# IV.F.2 Development of Low-Cost, High-Strength Commercial Textile Precursor (PAN-MA)

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Project Start Date: April 21, 2011
Project End Date: December 31, 2014

## Overall Objectives

- Develop a carbon fiber precursor that yields carbon fiber that is 25% less expensive to manufacture than commercially available carbon fibers and has a strength of at least 650 KSI and a modulus of at least 35 MSI.
- Down-select from 11 polymer candidate polymer compositions to three for spinning fibers.
- Evaluate three fiber compositions to yield guidance for selecting the best fiber composition.
- Demonstrate at least 300 KSI breaking strength and 30 MSI modulus by mid project. (Gate Milestone)
- Optimize the conversion protocol to achieve at least a 650 KSI ultimate strength fiber.
- Conduct a cost study to establish a baseline manufacturing costs for aerospace grade carbon fiber manufacturing.
- Evaluate the cost of manufacturing carbon fiber from the precursor developed in this project and compare to the baseline manufacturing costs.
- Assist manufacturer in implementing the technology in a precursor production facility and a carbon fiber manufacturing facility.

## Fiscal Year (FY 2014) Objectives

- Optimize the previously selected fiber composition.
- Increase finished carbon fiber tensile strength from 400 KSI to 650 KSI.
- Increase finished carbon fiber tensile modulus from 32 MSI to 35 MSI.
- Establish a firm commercialization commitment if final target properties are met at the end of the project.
- Establish a baseline cost model for the manufacture of aerospace grade carbon fiber.
- Determine the cost savings in the manufacture of carbon fiber from the newly developed precursor and compare to the baseline cost model.

## Technical Barriers

This project addresses the following technical barriers from the 3.3 section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(B) System Cost

(A) System Weight and Volume

## Technical Targets

The cost of the carbon fiber in hydrogen storage systems is 60-80% of the total system cost (Figure 1). Precursors account for 55% of the total cost of the carbon fiber (Figure 2). The precursor alone can account for 33-44% of the cost of the tank. The hydrogen storage team has been conducting projects to develop lower cost carbon fiber precursors to reduce the cost of carbon fiber for hydrogen

