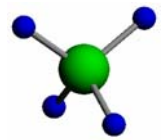
June 19-22, 2005, Lucca, ITALY
IPHE - Hydrogen Storage Technology Conference

Advanced Hydrogen Storage Functions of

Destabilized and Mixed Complex Hydrides



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Tohoku University

www.hydrogen.imr.tohoku.ac.jp

Research project

collaborated with

TOYOTA CRDL, INC.

S. Towata
www.tytlabs.co.jp

supported by

NEDO 技術開発機構

"Development for Safe Utilization and Infrastructure of Hydrogen"

www.nedo.go.jp/index.html

communicated with

E. Akiba, AIST-Tsukuba
H. Fujii, Hiroshima Univ.
C.M. Jensen, Univ. Hawaii
T. Kiyobayashi, AIST-Kansai
D.K. Ross, Univ. Salford
G. Sandrock, Sunatech.
S. Suda, Kogakuin/MERIT
H.T. Takeshita, Kansai Univ.
J.C.F. Wang, K.J. Gross, SNL
R. Zidan, SRNL
A. Züttel, Univ. Fribourg

focused on

1. Destabilization of $LiBH_4$ and $LiNH_2$
2. Combination of amide and hydride
3. Prevention of NH_3-contamination
4. Provision of new reaction pathway

Trinary collaboration

Ultrasoft-pseudopotential based on DFT (GGA)

Theory

K. Miwa, N. Ohba

First-Principles Calculation and Simulation

Material Synthesis

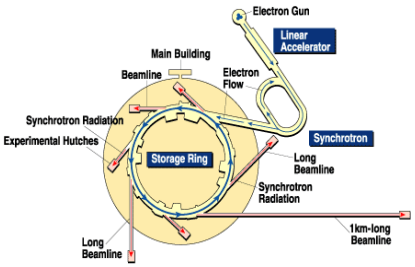
Y. Nakamori, M. Aoki

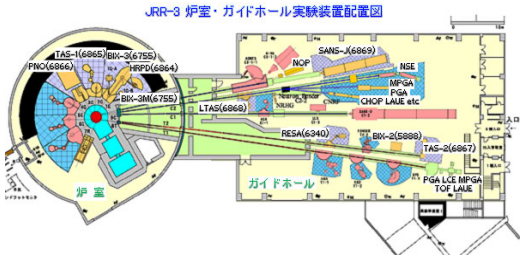
Solid-gas reaction, Milling Evaporation

Analysis

T. Noritake, G. Kitahara, A. Ninomiya, K. Ohyama

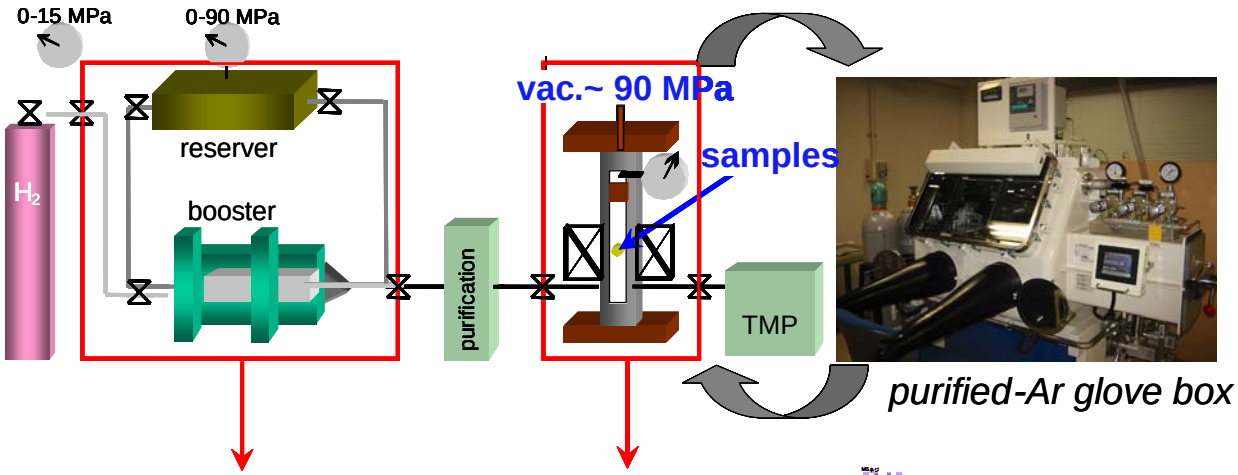
SR and Neutron Diffractions *In-situ* Characterization



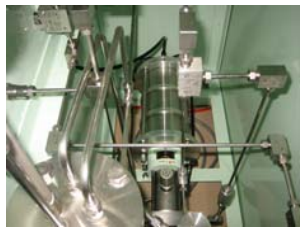


Metallurgical material synthesis

1) reactive synthesis (or sintering)

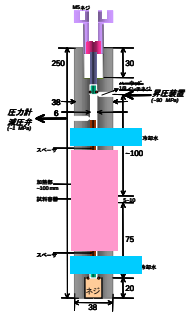


purified-Ar glove box



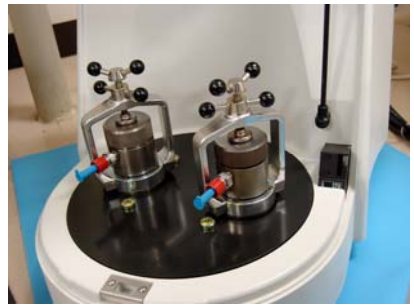
hydrogen booster
(without electricity)

reaction cell

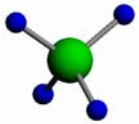


2) evaporation

3) milling



4 Guidelines



1. Destabilization of $LiBH_4$ and $LiNH_2$
   cation with larger electronegativity

2. Combination of amide and hydride
   lower T_d / faster reaction with "NH_3"

3. Prevention of NH_3-contamination
   "tunable" composition / starting material

4. Provision of new reaction pathway
   intermediate phase formed by dehydriding

Dehydriding reaction

A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Alloys Compd. 356-357* (2003) 515

$$LiBH_4 \Leftrightarrow LiH + B + 3/2\ H_2$$

69 (74 *) kJ/molH_2

*obtained from calculation

P. Chen Z. Xiong, J. Luo, J. Lin, K.L. Tan, *Nature 420* (2002) 302

$$LiNH_2 + 2\ LiH \Leftrightarrow Li_2NH + LiH + H_2 \Leftrightarrow Li_3N + 2\ H_2$$

