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Thermodynamics and performance of the Mg–H–F system for thermochemical energy storage applications


Magnesium hydride (MgH₂) is a hydrogen storage material that operates at temperatures above 300 °C. Unfortunately, magnesium sintering occurs above 420 °C, inhibiting its application as a thermal energy storage material. In this study, the substitution of fluorine for hydrogen in MgH₂ to form a range of Mg(HₓFₙ₋ₓ₂)₂ (x = 1, 0.95, 0.85, 0.70, 0.50, 0) composites has been utilised to thermodynamically stabilise the material, so it can be used as a thermochemical energy storage material that can replace molten salts in concentrating solar thermal plants. These materials have been studied by in situ synchrotron X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, temperature-programmed desorption mass spectrometry and Pressure-Composition-Isothermal (PCI) analysis. Thermal analysis has determined that the thermal stability of Mg–H–F solid solutions increases proportionally with fluorine content, with Mg(H₀.₅F₀.₅)₂ having a maximum rate of H₂ desorption at 434 °C, with a practical hydrogen capacity of 4.6 ± 0.2 H₂ wt% (theoretical 5.4 wt% H₂). An extremely stable Mg(H₀.₅F₀.₅)₂ phase is formed upon the decomposition of each Mg–H–F composition of which the remaining H₂ is not released until above 505 °C. PCI measurements of Mg(H₀.₅F₀.₅)₂ have determined the enthalpy (ΔH_m) to be 73.6 ± 0.2 kJ/mol H₂ and entropy (ΔS_m) to be 131.2 ± 0.2 J/K/mol H₂, which is slightly lower than MgH₂, with ΔH_m of 74.06 kJ/mol H₂ and ΔS_m = 133.4 J/K/mol H₂. Cycling studies of Mg(H₀.₅F₀.₅)₂ over six absorption/desorption cycles between 425 and 480 °C show an increased usable cycling temperature of ~80 °C compared to bulk MgH₂, increasing the thermal operating temperatures for technological applications.

Introduction

Metal hydrides have been identified as next generation storage materials for multiple applications including hydrogen and thermal energy storage, as well as solid state electrolytes.¹ ¹ Magnesium hydride was first identified as a hydrogen storage material in the early 1950s with one of the first thermal decomposition studies published in 1960.² ³ Due to its high gravimetric hydrogen content (7.6 wt% H₂), its high volumetric storage density of 111 kg m⁻³ H₂ and the relatively low cost of magnesium, this material, and many other magnesium based metal hydrides have been identified having potential for a variety of technologies.⁹ ¹³ To date, MgH₂ has been targeted as a stationary hydrogen storage material and thermochemical energy storage (TES) material due to its relatively high thermal stability. Upon thermal treatment at 330 °C, MgH₂ decomposes into Mg and H₂ with ΔH_des = 74.06 kJ/mol H₂ and ΔS_des = 133.4 J/K mol⁻¹ H₂.¹⁴ The implementation of MgH₂ as a TES material was discussed as early as 1987 and since this time, a number of MgH₂-based hydrogen storage tanks have been developed and prototype systems manufactured.¹⁵-²¹ One of the most promising applications for MgH₂ is as a TES material in concentrating solar (CSP) plants.²² ²⁶ The current operating temperature for a conventional CSP power plant with TES is approximately 565 °C,²² while for next-generation CSP plants, operating temperatures between 600 °C to 800 °C are proposed.²³ ²⁴ Although the thermal properties of MgH₂ confirm that it is a good candidate as a high-temperature metal hydride (HTMH) coupled with a low-cost metal hydride pair for energy storage, the typical operating temperature (~400 °C) is not high enough to meet the targets set by industry. In addition, other contributing factors inhibit the use of pure MgH₂ as TES material due to poor cycling stability above 400 °C with a significant reduction in the H₂ storage capacity over tens to hundreds of absorption/desorption cycles due to sintering of the Mg particles.²⁵ Furthermore, the high H₂ equilibrium pressure of MgH₂ at 550°C, ~210 bar, makes its use impractical from an engineering perspective.¹⁴ The focus of the current study is to enhance the cyclic stability and to decrease the H₂ equilibrium pressure of MgH₂ by forming a solid solution between MgH₂ and MgF₂. Sheppard et al. recently reported that one method to increase the operating temperature of a metal hydride (MH) is to partially replace hydrogen by fluorine, as this thermodynamically stabilises the corresponding solid-solution metal hydride-

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J. Name., 2013, 00, 1-3 | 1

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fluoride. 26-28 As such, many materials that operate below the target temperature of ~500 °C may become feasible for higher temperature applications. Furthermore, the addition of fluorine can reduce the cost of a TES system and improve metal hydride reversibility, which is a key factor given the typical 30-year lifetime of a CSP plant. 27, 29

To increase the operating temperature of the Mg–H system, fluorine substitution to form Mg(HF1-xFx) solid solutions have been studied herein. Previous studies on mixtures of MgH2 + xMFy (M = Mg, Zr, Ti, Fe, Ta, Ni, Nb; x = 5 - 7 mol%; y = 2 - 5) have concentrated on improving the kinetics of MgH2 for operation at lower temperatures. 30-35 The kinetics of decomposition were determined to be considerably faster than pure MgH2 with full H2 release within 600 s, 30 with negligible loss in H2 cycling capacity at 310 °C. The reason for the improved kinetics has been explored by a variety of techniques including X-ray photoemission spectroscopy (XPS) and powder X-ray diffraction (XRD). 33, 34 although there are mixed reports on whether the transition metal or MgF2 species forms is responsible for the enhanced performance. 30, 33, 34

