High temperature thermal energy storage in the CaAl$_2$ system

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ABSTRACT

Concentrated solar power (CSP) has been gaining significant attention as a method to produce electricity, but requires a suitable thermal energy storage (TES) system for continuous operation when the sun is unavailable. Thermochemical energy storage systems based on metal hydrides have advantages due to their high energy densities, potential for cost reductions, and higher operating conditions versus commonly utilized molten salts. Higher operational temperatures are desired for CSP power plants to achieve higher efficiencies and therefore lower costs. Herein, we demonstrate the feasibility of CaAl$_2$ as a high temperature thermal energy storage material for concentrated solar power applications. CaAl$_2$ is demonstrated to operate at 600 °C and have excellent reversibility, reasonable thermal conductivities, and equilibrium pressures practical for metal hydride based thermal energy storage systems. CaAl$_2$ was determined to hydrogenate in a two-step process mechanism to form CaH$_2$ and Al and dehydrogenate to reform CaAl$_2$ at 600 °C by adjusting hydrogen pressure. To our knowledge, this material represents the lowest cost metal hydride TES material capable of operating at or above 600 °C.

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1. Introduction

As global energy demands have increased, concerns of diminishing fossil fuel supplies and the adverse effects of their combustion products on the global climate has inspired a significant amount of research in renewable energy technologies. Solar energy represents the largest source of sustainable energy available on our planet. Concentrated solar power (CSP) is positioned to provide a large contribution of the future solar energy supply due to its scalability and potential for providing low cost electricity. Since solar irradiance is only available in the day, continuous operation of the power block is only feasible when interfaced with an appropriate thermal energy storage (TES) system or hybrid system. Hybrid solar/natural gas systems have been constructed, such as the Martin Next Generation Solar Energy Center in Martin county, Florida, which generates steam produced from CSP to reduce the amount of natural gas consumed for power plant operation. In

order to eradicate the use of fossil fuels for continuous operation, a TES system which can store excess thermal energy acquired during the day needs to be interfaced with the CSP system. These types of systems typically utilize one of three different methods of storing heat: (1) materials which store sensible heat, (2) latent heat, or (3) thermochemical heat. While sensible and latent heat materials, namely molten salts, are the current state-of-the-art TES, the achievable energy densities and heat storage periods are far less than thermochemical energy storage systems [1]. Solar salt, the most commonly utilized TES molten salt, faces challenges of high rates of corrosion and decomposition at temperatures above 600 °C [2]. Thermochemical energy storage materials based on metal hydrides have the potential to store large energy densities of heat and operate at high temperatures.

Numerous types of chemical systems can be utilized to store thermochemical energy. These systems include metal hydrides, carbonates, hydroxides, peroxides, ammonia decomposition systems, and various organic systems [3—9]. Metal hydrides have a distinct advantage due to the significant amount of research which has been conducted on the cycle stability of hydrogen storage materials, and the ability to provide a self-regulating system when an appropriate metal hydride pair is selected [9,10]. The light

weight of hydrogen typically leads to a higher gravimetric energy density for metal hydride based TES systems depending on the enthalpy of the reaction and the hydrogen gravimetric capacity.

Recently, there has been a significant push to operate next generation CSP power plants at temperatures of 600 °C and above due to the higher efficiencies which can be achieved. The use of MgH_2 to store thermochemical energy was evaluated in the early 1990s by Bogdanović et al. [11,12]. Unfortunately, the high equilibrium pressures at higher temperatures and significant vapor pressure of magnesium at temperatures greater than 500 °C hinder the use of MgH_2 in next generation TES systems. The push for higher operational temperature creates a variety of technical and material challenges to overcome for these systems [13,14].

