U.S. Coal to Conductive Inks

DE-SC0018694

Minus 100

- Speaker: James G. Hnat, Ph.D.
- Organization: Minus 100, LLC

- Project Primary Investigators
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U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
October 25 - 27, 2022

Project Overview

Funding & Performance Dates

Date	Activity	DOE Funding Level
2-Jul-2018	Phase I Effective Project Start	$ 224,813
7-Dec-2018	DOE Project Review Mtg	
1-Apr-2019	Phase I End Date	
30-Apr-2019	Phase I Final Report	
19-Aug-2019	Phase II Effective Project Start	$ 1,549,676
20-Oct-20	DOE Project Review Mtg	
28-Apr-21	DOE Project Review Mtg (virtual)	
18-Aug-2021	Phase II End Date	
17-Sep-2021	Phase II Final Report	
27-Aug-2021	Phase IIA Effective Project Start	$ 1,149,896
27-Oct-2022	DOE Project Review Mtg	
26-Aug-2023	Phase IIA End Date	
27-Oct-2023	DOE Project Review Mtg (assumed date)	
26-Dec-2023	Phase IIA Final Report	
	Total DOE Funding to Date	**$ 2,924,385**

Project Participants

- Ink Solutions LLC
- Several Major Ink Manufacturers
  - NDAs prevent their name disclosure
- Asbury Carbons Corporation
- Faraday Technologies, Inc.
- Butler Technologies, Inc.
- Jeddo Coal Co.
- Pennsylvania State University
- NAC Carbons

Minus 100, LLC Technical Objectives & Goals

Phase I

- Evaluate the use of anthracite coal for the production of electrically conductive inks
- Goal to achieve printed ink sheet resistivity < 1000 ohm/sq/mil
- Developed 3 electrically conductive pigments and 3 water-based ink formulations
- Phase I goal was achieved for all three pigments

Phases II & IIA

- Evaluate the use of bituminous coal-derived feedstocks for the production of electrically conductive inks
- Goal to achieve printed ink sheet resistivity < 100 ohm/sq/mil
- Phase II & IIA goals were achieved
- Current resistivities < 10 ohm/sq/mil
- Pursuing commercial implementation of coal-based thermal heating assemblies

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Technology Development Challenges & Solutions

Challenges

- Coal is an amorphous carbon that is naturally non-conductive
- Particle size and morphology are critical process requirements
- Ink Industry is very fragmented and niche ink formulations are based on the specific printing method used and the substrate upon which the ink is printed
- Typical printing methods include: gravure, flexographic, offset/lithographic, screen, & digital
- Typical substrates include: paper, cardboard, wood, metal, ceramics, plastics & composites
- Each printing method/substrate has its own set of design requirements, pigment size is a critical quality requirement.
- Electrically conductive inks are a specialty subset of the spectrum of the ink formulations

Solution

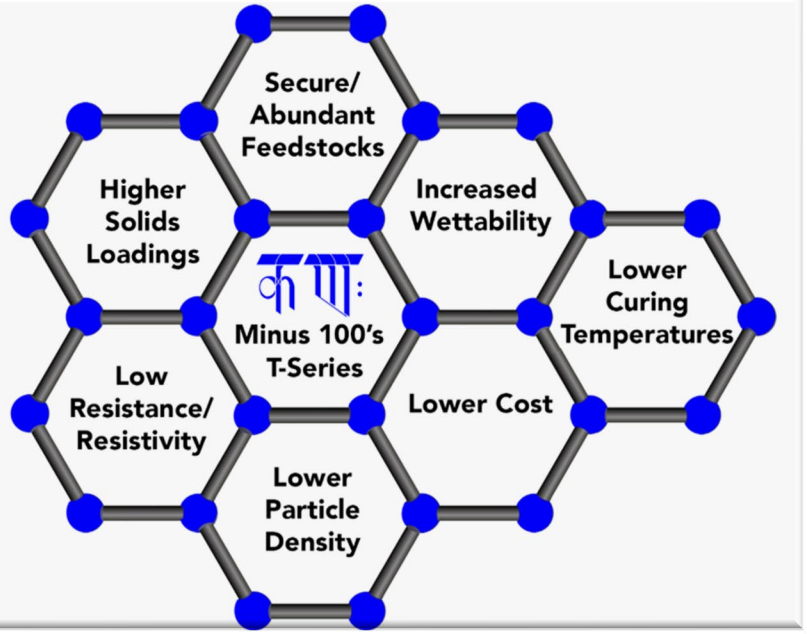
- Previous PSU work sponsored by DOE served as point of departure for the development of conductive pigments
- Focus on selected printing methods (screen, digital and flexographic)
- Utilize a spectrum of technologies to develop suitable/improved processes for printing on selected substrates (paper & plastic substrates)
- Improve & scale-up comminution & classification processes for the production of micron and nano-size pigments (0.02-30 µm)
- Continue Development of proprietary technology for the thermo-chemical processing of coal-based feedstock
- Develop/Improve Ink and suspension dispersions

Project Purpose/Objectives & Minus 100 Value Proposition

Project Objectives

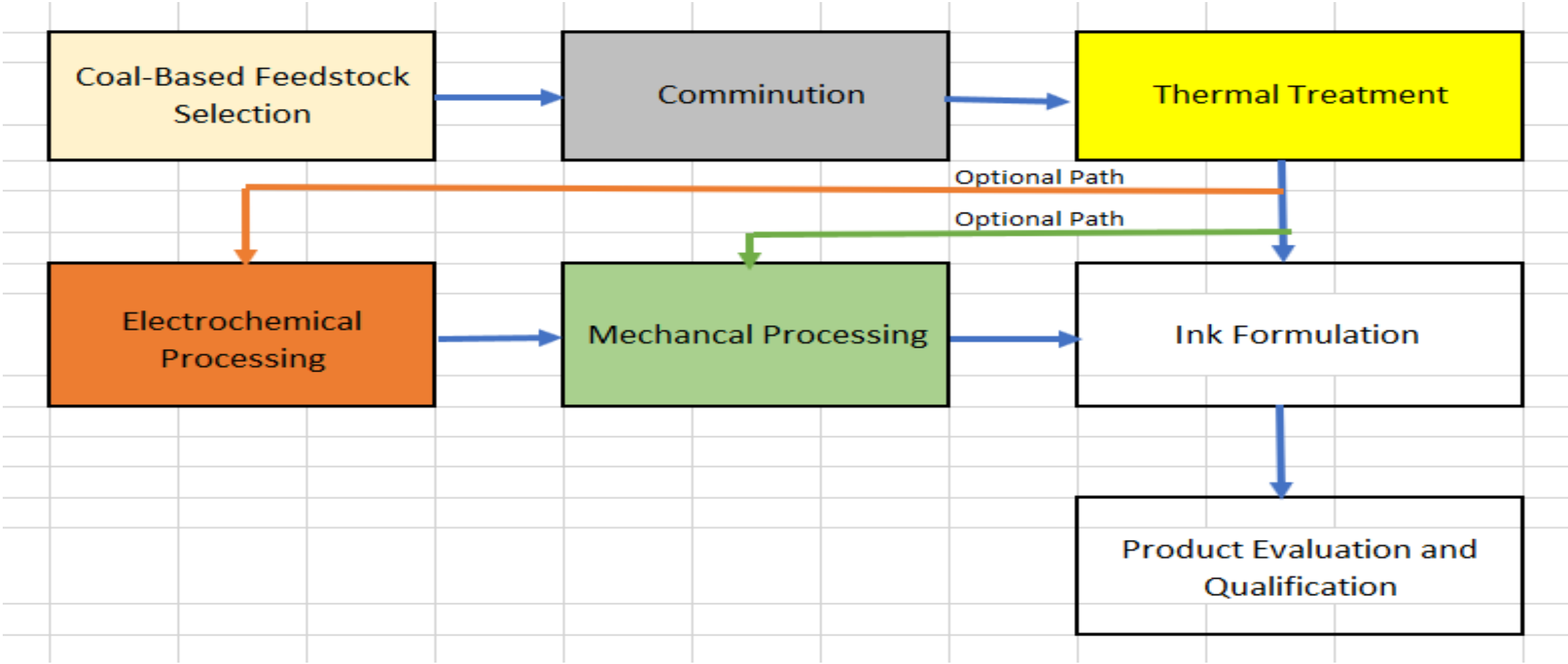
- Increase use of U.S. coal utilization through the development of technologies that produce value-added products that use U.S. Coal Supplies as a primary feedstock
- Focus on the development of electrically conductive pigments/inks