Recently a preliminary study has shown that MgH2 and MgF2 forms solid solutions with Mg(H0.50F0.50)x2 reversibly absorbing 5.5 wt % H2 in less than 3 min at 440 °C. 36 Thermal analysis by differential scanning calorimetry (DSC) indicates that ΔHdes for Mg(H0.50F0.50)x2 is close to that of MgH2 (74.0 kJ·mol⁻¹·H2) 14 and decreases with decreasing H content. However, without the determination of ΔSdes the stability of the material can’t be truly assessed. Previous studies have shown that an incremental substitution of F causes a decrease in ΔHdes although a concomitant decrease in ΔSdes causes an overall stabilisation of the material. 27 Further analysis of this system by pressure-composition-isotherm (PCI) analysis is required to precisely determine the decomposition pathway and the associated thermodynamics. These properties are required to assess the viability of Mg(HF1-xFx)2 as a TES material, especially at temperatures > 400 °C.

In this study, MgH2 has been ball-milled with MgF2 followed by annealing to successfully form solid solutions of Mg(HF1-xFx)2 (x = 1, 0.95, 0.85, 0.70, 0.50, 0) to determine differences in their structural and thermodynamic properties. Time resolved synchrotron radiation powder X-ray diffraction (SR-XRD) studies have been carried out on a range of Mg(HF1-xFx)2 compositions to ascertain the differences in thermal decomposition pathways of these compounds. The thermodynamic and kinetic properties of these solid solutions have been determined by PCI analysis using the van’t Hoff method, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), temperature-programmed-desorption mass spectrometry (TPD-MS). Cycling studies have also been carried out to determine the feasibility of the Mg–H–F system for CSP application.

Experimental

All manipulations of chemicals were undertaken in an argon atmosphere using an Mbraun Unilab glovebox to prevent air exposure and to minimise oxygen (O2 < 1 ppm) and water (H2O < 1 ppm) contamination. Mg(HF1-xFx)2 (x = 1, 0.95, 0.85, 0.70, 0.50, 0) samples were prepared by ball milling (BM) various ratios (Table 1) of MgH2 and MgF2 (Sigma-Aldrich, >99.99 %) at room temperature. MgH2 powder (95 wt% purity from Rietveld refinement) was first synthesised by annealing Mg powder (Aldrich, >99 %) at 400 °C under 30 bar hydrogen pressure for 18 hours. The partially hydrogenated Mg was then BM for 3 hours with a ball-to-powder mass ratio of 10:1 in a Shaker Mill (Turbula T2C shaker-mixer) and annealed once again under identical conditions (400 °C, 30 bar H2, 18 h). BM of MgH2 and MgF2 was undertaken at 400 rpm for 10 hours (labelled S) or 40 hours (labelled L) in an Across International Planetary Ball Mill (PQ-N04) with a ball-to-powder mass ratio of 50:1 using stainless steel vials and balls (6 and 8 mm in diameter) under an Ar atmosphere. After milling, samples were annealed under a hydrogen atmosphere of 60 bar at 450 °C for a period of 90 hours to form uniform solid solutions. Annealing samples under H2 prevents hydrogen release from the material. 27

Before and after annealing the Mg(HF1-xFx)2 powders, quantitative phase analysis was undertaken by conducting ex situ XRD analysis on each sample. The powders were mixed with ~10 wt% Si (~325 mesh, Aldrich) as an internal standard (α = 5.42960(4) Å), used to extract reliable lattice parameters for the solid solutions. Ex situ XRD was performed using a Bruker D8 Advance diffractometer (Cu-Kα2 radiation, λ = 1.5418 Å) with flat-plate sample holders sealed by a polymethylmethacrylate (PMMA) dome in order to prevent oxygen/moisture contamination during data collection. The PMMA dome resulted in a broad hump in XRD patterns centred at ~20° 2θ. Acquisition of data was subsequently restricted to 2θ = 20 – 80°, with a Δ2θ = 0.02° and 2 s/step scanning rate with a sample rotation rate of 60 rpm. In situ synchrotron radiation SR-XRD was performed at the Australian Synchrotron in Melbourne, Australia. 27 Without exposure to air, the Mg(HF1-xFx)2 powders (ball milled for 40 h) were loaded into borosilicate or quartz capillaries (outer diameter 0.7 mm, wall thickness 0.01 mm) that were then, using graphite ferrules, mounted in 1/16 tube fittings connected to a gas manifold. The samples were kept under dynamic vacuum while heated with a hot air blower up to 615 °C (Room Temperature (RT) → 200 °C at 10 °C/min, 200 → 615 °C at 5 °C/min). Mg(H0.50F0.50)x2 was measured with a temperature heating rate of 8 °C/min from 150 to 785 °C. One-dimensional SR-XRD patterns (monochromatic X-rays with λ = 1.000389(1), 0.826307(1) or 0.774541(1) Å) were collected using a Mythen microstrip detector with an exposure time of 54 s per pattern. The capillaries were continuously oscillated through 120° during exposure to improve powder averaging. Diffraction patterns were quantitatively analysed using the Rietveld refinement method with TOPAS software (Bruker-AKS). The temperature of the hot-air blower was calibrated against the known thermal expansion coefficients for NaCl and Ag. 27, 39

