



Composite Materials for Hazard Mitigation of Reactive Metal Hydrides

Project ID# ST013

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Project Overview

- **Timeline**

- Project start date: June 2007
- Project end date: Sept. 2011
- Percent complete: 90%

- **Budget**

- Total project funding
- DOE share: \$2.6M
- Funding received in FY10: \$310
- Funding for FY11: \$475

- **Barriers & targets addressed**

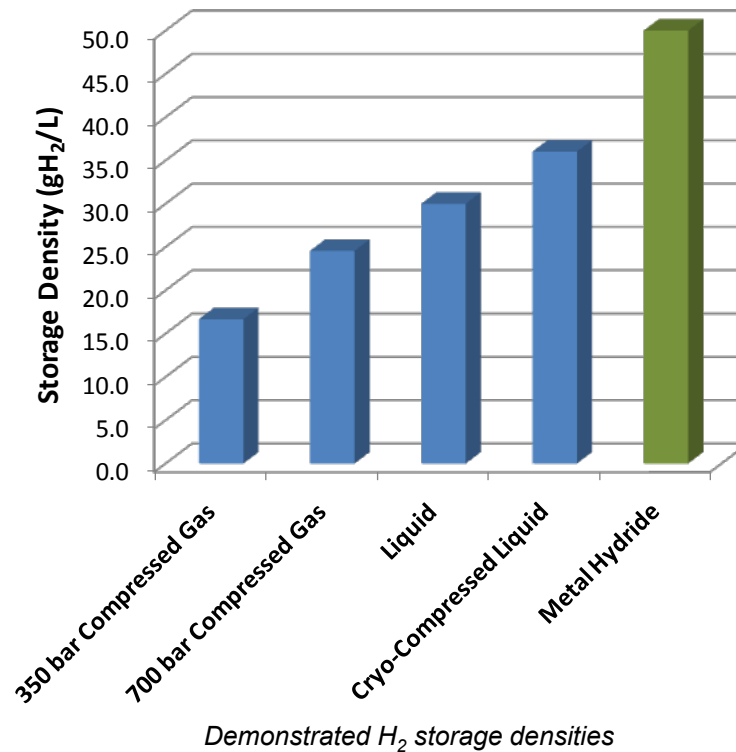
- On-Board Hydrogen Storage
- Durability/Operability (D)
- Codes and Standards (F)
- Reproducibility of Performance (Q)
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- **Partners**

- Collaboration with United Technologies Research Center

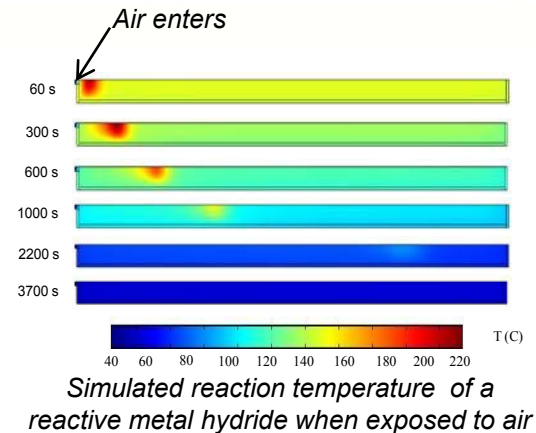
Relevance

- Metal hydrides show promise for compact hydrogen storage, enabling hydrogen usage in diverse applications.



Relevance (continued)

