Combinatorial Approach for Hydrogen Storage Materials

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Outline

Approach: Parallel synthesis accompanied by high throughput screening for a desired property.

– Methods
  • Preparation/parallel synthesis
  • Analytical techniques
  • Scale-up

– Selected results
  • Al-Li-Si system
  • Al-Mg-Ti system
  • AlH₃ + Si
  • Mg(BH₄)₂

– Summary
Down-selection of the combi process

Production of multiple compositions

Diffusion multiples

Co-sputtering

High energy 96-well Shaker

HTS Analytical Tools

ToF-SIMS

WO₃ sensor

Thermography
Hydrogen Sorption in Diffusion Multiples

Traditional DM w/ LaNi
several new concepts.

Activation 80 °C / 100psi H₂

Cycling 80 °C / 100psi H₂

Si DM with Li and Na

Sliced cross section

Subtracted Image

Rapid in-situ screening method but low spatial resolution
Hydrogen Sorption in Diffusion Multiples

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**Thin Film Sputtering**

Multi-Target Co-sputtering

- Start Mg₃-Al₀.₀₃
- End Mg₀.₀₃Al₃

Sputtered Array

Imaging A/B ratio

**Spatially Resolved Programmed Arrays**

**Continuous Compositional Gradients**
Reversible Catalyst Screening

Validation w/ 3NaAlH₄ + Ti (catalyst) 120 °C → Na₃AlH₆ + 3H₂ + 2Al (Endothermic)

Increasing Ti(m) 

Increasing Ti 

NaAlH₄ pellet 

Equivalent emissivity at 80 °C 

Increasing Ti 

At 130 °, lower temperature contains, higher [Ti]. Evidence of decomposition by XRD and H₂ pressure.

• High pressure thermography. 
• XRD

Ti(m) increasing

ZnB₂, MgB₂, Mg, Mn, Ti on ZnB₂

>200 catalyst composition screened
Down-selection of the combi process

Production of multiple compositions

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HTS Analytical Tools

ToF-SIMS

WO$_3$ sensor

Thermography
Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests.
Multi-well Reactive Ball Milling
Entire process in glove box

Catalyst Doping
- Validated with NaAlH₄, previously screened over 2000 catalyst.
- New MH candidates.

Synthesis
- Metal substitution in amides.
- Li – Alumides, AlLiMg
- Li – Silicides, LiSiMg

Improved method for the synthesis of ternaries.

PCI Measurement

Catalyst/Reactant Mixtures

Optical image

Thermography

96-well sample holder

High energy shaker
2x, 4x, or 96

96-well H₂ sensor for H₂ desorption
25 – 300 °C

High T and P Reactor

Improved method for the synthesis of ternaries.
Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests.
Hydride Screening with IR Imaging

Hydrogen Sorption and Desorption

- Benchmarked with LaNi₅, LaAlNi₅, and FeTi powders, 100 mg.
- 10 replicates 3% rsd.
- Distinguish between surface absorption and bulk hydriding.
- Synthesis and hydride w/o sample removal.

Risks

- Indirect measurement.
- Surface differences
- Resolution limited, need magnification lens for DMs

Surface sorption may mask hydrogenation
Thermographic Imaging

Mixed samples of LaNi$_5$ diluted with Al powder hydrided at 55 bar, 40°C.

Capability to rapidly and quantitatively screen for reversible, hydrogen storage up to 400°C / 55 bar.

Thermal camera response for the hydrogen sorption of LaNi$_5$

Linear response for H$_2$ sorption
0.3 wt% hydrogen detection limit.

Thermographic Imaging

Sorption

H$_2$ Desorption

Lemmon

y = 31.339x + 4.7116
$R^2 = 0.9118$
Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests.
6-Pak Test Setup – secondary screening

Capacity:
• Temp: RT~450°C
• Pressure: 0~1600 psi
• Resolution: 1 wt%

Features:
• 6 reactors/samples run simultaneously & independently
• 6 separate temperature/pressure controls
• Monitor/control through internet

Cui, Raber, Rubinsztajn, Rijssenbeek, Lemmon
6-Pak example results

pressure change during \( \text{H}_2 \) uptake/release

<table>
<thead>
<tr>
<th>Weight Percent</th>
<th>12Al+34LiBH4+17MgH2</th>
<th>12Al+34LiBH4+17MgH2+2M%\text{VCl}_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>350C12hr</td>
<td>0psi</td>
<td>400C12hr 1000psi</td>
</tr>
<tr>
<td>280C12hr</td>
<td>1000psi</td>
<td>400C12hr 1000psi</td>
</tr>
<tr>
<td>400C12hr</td>
<td>1000psi</td>
<td>350C12hr 1000psi</td>
</tr>
</tbody>
</table>

Weight change after \( \text{H}_2 \) charge/discharge

Number of Charge-Discharge
Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests.
Combined *In-situ* XRD and gas analysis

Sample holder

Image plate readout

Time resolved patterns (reaction pathway)

**max T: 550 °C**  **max P: 140 bar**

Diffraction setup

RGA (gas analysis)

Integrated diffraction pattern (crystal structure)

Unique apparatus to provide unmatched information about reaction pathways / mechanism

Gao & Rijssenbeek
Li-Al-Si System

Li$_{12}$Al$_3$Si$_4$ + H$_2$ ⇌ AlLiSiH$_{0.9}$

In-situ XRD: Hydrogen Sorption

- 270°C
- 240°C
- 200°C
- 150°C

Al$_{18}$Li$_2$Si$_6$
Al$_{13}$Li$_2$Si$_4$
Al$_{3}$Li$_2$Si$_4$
Li$_{15}$Si$_2$
Li$_{12}$Si$_7$
Al$_{12}$Li$_3$Si$_2$
Al$_{3}$Li$_5$Si$_2$
Al$_{3}$Li$_8$Si$_5$

Thermal camera response for H$_2$ sorption, 150°C, 55 bar.

