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Composite Materials for Hazard Mitigation of Reactive Metal Hydrides

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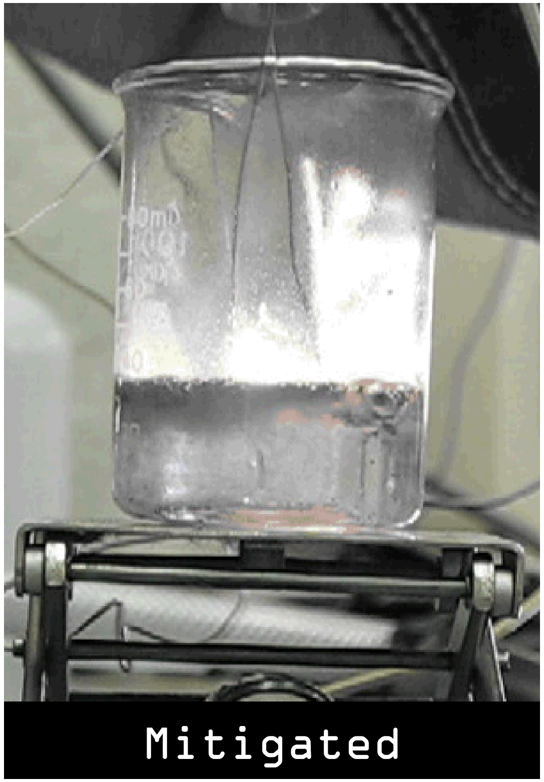
Unmitigated


Mitigated

Sandia has been working on hazard mitigation for several years.

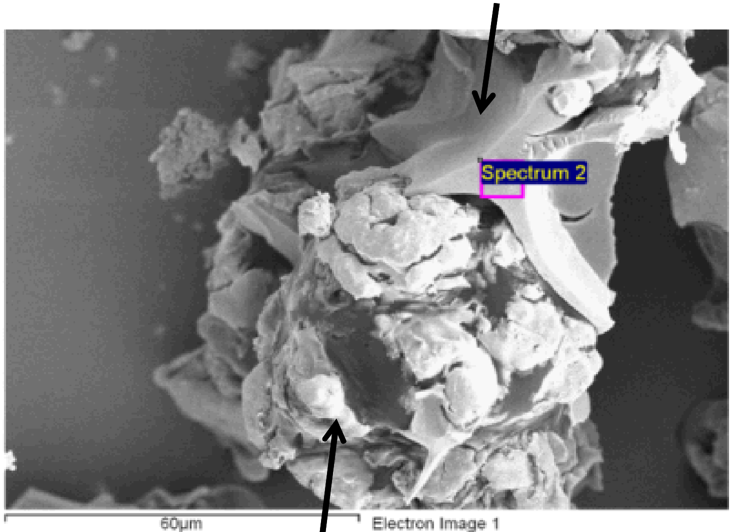
- CO_2 treatment of sodium alanate (SA).
  - Good for disposal but not for normal use.
- Tank liner to encapsulate bulk volume of SA during accident.
  - Liner materials showed too much interaction with the SA.
- Composite mixture of SA with mitigating material.
  - Normal operation until accident, then mitigation.

→ Purpose: Increase safety to enable wide-spread deployment of reactive metal hydride-based hydrogen storage materials.

Outline

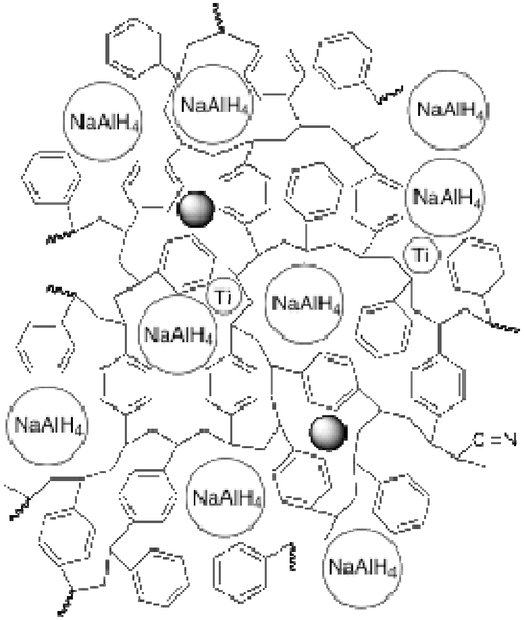
- Materials Development
- Experimental
- Results
- Conclusions

The composite is a mitigating material mixed with the active material.



Polymer (polystyrene)

Metal Hydride ($NaAlH_4$)



The mitigating material should:

- Slow the reaction rate,
- Stop the penetration of oxygen, and/or
- Absorb the heat of reaction.