45~60 (78*) kJ/molH_2

116 (124*) kJ/molH_2

~ 10 mass% H_2

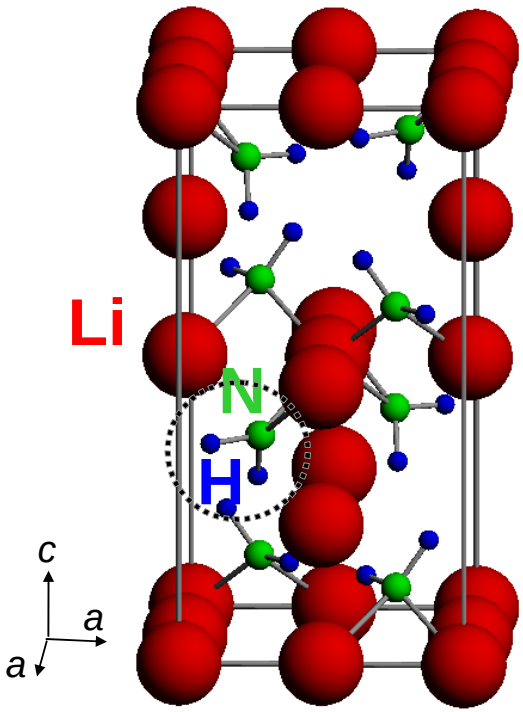
dehydriding temp. > 473-550 K

IEA target temp. < 353 K

Atomic and electronic structures

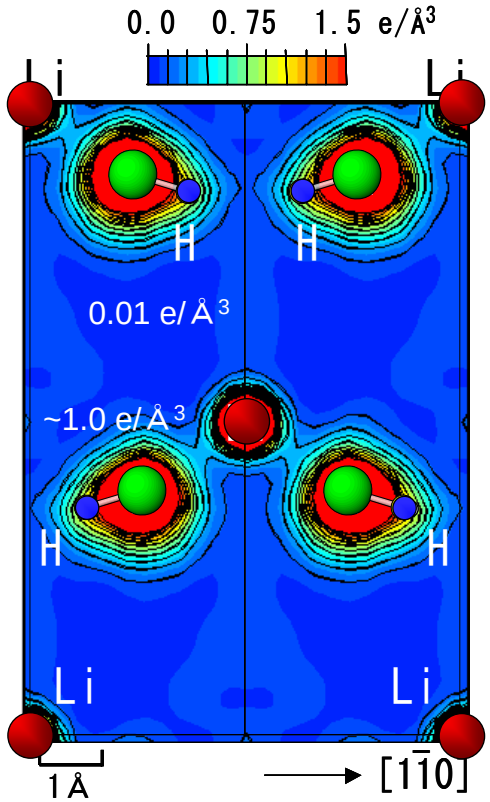
$LiNH_2$

Tetra., $I\bar{4}$ (No. 82)
a = 0.5037 nm
c = 1.0278 nm



V.H. Jacobs, R. Juza,
Z. Anorg. Allg. Chem.
391 (1972) 271

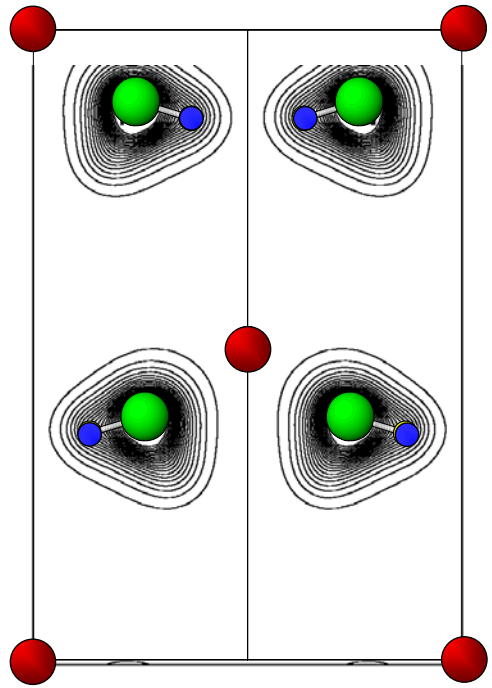
SR-XRD & MEM
(Spring-8, JAPAN)



T. Noritake, H. Nozaki, M. Aoki, S. Towata,
G. Kitahara, Y. Nakamori, S. Orimo,
J. Alloys Compd. 393 (2005) 264.

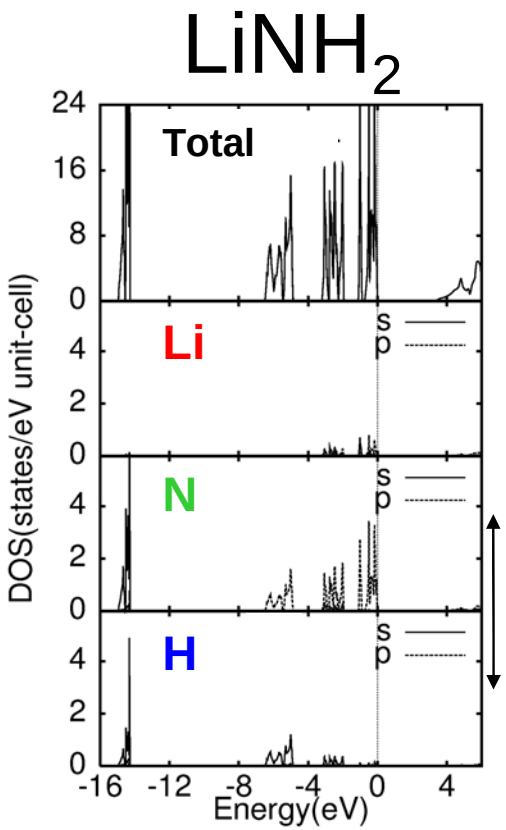
First-Principles
Calculation

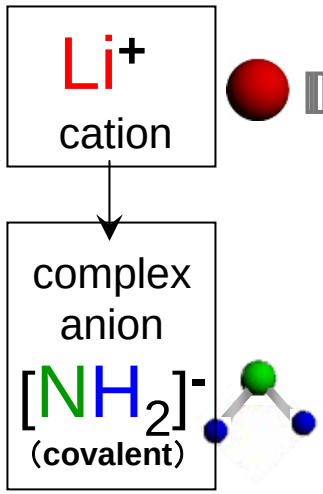
(110)



K. Miwa, N. Ohba, S. Towata,
Y. Nakamori, S. Orimo,
Phys. Rev. B 71 (2005) 195109

Charge transfer





cation substitution…

cation *M*	*valence*	*ionic radius*	*electro-negativity*
Li	1+	0.068 nm	1.0
Mg	2+	0.066 nm	1.2

by the other element with

larger electronegativitiy

Proposed in E-MRS 2003, Strasbourg, June 10-13, 2003

S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, *Appl. Phys. A (Rapid Commun.) 79* (2004) 1765

K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, *Phys. Rev. B 71* (2005) 195109

