Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

June 17, 2014

Status as of early April 2014

Dr.–Eng. Felix L. Paulauskas
MS&T Division

Oak Ridge National Laboratory
Phone: 865-576-3785
Email: paulauskasfl@ornl.gov

Project ID: LM006

Oak Ridge National Laboratory
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Project Overview

Timeline

Phase **I – Basic Science**

- Completed in 2011

Phase **II – Scale Up**

- Start 2011
- End 2015-16

Barriers

- High cost of carbon fiber
- Long conventional processing times for oxidative stabilization are the bottleneck in production
- Inadequate supply base for low cost carbon fibers/high volume production

Budget

- FY2013 $1,000,073
- FY2014 $1,500,000.

Partners

- **ORNL** (Host site), carbon fiber production, characterization, recipe development
- **RMX Technologies** (Experimental site), atmospheric plasma and hardware development.

Project Objectives and Relevance

- **Phase I: Produce multiple tows of carbon fiber meeting minimum program specifications using oxidation residence time of 40 minutes or less.**
  - Oxidation is the bottleneck in production often requiring 80 to 120 minutes. By developing a 2-3X faster oxidation process, higher throughput can be achieved.
  - This phase is Complete.
- **Phase II: Demonstrate Phase I capability at Pilot Scale.**
  - This will involve multiple tows and larger tows at less than 35 min residence time (increased throughput).
  - This phase is In Progress.
- **Current Project Year Objectives (FY14):**
  - Make Large Reactor operational
  - Optimize Large Reactor through parametric studies

FY14 Milestones

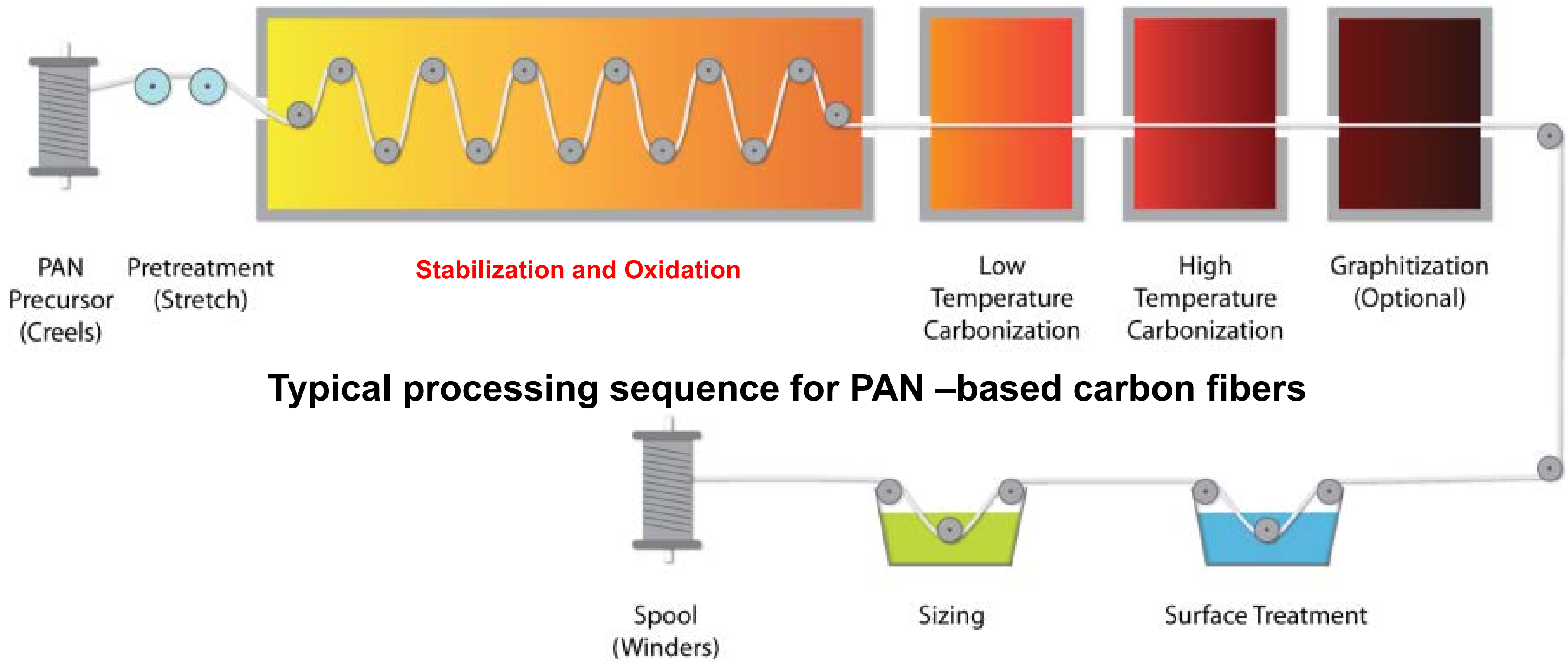
Date	Milestone	Status
November 30, 2013	**M1:** Establish definable relationships between tensile strength and modulus of oxidized fiber with primary advanced oxidation parameters.	**Complete**
January 5, 2014	**M2:** Complete construction of all components for the Large Reactor for plasma oxidation.	**Complete**
April 5, 2014	**M3:** Complete installation and make operational the Large Reactor for plasma oxidation of multiple tows of lower cost, commodity precursor fibers.	**Complete**

FY14 Milestones

Date	Milestone	Status
June 30, 2014	**M4:** Plasma oxidize in 35 minutes or less (and conventionally carbonize) two – 20,000+ filament tows of low cost commodity or textile grade PAN precursor yielding carbonized mechanical properties greater than 250 Ksi tensile strength and 25 Msi Modulus using multiple zone processing in the Large Reactor. Two 50 ft. tows of 24k of carbon fiber meeting the performance requirements of 250 KSI tensile strength and 25 MSI Modulus.	**In Progress**
August 30, 2014	**M5:** Establish an industrial partnership with a carbon fiber industry partner and obtain commitment letter from industrial partner.	**In Progress**