Minus 100, LLC Product Advantages



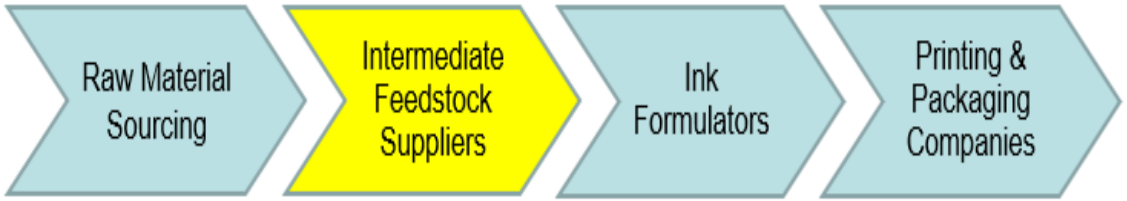
Technology/Product Development Approach

Integration of commercially Available Technology with Advanced Processing Systems



Printing Value Chain & Important ink Processing Parameters

Minus 100 Position within the Printing Value Chain



Typically Mined Materials, Domestic Raw Material Supply Eliminates Reliance on Uncertain Global Conditions	Pigments/Suspensions Base Vehicles & Additives (e.g., Binders, Coatings, Preservatives, Dispersants, Curing Agents)	Formulates Inks in Accordance with Printing Method Utilized and Substrate to be Utilized Paper & Cardboard Plastic & Metals	Lithographic Printing Flexographic Printing Gravure Printing Screen Printing Inkjet Ink Printing

Important Performance Parameters of Conductive Carbon Pigments Inks

Pigment Properties

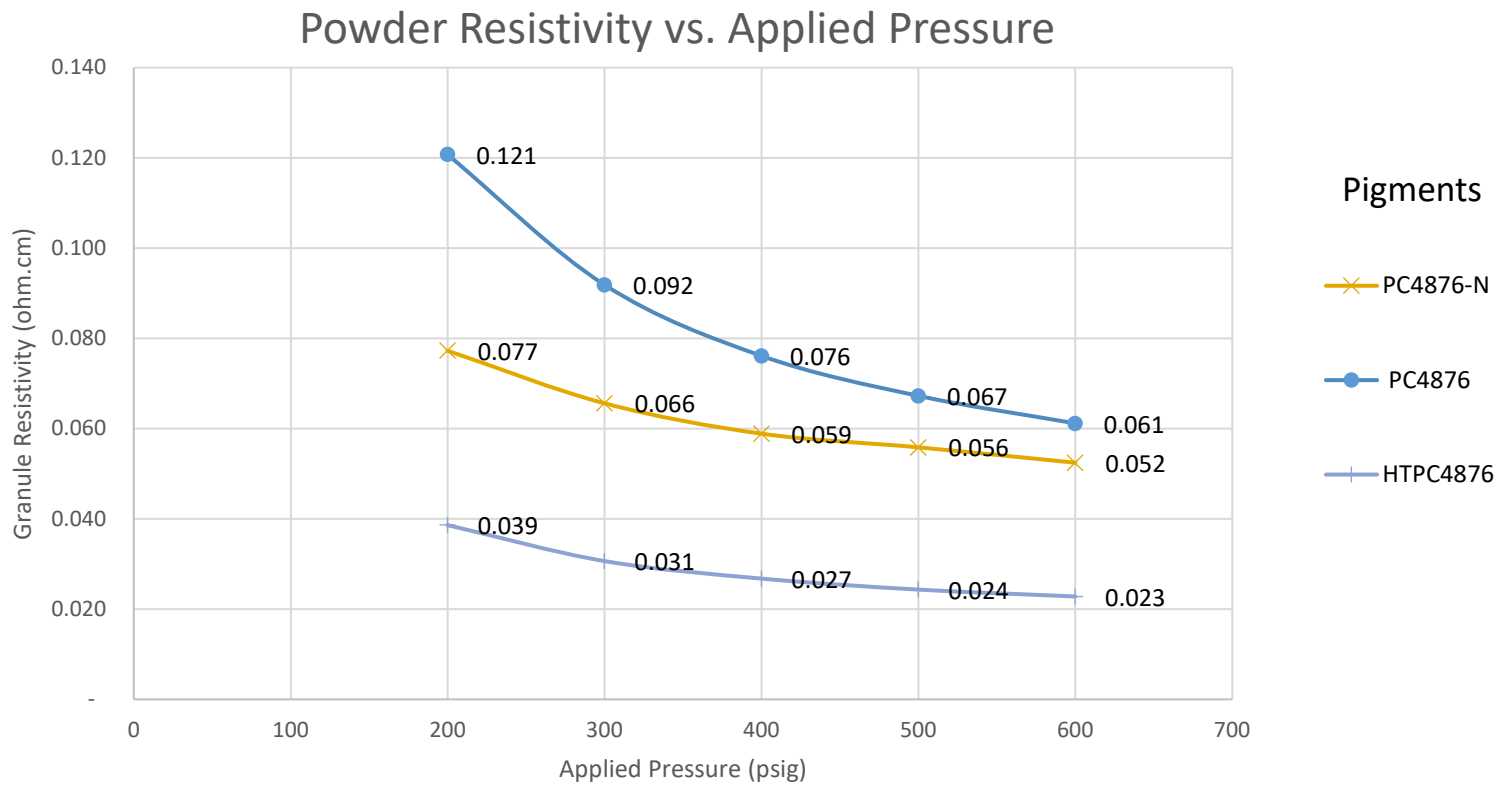
- Powder Resistivity (ohm-cm)
- Particle Size (µm)
- Surface Area (m2/g)
- Density (g/cc)

Ink Properties

- Sheet/Volume Resistivity (ohm/sq), (ohm/sq/mil)
- Viscosity (Pa·s)
- Surface Tension (dyne/cm)
- Substrate Surface Energy & Surface Adhesion
- Curing/Drying Rate & Temperature
- Abrasion Resistance
- Flexibility
- Color/Transparency
- Toxicity

Technology/Product Development Approach

Typical Powder Resistivity Measurement Results



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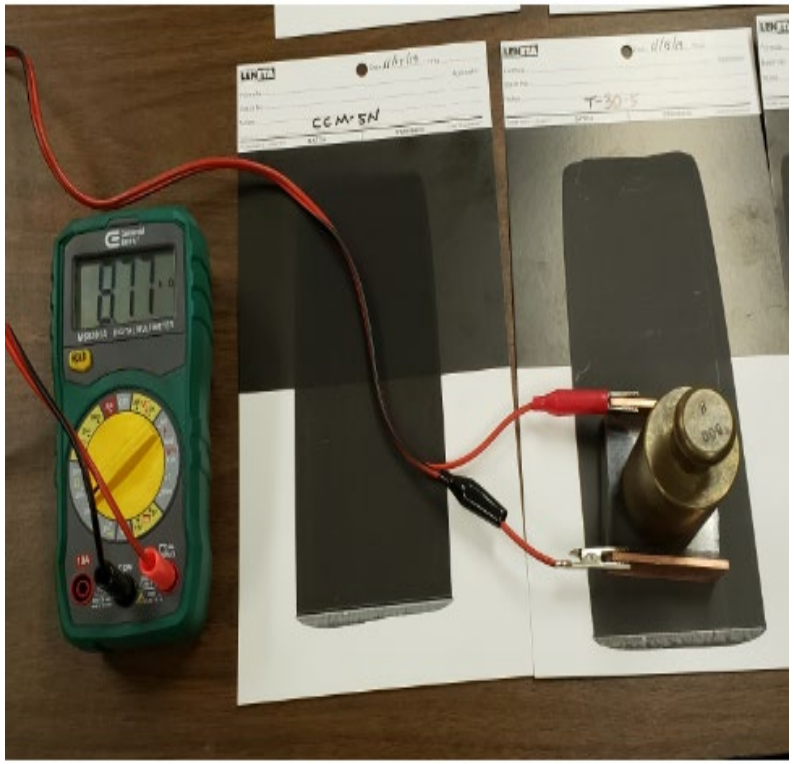
Technology/Product Development Approach

