Destabilised calcium hydride as a promising high-temperature thermal battery

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ABSTRACT

Calcium hydride (CaH₂) is considered an ideal candidate for thermochemical energy storage (thermal battery) due to its high energy density and low-cost. Its very high operating temperature and poor cycling stability are the main factors that hinder its development and implementation as a thermal battery for concentrated solar power (CSP) plants. In this work, CaH₂ was thermodynamically destabilised with aluminium oxide (Al₂O₃) at a 1:1 molar ratio to release hydrogen at a lower temperature than the hydride alone. Temperature programmed desorption measurements showed that the addition of Al₂O₃ destabilised the reaction thermodynamics of hydrogen release from CaH₂ by reducing the decomposition temperature to ~ 600 °C in comparison to ~1000 °C for pure CaH₂ at 1 bar H₂ pressure. The experimental

enthalpy and entropy of this system were determined by pressure composition isotherm measurements between 612 and 636 °C. The enthalpy was measured to be $\Delta H = 100 \pm 2$ kJ.mol⁻¹ H₂ and entropy $\Delta S = 110 \pm 2$ J.K⁻¹mol⁻¹ H₂. The XRD after TPD and *in situ* XRD data confirmed the main product as Ca₁₂Al₁₄O₃₃. The system exhibited a loss of capacity during hydrogen cycling at 636 °C, which was found to be due to sintering of excess Al₂O₃, as confirmed by X-ray diffraction and scanning electron microscopy. The hydrogen cycling capacity was significantly improved by reducing the initial amount of Al₂O₃ to a 2:1 molar ratio of CaH₂ to Al₂O₃, deeming it as a highly promising high-temperature thermal battery for the next generation of CSP plants.

1. INTRODUCTION

There is an increasing trend of energy consumption across the world, and according to the International Energy Agency, the global energy demand rose by 2 % in 2017¹. This has been the fastest rise during the decade, and an urgent requirement for managing the emerging energy crisis, as well as global warming, has been deemed essential. Renewable energy such as solar, wind, geothermal and biomass are encouraged in every country. Among these, solar energy is by far the most prominent solution for addressing present and emerging problems such as climate change, pollution and energy insecurity, since it is unlimited, clean, and available in almost all parts of the world²⁻⁵. However, there are many problems associated with its use, mainly it is a dilute form of energy, and its availability varies widely over time. Consequently, large collection areas and storage are required⁵⁻⁶.

Solar photovoltaic cells (PV) and concentrated solar power (CSP) are the two most mature technologies that utilise sunlight directly to produce electricity. From the 1990s, PV played a central role, while CSP gained attention in recent years and is growing at a 40% annual rate⁷. Compared with PV systems, CSP has a higher life span, and on a large scale, storing heat energy is cheaper than storing electrical energy^{8, 9}. The integration of a thermal energy storage

system makes CSP dispatchable and unique among all other renewable energy-generating alternatives. The aim of CSP technologies is to concentrate the sun's light using solar receivers and convert it into heat, to create steam, to drive turbines or engines, which generate electricity⁸, ⁹. Due to the intermittent nature of solar power, a reliable energy storage system is required to overcome this instability in power generation and to meet grid demand¹⁰. The selection of a suitable thermal energy storage (TES) system is the focus in a CSP technology. An ideal TES system should possess both high energy storage density 0.5 - 1.0 kWh/kg, and working temperatures above 600 °C, as required for a high-efficiency Stirling engine to operate for electricity production¹¹.

Sensible, latent and thermochemical energy storage are the three developed thermal energy storage systems for CSP plants. Half of the current CSP plants use the mature molten salt storage technology⁷. Molten salts store heat depending on their temperature change, with their maximum operating temperature limited to below 570 °C^{7, 13-16}.