Background

Conventional PAN Processing



Typical processing sequence for PAN –based carbon fibers

Major Manufacturing Costs

Precursor	43%
Oxidative stabilization	18%
Carbonization	13%
Graphitization	15%
Other	11%

Not selling price

- Automotive cost target is \$5 - \$7/lb
- Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain
- ORNL is developing major technological breakthroughs for major cost elements

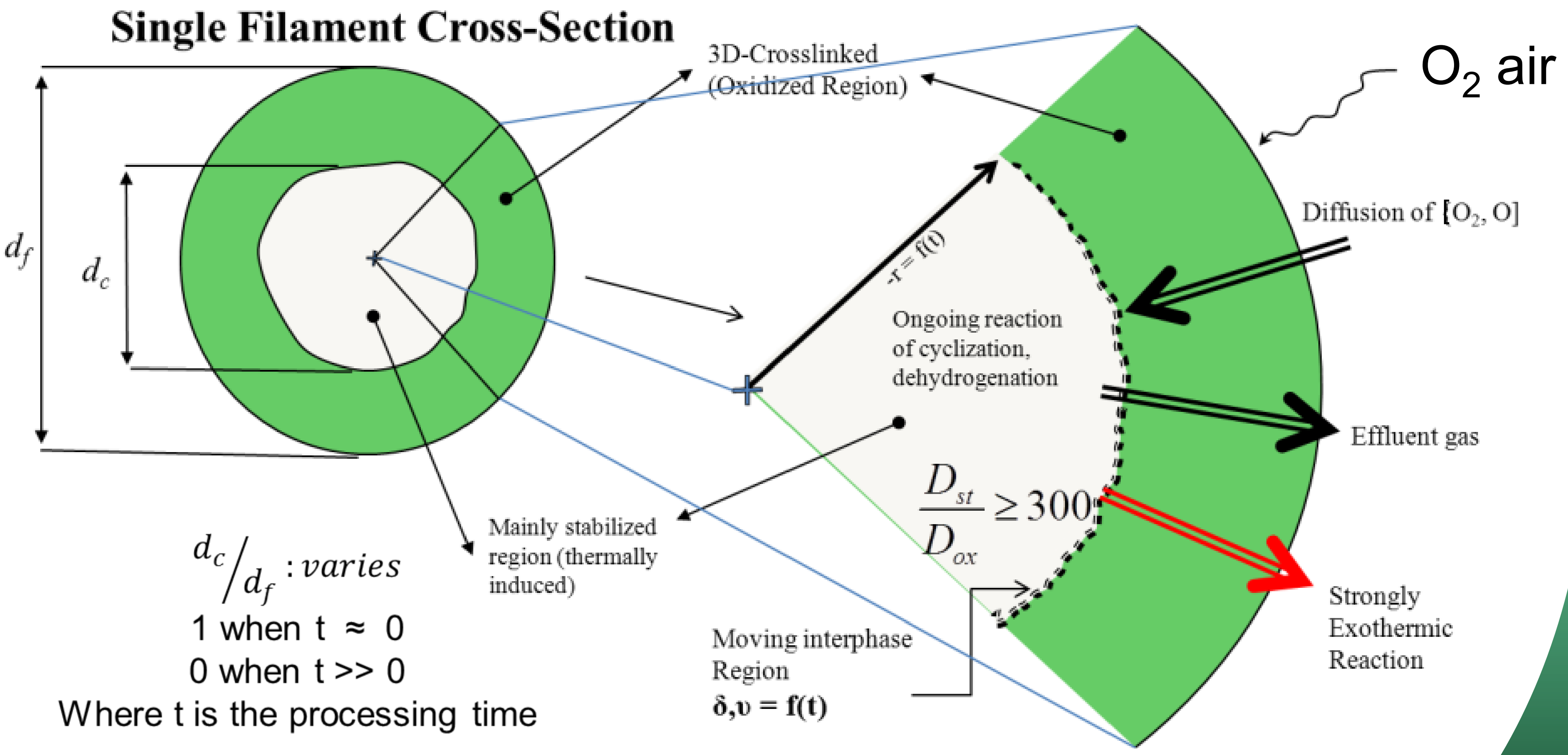
Approach/Strategy
Plasma-Based Oxidation

- Addresses diffusion-controlled stages of conventional oxidation.
- Utilization of non-thermal atmospheric pressure plasma based on Close Proximity Indirect Exposure (CPIE).
- After carbonization – good physical, morphological, and mechanical properties.
- Residence time reduced by 2 - 3X (less than 35 minutes).
- Large Reactor was tested for proper performance and is now operational for fiber oxidation (March 24, 2014).

