

Supporting information

Belonging to the manuscript

Complex hydrides as multifunctional materials: characterisation and thermal decomposition of $\text{Na}_2\text{Mg}_2\text{NiH}_6$

Terry D. Humphries,^{a,b*} Drew A. Sheppard,^a Guanqiao Li,^b Matthew R. Rowles,^a Mark Paskevicius,^a Motoaki Matsuo,^{c,d} Kondo-Francois Aguey-Zinsou,^d M. Veronica Sofianos,^a Shin-ichi Orimo^{b,e} and Craig E. Buckley^a

^a Department of Physics and Astronomy, Fuels and Energy Technology Institute, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

^b WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

^c School of Science and Technology, Kwansai Gakuin University, Sanda 669-1337, Japan

^d Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

^e Merlin Group, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

E-mail: terry_humphries81@hotmail.com

Additional experimental considerations

Thermal analysis of $\text{Na}_2\text{Mg}_2\text{NiH}_6$ shown in Fig. S3

Temperature Programmed Desorption (TPD) experiments were carried out using a RGAPro residual gas analyser. The sample was heated from room temperature to 400 °C at a ramp rate of 2 °C/min. Hydrogen desorption was measured using a mass spectrometer by analysing the intensity of ions with the $m/z=2$ (H_2).

The differential scanning calorimetry (DSC) analysis was conducted simultaneously with thermogravimetric analysis (TGA) on a Mettler Toledo Star1 analyser. The powdered sample (~10 mg) was loaded into an alumina crucible of 70 μl volume and covered with alumina powder (~53 mg) to prevent the oxidation and hydrolysis during the quick transfer to the analyser and also to avoid a volatile foaming and flowing out of the crucible if the powder sample melted. An argon flow of 20 ml/min was set as a protection gas flow with a purge gas rate of 50 ml min^{-1} . The sample was heated up to 400 °C at a heating rate of 2 °C min^{-1} .

Powder XRD analysis of $\text{Na}_2\text{Mg}_2\text{NiH}_6$ shown in Figs. S4 and S5

Powder X-ray diffraction (XRD) measurements were conducted using a PANalytical X'Pert-Pro using CuK α radiation inside a 0.7 mm borosilicate capillary. Data were collected using a X'Celerator X linear position sensitive detector within a 2θ range of $10 - 90^\circ$ using 0.021 steps at 0.041/s with X-ray generator operating conditions of 45 kV and 40 mA. The XRD samples were loaded in an Ar glovebox to prevent oxygen/moisture contamination during data collection.