Y. Nakamori, S. Orimo, *Mater. Eng. Sci. B 108 (2004)* 51

Y. Nakamori, S. Orimo, *J. Alloys Comp. 370 (2004)* 271

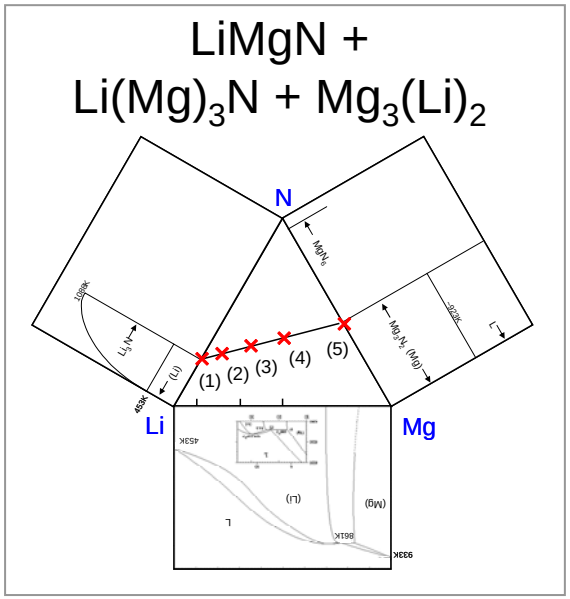
Dehydriding temperatures

$Li_{1-x}Mg_x$

833 K, 2 h, 0.3 MPa N_2

↓

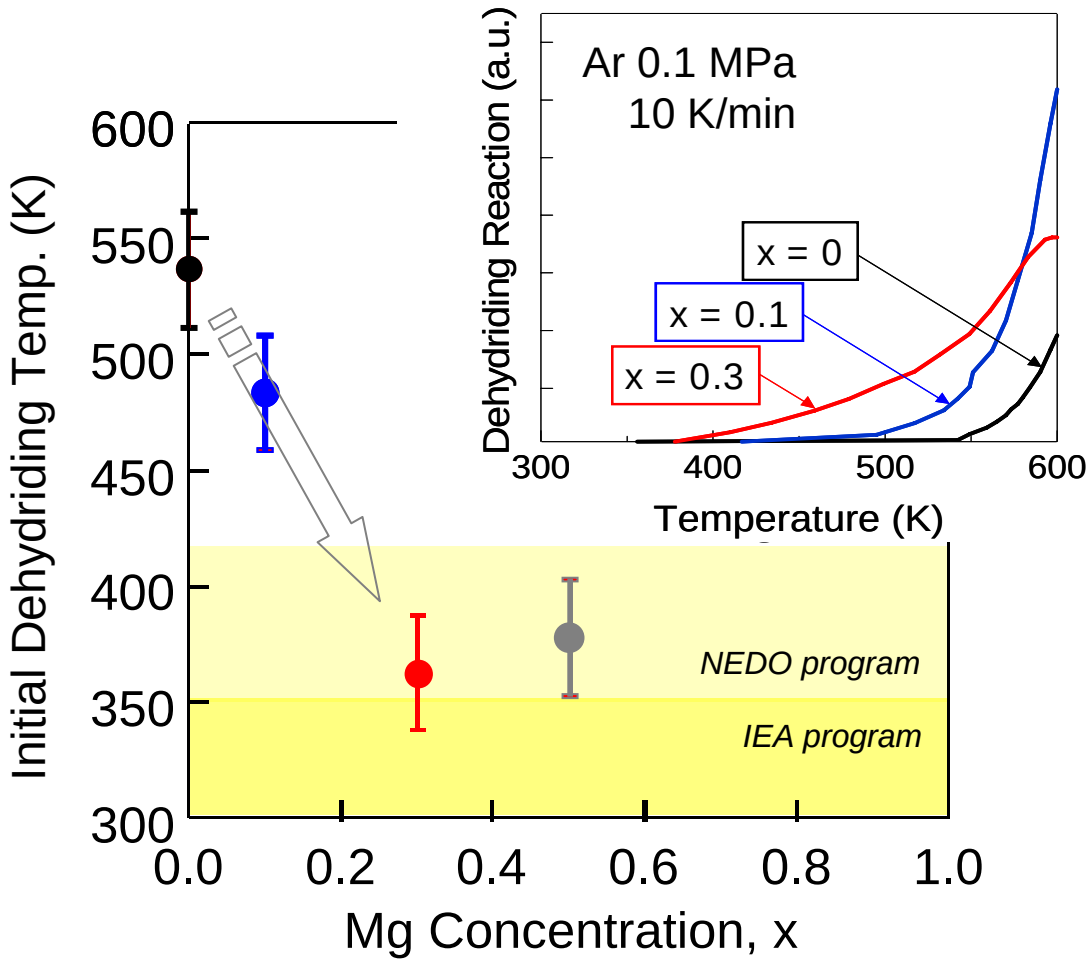
LiMgN +
$Li(Mg)_3N + Mg_3(Li)_2$



623 K, 2 h, 35 MPa H_2

↓

$Li(Mg)NH_2$ +
$Li(Mg)H + Mg_3(Li)_2$

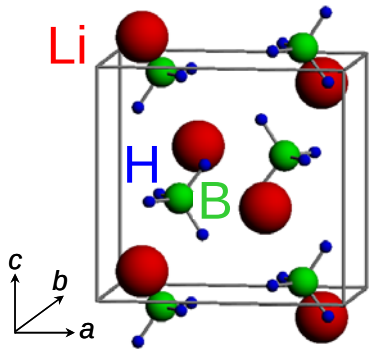


S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, *Appl. Phys. A (Rapid Commun.)* *79* (2004) 1765-1767