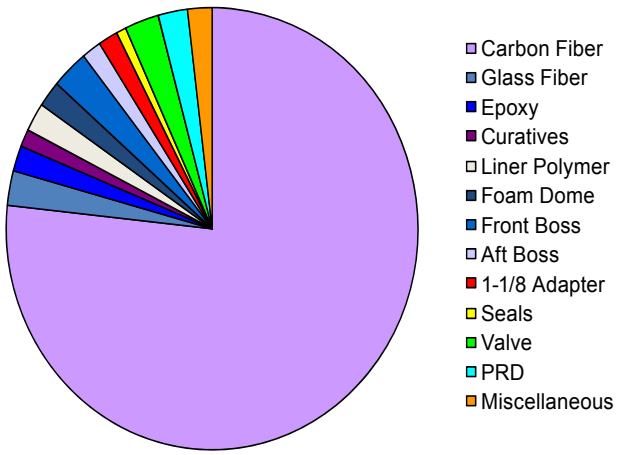


**FIGURE 1.** Cost of Hydrogen Storage System Broken Out by Major Components and Materials

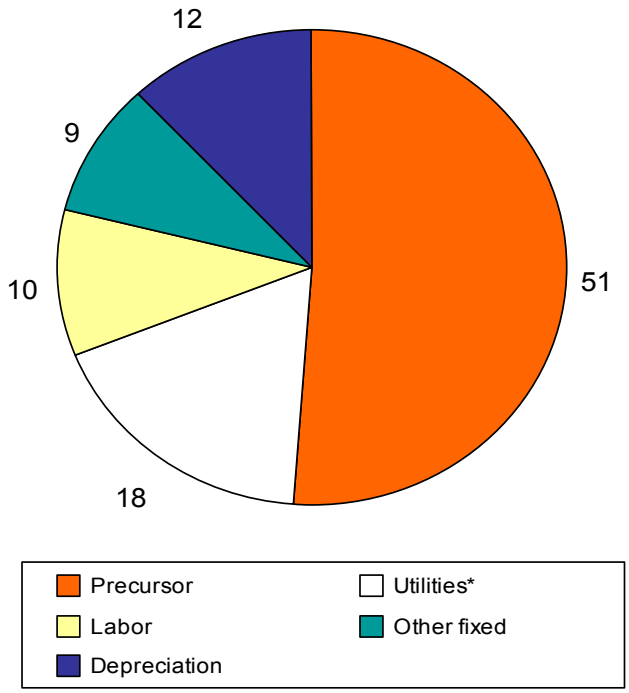


**FIGURE 2.** Carbon Fiber Production Costs

storage tanks. This effort is to develop a solution spun textile grade polyacrylonitrile with methyl acrylate (PAN-MA) precursor with strengths in the range of 650-700 KSI. This project is a shorter term, lower risk approach to addressing the same issue as is being addressed by the melt-spun polyacrylonitrile (PAN) project. The fiber developed in this proposal will be ready for commercialization within one to two years.

**TABLE 1.** Progress towards Meeting Technical Targets for PAN-MA Based Lower Cost Carbon Fiber for Hydrogen Storage Tanks

| | Strength (KSI) | Modulus (MSI) | Estimated Production Costs |
|---|---|---|---|
| Current Market Fibers | 750 | 38 | $15-20/lb |
| Target | 650-700 | 35-38 | $10-12/lb |
| Status of Developmental Precursor | 648 | 38 | $10-12/lb |

## FY 2014 Accomplishments (as of July 1, 2014)

- Completed 19 of 21 steps for optimizing selected fiber composition conversion conditions.
- Increased finished carbon fiber tensile strength from 405 KSI to 649 KSI.
- Increased finished carbon fiber tensile modulus from 33 MSI to 38 MSI.
- Developed a baseline cost model for the manufacture of aerospace grade carbon fiber.
- Partner is finalizing refinement of conversion conditions for their plant and has agreed to provide fiber for sampling to a tank manufacturer.

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## INTRODUCTION

In previous years, the Vehicle Technologies Office developed technologies for the production of lower cost carbon fiber for use in body and chassis applications in automobiles. Program goals target materials that have tensile strengths in excess of 250 KSI and modulus of at least 25 MSI. Past work included the development of a vinyl-acetate co-monomered, lower cost precursor and methods for manufacturing precursors into finished carbon fiber. The basic premise of the project was to be able to use PAN material produced in a high volume textile production process for a carbon fiber precursor rather than the specialty material that is typically used for carbon fiber precursors. A textile line that formerly made knitting yarn has been retrofitted and that precursor is being commercialized.

The previously developed fiber had strengths slightly below 500 KSI, which is far above strengths suitable for automotive structural applications but insufficient for many higher demanding applications with higher performance requirements such as the manufacture of hydrogen storage tanks. In order to preserve the cost advantages of using a high-volume PAN fiber and simultaneously meet the needs of higher performance applications, it was proposed to develop the capability to use methyl-acrylate based, textile grade, PAN as a carbon fiber precursor and to manufacture that precursor on a textile line.

The purpose of this current project is to take one precursor technology, textile-based PAN, while using a higher performance chemical formulation, from the technical feasibility stage and scale up to technology demonstration. This project has resulted in the determination of the best polymer formulation and conversion protocol (time-temperature-tension profiles) to produce the best carbon fiber while the precursor is readily and inexpensively manufacturable in existing textile PAN plants. Successful completion of this project resulted in defining the precursor formulation and manufacturing methods to produce carbon fiber. SGL Carbon Fibers is the partner for this work and has both the commitment and ability to commercialize the technology. SGL purchased FISIPE after FISIPE's involvement in the development of the first precursor. Therefore the team that developed the first textile based precursor is involved in this work. Deliverables include spools of fully carbonized, surface treated and sized carbon fiber. This project is on the critical path for the development of lower cost carbon fiber.

## APPROACH

The first step to developing a new precursor is to define and analyze candidate precursor formulations. Those are then down-selected and multiple candidate polymer formulations are produced. For this project, SGL/FISIPE down-selected to 11 candidate formulations. Those polymer formulations were sent to ORNL for evaluation from which three polymer formulations were selected to be spun into precursor fiber for attempted conversion into carbon fiber. SGL/FISIPE worked to determine how to spin each of those three formulations into precursor fiber tows and sent them to ORNL for conversion trials. Developing uniformly round fibers and maintaining fiber consistency from fiber to fiber and along the length of each fiber were critical parameters.