Thermochemical energy storage uses heat from the sun to induce an endothermic chemical reaction. Metal hydrides are one of the most promising next-generation high-temperature thermochemical storage materials. Libowitz *et al.* first studied metal hydrides as thermochemical energy storage systems in 1974¹⁶. A large collection of metals can reversibly react with hydrogen over a wide range of temperatures and have theoretical heat storage capacities higher than other thermal energy storage systems (sensible and latent). Even though metal hydrides are potential candidates for the next-generation storage systems for CSP plants, there are many technical challenges, from material selection to engineering issues that need to be overcome and operate at temperatures > 600 °C. For instance, calcium, barium, strontium and titanium hydrides are some of the systems that can operate in the high-temperature range (> 600 °C) for operation in higher efficiency CSP plants^{17, 18}. Calcium hydride has interesting properties including a high heat of formation 4312 kJ/kg at 25 °C, high thermal gravimetric

 heat storage capacity 4494 kJ/kg at 950 °C and a low cost compared with other metal hydrides, for instance, cost of pure LiH is 50 US Wh_{th}^{-1} and that of CaH₂ is 2.84 US Wh_{th}^{-1} ^{11, 12}. Due to the high energy density and operating temperature, CaH₂ was identified in 2010 as a solar thermochemical storage material¹⁹. Ward *et al.* showed that CaH₂ could operate as a hightemperature material with TiFeH₂ as a hydrogen storage tank while being economically suitable for solar thermochemical energy storage¹⁷. Unfortunately, its operating temperature is too high (> 1000 °C), and needs to be reduced to below 1000 °C. The melting point of both CaH₂ and Ca metal are 983 °C and 842 °C respectively, and are highly corrosive which could lead to expensive containment vessels²⁰⁻²². The decomposition temperature of CaH₂ can be reduced by adding suitable additives to it, and this process is called thermodynamic destabilisation²³. Veleckis ²⁴ successfully showed this method in 1981 by adding Al to calcium hydride, where a multistep reaction was detected:

$$CaH_2 + 4Al \rightleftharpoons Al_4Ca + H_2$$
 (1)

$$CaH_2 + Al_4Ca \rightleftharpoons 2Al_2Ca + H_2$$
 (2)

The enthalpy of reaction (1) was found to be $\Delta H \approx 74$ kJ.mol⁻¹ H₂ at 1 bar of H₂ pressure and 414 °C²³. In 2017, Ward *et al.*²⁵ extended this method and demonstrated the feasibility of the Al₂Ca system as a potential high-temperature thermal battery for CSP applications.

This work is the first ever to demonstrate the destabilisation of CaH_2 by adding Al_2O_3 , and its contribution to developing novel low-cost and highly-efficient thermal batteries that can operate at the required conditions for the next generation of CSP plants. Aluminium oxide or alumina is the most common naturally occurring thermally stable oxide of aluminium, which is also known as mineral corundum or α -Al₂O₃. Properties such as high melting point, catalytic activity, low cost and abundance in nature make it attractive all over the world for different industrial applications²⁶⁻²⁸. The aim of this study was to focus on the thermal analysis, thermodynamic characterisation and cycling stability of the CaH₂-Al₂O₃ system by applying temperature-programmed desorption (TPD), pressure composition isotherms (PCI), *ex situ* and

 in situ XRD analysis. The cycling stability of the $CaH_2-Al_2O_3$ system was significantly improved when a 2:1 molar ratio of CaH_2 to Al_2O_3 was achieved. The morphological differences of the sample before and after cycling were studied by field emission scanning electron microscopy (FE-SEM). The experimental enthalpy and entropy for the $CaH_2-Al_2O_3$ system between 612 and 636 °C were calculated, and so was the raw material cost, deeming this system as a highly promising thermal battery for the next generation of CSP plants.

2. EXPERIMENTAL METHODS

2.1. Theoretical thermodynamic calculations

HSC Chemistry software²⁹ was used to initially identify whether the chemical reaction between $CaH_2-Al_2O_3$ is thermodynamically favourable, without taking into consideration reaction kinetics. The enthalpy, entropy, Gibbs free energy and heat capacity for the different chemical reactions between CaH_2 and Al_2O_3 were calculated. Thermodynamic data for pure elements (Ca, Al) and compounds (CaH_2 , Al_2O_3) were collected from Dinsdale *et al.* and Binnewise et al.^{30, 31} The phase diagram of CaO-Al₂O₃³² provided the necessary information regarding the formation of various calcium aluminium oxide compounds at a particular molar ratio at the temperature of interest.

