Utilization of Carbon Supply Chain Wastes and Byproducts to Manufacture Graphite for Energy Storage Applications

FE0032144

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Ohio University

U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
April 2-4, 2024

Project Overview

Project Specifics

- DOE/NETL Cooperative Agreement No. DE-FE-0032144
- DOE Project Manager: Jason Montgomery
- Principal Investigator (PI): Jason Trembly
- Participants: GM, CONSOL Innovations, Americarbon, Koppers, and AEP

Project Budget

- Federal: $1,000,000
- Non-Federal: $250,000

Project Duration

- February 14, 2022 – February 13, 2025

DOE-NETL Carbon Ore Processing Program

Project Objectives

Overall: Develop coal-derived graphite materials for transportation and grid-scale energy storage applications. Coal waste(s) will be given preference as the process feedstock with caking coals from reclaimed mining wastes, currently operating mines, coal tar pitches, and combinations thereof.

Budget Period 1

- Characterize coal-derived waste feedstocks
- Manufacture coal-derived graphite and quantify relevant properties
- Construct and validate coin cells using coal-derived graphite as the negative electrode
- Develop initial porous electrode models for half and full coin cells
- Conduct initial modeling of aging and degradation mechanisms
- Develop initial microstructure models

Project Objectives

Overall: Develop coal-derived graphite materials for transportation and grid-scale energy storage applications. Coal waste(s) will be given preference as the process feedstock with caking coals from reclaimed mining wastes, currently operating mines, coal tar pitches, and combinations thereof.

Budget Period 2

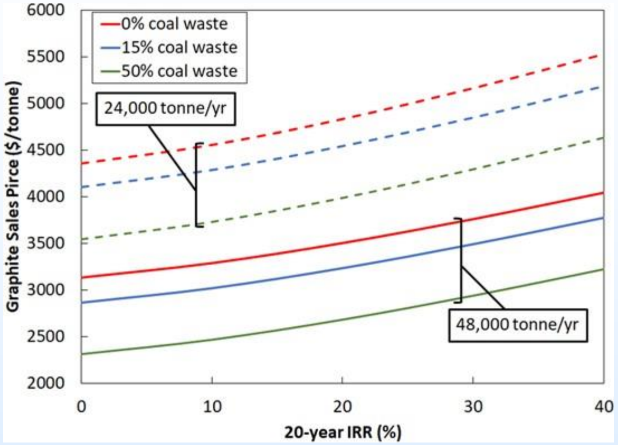
- Synthesize 1 kg batch of coal-derived graphite
- Conduct analysis of large format (pouch) cells using coal-derived graphite as the negative electrode
- Complete computational modeling
- Develop preliminary techno-economic analysis

Technology Background

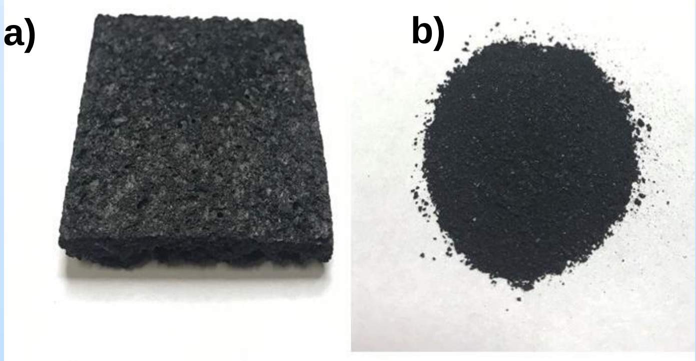
- Electric vehicle (EV) market is significant and growing
  - Projected to grow to $800 billion by 2027
- Graphite is critical negative electrode material
- United States highly dependent upon foreign sources
- Only 9% of global LiB manufacturing capacity in the U.S.
- Current processing wastes up to 70% of the graphite – battery grade graphite is $3,000 – $10,000/tonne
- IRA critical mineral requirements

Technology Background

- Conversion of coal wastes into graphitizable carbon foams to establish a U.S. supply chain
- Utilizing nation's coal resources as energy storage materials for LiBs
- Diversifying and securing U.S. battery/energy storage supply chains
- Lower graphite prices than currently realized
- Converti rural mining brownfields into energy storage material manufacturing hubs with prevailing wage jobs



Preliminary Estimated Graphite Selling Prices vs. 20-year Internal Rate of Return.