Mg substitution in $LiBH_4$

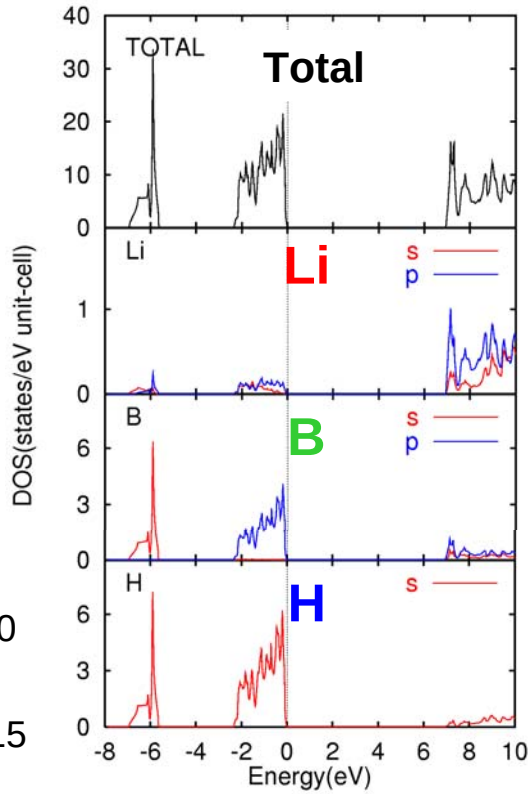
$LiBH_4$

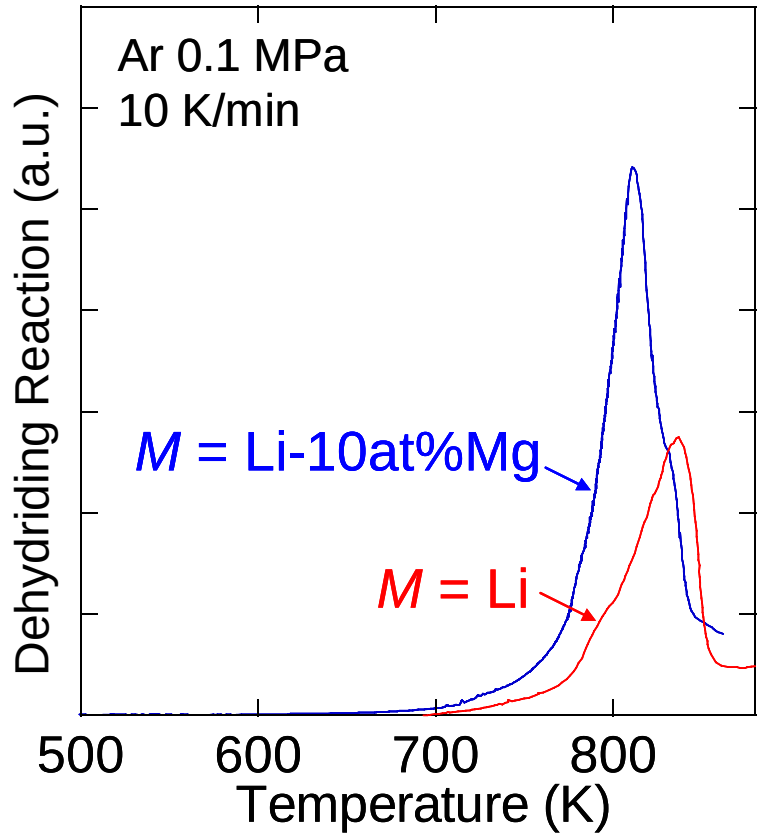
Ortho., Pnma (No. 62)
a = 0.718 nm
b = 0.444 nm
c = 0.680 nm, at 408 K



J-Ph. Soulié et al.,
J. Alloys Compd.346 (2002) 200

A. Züttel et al.,
J. Alloys Compd. 356 (2003) 515





$LiBD_4$

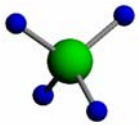
A. Züttel et al.,
J. Alloys Compd.
(to be submitted)

K. Miwa, N. Ohba, S. Towata,
Y. Nakamori, S. Orimo,
Phys. Rev. B 69 (2004) 245120

S. Orimo, Y. Nakamori, G. Kitahara,
K. Miwa, N. Ohba, S. Towata, A. Züttel,
J. Alloys Compd., in press

4 Guidelines

1. Destabilization of $LiBH_4$ and $LiNH_2$



2. Combination of amide and hydride
   lower T_d / faster reaction with "NH_3"

3. Prevention of NH_3-contamination

4. Provision of new reaction pathway

Amide and hydride

dehydriding process →			Ideal Hydrogen (mass%)	Ref.
Hydriding	Partial Dehyd.	Dehyd.		
$LiNH_2 + 2LiH$	$Li_2NH + LiH + H_2$	$Li_3N + 2H_2$	**10.4**	Dafert et al., *Monatsh. Chem.* (1910) , Chen et al., *Nature* (2002)
$Ca_2NH + CaH_2$	$CaNH + 2H_2$		**2.1**	
$LiNH_2 + NaH$	$LiNaNH + H_2$		**4.2**	Ichikawa et al., *JPChem B* (2004)
$2LiNH_2 + MgH_2$	$Li_2Mg(NH)_2 + 2H_2$		**5.6**	Luo, *JALCOM* (2004) Wang, *DOE Report* (2004)
$3Mg(NH_2)_2 + 12LiH$	$Mg_3N_2 + 4Li_2NH + 4LiH + 8H_2$	$Mg_3N_2 + 4Li_3N + 12H_2$	**9.1**	Nakamori et al., *Appl. Phys. A, J. Power Sources* (2004)
$3Mg(NH_2)_2 + 8LiH$	$Mg_3N_2 + 4Li_2NH + 8H_2$		**7.0**	Leng et al., *JPChem B* (2004)
$3Mg(NH_2)_2 + 6LiH$	$3Li_2Mg(NH)_2 + 6H_2$		**5.6**	Luo et al., *MH2004*, Xiong et al., *Adv. Mater.* (2004)

and so on…

Dehydriding process

"*redox process*"

H in $LiNH_2$: $H^{\delta+}$

in LiH : $H^{\delta-}$

→ *redox pair* $H^{\delta-} + H^{\delta+} \rightarrow H_2$

$N^{\delta-} + Li^{\delta+} \rightarrow Li_3N$

P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, *J. Phys. Chem. B 107* (2003) 10967

"*NH_3 mediating process*"

1st step

$M(NH_2)_2 \rightarrow$ "NH_3" + MNH

$\rightarrow$ "NH_3" + M_3N_2

2nd step

MH + "NH_3" $\rightarrow$ MNH_2 + H_2

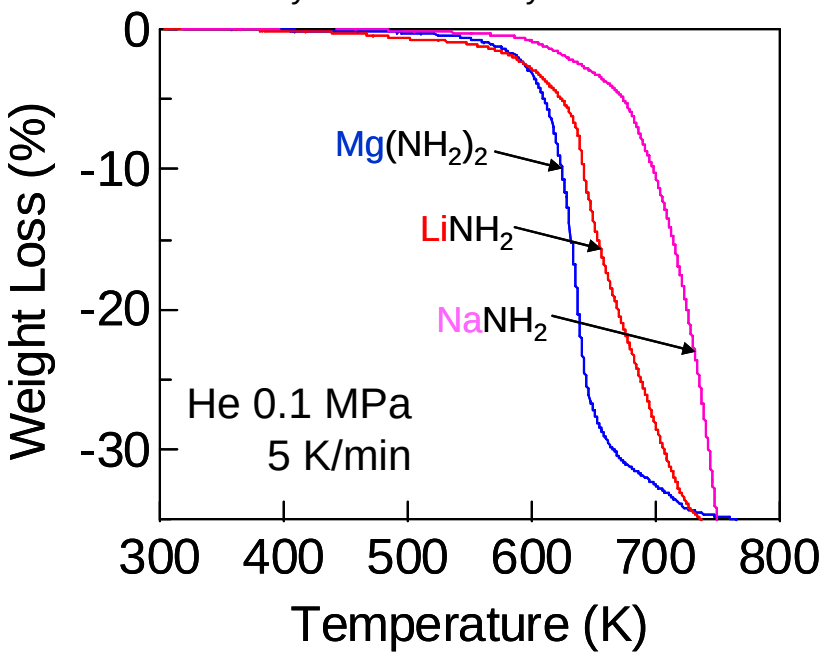
Y.H. Hu, E. Ruckenstein, *J. Phys. Chem. A 107* (2003) 9737

T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, *J. Phys. Chem. B 108* (2004) 7887

1st step (formation of "NH_3")