Approach: Reduce PAN-Oxidation

LM006

Two Zone Morphology



d_c / d_f : *varies*

1 when t ≈ 0

0 when t >> 0

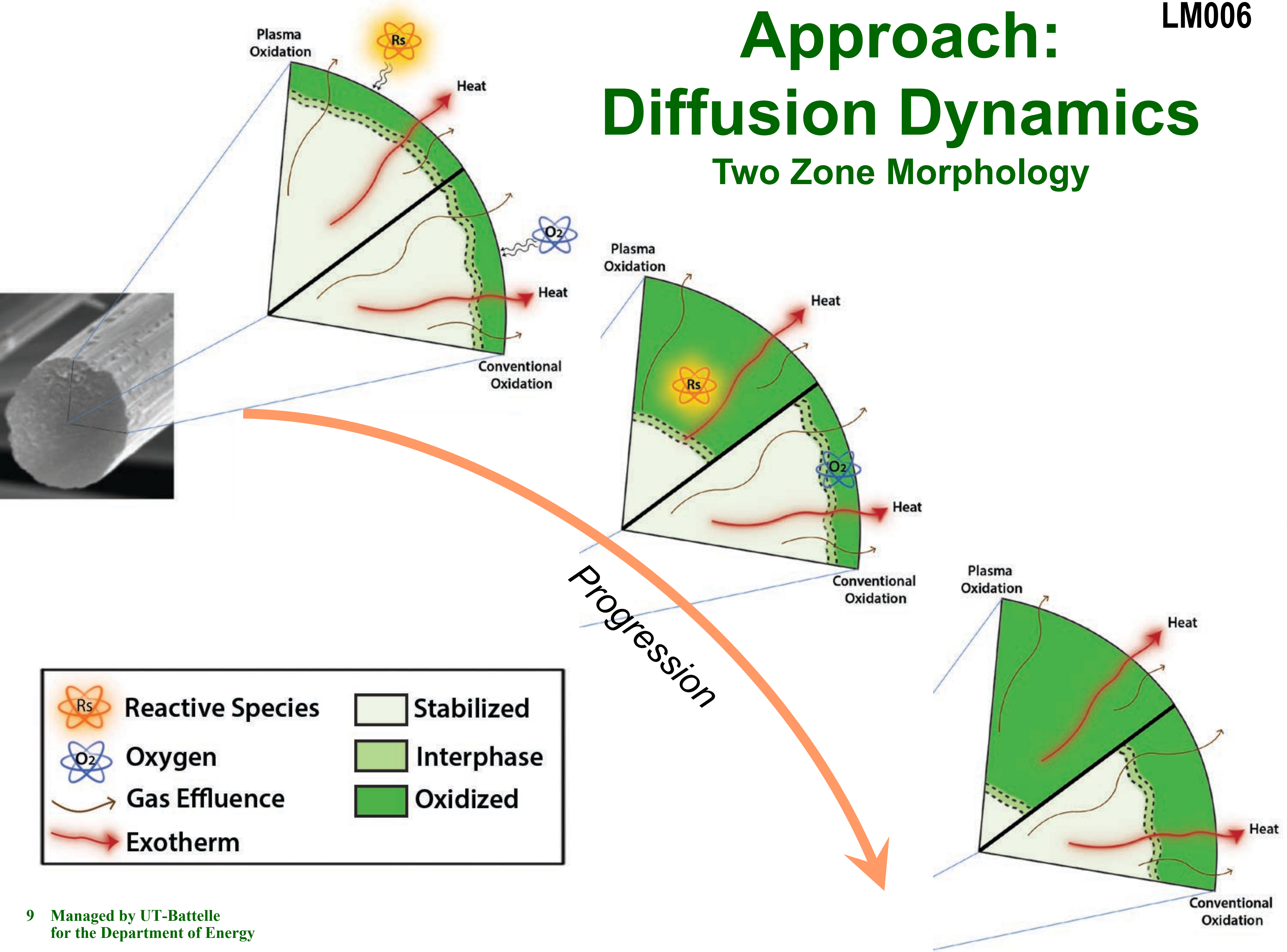
Where t is the processing time

- Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly
- The limiting factor in the oxidative processing is the diffusion-controlled phase