Graphitized OHIO Coal-derived a) Foam (4 in by 3 in) and b) Pulverized Powder

Project Scope

Success Criteria

- Produce a coal-derived graphite material using continuous manufacturing methodologies
- Produce coal-derived graphite meeting battery-grade graphite specifications
- Demonstrate coal-derived graphite-containing pouch battery with 80% capacity of commercial materials (~300 $mAh/g_{graphite}$)
- Estimated coal-derived graphite 20-year 40% IRR sales price of ≤$8,000/tonne

Project Scope

Project Milestones

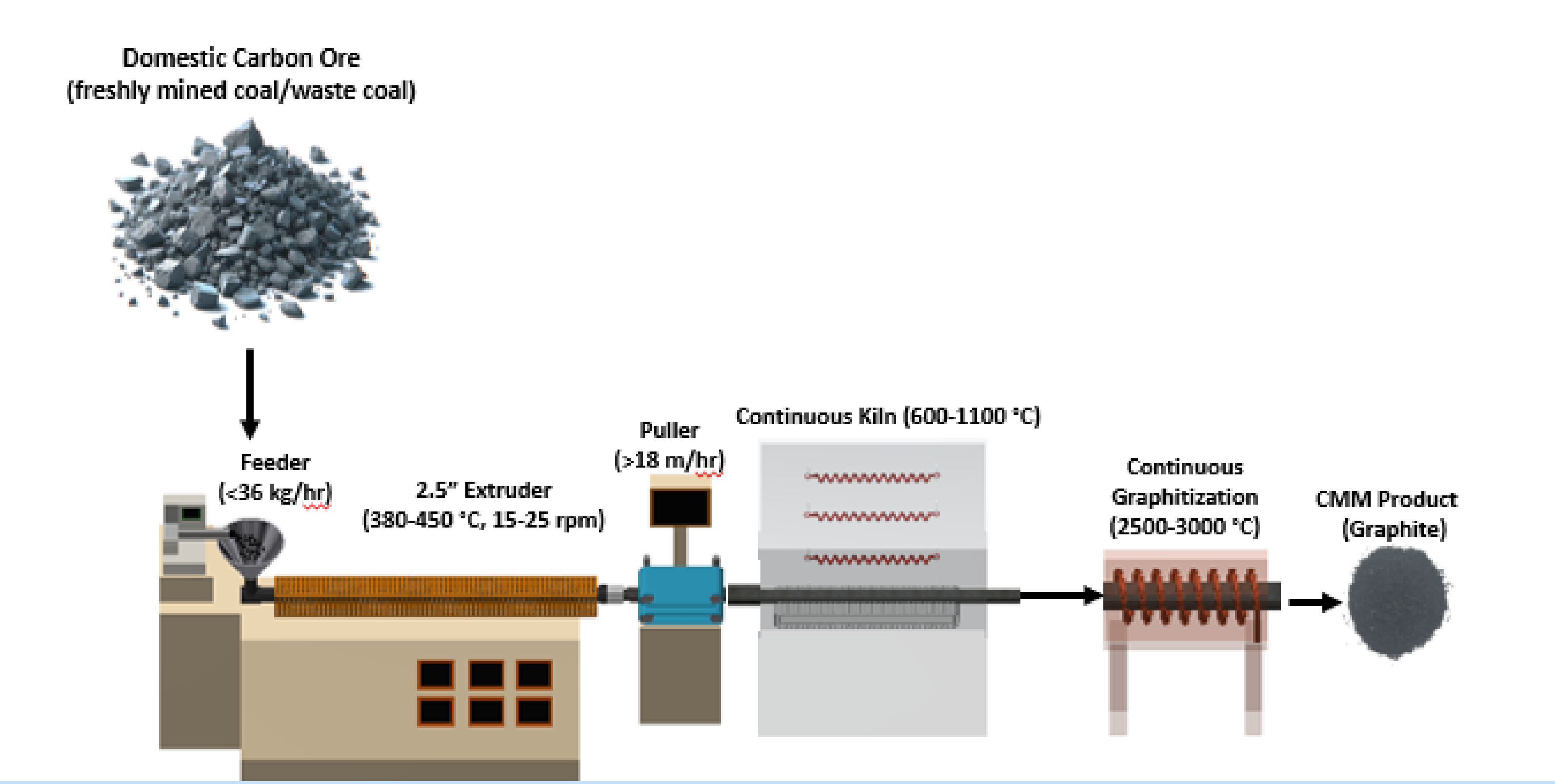
Task	Description	Planned Completion Date	Actual Completion Date	Verification Method
1.1	Updated PMP submitted	March 23, 2022	March 23, 2022	File Submitted
1.1	Project Kick-Off meeting held	May 23, 2022	July 9, 2022	Presentation file
1.2	Technology Maturation Plan (TMP)	May 23, 2022	June 10, 2022	Report file
4.0	Construction of first coin cell with coal-derived graphite	November 23, 2022	October 10, 2022	Quarterly report
5.0	Complete development of porous half-cell model	February 23, 2023	October 2, 2023	Quarterly report
3.0	Quantification of coal-derived graphite properties	May 23, 2023	March 15, 2023	Report file
4.0	Coin cell performance data for model verification	May 23, 2023	March 25, 2023	Quarterly report
3.0	Synthesize 1 kg batch of coal-derived graphite	February 23, 2024	September 7, 2023	Quarterly report
6.0	Preliminary techno-economic analysis	July 23, 2024		Quarterly report

