Electronic Supplementary Information

Enhancement of initial hydrogenation of Mg by ball milling with alkali metal amides MNH_2 (M = Li or Na)

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Experimental details:

The starting materials Mg powder (99.8%, -325 mesh, Alfa Aesar), $LiNH_2$ (95%, Alfa Aesar), $NaNH_2$ (95%, Sigma Aldrich), MgH_2 (98%, Alfa Aesar), Li (99%, Sigma Aldrich), NaCl (95%, Fluka), and NaBr (99%, Alfa Aesar) were all used as received. The samples were prepared by ball milling a 2 g mixture of Mg and MNH_2 (4 wt%, M = Li and Na) in a Spex 8000 mill. For comparison, a mixture of Mg and 4 wt% of MgH_2, Li, NaCl, or NaBr was ball milled under the same conditions. The ball-to-powder weight ratio was 7.5:1 and the milling time was fixed at 30 min due to the ductile nature of Mg. Milling was performed in stainless steel vials with three hardened steel balls under argon ambient atmosphere. The samples were handled inside a glove box filled with argon atmosphere to avoid excessive oxidation of the powders.

The crystal structure was studied by X-ray diffraction (XRD) using Bruker D8 Focus X-ray apparatus with Cu Kα radiation. Phase abundance, crystallite size and microstrain were determined from Rietveld analysis using TOPAS software [S1]. The powder's morphology was characterized by scanning electron microscopy (SEM) using a JEOL JSM-5500 microscope. The microscope was equipped with energy dispersive X-ray spectroscopy (EDX) (Oxford Instruments), which allowed for the determination of elemental composition. The samples were prepared by pressing the powder into a pellet under 30 MPa of pressure.

The hydrogen sorption properties were measured with a homemade Sieverts-type apparatus. All measurements were performed at 573 or 608 K under a hydrogen pressure of 2 MPa for absorption and 0.05 MPa for desorption. Each sample was loaded in the reactor inside a glove box. Prior to measurement the system was heated under dynamic vacuum at the absorption temperature in order to remove the gaseous products like ammonia from decomposition of alkali metal amides.

Figures and Tables

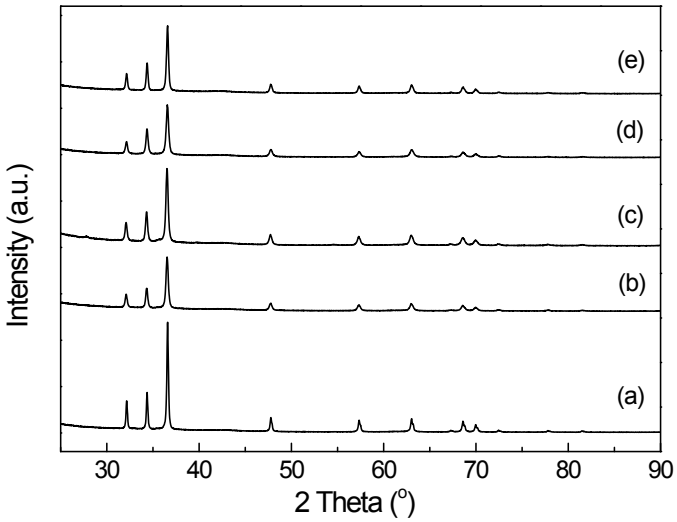
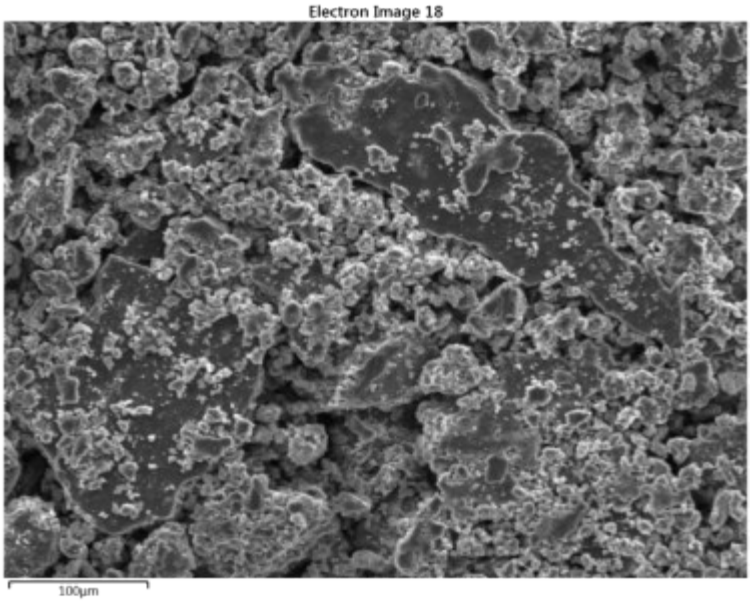
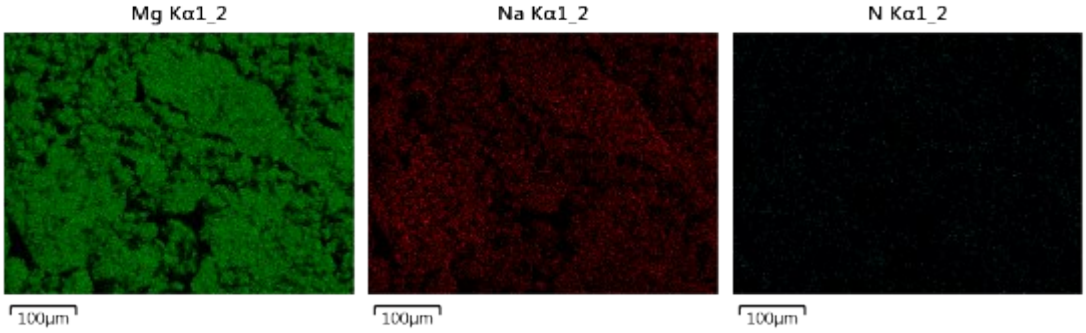


