High Performance Metal Hydride Based Thermal Energy Storage Systems for Concentrating Solar Power Applications

Patrick A. Ward[†], Claudio Corgnale[†], Joseph A. Teprovich Jr.[†], Theodore Motyka[†], Bruce Hardy[†], Brent Peters[†], Ragaiy Zidan^{*†}

[†] Savannah River National Laboratory, 999-2W, Aiken, USA, 29808

Abstract

Thermal energy storage systems based on metal hydride pairs using high efficiency materials are evaluated. The low temperature metal hydrides NaAlH₄ and Na₃AlH₆ were cycled to determine stability of hydrogen capacity over extended cycling. Addition of aluminum and expanded natural graphite were found to enhance the cycling stability of NaAlH₄. Potential high temperature metal hydrides were investigated based on NaMg materials. A techno-economic analysis was performed to evaluate the performance a thermal energy storage system based on two metal hydride pairs: NaMgH₃:NaAlH₄ and NaMgH₂F:Na₃AlH₆. The resulting analysis suggests that the two systems have the potential to reach low cost and high efficiency performance targets.

Keywords: Concentrating Solar Thermal, Metal Hydrides, Solar Thermal Energy, Heat Storage

1. Introduction

Development of renewable energy technologies to curb fossil fuel consumption has been gaining acceptance with the realization of fossil fuel depletion and concerns related to greenhouse gas emission. Solar energy represents a nearly endless supply of energy in the form of electromagnetic radiation with a greater potential for providing dispatchable power among all the different renewable options.^[1,2] Solar thermal concentrators are among the technologies aimed at harnessing this energy source. High temperature solar plants have the potential to reach low cost electric power production, similar to conventional power plants, only if equipped with thermal energy storage systems.^[3] The common approaches for the storage of heat is through sensible heat in which the heat is simply transferred from a material, latent heat in which a phase change occurs, or thermochemical heat which involves a chemical reaction to release or store heat energy.

A significant amount of research has been applied toward storing sensible heat in molten salts. This technology is currently being employed in concentrated solar thermal power plants such as Solar One. While this technology is the most mature, sensible heat materials suffer from low energy densities and limited transport distances due to thermal losses.^[4] Latent heat

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* Corresponding Author Tel: (803) 646-8876 E-mail: Ragaiy.Zidan@srnl.doe.gov

materials can offer the advantage of higher energy densities and smaller temperature ranges for heat transfer,^[5] but the high cost and the corrosive nature of many high temperature phase change materials limit their practicality in concentrated solar thermal storage systems. Thermochemical heat storage systems can provide very high energy densities and economic systems with the right choice of materials. Thermochemical storage materials based on carbonation, oxidation, hydration, and hydrogenation reactions have received the most attention. Of these different reaction types, hydrogenation of metal hydrides has advantages of being able to reversibly de/hydrogenate the material by simply changing the pressure at a constant temperature. Metal hydride (MH) systems can offer energy densities on the order of 15-20 times higher than molten salts-based thermal energy storage (TES) systems.^[6] This can substantially lower the size and the capital cost of many concentrating solar power (CSP) TES systems. Using only small pressure changes, hydrogen can be transferred from one metal hydride bed to another to exchange large quantities of heat at high temperatures. Here the progress in the development of metal hydride pairs based on sodium aluminum hydride (as the low temperature material) and sodium magnesium hydride (as the high temperature material) for solar thermal energy storage applications is described.

2. Metal hydride based TES system

Among the power cycles driven by renewable sources, solar power plants have been identified by the Department of Energy (DOE) as a baseline renewable source due to their potential of meeting economic and technical targets and their potential for dispatchability.^[3] One of the most common solar electric plants is based on the steam Rankine cycle. A diagram of the overall solar plant is shown in Figure 1 and it is comprised of the solar concentration section, the TES section (based on the MH system concept), and the power plant (based on a steam Rankine cycle). The same MH based storage system can be adapted for use with other power plants (e.g. Brayton cycle), with only a few minor variations.

