Development of Low-Cost, High Strength Commercial Textile Precursor (PAN-MA)

June 2014
Status as of mid April 2014

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Project Overview

Timeline

• Start   April 2011
• End     December 2014

Budget

• FY 2011: $350K
  ($125k from VT)
• FY 2012: $300K
• FY 2013: $550K
• FY 2014: $0
• DOE Total: $1200K
• FISIPE & SGL Cost Share: $1,277K
• Cost Share: 52%

Barriers

• Barriers addressed
  ➢ High cost of carbon fiber
  ➢ CF largest cost component of high pressure storage tanks.
  ➢ Inadequate supply base for low cost carbon fibers

Partners

• ORNL: carbon fiber conversion, precursor characterization, carbon fiber characterization
• FISIPE: Precursor formulation, precursor spinning
• SGL: Carbon fiber conversion
The CF material represents a significant portion of the overall cost of pressure vessels (60-80%).

There is a strong need for a reduction in the cost of CF.

Precursor is 55% of the cost of the Carbon Fiber.

Target properties: 35-38 MSI Modulus; Strength ~650 - 700 KSI.

Cost Breakdown Of Hydrogen Storage

<table>
<thead>
<tr>
<th>Component</th>
<th>Strength (KSI)</th>
<th>Modulus (MSI)</th>
<th>Estimated Production Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Market Fibers (Aerospace Grade)</td>
<td>700</td>
<td>35-38</td>
<td>$15-20/lb</td>
</tr>
<tr>
<td>Project Target</td>
<td>650-700</td>
<td>35-38</td>
<td>$10-12/lb</td>
</tr>
<tr>
<td>Current Status</td>
<td>592-619</td>
<td>35-39</td>
<td>$10-12/lb</td>
</tr>
</tbody>
</table>
Relevance – Project History

Project built off 2 previous projects funded by Vehicle Technologies.

1st was conducted by Hexcel: Feasibility of using “textile” grade PAN (carpet and sweater fiber) as a precursor. Properties: 20 MSI, 240 KSI.

2nd was conducted by ORNL and FISIPE (Lisbon, Portugal): Develop a textile based precursor for vehicles.

Target Properties: 250 KSI and 25 MSI

Final properties: 540 KSI and 38 MSI
<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 2011</td>
<td>Down select to most promising precursor formulation.</td>
<td>Complete</td>
</tr>
<tr>
<td>August 2011</td>
<td>Conduct first chemical pretreatment trials.</td>
<td>Determined not Needed</td>
</tr>
<tr>
<td>September 2012</td>
<td>Achieve carbonized fiber properties of at least 150KSI strength and 15MSI modulus.</td>
<td>Complete</td>
</tr>
<tr>
<td>March 2012</td>
<td>Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus.</td>
<td>Complete</td>
</tr>
<tr>
<td>October 2012</td>
<td>Downselect to the most promising precursor.</td>
<td>Complete</td>
</tr>
<tr>
<td>April 2013</td>
<td>Carbonize tows and achieve 450 KSI and 31 MSI.</td>
<td>Complete</td>
</tr>
<tr>
<td>Date</td>
<td>Milestone</td>
<td>Status</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>December 2013</td>
<td>Carbonize tows and confirm that material properties meets performance requirements of &gt; 500 KSI &amp; 30 MSI modulus.</td>
<td>Complete 1/13/2013</td>
</tr>
<tr>
<td>March 2014 Go/No/Go</td>
<td>Carbonize tows and confirm that material properties meets performance requirements of &gt; 550 KSI &amp; 31 MSI modulus.</td>
<td>Complete 1/13/2013</td>
</tr>
<tr>
<td>June 2014</td>
<td>Carbonize tows and confirm that material properties meets performance requirements of &gt; 600 KSI &amp; 32 MSI Modulus.</td>
<td>Complete 3/30/2014</td>
</tr>
<tr>
<td>July 2014</td>
<td>Complete cost report and estimate the cost savings if the precursor under development were used to manufacture carbon fiber as compared to the precursors that are currently used by industry. Metric: Cost savings in carbon fiber manufacturing cost of at least 25% when compared to precursors currently used by industry.</td>
<td>Phase I Baseline 6/30</td>
</tr>
</tbody>
</table>
# FY2014 Milestones