Point : ***M***NH_2 with lower decomp. temp. T_d

$M(NH_2)_y \rightarrow y/2\ M_{2/y}NH + y/2\ NH_3$



T_d : $Mg(NH_2)_2 < LiNH_2 < NaNH_2$

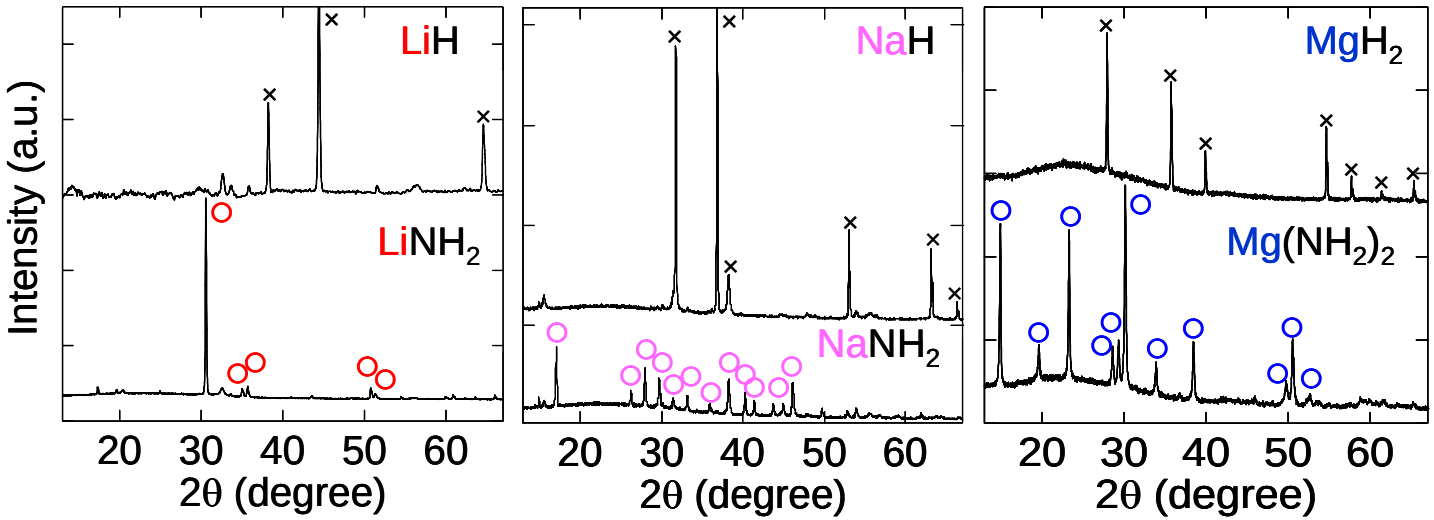
→ **Mg** for ***M***

Y. Nakamori et al.,
Mater. Trans., in press

2nd step (H_2 emission)

Point : ***M***H with faster reaction with "NH_3"

$$MH_y + y\ NH_3 \rightarrow M(NH_2)_y + y\ H_2$$



*M*H	temp. (K)	time (hour)
LiH	493	12
NaH	573	48
MgH_2	613	168

→ **Li** for ***M***

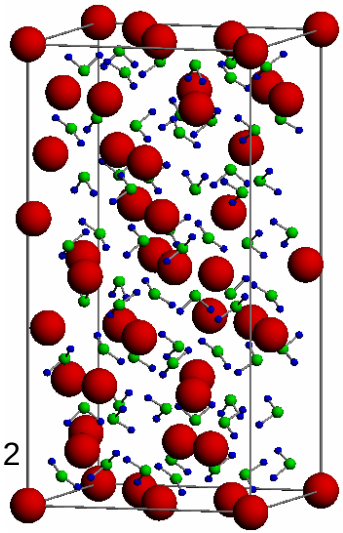
Y. Nakamori et al.,
Mater. Trans., in press

Optimized combination

$Mg(NH_2)_2 \rightarrow$ "NH_3" + MgNH

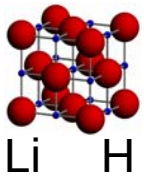
$\rightarrow$ "NH_3" + Mg_3N_2

Lower decomposition temp.



LiH + "NH_3" $\rightarrow$ $LiNH_2$ + H_2

faster reaction with "NH_3"



$Mg(NH_2)_2 + x\ LiH$

?

