DOE/NETL Virtual Project Review 19-20 Oct 2020

Production of High Value Products from Coal

U.S. Coal to Conductive Inks

DOE Grant DE-SC0018694

NATIONAL ENERGY TECHNOLOGY LABORATORY

DOE/NETL Virtual Project Review Meeting 19-20 Oct 2020

Investigators: James Hnat, PhD (PI) & Kevin Kerns, President (PM)

Contact Information

E-mail: jghnat@minus100.com, Tel:610-331-1772

E-mail: kckerns@minus100.com, Tel: 570-212-3261

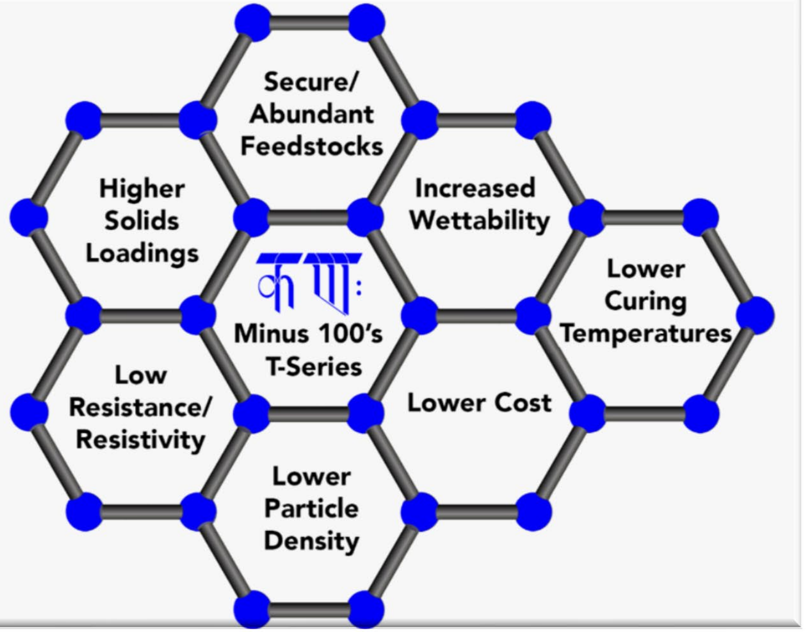
Project Purpose/Objectives

Fossil Energy/Minus 100, LLC Objectives

Fossil Energy Objective

- Increase use of U.S. coal utilization through the development of technologies and value-added products that use U.S. Coal Supplies as a primary feedstock