Upon receipt of the precursor spools, ORNL began the thermal evaluations to pinpoint conversion temperatures of the precursor, particularly the temperatures to be used for oxidative stabilization. The next step was to determine the limits of fiber stretching that can be achieved in each of the oxidative stabilization stages. As a general rule, higher levels of tension (i.e., percentage of stretching) will promote better polymer chain alignment along the axis of the fiber and will result in higher breaking strengths of the fiber. It is therefore necessary to apply the maximum tension to the fiber, especially during the early stages of oxidative stabilization, without breaking the filaments and without damaging the filaments.

The amount of stretching in each stage of conversion, the optimum temperatures for conversion and the time that the precursor is exposed to those conditions must be developed for each of the seven stages (Prestretching, Oxidation 1, Oxidation 2, Oxidation 3, Oxidation 4, Low Temperature Carbonization and High Temperature Carbonization) of processing. These must be done sequentially, completing each processing step before proceeding to the next. Only after completing all of these steps, can the final properties of the fiber be determined. The plan was to evaluate the three formulations, pinpointing processing parameters in approximate ranges and then down-select to one final formulation. For that formulation, all spinning and conversion parameters are now being optimized. That down-selection has been made to the F2350 formulation.

The main challenges to be addressed in optimizing the performance of the selected precursor are:

- Adapting high-speed processes for producing fiber containing higher acrylonitrile (AN) concentrations.
- Adapting high-speed processes for producing fiber containing methyl-acrylate (MA) co-monomers.
- Adapting high-speed processes for producing fiber with increased chemical purity in order to minimize defects.
- Spinning of round fibers rather than the kidney shaped fibers that are typically produced during textile fiber production.
- Improving the fiber consistency from fiber to fiber and along the fiber length without sacrificing production speed and throughput.
- Determining the optimal conversion protocol by balancing residence time, temperature and applied tension during each of the multiple steps in precursor conversion to carbon fiber.

## RESULTS

The down-selection of chemical compositions and fiber formulations started in April of 2011. The main issue related to achieving the proper formulation was the generation of the PAN-polymer with a higher AN content and with a MA comonomer. Dealing with MA co-monomered polymer required some changes to SGL/FISIPE's equipment and standard practices, which required three months. SGL/FISIPE generated 11 candidate compositions. Those 11 compositions were sent to ORNL for evaluation. Differential scanning calorimetry (DSC) curves and other technical data for those compositions were generated for comparison to each other and to known aerospace and industrial grade precursors. The research team then selected three fiber compositions from the first 11 formulations for fiber spinning and preliminary evaluation trials.

Upon receipt of the three fiber candidates, ORNL began the thermal evaluations to pinpoint conversion temperatures of the precursor, particularly the temperatures to be used for oxidative stabilization. Two features are prominent and were expected from the thermal evaluations: (1) the onset of the exotherm occurs at a slightly different temperature from traditional precursors indicating a different starting

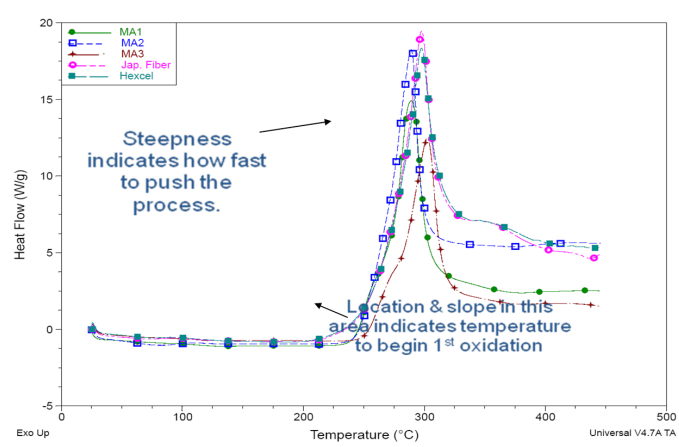


**FIGURE 3.** DSC Scans of the Three Fiber Compositions Compared to Aerospace and Industrial Grade Precursors

temperature for oxidative stabilization; (2) the exothermic curve is steeper for the PAN-MA precursors than it is for the PAN-VA precursors indicating a slower temperature ramp up being necessary during oxidative stabilization.

