Chemical Reactions of Amides and Hydrides-A Methodology for Synthesis of Hydrogen Storage Materials

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Introduction

There are strong pushes towards hydrogen economy worldwide. To overcome one of the technical barriers - onboard hydrogen storage, great efforts have been devoted to the development of solid-state materials. NITRIDE and IMIDE possess strong affinity towards hydrogen, which enables them as potential storage medias. Our discovery on amide-hydride system designed for reversible hydrogen storage was regarded as a big step forward over the promise of clean hydrogen energy.

First amide-hydride system, Li-N-H system, was proposed for hydrogen storage based on the discovery of hydrogenation of Li_3N

Hydrogenation $Li_3N + 2H_2 \rightarrow LiNH_2 + 2LiH$ 11.4wt%

Dehydrogenation $LiNH_2 + 2LiH \leftrightarrow Li_2NH + LiH + H_2$ 5.41wt%

thus, starting from hydrogenation of Li_2NH

$Li_2NH + H_2 \leftrightarrow LiNH_{2\ (amide)} + LiH_{\ (hydride)}$ 6.89wt%

Drawback: to reach the plateau pressure for hydrogen desorption of 1bar, temperature of 285°C is applied.

P. Chen, Z. Xiong, et.al., Nature 420 (2002) 302-304

Second amide-hydride system, Li-Mg-N-H system, was found by substituting lithium hydride with magnesium hydride and so far it's the most promising system for hydrogen storage

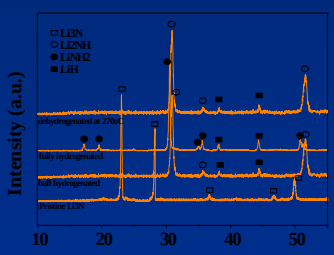
Dehydrogenation $2LiNH_2 + MgH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2$ 5.56wt%

Hydrogenation & dehydrogenation cycle

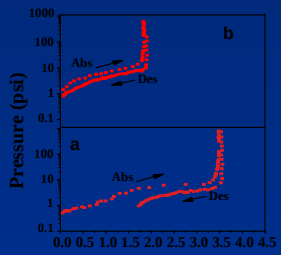
$Li_2Mg(NH)_2 + 2H_2 \leftrightarrow Mg(NH_2)_{2\ (amide)} + 2LiH_{\ (hydride)}$ 5.88wt%

Advantage: Temperature for hydrogen desorption decreased to 180°C with plateau pressure enhanced to above 20bar. Fast kinetics, 80% of H_2 can be hydrogenated & dehydrogenated in 1 hour.

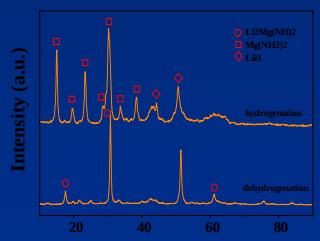
Z. T. Xiong, G. T. Wu, J. J. Hu and P. Chen, Adv. Mater. 2004, 16, 1522



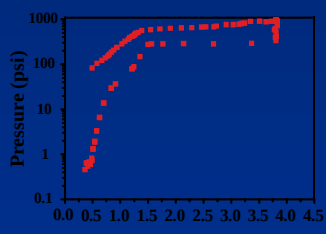
XRD patterns of hydrogenation&dehydrogenation over Li_3N



Pressure-Composition (P-C) Isotherms of Li_3N (a) and Li_2NH (b) samples at temperature 250°C.



XRD patterns of hydrogenated&dehydrogenated $Li_2Mg(NH)_2$ sample



Pressure-Composition (P-C) Isotherms of $Li_2Mg(NH)_2$ samples at temperature 180°C.

Other successful amide-hydride system including:

Amide	Hydride	H_2 amount for cycle
$LiNH_2$	CaH_2	2.71wt%
$Mg(NH_2)_2$	NaH	2.17wt%
$LiNH_2$	$LiAlH_4$	2.3wt%
$Mg(NH_2)_2$	MgH_2	H_2 can only be released
$Mg(NH_2)_2$	CaH_2	H_2 can only be released

Z. T. Xiong, G. T. Wu, J. J. Hu and P. Chen, Adv. Mater. 2004, 16, 1522

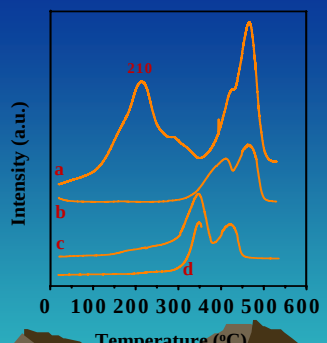
Z. Xiong, J. Hu, G. Wu and P. Chen, J. Alloy. Compd, 2005, 395, 209-212

Simple mechanism proposed to explain interactions between Amides and Hydrides

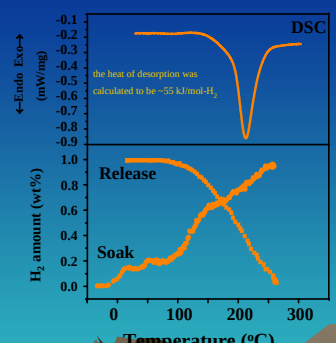
H atoms attached to N normally possess positive charges, however, H in ionic hydrides have negative one. The strong chemical potential for the combination of H^+ and H^- is one of the important driving forces!

By changing amide or hydride, new reactions and new materials may be discovered.

$Ca(NH_2)_2$-NaH system was investigated recently for reversible hydrogen storage

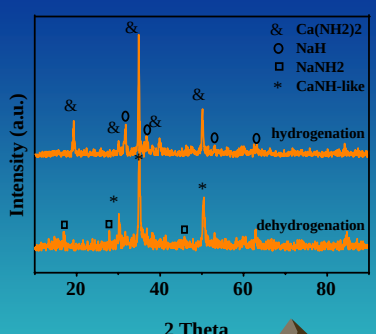


Temperature Programmed Desorption (TPD) spectra of post milled $Ca(NH_2)_2$-NaH 1/1 a) H_2 signal; b) NH_3 signal with c) pure $Ca(NH_2)_2$ and d) NaH included as comparison



DSC and Volumetric measurement of hydrogen desorption/absorption over $Ca(NH_2)_2$-NaH system

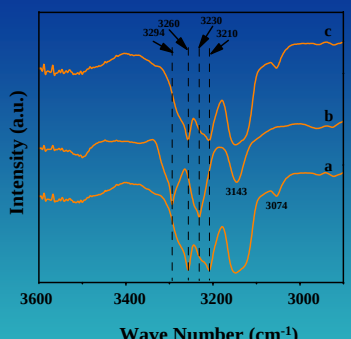
1H atom per $1Ca(NH_2)_2$-1NaH molecule can be reversibly stored



XRD patterns of hydrogenated & dehydrogenated $Ca(NH_2)_2$-NaH sample

Reaction formula can be written as:

$Ca(NH_2)_2 + NaH \leftrightarrow NaNH_2 + Ca\text{-}N\text{-}H$ solid solution



FTIR spectra of: a) dehydrogenated b) subsequently hydrogenated and c) again dehydrogenated $Ca(NH_2)_2$-NaH sample

Dehydrogenation:
$NaNH_2$ with signal at 3260, 3210, 3074 cm-1. CaNH-like structure 3143cm-1

Hydrogenation:
$Ca(NH_2)_2$ with characteristic N-H vibration at 3294 and 3230cm-1

Acknowledgement

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