Irreversible nanoconfinement of a 1:1 $Mg(NH_2)_2$ and $LiNH_2$ mixture in mesoporous carbon scaffolds

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Introduction

How to decrease the hydrogen release temperature of amines (or hydrides)?

The confinement of amines (and hydrides) in nanopores is one of the several methods that can improve the kinetic (and sometimes thermodynamic) properties of the solid state hydrogen stores.
The reduction of the particle sizes increases the surface energy and improves their reactivity.

Why a mixture of $Mg(NH_2)_2$ and $LiNH_2$?

- $Mg(NH_2)_2$ contains 7.2 wt% hydrogen
- $LiNH_2$ contains 8.7 wt% hydrogen

Both decompose at temperatures higher than 350 °C

The 1:1 mixture of $Mg(NH_2)_2$ and $LiNH_2$ melts at 350 °C and decomposes above 375 °C

It is possible to melt infiltrate in nanopores (350 °C <θ<375 °C).

The decomposition leads to $Li_2Mg_2(NH)_3$ or LiMgN.

$Li_2Mg_2(NH)_3$ and LiMgN can be reversibly hydrogenated to $Mg(NH_2)_2$ and LiH

- LiH contains 12.7 wt % hydrogen

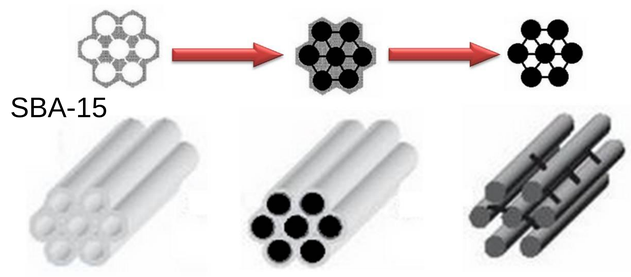
$Li_2Mg_2(NH)_3$ and LiMgN or $Mg(NH_2)_2$ and LiH cannot melt and escape from the pores, maintening their nanosize during cycling.

Synthesis of the mesoporous scaffolds

CMK-3

(Carbon Molecular sieves Korean Advanced Institute of Science and Technology)[1]

Hard template sythesis



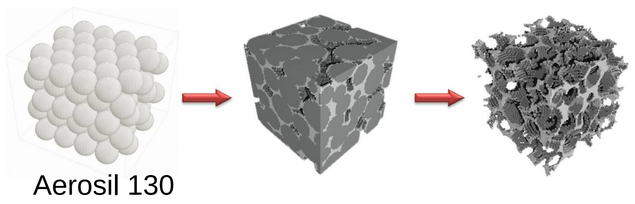
- Surface area (BET): 1270m²/g
- Total pore volume: 1.1 cm³/g
- Average pore diameter (QSDFT): 5.5 nm
- Regular hexagonal structure
- Cylindrical pores
- Amorphous carbon

1 – R. Ryoo et al, J. Am. Chem. Soc., 122, 43, (2000),10712-10713.

ASM

(Asemosil Carbon)

Hard template sythesis



- Surface area (BET): 590m²/g
- Total pore volume: 2.1 cm³/g
- Average pores diameter: 20 nm
- Random structure
- Spherical pores
- Amorphous carbon

Synthesis of the $Mg(NH_2)_2$ – $LiNH_2$ mixture

Synthesis of $Mg(NH_2)_2$

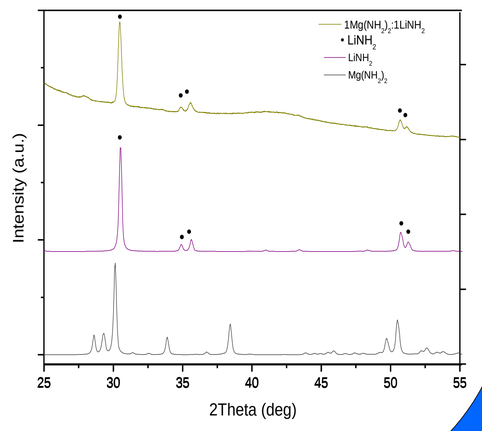
Starting materials:
MgH_2
NH_3 (7 bar)
Equipment:
Planetary ball mill
Jar with gas valve
Stainless steel balls (3g)