TGA and DSC in conjunction with MS (DSC-TGA-MS) analyses were conducted using sample masses of ~10 mg at a heating rate of 10 °C/min under an argon flow of 20 mL/min using a Mettler Toledo TGA/DSC 1 coupled with an Omnistar MS.
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J. Name., 2013, 00, 1-3 | 3

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Table 1. Structural properties of Mg(HₓF₁₋ₓ)₂-L mixtures (P42/mnm) at room temperature. Estimated standard deviations (esds) of lattice parameters and H occupancies in the 4f site are in parentheses.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>MgH₂:MgF₂ Molar ratio (target)</th>
<th>Lattice Parameter (Å)</th>
<th>H Occupancy</th>
<th>Unit cell volume (Å³)</th>
<th>Mg₂FeH₆ impurity (wt%)</th>
<th>Mg,H₂ content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH₂</td>
<td>1:0</td>
<td>4.51746(5)</td>
<td>3.02215(6)</td>
<td>1(0)</td>
<td>61.674(2)</td>
<td>0</td>
</tr>
<tr>
<td>Mg(H₀.₅F₀.₅)₂</td>
<td>0.95:0.05</td>
<td>4.52109(4)</td>
<td>3.02306(4)</td>
<td>0.919(9)</td>
<td>61.792(1)</td>
<td>0</td>
</tr>
<tr>
<td>Mg(H₀.₈F₀.₂)₂</td>
<td>0.85:0.15</td>
<td>4.54238(6)</td>
<td>3.02917(7)</td>
<td>0.801(2)</td>
<td>62.509(0)</td>
<td>3</td>
</tr>
<tr>
<td>Mg(H₀.₇F₀.₃)₂</td>
<td>0.7:0.3</td>
<td>4.55932(3)</td>
<td>3.03417(3)</td>
<td>0.7275(5)</td>
<td>63.072(1)</td>
<td>7</td>
</tr>
<tr>
<td>Mg(H₀.₅F₀.₅)₂</td>
<td>0.5:0.5</td>
<td>4.59133(2)</td>
<td>3.04372(2)</td>
<td>0.393(4)</td>
<td>64.162(1)</td>
<td>12</td>
</tr>
<tr>
<td>MgF₂</td>
<td>0:1</td>
<td>4.62312(2)</td>
<td>3.05195(2)</td>
<td>0(0)</td>
<td>65.230(1)</td>
<td>---</td>
</tr>
</tbody>
</table>

Masses (m/e = 2 – 100) were monitored up to 550 °C, however the Mg(H₀.₅F₀.₅)₂ was measured up to 850 °C. The instrument was installed in an Ar filled glovebox to avoid air contamination during sample handling. The temperature accuracy of this instrument is ±0.2 °C, while the balance has an accuracy of ±20 μg.

All hydrogen absorption/desorption measurements were performed by using a computer controlled Sieverts/volumetric apparatus previously described elsewhere.²⁸ The digital pressure transducer (Rosemount 3051S) had a precision and accuracy of 14 mbar, whilst room temperature measurements were recorded using a 4-wire platinum resistance temperature detector (RTD). Isothermal PCI curves were performed at 437, 444, 450 and 461 °C and monitored by a K-type thermocouple (± 4 °C). Above ~420 °C, the permeation of hydrogen directly through the walls of the stainless steel sample cell becomes an issue and the measured hydrogen content at each PCI data point has to be corrected for this loss, as previously explained.²⁸ In addition, hydrogen absorption PCI measurements were carried out at ~450 °C on the same apparatus.

Hydrogen absorption/desorption cycles were conducted by heating a sample of Mg(H₀.₅F₀.₅)₂ at 4 °C/min from room temperature to 425 °C followed by a 6 h isothermal period. The temperature was then heated at 2 °C/min to 480 °C followed by another 6 h isothermal step; it is during this stage the first decomposition begins. The temperature was then cycled between 425 °C (hydrogen absorption) and 480 °C (hydrogen desorption) 6 times under a closed gas system pressure varying between 30 - 42 bar.