LM006

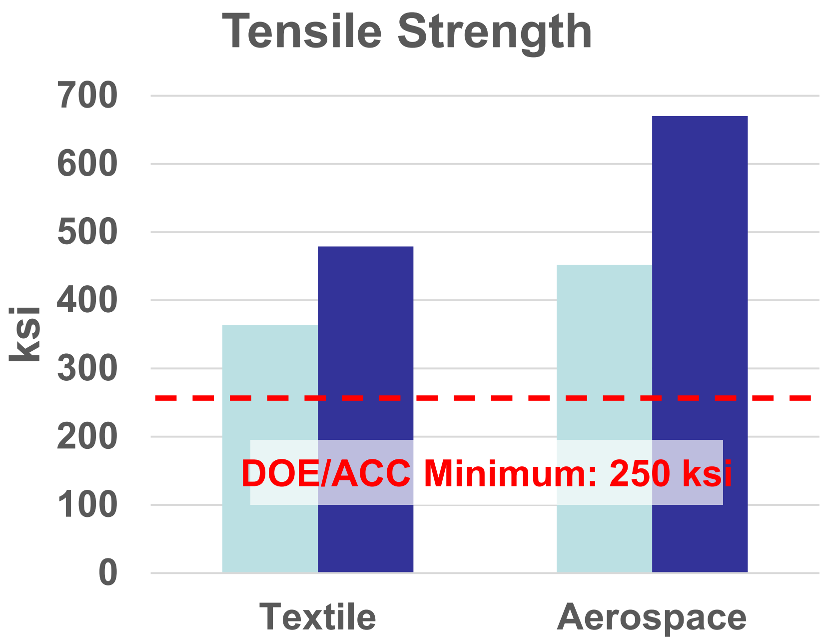
Approach: Diffusion Dynamics

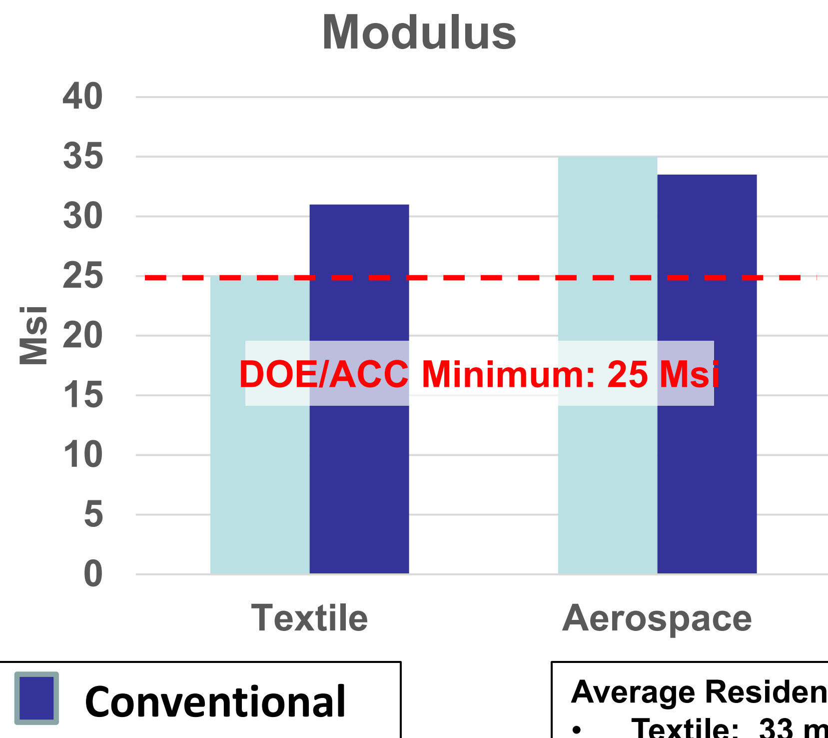
Two Zone Morphology



Technical Accomplishments FY13

Small Reactor (now in standby condition)





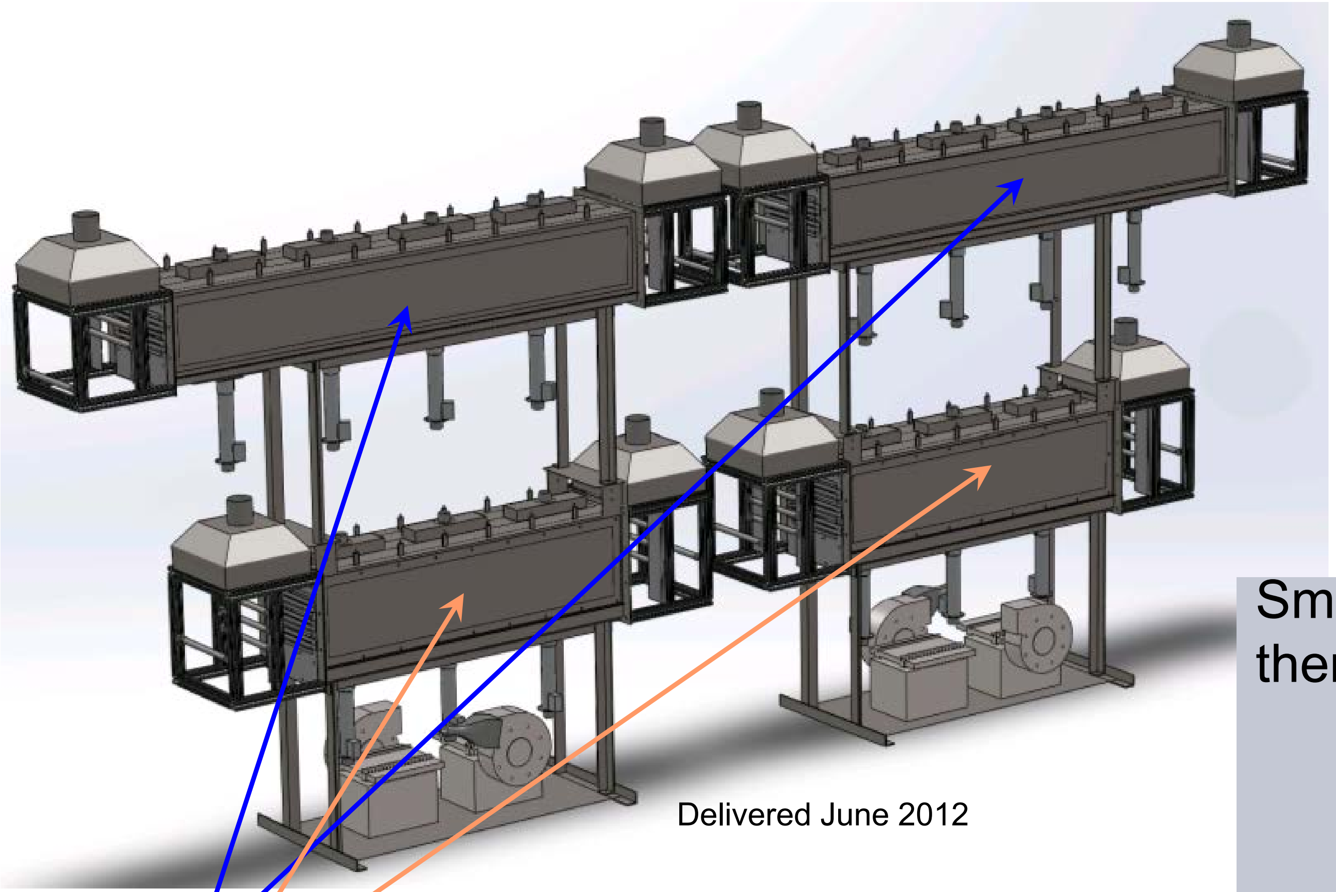
Average Residence Time
- **Textile: 33 min**
- **Aerospace: 30 min**

ORNL Mechanical properties to date

- Plasma Oxidation with ORNL Conventional Carbonization
- Mechanical properties matching conventional are expected with the new 1- ton/year Plasma Oxidation Oven due to better fiber handling equipment.