2.2. Sample preparation

Metal hydrides are sensitive to moisture and oxygen; therefore all chemical storage and handling were completed inside an argon-filled glove box (MBraun, Germany), where the H_2O/O_2 levels were less than 1 ppm. CaH₂-Al₂O₃ mixtures were synthesised by ball-milling calcium hydride and aluminium oxide (both purchased from Sigma Aldrich with purity > 95 % and > 98 % respectively) in 1:1 and 2:1 molar ratios, under an argon atmosphere at room temperature using an Across International Planetary Ball Mill (PQ-N04) and employing stainless steel vials. An equal number of 10 mm and 6 mm diameter stainless steel balls were

used with a 40:1 ball to powder mass ratio. The samples were ball milled for 3 hours at a rotational speed of 400 rpm. The direction of the vial rotation was altered every 30 min without pausing between each rotation.

2.3. Sample characterisation

Crystalline phase analysis of the starting materials for the and thermally analysed samples was done by *ex situ* powder X-ray diffraction, using a Bruker D8 Advance diffractometer that uses Cu K α wavelength radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA). An airtight sample holder covered with a polymethyl methacrylate dome was used for all air and moisture sensitive samples to prevent contamination. Data were collected over a 10° - 80° 2 θ range using 0.3° divergence slits and 0.3° antiscattering slits with a 0.03° step size. The counting time was 1.6 s/step associated with a rotational speed of 30 rpm. Bruker EVA and the International Centre for Diffraction Data (ICCD) PDF4 database were used to identify the phases. Quantitative analysis of peaks present in the X-ray diffraction patterns of all samples used was completed with TOPAS software³³ using the Rietveld method³⁴. Both ICDD PDF4 and the Crystallography Open Database (COD) were used for structural information³⁵.

In situ X-ray diffraction ($\lambda = 0.7093$ Å, Mo-K α) was conducted on the CaH₂-Al₂O₃ mixture using a Thermo Fisher ARL Equinox 5000 diffractometer by heating from room temperature to 750 °C using a hot air blower with a 2 °C/min heating rate; the sample was cooled at the maximum rate. Data were collected for 60 s exposures while heating and cooling. The powder sample was loaded inside a quartz capillary (0.7 mm outer diameter, 0.01 mm wall thickness), sealed under argon pressure and mounted onto a sample holder. The temperature of the hot air blower was calibrated against the known thermal expansion coefficient of both NaCl and Ag³⁶⁻³⁸

Temperature programmed desorption-mass spectrometry (TPD-MS) using a Stanford Research Systems (SRS) residual gas analyser (RGA-200) consisting of a quadrupole mass spectrometer

 was used to detect the gases released from CaH₂ and CaH₂-Al₂O₃ mixtures under high vacuum ($< 7 \times 10^{-4}$ mbar) while heating samples to 900 °C at 5 °C/min. The RGA separates the ionised gas molecules according to their respective masses and measures the ion currents at each mass. A 3 mg sample of pure CaH₂ and CaH₂-Al₂O₃ mixture (1:1 molar ratio) as prepared was taken in the silicon carbide reactor and connected to the RGA mass spectrometer separately and the corresponding analogue scan (partial pressure vs mass to charge ratio) was obtained. Temperature data was collected using a K-type temperature sensor that connected externally to the reactor. The data was collected every 5 s.