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>September 2014</td>
<td>Carbonize tows and confirm that material properties meeting performance requirements of &gt; 650 KSI &amp; 33 MSI modulus.</td>
<td>In Process</td>
</tr>
<tr>
<td>October 2014</td>
<td>Issue final project report which will include identification of other potential commercialization routes, materials and possible corporate entrants to achieve the same goals as this project (i.e. high strength at minimal cost and a good commercial pathway).</td>
<td>Not Started</td>
</tr>
<tr>
<td>October 2014</td>
<td>Deliver 20 Kg of fiber for evaluation to a tank manufacturer selected by DOE.</td>
<td>In Planning</td>
</tr>
<tr>
<td>November 2014</td>
<td>Commitment by a carbon fiber manufacturer to use the fiber developed in this project in production.</td>
<td>Scale-Up has begun.</td>
</tr>
</tbody>
</table>
Two Reference Cost Models (Industrial not Aerospace)

**H₂ Storage**

Diagram from Harper International

**Cost Per Pound of Carbon Fiber**

<table>
<thead>
<tr>
<th></th>
<th>Precursors</th>
<th>Stabilization &amp; Oxidation</th>
<th>Carbonization/Graphitization</th>
<th>Surface Treatment</th>
<th>Spooling &amp; Packaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEW TRJ</td>
<td>$6.61</td>
<td>$1.61</td>
<td>$2.65</td>
<td>$0.93</td>
<td>$0.50</td>
</tr>
<tr>
<td>High Volume Not Done</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline Today</td>
<td>$5.56</td>
<td>$1.78</td>
<td>$1.41</td>
<td>$0.80</td>
<td>$0.65</td>
</tr>
<tr>
<td>High Volume Today</td>
<td>$5.23</td>
<td>$1.62</td>
<td>$1.27</td>
<td>$0.72</td>
<td>$0.49</td>
</tr>
</tbody>
</table>

Baseline: 3M lb/yr line
High Volume: 12-15M lb/yr line

**NEW Textile Research Journal (TRJ) Model**
- 24 K
- Industrial Grade
- Based on Moses Lake Facility

**ORNL Model**
- 48K
- Industrial Grade
- Based on Multiple Manufacturers

Precursor Cost is by far the Greatest (55%) followed by Oxidation and Carbonization

Oxidation is the rate limiting step and thus mass throughput limiting step.
Current CF Precursors

- Cost drivers are polymerization materials (i.e. acrylonitrile) and high spinning equipment cost

<table>
<thead>
<tr>
<th>Commodity PAN</th>
<th>$0.00</th>
<th>$0.50</th>
<th>$1.00</th>
<th>$1.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerization</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spinning</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Textile Precursors

- Cost savings driven by substantially higher mass throughput per $ invested in spinning equipment versus commodity PAN

<table>
<thead>
<tr>
<th>Tex. PAN</th>
<th>Com. PAN</th>
<th>Savings</th>
</tr>
</thead>
<tbody>
<tr>
<td>7500 t/y Plant</td>
<td>7500 t/y Plant</td>
<td>$0.58 (25%)</td>
</tr>
<tr>
<td>$1.78 /lb</td>
<td>$2.37 /lb</td>
<td></td>
</tr>
</tbody>
</table>

Energy 8%
Labor 14%
Capital 23%
Materials 55%
Cost drivers are high precursor cost and with low conversion yield (47.6%).

Cost savings over commodity PAN mostly from lower cost precursors.
Developing a 700 KSI Fiber production cost model in two phases:

- **Phase I:** Baseline **Completion:** 30 June 2014
- **Phase II:** Project Benefit **Completion:** 31 July 2014

- Precursor model (7500 t/year line capacity)
  Evaluate precursor manufacturing at the level of two major process steps

- CF model (1500 t/year line capacity) Evaluate carbon fiber manufacturing at the level of nine major process steps
Precursor Cost $6.40/Kg ($2.91/pound)

Carbon Fiber Cost $29.40/Kg ($13.36/pound)
1. Identify candidate PAN-MA resins.
2. Determine fiber spinning parameters. (Purity level, molecular weight, AN concentration, 3\textsuperscript{rd} components such as itaconic acid, temperature, solvent concentration, etc.)
3. Down Selection from 11 polymers to 3 candidate fibers to 1 final fiber.
4. Improve fiber purity and “roundness”
5. Determine the conversion protocol.
6. Optimize all above parameters.