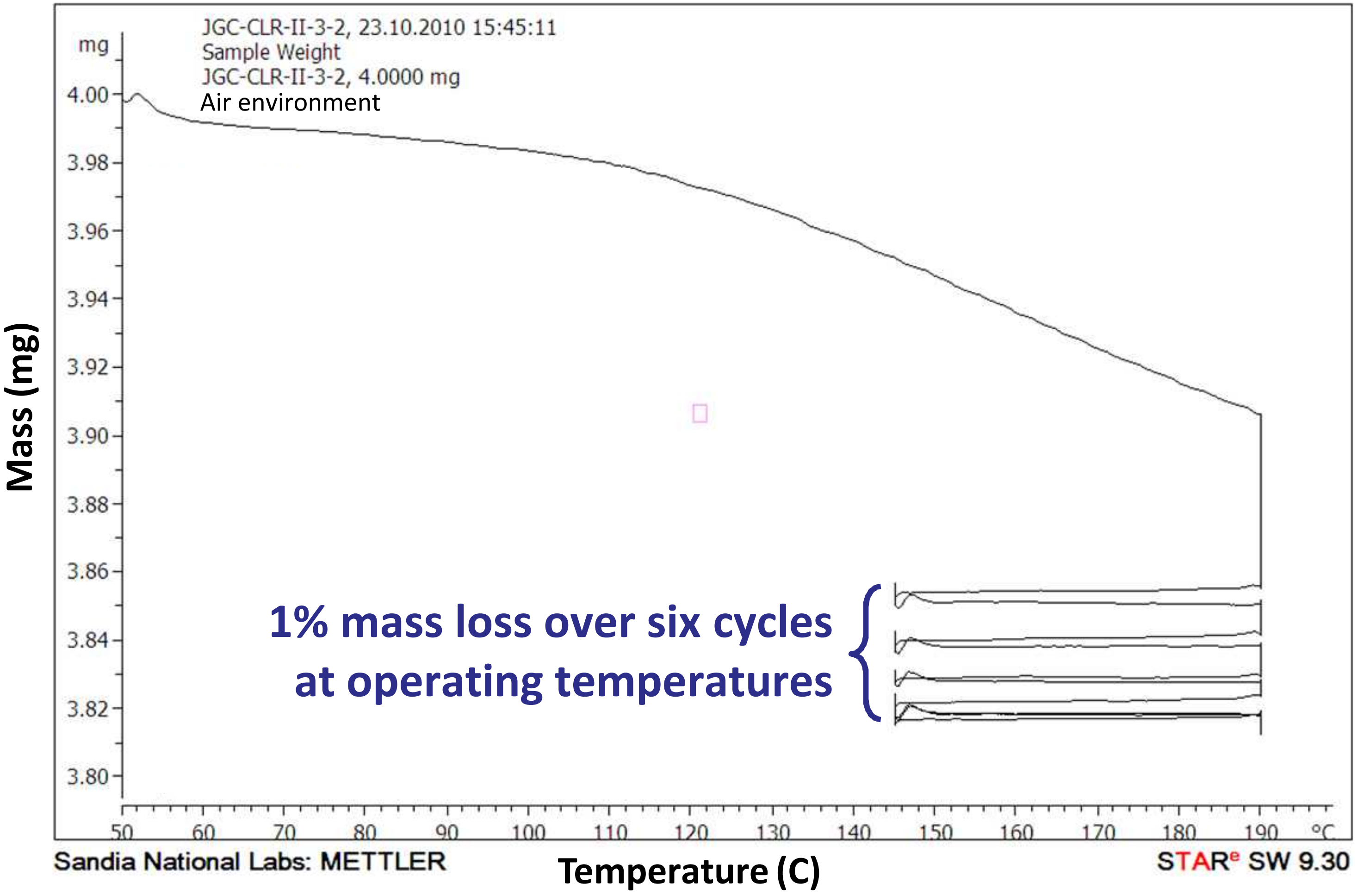
Without affecting the H_2 storage function during normal operation.

Recently we have been searching for mitigating materials that can accomplish this.

- Requirements:
  - Able to form a cross-linked polymer matrix to act as a “scaffold” for the active material.
  - Able to be polymerized in situ with the active material.
  - Able to withstand the operating environment.
  - Has a mitigating feature.

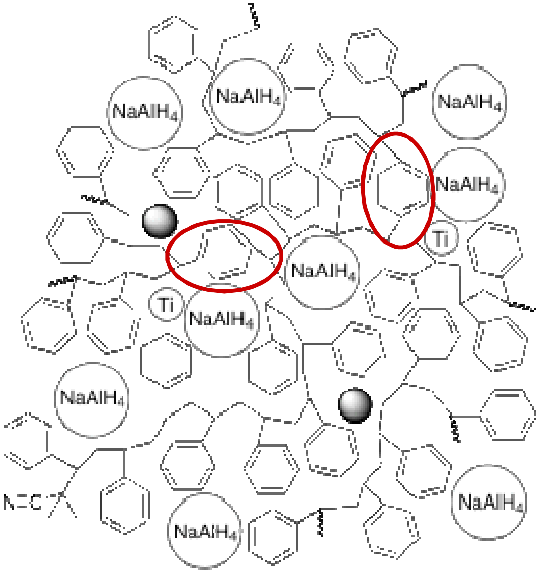
- Candidates:
  - Polystyrene + divinyl benzene (DVB)
  - Siloxane (-R_2SiO-)
  - Polystyrene+DVB -siloxane mixtures

Polystyrene + DVB by itself is thermally stable at temperatures needed for system operation.

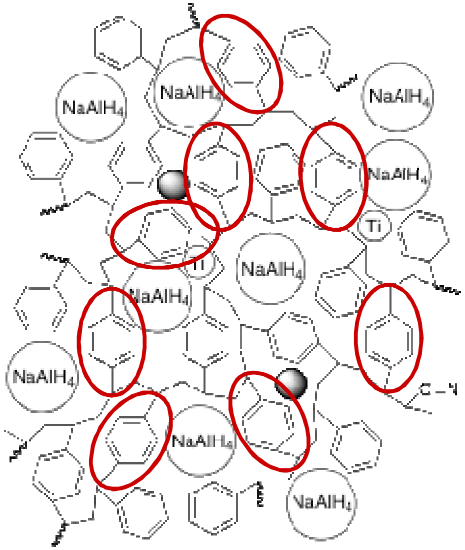


1% mass loss over six cycles at operating temperatures

Different degrees of crosslinking can change the matrix and bulk mechanical properties.