Thermal analysis of the CaH₂-Al₂O₃ mixture was also studied by TPD, PCI, and cycling measurements by using a computer-controlled Sieverts apparatus described elsewhere³⁹. TPD measurements were conducted from vacuum to an H₂ pressure of 2 bar. PCI measurements were performed between 612 °C and 636 °C with pressure increments of 3 bar after 3 h for 636 °C and 5 h for the rest of the temperatures as waiting time. As the melting point of aluminium is 660 °C⁴⁰, the PCI measurements were constrained to < 660 °C to provide consistent thermodynamics. The CaH₂-Al₂O₃ mixtures (1:1 and 2:1 molar ratios) were pressure cycled at 636 °C at a ramping rate 5 °C/min for 10 h steps. The hydrogen pressure increment during charging and discharging was 10 and 3 bar respectively. For the gas measurements, a silicon carbide (SiC) sample cell was used. The hydrogen permeation through SiC cells at high temperature is negligible^{39, 41}. All samples were loaded into a stainless steel sample holder within the SiC sample cell.

The morphological changes of the CaH_2 - Al_2O_3 mixtures before and after hydrogen cycling were studied by field emission scanning electron microscopy (FE-SEM) using a Zeiss Neon (40EsB). The specimens were placed onto carbon tape mounted on an aluminium stub inside the argon-filled glove box. To reduce exposure to air, the samples were transferred to the vacuum chamber of the SEM using a custom-made holder.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic predictions

Thermodynamic predictions of the CaH₂ destabilisation reaction with Al₂O₃ at different molar ratios were calculated as presented in Table 1. The predicted reaction pathways demonstrate favourable reaction enthalpies that might meet the US DOE Sunshot's target for the next-generation TES systems⁴². It is clear that reaction 1 and 2 from Table 1 is the most favourable reaction, according to HSC. These two reactions are favourable in the high-temperature region, and both significantly starts from 400 °C and 500 °C, respectively (Figure S1). However, these are thermodynamically favourable according to prediction but have not been tested, and the kinetics are unknown.

Table 1. Thermodynamic predictions of the reaction between CaH_2 and Al_2O_3 at 1 bar of H_2 pressure.

		Theoretical	5.4.4		
No.	Predicted Reaction	operating	Theoretical	al Enthalpy kJ/kg	Enthalpy ΔH
		temperature	H_2 wt%		
		°C			kJ.mol ⁻¹ H ₂
1	$3CaH_{2+}Al_{2}O_{3} \leftrightarrow 3 CaO + 2Al + 3H_{2}(g)$	510	2.65	1446	110
2	$12\text{CaH}_{2+}11\text{Al}_2\text{O}_3 \leftrightarrow \text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + 8\text{Al} + 12\text{H}_2(\text{g})$	375	1.48	760	103
3	$1.5CaH_{2}+2\ Al_2O_3 \leftrightarrow Ca_{1.5}Al_3O_6 + Al + 1.5H_2(g)$	340	1.13	528	94
4	$1.5CaH_{2+}3.5Al_{2}O_{3} \ \leftrightarrow Ca_{1.5}Al_{6}O_{10.5} + Al + 1.5H_{2}(g)$	240	0.7	307	86
5	$1.5\text{CaH}_{2+}9.5\text{Al}_2\text{O}_3 \leftrightarrow \text{Ca}_{1.5}\text{Al}_{18}\text{O}_{28.5} + \text{Al} + 1.5\text{H}_2(g)$	175	0.2	77	79

3.1. Initial phase analysis

Ex situ X-ray diffraction patterns of the starting material (CaH₂ and Al₂O₃), together with the CaH₂-Al₂O₃ mixture (1:1 molar ratio) are presented in Figure 1 (a), (b) and (c) respectively. Diffraction patterns were refined by the Rietveld method to determine their purity. It was found that the CaH₂ sample comprised of 91 \pm 1.5 % CaH₂ with 9 \pm 1.5 % CaO as an impurity (Figure

S2). The diffraction pattern of CaH₂-Al₂O₃ mixture as prepared consisted of only peaks that were assigned to CaH₂ (27.88 \pm 0.5 wt%), CaO (0.54 \pm 0.2 wt%) and Al₂O₃ (71.58 \pm 0.5 wt%) (Figure S3), indicating that CaH₂ and Al₂O₃ did not react with each other during ball milling to form a calcium aluminium oxide. The CaO weight percentage in the CaH₂-Al₂O₃ mixture is lower than expected; this may be due to the ball milling process were CaO particles have become smaller and hence their diffraction peaks broaden and are lost in the background. It can be seen that the intensity associated with the diffraction peaks of Al₂O₃ is much higher and narrower than the CaH₂ peaks. This is due to Al₂O₃ being more crystalline than CaH₂.