Ink Resistivity Measurements

Draw Down with a Mayer Rod



Measurement of Square Resistance

Measurement of Ink Film Thickness

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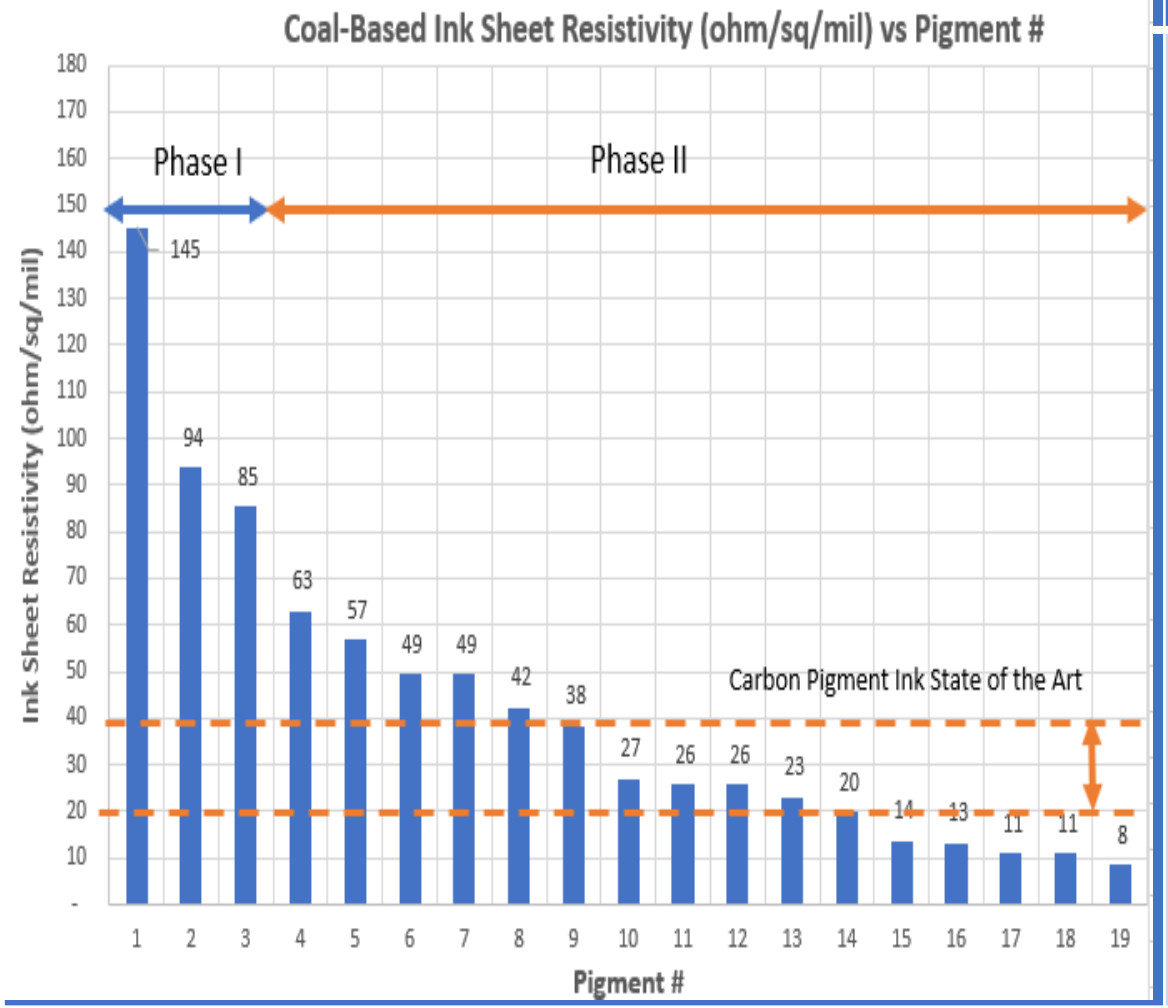
Technical & Commercialization Accomplishments

Technical Accomplishments/Activities

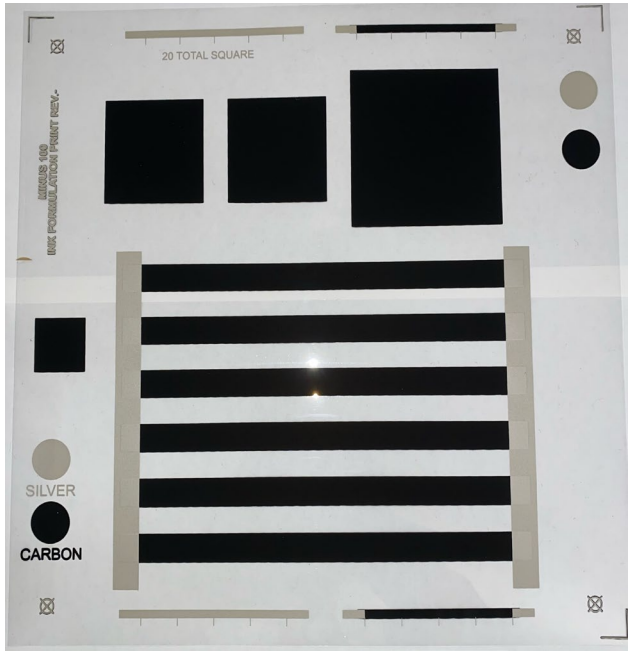


Commercialization Activities

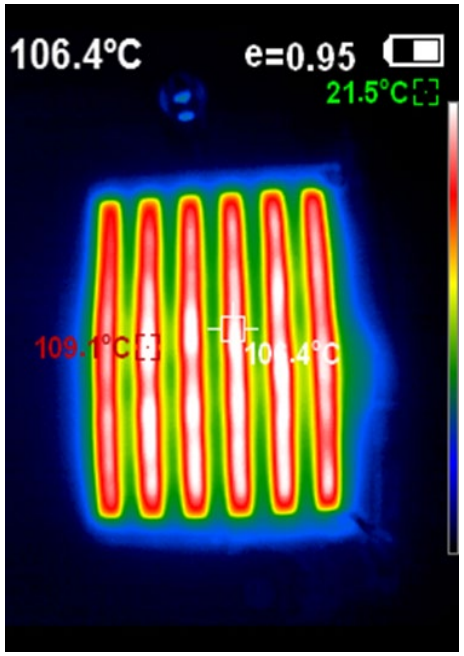
- Accomplished Phase II & IIA Objective of ≤ 100 ohm/sq/mil
- Ink Manufacturers/Printers are Evaluating Coal-Based Pigment & Ink Suspensions for Conductive Ink Applications
- Working Toward Qualification of our Pigments/Suspensions for Specific Commercial Applications (Floor & Wall Panel Heating) via Testing with Lab-scale & Commercial-scale Proto-type Heating Element Assemblies
- Working with Commercial Screen Printer to Evaluate & Scale-up Heating Element Assembly Designs
- Developing Lower Resistivity Pigments/Suspensions to Expand the Application Scope of our Coal-Based Pigments/Suspensions

Resistive Heating Element Application

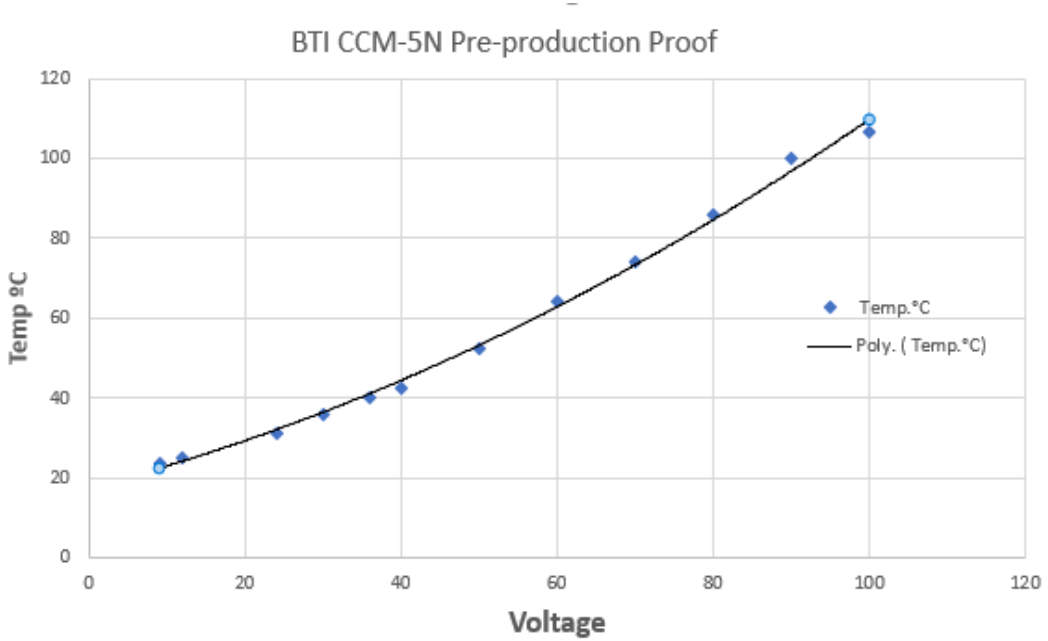
Carbon-Based Heating Element Laboratory Pre-Production Proof



Screen Printed Proof Utilizing CCM-5N Pigment From Minus 100 LLC. In a Commercial Grade Screen Ink.



