Close Proximity Electromagnetic Carbonization
(*Low Temperature Carbonization, LTC*)

Mat122

Status: as Apr. 10, 2018

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Partner:
RMX Technologies, LLC.

June 19, 2018, 9:30 AM

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Overview

Timeline

- Project Start: 10/1/17
- Project End: 9/30/18*
- Progress: ca. 60%

* Extension will be requested

Budget

Initial budget planning

- FY16 – FY18: $4.5M

Effective budget:

- Funding received in FY16: $1.5M
- Funding for FY17: $1.35M
- Funding for FY18: $1.5M

Barriers

- Barriers addressed
  – Cost: A goal of this project is to reduce energy consumption in the carbon fiber conversion process and therefore total carbon fiber cost.
  – Inadequate supply base: Another goal of this project is to reduce the require processing time for carbonization and therefore increase overall throughput.

Partners

- Project lead: ORNL
- Partner: RMX Technologies

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Relevance

- Close Proximity Electromagnetic Carbonization (CPEC) is a new low temperature carbonization (LTC) process that relies on dielectric heating instead of convective heating. It is faster and more efficient than the conventional process **at atmospheric pressure**.
- Project Goals
  - Reduce unit energy consumption of LTC stage (kWh/kg) by ca. 50% (which represents ca. 5% of the cost reduction on the CF overall manufacturing process).
  - Produce the same or better quality carbon fiber.
  - Scale the technology to a nameplate capacity of 1 annual metric ton and demonstrate by project end date.

FY16-17 Milestones

Date	Milestone	Status
January 31, 2017	**M5:** Successfully carbonize material on a continuous basis in the CPEC-3 with carbonized material achieving a minimum density of 1.5 g/cc.	**Complete**
September 18, 2017	**M6:** Successfully carbonize material on a continuous basis in the CPEC-3 with carbonized material achieving a minimum density of 1.5 g/cc in under 90 seconds achieving minimum mechanical properties of 150 ksi tensile strength, 15 Msi Modulus.	**Rescheduled and Complete** **(MS originally 6/30/2017)**
November 30, 2017	**Go/No Go M7:** Successfully carbonize material on a continuous basis in the CPEC-3 with carbonized material achieving a minimum density of 1.5 g/cc in under 90 seconds achieving minimum mechanical properties of 250 ksi tensile strength, 25 Msi Modulus, and 1% strain.	**Rescheduled and Complete** **(MS originally 9/30/2017)**

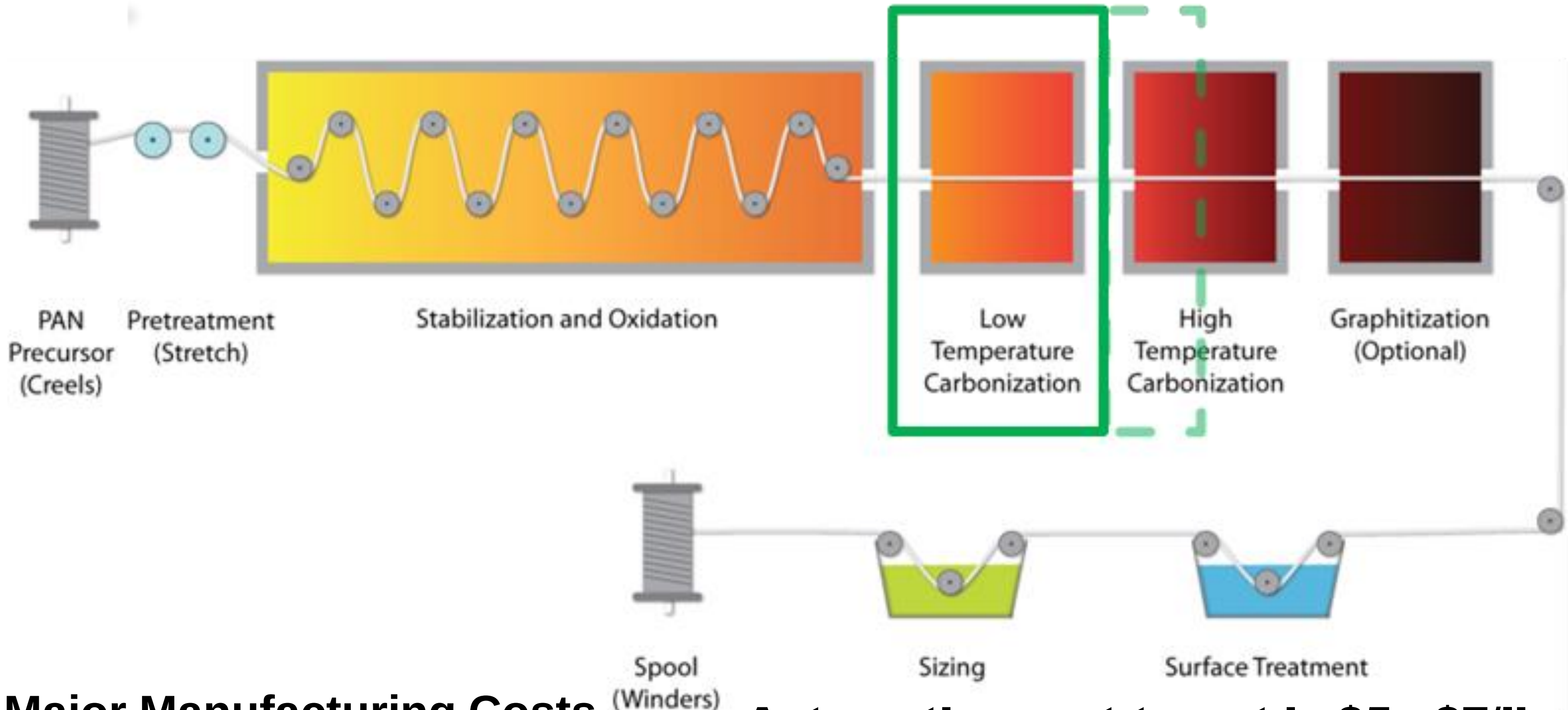
NOTE: Previous programmatic M1, M2, M3, and M4 milestones were completed on time