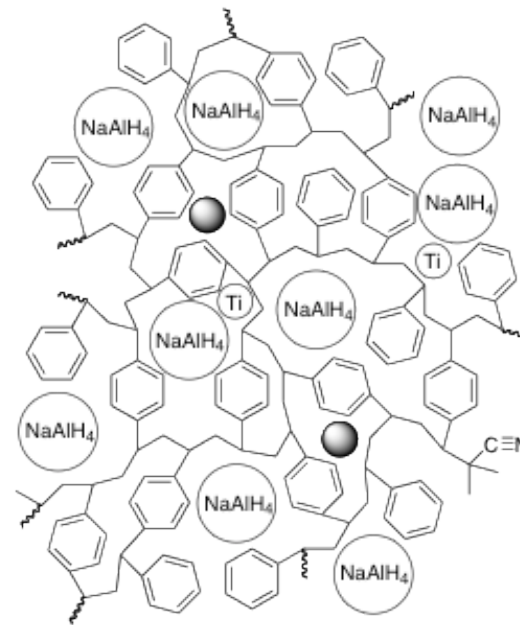
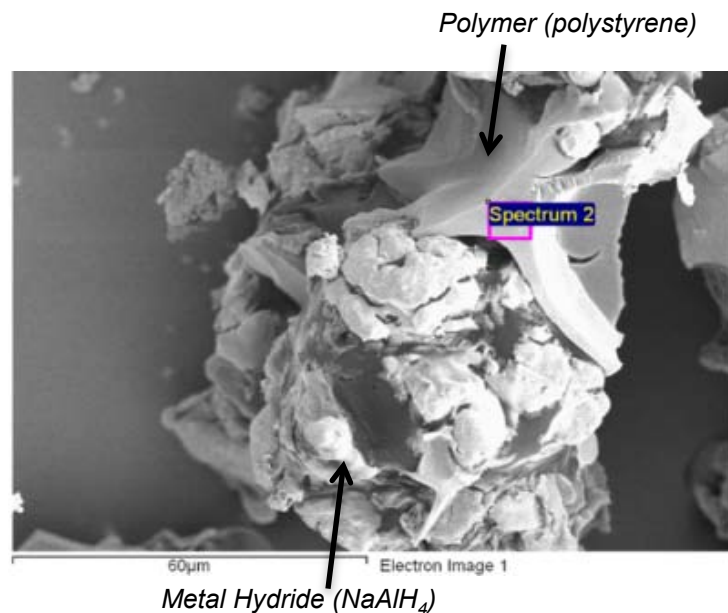
- However some show unfavorable reactivity when exposed to air or water (i.e., in an accident).



- A hazard mitigation strategy would help enable widespread use and commercialization of metal hydrides. Upon a breach in tank, something that:
 - Slows the reaction rate
 - Stops the penetration of oxygen, and/or
 - Absorbs the heat of reaction.

Approach

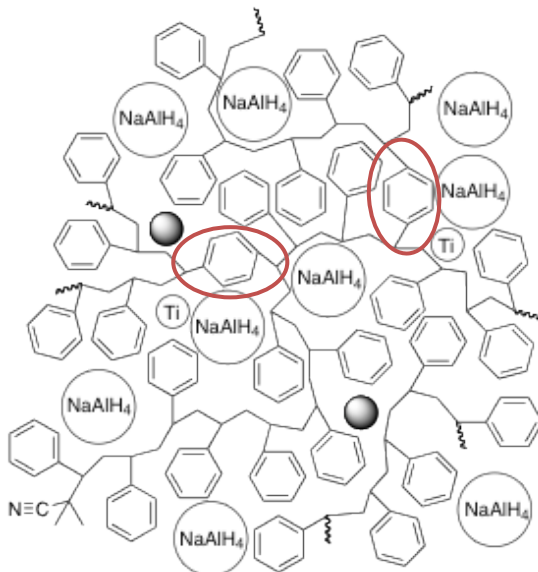
- A composite mixture of the metal hydride with a polymer may have these mitigating features.



→ This methodology is applicable to other metal hydrides with similar reactivity issues.

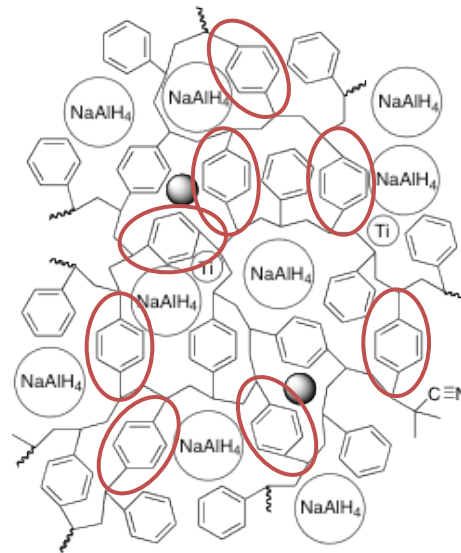
Technical Accomplishments and Progress: Materials Development Task

1. A metal hydride composite with copolymer polystyrene-divinylbenzene (dvb) was successfully synthesized, including differing cross-linking ratios.



High sty:dvb ratio (10:1)

Lower Cross-linking Density
Flexible matrix, tough material
→ holds together



Low sty:dvb ratio (3:4)