The next step was to determine the limits of fiber stretching that can be achieved in each of the stages during oxidative stabilization. As a general rule, higher levels of tension (i.e., percentage of stretching) will promote better polymer chain alignment along the axis of the fiber and will result in high breaking strength of the fiber. It is therefore necessary to apply the maximum tension to the fiber, especially during the early stages of oxidative stabilization, without breaking the filaments. Damage to the filaments that is hidden can also be induced by the tensioning. That damage many not show up until later processing stages. After determining the temperature and tension limits for processing, precursor conversion trials were conducted for those three fiber formulations. The results of those trials are shown below in Table 2. The F2000 formulation was selected for full program development but due to a further refinement by FISIPE was changed to the F2350 formulation. Filament diameters for the new precursor were measured at 11.7 microns which is within the desired range for an oxidized precursor. Normal ranges are 11-12 microns which, after carbonization, produce an ~7 micron diameter carbonized fiber.

Table 2. Final Fiber Properties for Three Candidate Precursor Systems

| Fiber Designation | Tensile Strength (KSI) | Tensile Modulus (MSI) |
|---|---|---|
| F1921 | 324.7 | 26.9 |
| F2000 | 372.8 | 36.0 |
| F2027 | 252.7 | 27.2 |

At this point precursor optimization began. Using the three spools of laboratory-produced F2000 that ORNL had, temperature profiles during oxidation were then determined. The temperature profiles are the temperature setting of each of the oxidation ovens and dwell times before significant polymer stretching (tensioning) is applied. Figure 4 shows the DSC curves used for that evaluation. Axis data labels are intentionally omitted for this and all DSC curves in this report due to export control restrictions. The closeness of the Stage 1 and Stage 2 curves is indicative of further improvements that can still be made in the oxidation temperature profile.

The processing parameters (temperature, time at that temperature, and tension applied during oxidative stabilization) during oxidation are interdependent. If any one of the processing conditions in the first stage of oxidation is changed, then the processing conditions that will be optimal in Stage 2 are altered. If Stage 2 parameters are changed then Stage 3 will be altered, etc. As a result, it is critical when optimizing a precursor to finish each processing stage in series rather than in parallel. As an example, if the

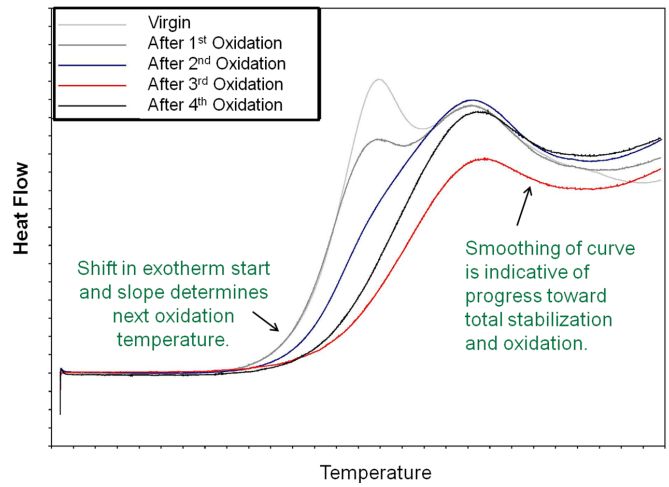


**FIGURE 4.** DSC Curves for the F2000 Precursor after Various Stages of Oxidative Stabilization

temperature is increased during one stage of oxidation, or the residence time at temperature is increased, then the resulting material will be more highly crosslinked and the amount of oxygen diffusion into the fiber will have increased as will the degree of polymer crosslinking. Likewise, if the fiber is more highly stretched, then the fiber diameter will have decreased, affecting oxygen diffusion into the fiber. For each of these parameters—time, tension and degree of stretch—there is an optimal processing condition for each production step. Too little of each of these and the fibers final properties are compromised. Too much of each of these and the fibers are damaged. Fortunately, once these conditions are optimized, as long as the precursor chemistry is not changed, the processing conditions will not change either.