Thermographic Image of Pre-Production Proof
Heating Assembly



Thermoprofile of Pre-Production Proof Heating Element Assembly

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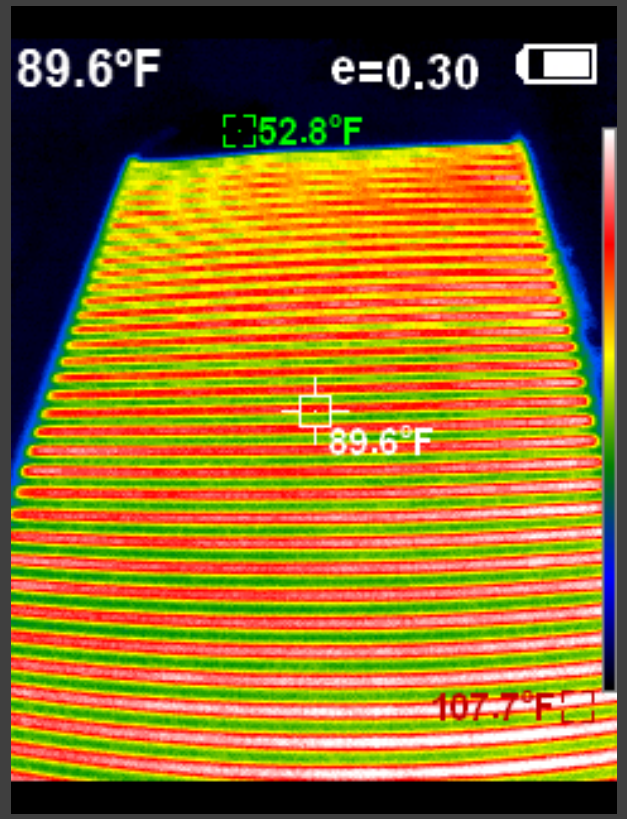
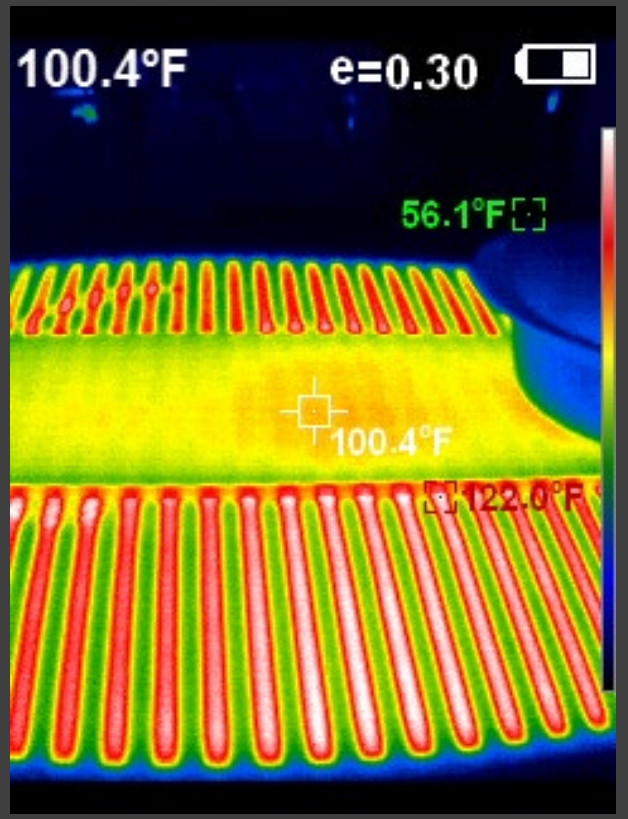
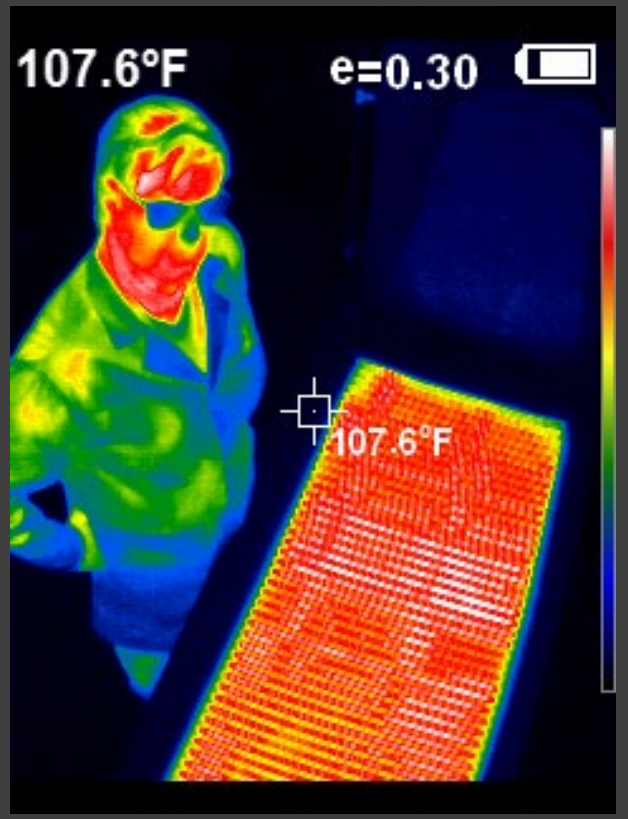
Minus 100 Underfloor Fully Printed Heating Element.



120v Underfloor Heating Element



Shown with section of Laminate Flooring To demonstrate Heating Potential. Floor temp. 100°F



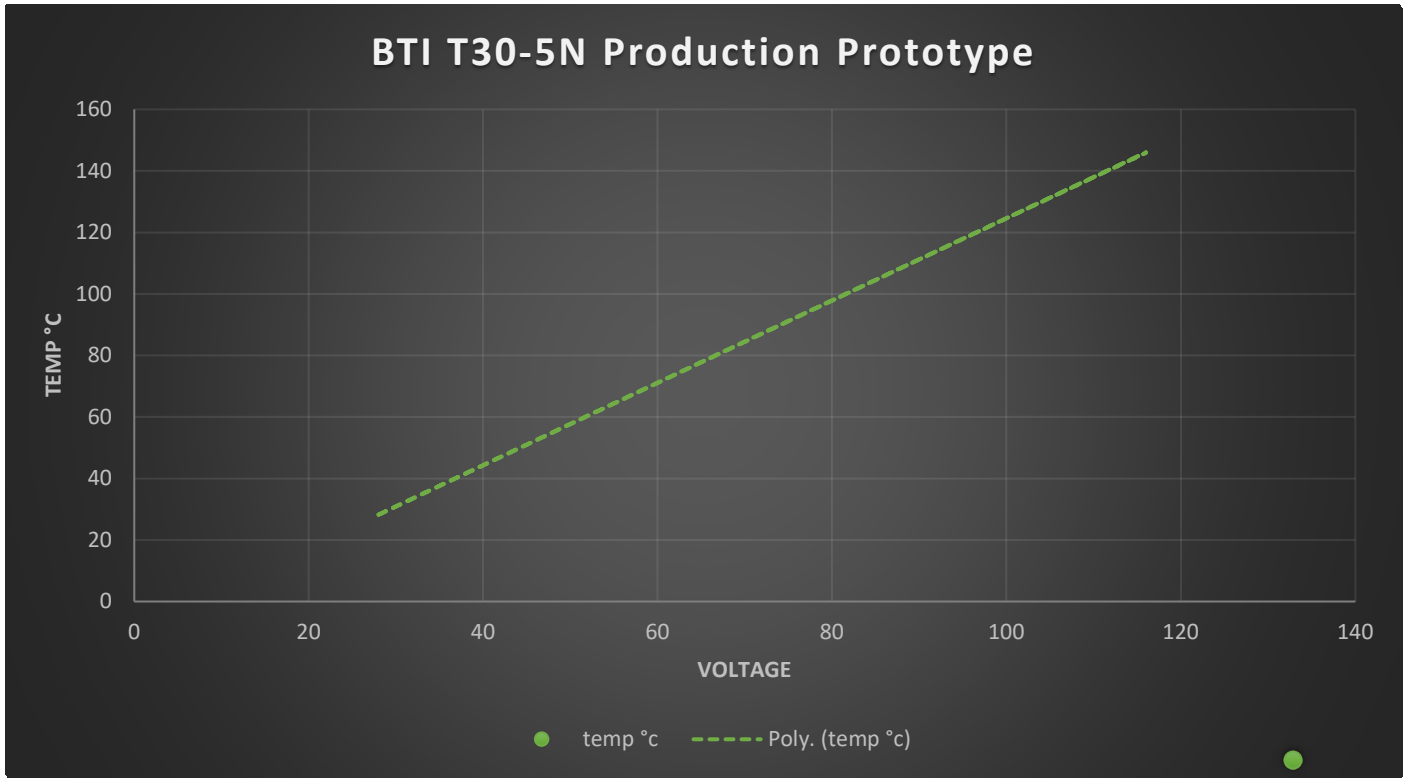
Same Heating Element with proprietary underfloor heat shield