Results and Discussion

Structure and Composition.
The BM powders were analysed by ex situ XRD before and after annealing to confirm that a Mg(HF\textsubscript{1-x}L\textsubscript{x}) solid solution was formed and that neither of the MgH\textsubscript{2} and MgF\textsubscript{2} starting materials were present (Fig. S1). Due to the fact that MgH\textsubscript{2} and MgF\textsubscript{2} both exist in a tetragonal rutile crystal structure (P4\textsubscript{2}mm\textsubscript{2}),\textsuperscript{40, 41} the solid solutions of Mg(HF\textsubscript{1-x}L\textsubscript{x}) also possess identical structures, as predicted by Messer.\textsuperscript{42} The annealing process, while also enhancing the crystallinity of the samples, was necessary to allow the H and F atoms to substitute in to the 4f sites and form a uniform solid solution (Table 1). Milling alone is not enough to facilitate the formation of a uniform single phase, although extended milling time aids in attaining a uniform sample composition. However, extended milling may lead to the introduction of iron impurities from the stainless-steel canisters and balls, resulting in the formation of small amounts of MgFe\textsubscript{6} being evident after annealing (Fig. 1, Table 1).\textsuperscript{43, 44} Therefore, it is important to restrict long milling times in order to reduce the quantity of impurities. After BM for 40 h the samples were analysed by XRD and it can be seen that the samples exhibit broad diffraction peaks suggestive of a single tetragonal phase or an extended range of Mg(HF\textsubscript{1-x}L\textsubscript{x}) compositions (Fig. S1), but annealing promotes crystallisation into single phase compositions (Fig. 1). Quantitative phase analysis of each the mixtures identifies that Mg(H\textsubscript{0.50}F\textsubscript{0.50})\textsubscript{L} contains the largest quantity of MgF\textsubscript{6}\textsuperscript{43, 44} (Table 1) and it is deemed that the greater hardness of MgF\textsubscript{2} compared to stainless-steel is responsible (MgF\textsubscript{2} has a hardness of 415 kg/mm\textsuperscript{2} Knoop,\textsuperscript{45} whereas stainless steel has a hardness of 166 kg/mm\textsuperscript{2} Knoop).\textsuperscript{46} Therefore, increased MgF\textsubscript{2} content in the sample promotes erosion of the stainless-steel and, by consequence, incremental quantities of MgFe\textsubscript{6} are observed. In addition, Fe metal is observed in only the Mg(H\textsubscript{0.50}F\textsubscript{0.50})\textsubscript{L} materials. Some MgO is observed in sample Mg(H\textsubscript{0.70}F\textsubscript{0.30})\textsubscript{L} due to an inadvertent exposure of the sample to air during mounting of the capillary before XRD. MgO and other impurities may also be formed due to reaction with the borosilicate or quartz capillaries. In this study, no additional impurity phases were identified to form during the in situ heating experiment.

Fig. 1 illustrates the SR-XRD patterns for each of the L-solid solutions at room temperature. It is noted that the peaks for Mg(HF\textsubscript{1-x}L\textsubscript{x}) move to lower angles (higher d-spacing) with increased F content. This is emphasised in Fig. S2. This shift causes a concomitant increase in unit cell volume from 61.674(2) Å\textsuperscript{3} for MgH\textsubscript{2} to 65.230(1) Å\textsuperscript{3} for MgF\textsubscript{2} (Table 1). This is expected due to the longer Mg–F bond distances of 1.9968 Å\textsuperscript{47} in MgF\textsubscript{2} compared to the apical Mg–H distance of 1.94(2) Å and the equatorial Mg–H distance of 1.97(2) Å in MgH\textsubscript{2}.\textsuperscript{48} The lattice parameters for the Mg–H–F solid solution are illustrated in Fig. 2a and clearly show that the a and c parameters increase with increasing fluorine content, with a having a dominant influence on the unit cell expansion. Previous studies have used the lattice parameters to predict the H/F compositions of the materials after hydrogen absorption/desorption cycles,\textsuperscript{27} while the unit cell volume can also be utilised (Fig. 2b). The H occupancy factor may also be employed as a measure of substitution between H and F (Fig. 2b). Despite H having a negligible scattering factor, the X-ray cross section of F allows for appreciable determination of the occupancy of the 4f site of which the F and H share. To avoid Fe impurities the milling time of the samples were reduced to 10 h while maintaining the annealing conditions (90 h at 450 °C at 60 bar H\textsubscript{2}). These samples are labelled as Mg(HF\textsubscript{1-x}L\textsubscript{x})S. The annealed S samples were analysed by XRD and show no presence of MgFe\textsubscript{6} although the shape of the Mg(HF\textsubscript{1-x}L\textsubscript{x}) solid solution Bragg peaks were asymmetric (Fig. S3).

![Figure 2](image2.png)

**Fig. 2.** Refined lattice parameters of Mg(HF\textsubscript{1-x}L\textsubscript{x}) mixtures from room temperature in situ XRD. (a) Quadratic fit for lattice parameters a and c versus composition.
\[ a = -0.8762x^2 + 0.0326x + 4.6236, \quad c = -0.0239x^2 - 0.0069x + 3.0521 \]
(b) Quadratic fit for unit cell volume and H occupancy versus composition. Unit cell volume \( V = -2.5527x^2 - 1.1113x + 65.246 \), H Occupancy = 0.2073x\textsuperscript{2} + 0.7952x - 0.0064.