Fiber formulation being done in Portugal.

Fiber conversion optimization being done in two teams:
- ORNL (US) – High tension oxidation approach.
- SGL (Germany) – Low tension oxidation approach.

\[
\text{PAN:} \quad \begin{array}{c}
  \text{H} \\
  \text{C} \\
  \text{C} \equiv \text{N} \\
\end{array} \quad \begin{array}{c}
  \text{H} \\
  \text{C} \\
  \text{C} \equiv \text{N} \\
\end{array} \quad \begin{array}{c}
  \text{H} \\
  \text{C} \\
  \text{C} \equiv \text{N} \\
\end{array}
\]  

\[T_g \approx 120^\circ\text{C}\]
FY11-12 Status

Kick-off Telecon 21 April 2011. Several months of retrofit to produce a PAN-MA precursor. Downselected from numerous potential formulations.

11 polymer compositions sent to ORNL for screening.

3 were selected for further development using analytical techniques. (critical: high molecular weight, high AN content, uniform exotherm during oxidation, etc.)

First trial: 282 KSI, 28.4 MSI with F1921.

Preliminary Conversion Trials were held with all 3 Precursors.

Go/No-Go MILESTONE 3/31/12: Achieve properties of at least 300 KSI strength and 30 MSI modulus.

- F1921 Precursor: 324.7 KSI; 26.9 MSI
- F2350 Precursor: 372.8 KSI; 36.0 MSI
- F2027 Precursor: 252.7 KSI; 27.2 MSI

The F2350 Precursor was downselected for further development.
Optimization through iterative optimization of Temperatures, Exposure Times and Tension (Stretch %) in each of 7 stages of conversion.

Once process is optimized, produce 20 Kg of fiber and send to Hexagon Lincoln for testing.
Sample Data Analysis

H₂ Storage

Processing Conditions Systematically Varied

Strand Tests conducted using ASTM4018 at the Oak Ridge Carbon Fiber Technology Facility

Processing Conditions Omitted for Export Control Compliance
Conclusion: Optimum HT Relaxation Identified*, Optimum LT Stretch Identified**
Conclusion: High Amount of Stretch in Oxidation* & Increased Relaxation in HT Carbonization** & Increase Stretch in LT***
FY13Q4 Milestone: Reach an intermediate goal of 450 KSI tensile strength and 33 MSI modulus. Milestone exceeded.

Intermediate milestone of 450 KSI Strength and 33 MSI modulus exceeded. Current properties: 576.9 KSI strength and 39.8 MSI modulus. Verified using ASTM4018 at ORNL CFTF.
**FY13-14 Status – Accomplishments**

**H₂ Storage**

**Strength over Project Duration**

Yield Strength Progression

Goal

<table>
<thead>
<tr>
<th>Date</th>
<th>Yield Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 Jan</td>
<td>250</td>
</tr>
<tr>
<td>7 Feb</td>
<td>300</td>
</tr>
<tr>
<td>7 Feb</td>
<td>350</td>
</tr>
<tr>
<td>26 Jun</td>
<td>400</td>
</tr>
<tr>
<td>26 Jun</td>
<td>450</td>
</tr>
<tr>
<td>24 Feb</td>
<td>500</td>
</tr>
<tr>
<td>30 Jul</td>
<td>550</td>
</tr>
<tr>
<td>8 Oct</td>
<td>600</td>
</tr>
<tr>
<td>8 Oct</td>
<td>650</td>
</tr>
<tr>
<td>23 Jan</td>
<td>700</td>
</tr>
<tr>
<td>14 Mar</td>
<td>750</td>
</tr>
<tr>
<td>14 Mar</td>
<td>800</td>
</tr>
</tbody>
</table>