FY18 Up Coming Milestones

Date	Milestone	Status
February 28, 2018	**M8:** Complete assembly of CPEC-4 and demonstrate stable/proper operation of all subcomponents for 20 minutes.	**Extended to Sep 15, 2018**
June 30, 2018	**M11:** Successfully carbonize 4x24k tows with final mechanical properties of greater or equal to 250 ksi tensile strength and 25 Msi Modulus in under 60 seconds.	**Extended to Feb 28, 2019**
September 30, 2018	**Go/No Go M10:** Demonstrate at least 5% cost savings of the overall CF manufacturing process using CPEC technology versus conventional carbonization.	**Extended to Mar 31, 2019**

Approach Background

Conventional PAN Processing



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

- **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**

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Approach

- Conventional furnaces consume significant energy heating large volumes of inert gas surrounding the fiber.
- If thermal energy could be directly coupled from an energy source to the fiber, tremendous energy savings could be realized.
- This project uses electromagnetic coupling to directly heat the fiber – not the surrounding (walls, gas, etc.).
- The Dielectric and Maxwell-Wagner heating mechanisms are utilized.

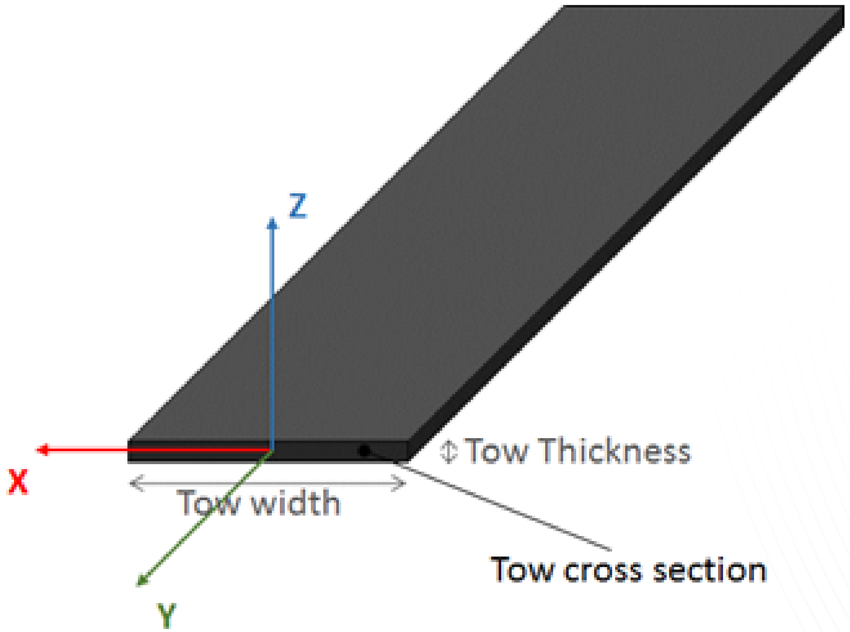
Approach

- Based on volumetric power loss due to dipolar electromagnetic heating
  - P_v volumetric power transferred to the material.
  - ε' is the relative dielectric constant.
  - ε_0 is permittivity of free space, 8.85418782 x 10^{-12} F/m.
  - $|E|$ is the magnitude of the local electric field intensity (V/m).
  - $tan\delta$ is the loss tangent of the material.
  - f is the operational frequency.

$$P_v = 2\pi f|E|^2\varepsilon_0\varepsilon' tan\delta$$

Approach

- CPEC-3 (current setup) is capable of Processing 1 x 48k tow.
- CPEC-4 (in construction) will be capable of processing up to 8 x 48k tows (approx. 8in wide):
  - Operation of CPEC-4 will start with 4 tows or equivalent.



Technical Accomplishments

- Project flow:

Material Measurement → Computational Electromagnetic Modeling (CEM) → (CPEC-2V) → Prototype Design and Build (CPEC-3) → Prototype tested → Prototype altered → Fiber production Material characterization → CEM for CPEC-4

- Material measurement/data acquisition (FY16)
  - 163 different samples measured (Novocontrol/Keysight) consisting of:
    - 10 different carbonization levels or temperatures.