High sty:dvb ratio (10:1)



Low sty:dvb ratio (3:4)

Lower Cross-linking Density

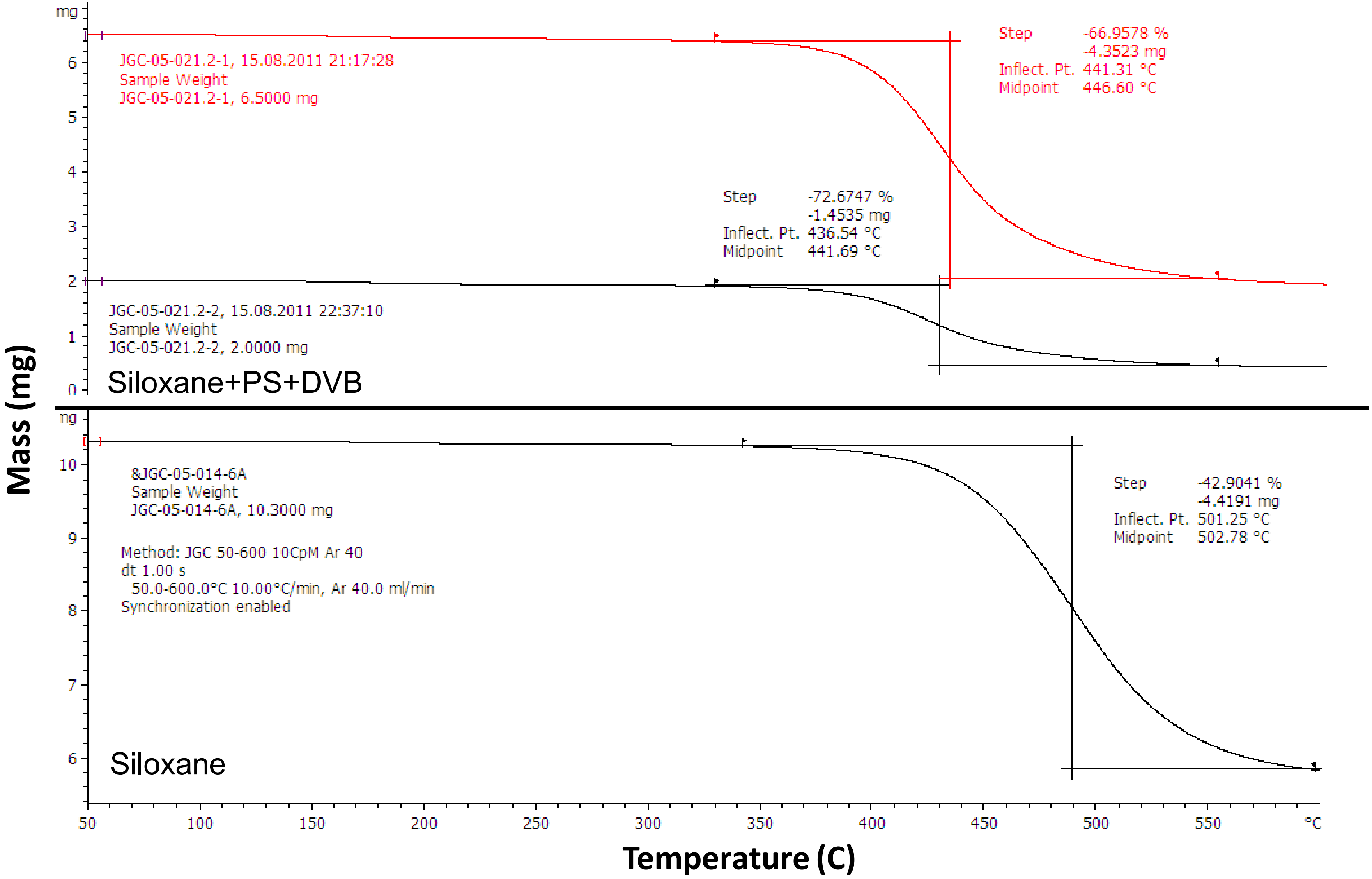
Flexible matrix, tough material
→ *holds together*

Higher Cross-linking Density

Stiff matrix, brittle material
→ *easily crushed*

○ Red circles indicate **styrene cross link** between polystyrene chains

Siloxane materials are also stable, with decomposition starting about 350 C.



JGC-05-021.2-1, 15.08.2011 21:17:28
Sample Weight
JGC-05-021.2-1, 6.5000 mg

Step -66.9578 %
-4.3523 mg
Inflect. Pt. 441.31 °C
Midpoint 446.60 °C

Step -72.6747 %
-1.4535 mg
Inflect. Pt. 436.54 °C
Midpoint 441.69 °C

JGC-05-021.2-2, 15.08.2011 22:37:10
Sample Weight
JGC-05-021.2-2, 2.0000 mg

&JGC-05-014-6A
Sample Weight
JGC-05-014-6A, 10.3000 mg

Method: JGC 50-600 10CpM Ar 40
dt 1.00 s
50.0-600.0°C 10.00°C/min, Ar 40.0 ml/min
Synchronization enabled

