Supporting Information

The thermodynamics of hydrogen desorption from $NaMgH_3$ and its application as a solar heat storage medium

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$NaMgH_3$ decomposes in two-steps according to the following equations:

$NaMgH_3 \rightarrow NaH + Mg + H_2$ - 4.0 wt.% H_2 Eq. 1

$NaH + Mg \rightarrow Na_{(l)} + Mg + ½ H_2$ - 2.0 wt.% H_2 Eq. 2

Analysis of Previous Studies

None of the previous studies on the thermodynamics of $NaMgH_3$ reported experimental information on the sample mass used for PCI, sample temperature measurement methods and, most importantly, the amount of time waited for each data point to reach equilibrium in the PCI measurements. Table S1 shows the reported enthalpy (ΔH) and entropy (ΔS) values with respect to Equation 1 from previous studies.[1-3] Enthalpy and entropy values recalculated from the pressure and temperature values reported in these previous studies is also indicated.

Table S1: Previously reported thermodynamic values for $NaMgH_3$ with respect to Equation 1.

Source	Temperature (K)	Reported ΔH (kJ/mol H_2)	Reported ΔS (J/mol H_2/K)	Est. Eq. Press. (bar)	Recalculated ΔH (kJ/mol H_2)	Recalculated ΔS (J/mol H_2/K)
Ikeda et al. [1]	653	93.9	116.2	1	74.2	113.6
	673			1.5		
	693			2.2		
Komiya et al. [2]	673	94	140	1.15	94.4	141.1
	698			1.9		
	723			3.7		
Pottmaier et al. [3]	650	92	123	0.3	95.7*	146.1*
	670			0.9		
	680*			1.9		
	700*			3.1		
	723*			5.2		
This Work	671.45	-	-	1.471	86.6	132.2
	683.85			1.965		
	691.95			2.355		
	702.85			2.964		
	712.05			3.559		

*The two lowest temperatures in Pottmaier et al.'s work are clearly affected by poor kinetics, as shown by the van't Hoff plot in Figure S1, and have thus been excluded from the thermodynamic calculations.

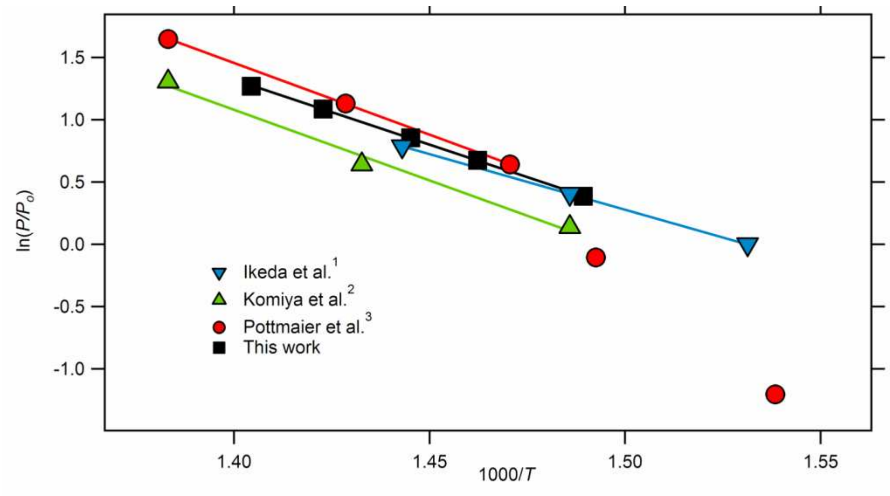

Figure S1. van't Hoff plot for $NaMgH_3$ hydrogen desorption data published in the literature.

Ikeda et al. [1] first reported the enthalpy (ΔH) and entropy (ΔS) value for $NaMgH_3$ decomposition, according to Eq. 1, as -93.9 kJ/(mol H_2) and 116.2 J/(mol H_2.K) from their van't Hoff data. Using these reported thermodynamic values to calculate the expected pressure at their experimental temperatures yields pressures that are more than an order of magnitude less than their experimentally measured pressures. From the same experimental measurements they reported an enthalpy and entropy for NaH decomposition of 102.4 kJ/(mol H_2) and 125.9 J/(mol H_2.K). The discrepancy with the accepted values for NaH of 115.8 kJ/mol and 166.4 J/mol.K should have raised concerns about either their data or their data analysis. Using the temperatures reported by Ikeda et al. [1] and the estimated pressure values from the reported PCI data, the enthalpy and entropy values were recalculated and are presented in Table 1. Their van't Hoff plot was constructed from just three PCI's with the resulting enthalpy and entropy being highly sensitive to even small variations in the reported equilibrium pressures (or small variations in the reported temperature). The limited data points measured across the equilibrium plateau could introduce the large aliquot effect [4]: localised sample cooling that would decrease the observed hydrogen pressure unless sufficient time is allowed for the sample to return to the furnace temperature. Later work by Komiya et al. [2] raises similar concerns where only three PCI's were measured and only limited data points were collected across the equilibrium plateau. A lack of sufficient data points across the plateau can cause problems with measuring the correct equilibrium pressure. Komiya et al [2] reported an enthalpy and entropy of 94 kJ/mol H_2 and 140 J/mol H_2.K respectively. In this case, the enthalpy and entropy reproduce the experimentally observed data reasonably well. However, with only three data points, the calculated enthalpy and entropy are highly sensitive to even small variations in the observed pressure.

