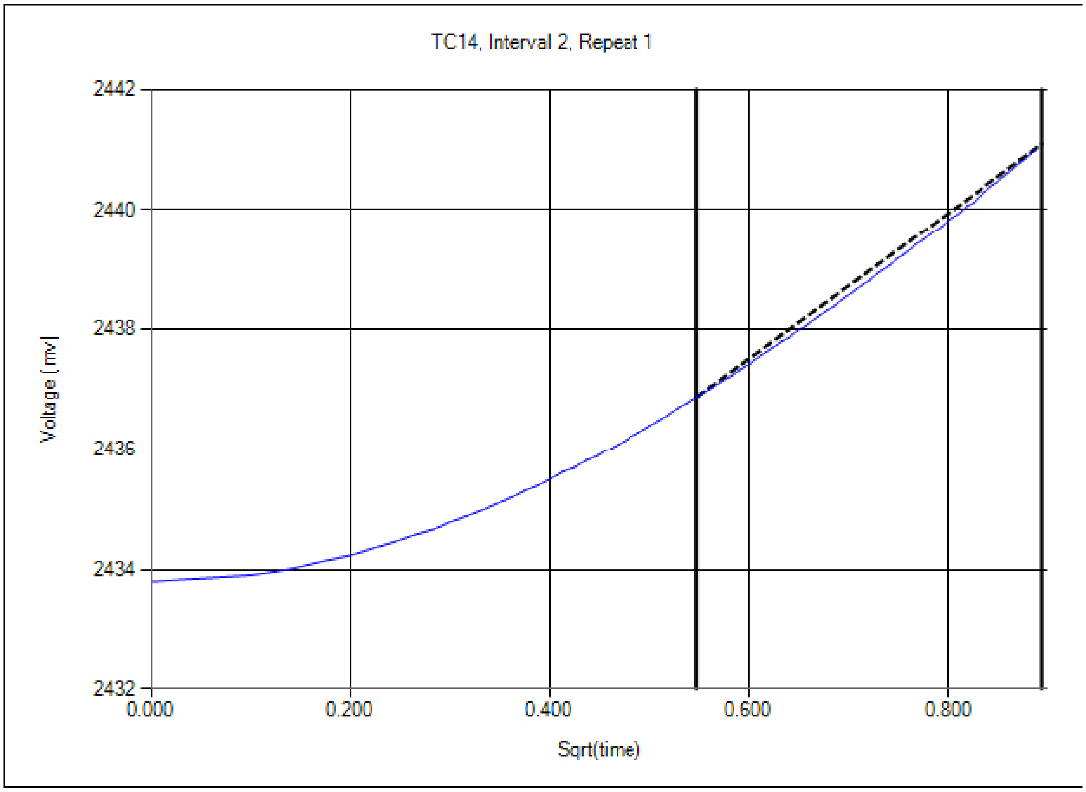
Figure 1 – Representative Voltage vs. square root of time (Sqrt(Time)) Plot from a TCi thermal conductivity probe

Figure 2 – Images of C-Therm's probe being used inside a glove Box

Figure 3 - Thermal conductivity of pressed vs. powdered metal hydrides

Figure 4 – Solid Works schematic of the hydrogen storage device being built by HSM Systems

Table 1 - Thermal conductivity (k) and specific heat measurements (Cp) for select, commonly studied metal hydrides