Step -42.9041 %
-4.4191 mg
Inflect. Pt. 501.25 °C
Midpoint 502.78 °C

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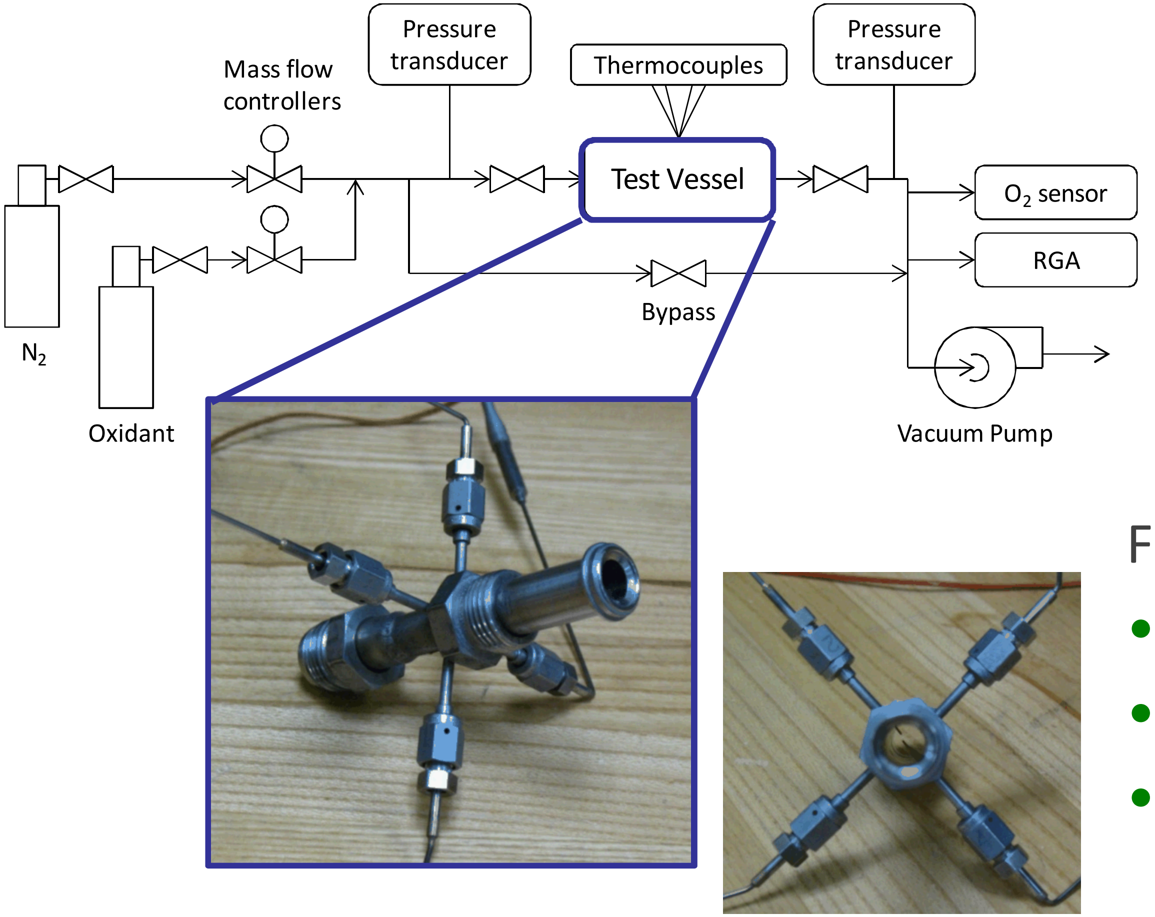
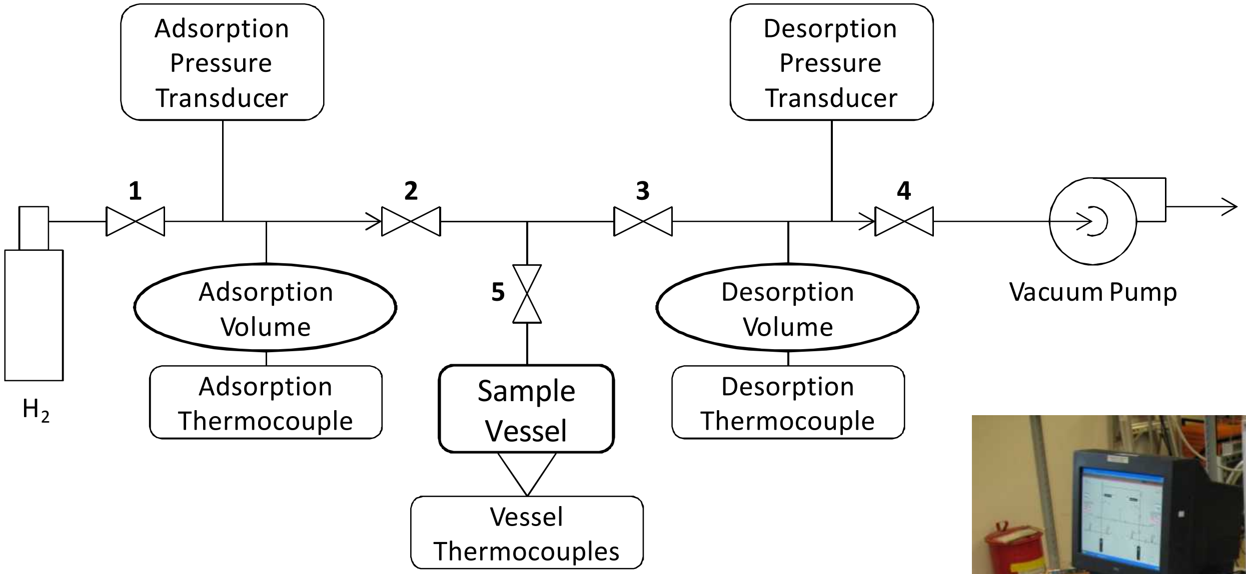
Oxygen is flowed through the sample and the heat released by the reaction determines the mitigating material's effectiveness.



Flow-through Conditions:

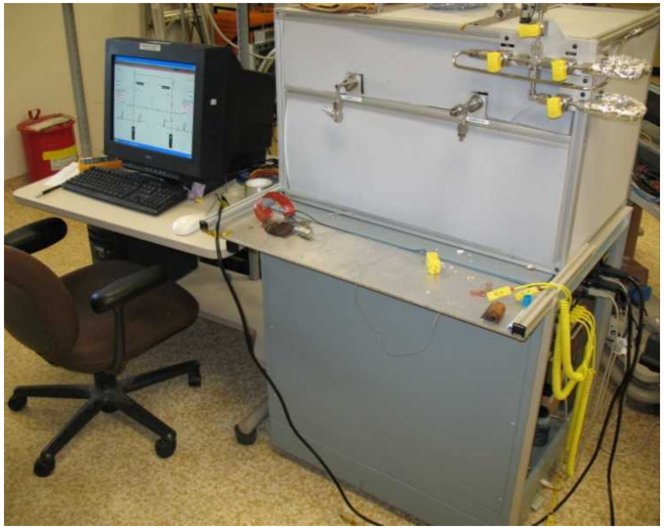
- 24% O_2, 75% N_2, 1% He
- 200 C at start
- 0.1 SLPM

Hydrogen adsorption/desorption cycling at normal operating temperatures tests the capacity and durability of the composite material.