Prototypes undergoing extensive testing with a variety of insulating systems.

Commercial Scale Coal-based Heating Panel (Testing/Qualification)

Prototype of 2’ x 4’ Commercial-Scale Wall Heating Panel

Thermal Profile vs Applied Voltage of Prototype Wall Heating Panel



Minus 100 Series 1 Wall Panel Fully Printed Wall Heating Element

Power Control Panel

Raised the temperature in a 2762 ft^3 10° F in 20 minutes.

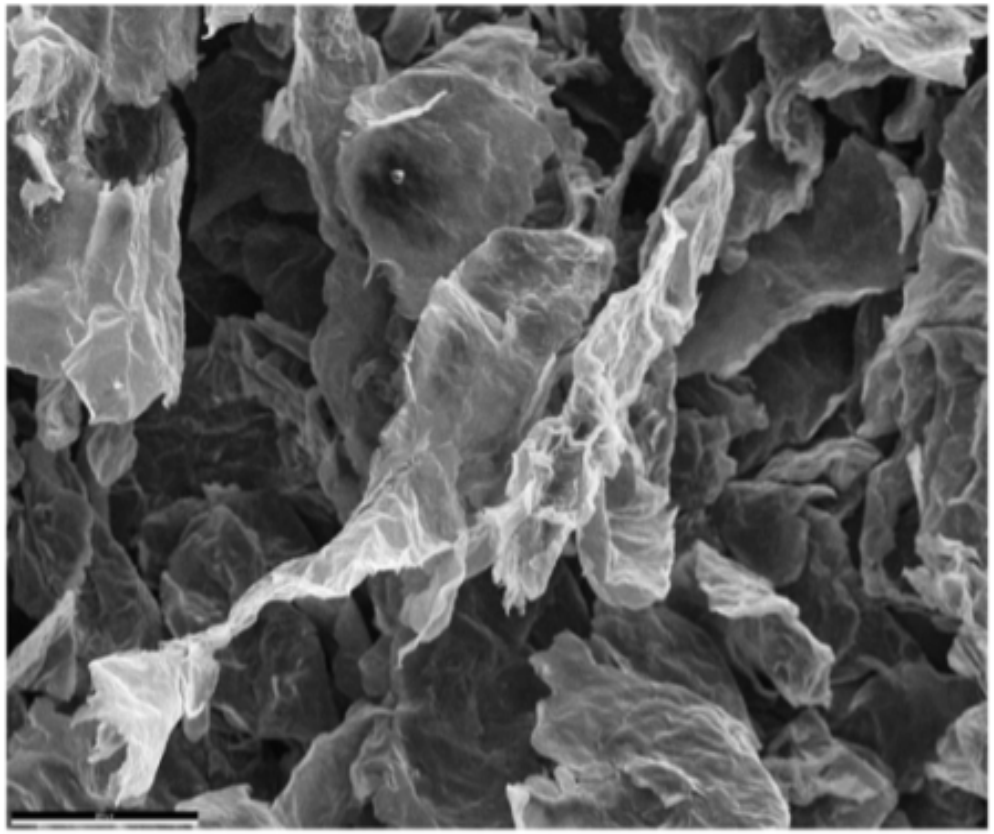
Minus 100 Proprietary Thermal Treatment Process

- Elevated temperatures enhance the electrical conductivity of coal-based feedstocks.
- Minus 100, LLC has developed a novel high temperature process for converting coal-based feedstocks into electrically conductive materials.
- This process is suitable for the production of synthetic graphite, a strategic material, from coal-based feedstocks
- Patent application restrictions preclude disclosure of details

Electrochemical Processing Development

Lab-Scale Electrochemical Testing

SEM of Intercalated & Exfoliated Graphite Foil



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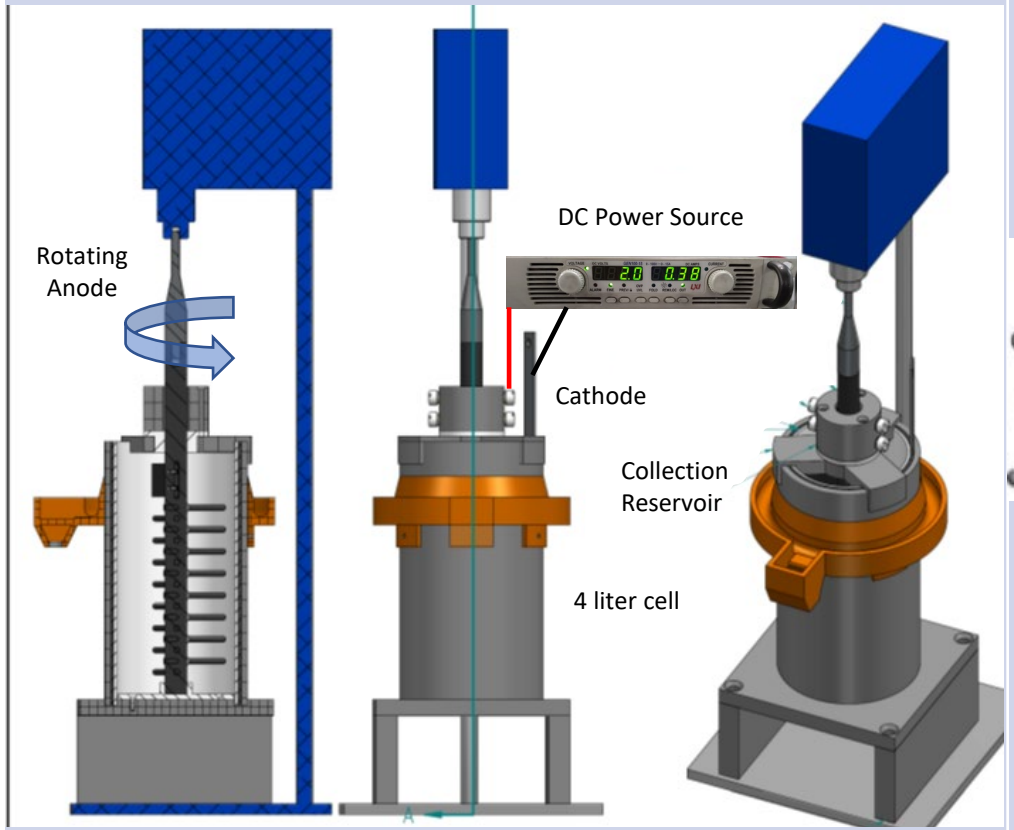
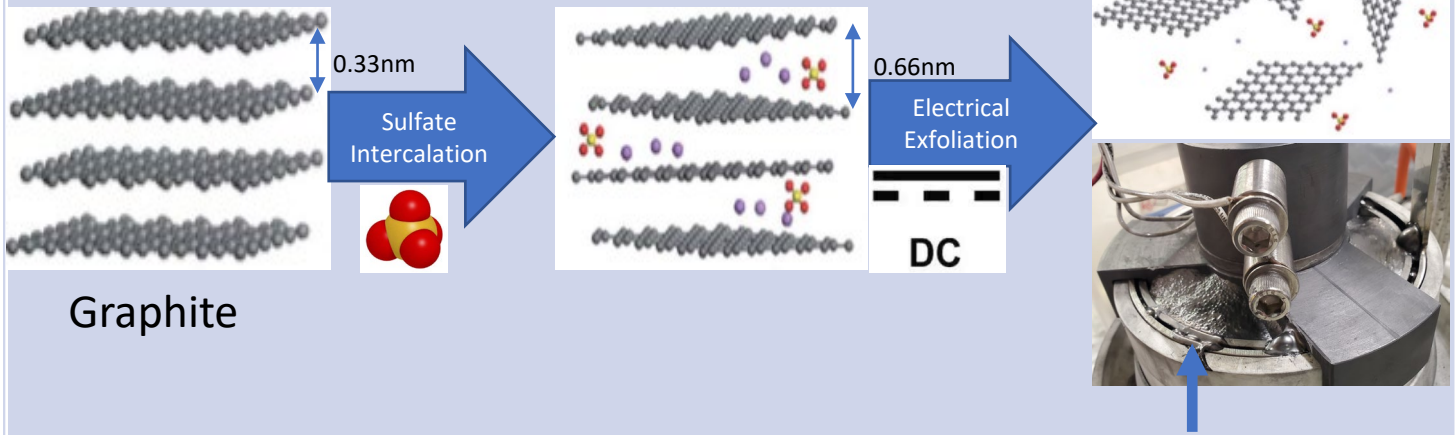
Pilot-Scale Assembly for Exfoliation of Graphite Flakes