Project Scope

Risks & Mitigation Strategies

Risk	Mitigation Strategy
Feedstock Availability	Test a host of feedstock and a mixture thereof to increase supply chain security to meet future domestic graphite demands.
Graphite Purity	Analyze a range of coal-derived materials for impurities and utilize this information to select feedstock or mixtures thereof capable of achieving battery graphite purity specifications.
Market Acceptance	To create market acceptance the project team plans to conduct LIB coin and pouch cell tests to demonstrate acceptable performance with coal-derived graphite. Additional potential market segments will also be identified.
Process Economics	To minimize coal-derived graphite manufacturing costs multi-variable techno-economic studies will be completed including but not limited to feedstock pricing, project financing, product sales price, location, and production capacity.

Progress and Current Status of Project



Carbon Foam Extrusion

Carbon Foam Extrusion

Low Sulfur Pittsburgh No. 8 Ultimate/Proximate Analysis (%)			
Proximate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Moisture	0.76	0.00	0.00
Ash	9.42	9.49	0.00
Volatile Matter	36.21	36.49	40.31
Fixed Carbon	53.61	54.02	59.69
Ultimate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Hydrogen	4.96	4.91	5.43
Carbon	75.42	76.00	83.97
Nitrogen	1.53	1.54	1.70
Sulfur	2.46	2.48	2.74
Oxyen	6.21	5.58	6.16
Ash	9.42	9.49	0.00