Minus 100, LLC Value Proposition

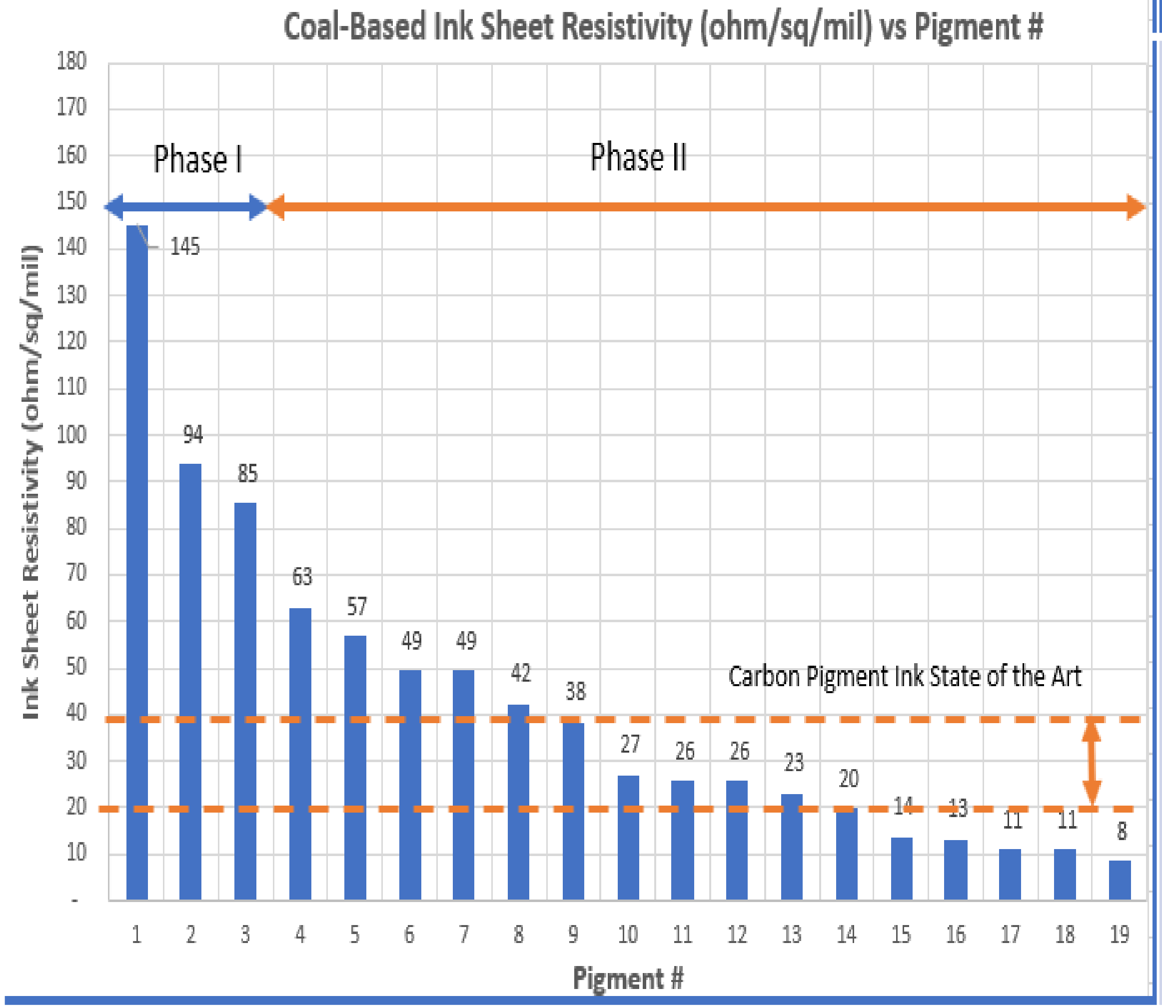


Conductive Pigment Markets

- Conductive Inks
  - Current Market (~ $ 3.0 B/yr) Growing at 4-8% CAGR
  - Conductivity Enhancement Methods Under Evaluation
  - Lower Resistivity Leads to Electronic Printing Market Expansion
- Conductive Paints & Coatings
  - Significantly Larger Market (~ $ 17.5 B/yr) Growing at 6.8% CAGR
  - Application Methods are Simpler
- Synthetic Graphite Manufacturing
  - Significantly Larger Market (~ $ 17.4 B/yr) Growing at 5.2% CAGR
  - Precursor to Various Carbon Allotropes
    - Graphene, Carbon Nanotubes
  - Strategic Material with Limited U.S. Manufacturing Capacity
- Underfloor Heating Market
  - (~$6 B/yr) Growing at 4.5% CAGR

Technical & Commercialization Accomplishments

Technical Accomplishments/Activities



Commercialization Activities

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

Carbon-Based Conductive Ink Applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

Henkel Web Page

Sheet Resistivity (ohm/sq/mil)	Printing Method	Potential Application
1,000,000 ± 15%	Screen-printing, thermoset, rigid carbon ink, blending for specific resistance targets	Printed resistors, heaters, potentiometers, friction
100,000 ± 15%	Screen-printing, thermoset, rigid carbon ink, blending for specific resistance targets	Printed resistors, heaters, potentiometers, friction
10,000 ± 15%	Screen-printing, thermoset, rigid carbon ink, blending for specific resistance targets	Printed resistors, heaters, potentiometers, friction
1,000 ± 15%	Screen-printing, thermoset, rigid carbon ink, blending for specific resistance targets	Printed resistors, heaters, potentiometers, friction
100 ± 15%	Screen-printing, thermoset, rigid carbon ink, blending for specific resistance targets	Printed resistors, heaters, potentiometers. friction
< 40	Flexographic, Gravure, Screen, Digital	Printed resistors, heaters, potentiometers, friction
1	Flexographic, Gravure, Screen, Digital	RFID Applications

Position of Minus 100 in the Printing Value Chain

NATIONAL ENERGY TECHNOLOGY LABORATORY

Position within the Printing Value Chain & Important Pigment/Ink Parameters

Minus 100 Position within the Printing Value Chain

Raw Material Sourcing	Intermediate Feedstock Suppliers	Ink Formulators	Printing & Packaging Companies
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

- Sheet/Volume Resistivity (ohm/sq), (ohm/sq/mil)
- Powder Resistivity (ohm-cm)
- Particle Size (µm)
- Surface Area (m2/g)
- Density (g/cc)