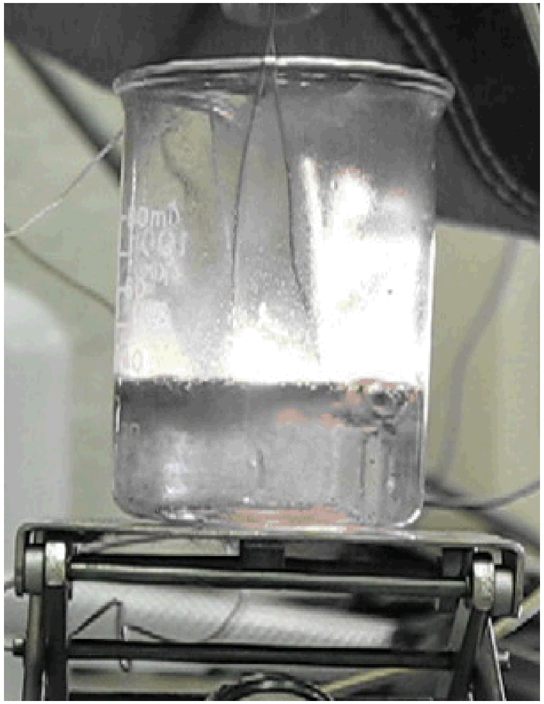
Cycling conditions:

- Adsorption: 30 min at 145 C;
  1900 psia (130 bar) supply pressure.
- Desorption: 60 min at 190 C; to vacuum.
- Number of cycles set by user.



Qualitative experiments visually compare mitigated and unmitigated pellets and powder dropped into water.

Unmitigated powder



Composite powder (polystyrene-DVB mixture)

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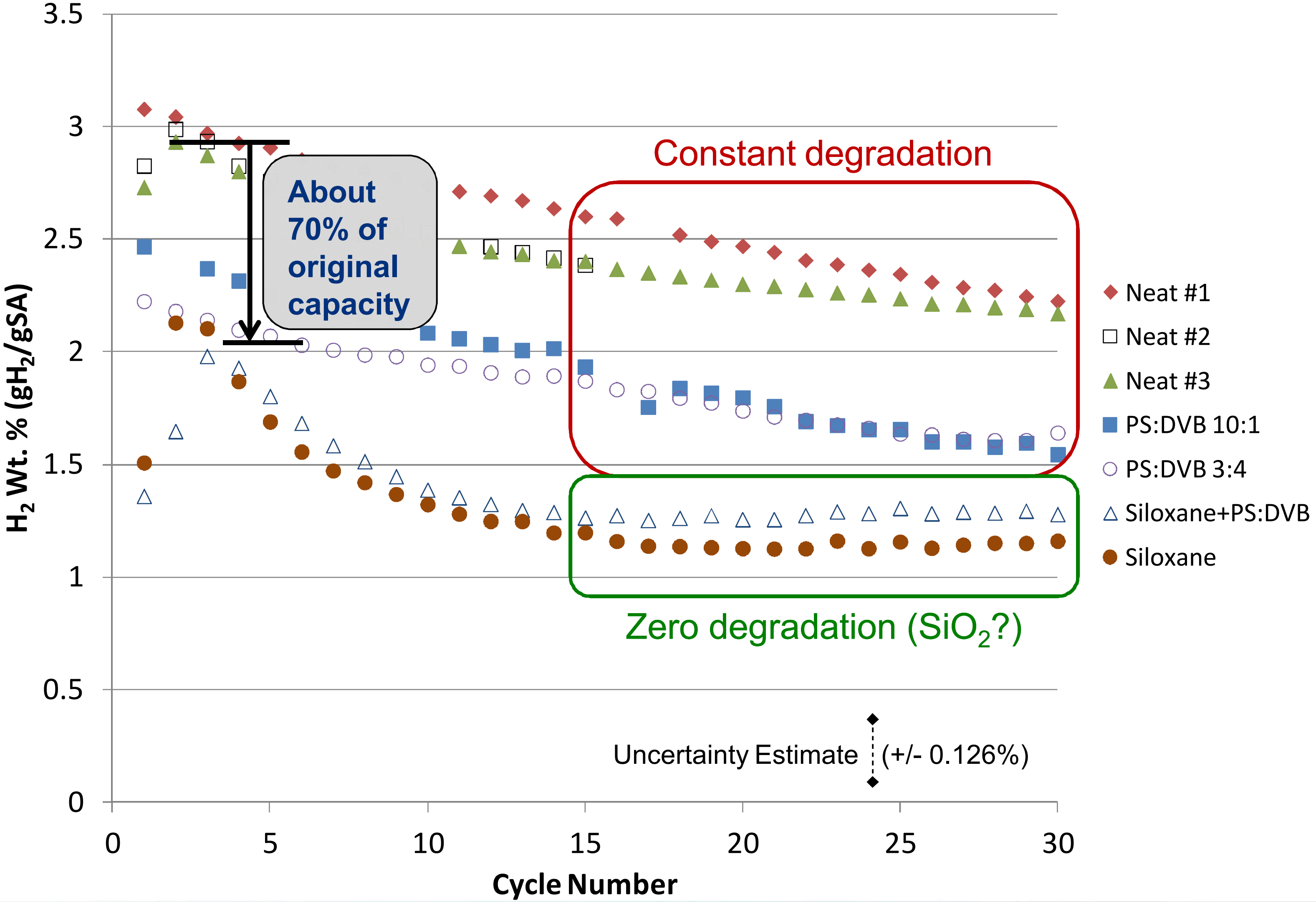
Qualitative experiments visually compare mitigated and unmitigated pellets and powder dropped into water.

Addition of the mitigating material decreases the hydrogen capacity of the metal hydride and effects vary with number of cycles.