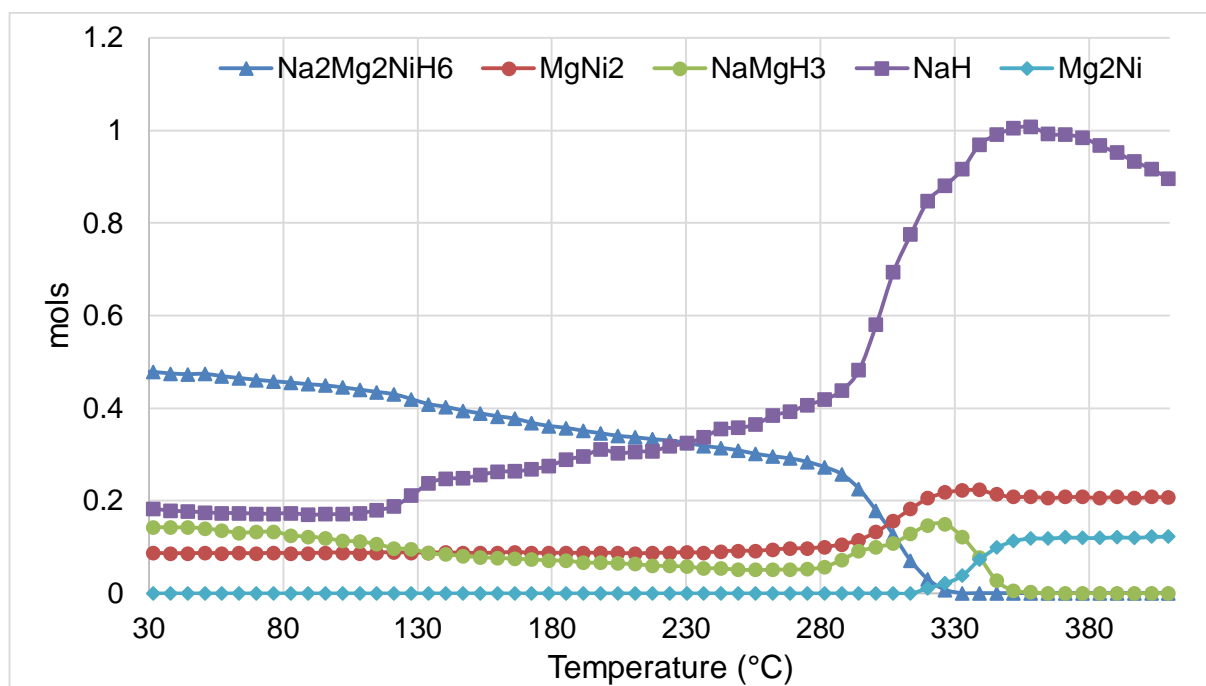


Fig. S1. Moles of crystalline phases calculated directly from quantitative Rietveld refinement of *in situ* SR-XRD data.

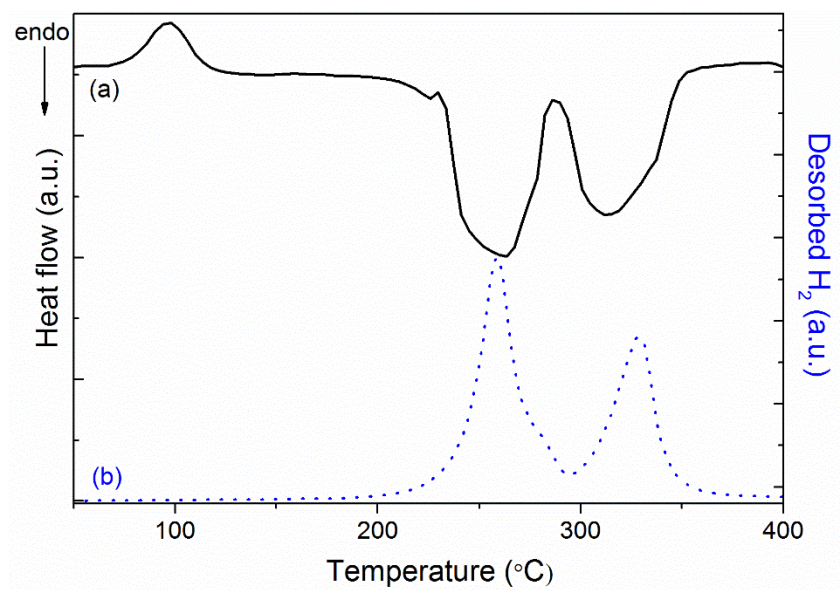


Fig. S2. DSC (a) and TPD-MS (b) analysis of Na₂Mg₂NiH₆. $\Delta T/\Delta t = 2$ °C/min.