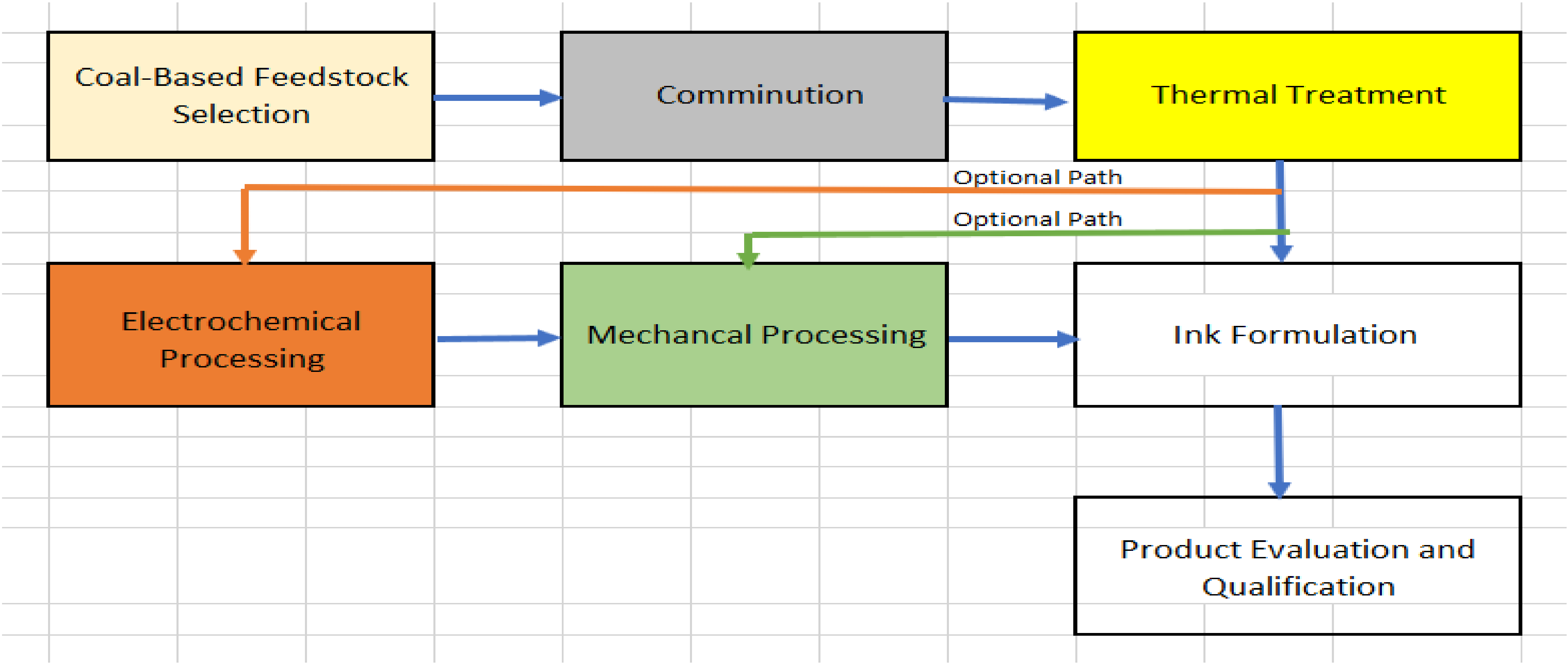
Ink Properties

- 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

NATIONAL ENERGY TECHNOLOGY LABORATORY

Technical Approach



Technology/Product Development Approach