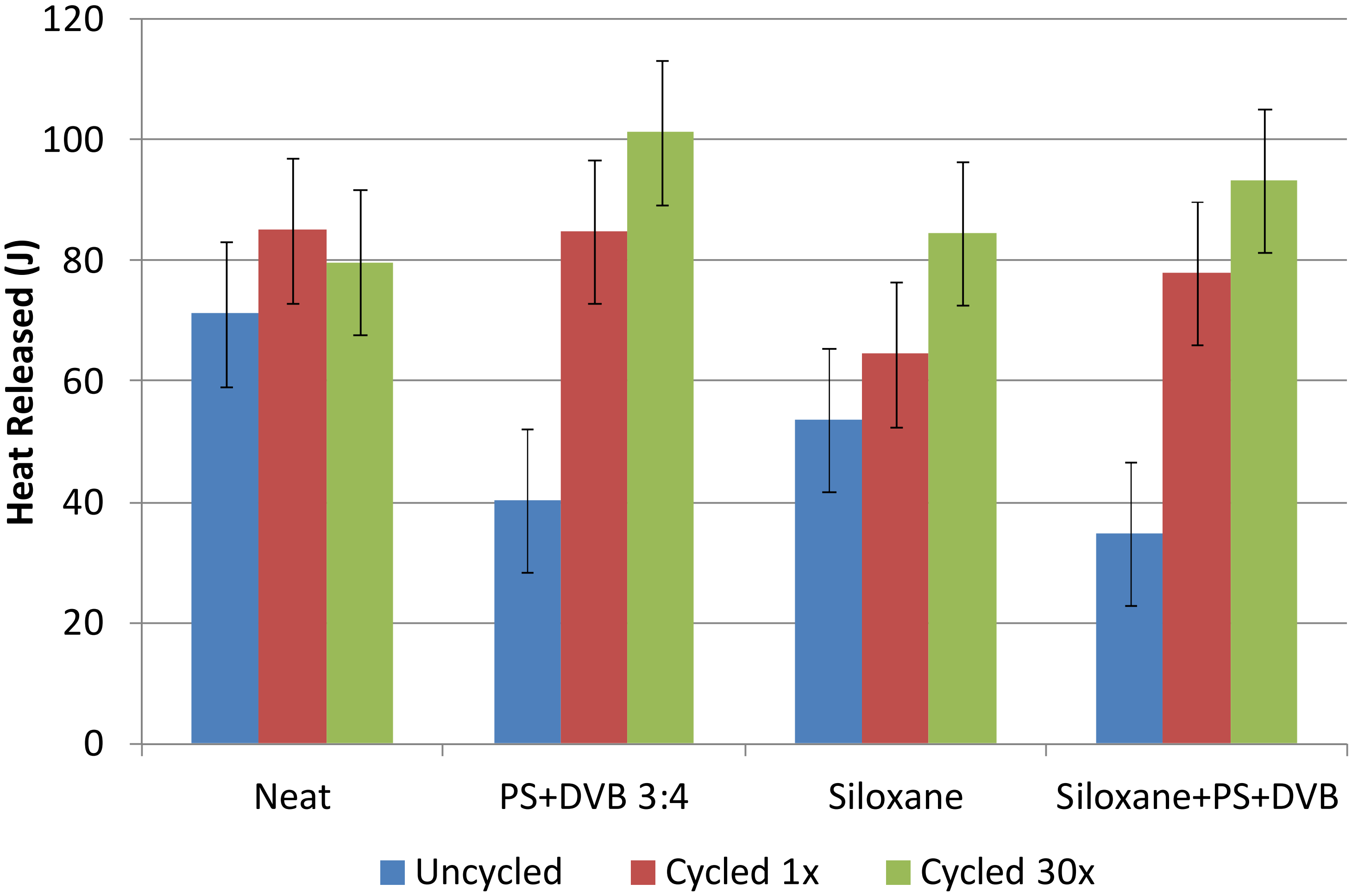
About 70% of original capacity

Constant degradation

Zero degradation (SiO_2?)

Uncertainty Estimate (+/- 0.126%)

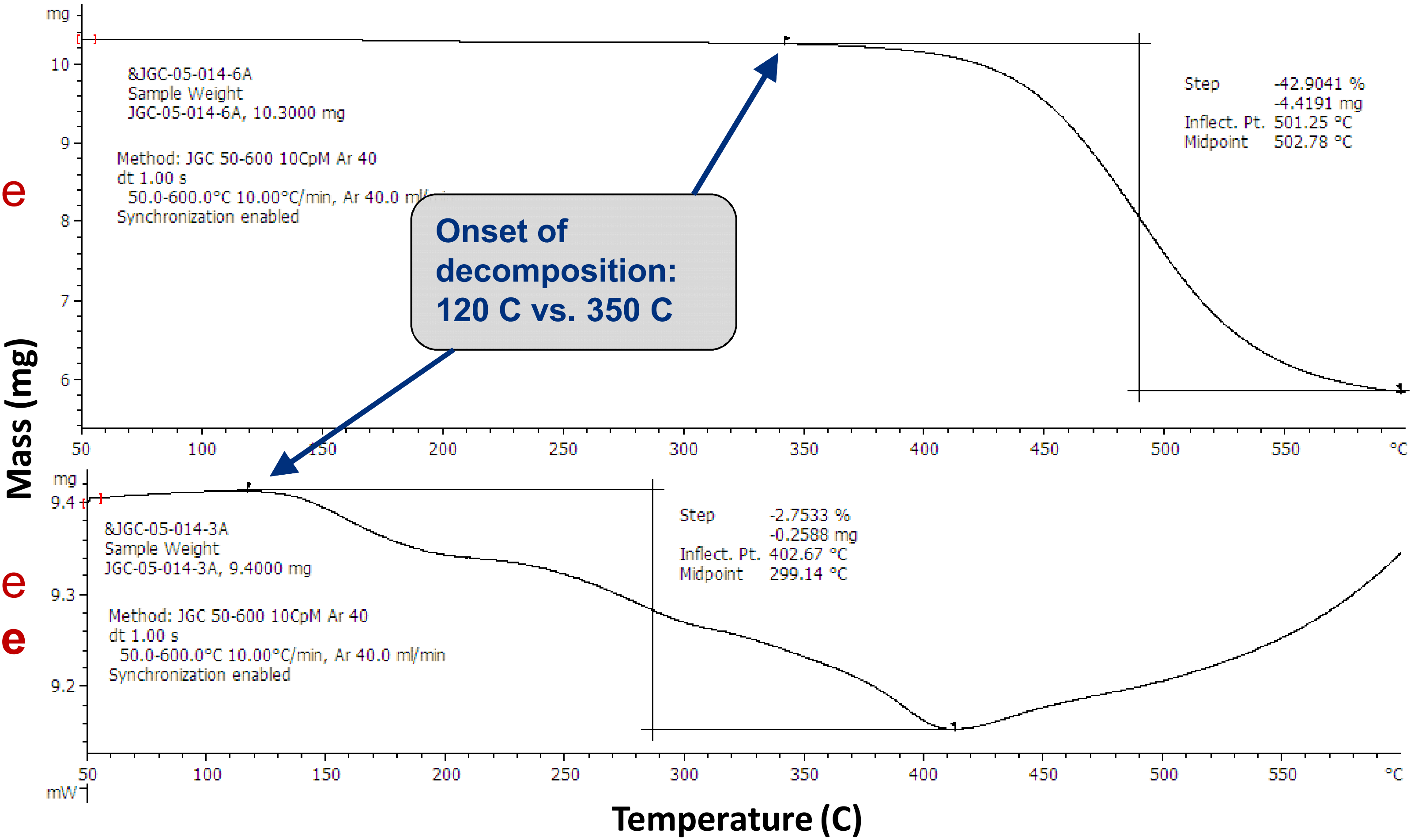
The composites mitigate well initially, reducing heat release to between 49% and 75% of its original amount, but degrade under repeated cycling.



