Low-cost Magnetocaloric Materials Discovery

Phase II STTR Project ID PD172

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Overview

Timeline
Phase I Project Start Date: 06/13/2016
Phase II Project Start Date: 07/31/2017
Phase II Project End Date: 07/30/2019

Barriers
H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

Ultimate Target: Energy Required < 6 kWh/kg of LH2 at 300,000kg/day facility.

Budget
Total Project Budget: $1,150,000
• Phase I - $150,000
• Phase II - $1,000,000
• Total DOE Funds Spent*: $450,000
• As of 3/31/18 – late start due to delay in funds

Partners
UCSD – Project Partner
US DOE – Project sponsor and funding
California Energy Commission – additional business development funding
San Diego Region Energy Innovation Network - Incubator for CleanTech companies
Interactions/collaborations
• Hydrogen Delivery Tech Team
• Other Industrial Partners
Objective:
Develop low cost energy efficient magnetic refrigeration technology for hydrogen liquefaction.

**Barrier**

- High-Cost and Low Energy Efficiency of Hydrogen Liquefaction
  - Energy required for hydrogen liquefaction at point of production too high.
  - Hydrogen boil-off from cryogenic liquid storage tanks needs to be minimized.

**PNNL Task (PD131)**
Developing magnetocaloric hydrogen liquefaction prototype to establish viability of concept.

**GE&R Task**
Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.

<table>
<thead>
<tr>
<th>DOE Current Targets</th>
<th>FY 2015 Status</th>
<th>FY 2020 Target</th>
<th>Ultimate Target</th>
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<tbody>
<tr>
<td><strong>Small Scale Liquefaction (30,000 kg H2/day)</strong></td>
<td>70 million</td>
<td>70 million</td>
<td>-</td>
</tr>
<tr>
<td>Installed Capital Cost ($)</td>
<td>70 million</td>
<td>70 million</td>
<td>-</td>
</tr>
<tr>
<td>Energy Required (kWh/kg of H2)</td>
<td>15</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td><strong>Large Scale Liquefaction (300,000 kg H2/day)</strong></td>
<td>560 million</td>
<td>560 million</td>
<td>142 million</td>
</tr>
<tr>
<td>Installed Capital Cost ($)</td>
<td>560 million</td>
<td>560 million</td>
<td>142 million</td>
</tr>
<tr>
<td>Energy Required (kWh/kg of H2)</td>
<td>12</td>
<td>11</td>
<td>6</td>
</tr>
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Relevance

Magnetic refrigeration is a promising breakthrough technology to replace conventional compression based systems.

Magnetocaloric Effect (MCE)
The variation in temperature of a magnetic material when exposed to a change in magnetic field.

PROS
- Solid state material – NO HFCs
- Lasts forever
- High Efficiency (H2 liquefaction >50% energy reduction)*

CHALLENGES
- Rare-Earth - $ to $$$$
- Not easy to make - Processing $$$$$
- Limited commercially available materials
- Limited work demonstrating these systems
- MCE material only works at its curie temp, Tc

Approach

Objective: Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.

**Phase I Milestones - Completed**
1.1 Discover low cost high performance MCE materials for sub 50K

**Phase II Milestones – In progress**
2.1 Discover novel MCE materials for >50K temperature applications

2.2 Testing in Magnetic Refrigeration Environment
   a) Characterize $\Delta T$.
   b) Evaluate heat capacity/thermal transport – **Build prototype**

2.3 Optimize material synthesis processing to achieve:
   a) High performance – need $\Delta T$ equivalent or better than Gd
   b) Low cost – Target selling price of $5,000/kg
   c) High stability form - spheres or thin plates

2.4 Commercially Available MCE Products on [www.geandr.com](http://www.geandr.com) webstore.

New! Small scale, room temp. Will need additional funding to achieve low temp.
Lots of work on MCE Materials in last few decades

- No known commercial magnetic refrigerators yet for >4K applications.

**Traditional Approach to MCE Materials Research**
- Maximize $\Delta S$
  - GdSiGe
  - LaFeSi
- Avoid rare-earth materials due to cost/availability
  - MnFeAs
  - NiMnSn

$\Delta S$ not a good measure of performance for 1st order materials.

**GE&R Approach to MCE Materials**
- Materials with 2nd order only response
  - Maximize $\Delta T$ – high cooling power
  - Mechanically stable
- Use low cost rare-earth (Ce, Nd, Gd)
  - Need high performance to keep cost of Magnetic field reasonable

Performance is too low
Accomplishments and Progress

MCE Materials 9K to 300K

For 9~50K,
-> Nd/Ce based ternary

For 50~325K,
-> Nd/Gd ternary or quaternary

NEW PATENTS FILED
Low cost 2nd order MCE compositions discovered for entire temperature range 9K – 325K
Significant Improvement in Performance with composition optimization.
For further performance improvements - Long high temp anneals typically required

**Challenge:** low melting temperature
- Anneal may not work to improve performance
- New melt furnace installed onsite

**GOAL:** Synthesize alloys on-site and optimize melt step to avoid additional anneal.
Accomplishments and Progress

High Stability Form – Spheres and Thin Plates

Rotating Disk Atomization

- Performed by Arcast Inc
  - Sub mm size spheres
  - Performance maintained (or better)
  - Reasonable cost – several kg for $1k
  - Our material works well
  - Process optimization needed

- Thin Plates – need to develop

Materials Successfully formed into sub mm size spheres
Accomplishments and Progress

Cryogenic/Magnetic System

- The magnetic field can reach up to ~0.37 T.
- The cryogenic chamber can reach down to 20 K.
- The chamber can be moved in and out of magnetic field by mechanical rotation.