The enthalpy of the reaction of $CaAl_2$ with H_2 to produce CaH_2 and Al has been predicted by DFT calculations to be −72 kJ/mol [15]. Experimental measurements of the reaction of $CaAl_2$ with H_2 have measured this enthalpy to be −83.1 kJ/mol [16]. Using the experimentally measured value, this material can theoretically store 865 kJ per kilogram of $CaAl_2$. Herein, we demonstrate that this material is reversible with very little capacity degradation and possesses a reasonably high thermal conductivity. The cycle stability and thermal conductivity of $CaAl_2$ reported herein are two essential aspects necessary for the development of an economically feasible thermal energy storage system.

2. Experimental procedure

Calcium hydride (99.99%) was purchased from Sigma Aldrich and used as received. Aluminum hydride (α phase) was purchased from ATK. All materials were handled in an argon filled glovebox. Calcium hydride and aluminum hydride were planetary milled on a Fritch Pulverisette 7 planetary mill, at 500 RPM, for 15 min in each direction with a 5 min cooling period between milling sessions. 2.6 mm stainless steel ball bearings were used with a sample to ball bearing weight ratio of 1:30. The resulting mixed powder was then annealed under vacuum at 600 °C for 6 h to produce $CaAl_2$.

Hydrogen capacity cycling was performed on a Hy Energy Pro PCT at 600 °C with a custom designed Incoloy 625 reaction vessel. Hydrogen absorption was carried out on approximately 2 g of $CaAl_2$ at 23 ± 1 bar H_2 starting pressures over 3 h followed by a hydrogen desorption cycle at 2 bar H_2 over 3 h with a 5 min evacuation period after desorption. The thermal diffusivity was measured on a NETZSCH LFA 457 microflash. As prepared $CaAl_2$ and hydrogenated $CaAl_2$ powder was cold pressed into a 10 mm pellet at 4 tons of applied pressure. The $CaAl_2$ pellet was then annealed at 600 °C for 1 h under argon. The packing density was found to be 1.72 g/cm^3, which is ~80% of the crystal density of $CaAl_2$ (2.15 g/cm^3). The pellets were loaded into a sputtering chamber under an argon atmosphere and ~40 nm of Au sputtered onto each side. The pellet was then coated with graphite spray to reduce the reflectivity of the sample. Thermal diffusivity was measured over a temperature range of 200 °C to 600 °C for the $CaAl_2$ sample and 80 °C–200 °C for the hydrogenated $CaAl_2$ sample (CaH_2 + 2Al). Three data points were taken at each temperature after stabilizing for about 3 min and at a 1 min interval. The signal was fit to the Cowan + pulse model. The packing densities of the pellets before and after laser flash measurements were confirmed to have no discernible change. Specific heat was measured on a SynSys Evo Pro with sealed aluminum crucibles. Samples were referenced to Al_2O_3. Powder X-ray diffraction patterns were measured on a PANalytical X'pert Pro with Cu Kα radiation. Samples were prepared in an argon filed glovebox and protected with a Kapton film to avoid oxidation of the sample. Thermal gravimetric analysis/residual gas analysis (TGA/RGA) was performed on a Perkin Elmer Pyris 1 with a heating rate of 10 °C/min under argon flow.

3. Results and discussion

Planetary milling of CaH_2 and AlH_3, followed by annealing at 600 °C under vacuum for 6 h, resulted in a finely divided, dark purple powder which consisted of $CaAl_2$ with a trace amount of $CaAl_4$ as shown in the powder XRD patterns in Fig. 1. XRD of the milled sample before annealing determined that the powder consisted of CaH_2, AlH_3, and Al. No traces of $CaAlH_5$ were detected in our milled samples which have been shown to be produced by longer periods of milling under a hydrogen atmosphere [17]. After hydrogenation of $CaAl_2$ for 2 h at 600 °C and 25 bar H_2, the crystalline species observed were CaH_2 and Al. Subsequent dehydrogenation of the material resulted in the formation of $CaAl_2$ once again (Supporting Information).