Siloxane decomposes at a lower temperature when mixed with the active material, which must be causing a major chemical change to the polymer network.

Siloxane

Siloxane Composite



Onset of decomposition: 120 C vs. 350 C

&JGC-05-014-6A
Sample Weight
JGC-05-014-6A, 10.3000 mg

Method: JGC 50-600 10CpM Ar 40
dt 1.00 s
50.0-600.0°C 10.00°C/min, Ar 40.0 ml/
Synchronization enabled

Step -42.9041 %
-4.4191 mg
Inflect. Pt. 501.25 °C
Midpoint 502.78 °C

&JGC-05-014-3A
Sample Weight
JGC-05-014-3A, 9.4000 mg

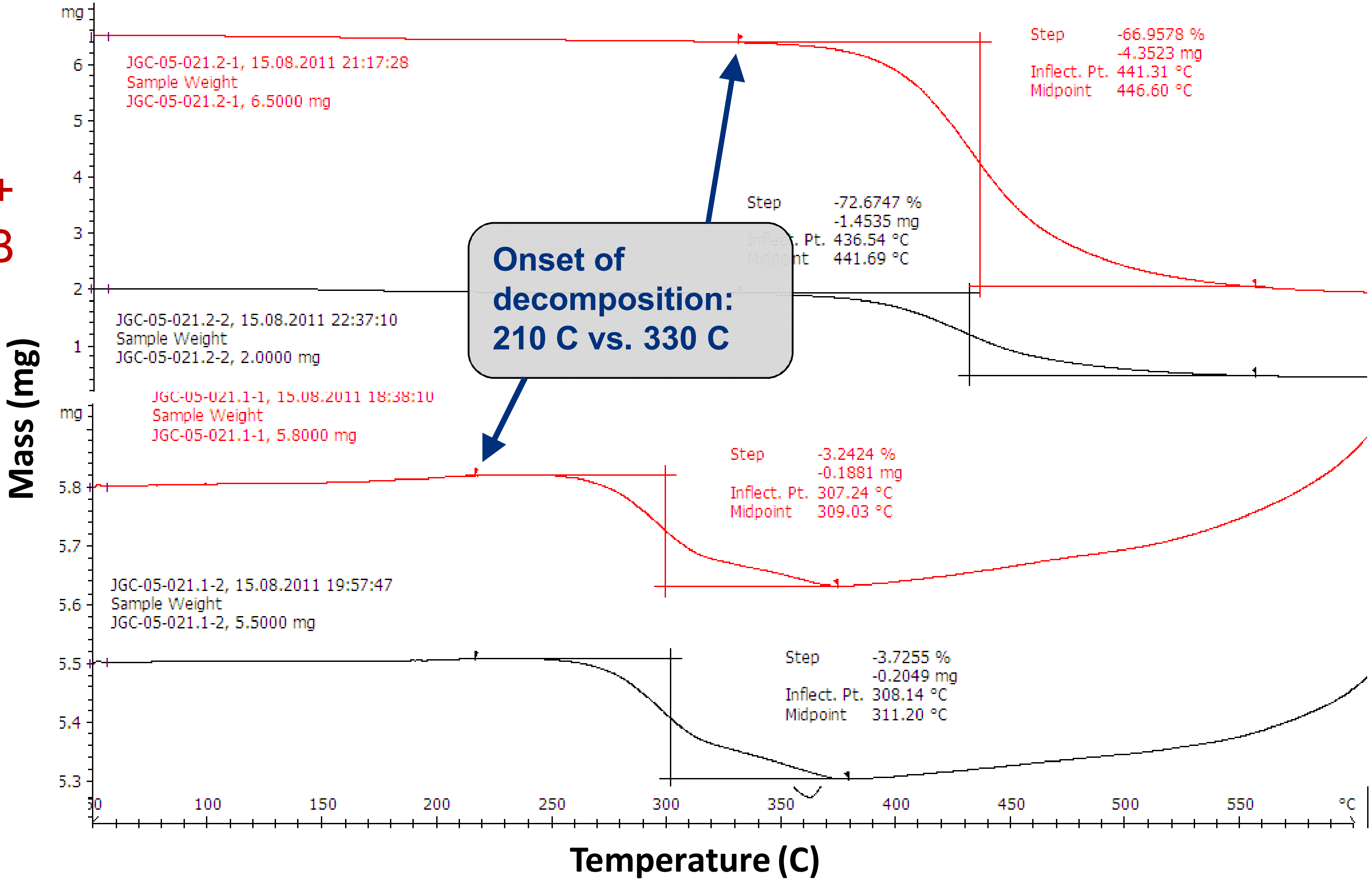
Method: JGC 50-600 10CpM Ar 40
dt 1.00 s
50.0-600.0°C 10.00°C/min, Ar 40.0 ml/min
Synchronization enabled

Step -2.7533 %
-0.2588 mg
Inflect. Pt. 402.67 °C
Midpoint 299.14 °C

The mixed polymer, siloxane with polystrene, shows similar but less-pronounced decomposition differences.