Higher Cross-linking Density
Stiff matrix, brittle material
→ easily crushed

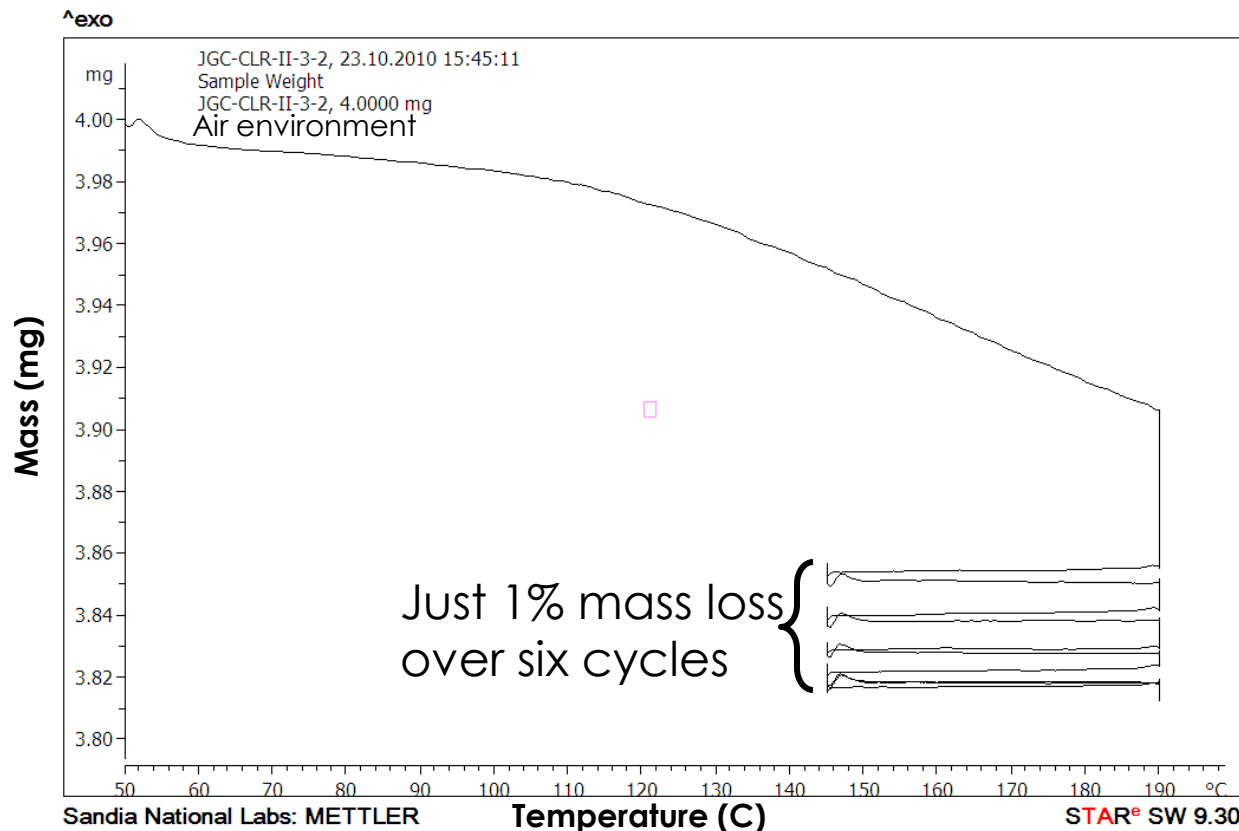
Technical Accomplishments and Progress: Materials Development Task

2. Large-scale synthesis was attempted at the 30 g, 50 g, and 300 g scales (compared to 2 g typical for other tests):
 - NaAlH₄ with 20 wt% copolymer polystyrene-divinylbenzene (ps-dvb) composite.
 - Initial attempts in a steel-reaction vessel gave heterogeneous mixtures.
 - Further attempts to make composite material with mechanical agitation of the mixture were unsuccessful due to incomplete polymerization.
 - Further attempts at large scale synthesis of ps-dvb composite deferred due to subsequent findings showing it is not a suitable material.
 - If future large scale syntheses with a successfully performing composite material (in development) are attempted, a more suitable reaction vessel must be acquired.



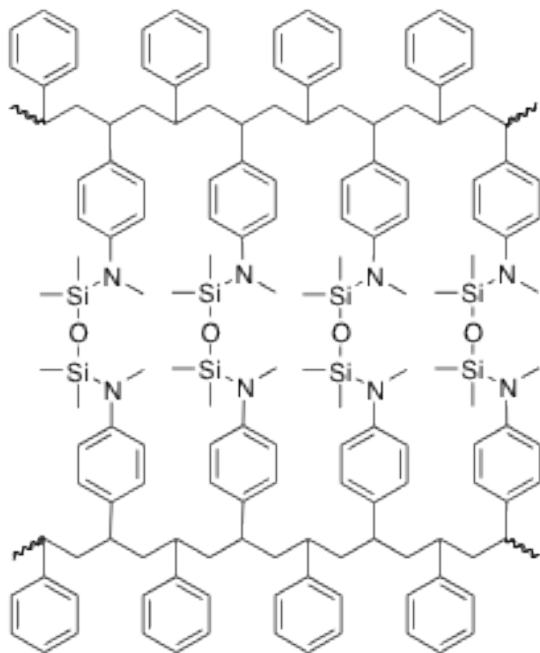
Technical Accomplishments and Progress: Materials Development Task

- The polystyrene backbone was verified to be thermally stable (in air at the same thermal conditions as the H₂ charge/discharge cycling: 30 min. at 145 C and 60 min. at 190 C).