Description of Rotary Electro-Chemical Reactor (ECR) Assembly

Electrochemical Reactor for Processing Carbon Powders (Faraday Technologies, Inc.)



Intercalation-Exfoliation Mechanism



Bench-Scale ECR & Typical Results

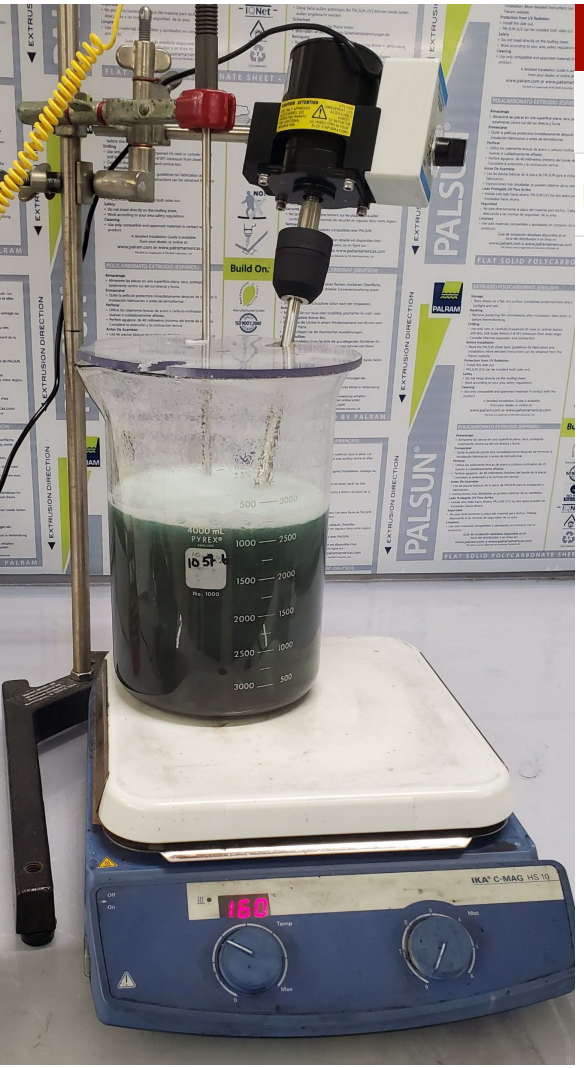
Photo of ECR Assembly During Test

Powder Resistivity Results with Exfoliated Graphite Platelets (ohm.cm)

- Exfoliated Graphite was dried and made into a powder,
- No Significant Improvements in powder electrical resistivity resulted from the ECR Trials with coal-based feedstocks

Hybrid Metal/Carbon Pigment/Ink Development

Metallization of Coal-Based Pigments via Electroless Nickel Plating



Property / Level of alloy	High[a]	Mid[a]	Mid-Low[a]	Low[a]	
% Phosphorous	10 - 13	7 - 9	4 - 6	1 - 3	
Electrical resistivity[h]	75 - 110	40 - 70	15 - 45	10 - 30	uOHM-CM

$$2Ni^{2+} + 8H_2PO^-_2 + 2H_2O \rightarrow 2Ni_0\,(s) + 6H_2PO^-_3 + 2H^+ + 2P\,(s) + 3H_2\,(g)$$

- <u>Stage I</u>
- 5µm coal based conductive particles were successfully coated with nickel alloy.
- Lowers overall weight and cost compared to silver.
- <u>Stage II</u>
- NiP alloy coating with targeted resistivity 15-45 µohm-cm range

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Hybrid Carbon/Metal Pigment/Suspension Development

(All-Carbon Pigment (CM5) vs Nickel/Carbon Pigment (CM5-Ni))

Typical PSD Test Results CM5-Ni

Microtrac — Total Solutions in Particle Characterization

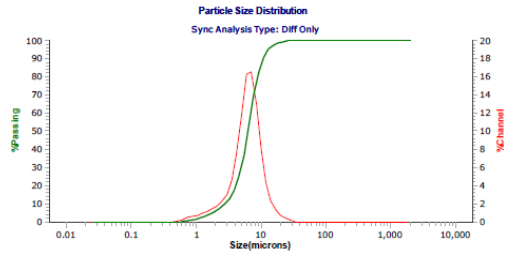
- Particle Size Analysis -

C:\Microtrac\FLEX 12.0.0.1\Databases\Coatings.MDB

Tabular Data

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
2000	0.00	100.00	3.89	4.61	17.38
1674	0.00	100.00	3.27	3.05	12.77
1408	0.00	100.00	2.750	2.23	9.72
1184	0.00	100.00	2.313	1.77	7.49
995.6	0.00	100.00	1.945	1.44	5.72
837.2	0.00	100.00	1.635	1.16	4.28
704.0	0.00	100.00	1.375	0.93	3.12
592.0	0.00	100.00	1.156	0.73	2.19
497.8	0.00	100.00	0.972	0.58	1.46
418.6	0.00	100.00	0.818	0.48	0.88
352.0	0.00	100.00	0.688	0.28	0.40
296.0	0.00	100.00	0.578	0.12	0.12
248.9	0.00	100.00	0.486	0.00	0.00
209.3	0.00	100.00	0.409	0.00	0.00
176.0	0.00	100.00	0.344	0.00	0.00
148.0	0.00	100.00	0.2890	0.00	0.00
124.5	0.00	100.00	0.2430	0.00	0.00
104.7	0.00	100.00	0.2040	0.00	0.00
88.00	0.00	100.00	0.1720	0.00	0.00
74.00	0.00	100.00	0.1450	0.00	0.00
62.23	0.00	100.00	0.1220	0.00	0.00
52.33	0.00	100.00	0.1020	0.00	0.00
44.00	0.00	100.00	0.0860	0.00	0.00
37.00	0.00	100.00	0.0720	0.00	0.00
31.11	0.21	100.00	0.0610	0.00	0.00
26.16	0.46	99.79	0.0510	0.00	0.00
22.00	0.73	99.33	0.0430	0.00	0.00
18.50	1.26	98.60	0.0360	0.00	0.00
15.56	2.31	97.34	0.0300	0.00	0.00
13.08	4.36	95.03	0.02550	0.00	0.00
11.00	7.98	90.67			
9.25	12.90	82.69			
7.78	16.56	69.79			
6.54	16.24	53.23			
5.50	12.05	36.99			
4.63	7.56	24.94			

WARNING: NONE



Measurement Info

Title	
CCM5-Ni	
Identifiers	
0920E-01	
-	
Database Record	240
Run Number	Avg of 3
Date	9/21/2022
Time	9:09 AM
Acquired Date	9/21/2022
Acquired Time	9:09 AM
Serial Number	H0065
Sample Cell ID	20063
Calculated Data	
Above Residual	0
Below Residual	0
Loading Factor	0.0248
Transmission	0.949
RMS Residual	0.731%
Calc SW Ver	12.0.0.1
User Defined Calculations	
Name	Value
Recalculation Status	
DB-Meas : : Original :	