Siloxane+
PS+DVB

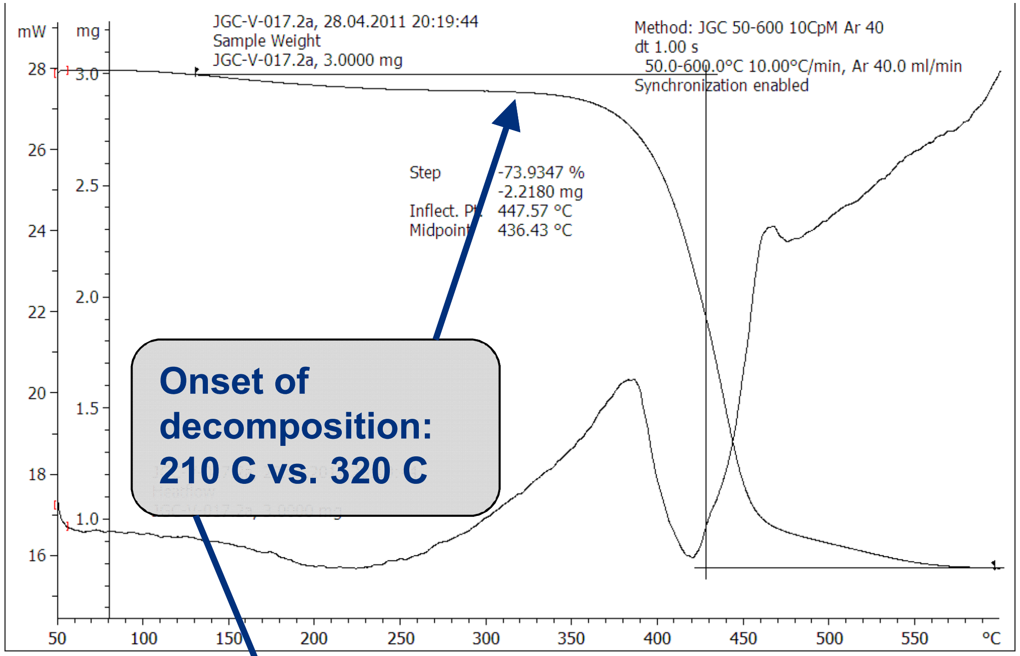
Siloxane+
PS+DVB
Composite



Onset of decomposition: 210 C vs. 330 C

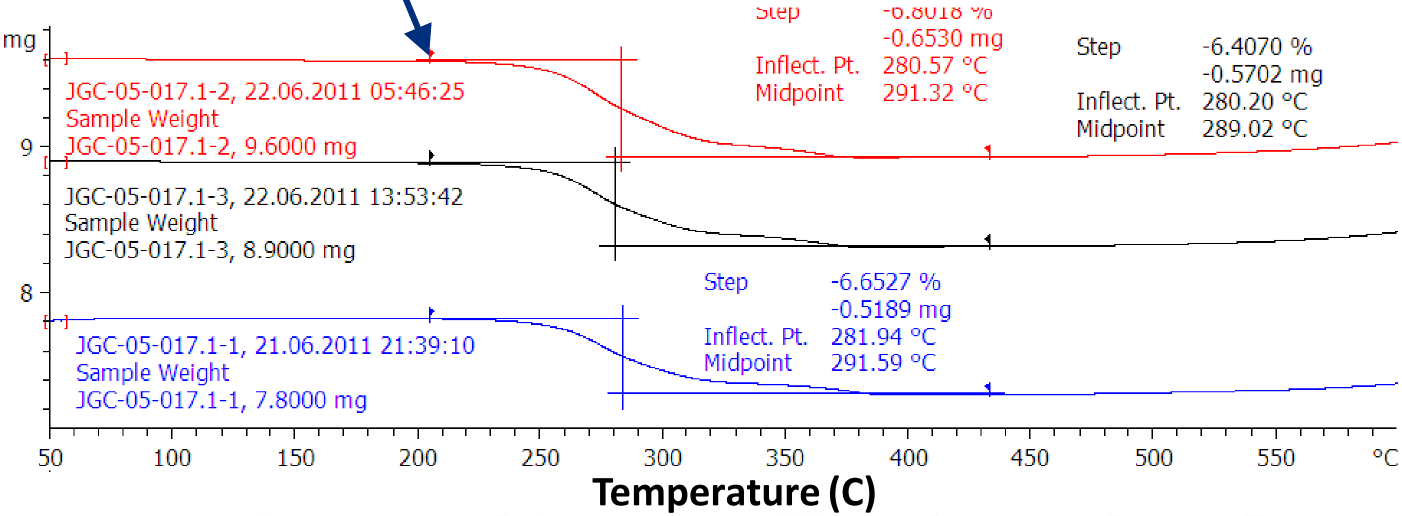
Polystyrene+DVB composite materials begin to decompose at 210 C, also indicating a chemical change.

PS:DVB



Onset of decomposition: 210 C vs. 320 C

PS:DVB **Composite**



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Conclusions

- Addition of the polymer will reduce the hydrogen capacity of the metal hydride to about 70% of its original capacity.
- The composite materials mitigate well initially, reducing heat release to between 49% and 75% of its original amount.
- However, the composite materials are not robust under cycling conditions.
- Although the polymers are stable by themselves, they undergo a major chemical change when mixed with the active material, causing them to decompose at a much lower temperature.

Suggested Future Work

- For mitigation, an approach to new materials that more-emphasizes *robustness* may be an effective strategy.
- The additive's interaction with the metal hydride may have unintended consequences that need quantification:
  - Bad: Possible introduction of contaminants into the H_2 stream as the polymer degrades.
  - Good: Stabilizing effect / reduction of degradation?

Acknowledgements

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Craig Reeder

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