Figure 1. *Ex situ* powder diffraction patterns of (a) CaH₂, (b) Al₂O₃ and (c) CaH₂ -Al₂O₃ mixture as prepared using Cu K α radiation($\lambda = 1.5418$ Å).

3.2. Thermal analysis

TPD-MS measurements were performed on CaH_2 and the CaH_2 -Al₂O₃ mixture to both determine and compare their hydrogen desorption profiles. As vacuum was used, CaH_2 started to release hydrogen at 500 °C and reached its highest intensity of desorption at 600 °C (Figure 2 (a)). Figure 2(b) shows the hydrogen desorption profile of the CaH_2 -Al₂O₃ mixture, with the main peak lowered by ~400 °C in comparison to pure CaH_2 . This clearly indicates that the

addition of Al_2O_3 to CaH_2 reduces the decomposition temperature. No other gasses were detected by the mass spectrometer in the mass range 1 -150 amu.



Figure 2. Hydrogen desorption profiles as observed by TPD-MS measurements of (a) CaH_2 and (b) the CaH_2 -Al₂O₃ mixture in 1:1 molar ratio at a heating rate of 5 °C/min under vacuum.

Temperature programmed desorption was performed from room temperature to 800 °C on the $CaH_2-Al_2O_3$ mixture. According to Figure 3 (b), a small amount of gas is released at lower temperatures (200 - 550 °C) than expected, and it may be due to the presence of impurities. The reaction between CaH_2 and Al_2O_3 becomes significant from 560 °C reaching maximum hydrogen desorption of 1.2 % H_2 at 700 °C. The measurement started at vacuum and reached a maximum H_2 pressure of 2 bar.

The *in situ* X-ray diffraction data of CaH_2 -Al₂O₃ mixture is presented in Figure 3 (a) and compared with the TPD curve (collected separately). From Figure 3 (a) it is evident that the

 reaction between CaH_2 and Al_2O_3 is significant above 500 °C, which is in agreement with the TPD curve in Figure 3 (b). In addition, the CaH_2 completely reacts by 500 °C and commences to form a new compound $Ca_{12}Al_{14}O_{33}$.



Figure 3. (a) *In situ* X-ray diffraction patterns using Mo K α of $\lambda = 0.7093187$ Å and (b) TPD profiles of the CaH₂-Al₂O₃ mixture from vacuum to a maximum H₂ pressure of 2 bar.

The decomposition products after the TPD measurement for the CaH₂-Al₂O₃ mixture were determined by *ex situ* X-ray powder diffraction (Figure 4) and quantified by the Rietveld refinement method. Ca₁₂Al₁₄O₃₃ was the main decomposition product ($48.78 \pm 0.7 \text{ wt }\%$), along with $7.35 \pm 0.3 \text{ wt }\%$ of CaO, $7.93 \pm 0.4 \text{ wt }\%$ of Al and $35.9 \pm 0.7 \text{ wt}\%$ of unreacted Al₂O₃ (Figure S4). These experimentally determined decomposition products are the same as predicted in reactions (1) and (2), when combined, as seen in Table 1. Hence, the actual

destabilisation reaction of CaH_2 with Al_2O_3 is different from the predicted reactions from HSC. Table 2 shows the comparison between the predicted and experimental destabilisation reactions for CaH_2 with the addition of Al_2O_3 .



Figure 4. *Ex situ* X-ray diffraction (Cu K α , $\lambda = 1.5418$ Å) pattern of the CaH₂-Al₂O₃ mixture as prepared after the TPD experiment.