In-situ XRD: Hydrogen Desorption

- 330°C
- 300°C
- 50°C

- Li$_{12}$Al$_3$Si$_4$ + H$_2$ ⇌ AlLiSiH$_{0.9}$
- New intermetallic compound reversibly absorbs up to 1.2 wt % H$_2$ at 150°C, 55 bar (desorption at 300°C)
- Found using diffusion multiple
Thermographic Images: Hydrogen Sorption 55 bar, 300°C, blank subtracted.

Before H₂ addition.

Immediate surface sorption.

10 sec after H₂ addition

30 sec after H₂ addition

40 sec after H₂ addition
AlH$_3$ + 2 MgH$_2$ + TiH$_2$ \textit{in-situ} XRD

Hydrogen Desorption

Al$_{12}$Mg$_{17}$, Mg, TiH$_2$

WC, MgO

→ 290 °C

Al, MgH$_2$, TiH$_2$

WC, MgO

MgH$_2$ + 0.71 Al ↔ MgAl$_{0.71}$ + H$_2$

Hydrogen Sorption (130 bar)

Al, MgH$_2$, TiH$_2$

WC, MgO

→ 230 °C

Al$_{12}$Mg$_{17}$, Mg, TiH$_2$

WC, MgO

→ 185 °C

Reduced T & wt.% but faster kinetics

Found independently using multi-well shaker
Over 100 composition investigated, only Si demonstrates reversibility.
Reversible $\text{AlH}_3 + \text{Si}$

H$_2$ Desorption, 460°C 1$^{\text{st}}$ Cycle

2.5 – 3.2% (6$^{\text{th}}$ cycle)

XRD Hydride State

- Reversible store ~3 wt.% (400-460°C)
- Found using multi-well shaker
- Surprising finding
- Don’t understand what’s going on yet
- Shows the power of Combi/HTS
Thermal decomposition of Mg(BH₄)₂

Step 1.  Mg(BH₄)₂ → 2 B + MgH₂ + 3 H₂ (11.2 wt % H₂)
Step 2.  MgH₂ ↔ Mg + H₂ (3.7 wt % H₂)

- Partial recharging possibly produced MgH₂ but with much lower T_{des}
- T_{des} decreased with Zn and Ti doping
- Mg(BH₄)₂ prepared in gram quantities – dopant & catalyst screening ongoing
Substitution and Catalyst Screening of Mg(BH₄)₂

Catalyst Doping

As chlorides and metals.

Substitution Concepts

Promising concept to form metal boride alloys.

Also with addition of other hydrides

Over 100 combinations of single, binary and ternary compositions screened...no reversibility demonstrated for the first step.
Catalyst Screening for Mg(BH₄)₂

Hydrogen desorption from catalyzed Mg(BH₄)₂

- Catalysts decrease the decomposition temperature by 50 – 70 °C and improve hydrogen desorption kinetics
- Found using 6-pack unit
Metal hydrides against DOE targets

**DOE 2010 Goal**

**DOE 2015 Goal**

Assume 1/3 for balance of plant

Borohydrides

(not yet fully reversible)

Aluminides & silicides

Amides & imides

Assume 1/3 for balance of plant

Mg(BH$_4$)$_2$

2LiBH$_4$ + MgH$_2$

Li$_6$Mg(NH)$_4$

MgH$_2$ + 2LiNH$_2$

MgH$_2$ + Al

Mg$_2$NiH$_4$

AlH$_3$ + Si

LaNi$_5$H$_6$

LiAlH$_4$

NaAlH$_4$

LiNH$_2$

MgH$_2$

LiAlSiH
HTS Challenges

• High sensitivity to O₂ and moisture
• High reactivity of metals – materials corrosion
• Low spatial resolution
• Combining high temperature and high pressure
• Parallel wet synthesis/desolvation
• Catalyst/dopant introduction in metal hydride phase
• Quantification of adsorbed/desorbed H₂ at small scale
• Scale up of HTS findings

New methods for parallel wet synthesis of complex hydrides and analysis of their hydrogen storage characteristics needed
Summary

• Developed effective HTS methodologies
• Down-selected parallel ball milling and thermal imaging
• Successfully scaled materials and validated methodology
• Screened the aluminide and silicide compositional space
  – Low weight percent
  – Disproportionate
• Found low temperature Al$_{12}$Mg$_{17}$, with improved kinetics compared to MgH$_2$
• Discovered reversible AlH$_3$ + Si system
• Lowered the decomposition temperature of Mg(BH$_4$)$_2$ with some catalysts