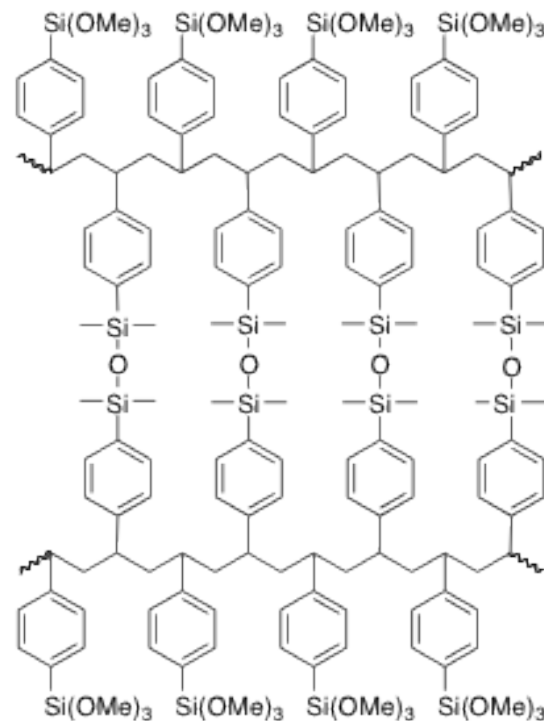


Technical Accomplishments and Progress: Materials Development Task

4. Synthesis routes for other polymer formulations (polystyrene with siloxane crosslinker, with and without siloxane moieties) have been devised.