    - Multiple temp ramping functions during material characterization.
    - Broad frequency range with at least 801 points in each sweep.
  - Characterized on 3 different measurement systems.
  - Compilation/data aggregation required additional software: custom *MATLAB* and *Visual Basic* Data Reduction.

Technical Accomplishments

- CPEC Furnace Evolution:
  - CPEC-1 was the initial proof of concept device (FY14).
  - CPEC-2V is the aforementioned modeling effort (FY16).
  - CPEC-3 current operational furnace (FY17-18).
  - CPEC-4 already modeled and ready for fabrication (FY18).

Technical details cannot be presented due to export control restrictions.

- CPEC-3 has been in operation since Q1-FY17. Operation was successful and has led to the CPEC-4 design.
- CPEC-4 design is complete and construction will start soon.

Technical Accomplishments

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Continuous Processing of Fiber with CPEC-3 Furnace

Mechanical properties of fully carbonized fiber (as of 11/2017)

Oxidation (conventional), LTC (CPEC-3), HTC (Conventional)*

Test#	Density (g/cc)	Diameter (Avg) µm	Std. Deviation	Tensile Strength (Avg) ksi	Std. Deviation	Modulus (Avg) Msi	Std. Deviation	Strain (Avg) %	Std. Deviation	Residence Time
1	1.8032	8.05	0.35	348.70	77.50	23.42	1.84	1.49	0.28	Long
2	N/A	8.20	0.41	303.00	87.50	22.73	2.76	1.40	0.32	Short
2	1.7924	8.44	0.74	356.60	135.30	24.88	3.83	1.42	0.47	Long
2	N/A	8.00	0.80	254.20	88.90	21.42	2.59	1.22	0.43	Long
3	N/A	8.40	0.53	333.00	149.80	25.44	3.45	1.29	0.51	Short
3	N/A	8.22	0.63	292.00	91.70	22.79	3.31	1.27	0.27	Short
3	N/A	8.42	0.46	331.30	125.00	23.44	1.84	1.48	0.55	Long
4	N/A	8.09	0.62	354.60	97.60	23.64	2.42	1.48	0.32	Short
4	N/A	8.06	0.72	263.60	132.80	22.31	3.61	1.13	0.44	Short
4	1.8138	8.91	0.63	340.20	101.70	25.14	1.73	1.39	0.43	Long
4	1.8135	8.73	0.56	285.50	98.50	23.07	2.03	1.23	0.37	Long

Table 1: Mechanical properties of fully carbonized samples at HTC (HTC at constant parameters). In the low temperature carbonization stage (LTC), using CPEC-3, temperature and residence time were the only parameters that were changed. The residence time is indicated in the last column as "Long" or "Short". Both residence times in CPEC-3 are shorter than 90 seconds. The values highlighted in green surpassed the dual programmatic requirements of 250ksi tensile and 25Msi modulus simultaneously. No parameter optimization was undertaken.