NATIONAL ENERGY TECHNOLOGY LABORATORY

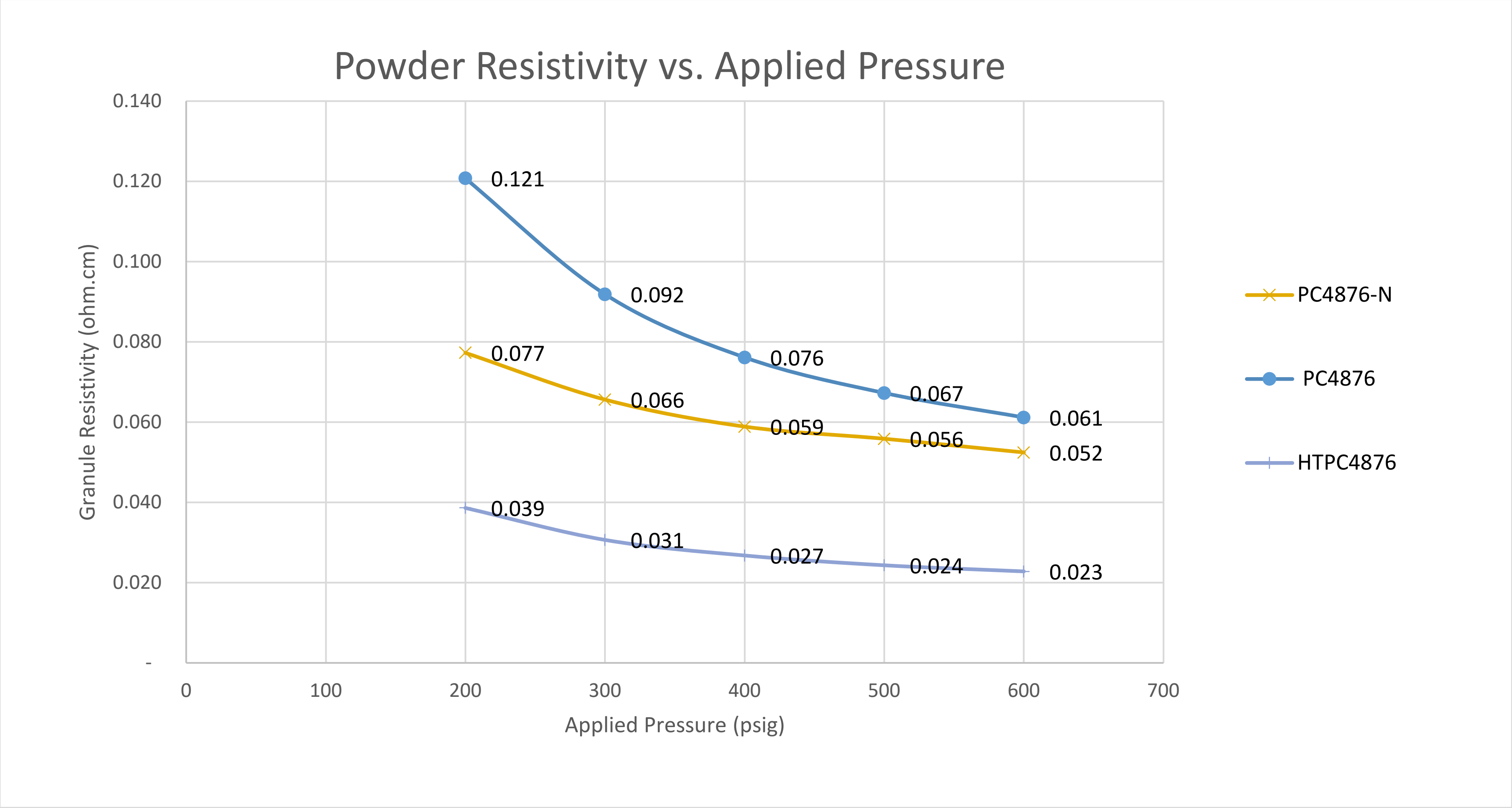
Proprietary Thermal Treatment

Heat Treated Coal-Based Product

- 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.