Syntetic conditions:
MgH_2 under 7 bar of NH_3
Mass ratio MgH_2 – Balls= 1 : 10
300 RPM for 40h

Mixing conditions

Starting materials:
$Mg(NH_2)_2$
$LiNH_2$
Equipment:
Planetary ball mill
Jar with gas valve
Stainless steel balls (3g)

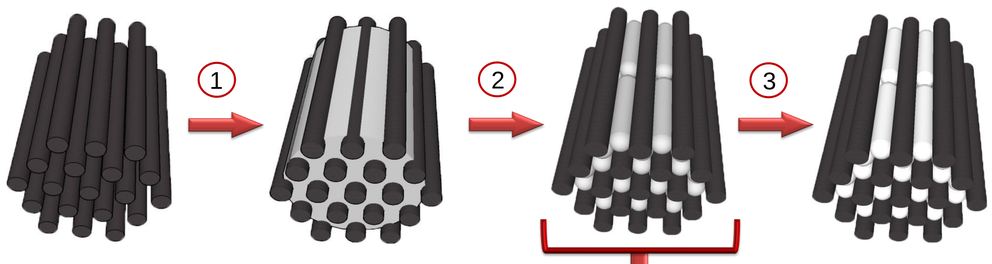
Syntetic conditions:
$Mg(NH_2)_2$ and $LiNH_2$ under Ar atmosphere
Mass ratio Amide Mixture – Balls= 1 : 10
300 RPM for 1h



Carbon infiltration

Starting materials:
Degassed carbon – 300 °C under vacuum overnight
1 $Mg(NH_2)_2$: 1 $LiNH_2$ homogeneous mixture
Equipment:
Parr reactor
Furnace

Infiltration contidions:
Amount of 1 $Mg(NH_2)_2$: 1 $LiNH_2$ mixture equal to the total pore volume
Starting overpressure of NH_3 (4bar)



1. **Thermal treatment at 350 °C**
The 1$Mg(NH_2)_2$: 1$LiNH_2$ mixture melts and fills the carbon pores

2. **Thermal treatment at 380 °C**
The 1$Mg(NH_2)_2$: 1$LiNH_2$ mixture inside the pores becomes solid and starts to release NH_3 to afford $Li_2Mg_2(NH)_3$

3. **Thermal treatment at higher temperatures**
Complete dehydrogenation to LiMgN

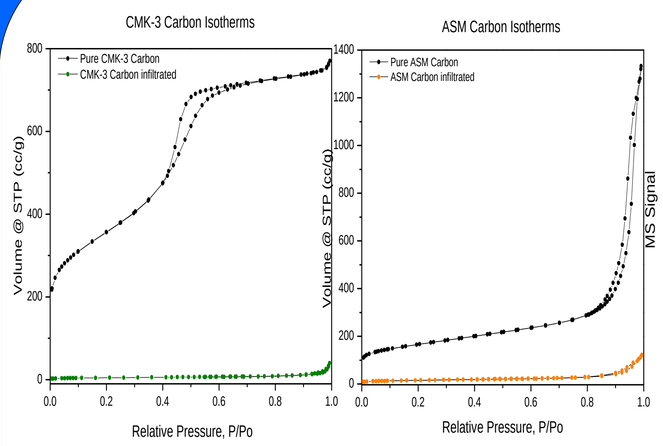
$$2Mg(NH_2)_2 + 2LiNH_2 \xrightarrow{+374\,^oC} Li_2Mg_2(NH)_3 + 3NH_3 \quad (2)$$

$$\xrightarrow{+450\,^oC} LiMgN + H_2 \quad (3)$$

$$2LiMgN + 4H_2 \longleftrightarrow Mg(NH_2)_2 + MgH_2 + 2LiH$$

Final system
Reversible reaction

Material characterization



CMK-3 infiltrated

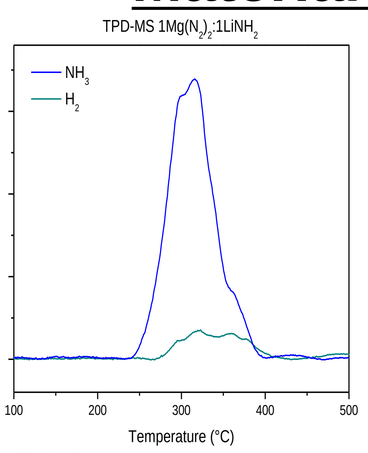
Total pore volume: 0.1 cm³/g
BET Surface area: 17 m²/g