Multiple samples with similar process parameters had comparable mechanical properties → Reproducibility

* HTC: High Temperature Carbonization

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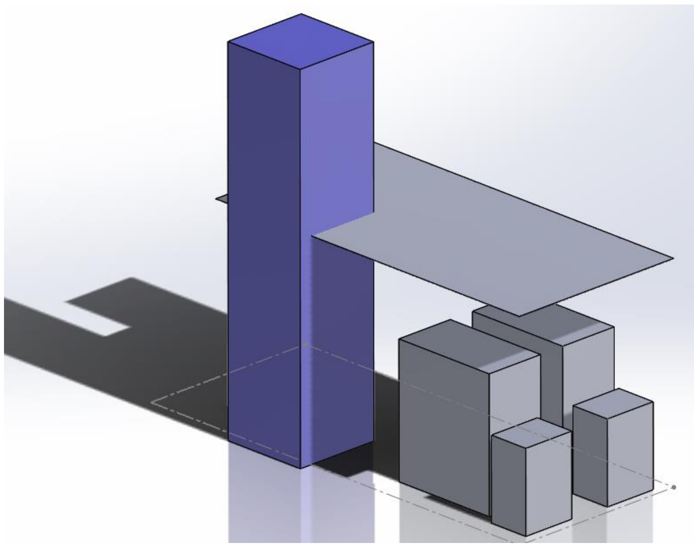
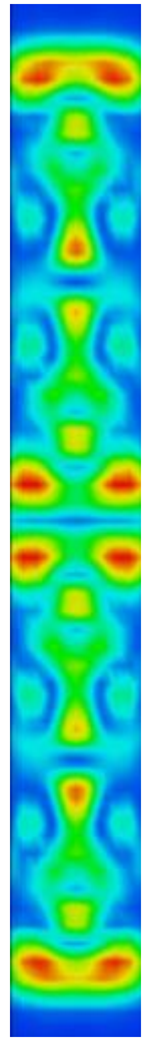
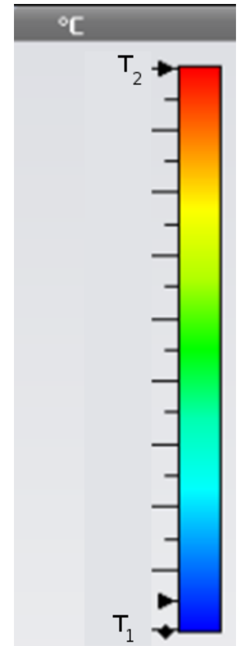
Technical Accomplishments

CPEC-4: CEM and CAD representation



Representation of CPEC-4 and its two power supplies (completion expected by Aug. 2018). The pre-carbonization stage and the applicators will be set vertically (purple parallelepiped on the picture. A mezzanine will help to maintain the vertical structure and provide access to the equipment safely. This setup will be at RMX (Capacity: 4 – 8 continuous tows of 48k)





$T_2 >> T_1$

Just one example of a simulation using CEM:

<u>*Middle*:</u> on a strip of 8 x 48k tows seen from the top.

<u>*Right*:</u> related temperature scale.