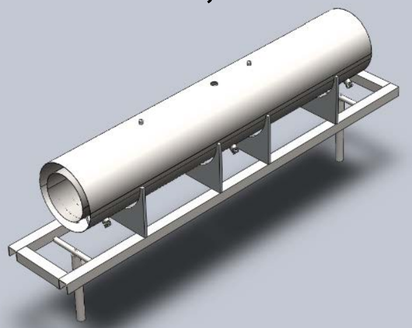
Previous Work

Equipment Comparison



- Two 2-Pass Modules (Upper Level)
- Two 3-Pass Modules (Lower Level)

Small Reactor: Single thermal zone, uni-tensional



Technical Accomplishments

Timeline of Large Reactor

Jan 2011	• CPIE technique first demonstrated
Jan 2012	• Design of Large Reactor complete
Jun 2012	• Large Reactor structural components delivered
Apr 2013	• Stretching system delivered
Jan 2014	• Large Reactor construction complete
Apr 2014	• Large Reactor operational

Technical Accomplishments

Subsystem Functionality

Thermal	Controls temperature independently in each module. Must maintain uniform heating across the width and length of each module.
Flow	Control the chemical mix and flow rate to all modules. Must precisely control these and produce a uniform flow of gas across the width of each module.
Fiber	Includes creels, stretchers, dancers, and winders. Controls fiber tension and distribution in the modules.
Exhaust	Must adequately remove and treat the exhaust stream from the oven.
Plasma	Control the generation of reactive species uniformly across the module width, independently for each module.
Control	Unifies control of all other subsystems and components.

Large Reactor Progress

LM006

Overview
As of April 2014

Sub-system	Acquire	Assemble	Install	Connect /Integrate	Subsystem Test	Full System Test	Full System Optimize
Thermal	Complete	Complete	Complete	Complete	Complete	Complete	Working
Flow	Complete	Complete	Complete	Complete	Complete	Complete	Working
Fiber	Complete	Complete	Complete	Complete	Complete	Complete	Working
Exhaust	Complete	Complete	Complete	Complete	Complete	Complete	Working
Plasma	Complete	Complete	Complete	Complete	Complete	Complete	Working
Control	Complete	Complete	Complete	Complete	Complete	Complete	Working

M2

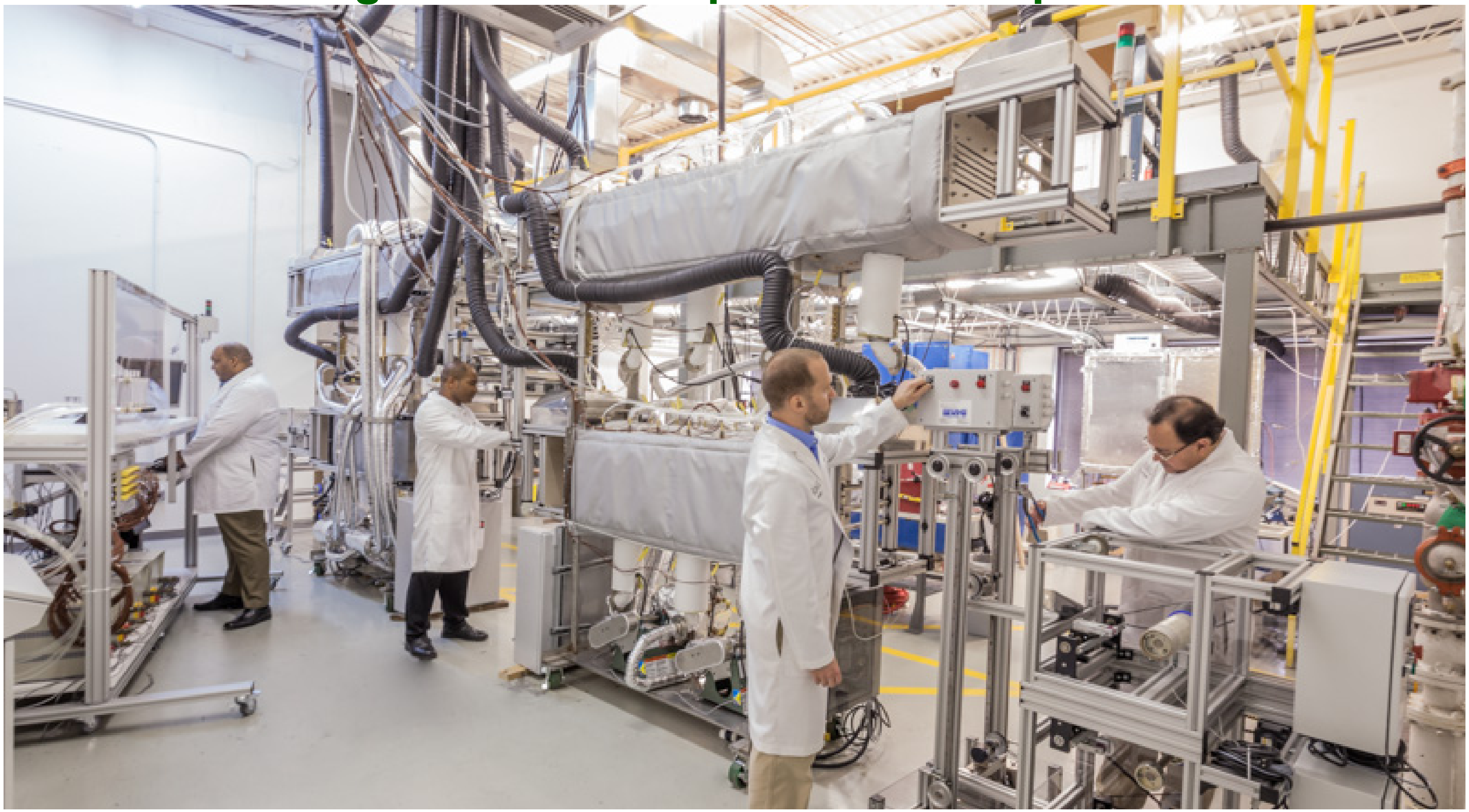
Jan-5, 2014

M3

Apr-5, 2014

Technical Accomplishments

Large Reactor – Operational in April 2014



As of April 2014, the research team is processing fiber in the Large Reactor conducting parametric studies to optimize all processing conditions. Currently processing 1 tow. Once optimized, will process two tows to meet milestone M4 in June.