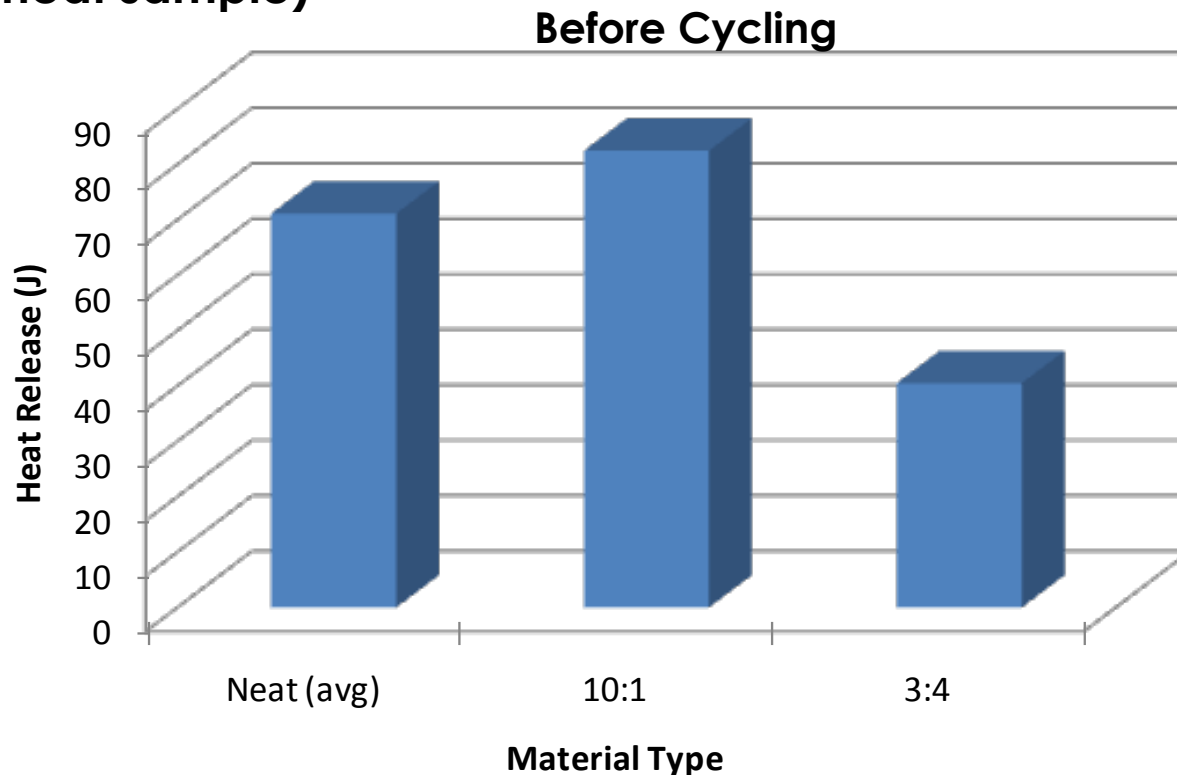
Polystyrene with siloxane crosslinker



Polystyrene with siloxane crosslinker and siloxane moieties

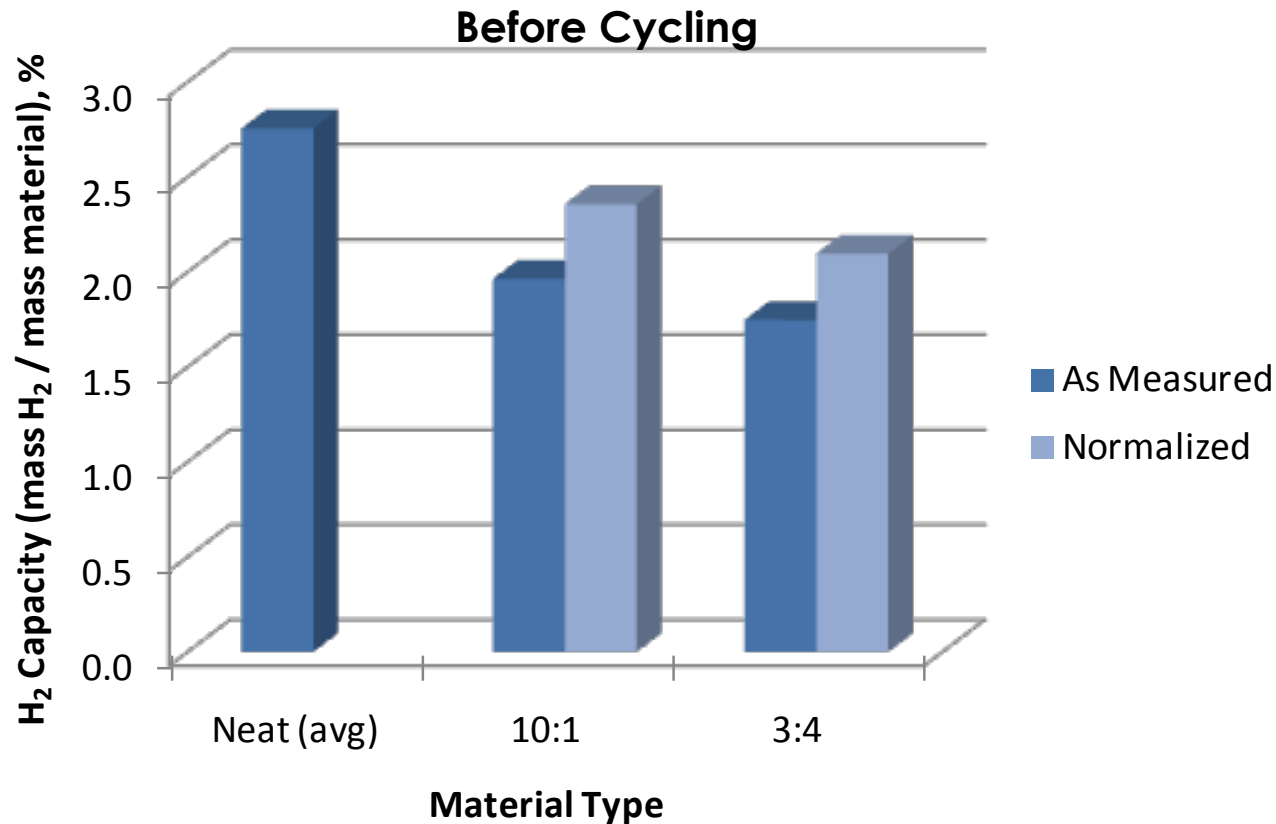
Technical Accomplishments and Progress: Characterization Task

1. Reactivity was measured by the heat released during oxidation flow-through calorimetry. Before cycling:
 - 10:1 (ps:dvb ratio) did not reduce the reactivity (measured increase in heat release attributed to experimental error).
 - 3:4 (ps:dvb) was effective (approx. 60% of heat released by the neat sample)