**Thermal analysis.**

*In situ* SR-XRD was carried out up to 615 °C on all sample compositions with Fig. 3a illustrating Mg(H\textsubscript{0.85}F\textsubscript{0.15})S and exemplifying the decomposition process (also see Fig. S4-S6). As temperature increases, thermal expansion causes the lattice parameters of Mg(H\textsubscript{0.85}F\textsubscript{0.15})S (and the minor MgFe\textsubscript{6} phase) to expand (2θ decreases) before both materials decompose simultaneously at an onset temperature of 433 °C with total decomposition occurring by 440 °C. The decomposition observed in XRD data is also mirrored in the TGA-DSC-MS data (Fig. 3b - d). The DSC data show a single endothermic event between 350 - 450 °C for all hydrogen
containing samples (Fig. 3b, Table 2). The onset temperature for the decomposition of pure MgH₂-S is ~394 °C with a maximum H₂ release at ~413 °C. The decomposition temperature of the pure hydride is greater than that of Mg(HₓF₁₋ₓ)₂-S, which has on onset temperature of 360 °C and a maximum H₂ release temperature of 405 °C. From this it can be inferred that Mg(HₓF₁₋ₓ)₂-S has faster kinetics of desorption than pure MgH₂-S. A result that has also been noted previously. Further substitution of H by F appears to kinetically and/or thermodynamically stabilise MgH₂ with Mg(HₓF₁₋ₓ)₂-S having a decomposition onset of 405 °C (peak maximum of 434 °C), while Mg(HₓF₁₋ₓ)₂-S has an onset of ~415 °C (peak maximum of 437 °C). One of the most intriguing results is that Mg(HₓF₁₋ₓ)₂-S shows no obvious decomposition event during DSC measurement up to 550 °C (Fig. 3b). This is in agreement with the in situ SR-XRD measurement of Mg(HₓF₁₋ₓ)₂-L up to 615 °C, Fig. S5. This particular in situ SR-XRD pattern also shows the presence of Mg₂Feₓ which disappears at ~450 °C in conjunction with the appearance of Mg at the same temperature. The disappearance of the Mg at ~530 °C is due to the migration of Mg vapour from the hot-zone during measurement.

The decomposition onset for the Mg₂Feₓ impurity phase determined in each of the Mg(HₓF₁₋ₓ)₂ (x = 0.85, 0.70, 0.50) samples measured by in situ XRD occurs at ~430 °C. A previous in situ XRD decomposition study of Mg₂Feₓ shows the onset of decomposition to occur at ~340 °C under 1 bar Ar. To ascertain if F substitution had occurred within Mg(HₓF₁₋ₓ) during annealing, refinement of the lattice parameter and H/F occupancy factors on the 24e site in the Fm3m unit cell was undertaken. At room temperature the unit cell dimension was determined as 6.46277(8) Å, which is only 0.25% larger than 6.44686(2) Å determined in a previous study, while the hydrogen occupancy was refined to be 100%. At ~380°C the hydrogen occupancy was determined to be 96.8(9) %, which indicates that some F substitution may have occurred at higher temperatures, and in turn may have increased the thermal stability of the Mg₂Feₓ material.

DSC and TPD-MS data were also collected for the samples milled for 40 h (L, Fig. S7). Upon comparing the L and S samples measured by DSC, it appears that extended milling times reduce the observed temperature of the endothermic peak compared to the corresponding compositions milled for 10 h. For instance, the maximum rate of H₂ release for Mg(HₓF₁₋ₓ)₂-S is 437 °C, whereas it is 367 °C for Mg(HₓF₁₋ₓ)₂-L. Extended milling decreases the crystallite and particle size, decreases diffusion pathways, increases the specific surface area and introduces defects. All of these factors contribute to faster kinetics that allow the hydride to decompose at a lower temperature.

TPD-MS was used to analyse the gases released by materials upon thermal treatment. In this study, the gases released during DSC-TGA were analysed for all m/e up to 100 showing that only H₂ was released during thermal treatment (Fig. 3d, log scale). The most striking result is that for Mg(HₓF₁₋ₓ)₂-S only minor H₂ evolution is observed between 290 and 475 °C. In fact, all samples apart from Mg(HₓF₁₋ₓ)₂-S start to desorb hydrogen between 290 and 340 °C, while it is only the peak rate of release that differs between the samples.

Considering that the thermal analysis experiments have indicated that increasing the F content in the samples increases thermal stability compared to pure MgH₂, it would be assumed that the Mg(HₓF₁₋ₓ)₂ sample would be the ideal candidate for further studies as a HTMH for TES applications. However, the larger practical hydrogen capacity of Mg(HₓF₁₋ₓ)₂ is far greater than Mg(HₓF₁₋ₓ)₂ below 550 °C (5.06 ± 0.02 wt% H₂ and 0.77 ± 0.01 wt% H₂, respectively). As such, Mg(HₓF₁₋ₓ)₂-S was deemed an ideal candidate to be studied by PCI between 437 and 461 °C to determine its thermodynamics of.
Table 2. Decomposition temperatures and hydrogen capacities and values of Mg(HₓF₁₋ₓ)₂-S mixtures measured by DSC-TGA up to 550 °C. ΔT/Δt = 10 °C/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Practical / theoretical H₂ capacity (TGA, wt %)</th>
<th>Hydrogen yield (%)</th>
<th>Onset/Peak Temperature of H₂ desorption (DSC, °C) *</th>
<th>Temperature in middle point of step (TGA, °C) *</th>
<th>Peak Temperature of H₂ desorption (MS, °C) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH₂</td>
<td>7.50 ± 0.03 / 7.66</td>
<td>97.9</td>
<td>394/413</td>
<td>413</td>
<td>412</td>
</tr>
<tr>
<td>Mg(HₓF₀.₉₅)₂</td>
<td>6.60 ± 0.03 / 6.81</td>
<td>96.9</td>
<td>360/405</td>
<td>400</td>
<td>403</td>
</tr>
<tr>
<td>Mg(HₓF₀.₈₅)₂</td>
<td>5.06 ± 0.02 / 5.4</td>
<td>93.7</td>
<td>405/434</td>
<td>430</td>
<td>435</td>
</tr>
<tr>
<td>Mg(HₓF₀.₇₅)₂</td>
<td>1.60 ± 0.01 / 3.8</td>
<td>42.1</td>
<td>415/437</td>
<td>433</td>
<td>436</td>
</tr>
<tr>
<td>Mg(HₓF₀.₅₀)₂</td>
<td>0.77 ± 0.01 / 2.27</td>
<td>33.9</td>
<td>---</td>
<td>---</td>
<td>~414</td>
</tr>
</tbody>
</table>