Technology/Product Development Approach

Enhanced Conductivity of Bituminous Feedstocks via Thermal Treatment

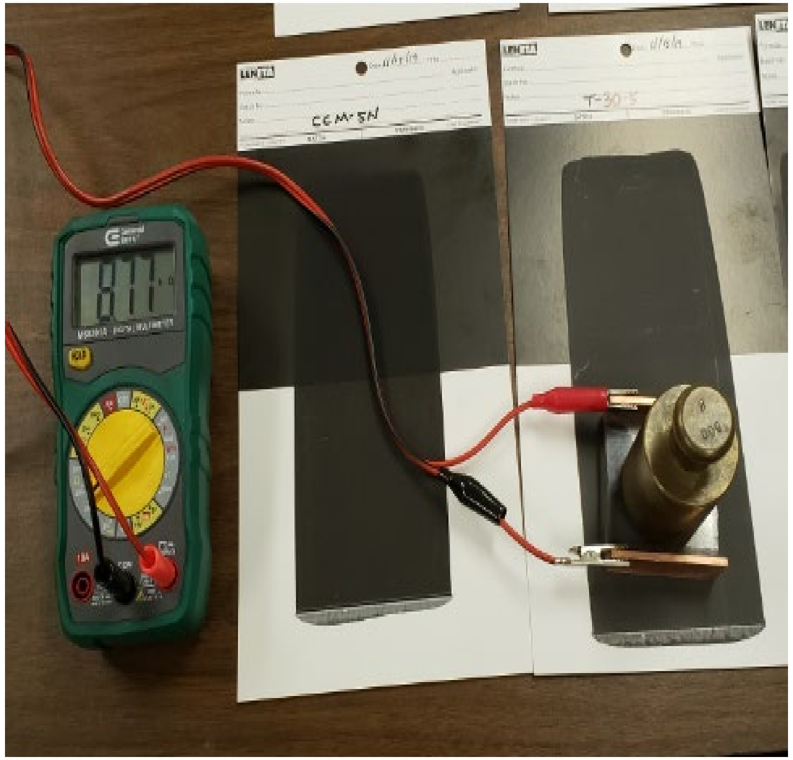


Technology/Product Development Approach

NATIONAL ENERGY TECHNOLOGY LABORATORY

Ink Resistivity Measurements

Draw Down with a Mayer Rod

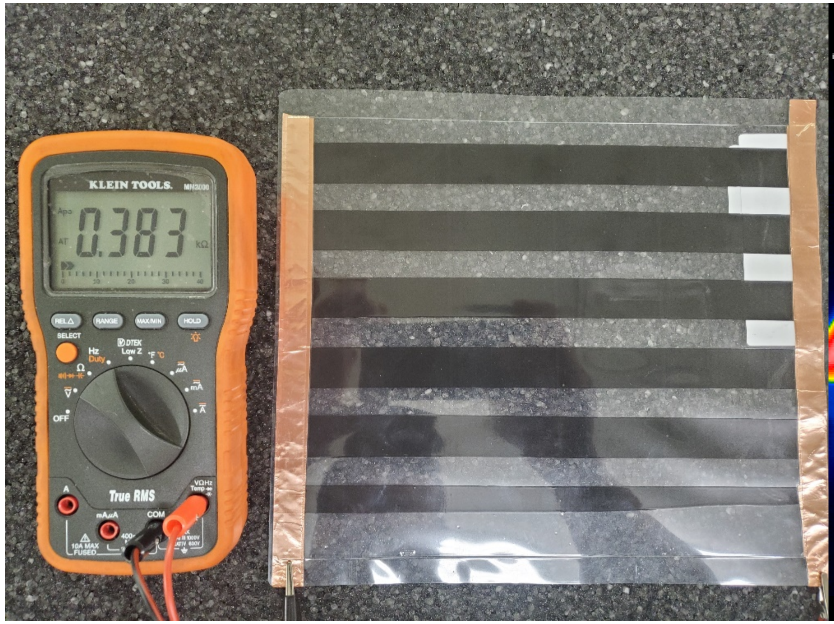


Measurement of Square Resistance

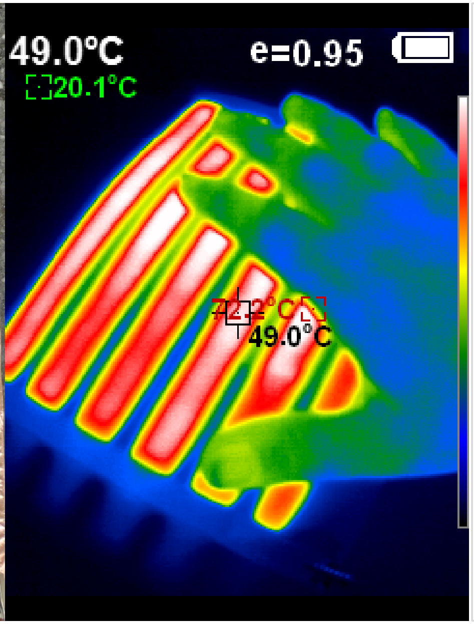
Measurement of Ink Film Thickness

Lab-Scale Resistive Heating Element Testing Underway

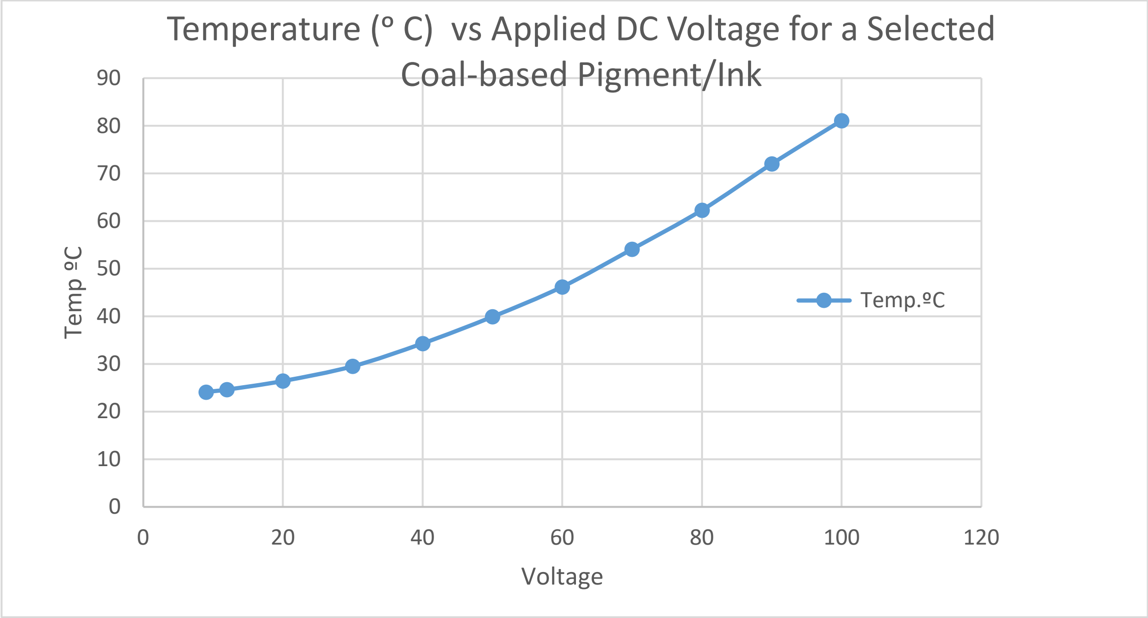
Coal-Based Heating Element Assembly Test Arrangement