SOP Info

CCM-5(*)	
Timing	
Setzero Time	30 (sec)
Run Time	30 (sec)
Number of Runs	3
Multi-Run Delay	0 (min)
Delay First Meas.	Disabled
Analysis	
CCM-5	
Refractive Index	N/A
Transparency	Absorb
Shape	Irregular
WATER	
Refractive Index	1.33
Options:	
Filter	Enabled
Analysis Gain	Default(2)
Analysis Mode	3R/Img L
Analysis Type	Diff Only
Img Cor File:	Default
Perspective	
Progression	Geom 4 Root
Distribution	Volume
Upper Edge(um)	2000
Lower Edge(um)	0.0215
Residuals	Disabled

Summary

Data	Value
MV(um):	6.78
MN(um):	1.300
MA(um):	4.73
CS:	1.269
SD:	2.876
Mz:	6.51
si:	3.15
Ski:	0.1439
Kg:	1.265

Percentiles

%Tile	Size(um)
10.00	2.801
20.00	4.17
30.00	5.01
40.00	5.69
50.00	6.33
60.00	7.01
70.00	7.80
80.00	8.87
90.00	10.80
95.00	13.06

Peaks Summary

Dia(um)	Vol%	Width
6.33	100	5.75

FLEX
12.0.0.1

9/21/2022 12:21 PM

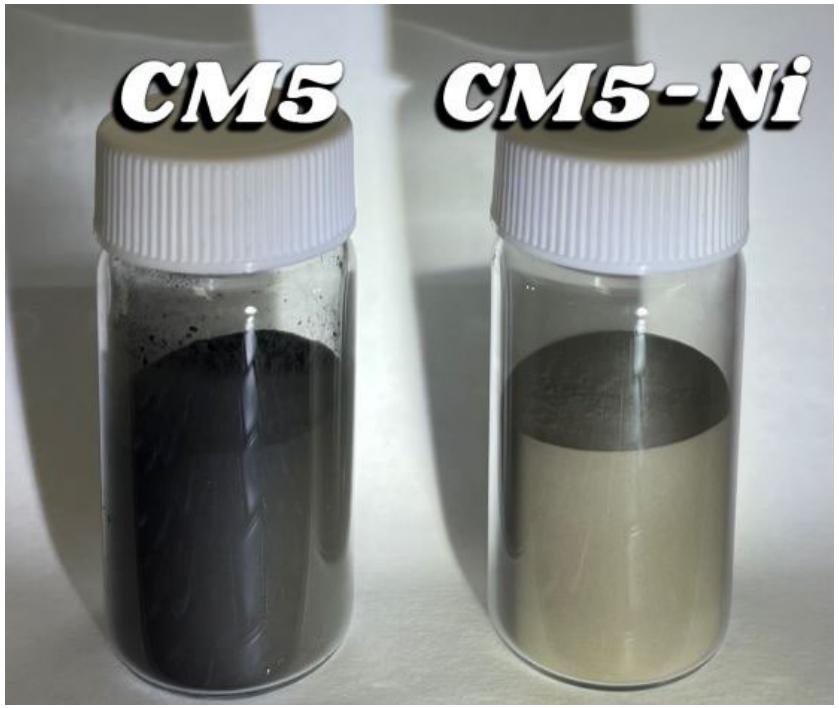
Notes

-0225D-3.2N-2

Sample System(Wet)	
Number of Rinses	4
Flow Rate (%)	50%
Deaeration Cycles	3

Comparative Results

- Nickel coating of 5micron coal-based pigments results in significant reduction in powder resistivity.
- Development of electroless coating of coal-based particles will continue.



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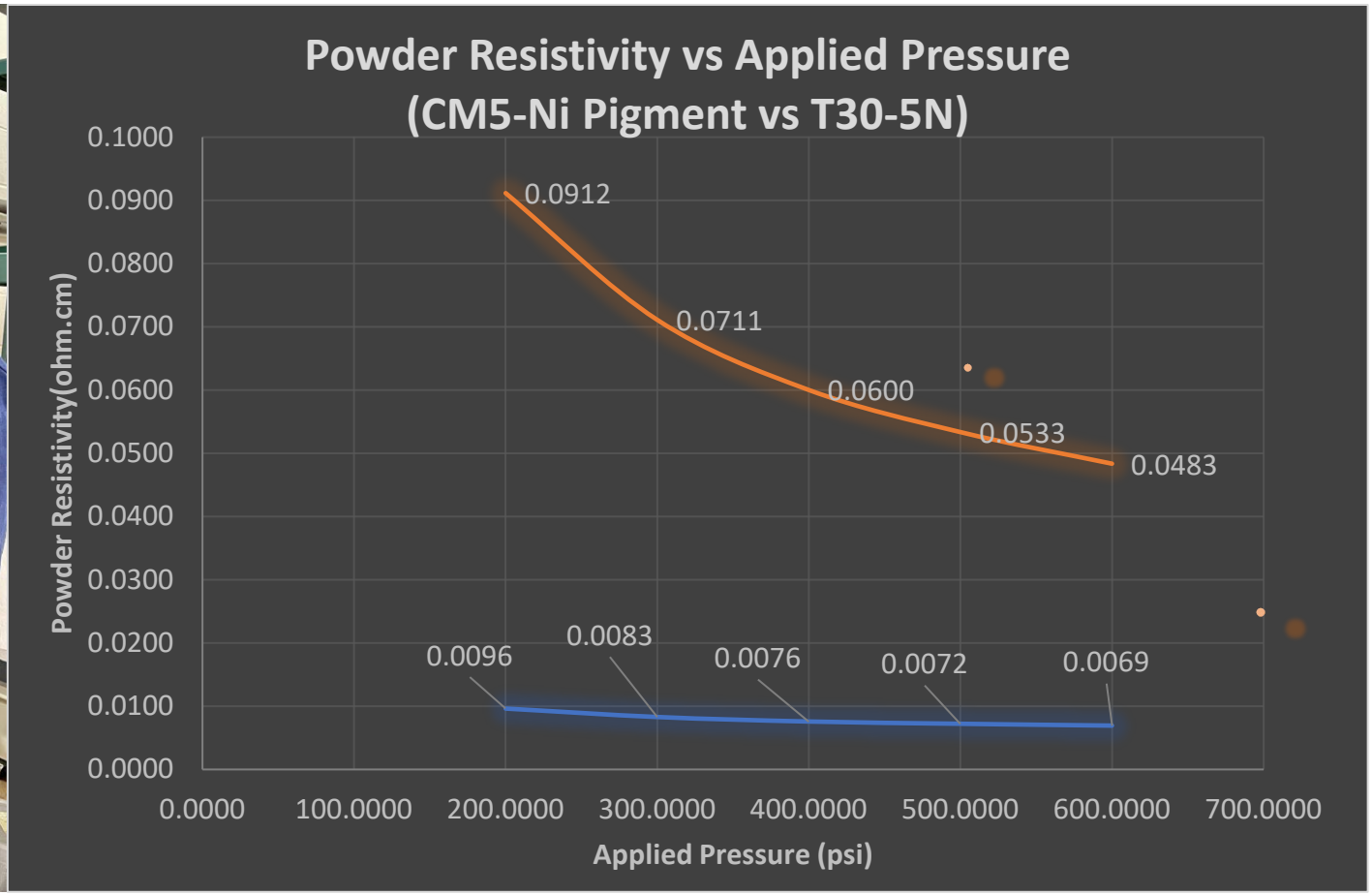
Technology/Product Development Approach

Typical Powder Resistivity Measurement Results



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Plans for Future Testing/Development/Commercialization

- Current Project
  - Continue Evaluation/Testing of Heating Panel Prototypes of Coal-Based Heating Panels by a Contractor/Distributor for Commercial Applications
  - Continue Development/Testing of All-Carbon Pigments & Inks
  - Continue Development/Testing of Metal/Coal Hybrid Pigments & Inks
- Next Project
  - Continue Development of Advanced Thermo-Chemical Heating Process for Processing Coal-based Feedstocks
  - Seek Commercialization Partners for Testing/ Implementing of Coal-Based Heating Panels
  - Seek Commercialization Partners for Other Printed Circuit Applications
- Scale-up Potential
  - Some aspects of the technologies being developed have good scale-up potential
  - Other aspects of said technologies will require further investigation

Commercialization of Wall and Floor Heating Panels

WALL PANEL HEATER

UNDER FLOOR HEATING SYSTEM

Heat your Living Space with Coal without Generating any Greenhouse Emissions

- Rendering of Prototype wall panel
- Underfloor heating shown in kitchen floor

Outreach and Workforce Development Efforts or Achievements

- Minus 100, LLC hired one college intern majoring in nano-technology for the summer (sophomore at BU). Said intern has expressed interest in being hired for an internship for the summer of 2023.
- New Hire (Lead Chemist) to come on-board in late 2022 or early 2023. His role will be to oversee the hybrid metal/carbon ink formulation development.
- New Hire (Lab Tech. Level 1) Associates Degree in Mechanical Engineering, BS in Plastics Engineering Technology.

