



High performance metal hydride based thermal energy storage systems for concentrating solar power applications



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ABSTRACT

Thermal energy storage systems based on metal hydride pairs using high efficiency materials are evaluated. The low temperature metal hydrides NaAlH_4 and Na_3AlH_6 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 NaAlH_4 . 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: $\text{NaMgH}_3\text{:NaAlH}_4$ and $\text{NaMgH}_2\text{F:Na}_3\text{AlH}_6$. The resulting analysis suggests that the two systems have the potential to reach low cost and high efficiency performance targets.

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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 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 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

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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 Fig. 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.

The power plant shown in Fig. 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 Fig. 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 Fig. 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). This 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 Fig. 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.

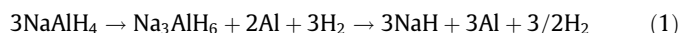
An ideal HTMH material is characterized by high operating temperatures and high reaction enthalpies whereas the ideal LTMH would possess low operating temperatures and low reaction enthalpies. This allows it: (1) to store large amount of heat, during the release of hydrogen from the HTMH; and (2) to 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: NaMgH_3 , TiH_2 and CaH_2 . The highest temperature system, which is comprised of CaH_2 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 (NaMgH_3 and TiH_2) presented TES specific installed costs on the order of 35–50 \$/kW h th, which is beyond the 2015 DOE target for tower based CSP plants of 30 \$/kW h th [10]. In order to reduce the cost of the NaMgH_3 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 in cost of the heat exchanger and pressure vessel for both HTMH and LTMH systems is needed [9]. Our current focus is to examine possible low cost LTMH materials, in particular NaAlH_4 and Na_3AlH_6 , 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 NaAlH_4 possesses a higher gravimetric hydrogen density, Na_3AlH_6 requires lower pressures for rehydrogenation and releases hydrogen through a one-step process. The decomposition reaction pathway for NaAlH_4 is shown below in Eq. (1). Fig. 2 displays the cycling data for the NaAlH_4 materials with various additives compared to Na_3AlH_6 . TiCl_3 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 Fig. 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

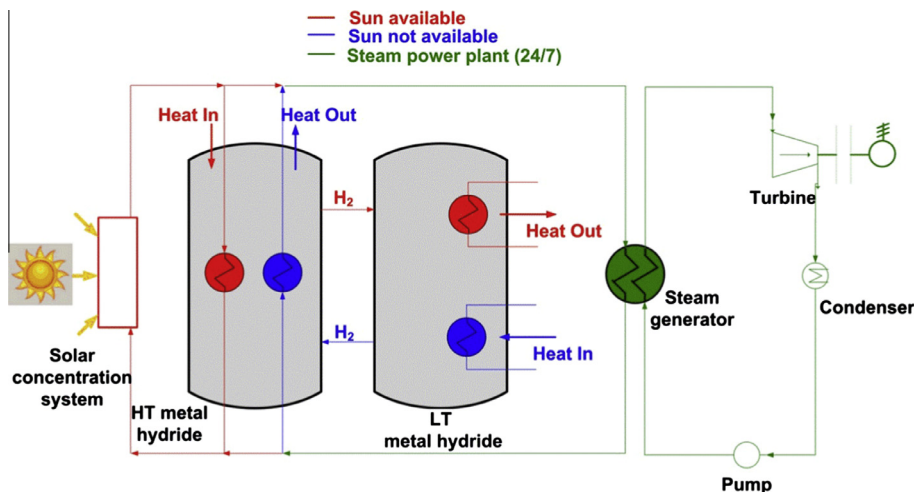


Fig. 1. Steam power plant based CSP plant, comprised of the solar concentration system, the TES system (constituted by HT metal hydride and LT metal hydride materials) and power plant system, based on Rankine cycle.

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