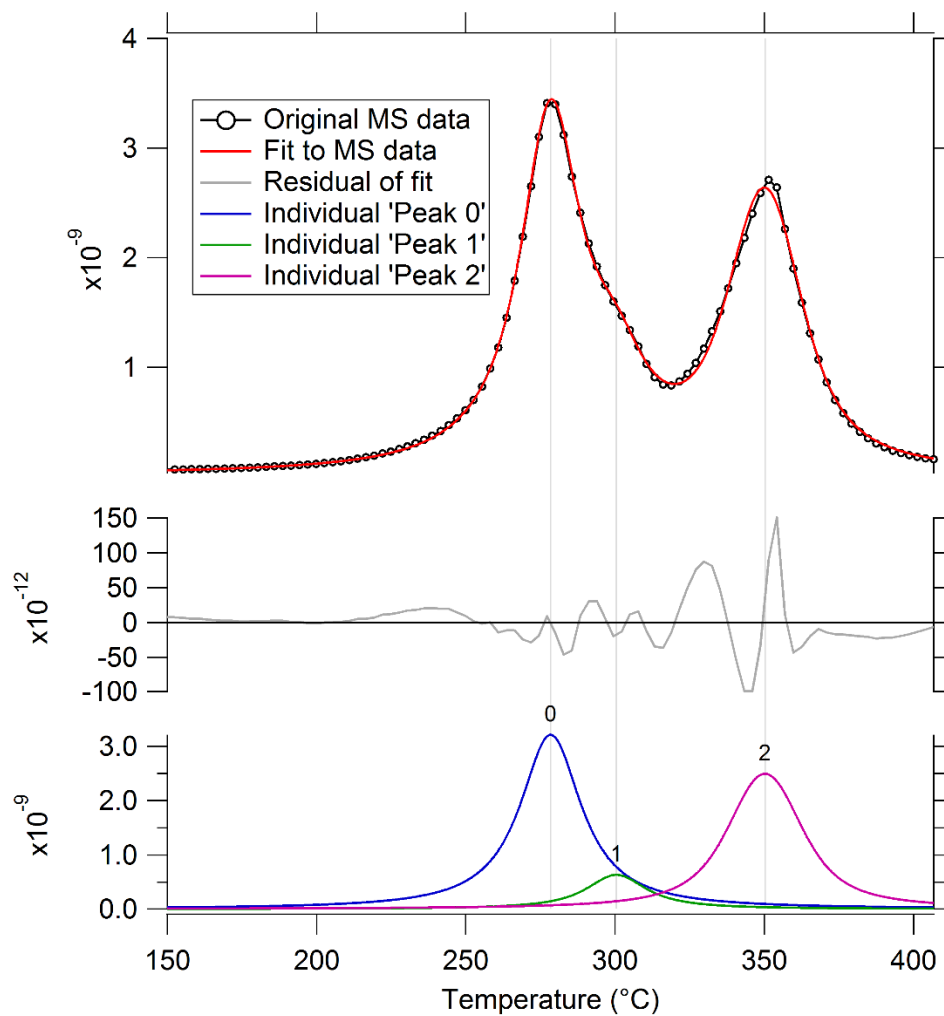


Fig. S3. Multi peak fitting of the MS analysis of $\text{Na}_2\text{Mg}_2\text{NiH}_6$. Temperature of peak 0 = 278 °C, peak 1 = 300 °C, peak 2 = 350 °C.

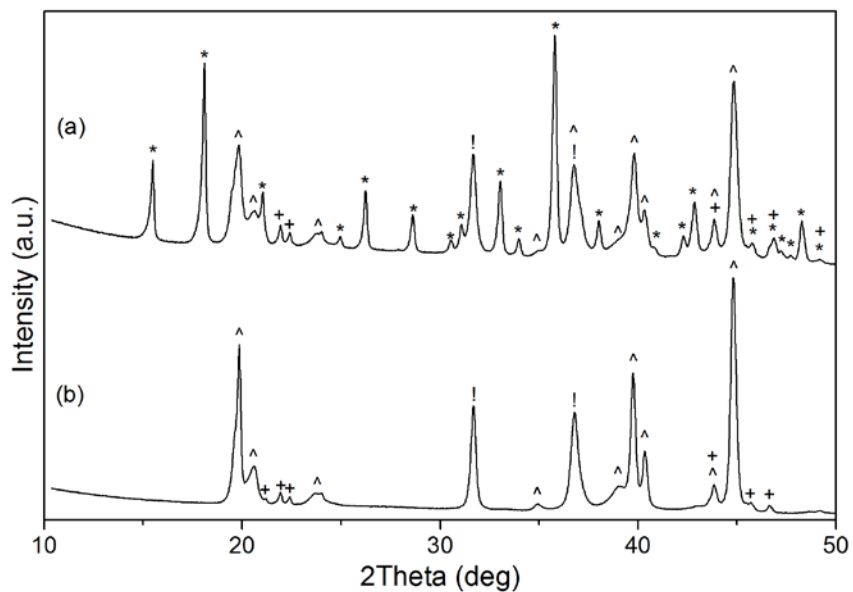


Fig. S4. Room temperature XRD patterns of Na₂Mg₂NiH₆ performed after heating to (a) 260 °C and (b) 330 °C *in vacuo* before quenching. * = Na₂Mg₂NiH₆; ^ = Mg₂NiH_{0.3}; ! = NaH; + = MgNi₂. λ = CuK_α.