Pottmaier *et al.* conducted a further study on $NaMgH_3$ in 2011 [3] where the enthalpy and entropy of decomposition were reported as 92 kJ/mol H_2 and 123 J/mol H_2.K. Here 5 PCI's are reported but unfortunately the data quality is poor, especially at temperatures below 427°C. Firstly, the equilibrium pressure plateaux are not flat, as is expected for a chemical hydride (non-interstitial) (likely caused by insufficient wait time for each equilibrium measurement). Secondly, there are large pressure variations across the plateaux, particularly at the lower temperatures examined (insufficient pressure resolution or wait time). The consequence is that the two lowest temperature PCIs are unsuitable for extracting reliable thermodynamic data. In addition to these problems, the presented van't Hoff plot for these PCI's contains data points at temperatures that do not match the reported temperatures at which the PCI data was collected. Careful consideration of the van't Hoff equation also reveals its incorrect application by Pottmaier to their data. The full van't Hoff equation can be written as:

$$ln\left(\frac{f_{eq}}{f_o}\right) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{Eq. 2}$$

Where f_{eq} is the fugacity of hydrogen at equilibrium at a given temperature T (K), f_o is a reference fugacity of hydrogen at a pressure of 1 bar, ΔH is the enthalpy in J/(mol H_2), ΔS is the entropy in J/(mol H_2.K), R is the universal gas constant (8.31447 J/(mol.K)) and T is the temperature in Kelvin. The fugacity is the activity of the real gas which provides a better representation of the chemical potential of the system than pressure. However at low pressure, the pressure is often assumed equal to the fugacity due to the near-ideal gas behavior of hydrogen

If we assume the approximation that fugacity and pressure are equal and that the pressure is not plotted in units of bar, as in the case for Pottmaier et al's data, then P_o must be retained in the van't Hoff equation as follows:

$$ln(P) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + ln(P_o) \qquad \text{Eq. 3}$$

As we can see from this, the enthalpy determined from a van't Hoff equation is independent of the units used for pressure. However, the entropy value is determined from

$$\Delta S = c*R - R*ln(P_o) \qquad \text{Eq. 4}$$

where c is the intercept of the van't Hoff fit. If the units of MPa is used for pressure in the van't Hoff plot then P_o must be equal to 0.1 MPa. Thus, ln(P_o) equals -2.30 and $R*ln(Po)$ equals -19.1. Correcting Pottmaier's reported entropy value (of 123 J/(mol H_2.K)) by this amount yields a new value of 142 J/mol.K which is closer to that reported by Komiya et al.

Experimental

All handling of chemicals and sealable milling canisters was undertaken in an argon-atmosphere glovebox in order to minimize oxygen ($O_2 < 1$ ppm) and water ($H_2O < 1$ ppm) contamination. NaH (98 %) and MgH_2 (> 96.5 %) were both purchased from Sigma-Aldrich.

Milling was performed cryogenically (77 K) using a Spex 6850 freezer mill. NaH and MgH_2 were combined in a 1:1 molar ratio in a 14.3 cm^3 440c stainless steel canister sealed with Teflon tape. Milling was undertaken on a 1 g sample using a 2 minute milling, 1 minute cooling cycle for a total of 30 minutes of milling. Following this, the sample was evacuated at room temperature and then placed under 50 bar of H_2 pressure (99.9995% purity), raised to 300°C and held at this temperature for 24 hours.

X-ray diffraction (XRD) was performed using a Bruker D8 Advance diffractometer (CuK_α radiation) equipped with a LynxEye 3° linear position sensitive detector with a 2θ range of 10 - 80° using 0.02° steps with 0.8 s of count time per step with operating conditions of 40 kV and 40 mA. The XRD instrument was equipped with a LynxEye 3° linear position sensitive detector (PSD) with 192 pixels. The XRD samples were loaded into an XRD sample holder in an argon glovebox and sealed with a poly(methylmethacrylate) (PMMA) air-tight bubble to prevent oxygen/moisture contamination during data collection.