Project Timeline

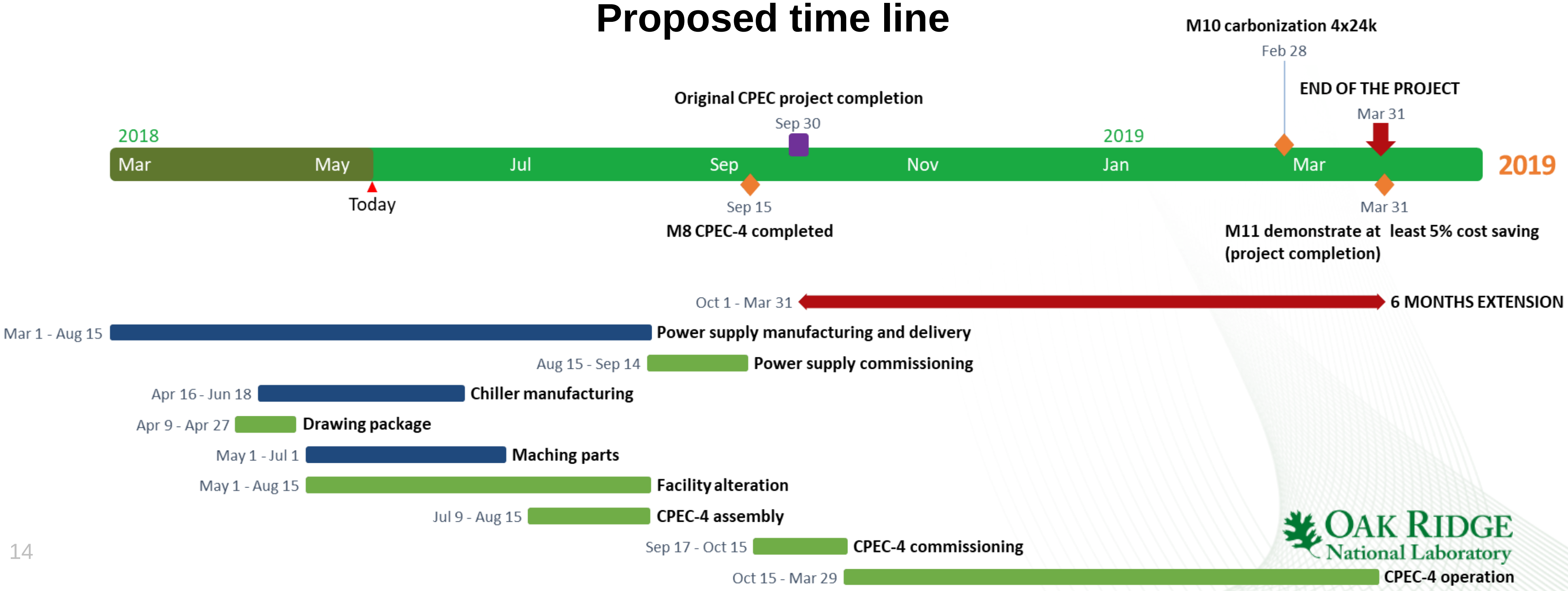
Budget FY17/FY18 reduction/delays and their impacts

- Budget cut: -10% on FY2017.
- Funding supply reduced and sparse over the period Jul.17 – Apr.18 (“Continuing Resolutions").
- Major project funding availability started again on Apr.5th, 2018.

→ Labor only over the Jul.17 – Apr.18 period (effort).
→ Budget uncertainty jeopardized purchase planning and construction:
  → Delay of all hardware purchases for CPEC-4.
  → Subsequent purchases for long lead time items creates further delays.

→ **An extension of the project at no cost has been requested.**

Proposed time line



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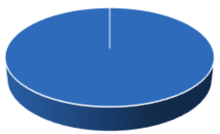
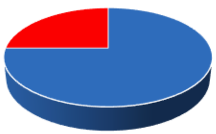
Response to Previous Year Reviewer's Comments

- Previous year scoring:





- Question 1

Approach to performing the work—the degree to which technical barriers are addressed, the project is well-designed, feasible, and integrated with other efforts.

- The practical steps to be pursued were more blurred [Due to Export Controlled (EC) policy.]
- how the technical challenges with respect to ensuring consistent properties (along and across the fiber) are addressed [This issue has been addressed with the elimination of the random arcing: Table 1 shows a relative good consistency in the mechanical properties of various samples, with similar process conditions, probed along a continuous tow of approximately 40m. Consistency across the tow will be explored in CPEC-4 with its wider processing width.]
- resistance along the strand varies from 76-ohms to 1295-ohms: [this was due to unstable and uncontrolled reactions at the time. Once stable operation is reached, these values become much more precise.]
- The reviewer noted that the team uses an average resistance to tune the energy source and as a result, the source frequency will be significantly off resonance for most of the fiber [An initial fiber state is considered in the modeling and during initial matching of the CPEC-3 device. CPEC-3 was manually tunable between operational runs. The CPEC-4 design will be able to respond to load changes during operation and will allow near real time active tuning, and will therefore not be "off resonance".]
- part of the fiber will heat up too much (melting was observed) or not heat enough [The feedstock of this process is already oxidized fiber which is an infusible thermoset and thus cannot melt. This engineering problem has been solved.]

Response to Previous Year Reviewer's Comments

- <u>Question 2</u>

Technical accomplishments and progress toward overall project and DOE goals—the degree to which progress has been made, measured against performance indicators and demonstrated progress towards DOE goals.