The theoretical gravimetric hydrogen capacity is 2.1 wt % for the overall reaction 1 below.

$$CaAl_2 + H_2 \leftrightarrow CaH_2 + 2\ Al. \tag{1}$$

Thermal gravimetric analysis (TGA) of $CaAl_2$ hydrogenated at 600 °C and 95 bar H_2 for 6 h displayed a weight loss of 1.8 wt % and two distinct hydrogen desorption events were observed by residual gas analysis (RGA) of the purge gas. Fig. 2 shows the overlay of the TGA/RGA data clearly demonstrating a two-step desorption process with an onset of hydrogen desorption at ~460 °C. Previous reports have described the first and second dehydrogenation steps to occur as described in equations (2) and (3) below [16]. Pressure composition isotherm (PCI) measurements of $CaAl_2$ (Supporting Information) are in agreement with a two-step absorption mechanism with equilibrium pressures of ~8 bar H_2 and ~19 bar H_2 at 600 °C. To verify the hydrogenation mechanism, $CaAl_2$ was hydrogenated at 11 bar H_2 and 600 °C for 3 h and the product of the hydrogenation analyzed by XRD as shown in Fig. 3. Since the equilibrium pressure for the second reaction step is ~19 bar H_2, only the first step of the reaction should go to completion. The products observed by XRD are CaH_2, $CaAl_4$, and Al. This data confirms that hydrogenation occurs in a two-step process through the formation of $CaAl_4$. The observation of Al would only be expected if some of the second hydrogenation step ($CaAl_4$ + H_2 → CaH_2 + 4 Al) were to occur. The equilibrium pressure of the second step drops significantly while lowering temperature, so it is likely that this reaction step partially occurred during the cooling of the reactor from 600 °C to room temperature under hydrogen pressure.

$$CaH_2 + 4\ Al \leftrightarrow CaAl_4 + H_2 \tag{2}$$

$$CaAl_4 + CaH_2 \leftrightarrow 2\ CaAl_2 + H_2 \tag{3}$$

For a practical thermal energy storage system, the material must be able to be cycled thousands of times with very little loss in capacity. The $CaAl_2$ system was cycled 100 times at 600 °C with starting absorption pressures between 22 and 24 bar H_2 for 3 h periods. Desorption of the material was carried out at 2 bar H_2 over 3 h. A helium calibration curve for the pressure drop in the reaction vessel during cycling was obtained and used to calibrate the hydrogen uptake measurements (supporting information). The slight differences in the starting pressures during hydrogenation are due to the slight differences in the starting reservoir pressure set by the software before each absorption cycle. Fig. 4 illustrates some variation in capacity between 2.0 and 1.9 wt % H_2 during the first 20 cycles. This is typically observed in metal hydride materials and is a result of the material reaching an equilibrium state with respect to particle proximity for dissociation and recombination. Once equilibrium was reached (cycle ~ 20), the capacity demonstrates only a very slight degradation from ~1.9 wt % to ~1.85 wt %.
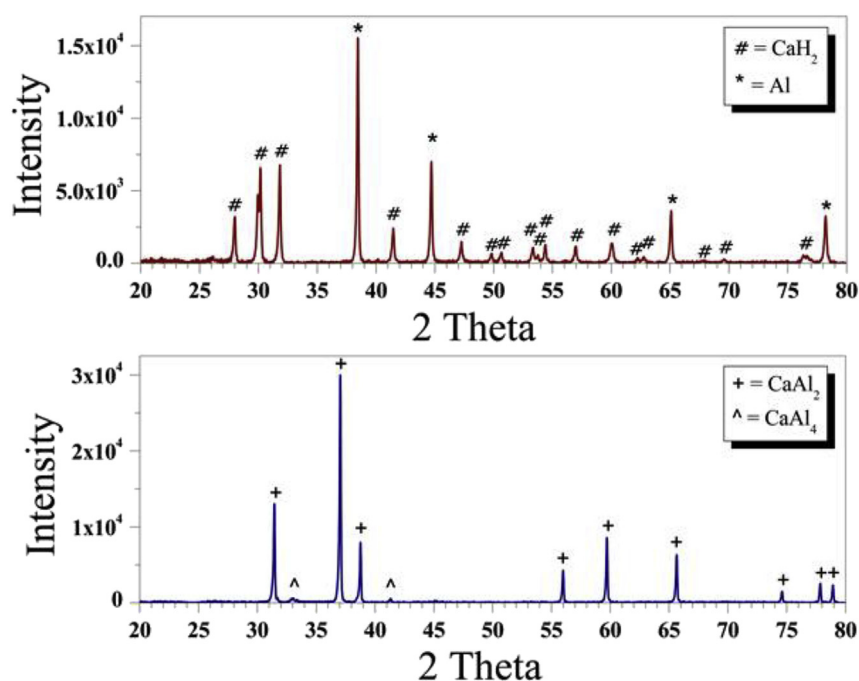
Fig. 1. Powder XRD pattern of (top) CaAl$_2$ hydrogenated for 2 h at 25 bar H$_2$ and 600 °C (bottom) CaAl$_2$ prepared by annealing ball milled AlH$_3$ and CaH$_2$ (2:1 M ratio) at 600 °C under vacuum for 6 h.