Custom built system to characterize $\Delta T$ of MCE materials.

- Measure $\Delta T$ - This is a better indicator of performance
  – not easy to measure
Accomplishments and Progress
Characterizing MCE materials in Refrigeration Environment

$\Delta T$ of Gd

Calculated $\Delta T$ (based on DS curve) $\sim 1.9K$ @ 0.37T

Measured $\Delta T$ $\sim 0.5K$

Measured $\Delta T$ of Gd
Accomplishments and Progress
Characterizing MCE materials in Refrigeration Environment

- Cryogenic chamber temperature: 
  $T = 190 \text{ K}$ (temp of max $\Delta T$)
- Magnetic field: $H = 0.37 \text{ T}$
- La-Fe-Si plate temperature change: $\Delta T = 0.3 \text{ K}$

$\Delta T$ of LaFeSi is lower than Gd, even though $\Delta S$ is nearly triple
Accomplishments and Progress

Small Room Temperature Magnetocaloric Cooler Prototype

In progress. Testing material performance, compatibility, etc.
Reviewer Responses

This project was not reviewed last year.
# A Collaborative Project

<table>
<thead>
<tr>
<th>Partner</th>
<th>Project Role</th>
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<tbody>
<tr>
<td>US DOE</td>
<td>Project sponsor and funding</td>
</tr>
<tr>
<td>University of California, San Diego (UCSD)</td>
<td>Project partner. Subcontractor. Assisting with materials development and optimization.</td>
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<tr>
<td>California Energy Commission (CEC)</td>
<td>Additional funding provided for business development through CALSeed Program. Participation in CleanTech Open business accelerator program.</td>
</tr>
<tr>
<td>San Diego Regional Energy Innovation Network (SDREIN)</td>
<td>Networking incubator for CleanTech companies in San Diego. GE&amp;R officially accepted into program. They provide network / mentor resources.</td>
</tr>
<tr>
<td>Hydrogen Delivery Tech Team</td>
<td>Annual reporting provided to HDTT</td>
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<tr>
<td>Other Industry Partnerships</td>
<td>In Progress - Proprietary</td>
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</table>
For MCE Materials Commercialization:

- MCE Materials - need continued process development and optimization to hit performance targets ($\Delta T \sim 1^\circ C$ in 1T field) to be viable in magnetic refrigeration systems.
- Commercialization – MCE materials market is small. Very few entities are actually working on systems.
  - Need more resources to work on system development – we added small prototype development to our Phase II milestones. Additional resources will be needed to develop commercial systems.

For Hydrogen Liquefaction:

- Both large scale magnetic refrigeration production plants and small scale magnetic refrigeration systems to prevent boil-off at point of use are needed.
- Only two known entities working on systems (Pacific Northwestern National Lab and Japanese National Institute of Material Science). Need industrial effort to move magnetic refrigeration technology forward.
# Proposed Future Work

## Remainder FY2018 and FY2019

<table>
<thead>
<tr>
<th>Phase II Milestones</th>
<th>Description</th>
<th>Percent Complete</th>
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| 1                   | Discover MCE for >50K applications  
- Low cost compositions with 2nd order response to cover 9-300K range have been discovered. We will investigate material doping to improve performance. Additional material set (such as known and public domain alloys of Gd, Dy, Er) may be investigated if needed. | 80% |
| 2                   | Evaluate performance in magnetic refrigeration environment  
- We have a custom built platform to evaluate $\Delta T$ of materials.  
- We are working on a small scale room temperature prototype. Additional funding/ resources will be needed to develop:  
  - LH2 production facility using Magnetic Refrigeration  
  - Zero boil-off magnetic refrigeration system for 1000kg LH2 gas station storage | 50% |
| 3                   | Optimize processing to achieve high performance, low cost, and stability.  
- New furnace installed for on-site alloy synthesis. We will develop melting/cooling conditions to achieve high performance and methods to form material into thin plates.  
Phase II Goal: 1kg available for $5000 | 50% |
| 4                   | Commercially Available MCE Products on [www.geandr.com](http://www.geandr.com) webstore.  
- Webstore is built. Just need to add products. | 50% |

Any proposed future work is subject to change based on funding levels.
Technology Transfer Activities

Additional Funding Received
• CALSeed Grant from the California Energy Commission is supporting business development activities for our Magnetic Refrigeration technologies.

Potential Future Funding
• Applied for ARPA-E funding to develop Zero boil-off LH2 storage system.
• Applied for NASA SBIR Phase I to develop Zero boil-off LH2 storage system.
• We will compete in the CALSeed Phase II pitch competition in Sept 2018 to raise additional funds for prototype development.
• Industrial Funding Sources – In progress.

Patents
• PCT application (US2018/012836) filed for our ternary based compounds.
• New provisional application (US 62/634078) filed on our quaternary compounds.
• New provisional application (US 62/551148) filed to cover zero boil-off LH2 storage system.
Summary Slide

- Novel 2nd order response MCE material set for entire temperature range 9 - 325K discovered with promising potential for high refrigeration performance.
- System to characterize ΔT developed.
- In-house manufacturing capabilities in progress.
- Additional CEC funding obtained for magnetic refrigeration development.
Technical Back-Up Slides