 Table 2. Comparison between theoretical (Table 1) and experimental reactions (XRD
 Rietveld data)

Theoretical	Experimental		
1. $12CaH_2 + 11Al_2O_3 \leftrightarrow Ca_{12}Al_{14}O_{33} + 8Al + 12H_2(g)$ $\Delta H = 102.8 \text{ kJ.mol}^{-1} \text{ H}_2,$ $\Delta S = 159.1 \text{ J.K}^{-1}\text{mol}^{-1} \text{ H}_2$	$3CaH_2 + 2Al_2O_3 \leftrightarrow \frac{1}{7}Ca_{12}Al_{14}O_{33} + \frac{9}{7}CaO + 2Al + 3H_2(g)$		
	$\Delta H = 100 \pm 2 \text{ kJ.mol}^{-1} \text{ H}_2,$		
2. $3CaH_2 + Al_2O_3 \leftrightarrow 3CaO + 2Al + 3H_2(g)$	$\Delta S = 110 \pm 2 \text{ J.K}^{-1} \text{mol}^{-1} \text{H}_2$		
$\Delta H = 110.2 \text{ kJ.mol}^{-1} \text{ H}_2,$			
$\Delta S = 140.8 \text{ J.K}^{-1} \text{mol}^{-1} \text{ H}_2$			

Pressure Composition Isotherm (PCI) measurements were performed at three different temperatures (612, 626 and 636 °C) (Figure 5a). The van't Hoff plot (Figure 5b) was 12

constructed by taking the mid-point values of each PCI profile (Figure 5a) as to determine the thermodynamic values (enthalpy and entropy) of the proposed destabilisation reaction. All three PCI profiles (Figure 5a) show a slightly slopping pressure plateau, which may influence the engineering of the container as hydrogen absorption and desorption at a constant pressure and temperature is desired due to the simplicity of the system⁴³. The kinetic data for the PCI measurements at 636, 626 and 612 °C (Figure S5) show that the equilibrium plateau was almost reached after each desorption step. PCI measurements were also obtained at 645 and 655 °C (Figure S6), which profiles exhibited slopping plateaus, and as such thermodynamic data from these measurements could not be trustable.

The enthalpy and entropy were determined from the van't Hoff plot as $\Delta H = 100 \pm 2 \text{ kJ.mol}^{-1}$ H₂ and $\Delta S = 110 \pm 2 \text{ J.K}^{-1}\text{mol}^{-1}$ H₂ respectively. The theoretical enthalpy and entropy were, $\Delta H = 103 \text{ kJ.mol}^{-1}$ H₂, $\Delta S = 160 \text{ J.K}^{-1}\text{mol}^{-1}$ H₂. The mismatch between the theoretical and experimental values may be due to the different reaction pathways observed between theoretical and experimental. However, for a more definite answer further investigation is required.



Figure 5. (a) Pressure Composition Isotherms of CaH₂-Al₂O₃ mixture between 612 and 636 °C and (b) corresponding van't Hoff plot.

In order to check the feasibility of the as prepared $CaH_2-Al_2O_3$ mixture (1:1 molar ratio) as a high-temperature thermal battery, the mixture was cycled at 636 °C by absorbing and releasing hydrogen. Figure 6 shows, four hydrogen desorption/ absorption cycles of the mixture. It is noted that each cycle reaches a plateau, indicating that the kinetics of the desorption and absorption reaction are fast enough to be completed within the 10 h of each step duration. It is evident that after each cycle, the material degrades by 50 % in comparison to the previous cycle. After the 3rd cycle, the mixture lost its reversibility with a 90 % loss in storage capacity.



Figure 6. H₂ desorption and absorption cycles of the CaH₂-Al₂O₃ mixture at 636 °C.

The reasons why the hydrogen capacity of the $CaH_2-Al_2O_3$ mixture degrades may be due to: (i) the presence of excess unreacted alumina (35.6 ± 0.5 wt %) that is present in the cycled mixture (Figure S7) that may hinder the reaction kinetics, (ii) the sample may also sinter after heating to high temperature. SEM was utilised to investigate these possibilities. The sintering effect can be seen from the SEM micrographs of the $CaH_2-Al_2O_3$ mixture before (Figure 7a) and after (Figure 7b) cycling, where the particle sizes of the cycled mixture are evidently bigger than the ones prior to cycling.