After determining these beginning temperatures, the amount of stretch that can be given to the precursors during each stage of processing had to be determined. This is done by systematically adding tension to precursors that have been processed through all earlier stages until the breaking point of the precursor at the next temperature is achieved. Figure 5 shows the tension and percent stretching for fibers after exposure to the temperatures determined in the previous step. Of particular interest are the ends of each curve which indicate the upper tension limit of the processing window for these precursors. The closeness of the first and second stage curves indicates that not much progress was being made during the first stage oxidation so either the temperature or the residence time will have to be increased. Since the goal of this effort is to develop a lower cost carbon fiber, a temperature increase of just a few degrees Celsius was used to combat this problem. The closeness of data and the magnitude of the data after the third and fourth stages is indicative of damage during earlier stages, likely due to over stretching the fibers. Export control restrictions require that all tension loads, stretching percentages, oven temperatures

and residence times not be publicly disclosed, therefore axis values are intentionally left off of these charts.

One issue that had to be dealt with for these precursors was "fuzzing" of the fiber tow during processing. Figure 6 shows an example of this. Fiber fuzzing is typically due to small, not fully developed "baby" fibers present in the precursor. Upon tensioning, these fibers see a higher than average stress, exceed their strength and break. This issue has been resolved.

As second issue that had to be dealt with was the cross-sectional geometry of the fibers. Typical textile production processes yield fibers that are kidney bean in shape (Figure 7A). These are fine and even preferable for making carpet fiber or knitting yarn but not for carbon fiber. Carbon fiber properties are enhanced by having uniformly round fibers (Figure 7B). To solve this problem a slightly different configuration for spinning the precursor into the solvent bath during solution spinning of the precursor had to be adopted. The details are proprietary.

Determination of the residence time, stretch percentage and oven temperatures for all oxidation stages has been completed. Determination of 19 of the 21 processing parameters for conversion of the precursor to the final carbon fiber has been completed. The remaining parameters are stretch percentage in low-temperature carbonization, stretch percentage in high-temperature carbonization and the optimum high-temperature carbonization temperature.

Figures 8 and 9 are the property as a function of time charts for tracking precursor progress. Each data point is the average of 18 tests. Blue indicates properties in 2012, purple indicates properties in 2013 and gold the properties in 2014.

Another task to be accomplished is to develop a baseline cost model for production of high-strength carbon fiber (700 KSI) based upon the technologies currently employed in industry today. The expected cost benefits of using the precursor that is being developed under this project will then be evaluated using that cost model and the processing conditions determined in this project. The baseline cost