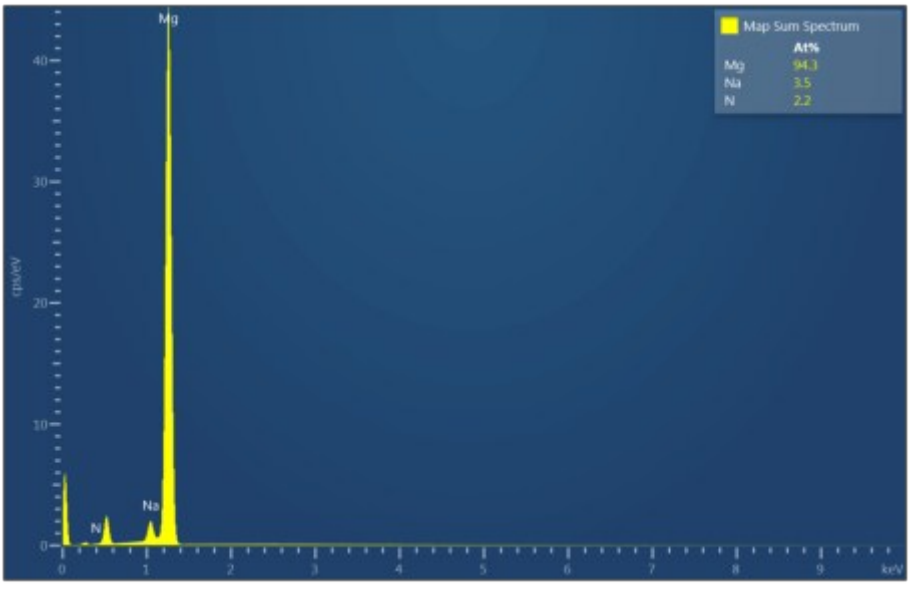
Fig. S1 XRD patterns of (a) as-received Mg, ball milled (b) Mg, (c) Mg-MgH_2, (d) Mg-$LiNH_2$ and (e) Mg-$NaNH_2$.



(a)



(b)



(c)

Fig. S2 (a) SEM image and (b) EDX elemental mappings of Mg-$NaNH_2$. Image (b) is corresponding to image (a). (c) The amount of elements.