- difficult to judge from the property data presented if milestone 6 on fiber properties is likely to be achieved [M6 has been achieved.]
- The results, however, suggest scalability and demand follow up [Scalability is the purpose of CPEC-4, which is the next milestone.]
- the trend of increasing modulus […] suggests a level of risk (i.e., insufficient peak strain) [Results presented here show acceptable peak strain.]
- The technology may also be applied in the range of high-temperature carbonization represents additional cost reduction opportunities and must be further explored. [This effort will be proposed and may involve reactivation of the MAP. Alternatively, upgrades to CPEC-4 may allow full temperature range processing to carbonization.]
- the milestone claims stable processing of the fiber, but in the speaker's own words, there was melting of the fiber [The equipment was operating with stability but the material had nonlinear behavior which generated random electro-thermal events, e.g. arcing and plasma formation. This engineering problem has been solved. The material shows a visible, more homogeneous, and intense dielectric heating without arcing on a continuous run of 40-60 minutes.]

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Response to Previous Year Reviewer's Comments

- Question 3

Collaboration and coordination with other institutions.

- – it might be helpful to include collaboration with an academic institution to support material characterization or provide specific targets for material performance. [The generation of the materials property data was obtained thanks to the support of several departments at ORNL Additional partnership with Prof. Sokolov of both ORNL and UTK as well as Dr. Sangoro of UTK has been fruitful for material characterization. This data was required for the Computational Electromagnetic (CEM) modeling. Despite all this support, the evaluative instruments were not able to cover the full range of interest. Thus, some material properties such as permittivity were extrapolated to required operational parameters. At this time, additional characterization of the material is not a high priority of this project – this might be the object of a subsequent proposal.]
- – more partners (such as OEMs, composite manufacturers) should be sought [The ideal partner for this project is a carbon fiber manufacturer that would integrate this technology in their production lines. Possibly 4M Carbon Fiber, with its established relationship with RMX, has the potential to become another partner.]
- – lack of collaboration with a partner that can quantify the efficiency and losses of the conventional process for the low temperature carbonization stage. [This will be a future step at the end or after finalization of this project. ORNL could be a candidate through its CFTF facility, as well as 4M Carbon Fiber.]

Response to Previous Year Reviewer's Comments

- Question 4

Proposed future research—the degree to which the project has effectively planned its future work in a logical manner by incorporating appropriate decision points, considering barriers to the realization of the proposed technology and, when sensible, mitigating risk by providing alternate development pathways.

- The reviewer asked (1) what is causing the temperature spikes that cause melting and (2) how is the efficiency of the electrical system being measured. [(1) The temperature spikes have been resolved. (2) CPEC-3 was too small of a device for accurate energy efficiency measurements. With CPEC-4, the efficiency will be measured by recording the overall power consumption (and thus energy over time) divided by fiber throughput. This "unit energy" measurement will be the basis for comparison to the conventional process].
- that an explicit target based upon properties of fiber produced with conventional thermal processes would be useful [The main goal of the project is to produce fully carbonized fiber with mechanical properties that achieve milestone commitments while using the CPEC technology instead a conventional setup for LTC. It is agreed with the reviewer that the final mechanical properties are not sufficient to fully track the efficiency of the process. Because LTC fiber corresponds to an in-between stage in the overall process of conversion, the LTC-"carbon fiber" is not a final product and is not commercially available. Neither it nor its properties are available/obtainable from industry. To circumvent this lack of data from the industry, ORNL generated its own dataset of partially carbonized fiber with its conventional pilot line and its characterization equipment using the same feedstock material (industrial PAN oxidized fiber) that is used to feed the CPEC-3 setup. These fibers were evaluated for their density, their electrical resistivity, and their mechanical properties. This data was presented in last year's AMR and is included again in the technical backup in this presentation. Based on this data, a comparison can be established between CPEC production and conventional carbonized fiber.
  For this reason, only fully carbonized fiber mechanical property goals were set in the milestones of the program. Later on, morphological evaluations will be undertaken to compare resulting morphologies of the carbon fibers produced by these two conversion processes.]