* Temperature reported as integers although accurate to 0.02 °C.

decomposition (Fig. 4a). The PCI curves in Fig. 4a show that decomposition follows a single step process that releases an average total of 4.6 ± 0.2 wt% H₂ for the four temperatures measured, with equilibrium pressures between 32 and 38 bar. Each of the curves exhibits a sloping plateau that is highly characteristic of a solid solution of this type, albeit not as sloped as those observed in the NaHₓFₓO.₅₀ or NaMgHₓF systems.²⁷ ²⁸ Sloping plateaus are not ideal in practical applications due to the fact that hydrogen absorption and desorption does not occur in an isobaric process,²⁸ and the range of operational system pressures over the equilibrium transition becomes larger.

Generally, the thermodynamics of absorption/desorption are determined by measuring the pressure at the midpoint of the equilibrium plateau and plotting this as a function of temperature in a van’t Hoff plot. In this study, due to the sloping plateau, each of the four curves were numerically fitted throughout the plateau region so that the enthalpy and entropy could be determined at any hydrogen content (Fig. 4).²⁸ All of the information obtained from the PCI measurements presented in Fig. 4, are summarised in Table 3. The enthalpy (ΔHₐbs) and entropy (ΔSₐbs) of hydrogen desorption are also presented in Table 3. The uncertainties for the data were calculated using the weighted least squares method with a 95% confidence interval as described in previous work.¹⁴ The enthalpy, ΔHₐbs, decreases from 74.7 to 72.2 kJ/mol H₂ between −1 wt% to −3 wt% H₂ desorption. With regards to entropy, these values also show the same trend, decreasing in value from 133.0 to 129.1 J/K/mol H₂. This means that at −2 wt% H₂ (middle point of the plateau), ΔHₐbs = 73.6 ± 0.2 kJ/mol H₂ and ΔSₐbs = 131.2 ± 0.2 J/K/mol H₂ are 0.66% and 1.65% lower than that of pure MgH₂.

Fig. 4. (a) Pressure–Composition Isotherms (PCI) for Mg(HₓF₀.₅₀)₂-S performed between 437 °C and 461°C. *ln(ΔP)/Δx = 0.0297x + 3.7850, *ln(ΔP)/Δx = 0.0279x + 3.6048, *ln(ΔP)/Δx = 0.0256x + 3.4978, *ln(ΔP)/Δx = 0.0227x + 3.3731, where x = wt% H₂ desorbed. (b) van’t Hoff plot of respective H₂ desorption equilibrium pressures, where T is temperature (K), P₀=1 bar.
Table 3. Thermodynamic properties at 5 different hydrogen contents for Mg(H$_{0.85}$F$_{0.15}$)$_2$-S

<table>
<thead>
<tr>
<th>At H$_2$ wt%</th>
<th>$\Delta H_{\text{des}}$ (kJ/mol H$_2$)</th>
<th>$\Delta S_{\text{des}}$ (J/K/mol H$_2$)</th>
<th>$\Delta G$ (J/mol H$_2$)</th>
<th>van’t Hoff plot ln(P/P$_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>74.7 ± 0.2</td>
<td>133.0 ± 0.3</td>
<td>21.2 ± 0.2</td>
<td>-8982/T + 15.99</td>
</tr>
<tr>
<td>-1.5</td>
<td>74.1 ± 0.2</td>
<td>132.1 ± 0.2</td>
<td>21.2 ± 0.2</td>
<td>-8916/T + 15.87</td>
</tr>
<tr>
<td>-2</td>
<td>73.6 ± 0.2</td>
<td>131.2 ± 0.2</td>
<td>21.1 ± 0.2</td>
<td>-8849/T + 15.78</td>
</tr>
<tr>
<td>-2.5</td>
<td>72.9 ± 0.2</td>
<td>130.2 ± 0.3</td>
<td>21.0 ± 0.2</td>
<td>-8772/T + 15.66</td>
</tr>
<tr>
<td>-3</td>
<td>72.2 ± 0.2</td>
<td>129.1 ± 0.3</td>
<td>20.9 ± 0.2</td>
<td>-8685/T + 15.53</td>
</tr>
<tr>
<td>Pure MgH$_2$</td>
<td>74.06</td>
<td>133.4</td>
<td>22.17</td>
<td>---</td>
</tr>
</tbody>
</table>