Hydrogen sorption experiments were performed in a manometric apparatus using 0.33 g of sample. The digital pressure gauge (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). Further details are provided elsewhere on the hydrogen sorption apparatus.[5] The sample temperature was monitored using an N-type thermocouple inserted into a hydrogen leak-test hole that formed part of the sample holder. The N-type thermocouple was calibrated by the manufacturer to be accurate to within 0.1 °C at 419 °C.

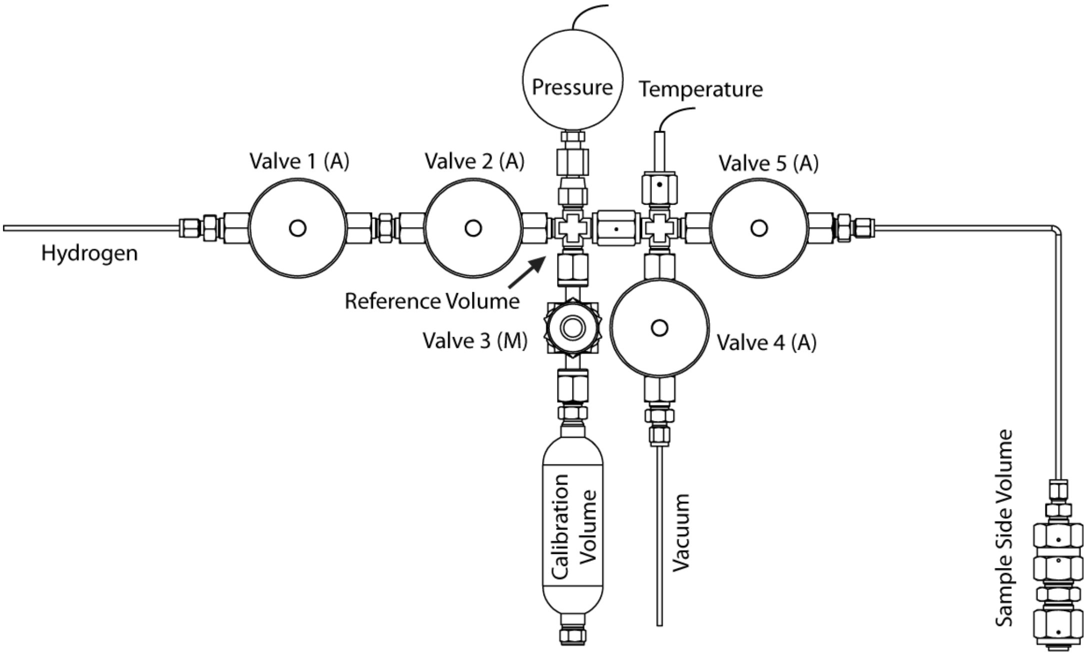

Figure S2. Custom-built, computer-controlled Sieverts apparatus utilized in equilibrium pressure measurements. Automated (A) and manual (M) valves are indicated.

Results

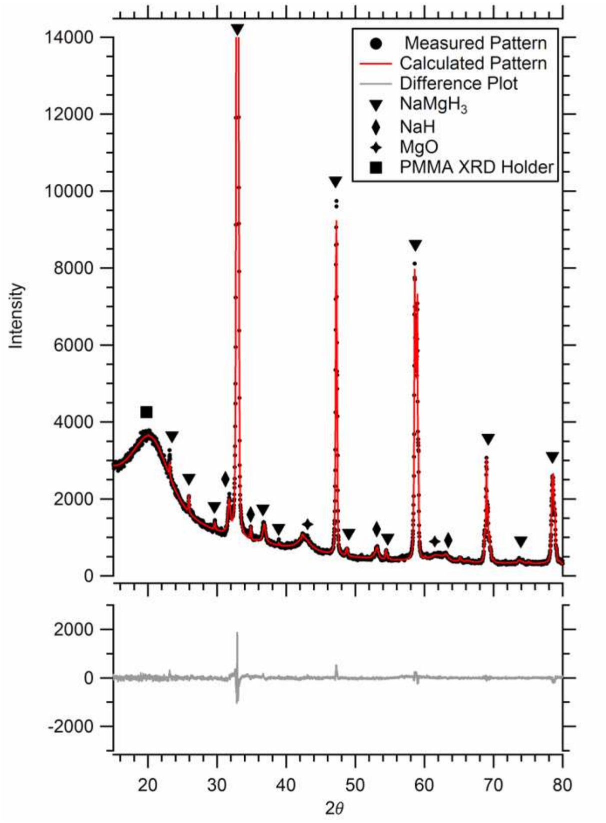

Figure S3: X-ray diffraction of synthesised NaMgH$_3$ showing the Rietveld refinement calculated pattern and the difference plot. Note that the NaMgH$_3$ peak intensity at 2θ = 32.9^o extends to ~55,000 counts.