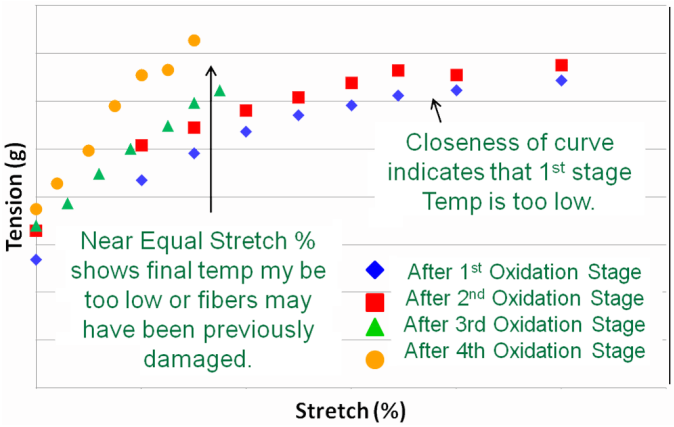


**FIGURE 5.** Stretch – Break Curves for F2000 Precursor

**FIGURE 6.** Top: "Fuzzing" of Filament Tow during Oxidative Stabilization; Bottom: Tow not exhibiting "Fuzzing"

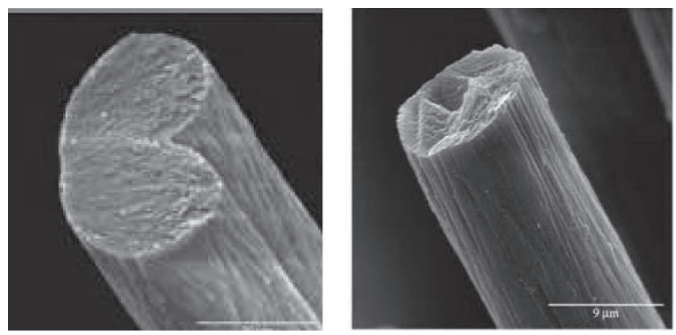


**FIGURE 7.** (A) Typical Textile Produced PAN Fibers; (B) Carbon Fiber Grade PAN Fibers

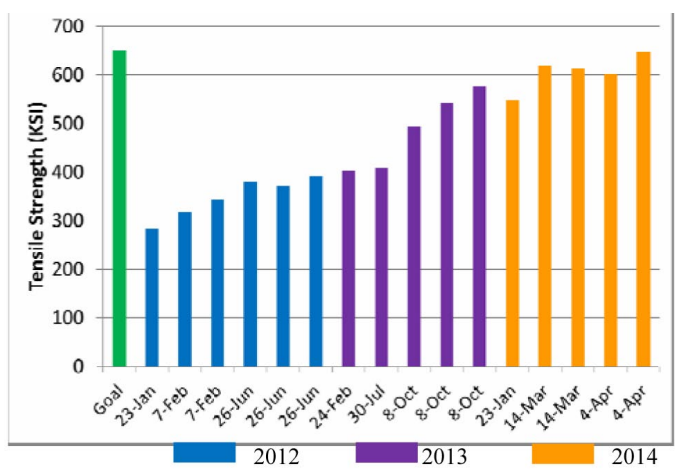


**FIGURE 8.** Tensile Strength as a Function of Time for the F2350 Precursor

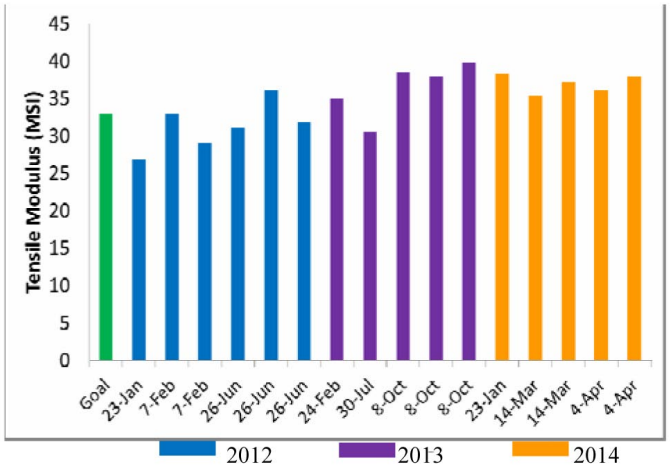


**FIGURE 9.** Tensile Modulus as a Function of Time for the F2350 Precursor

model nearing completion and preliminary results are presented in Figures 10 and 11.

While we have not yet achieved Hydrogen Storage Program goals, the properties achieved thus far are sufficient for this precursor to go into production for lower performance applications. As a result, SGL/FISIPE is now moving to produce the precursor that they are supplying for this work on their full-scale production line

## CONCLUSIONS AND FUTURE DIRECTIONS

The gate milestone for project continuation has been met. The original 11 polymer compositions have now been selected down to one final composition. That material is being produced on full-scale production lines while optimization of the conversion protocol is occurring. To

Precursor Cost $6.40/Kg ($2.91/pound)

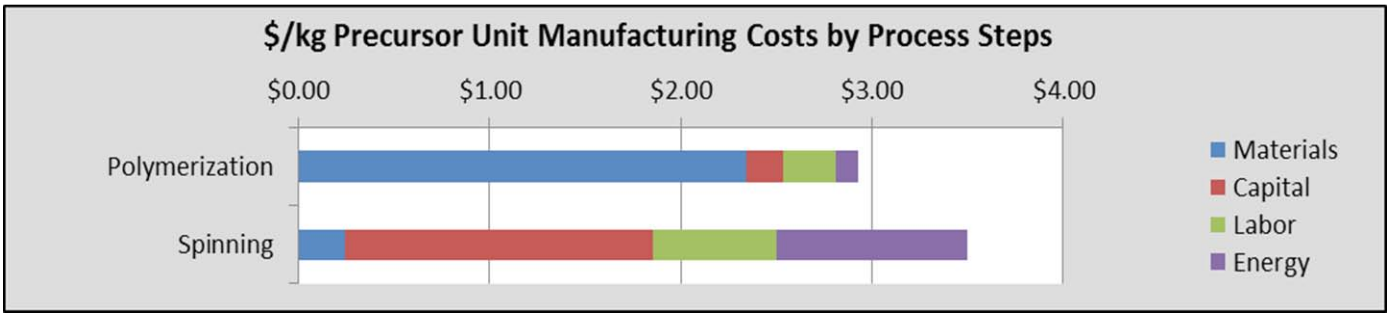


**FIGURE 10.** Baseline Precursor Cost for High-Performance Carbon Fiber (2.1 lbs of Precursor is required to make 1.0 lbs of Carbon Fiber)