MgH$_2$, respectively. This indicates that the equilibrium pressure at which decomposition will occur is insignificantly lower than that for MgH$_2$ at the same temperature. However, along the plateau the equilibrium pressures change (due to the sloping plateau) resulting in $\Delta H_{\text{des}}$ (Mg(H$_{0.85}$F$_{0.15}$)$_2$-S) > $\Delta H_{\text{des}}$ MgH$_2$ while < −1.58 wt%, and after this point (> −1.58 wt%) $\Delta H$ (Mg(H$_{0.85}$F$_{0.15}$)$_2$-S) < $\Delta H$ MgH$_2$. However, $\Delta S_{\text{des}}$ (Mg(H$_{0.85}$F$_{0.15}$)$_2$-S) < $\Delta S_{\text{des}}$ MgH$_2$ all along the plateau. Although these are only small changes in $\Delta H$ and $\Delta S$, it is still significant and are linked

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Fig. 5. (a) Reaction enthalpy and entropy for Mg(H$_{0.85}$F$_{0.15}$)$_2$. $\Delta S_{\text{des}}$ = 1.9181 × (wt% H$_2$) + 134.95, $\Delta H_{\text{des}}$ = 1.225 × (wt% H$_2$) + 75.995 (b) Predicted equilibrium pressures of MgH$_2$ and Mg(H$_{0.85}$F$_{0.15}$)$_2$ at 5 different values of H$_2$ wt% along the equilibrium plateau. For Fig 5b: pure MgH$_2$ and Mg$_2$FeH$_6$. 44
with the sloping nature of the plateau. Frequently, a flat equilibrium plateau is observed when a material decomposes into another with a different crystal structure. In this particular case, the same space group, P42/mnm, is shared for both the starting and final products. As a consequence, it is observed that during PCI experiments, H₂ is progressively desorbed allowing an F-rich phase to emerge. This F-rich phase also possesses the same crystal structure, allowing for changes to occur gradually, which explains the nature of the sloping plateau. For this reason, the thermodynamics of decomposition change gradually during the measurement. It needs to be mentioned that ΔG for hydrogen release from Mg(H₂₀.₈₅F₀.₁₅)₂ is equivalent to ΔG for hydrogen release from MgH₂, therefore ΔG = 0 (1 bar equilibrium temperature) is at 273.7 °C for both Mg(H₂₀.₈₅F₀.₁₅)₂ and MgH₂ within experimental uncertainty.

Figure 5b also shows that the H₂ equilibrium pressures of the Mg(H₂F₀.₈₅)₂ decreases and moves closer to that of Mg₂FeH₆ as the temperature increases. It should be noted that during PCI measurements the quantity of desorbed H₂ for Mg(H₂₀.₈₅F₀.₁₅)₂ (4.6 wt% H₂, Table S1) did not reach the theoretical hydrogen capacity of 5.4 wt%. This can be attributed to the formation of a stable Mg-H-F phase. An XRD pattern of Mg(H₂₀.₈₅F₀.₁₅)₂ prepared by in situ SR-XRD and DSC-TGA-MS. Rietveld refinement of the XRD pattern to determine the unit cell parameters corresponding to the fact that ~0.8 wt% H₂ remains within the sample (Table S1).

The high thermal stability of the Mg(H₂₀.₅₀F₀.₅₀)₂-L composition was subsequently investigated by TGA-MS and in situ SR-XRD up to 850 °C to determine the temperature at which the remaining H₂ could be desorbed (Fig. S8 and S9). As noted previously, during TGA measurement (Fig. 3c) of Mg(H₂₀.₅₀F₀.₅₀)₂, before 480 °C only 0.77 wt% H₂ is desorbed, but after 505 °C a major desorption event occurs (Fig. S8) releasing a total mass loss of 2.3 wt% before 830 °C. This value is slightly greater than the theoretical quantity of 2.27 wt% H₂ as Mg evaporates at this temperature due to its low vapour pressure. The first step of decomposition, observed at ~400 °C during TGA-MS, Fig. S8, is not clearly witnessed by in situ SR-XRD but at ~545 °C a significant expansion of the unit cell is observed, beyond that expected from of thermal expansion alone (Fig. S9). At the same time, the peaks become broader and asymmetric in shape. This is most likely a consequence of a variety of solid-solution compositions being present during decomposition. At ~755 °C the hydrogen occupancy factor is 2.9(5)% indicating that full decomposition has almost been achieved under vacuum conditions.

The extreme thermal stability of this material should be investigated by theoretical methods to understand the unexpected thermodynamic stability, while the thermodynamic properties should also be determined experimentally. Overall, each method of thermal analysis used in this study illustrates that the thermal stability of the Mg-H-F systems increase with addition of F. A previous report on this system mentions that data measured by DSC indicates a destabilisation due to a decrease in ΔH_des. As stated above, ΔS_des is required to ultimately determine the overall stability of the system. This study shows that for Mg(H₂₀.₈₅F₀.₁₅)₂, a concomitant decrease in ΔS_des is observed during addition of F to the mixture, which causes an overall increase in stability. This pattern has been established previously during the study of Na-H-F in which PCI measurements determined a ΔH_des of 106 ± 5 kJ·mol⁻¹ H₂ and ΔS_des of 143 ± 5 J·K⁻¹·mol⁻¹ H₂ for
Rehydrogenation studies