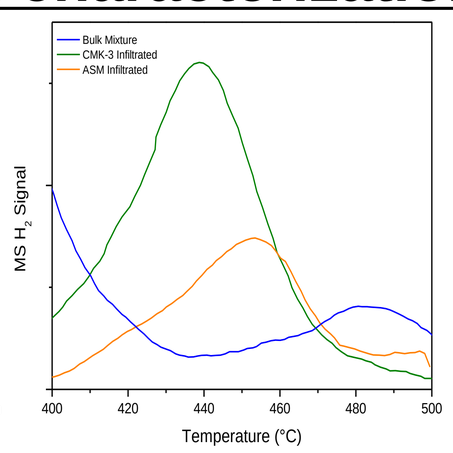
ASM infiltrated

Total pore volume: 0.2 cm³/g
BET Surface area: 56 m²/g

Surface analysis
Adsorption isotherm (77K)

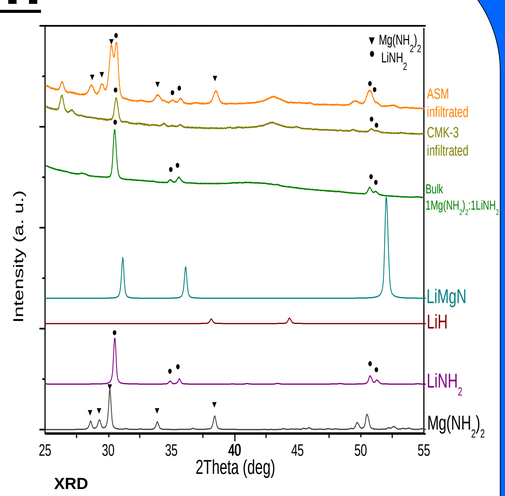
The surface analysis of the samples before and after the infiltration show a dramatic decrease of the surface area and total pore volume.
Practically all pores are filled (or blocked).





TPD-MS
(Thermal Programmed Desorption – Mass Spectrometry)
Performed up to 500 °C with a rate of 5 °C /min under He flow (20ml/min).
The 1$Mg(NH_2)_2$: 1$LiNH_2$ mixture shows NH_3 signals between 200 and 400 °C
The NH_3 signals appear also in the infiltrated samples, but with a very low intensity compared to the bulk (indication of a partial decomposition during the infiltration process).

At temperatures higher than 400 °C total dehydrogenation occurs and LiMgN is obtained.
The H_2 signals appear at:
483 °C - bulk mixture, with a broad peak
456 °C - ASM infiltrated
438 °C - CMK-3 infiltrated sharper peak



XRD
(X-Ray Diffraction)

The bulk 1$Mg(NH_2)_2$: 1$LiNH_2$ mixture shows the pattern of $LiNH_2$ only ($Mg(NH_2)_2$ is probably amorphous)
The intensities of CMK-3 infiltrated mixture have been significantly suppressed implying adequate infiltration.
The ASM infiltrated mixture shows $Mg(NH_2)_2$ peaks probably due to a more intense recrystallization (outside the pores?)

Conclusions

- The physical properties of the mixture 1$Mg(NH_2)_2$: 1$LiNH_2$ allows infiltration in mesoporous carbon structures.
- The nanoconfined mixture reveals decreased decomposition temperatures (T_{des}) compared to the bulk material.
- The decomposition temperatures can be a function of:
  - ✓ pore size (smaller pores → lower T_{des}), i.e. nanoconfinement effects.
  - ✓ surface area (higher SBET → lower T_{des}), i.e catalytic effects.

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