Lab Scale Under Floor Heating Element Assembly



Thermographic Image of Lab-Scale Heating Assembly

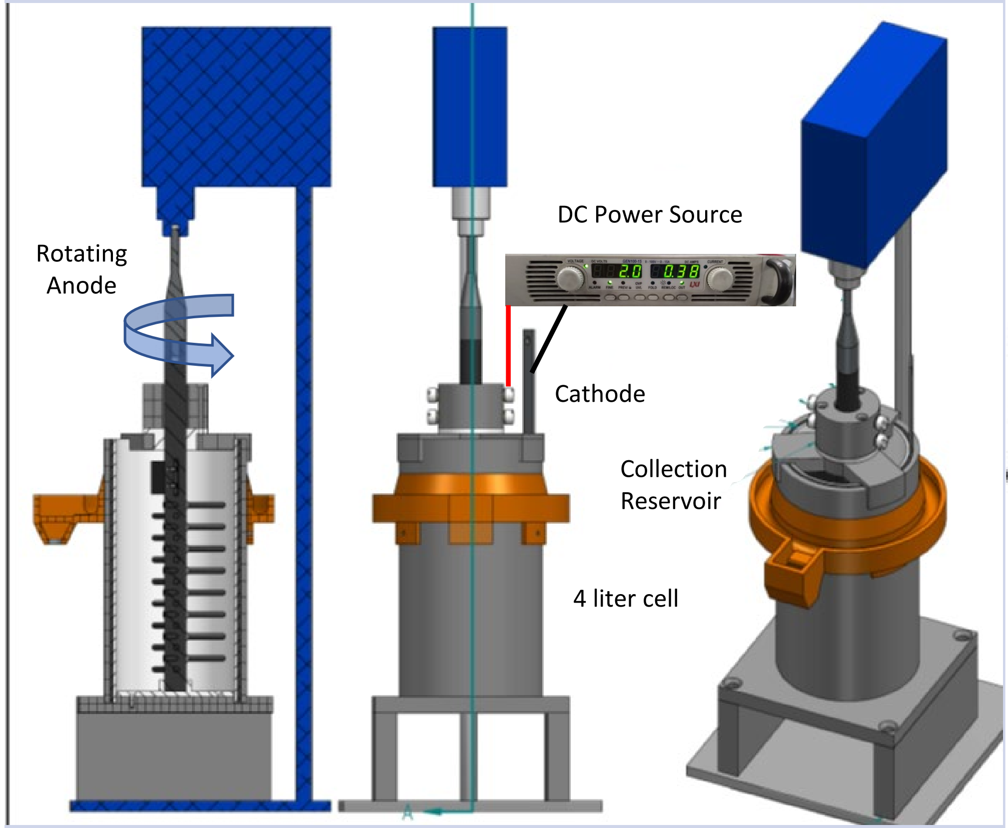


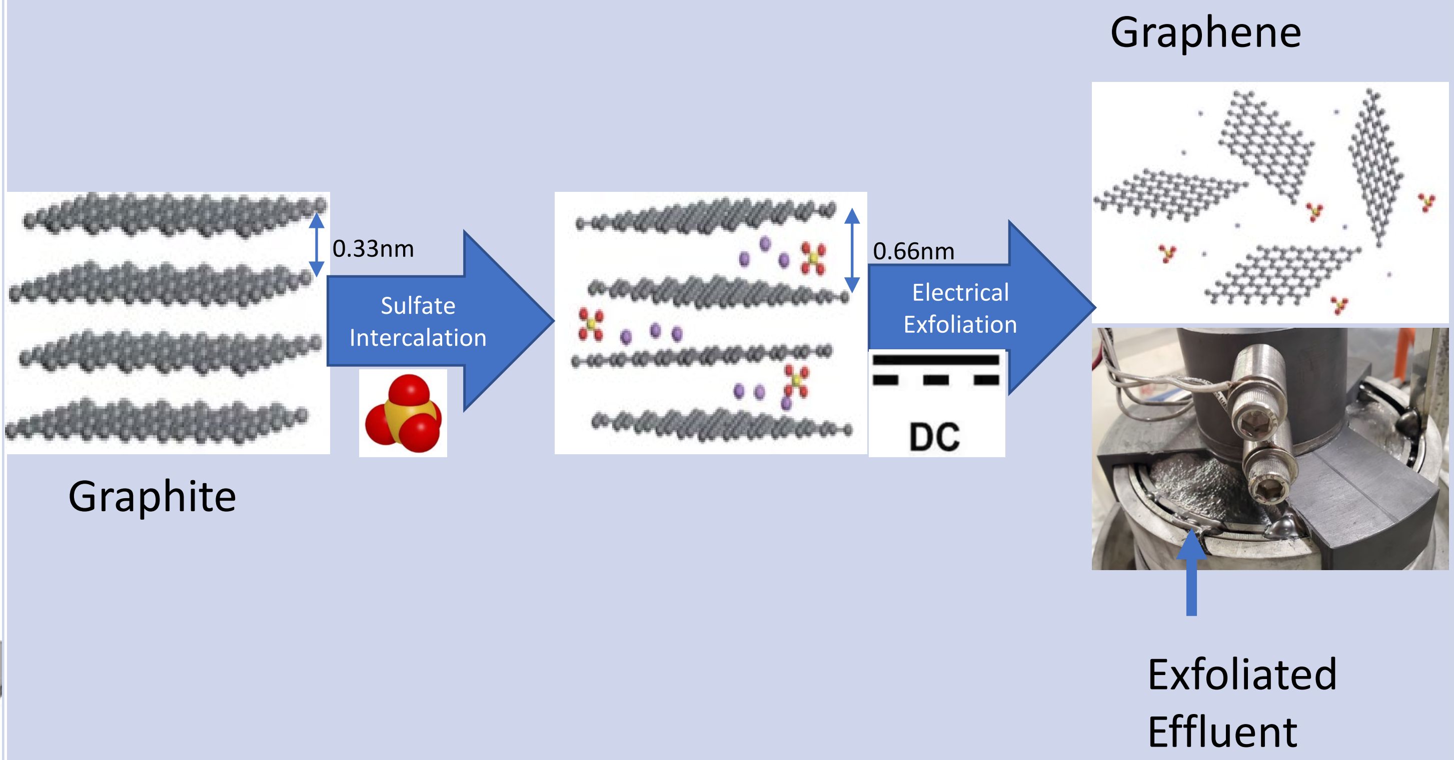
Thermoprofile of Lab-Scale Heating Element Assembly

Carbon Additive Enhancement of Coal-Based Pigments

Description of Electro-chemical Reactor Assembly

Electrochemical Reactor for Processing Carbon Powders	Intercalation-Exfoliation Mechanism

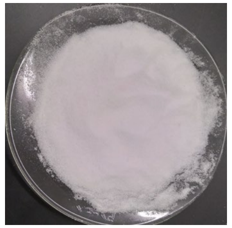




Additive Enhancement for Coal-Based Pigments

NATIONAL ENERGY TECHNOLOGY LABORATORY

Experimental Design (DOE) for the Production of Graphite/Graphene Platelets

Factor (X)		Levels	Experimental Trials	Results (Y)