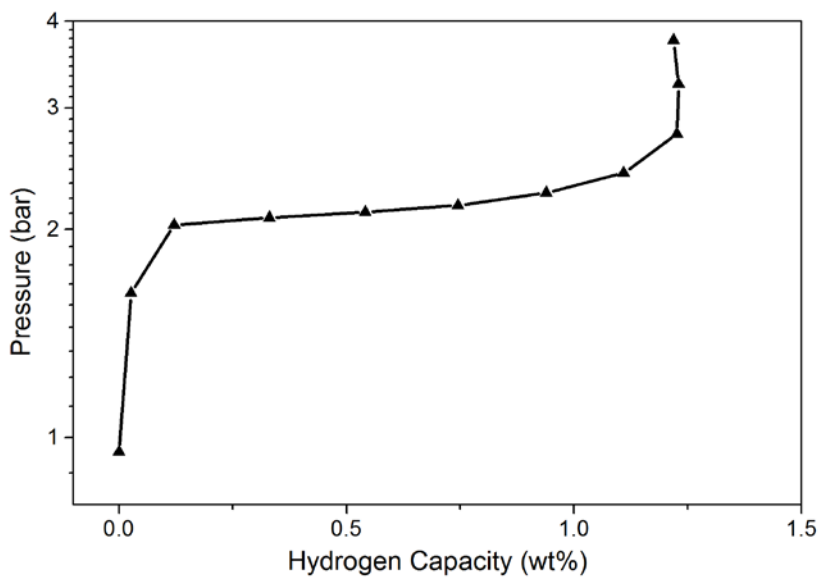


Fig. S5. PCI absorption measurement at 315 °C of previously decomposed Na₂Mg₂NiH₆.

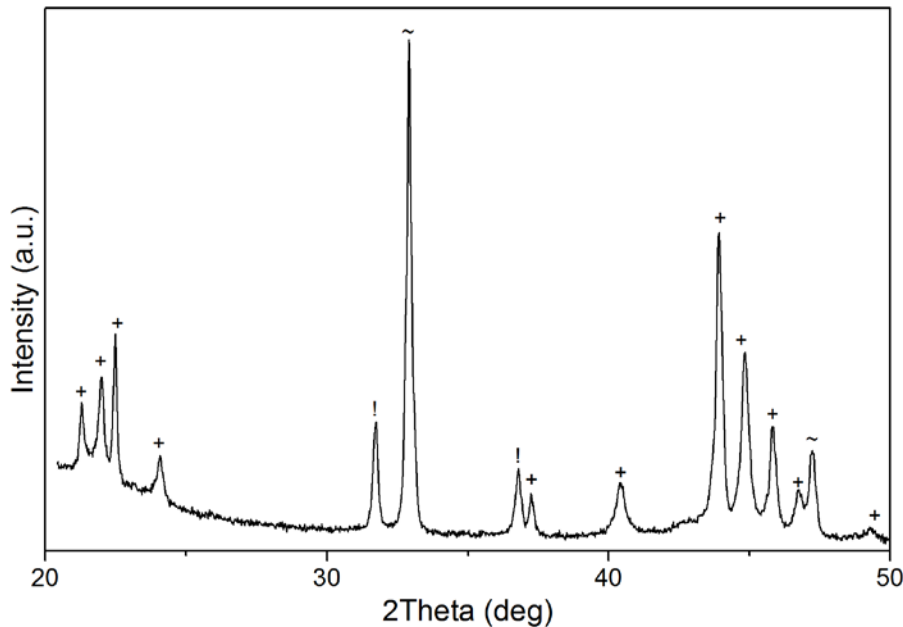


Fig. S6. Room temperature XRD pattern of material after a PCI absorption measurement at 315 °C of previously decomposed $\text{Na}_2\text{Mg}_2\text{NiH}_6$. $\sim = \text{NaMgH}_3$; $! = \text{NaH}$; $+ = \text{MgNi}_2$. $\lambda = \text{CuK}\alpha$.