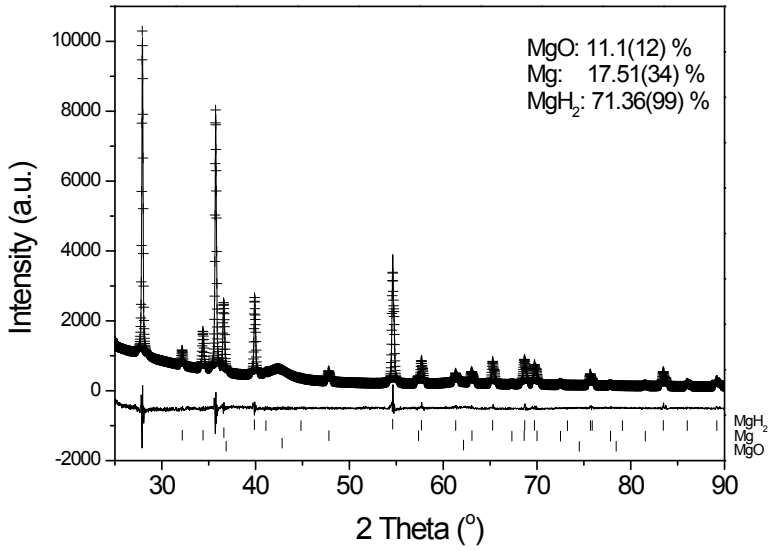


Fig. S3. XRD pattern and Rietveld refinement result of Mg-$NaNH_2$ after hydrogen absorption (R_{wp} = 8.87%).

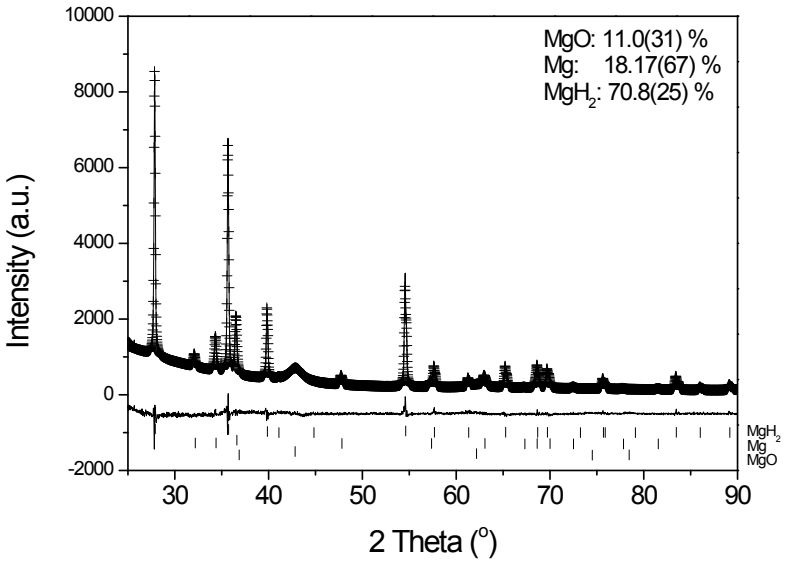


Fig. S4. XRD pattern and Rietveld refinement result of Mg-$LiNH_2$ after hydrogen absorption (R_{wp} = 7.19%).