Response to FY13 Reviews

Comments on Technical Accomplishments

- Comment on the "spread of the data (specifically Modulus)": One reviewer expressed some concern about this issue. The reason for the large variation of Modulus is that a wide variety of process conditions was being explored. The goal for this period of work was not to generate consistent results – the team was conducting parametric studies to look at the variations.
- Comment on "the modulus is a bit low, but improving": This is partly due to the above reason, but also due to the limitations of the small reactor, primarily in temperature gradient/control and tension limitations.
- Comment on "discussion of cost of plasma oxidation": There has been two major modeling studies at ORNL looking at this technology. These will be revisited as new data is generated with the large reactor.

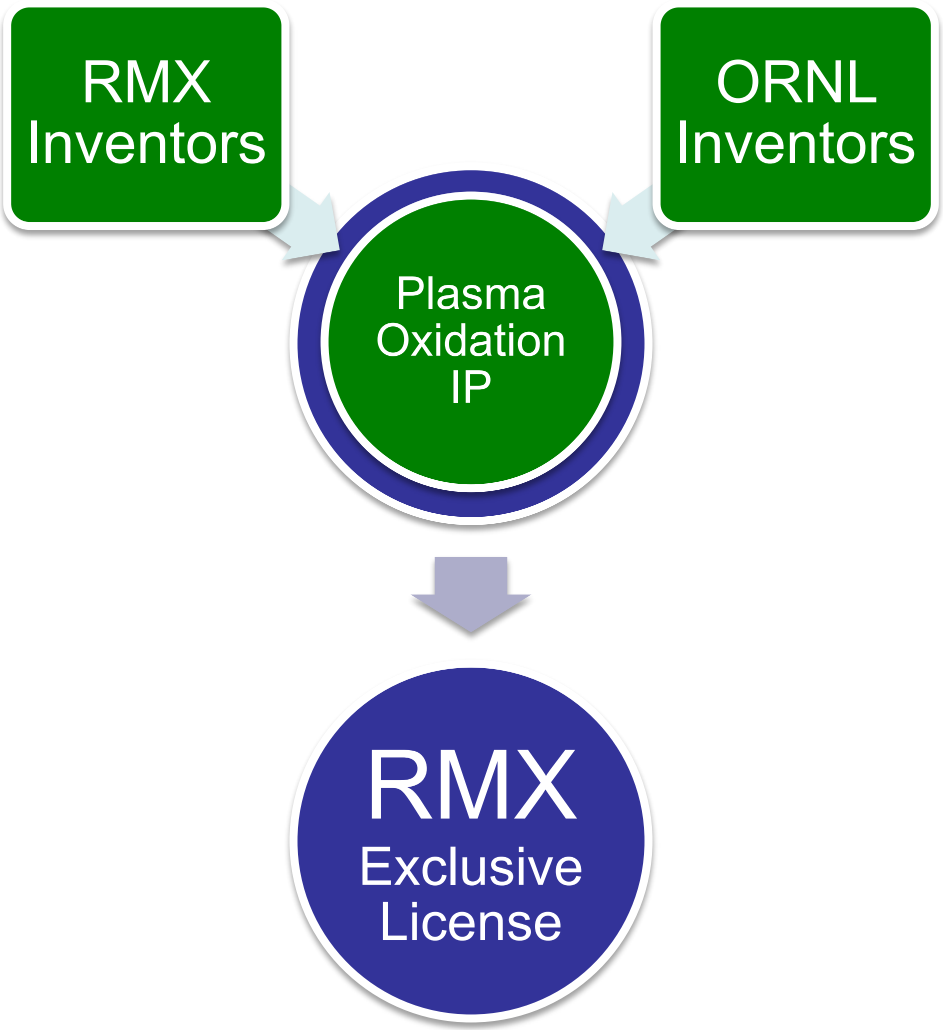
Comments on Future Work

- Comment on processing "3 tows or more of 20,000 in less than 30 minutes": This project has a milestone due in June 2014 to meet this request. The large reactor will be utilized for this task.

We appreciate the mostly positive remarks in the area of Approach to the Work, Collaboration, Future Work, Support of Overall DOE Objectives.

Collaboration and Coordination

Technology Transfer



- Intellectual Property (IP) covering Plasma Oxidation is co-owned by RMX and ORNL. RMX has executed an option to exclusively license.
- Interest in utilizing this technology has been expressed repeatedly by at least three companies. Several are in talks pursuing possible commercialization plans.
- RMX will lead commercialization effort.

contacts under limitations of IP and export control

Future Work

- FY14
  - Verify continuous operation capabilities of Large Reactor
  - Process multiple tows of large textile grade PAN with low variability among tows.
  - Obtain scaled energy consumption data.

- FY15
  - Coordinate interactive work of Large Reactor with the ORNL Small Pilot Line (SPL). Evaluation needed as standalone unit and with ORNL SPL.
  - Deliver equipment specification for a plasma oxidation oven for an advanced technology/demonstration pilot line (principal project deliverable) appropriate for integration with the Carbon Fiber Technology Facility.

Conclusions

- Project is on schedule.
- Large Reactor is operational and is currently being optimized.
- Interest from the carbon fiber industry is driving significant commercialization progress.
- The ultimate goal of this project is to successfully demonstrate this technology at a sufficiently large scale such that the carbon fiber industry *begins widespread utilization of this technology.*

Summary

Relevance

- This technology will reduce the required oxidation time during conversion, and hence will reduce the production costs of carbon fiber.

Approach/Strategy

- Develop an oxidation technology that addresses the diffusion time limitations of the conventional method and scale that technology sufficiently to demonstrate the success of this approach to the carbon fiber industry.

Technical Accomplishments

- Large Reactor assembly complete.
- All subsystems successfully tested for performance.
- Large Reactor first fiber dry runs mid-April.

Collaboration and Coordination

- ORNL and RMX are partners.
- RMX leading commercialization efforts with major industry players.

Future Work

- Develop specification for 25 ton/year plasma oxidation oven for CFTF.