Carbon Fiber Cost $29.40/Kg ($13.36/pound)

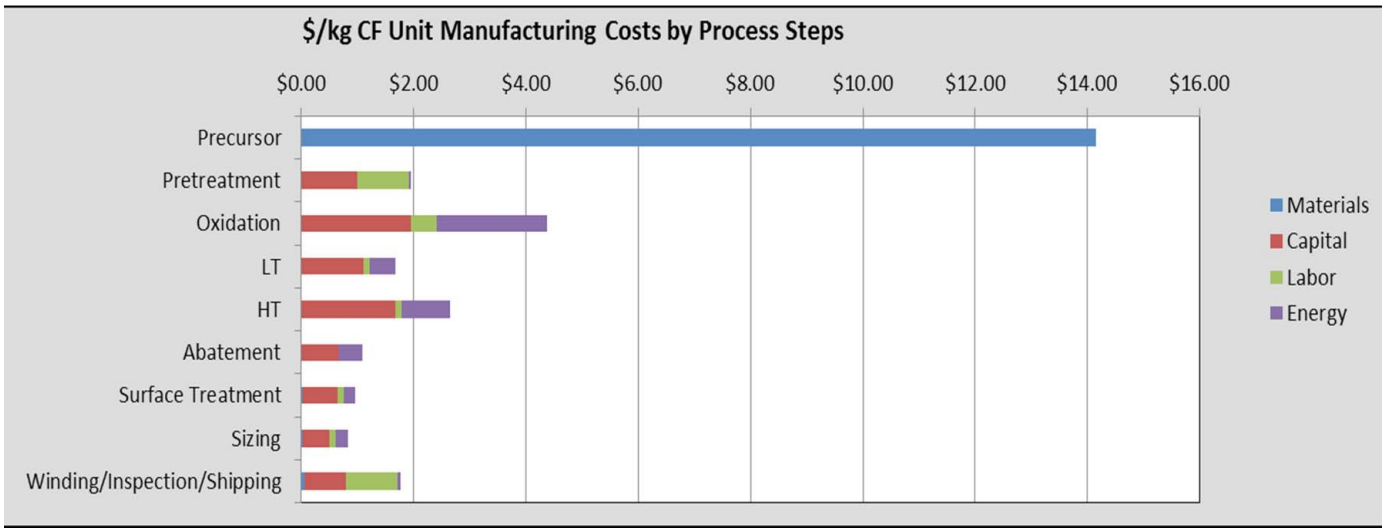


**FIGURE 11.** Baseline Carbon Fiber Cost for High-Performance Carbon Fiber

date, we are approximately half-way through the conversion protocol optimization phase. Work to improve fiber consistency from filament to filament and along the lengths of the filaments has mostly been completed. This is a task that manufacturers will continue throughout the production life of the precursor since it is critical to pushing the final carbon fiber properties higher.

## FY 2014 PUBLICATIONS

**1.** Warren, C.D., Wheatley, A. and Das S., "Low Cost Carbon Fibre for Automotive Applications Part 1: Low Cost Carbon Fibre Development", Chapter 3 in Advanced Composite Materials for Automotive Applications: Structural Integrity and Crashworthiness, (in final editing) Publisher: Wiley, Edited by: Ahmed Elmarkbi. (2013).

**2.** Warren, C.D., Wheatley, A. and Das S., "Low Cost Carbon Fibre for Automotive Applications Part 2: Applications, Performance and Cost Reduction Models" Chapter 17 in Advanced Composite Materials for Automotive Applications: Structural Integrity and Crashworthiness, (in final editing) Publisher: Wiley, Edited by: Ahmed Elmarkbi. (2013).