Summary

- Key Findings & Lessons Learned
  - Coal-based feedstocks can be converted to electrically conductive carbon-based pigments & Inks for commercial and military applications.
  - The carbon quality/purity of the products manufactured is dependent on the quality/purity of the feedstocks. Therefore, in many/most high-value carbon applications, coal refining/pre-processing is a requisite step in the overall manufacturing process
  - The technologies being developed for electrically conductive inks can be potentially applied to the manufacture of electrically conductive paints and coatings for which there are significantly larger markets.
- Technology Development
  - Development of a moderate-temperature thermo-chemical reactor assembly will continue with emphasis on improving operating reliability with high coal loads.
  - Development of an advanced high-temperature, thermo-chemical reactor assembly will be pursued in a separate DOE Project due to development cost.
  - Development of the electro-chemical technology reactor for exfoliating coal-based graphite has been put on hold because there was little difference in the ink sheet resistivity produced.
- Take-Away Message
  - Coal is an abundant natural resource in the USA that can help secure the supply chains of many critical specialty chemicals and carbon-based products. Coal refining/pre-processing will be a requisite step in the overall manufacturing process of producing high-value coal-derived products

End of U.S. Coal to Conductive Inks Presentation

DOE Grant DE-SC0018694

DOE/NETL Project Review Meeting 25-27 Oct 2022

Investigators: James Hnat, PhD (PI)
Kevin Kerns, President (PM)
Jeremy Rogers (Lab Manager)

DOE Project Managers
Anthony Zinn
Christian Robinson

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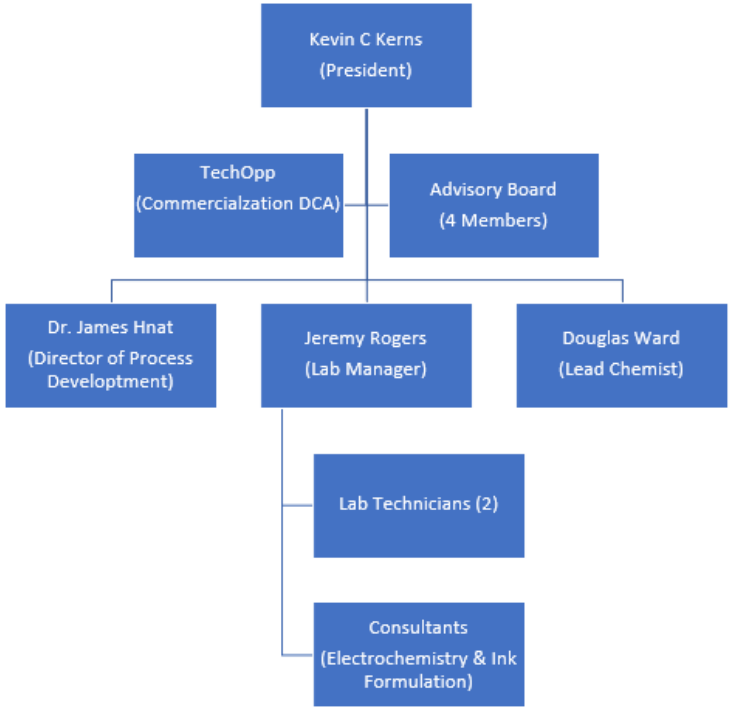
Appendix

- These slides will not be discussed during the presentation but are mandatory.
- Organization Chart
- Gantt Chart

Minus 100 Organization Chart & Relationship to Current Program

Minus 100 Organization Chart



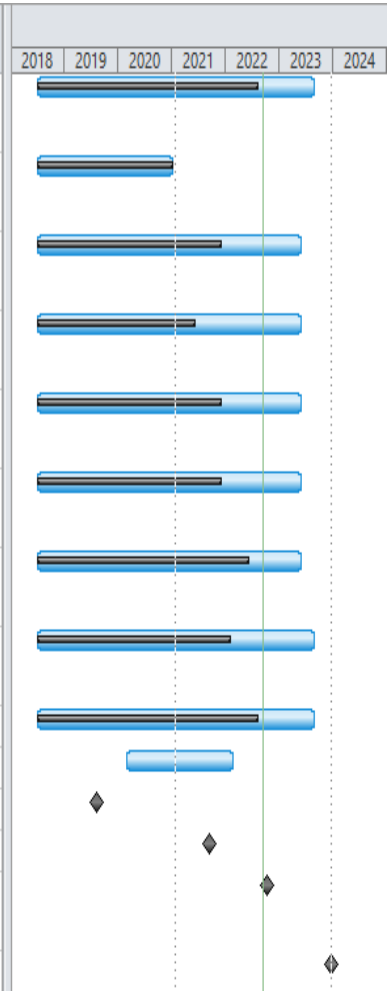
Relationship to Current DOE Program

- Kevin Kerns, President also acts as the Phase II, IIA Project Manager
- TechOpp assist Minus 100 in its commercialization efforts
- The Advisory Board provided advice to the President regarding the future course of business of Minus 100
- James Hnat, Director of Process Development serves as the Principal Investigator for the DOE Project
- Jeremy Rogers, Lab Manager manages the lab technicians who perform the test operations and interfaces with the electro-chemical and ink formulation consultants
- Douglas Ward, Lead Chemist is a new hire and will participate in the development of coal-based suspensions for a variety of applications

Gantt Chart & Summary for Appendix

Gantt Chart

Task Name	% Compl	Start	Finish
1. Purchase of Critical Feedstocks, Supplies, Instrumentation & Equipment	80%	Mon 7/2/18	Mon 8/28/23
2. Scaleup of Comminution Process Step to Pilot Scale	100%	Mon 7/2/18	Fri 1/15/21
3. Evaluation and Qualification of Minus 100 Pigments/Suspensions	70%	Mon 7/2/18	Thu 6/1/23
4. Development of High Temperature Microwave Furnace	60%	Mon 7/2/18	Thu 6/1/23
5. Development of Electrochemical Reactor Assembly	70%	Mon 7/2/18	Thu 6/1/23
6. Development of High Conductivity Pigments & Suspensions	70%	Mon 7/2/18	Thu 6/1/23
7. Characterization of Minus 100 Pigments & Suspensions	80%	Mon 7/2/18	Thu 6/1/23
8. Commercialization Planning & Heating Panel Development	70%	Mon 7/2/18	Mon 8/28/23
9. Project Management & Reporting	80%	Mon 7/2/18	Mon 8/28/23
COVID Delays	0%	Sun 3/1/20	Tue 3/1/22
Milestone 1 - Phase I Final Report	100%	Mon 8/19/19	Mon 8/19/19
Milestone 2 - Phase II Final Report	100%	Fri 9/17/21	Fri 9/17/21
Milestone 3 - Completion of Heating Panel Prototypes	0%	Fri 10/14/22	Fri 10/14/22
Milestone 4 - Phase IIA Final Report	0%	Tue 12/26/23	Tue 12/26/23



Summary

Task #	Remarks/Summary
1	All major equipment & Instrumentation Procurement Completed. Only feedstocks and supplies remaining to be purchased
2	Scale-up of comminution process to pilot-scale completed. Operational milling continuing
3	Evaluations by commercialization ink formulators terminated because of COVID. Engaged commercial screen printer to print prototype heating panels
4	Development of moderate temperature microwave furnace completed. Development of high temperature microwave furnace put on hold because of cost/risk.
5	Testing with electro-chemical reactor completed. Further testing put on hold because no significant difference in ink resistivity observed.
6	Progress being made on development of hybrid metal/carbon pigments/suspension. Further development/testing continues.
7	Characterization of pigments/suspensions basically on schedule
8	Commercialization efforts focused on heating panel development. Commercial prototype heating panels under development
9	Project Management & Reporting on schedule.