In order for Mg(H_{0.85}F_{0.15})_2 to be considered as potential material for hydrogen storage or thermal energy storage applications, characteristics such as hysteresis (absorption/desorption pressure), cyclic stability and reversibility need to be assessed. After the PCI measurement at 450 °C (Fig. 7a), a hydrogen absorption experiment was performed on the sample at the same temperature (450 °C) (Fig. 7b). An initial pressure of 3 bar was increased to 55 bar in a step-wise fashion, with 3.5 h equilibrium step times (identical to desorption measurements). According to the ΔH_{des} and ΔS_{des} for Mg(H_{0.85}F_{0.15})_2 determined by PCI, the sample is predicted to start absorbing H\textsubscript{2} at an equilibrium pressure of ~34 bar (Fig. 7b). As observed in Fig. 7c, the sample starts to absorb a significant amount of H\textsubscript{2} above ~36 bar. Figures 7a and 7b represent the kinetic data for desorption and absorption, respectively. These graphs show that Mg(H_{0.85}F_{0.15})_2 does not reach true equilibrium after 3.5 h, indicating that reaction kinetics during absorption are appreciably slower than observed during dehydrogenation. If a longer equilibration step time was afforded for each step then hysteresis may not be observed. Despite the kinetics of absorption being slow, the sample absorbed ~98% of the hydrogen that was previously desorbed and equates to ~88% of the theoretical value. At the end of the absorption PCI, quantitative Rietveld refinement of the XRD data shows that two compositions of Mg(H_{x}F_{1-x})_2 are identified, although due to the asymmetry of the peaks there are maybe a larger distribution of compositions (Fig. 6c). The compositions are determined, based on the unit cell volume method (Fig. 2b), to be approximately 90 wt% Mg(H_{0.86}F_{0.14})_2 and 10 wt% Mg(H_{0.56}F_{0.44})_2. Macroscopic flakes are evident in the rehydrogenated sample when visually inspected, which are attributed to the sintering of the material at high temperature. This was previously reported by Bogdanovic et al. by observing that Mg metal agglomerates during and is likely to be responsible for the reduced kinetics.

Cycling studies

The cyclability of Mg(H_{0.85}F_{0.15})_2-S was investigated to characterise its long-term reversibility and its potential use in technological applications. Cycling studies were conducted over six absorption/desorption cycles between 480 °C (desorption) and 425 °C (absorption) (Fig. 8a). A system pressure of ~27 bar was utilised to ensure full absorption and desorption could occur during the cycling studies. Over the course of the 6 consecutives absorption/desorption cycles, the
hydrogen capacity of the sample decreased gradually, as seen in Fig. 8a. For these conditions, the hydride desorbed 4.6 wt% H₂ for the first desorption with ~92% of hydrogen being desorbed after ~35 min. The sample then absorbed 4.08 wt% H₂ with 97% being absorbed in less than 30 min. After the first cycle, the capacity of Mg(H₃₀.₈₅F₀.₁₅)₂ was reduced by 19% and over the 6 cycles the sample lost a total of ~27% capacity. Sintering of the Mg in the sample is responsible for the decrease in capacity (clearly impacting kinetics) and was confirmed by visual observation of flakes inside the sample after cycling. The cycling measurement was stopped after absorption, at which point XRD was undertaken (Fig. 8b). Quantitative analysis shows that two Mg(HₓF₁−ₓ)₂ phases were present, both of which are H-rich, along with Mg metal, confirming what was previously observed in the absorption stage of the PCI experiment. The main phase is Mg(H₅₀.₈₅F₀.₁₅)₂ and the other is Mg(H₅₀.₈₅F₀.₅₃)₂.

Conclusions
A range of Mg(HₓF₁−ₓ)₂ (x = 1, 0.95, 0.85, 0.70, 0.50, 0) solid solutions have been synthesised by ball milling quantitative ratios of MgH₂ and MgF₂ followed by annealing under a hydrogen backpressure. Their potential use as hydrogen storage or thermal energy storage materials has been examined by in situ synchrotron XRD, DSC-TGA-MS and PCI analysis. Thermal studies were carried out on all Mg(HₓF₁−ₓ)₂ mixtures concluding that increased F content increases the thermal stability and decreases the absorption/desorption kinetics compared to pure MgH₂. As such, decomposition occurs in a single step with DSC data showing a maximum rate of H₂ desorption at 434 °C for Mg(H₅₀.₈₅F₀.₁₅)₂, with a practical hydrogen capacity of 4.6 ± 0.2 wt% (theoretical 5.4 wt% H₂). An extremely stable Mg(H₂₅F₀.₇₅)₂ phase is formed upon the decomposition of each Mg—H—F composition of which the remaining H₂ is not released until after 505 °C. PCI measurements of Mg(HₓF₁−ₓ)₂ determined an enthalpy of decomposition of 73.6 ± 0.2 kJ/mol H₂ and an entropy of 131.2 ± 0.2 J/K/mol H₂. In comparison with MgH₂, these values are decreased from 74.06 kJ/mol H₂ and 133.4 J/K/mol H₂, respectively. Cycling of Mg(H₅₀.₈₅F₀.₁₅)₂ has been investigated over six cycles between 420 and 480 °C, with a reduction of 27% of the practical hydrogen capacity of 4.6 wt% H₂. This represents an increased cycling temperature of ~80 °C compared to bulk MgH₂ which increases the thermal operating temperatures for technological applications, thereby increasing efficiency.

Conflicts of interest
There are no conflicts to declare.

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