Response to Previous Year Reviewer's Comments

- Question 4 (continuation)

  - a complete cost model that provides detail on the opportunity for cost reduction in terms of dollars per kilogram would be very useful to assess value of work [The economic evaluation is the final milestone of this project]
  - not clear if the technology can provide consistent fiber properties across the tow, across the fiber cross section, and along the fiber length [Fiber consistency is a main goal and challenge of this effort. The lack of consistency has been addressed in CPEC-3 with the removal of the random arcing: Table 1 shows a relative good consistency in the mechanical properties of various samples, with similar process conditions, probed along a continuous tow of approximately 40m. Since the arcing has been eliminated, CPEC-3 has been able to demonstrate homogeneous production. The homogeneity of the resulting mechanical properties is checked by randomly testing several filaments across the section. Consistency across the tow will be explored in CPEC-4 with its wider processing width. The main challenge is combining the thermal processing effect from electromagnetic coupling with motional averaging to produce thermally uniform treatment on the tow band both widthwise and lengthwise. As the reviewer recognized, this is a great challenge. The design of CPEC-4 has been completed with this in mind. Finally, the CPEC-4 power supplies have the ability to actively respond to changes in fiber processing parameters (the CPEC-3 power supply did not have this ability), which will improve the consistency of the process.]
  - In addition, the reviewer said that the future research does not explain how these consistent properties can be obtained with the current technology when scaled-up [See our answer above.]

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Response to Previous Year Reviewer's Comments

- Question 5

Relevance—Does this project support the overall DOE objectives of petroleum displacement?

  - with no OEM or composites manufacture present as partners, the project may not have a sharp focus [At this moment, the project is focused on the concept/feasibility (currently low Technology Readiness Level – TRL 3-4). This is too early for OEMs to be involved. OEMs utilize fiber that typically has been obtained from a bulk supplier and impregnated with some material to produce a product with woven fiber and some type of binder. The technology readiness level is not at the point to include end users. Potentially better partners for the CPEC technology could be carbon fiber manufacturers. Eventually as this technology matures, OEM will develop long term interest.]

- Question 6

Resources—How sufficient are the resources for the project to achieve the stated milestones in a timely fashion?

  - the team does not have enough details on the expected properties or process of the commercial low-temperature carbonization process [Answer to this statement was already elaborated for ***Question 4 section 2*** (slide 19), additional material is available in the technical backup (slide 28)]

Collaboration and Coordination with Other Institutions (additional to ORNL)

- RMX Technologies is a sub to ORNL.
  - Provides electrical engineering/plasma expertise.
  - RMX Technologies has previously partnered with ORNL to successfully develop plasma oxidation technology that is now being commercialized.
  - This same ORNL/RMX partnership is involved with the current project.
- 4M Carbon Fiber Corp. is utilizing technology created by RMX and ORNL to manufacture carbon fiber. Will utilize/commercialize this technology as it matures.
  - 4M became a public company in early 2017
- C.A. Litzler & Co., Inc. is RMX's oven manufacturing partner. Will be involved in commercialization at conclusion of project.

Remaining Challenges and Barriers

- Demonstrate safe levels of radiation in immediate local environment during operation.
- Enact a control system that monitors and reacts to:
  - Local area electromagnetic radiation levels.
  - Exhaust and flow controls within all stages.
  - Monitor and ensure low oxygen levels.
  - Vessel temperature monitoring and control.
  - Near real-time radiation response to material morphology.
- Ensure proper full scale operation of CPEC-4 as predicted with acceptable uniformity width-wise.

Proposed Future Research

Any proposed future work is subject to change based on funding levels.

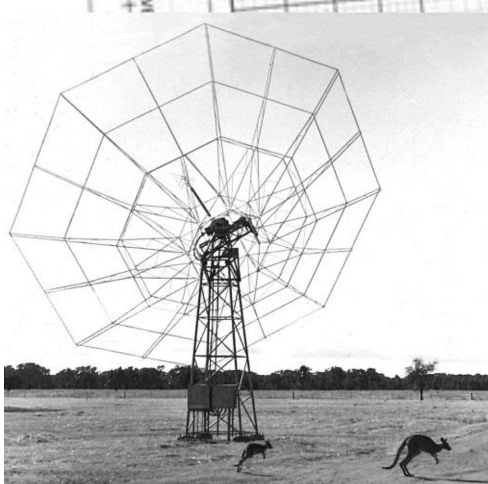
- FY18/FY19
  - Design and build the CPEC-4 furnace, a 1 ton low temperature carbonization furnace.
  - Operate CPEC-4 furnace and produce carbon fiber exceeding required mechanical properties.
  - Match or exceed power saving milestone requirements.
  - Economic evaluation of CPEC-4 process.
  - Propose follow-on research for a comprehensive solution for full carbonization process based on CPEC technology.