The temperature of the material was also monitored during absorption/desorption of H$_2$ at the same pressure and temperature conditions as the cycling experiements (Fig. S3, Supporting Information). The thermal profile of the material shows a large temperature spike ~80 °C during the hydrogenation and clearly illustrates the large amount of heat that can be rapidly generated and extracted from the system to facilitate 24 h operation of a future CSP plant. We also believe that this may be responsible for the slight degradation observed in the material. In a real system, this heat would be extracted to maintain an operational temperature of 600 °C and pressure would be altered very slowly in a controlled fashion. In our cycling reaction, no such heat extraction mechanism is possible and high pressure above both equilibrium pressure plateaus is given instantaneously. Therefore, the material exceeds 660 °C, which is the melting point of aluminum. Since the hydrogenated state of this material consists of CaH$_2$ and Al, it is quite possible that a small amount of phase segregation of the powdered material is responsible for the slight capacity loss observed.

Another important aspect to consider when developing a thermal energy storage system is the thermal conductivity of the material. Materials with low thermal conductivities will require additives to increase the thermal transport properties or a more costly engineering design to transport the heat effectively. For power tower applications, it is ideal to have the high temperature metal hydride at the top of the tower with the solar receiver to minimize heat loss. Since there are weight limitations for the support structure of the tower, the introduction of additional materials for enhancing the thermal conductivity of a TES system
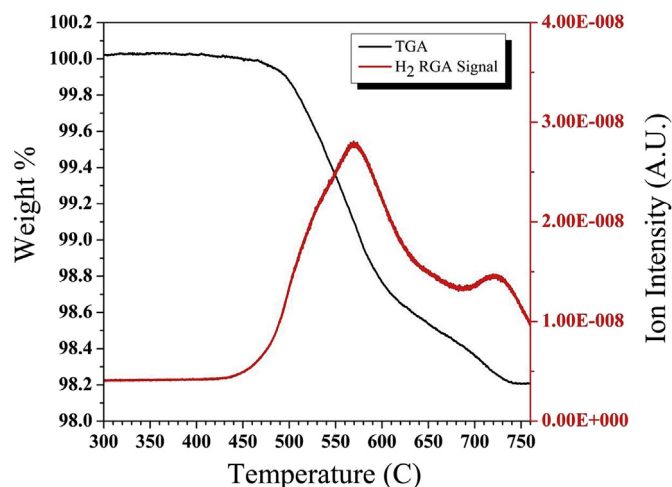