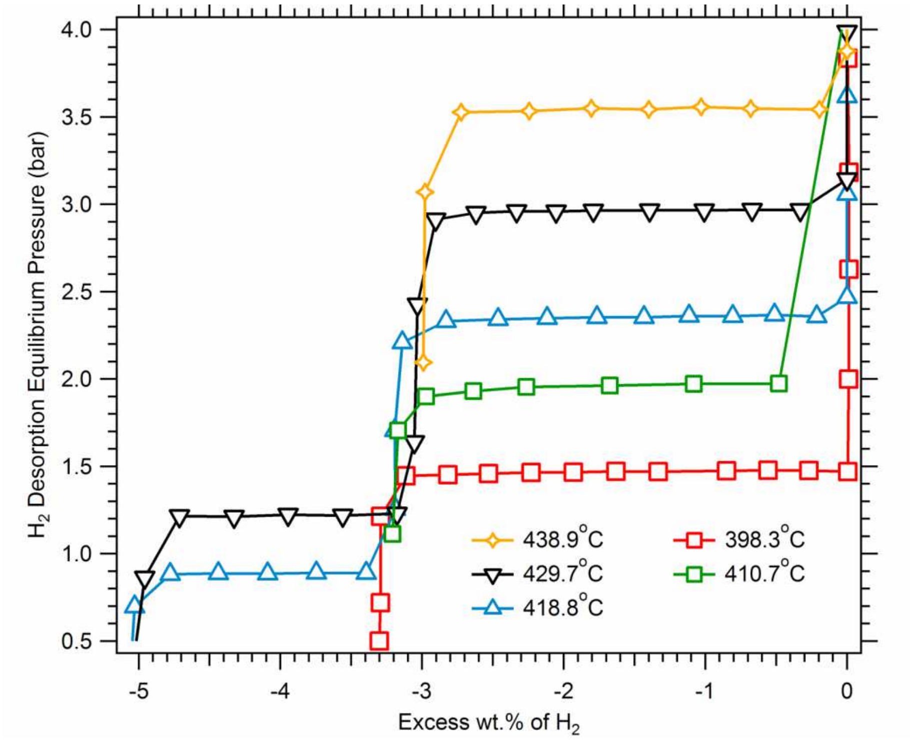

Figure S4. Full desorption PCI curves for NaMgH$_3$.

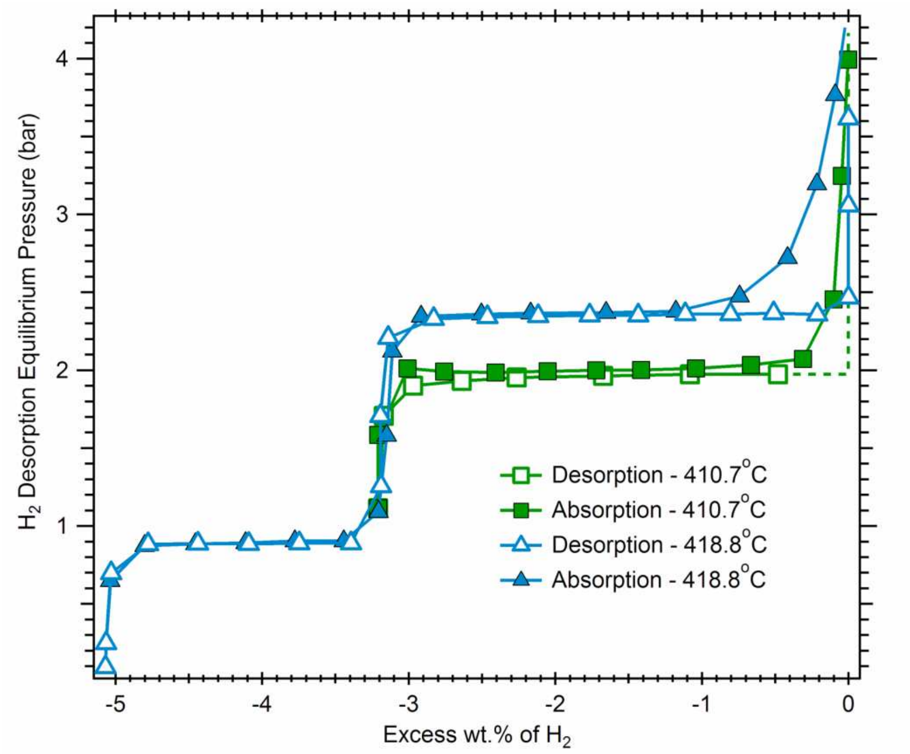

Figure S5. Absorption and desorption PCI data for $NaMgH_3$. The dashed line indicates inferred data.

References

1. Ikeda, K.; Kato, K.; Shinzato, Y.; Okuda, N.; Nakamori, Y.; Kitano, A.; Yukawa, H.; Morinaga, M.; Orimo, S., *Journal of Alloys and Compounds* **2007,** *446-447*, 162-165.

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