	Graphite Platelets	5wt% 10wt%	All possible level combinations yield **12** trials. Design results will be randomized and analyzed using Minitab Software	Sheet Resistivity Powder Resistivity Particle Size Expansion Fraction
	Na_2SO_4	0.5M 1.0M		
	Intercalation Time @ 2.00V	10min 20min 40min		

Additive Enhancement for Coal-Based Pigments

Preliminary Analysis for Electrochemical Reactor DOE

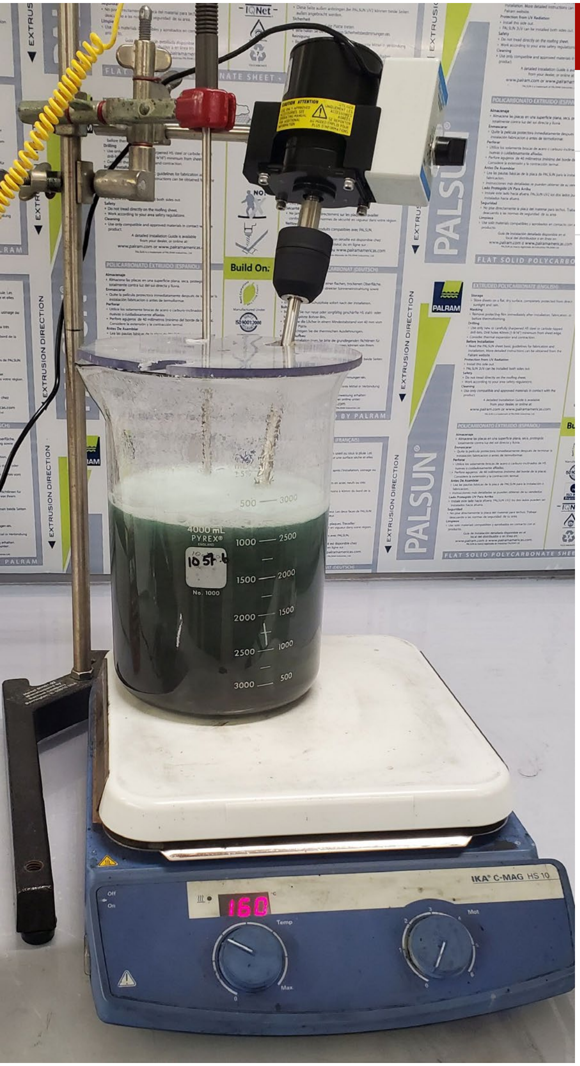
StdOrder	RunOrder	PtType	Blocks	Salt	Carbon %	I time	sheet resistivity
10	1	1	1	1	10	10	51.95
11	2	1	1	1	10	20	50.76
5	3	1	1	0.5	10	20	43.89
3	4	1	1	0.5	5	40	46.65
8	5	1	1	1	5	20	42.29
6	6	1	1	0.5	10	40	43.91
12	7	1	1	1	10	40	41.01
1	8	1	1	0.5	5	10	43.28
2	9	1	1	0.5	5	20	46.29
7	10	1	1	1	5	10	42.42
4	11	1	1	0.5	10	10	55.13
9	12	1	1	1	5	40	36.6