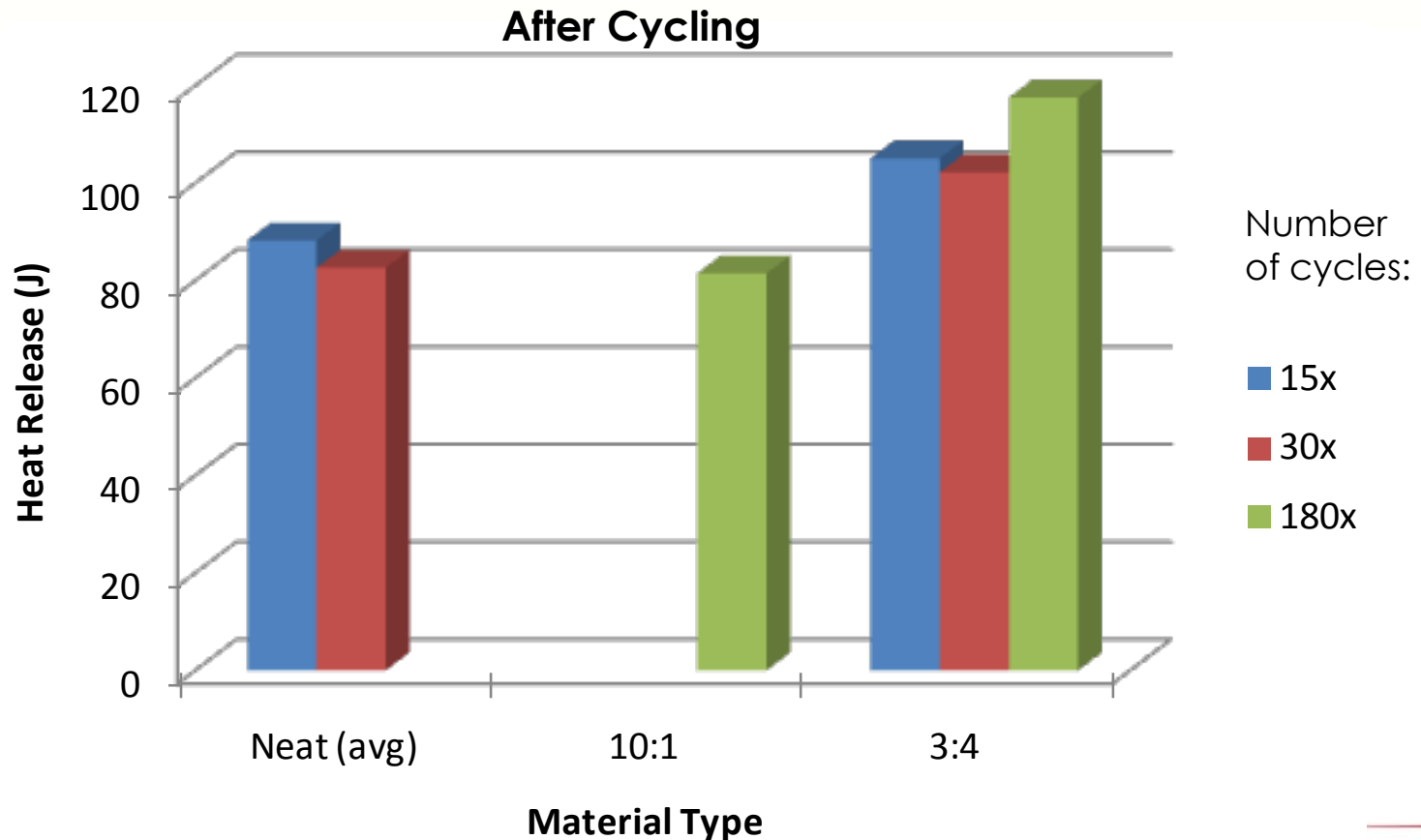
Technical Accomplishments and Progress: Characterization Task

2. The initial hydrogen capacity (before cycling) is decreased by the addition of polystyrene.
 - Decrease in capacity directly related to amount of crosslinking.