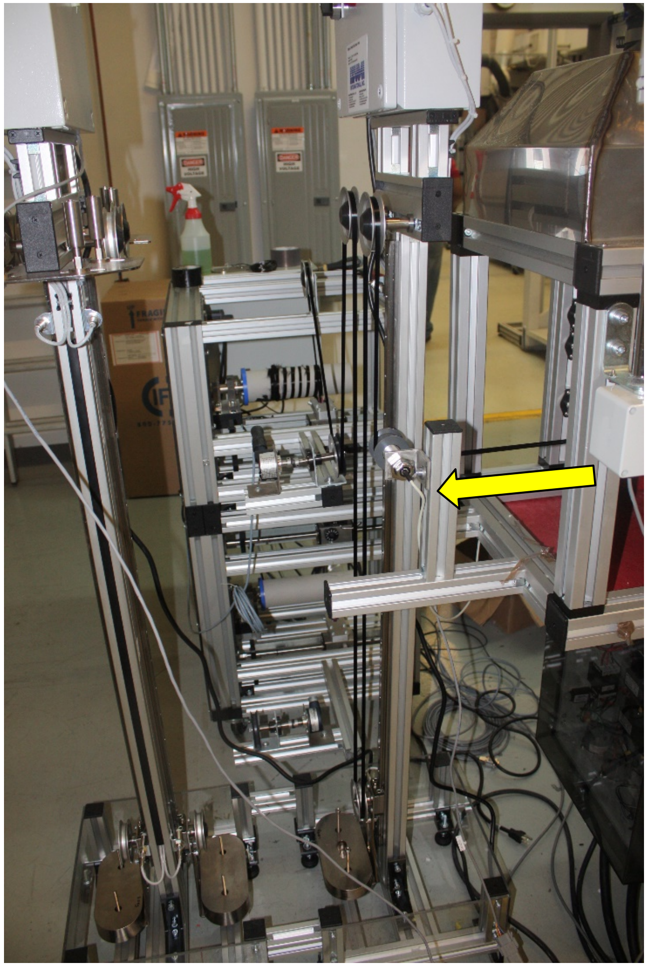
Thank you for your attention.

Questions?

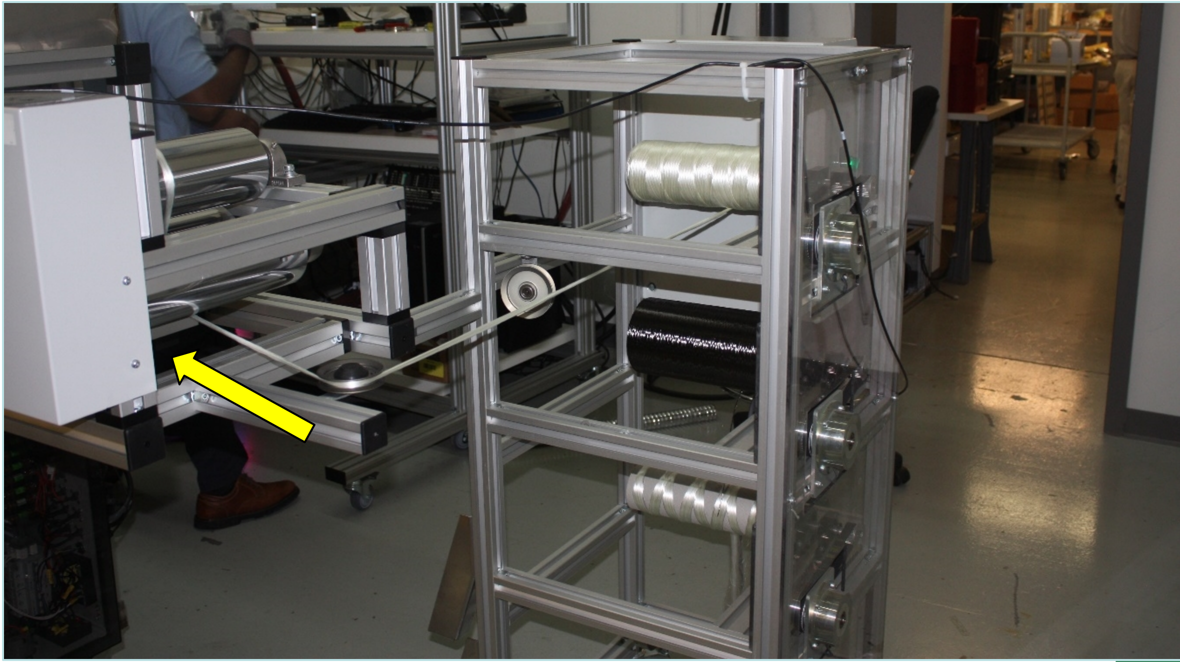
Technical Backup Slides

Technical Accomplishments

Large Reactor Initial Dry Runs (March 24 – April 7)