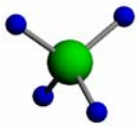
composition ratio

Y. Nakamori, G. Kitahara, S. Orimo, *J. Power Sources* 137 (2004) 309

4 Guidelines

1. Destabilization of $LiBH_4$ and $LiNH_2$

2. Combination of amide and hydride

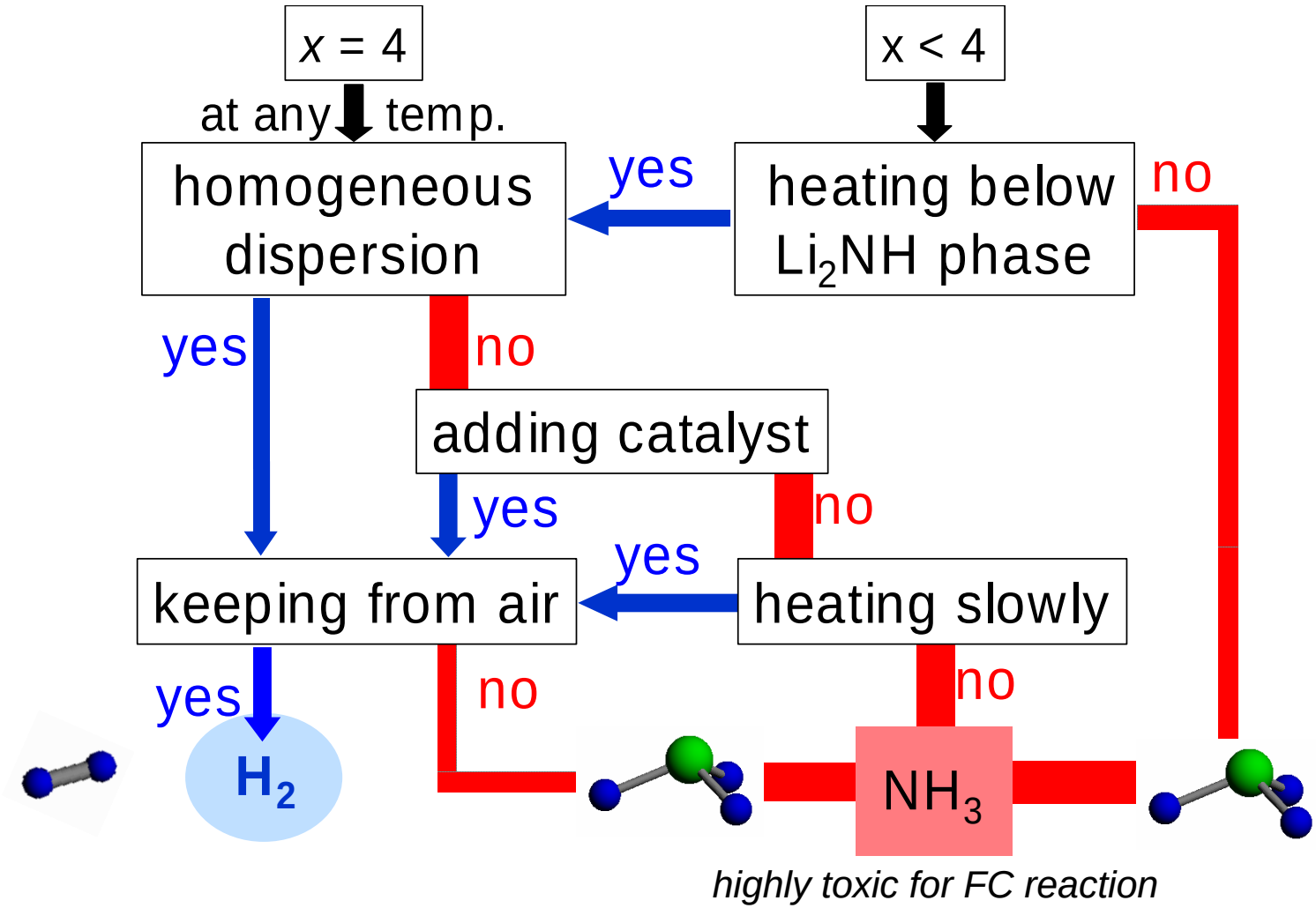


3. Prevention of NH_3-contamination

"tunable" composition / starting material

4. Provision of new reaction pathway

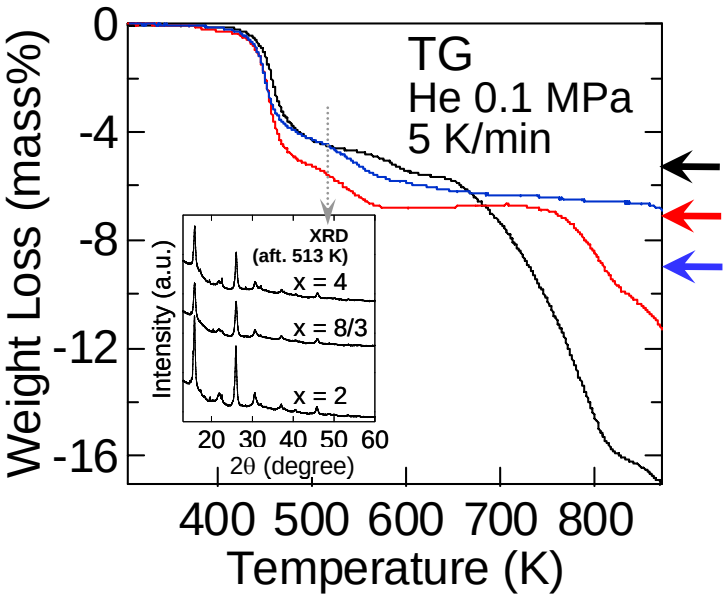
H_2 / NH_3 from $Mg(NH_2)_2$ + *x* LiH

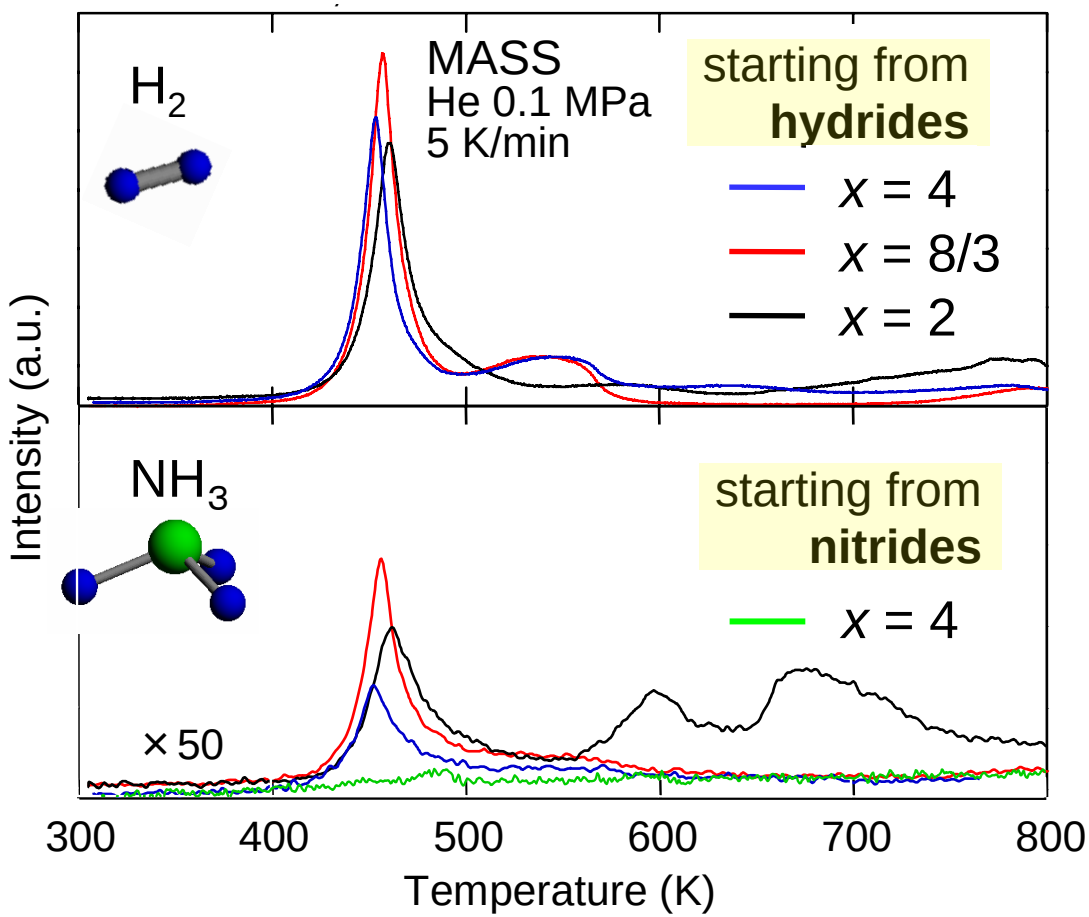


Y. Nakamori, S. Orimo, submitted

Affected by composition *and* …

$Mg(NH_2)_2 + x\ LiH$





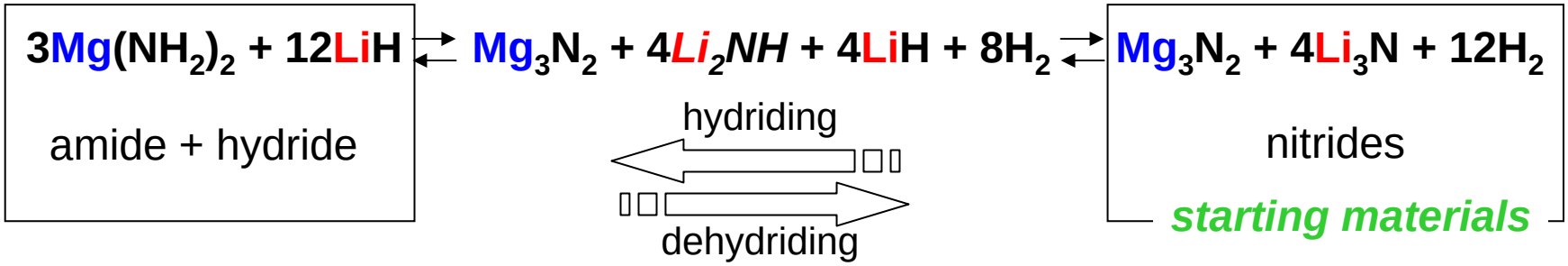
$x = 4$ (max. 9.1 mass%)