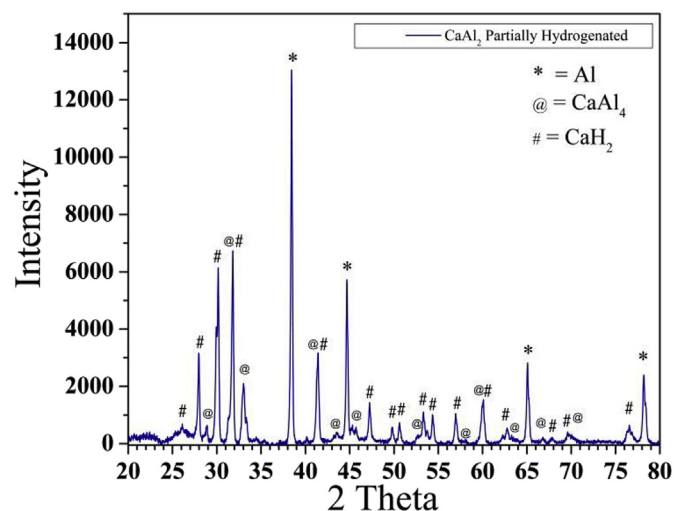**Fig. 2.** TGA/RGA of CaAl$_2$ hydrogenated at 600 °C for 6 h at 95 bar H$_2$.

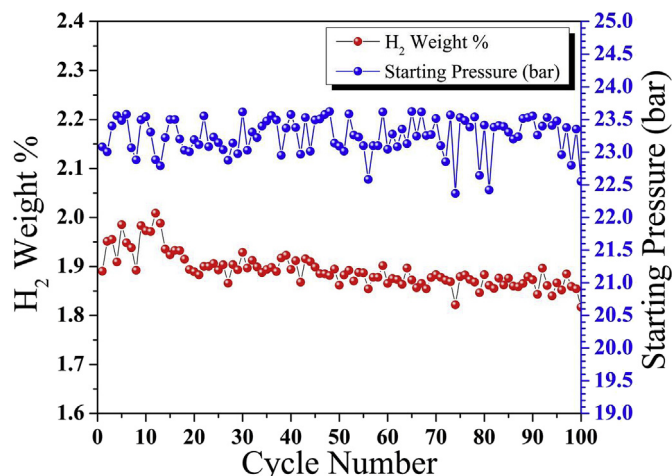**Fig. 3.** XRD pattern for CaAl$_2$ partially hydrogenated at 11 bar H$_2$ and 600 °C.

Fig. 4. Cycling capacity of CaAl$_2$ cycled at 600 °C for 3 h for each absorption and desorbed at 2 bar H$_2$ for 3 h followed by a 5 min evacuations. Starting pressures for absorption cycles are given by blue circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

reduces the amount of heat storage material that can be utilized or increases the cost needed for the support structure. Therefore, having a material with high thermal conductivity can play a significant role in reducing the cost of the TES system. Because of the lower thermal conductivities of most metal hydrides, enhanced thermal transport in these materials for hydrogen storage applications has been a subject of interest for many researchers [18,19]. Thermal conductivity (λ) can be calculated from the thermal diffusivity (α), density (ρ), and the specific heat (C_p) by the following equation.

$$\lambda = \alpha\,\rho\,C_p$$

Fig. 5 below shows the thermal conductivity of the as prepared CaAl$_2$ from 200 °C to 600 °C. The thermal conductivity at the desired operational temperature (600 °C) was determined to be
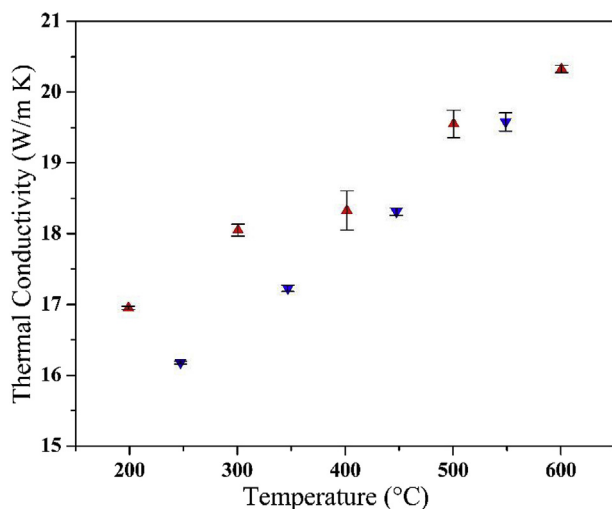