Figure 7. Scanning electron micrographs of the CaH_2 - Al_2O_3 mixture (1:1 molar ratio) (a) before and (b) after 4 cycles at 636 °C.

In order to improve the reversibility of the CaH₂-Al₂O₃ system a new mixture of CaH₂ and Al₂O₃ was synthesised in a 2:1 molar ratio to minimise the quantity of excess Al₂O₃. The 2CaH₂-Al₂O₃ mixture showed significant improvement regarding its cyclic hydrogen reversibility as seen in Figure 8, without much loss in hydrogen storage capacity, deeming this new mixture promising as a high-temperature thermal battery for CSP applications. It is noted from the same figure that each cycle has not reached a plateau, indicating that the kinetics of the desorption and absorption reaction are not fast enough to be completed within the 10 h of each step duration. This phenomenon could be due to the sample sintering as observed in Figure

9. Moreover, the unreacted Al_2O_3 left over after cycling was reduced to 5.5 ± 0.3 wt% (Figure S6) compared to 35.6 ± 0.5 wt% in the first mixture.

 Table 3 shows a comparison of the $CaH_2-Al_2O_3$ system with pure CaH_2 and the CaH_2-2Al system in terms of cost and operating conditions. It can be seen that the $CaH_2-Al_2O_3$ system operates at a high temperature and low pressure (636 °C at 1 bar) and is a low-cost material making it a promising high-temperature thermal battery for the next generation of CSP applications.



Figure 8. H₂ desorption and absorption cycles of the 2CaH₂-Al₂O₃ mixture at 636 °C.



Figure 9. Scanning electron micrographs of the 2CaH₂-Al₂O₃ mixture after cycling at 636 °C.

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	ΔH kJ.mol ⁻¹ H ₂	ΔH kJ/kg	US \$/ ton	US \$/ kWh- thermal	Operating conditions
3CaH ₂ +2Al ₂ O ₃ ⁴⁴	100	904.8	2460	9.7	636 °C 1 bar
CaH ₂ +2Al ^{12, 23, 24, 45}	84	875	3631	14.93	700 62 bar
CaH ₂ ⁴⁶	162	3857	6000	5.6	1000 °C 1.2 bar

4. CONCLUSIONS

The feasibility of CaH₂ destabilised with Al₂O₃ and used as a high-temperature thermal battery for the next-generation of CSP applications was investigated. Thermal desorption studies showed that the decomposition temperature of the CaH₂-Al₂O₃ mixture was ~600 °C and obtained a maximum gravimetric H₂ wt% of 1.2 when heated to 850 °C. *Ex situ* and *in situ* Xray diffraction studies showed that the main product of the destabilisation reaction was Ca₁₂Al₁₄O₃₃. The high enthalpy of reaction, high operating temperature at low pressure (636 °C at 1 bar) and low materials cost of this system, makes it a promising high-temperature thermal battery for the next generation of CSP applications. Though, due to the presence of excess unreacted alumina and sintering effects demonstrated a poor performance upon cycling initially, however, the hydrogen cycling capacity was significantly improved by reducing the initial amount of Al₂O₃ by half. Further investigation into the reaction kinetics, heat transfer, thermal conductivity and hydrogen cycling stability over 100 cycles are required to prove its overall efficiency as a TES material.

ASSOCIATED CONTENT

Supporting Information

HSC graphical simulation of CaH₂-Al₂O₃ system at 1bar of pressure, Rietveld refinement of the diffraction patterns for pure CaH₂, CaH₂/Al₂O₃ mixture after ball milling, CaH₂/Al₂O₃ after TPD, CaH₂/Al₂O₃ after cycling, 2CaH₂/Al₂O₃after cycling, equilibrium pressure curves of PCI measurements, comparison of Pressure Composition Isotherms of CaH₂-Al₂O₃ mixture between 636, 645 and 655 °C.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

 The authors declare no competing financial interest.

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