Technical Accomplishments and Progress: Characterization Task

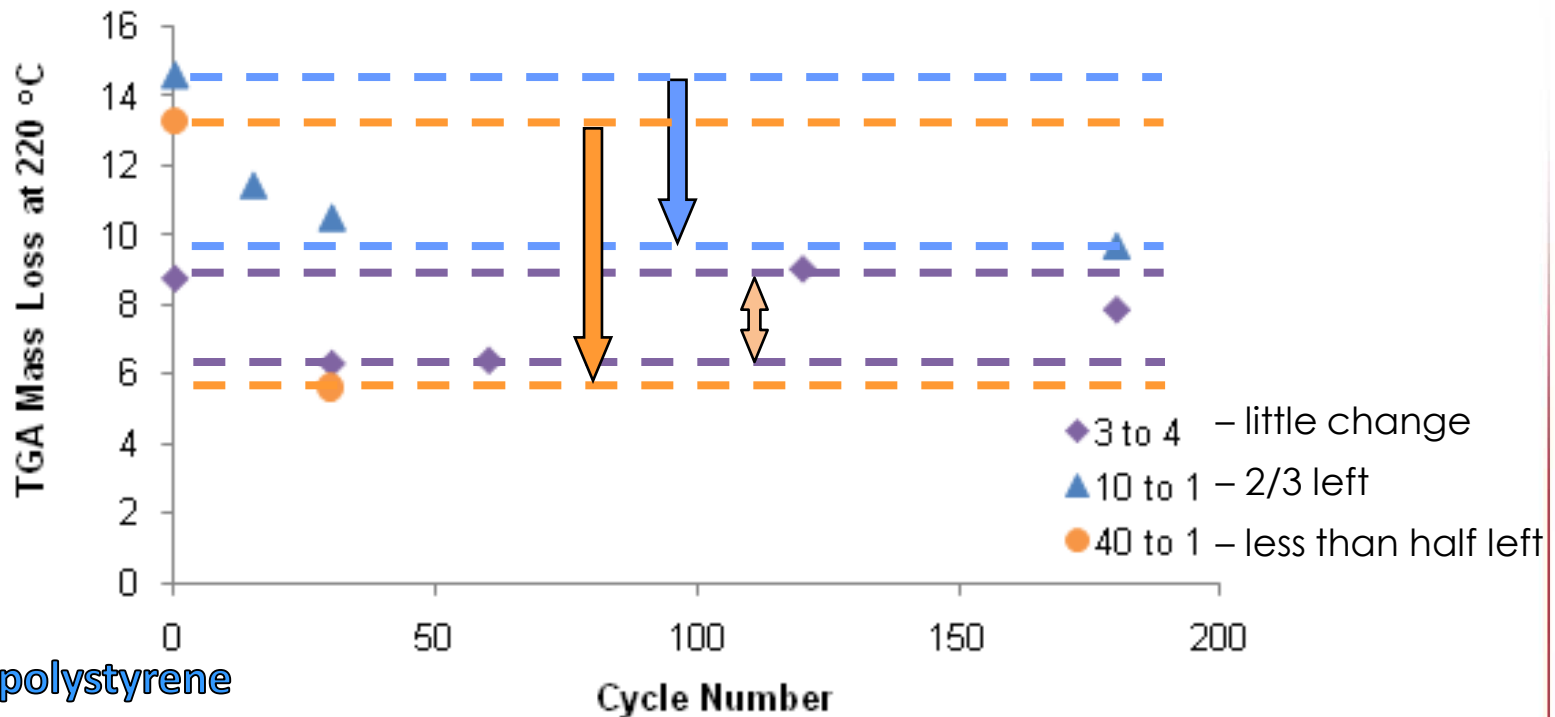
3. After cycling, no mitigating effect of any polymer is observed.
 - Polymer is not stable under actual cycling conditions.



Technical Accomplishments and Progress: Characterization Task

- Mass analysis shows polystyrene was lost during actual cycling, although the more crosslinked material experienced a smaller loss.