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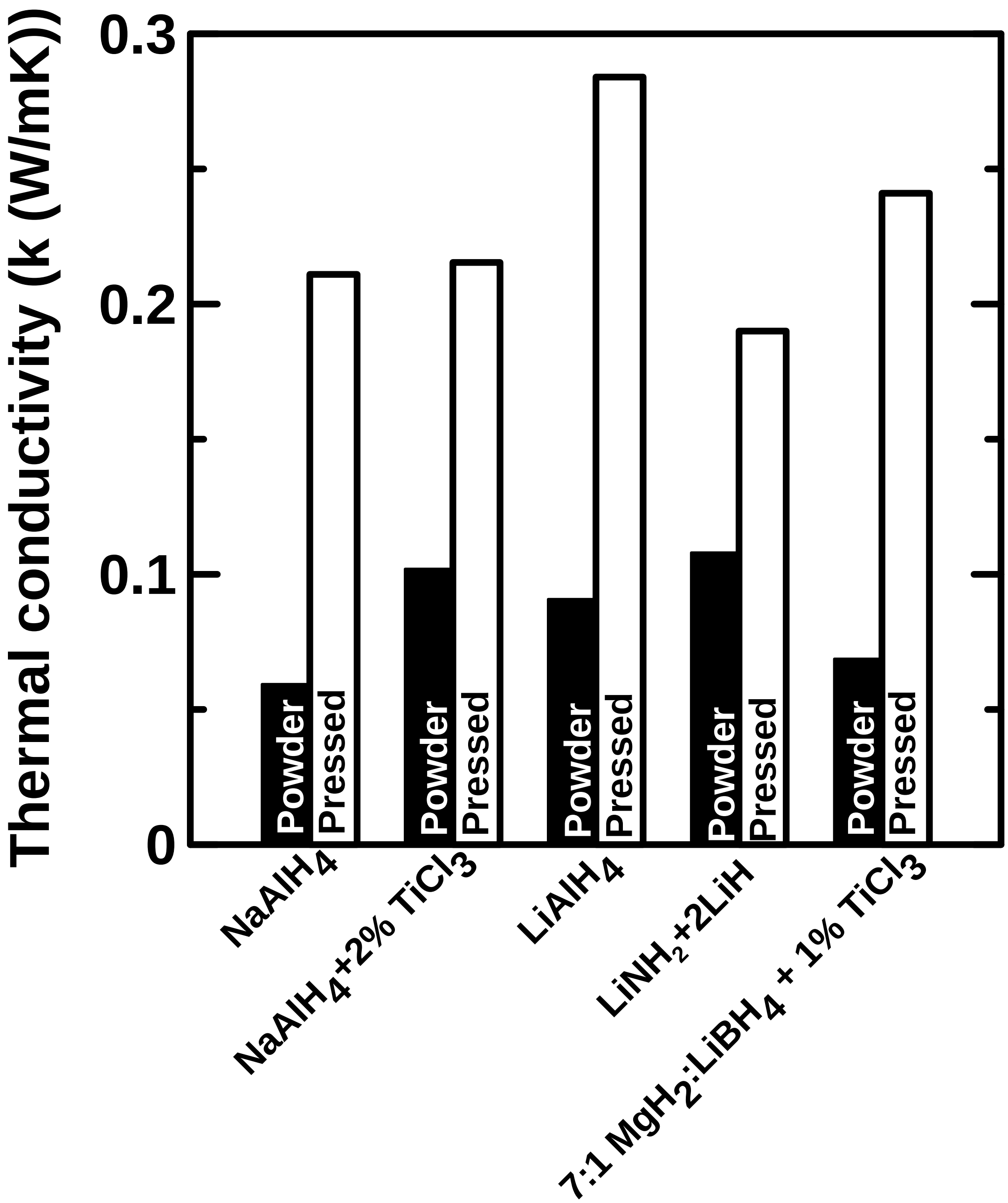

Figure 3 - Thermal conductivity of pressed vs. powdered metal hydrides

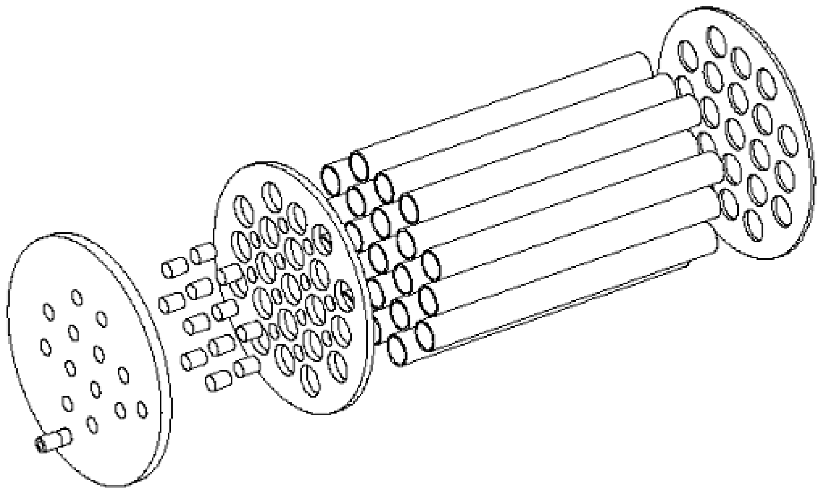

Figure 4 – Solid Works schematic of the hydrogen storage device being built by HSM Systems

Table 1 - Thermal conductivity (k) and specific heat measurements (C_p) for select, commonly studied metal hydrides

Sample/Measurement	Powder (k(W/mK))	Pressed (6 ton) (k(W/mK))	C_p, J/ g K (25.15 ^oC)	C_p, kJ/ mol K (25.15 ^oC)
$NaAlH_4$	0.0593	0.211	1.597	86.24
$NaAlH_4$ + 2% $TiCl_3$	0.102	0.2154		
$LiAlH_4$	0.0908	0.284	2.219	84.22
$LiNH_2$+2LiH	0.108	0.19	2.491	94.29
7:1 MgH_2:$LiBH_4$ + 1% $TiCl_3$	0.0687	0.241		

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