Fig. 5. Thermal conductivity of CaAl$_2$ from 200 °C to 600 °C. The red up arrows show measurements acquired during the heating ramp and blue down arrows show measurements acquired during the cooling ramp. Y axis is scaled to display the slight discrepancy (~6%) between the heating and cooling measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
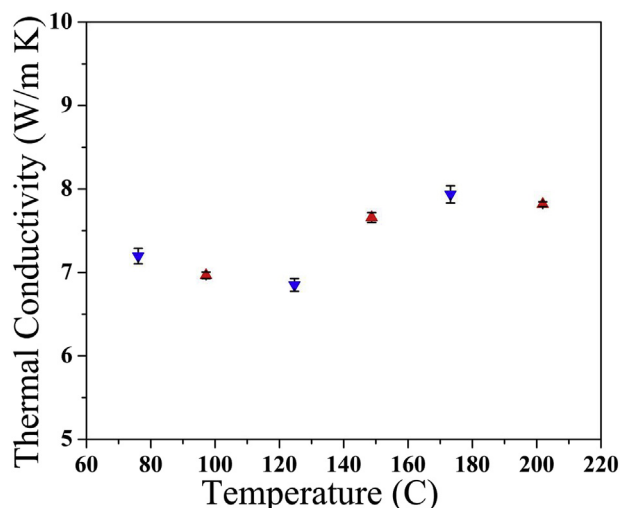

Fig. 6. Thermal conductivity of CaAl$_2$ (hydrogenated to CaH$_2$ + Al) from 80 °C to 200 °C. Red up arrows depict measurements acquired during the heating ramp and blue down arrows depict measurements acquired during the cooling ramp. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

20.3 W/m K. While this value is not a high as most metals (i.e. Aluminum 205 W/m K at 25 °C), it is exceptionally high for most metal hydrides and given that the measured pellet is only 80% of the theoretical crystal density of CaAl$_2$. It is well-known that the thermal diffusivity strongly depends on the packing density and inter-grain connectivity, hence further improvement in thermal diffusivity is expected upon increasing the cold-pressing pressure and/or further sintering the pellet. Obtaining thermal conductivities for the hydrogenated samples at 600 °C was not possible with the current instrumental setup due to hydrogen release at elevated temperatures without having the appropriate hydrogen overpressure. Therefore, the thermal conductivities for the hydrogenated materials were measured from 80 °C to 200 °C to ensure no hydrogen evolution. Fig. 6 displays shows that the thermal conductivity of the hydrogenated material falls within the range of 6.8 W/m K to 7.9 W/m K from 80° to 200 °C. This value still far exceeds the thermal conductivities of most metal hydrides and molten salts (usually less than 2 W/m K) that would be used for TES applications.

4. Conclusions

The feasibility for high temperature thermal energy storage in the CaAl$_2$ system was demonstrated. To our knowledge, this material represents the highest operating temperature metal hydride comprised of low cost elements which is suitable for thermal energy storage applications. CaAl$_2$ demonstrates excellent reversibility producing CaH$_2$ and Al upon hydrogenation and reforming CaAl$_2$ upon dehydrogenation with no observable inactive side reaction products. Furthermore, no significant hydrogen capacity loss over 100 cycles was observed. A capacity of 1.9 wt % can be achieved at 600 °C and the hydrogenation and dehydrogenation occurs in a two-step process. The mechanism of the hydrogenation reaction was confirmed to go through CaAl$_4$ before completely hydrogenating to CaH$_2$ and Al. The thermal conductivity of CaAl$_2$ is excellent in comparison with other thermal energy storage materials, which is a significant factor in the cost and complexity of designing a metal hydride based TES system. Further investigation into the thermodynamic properties, kinetics, mechanism, and techno-economic analysis of CaAl$_2$ for TES applications is currently

underway.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jallcom.2017.10.191.

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