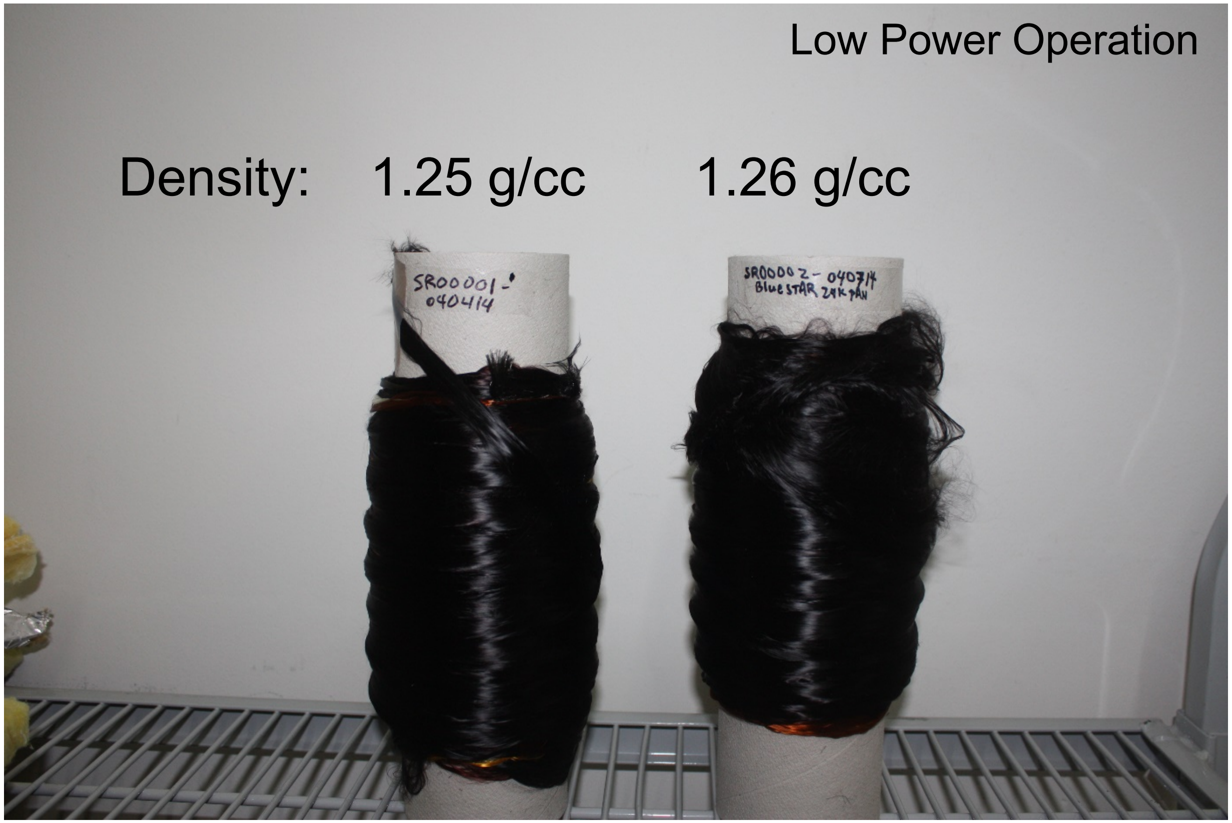
Oxidized PAN Fiber Out



Precursor In

Technical Accomplishments

Large Reactor Initial Dry Runs
(March 24 – April 7)



Approximate Length: 100 ft. each

Technical Accomplishments

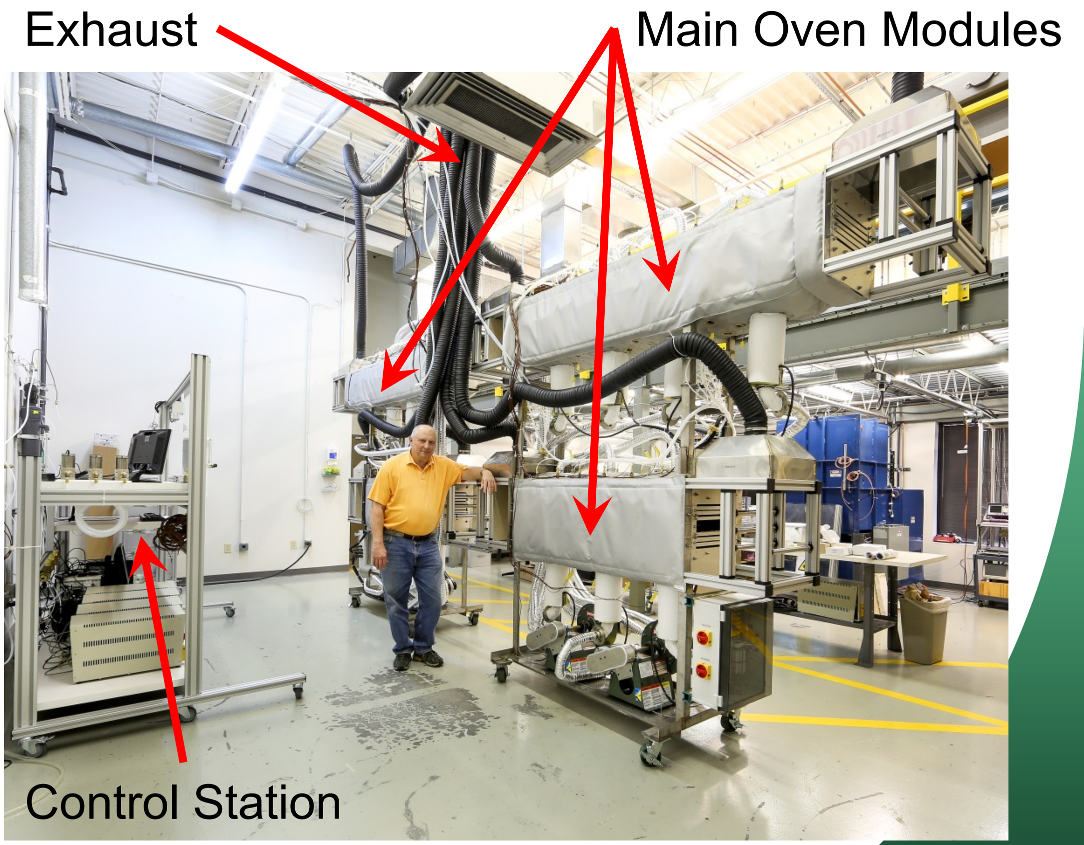
Large Reactor (as of February 2013)

The Large Reactor:

- At the Pilot-Line level, designed with a plate capacity circa 1 ton/year.
- If successful, can be directly integrated into the small ORNL Carbon Fiber Conversion Pilot Line.

Specifications:

- 4 independently controlled thermal zones
- Multiple passes in each zone
- Fiber movement system designed for a max of 6 large tows (not shown).
- Highly modular and flexible
- Utilizes CPIE technology (plasma hardware not shown)
- LabVIEW controlled



OAK RIDGE National Laboratory