Lightweight Intermetallics for Hydrogen Storage

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GE Global Research
Niskayuna, NY

– A Member of the DOE Metal Hydride Center of Excellence –

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GE Program Overview

Timeline
- Project start date: FY05
- Project end date: FY09
- Percent complete: New Project

Budget
- Expected Total Project Funding:
  - Phase I - 3 years: $2.00M
    - DOE Share: $1.60M
    - GE Share: $0.40M
  - Phase II - 2 years: $1.47M
    - DOE Share: $1.18M
    - GE Share: $0.29M
- Funding for FY05: $450K (DOE), $112K (GE)

Barriers
- Right heat of formation
- Absorption / desorption kinetics
- Hydrogen capacity and reversibility

Targets
- Gravimetric capacity: > 6%
- Volumetric capacity: > 0.045 kg H₂/L
- Min/max desorption temp: -30 / 85°C

Partners
- Member of DOE MHCoE
- Collaborations with MHCoE partners on modeling and characterization
- Member of the Coordinating Council of DOE MHCoE
Discover and develop a high capacity (> 6 wt.%) lightweight hydride that is practical and inexpensive for reversible vehicular hydrogen storage and delivery systems, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

FY05 Goals

• Develop a high-efficiency combinatorial synthesis and high-throughput screening methodology for metal hydride discovery
• Identify hydrides from combinatorial samples and validate them through gram-quantity sample tests
GE Approach

Materials Discovery Acceleration: Design for Six Sigma coupled with...

- Materials Expertise: Development & Processing
- High Throughput Screening (HTS): Composition Design Space
- Characterization: Composition, Microstructure & Performance
- System Performance: Characterization & Predictive Modeling
- Focused multi-disciplinary team
GE Metal Hydride Discovery Process

System Requirements
Thermodynamics
Reaction Path
Diffusion
Safety

Modeling

Concepts
Combi & HTS

Synthesis & Characterization
New Hydrideds

DOE 2015 Goal
DOE 2010 Goal

Reversible storage capacity (wt % H₂)

Temperature (°C)

MgH₂
Mg₂NiH₄
LiBH₄+MgH₂

MgH₂+2LiNH₂

(assume 50% debit for system)

Ge Program
Objective

LaNi₅

Limit of demonstrated reversibility

NaAlH₄

LiNH₂ (potential)

MgH₂ (potential)
GE Lightweight Intermetallics Approach

• **Focus:**
  Lightweight aluminides & silicides of Li, Mg, and Na (potential to 6 wt.%)

• **Opportunity:**
  Many intermetallic compounds exist in aluminide and silicide systems

• **Develop & Validate:**
  Combinatorial synthesis and high-throughput screening methodologies for hydride discovery in the target temperature – pressure – kinetics design space
Aluminides and Silicides

Aluminides

• Space to be screened: Al-Li, Al-Li-Si, Al-Li-Mg, Al-Ga, Al-Li-Cu, Al-Li-Mn, Al-Mg-Zn, Al-Mg-Cu, Al-Li-Ge, Al-Li-Si, …

• Al and Si are lightweight, high availability & low cost
• Many compounds known to exist but not evaluated for H₂ storage
• Minimal risk of forming volatile hydrides (e.g., BH₃, NH₃)

Silicides

• Space to be screened: Li-Si, Li-Mg-Si, Mg-Si, Na-Si, Li-Na-Si, Na-Al-Si, Li-Na-Al-Si Li-Na-Si, …
Diffusion Multiples & Alloy Development

Synthesize many compounds simultaneously
Identify, synthesize & test leads

Combinatorial Synthesis & HTS

• Slice & polish
• 1st-level characterization

React @ desired T and atmosphere

Charge with D₂

Effective combi synthesis methods developed

Screening with thermography

Screening with time-of-flight secondary ion mass spectroscopy

Effective combi synthesis methods developed
Combinatorial Synthesis & HTS: Results

Thin-film methods

Synthesis
- Complementary to diffusion multiple
- Great for exploring Mg, Al, Si alloys
- Map phase diagram at 6% intervals, 3 runs, 5hrs.
- 7 target co-sputtering, DC and RF power

Screening
- Optical reactor capability, 350 °C, 55 atm.

Screen for H₂ storage with thermography

Thermography is an effective screening tool
In-Situ XRD: Results

Literature:
LiAlSi + 0.45 H₂ ⇌ LiAlSiH₀.₉ 535°C, 80-82 bar

New result: 300-380°C, < 135 bar
AlLi + Li₁₂Si₇ + Al + H₂ ⇌ LiAlSiH₀.₉ + LiH + (Al)

Charging kinetics are very fast

LiAlSiH₀.₉

LiAl

LiAl (Al)
Decomposition without intermediates at 380 °C
LiAlSiH₀.₉ + Si + Al

Hydrogenation via intermediates at 300 °C
LiAl + Li₁₂Si₇ + Al

First intermetallic hydride in non-transition metal alloys
GE Lightweight Intermetallics Progress

1. Designed new diffusion multiple configuration and tested for alkali metals

2. Demonstrated the screening capability of thermography and ToF-SIMS

3. Studied/screened several compounds in the Li-Al-Si ternary system
   – *This system has the first reversible intermetallic hydride in non-transition metal alloys*
Future Work

Remainder of FY ’05:

• Team with modeling partners to identify promising concepts/systems
• Continue to make combi samples & screen the aluminides and silicides composition space
• Synthesize lab quantities of compounds identified from combi screening to validate the methodology

FY ’06:

• Continue with the hydride discovery task (Task 1)
• Begin Task 2: materials synthesis
• Prepare Task 3: system-level materials evaluation models and setup
GE Lightweight Intermetallics for Hydrogen Storage: Plan

<table>
<thead>
<tr>
<th>TASK</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
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</thead>
<tbody>
<tr>
<td><strong>Task 1: Materials discovery</strong></td>
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<td>Go/No-Go</td>
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<tr>
<td>Identify candidate intermetallics</td>
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<td>Go/No-Go</td>
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<tr>
<td>Make diffusion multiples</td>
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<td>Go/No-Go</td>
<td>Combi methodology validation</td>
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<td>Conduct initial screening</td>
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<td>Go/No-Go</td>
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<td>Hydrides &gt; 6.0 wt.%</td>
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<td>Identify promising compounds</td>
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<td>Go/No-Go</td>
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<tr>
<td><strong>Task 2: Materials synthesis</strong></td>
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<td>Go/No-Go</td>
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<td>Synthesize lab-scale quantities</td>
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<td>Go/No-Go</td>
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<td>Gram-quantity &gt; 6.0 wt.%</td>
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<td>Fully characterize the compounds</td>
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<td><strong>Task 3: System-level evaluation</strong></td>
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<td>Go/No-Go</td>
<td>Materials meeting DOE2010 targets</td>
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<td>Test operational performance</td>
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<td>Develop constitutive models</td>
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<td>Identify preferred system</td>
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<td><strong>Task 4: System-level evaluation</strong></td>
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<td>Scaleup materials process</td>
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<td>Evaluate product</td>
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Go/No-Go decisions are marked with orange dots.