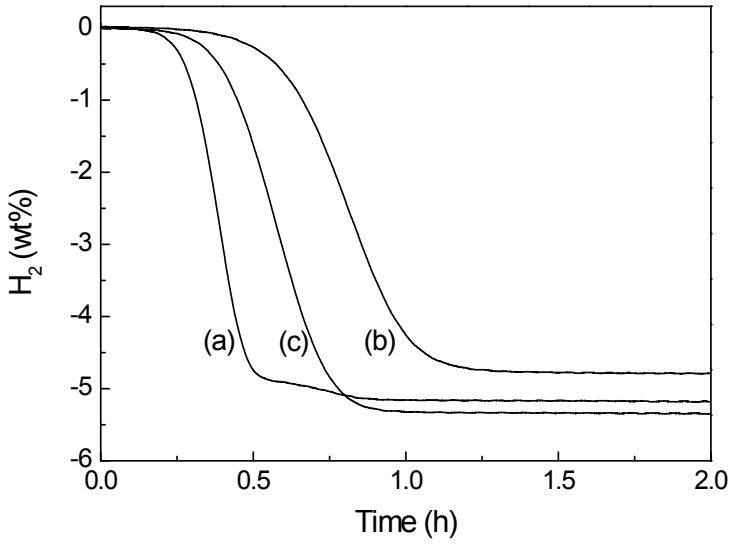


Fig. S5 Hydrogen desorption kinetic curves at 608 K under 0.05 MPa H_2 pressure for ball milled (a) Mg; (b) Mg-$LiNH_2$ and (c) Mg-$NaNH_2$.

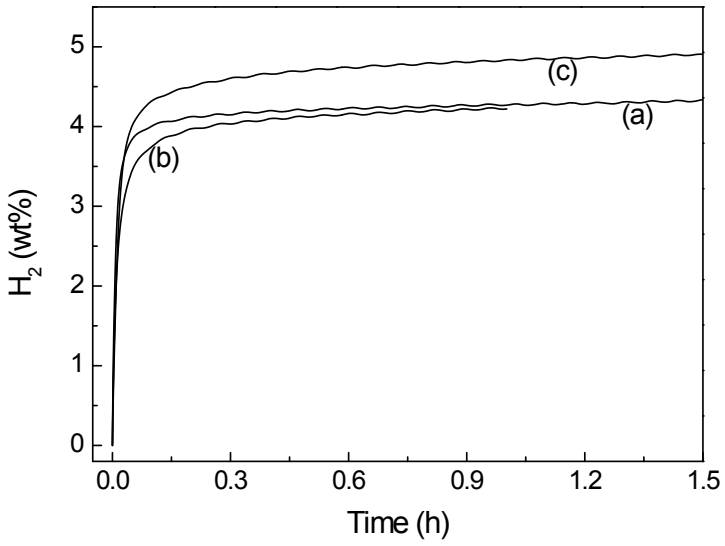


Fig. S6. Second (after initial activation) hydrogen absorption kinetic curves at 608 K under 2 MPa H_2 pressure for ball milled (a) Mg; (b) Mg-$LiNH_2$ and (c) Mg-$NaNH_2$.

Table S1

Crystallite size, microstrain and phase abundances of the Mg, MgH_2 phases in wt% determined from Rietveld refinement of all the samples. For crystallite size and microstrain values in parenthesis are uncertainties on the last significant digit.

Samples	Mg		MgH_2		Parameters of fit
	Size (nm)	Strain (%)	Size (nm)	Strain (%)	
As-received Mg	55.7(4)	0.155(6)			R_{wp} = 10.09%
Mg-BM	41.7(7)	0.449(9)			R_{wp} = 6.83%
Mg-BM-120 min	33.7 (6)	0.531(1)			R_{wp} = 6.95%
Mg-$LiNH_2$-BM	37.4(6)	0.479(9)			R_{wp} = 6.73%
Mg-$NaNH_2$-BM	55.1(1)	0.395(8)			R_{wp} = 7.53%
Mg-$LiNH_2$-BM-Heated for 1 h	42.6(1)	0.413(1)			R_{wp} = 7.32%
Mg-$NaNH_2$-BM-Heated for 1 h	82.0(2)	0.292(8)			R_{wp} = 7.71%
Mg-$LiNH_2$-BM-Absorption	41.6(2)	0.279(4)	69.9(1)	0.158(7)	R_{wp} = 7.19%
Mg-$NaNH_2$-BM-Absorption	49.8(4)	0.347(4)	70.8(1)	0.162(7)	R_{wp} = 8.87%
Mg-MgH_2-BM-Aborption	63.8(3)	0.338(2)	69.7(1)	0.239(7)	R_{wp} = 6.43%
Mg-$LiNH_2$-BM-Desorption	74.8(2)	0.258(9)			R_{wp} = 9.31%
Mg-$NaNH_2$-BM-Desorption	82.7(2)	0.256(8)			R_{wp} = 8.56%

Reference:

[S1] BRUKER AXS, TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data, Bruker AXS, Karlsruhe, Germany, 2008.