- Residual Carbon Fraction Analysis
- Main Effects Carbon Fraction Analysis
  - Lower carbon% = lower sheet resistivity
  - Higher intercalation time = lower sheet resistivity
  - Higher salt concentration = lower sheet resistivity
- Effluent Carbon Fraction Analysis in process with target date 10/31/2020.

Additive Enhancement for Coal-Based Pigments

NATIONAL ENERGY TECHNOLOGY LABORATORY

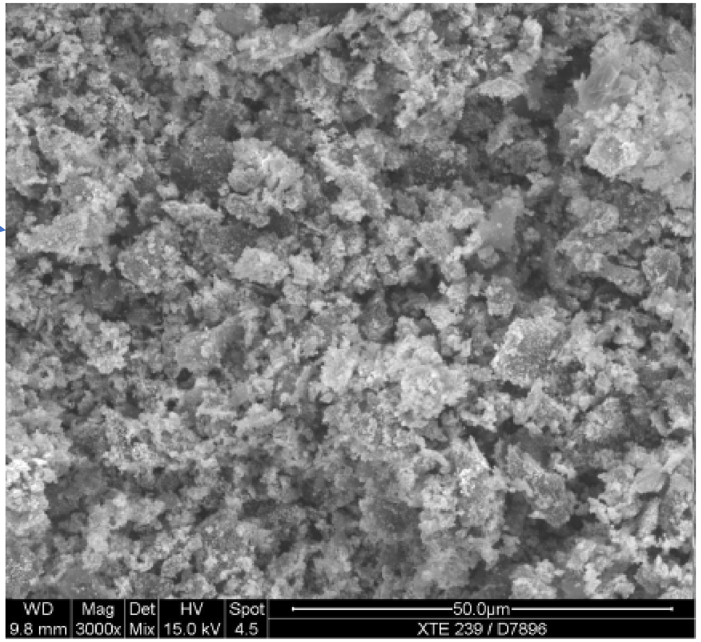
Metallization of Coal-Based Pigments via Electroless Nickel Plating



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



SWOT Analysis

Strengths

- Phase I Goal: < 1000 ohm/sq/mil - Achieved
- Phase II Goal: < 100 ohm/sq/mil - Achieved
- Internal Goal: < 10 ohm/sq/mil – Achieved 8 ohm/sq/mil
- Next Target: ≤ 1 ohm/sq/mil – In Progress
- Lab-Scale heating element prototype developed
- Development of novel high temperature process for conductive/graphitic enhancement
- Use of nontoxic electrolytes in ECR

Challenges

- Achieve ≤ 1 ohm/sq/mil with metallized pigment.
- HT Furnace construction materials
- Flue Gas Emissions
- Material handling of fine particles

Opportunities

- Seeking underfloor heating commercialization partner
- New electronic circuit printing
- Collaborating with major ink manufacturers
- Conductive Paints and Coatings
- Synthetic Graphite Production
- Semiconductor Chemical Mechanical Planarization (CMP) Spillover

Threats

- Covid-19 Fallout (supply and co-development)
- Demand destruction

Future Plans

1. Underfloor Heating Element Applications
    - Pursuing co-development commercial screen-printing partners to produce a protype.
2. Electro-Chemical Research
    - Complete Design of Experiment analysis to target optimum ECR conditions.
    - Evaluate intercalation/exfoliation potential of selected coal-based pigments with optimum ECR conditions
3. Hybrid Pigment Conductive Research
    - Complete carbon-based additive research
        - Conductive Carbon Black
        - Graphite/Graphene Platelets
        - Carbon Nanotubes
        - Metallization
4. Continue collaboration with major ink formulators to evaluate Minus 100, LLC conductive pigments.
5. Initiate lab-scale testing and evaluation of proprietary heating technology at elevated temperatures
6. Continue commercialization efforts with Tech-Opps.

Questions & Answers