Figure 1: Steam power plant based CSP plant, comprised of The Solar Concentration system, the TES system (constituted by HT Metal Hydride and LT Metal Hydride materials) and Power Plant system, based on Rankine cycle

The power plant shown in Figure 1 operates 24/7, with the TES system storing and releasing the needed thermal energy to maintain continuous operation of the power section. The storage system shown in Figure 1 is comprised of two MH materials operating at different temperatures and about the same pressure. The pressure spatial gradients inside the MH materials and the connecting tubes are, in general, negligible compared to the operating pressures^[7,8], resulting in slow hydrogen flow velocities and negligible pressure drops. During the day ('Sun available' in Figure 1), the power plant is driven by the thermal power directly available from the solar concentration system. The available surplus solar power is stored in the TES. When solar radiation is available the heat transfer fluid exchanges high temperature heat (from the solar concentrator) with the high temperature metal hydride (HTMH), which releases hydrogen (endothermic process) to the low temperature metal hydride (LTMH) material. The LTMH absorbs hydrogen (exothermic process) and releases low temperature heat, which is extracted from the TES system. During the night or times when additional thermal energy is required to run the power plant ('Sun not available' in Figure 1), the process is reversed. Hydrogen is allowed to flow from the LTMH and be absorbed by the HTMH exothermally providing the needed heat to the steam generator. This TES is a self-sustaining system, since the hydrogen moves between the two beds exploiting the small pressure gradients (i.e. negligible compared to the operating pressures) that are available inside the MH beds and in the connecting tubes, during charging and discharging processes.

An ideal HTMH material is characterized by high operating temperatures and high reaction enthalpies whereas the ideal LTMH would possess low operating temperatures and low reaction enthalpies. This allows it: (1) to store large amount of heat, during the release of hydrogen from the HTMH; and (2) to provide the LTMH with low thermal power (at low temperatures) during the reverse process (hydrogen release by the LTMH and uptake by the HTMH).

3. High performance MH material TES system

Recent work^[9] has identified three possible HTMH materials capable of being paired with suitable LTMH materials. These materials can result in TES systems capable of being integrated in high temperature CSP plants. These materials are: NaMgH₃, TiH₂ and CaH₂. The highest temperature system, which is comprised of CaH₂ material, has several technical hurdles such as corrosion associated with molten Ca, low equilibrium pressures at high temperatures, etc. These limitations currently impede practical applications with this material. The more practical materials (NaMgH₃ and TiH₂) presented TES specific installed costs on the order of 35-50 \$/kWhth, which is beyond the 2015 DOE target for tower based CSP plants of 30\$/kWhth.^[10] In order to reduce the cost of the NaMgH₃ system, improvement of the HTMH and LTMH material techno-economic properties (i.e. reduction of the raw material cost, increase of the HTMH

reaction enthalpy). In addition a reduction of the cost of the heat exchanger and pressure vessel cost for both HTMH and LTMH systems is also needed.^[9] Our current focus is to examine possible low cost LTMH materials, in particular NaAlH₄ and Na₃AlH₆, in order to reduce the cost and increase the performance of the overall TES system.

3.1 LTMH material

Materials based on sodium aluminum hydrides were investigated to serve as low enthalpy materials in solar thermal heat storage. While NaAlH₄ possesses a higher gravimetric hydrogen density, Na₃AlH₆ requires lower pressures for rehydrogenation and releases hydrogen through a one-step process. The decomposition reaction pathway for NaAlH₄ is shown below in equation 1. Figure 2 displays the cycling data for the NaAlH₄ materials with various additives compared to Na₃AlH₆. TiCl₃ is used in all of the sodium aluminum hydride materials to enhance the reversibility of the reaction as well as increase its rate of absorption and desorption.