$x = 8/3$ (max. 6.9 mass%)

$x = 2$ (max. 5.6 mass%)

Y. Nakamori, G. Kitahara, A, Ninomiya, K. Aoki, T. Noritake, S. Towata, S. Orimo, *Mater. Trans.,* in press

$Mg(NH_2)_2$ + *4* LiH



"NH_3 *mediating process*"

Y.H. Hu, E. Ruckenstein, *J. Phys. Chem. A 107* (2003) 9737

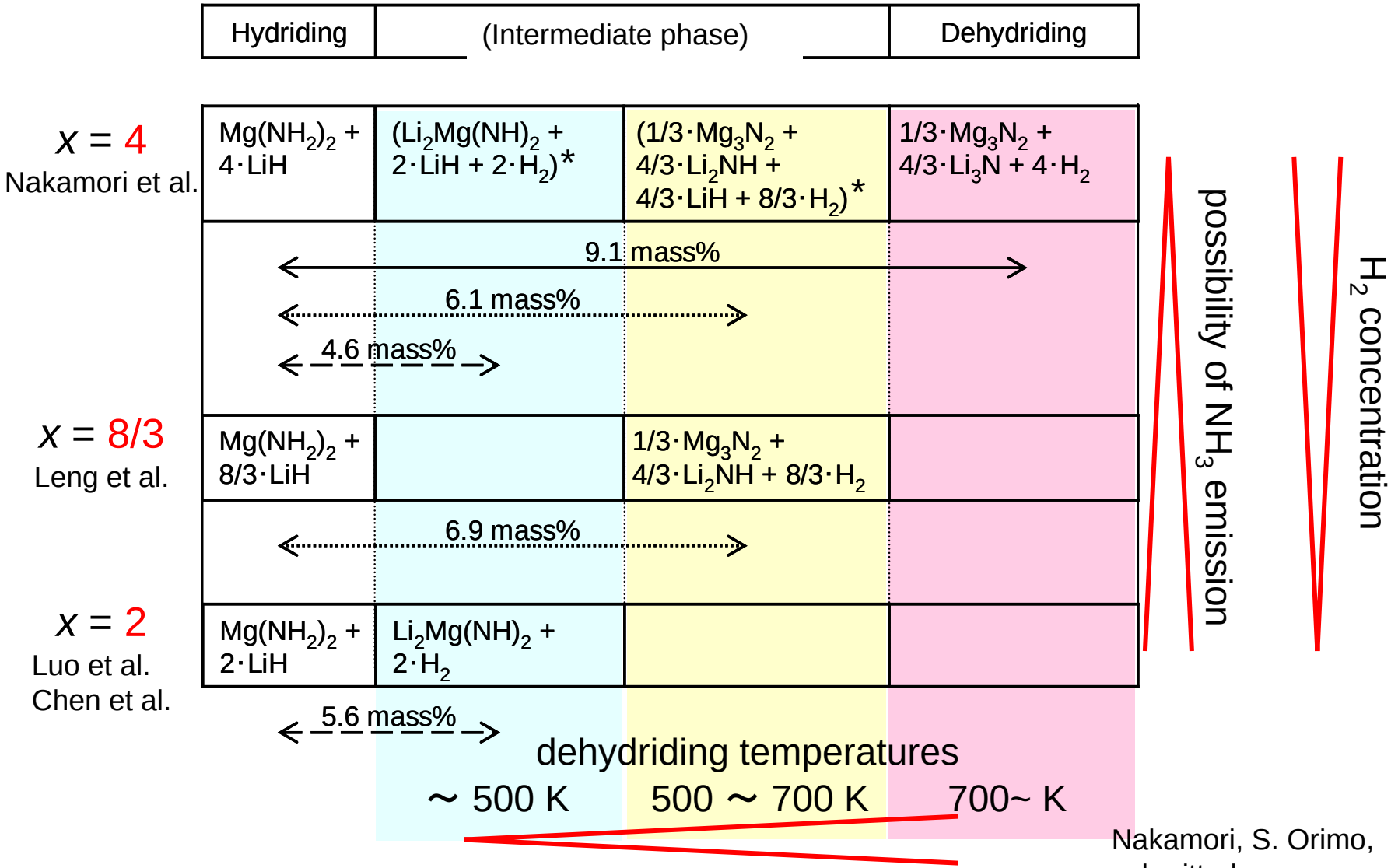
T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, *J. Phys. Chem. B 108* (2004) 7887

S. Hino, T. Ichikawa, N. Ogita, M. Udagawa, H. Fujii, *Chem. Commun.,* in press

Y. Nakamori, G. Kitahara, A, Ninomiya, K. Aoki, T. Noritake, S. Towata, S. Orimo, *Mater. Trans.,* in press

affected by… *composition,*
starting material (= elemental dispersion),
atmosphere,
heating rate,
open/close system, …

x, depending on applications



Nakamori, S. Orimo, submitted.

4 Guidelines

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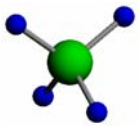


4. Provision of new reaction pathway

Intermediate phase formed by dehydriding

Mixing effect

$LiNH_2 \rightarrow 1/2\ Li_2NH + 1/2\ NH_3 \rightarrow 1/3\ Li_3N + 2/3\ NH_3$

NH_3 emission, 600 K

$LiH \Leftrightarrow Li + 1/2\ H_2$

13.8 mass%H_2, 953 K

○ $LiNH_2 + 2\ LiH \Leftrightarrow Li_2NH + LiH + H_2 \Leftrightarrow Li_3N + 2\ H_2$

5.5 mass%H_2, 473 K 5.2 mass%H_2, 700 K

Any intermediate phase after/during dehydriding?