Summary

- A CPEC furnace was successfully modeled and built based upon material characterization.
- CPEC-3 can produce fiber with properties exceeding those obtained from conventional Low Temperature Carbonization (LTC).
- CPEC-4 fully modeled with tunable and accessible design.

Thank You

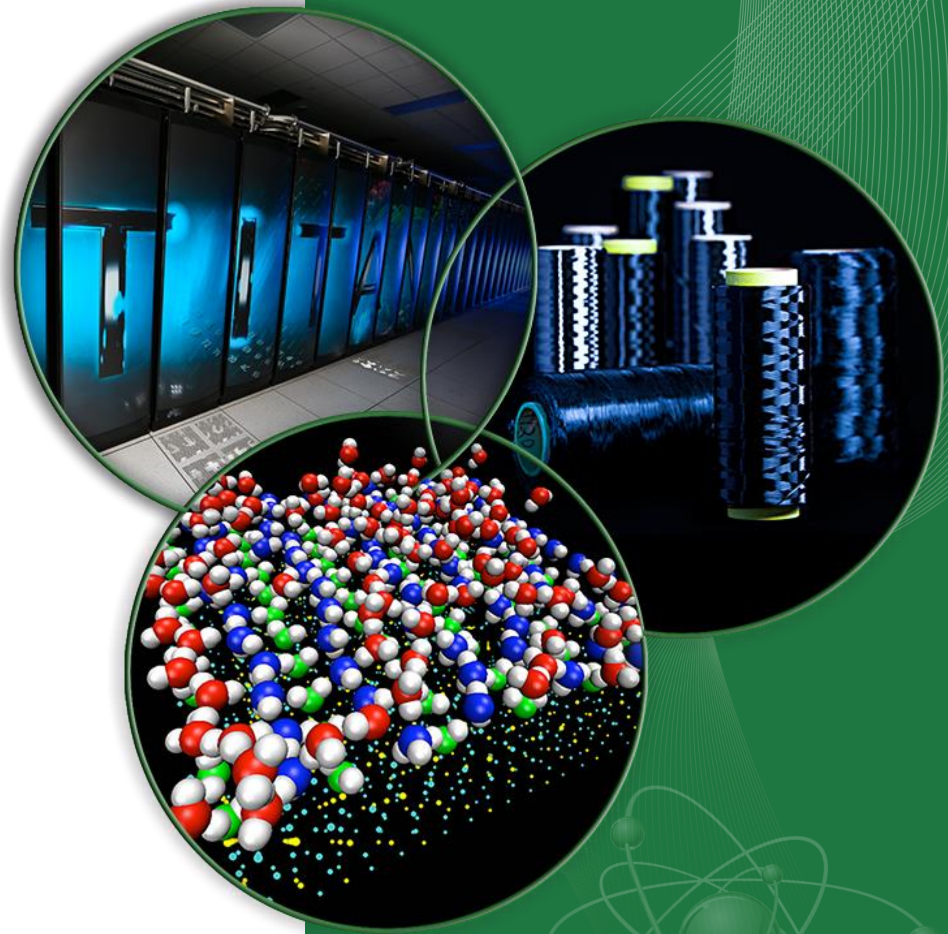
- THANK YOU for your attention



Hans Christian Ørsted
14 August 1777 – 9 March 1851

QUESTIONS?

Backup



Technical Backup

Tables of reference for process evaluation

Temperature, C	Density, g/cc
500	1.48
550	1.51
600	1.54
650	1.56
700	1.60
750	>1.60

Temperature vs. density of conventionally processed carbon fiber at ORNL.

Mechanical Properties of <u>Partially</u> Carbonized Fiber.

Sample	Temperature [C]	Diameter [µm]	Peak stress [ksi]	Modulus [Mpsi]	Strain peak stress [%]
CPEC-3_0035	EM	8.95	162.4	11.54	1.29
Sample A	300	13.52	29.2	1.05	21.62
Sample B	400	12.01	21	0.98	4.22
Sample C	500	11.45	40.1	1.35	7.45
Sample D	600	11	72.8	2.58	3.95
Sample E	700	10.69	117.3	5.52	2.03
Sample F	800	9.76	176.7	9.53	1.76
Sample G	900	9.87	108.3	12.32	1.37
Sample H	1000	8.8	208.4	16.25	1.18
Sample I	1100	9.07	308.6	21.05	1.33
Sample J	1200	8.77	329.2	21.99	1.36

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