The addition of aluminum and expanded natural graphite (ENG) was used to increase the thermal conductivity and stability of the material over multiple cycles. As shown in Figure 2, the addition of aluminum powder (325 mesh) and ENG (< 45 μm) by planetary ball milling reduces the rate at which the material starts to lose capacity. The degradation of capacity in the ENG and Al doped material is still evident after 400 cycles, but rate of degradation is slower than the undoped material demonstrating an enhancement with these additives. These additives allow for more efficient heat transfer during hydrogenation, which is believed to reduce the chance of material segregation by excessive heating at the molecular level. ENG and aluminum were chosen to enhance the thermal conductivity due to their inert nature on this material. Aluminum is already present in the dehydrogenated material (as shown in equation 1). ENG and other carbon based materials are known to be quite inert with metal hydrides and can provide hydrogen diffusion pathways to increase the kinetics of the reaction as well as providing a heat transfer pathway.^[11]

The observed capacity loss in NaAlH₄ is believed to be due to the incomplete reversibility of Na₃AlH₆ to NaAlH₄ during rehydrogenation. This results in a capacity drop over extended cycling. Therefore, Na₃AlH₆ was synthesized directly by a ball milling technique described elsewhere^[12] and cycled to assess the cycle stability of this material. As shown in figure 2, Na₃AlH₆ displays a much higher stability of hydrogen capacity than that of the modified NaAlH₄ over 300 cycles. Although the overall hydrogen capacity is lower, the stability between cycles is enhanced which is important for thermal energy storage applications. Furthermore, the pressure required for regeneration of the hexahydride (30 bar) is much lower than that of the NaAlH₄ (100 bar).

Figure 2: A) Cycling data for NaAlH_4 with 2 mole % TiCl_3 (blue) B) $\text{NaAlH}_4 - \text{TiCl}_3$ with 10 wt. % Al (red) C) NaAlH_4 with 10 wt. % Al and 10 wt. % ENG (black) D) Na_3AlH_6 with 2 mole % TiCl_3 (green).

3.2 HTMH material

NaMgH_3 was initially investigated as a high enthalpy heat storage material due to its favorable thermodynamic properties and low cost. Figure 3 shows the first 10 cycles of NaMgH_3 and NaMgH_2F at 500 °C. The material was cycled between 1 bar (desorption) and 45 bar (absorption) of hydrogen with cycle times of 3 hours. It was found that NaMgH_3 segregates into separate materials at high temperatures over cycling due to the volatile nature of sodium which is a product of the decomposition. This leads to the formation of NaH and MgH_2 in separate regions of the reactor. (The cooler region containing the NaH) In order to circumvent this limitation, NaMgH_2F was investigated due to the increased stability of the sodium product formed (NaF) and the higher enthalpy of the reaction. Since the enthalpy of the reaction determines the amount of thermal energy which can be stored, higher enthalpies provide higher thermal energy densities. To our surprise, NaMgH_2F displayed a lower cycle stability than NaMgH_3 . NaMgH_2F was determined to also lose capacity from loss of volatile Na. This suggests that the mechanism of the reaction proceeds through NaH or Na metal as some point instead of being bound to the fluorine at all times. The cycling stability at lower temperatures and additives to enhance the cycling stability of these materials are currently being investigated by our group.

Figure 3: Cycling data for NaMgH₃ (red squares) and NaMgH₂F (blue circles) at 500 °C and 45 bar H₂.

4. Techno-economic analysis of the TES system

The NaMgH₂F-Na₃AlH₆ couple has been identified as one of the most promising MH-based TES systems. The techno-economic performance of the pair has been analyzed and compared with the original couple: NaMgH₃-NaAlH₄. The thermodynamic properties of the selected pair are reported in Table 1, along with those of the original couple (NaMgH₃-NaAlH₄). Most of the NaMgH₂F material data (cost of raw material, weight capacity, reaction enthalpy, operating conditions) have been obtained from a previous work^[13] while the other data (reaction entropy) have been assumed based on the values available for the currently available Mg-based MH materials. The Na₃AlH₆ material data has been compiled from literature sources^[8, 14] and on the experimental data obtained by our group. The NaMgH₃-NaAlH₄ material data reported in Table 1 is from our previous work.^[9]

Table 1: Techno-economic properties of the original MH pair (NaMgH₃– NaAlH₄) and of the selected new MH pair (NaMgH₂F– Na₃AlH₆)

	NaMgH ₃ – NaAlH ₄ MH system		NaMgH ₂ F– Na ₃ AlH ₆ MH system	
	NaMgH ₃	NaAlH ₄	NaMgH ₂ F	Na ₃ AlH ₆
Cost of raw material (\$/kg)	4.15	3.00	1.73	3.00
Weight capacity (kgH ₂ /kgmatl)	0.040	0.037	0.029	0.025
Bulk density (kg/m ³)	1000	750	1390	750