○ $LiBH_4 + LiNH_2$: “Li-B-N(-H)” exists

× $LiBH_4 + LiAlH_4$: “Li-B-Al(-H)” may not exist

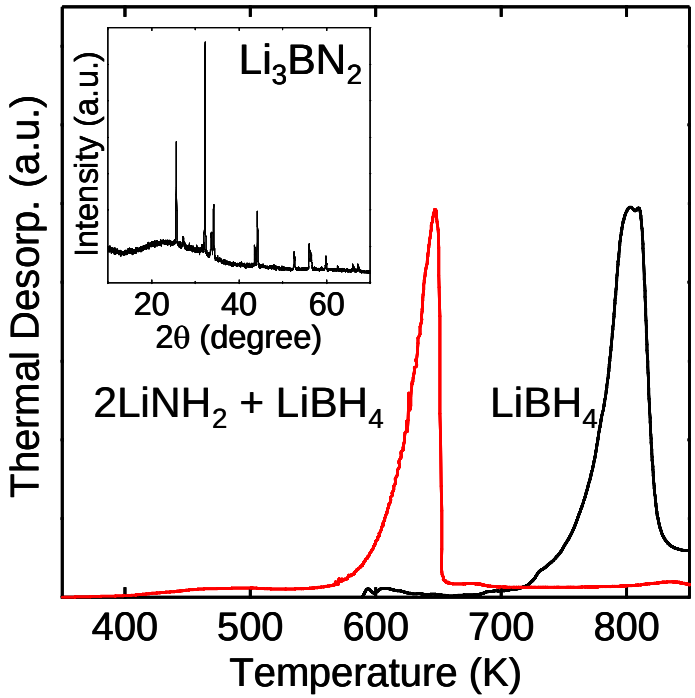
Combination of $LiBH_4$ + $LiNH_2$

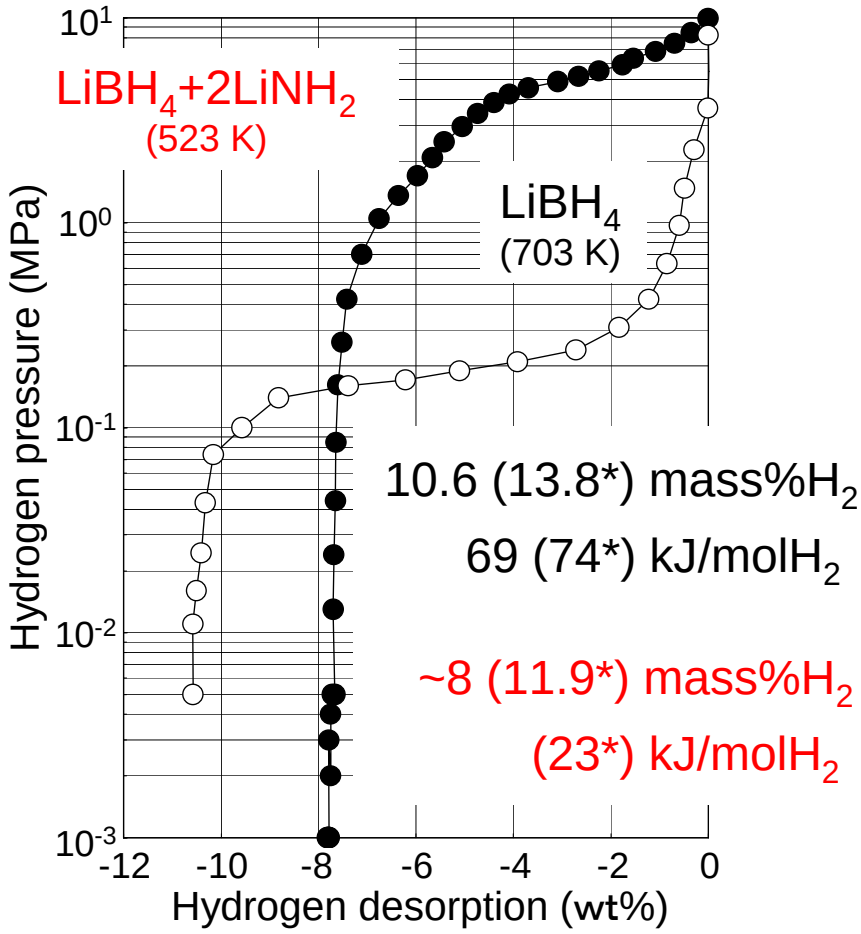
milling 650 K

$LiBH_4 + 2LiNH_2 \rightarrow Li_3BN_2H_8 \rightarrow$

$\rightarrow Li_3BN_2H_x$ (x~0) $\rightarrow$ α-Li_3BN_2

800 K





Y. Nakamori, A. Ninomiya, G. Kitahara, K. Aoki, T. Noritake, K. Miwa Y. Kojima, S. Orimo, *J. Power Sources* in press

M. Aoki, K. Miwa, T. Noritake, G. Kitahara, Y. Nakamori, S. Orimo, S. Towata, *Appl. Phys.A 80* (2005) 1409

4 Guidelines

1. Destabilization of $LiBH_4$ and $LiNH_2$
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   lower T_d / faster reaction with "NH_3"

3. Prevention of NH_3-contamination
   "tunable" composition / starting material

4. Provision of new reaction pathway
   intermediate phase formed by dehydriding

Recent publications

Theory

K. Miwa et al., "*First principles study on lithium borohydride $LiBH_4$*", *Phys. Rev. B 69* (2004) 245120

K. Miwa et al., "*First-principles study on lithium amide for hydrogen storage*", *Phys. Rev. B 71* (2005) 195109

Analysis

S. Orimo et al., "*Material properties of MBH_4 (M = Li, Na, and K)",* *Mater. Sci. Eng. B 108* (2004) 51

K. Ohoyama et al., "*Revised crystal structure model of Li_2NH by neutron powder diffraction*", *J. Phys. Soc. Jan. 74* (2005) 483

T. Noritake et al., "*Crystal structure and charge density analysis of Li_2NH by synchrotron X-ray diffraction*", *J. Alloys Compd.* 393 (2005) 264

Material Synthesis

Y. Nakamori, S. Orimo, *"Destabilization of Li-based complex hydrides", J. Alloys Compd. 370* (2004) 271

S. Orimo et al., "*Destabilization and enhanced dehydriding reaction of $LiNH_2$ – an electronic structure viewpoint*", *Appl. Phys. A (Rapid Commun.) 79* (2004) 1765

Y. Nakamori, et al., "*Synthesis and dehydriding studies of Mg-N-H systems*", *J. Power Sources 138* (2004) 309

M. Aoki et al., "*Destabilization of $LiBH_4$ by mixing with $LiNH_2$*", *Appl. Phys. A 80 (2005) 1409*.

Y. Nakamori et al., "*Reversible hydrogen storage functions for the mixtures of Li_3N and Mg_3N_2*", *Appl. Phys. A 80* (2005) 1

Y. Nakamori, et al., "*Guidelines for developing amide based hydrogen storage materials*", *Mater. Trans.,* in press

S. Orimo et al., "Dehydriding and rehydriding reactions of $LiBH_4$", *J. Alloys Compd.* in press

Y. Nakamori et al., "*Dehydriding reaction of mixed complex hydrides*", *J. Power Sources,* in press