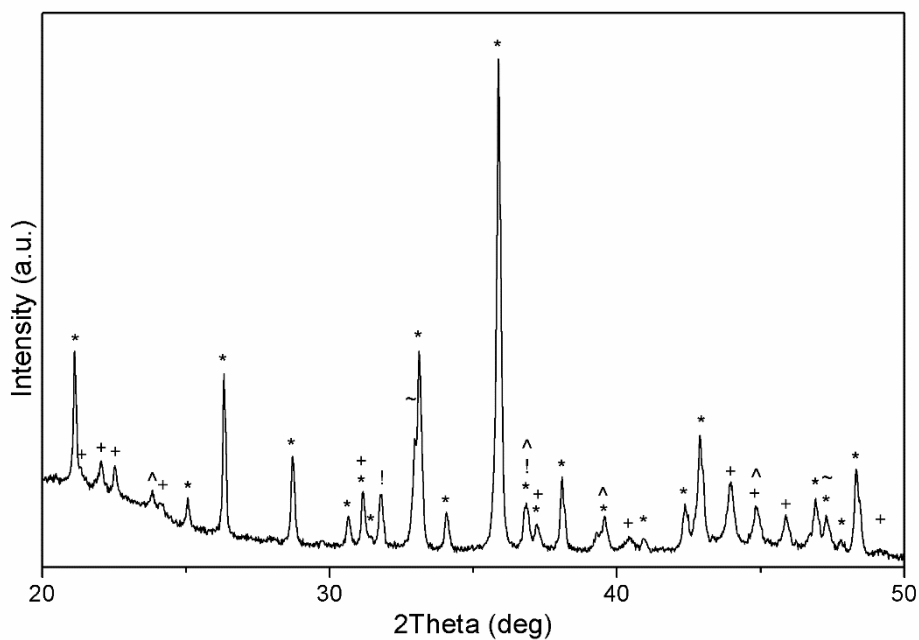


Fig. S7. XRD pattern of hydrogenated material after four absorption and three desorption cycles starting from the desorbed state. $* = \text{Na}_2\text{Mg}_2\text{NiH}_6$; $\sim = \text{NaMgH}_3$; $! = \text{NaH}$; $+ = \text{MgNi}_2$. $\lambda = \text{CuK}\alpha$.
 $T_{des} = 395$ °C and 0.2 bar H_2 ; $T_{abs} = 315$ °C and 60 bar H_2 .

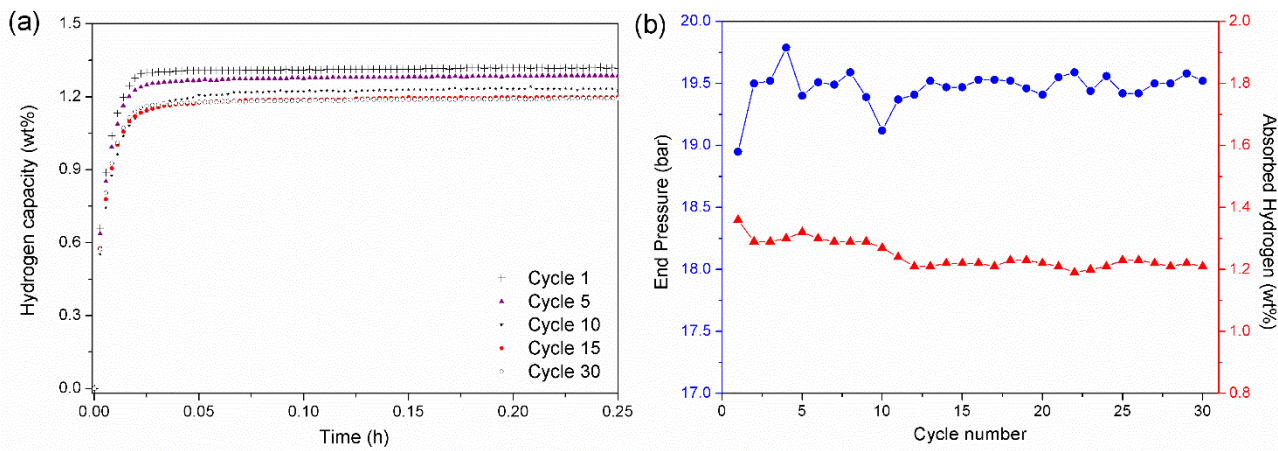


Fig. S8. (a) Absorption kinetics and (b) maximum hydrogen capacity of $\text{Na}_2\text{Mg}_2\text{NiH}_6$ for 30 cycles measured inside a Sieverts apparatus. $T_{des} = 400\text{ }^\circ\text{C}$ and 0.7 bar H_2 ; $T_{abs} = 400\text{ }^\circ\text{C}$ and 40 bar H_2 . The blue circles (b) indicate the end pressure after the absorption step. The red triangles indicate the wt % H_2 absorbed in each cycle.