MORE polystyrene

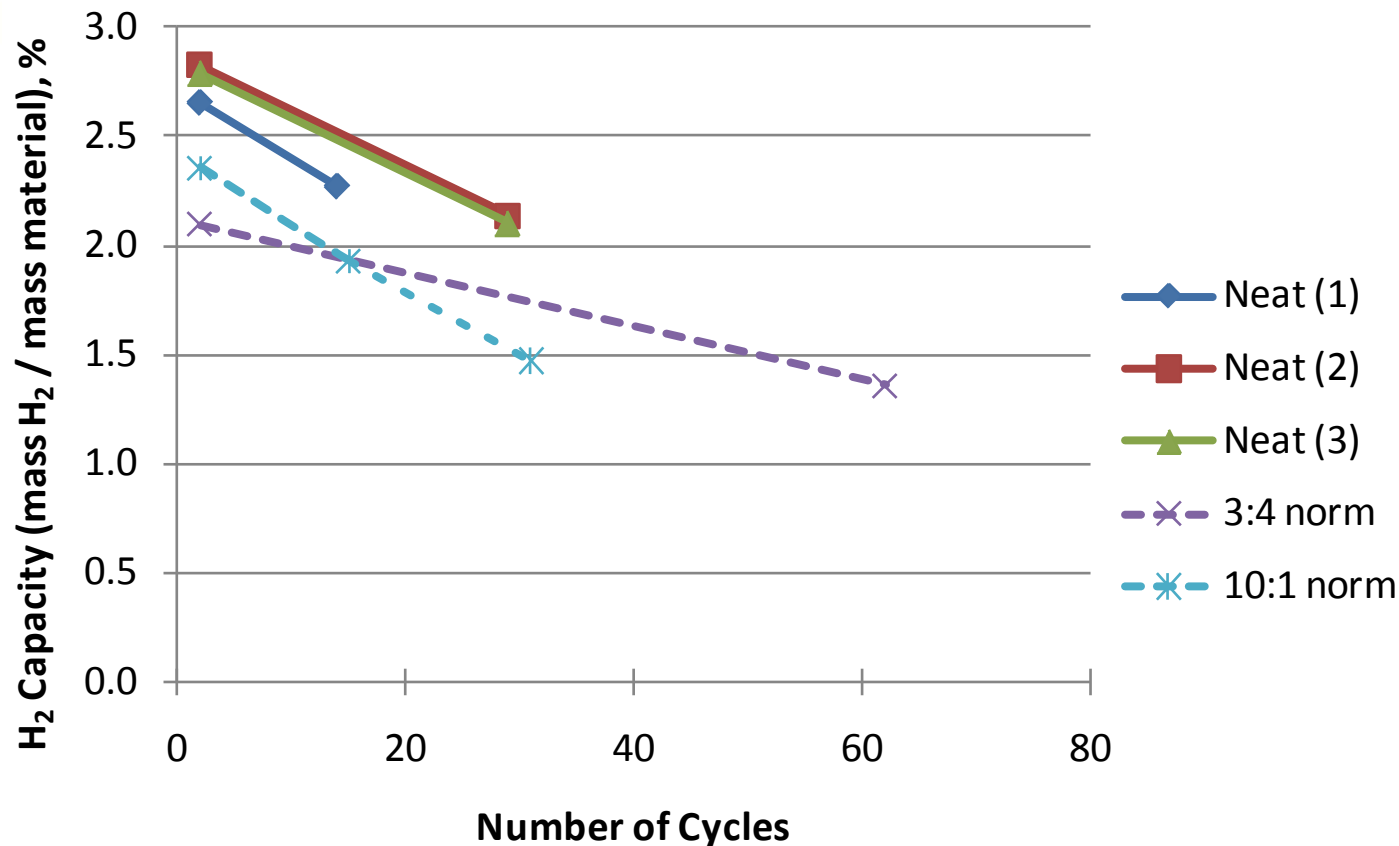


LESS polystyrene



Technical Accomplishments and Progress: Characterization Task

5. Less cross-linked (10:1) polystyrene has less impact on capacity, but is less stable with cycling.



Technical Accomplishments and Progress: Characterization Task

6. Qualitative reactivity demonstration: pellet of material dropped into water at room temperature.



Neat material
(no polystyrene)



Composite material
(with polystyrene)

Collaborative Efforts

- **Collaboration continues with United Technologies Research Center (Y. F. Khalil, PI). One example of tests done at UTRC:**
 - **While UTRC's wafer (unmitigated) ignited with flame on a hot surface at about 81 C, the Sandia (mitigated) sample did not ignite even at temperature of about 172 C.**
 - **Indicates the added polymer (polystyrene) was beneficial in preventing the ignition of the heated sample.**



Findings and Conclusions

- 1. Polystyrene backbone was found to be thermally stable in the same temperature conditions as cycling.**
 - 2. However, it broke down under actual cycling conditions (exhibited by loss of mitigating properties and verified by mass analysis).**
 - 3. The degree of breakdown is inversely related to the amount of crosslinking.**
 - 4. The degree of mitigation is directly related to the amount of crosslinking.**
- The crosslinking properties seem to be the key to finding a better mitigating and more robust composite.**

Future Work

- **The siloxane formulations are expected to have better mitigating properties and show more durability under charge/discharge cycling. The plan forward is to:**
 - **Demonstrate a reliable method to synthesize the polystyrene-siloxane polymer composites.**
 - **Evaluate their effectiveness in reducing heat release.**
 - **Evaluate their stability under cycling conditions.**
 - **Evaluate performance of systems during fire impingement.**

- **Highlights of the two project tasks over the last year:**
 - **Materials Development**
 - Composite mixtures of metal hydride and polymers with different cross-linking ratios have been successfully synthesized.
 - Lessons learned from large scale synthesis attempt will be applied to future attempts.
 - Polystyrene backbone verified to be thermally stable.
 - Synthesis routes for more promising materials have been identified.
 - **Characterization**
 - Crosslinking ratios affect hydrogen capacity and mitigating ability.
 - Polystyrene composite initially mitigated heat release, but was not robust enough to withstand charge/discharge cycling.
- **Collaboration is proving useful in characterization efforts**
- **Current and future work focuses on developing composite materials with better mitigating and stability properties.**



Acknowledgements

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