Reaction entropy ΔS (J/molH ₂ K)	133	130	134	134
Reaction enthalpy ΔH (kJ/molH ₂)	88	40	96.8	47
MH material range of operating temperature (°C) /pressure (bar)	550-600/50-60	100-120/50-70	600-650/30-50	120-150/10-30
TES MH specific cost (\$/kWhth)	17.6	15.9	11.6	18.2
TES MH exergy efficiency (%)	81		86	

The techno-economic analysis of the NaMgH₂F-Na₃AlH₆ material pair has been carried out based on the methodology and assumptions reported previously.^[9] The analysis has been carried out examining a power plant producing 100 MW_{el} (average during the year), assuming a plant capacity factor of 0.63, assured by a storage time of 13 hours. The shell and tube heat exchanger has been assumed as the baseline heat transfer system, with the assumptions for the material thermal conductivity (7 W/mK), fluid convective heat transfer coefficients (2000 W/m²K) and temperature differences between fluid and MH material (25 °C) reported in previous publication^[9]. The specific installed cost of the MH TES system reported in Table 1 shows the contribution of the HTMH and LTMH system on the overall TES cost. The value has been assessed accounting for: (1) the material cost (including an additional cost due to manufacturing, work and handling of the material); and (2) the heat transfer system (based on the shell and tube heat exchanger) and pressure vessel cost, following the methodology reported previously.^[9] The overall efficiency has been assessed as the ratio between the system exergetic efficiency during heat storage (i.e. hydrogen moving from HTMH to LTMH) and the system exergetic efficiency during heat release (i.e. hydrogen moving back from LTMH to HTMH) considering the exergy content of the heat transfer fluids^[9].

Results show a large reduction of the HTMH system cost (about 34%) from the original MH pair to the NaMgH₂F-Na₃AlH₆ materials. This is due to the higher reaction enthalpy, as well as to the lower material price and lower operating pressures. This results in a reduction of both the material cost and the pressure vessel and heat exchanger cost. On the other hand, the LTMH system cost increases of about 14% as shown in Table 1. The reduction of the LTMH material weight capacity, by substituting NaAlH₄ with Na₃AlH₆ material, and the higher reaction enthalpy result in increased cost. However, this cost is negated by the operating pressure reduction which results in a pressure vessel and heat exchanger cost reduction. The increased operating temperature (substituting the original MH pair with NaMgH₂F-Na₃AlH₆) also results in an increased exergetic efficiency of about 5%.

5. Conclusions

LTMH materials based on sodium aluminum hydride were investigated for their potential as TES materials in CSP applications. It was found that the addition of aluminum and expanded natural graphite to NaAlH₄ enhanced the cycle stability of the material which is likely the result

of enhanced thermal conductivity. It was also demonstrated that Na_3AlH_6 possesses better cycle stability than NaAlH_4 without the use of additives. This is likely due to the one-step reaction mechanism for the decomposition of Na_3AlH_6 compared to the two step reaction mechanism with NaAlH_4 . While Na_3AlH_6 has a lower capacity than NaAlH_4 , the pressures required for the materials regeneration are significantly lower. HTMH materials based on NaMgH_3 were investigated due to their appropriate enthalpy and cost values. It was found that segregation of the material due to vaporization of Na make this material impractical for solar thermal storage applications greater than 500 °C without the incorporation of product stabilizing additives. The addition of fluorine to the material to form NaMgH_2F was unsuccessful in stabilizing the sodium atom and it also led to material segregation. A techno-economic analysis of the new MH based TES system has been carried out. It demonstrated that the new TES system ($\text{NaMgH}_2\text{F}:\text{Na}_3\text{AlH}_6$) can achieve a system installed cost less than 30 \$/kWh, with a reduction of about 11% compared to the original couple ($\text{NaMgH}_3:\text{NaAlH}_4$). An increase of the system exoegetic efficiency of about 5% has also been predicted using the $\text{Na}_3\text{AlH}_6:\text{NaMgH}_2\text{F}$ material pair. These pairs are found suitable to operate at temperatures less than 500 °C.

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