- **2012**
- **2013**
- **2014**
Modulus over Project Duration

Modulus Progression

Goal
Major Issues Resolved:

Fiber fuzzing
   (Diameters: 11-13 as a precursor)
Consistency along the Tow
   (< 8% Variability)
Tow to Tow Variability
   (<5% in filament count)
Fiber Uniformity in Roundness
   (width/thickness ratio: 1.1-1.4)

Resolved by optimization of spinning conditions, such as temperature, spin rate, solvent concentration, etc.
ORNL identified issues that are critical for CF precursors but not textile fiber. FISIPE resolved those in their process.

Their process conditions are proprietary.
We have completed optimization of all 4 oxidation zones and most of the way through the carbonization.

15 of 18 Processing Parameters Completed: 83%
(6 Zones – Temperature, Time, Stretch % in Each)
Remaining: LT Stretch %, HT Stretch % & HT Final Temperature

Current Test Matrix:
- 2 Different Oxidation Profiles
- 5 Low Temperature Carbonization Stretch Conditions
- 3 High Temperature Carbonization Stretch Conditions
- 3 Different High Temperature Carbonization Temperatures
- 90 Combined Condition Variations
ORNL:
- Conducts conversion from precursor to carbon fiber. (multiple profiles)
- Develops relationships between processing conditions and fiber properties.
- Precursor characterization and advises on modification.
- Carbon fiber characterization.
- Composite characterization and coordinates activities.

FISIPE:
- Formulates the polymer.
- Spins the polymer into precursor fiber.
- Analyses of the precursor.

SGL:
- Conducts conversion from precursor to carbon fiber for multiple applications.
- Carbon fiber characterization.

Hexagon Lincoln:
- Will evaluate the finished fibers for composite (tank) applications.
Proposed Future Work

Future Plans


2. Scale-up ability to make precursor to an industrial scale. (Transfer process from pilot precursor line to industrial fiber line.)

3. Complete cost model & brief to DOE & HSTT.

4. Deliver fiber to a tank manufacturer (Hexagon Lincoln) and conduct preliminary composite coupon testing, will also conduct parallel testing at ORNL

5. Make preliminary composite samples. Test and compare to baseline industrial fibers.
1. The research team should add a partner or effort in the area of cost estimating. It should also consider including others in the fiber industry beyond FISIPE to ensure that precursor development will have a wider impact rather than simply to SGL Group before the project is complete.

In FY 14 the team has added a cost estimating effort. While additional partners would be eagerly welcomed, the proprietary nature of the work dictates that each project be conducted with a single precursor manufacturer. We have developed similar efforts with 2 additional textile manufacturers targeting lower fiber strengths.

2. It would be good to develop a better understanding of the impact on final materials properties of polymer dope filtration as well as other aspects of the spinning process that could reduce the number of large-scale pilot trials. It is unclear if SGL Group plays a role in the project. If so, its role should be described. It has manufacturing expertise that can be brought to bear on this project.

The polymer processing details are understood but highly proprietary and cannot be presented in this forum. SGL is also conducting conversion trials.
3. The project team needs to include specific metrics for developing a high-quality aerospace CF. The team needs to have an update on the cost estimate based on the current assumptions.

The project metrics are tied to the milestones and are basically to develop fibers with properties equivalent to lower cost aerospace carbon fibers. i.e. 700 KSI strength and >33 MSI modulus in a 24K tow size. A cost model is being developed.
Summary

Relevance
- Carbon fiber composites make up 60-80% of the hydrogen storage system and the cost of the fiber makes up the majority of that cost.

Approach/Strategy
- Developing lower cost precursors, building off of previous project, to meet performance requirements while preserving high production rate cost benefits.

Technical Accomplishments
- Chose 11 Formulations, down selected to 3 candidate fibers and then down selected to 1 development system.
- About 83% through optimization

Collaboration and Coordination
- Building off Vehicle Technologies Work
- FISIPE (Precursor supplier) and SGL Carbon Fibers are partners

Future Work
- Complete Optimization of current formulation. Test fibers.
Thank you for your attention.

Questions?