Extrusion

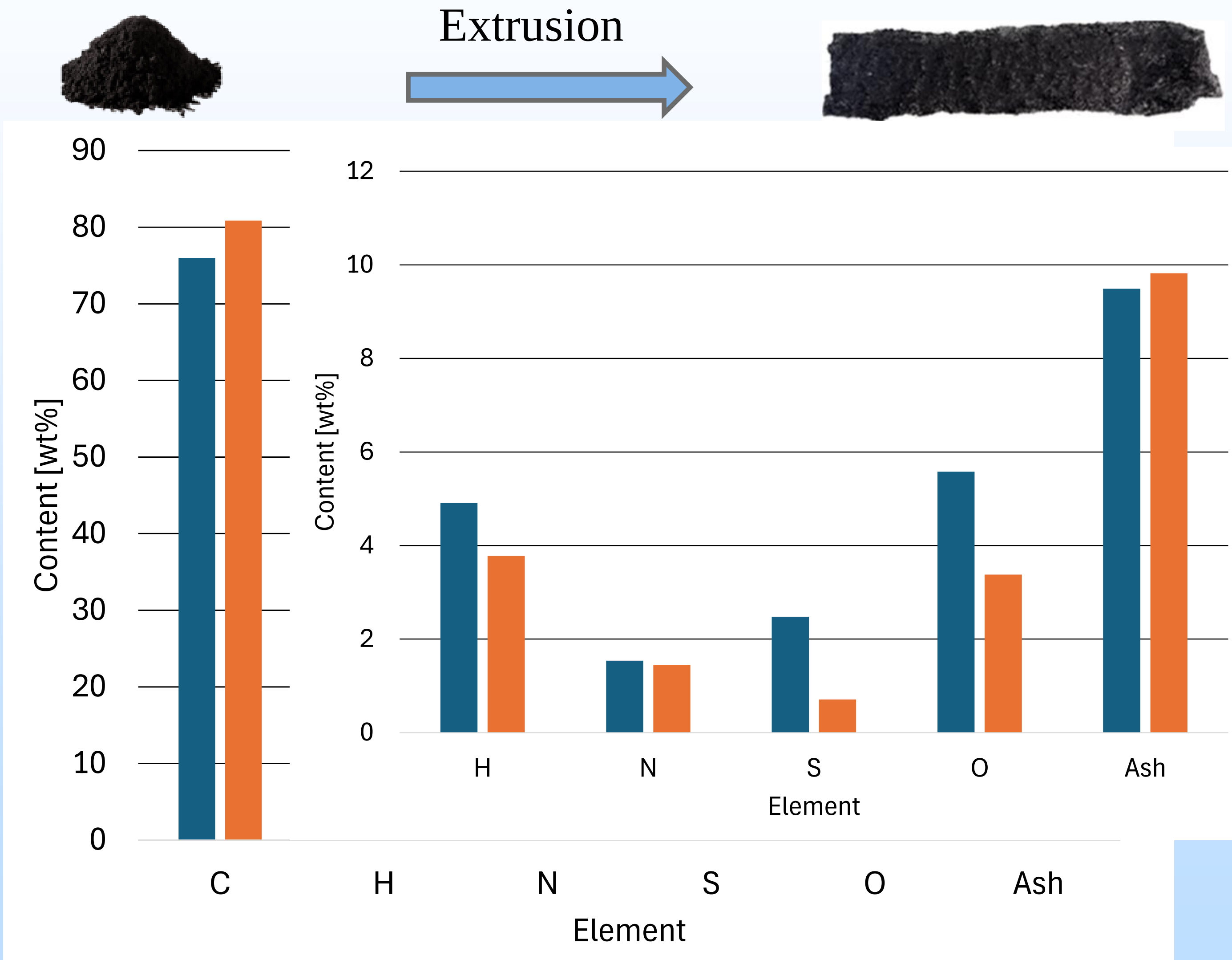
Low Sulfur Pittsburgh No. 8 - Green Foam - Ultimate/Proximate Analysis (%)			
Proximate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Moisture	0.67	0.00	0.00
Ash	9.75	9.82	0.00
Volatile Matter	31.64	31.85	35.32
Fixed Carbon	57.94	58.33	64.68
Ultimate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Hydrogen	3.83	3.78	4.19
Carbon	80.32	80.86	89.66
Nitrogen	1.44	1.45	1.61
Sulfur	0.71	0.71	0.79
Oxyen	3.95	3.38	3.75
Ash	9.75	9.82	0.00

White Forest Ultimate/Proximate Analysis (%)			
Proximate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Moisture	0.57	0	0.00
Ash	7.75	7.79	0.00
Volatile Matter	25.24	58.38	27.53
Fixed Carbon	66.44	66.83	72.47
Ultimate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Hydrogen	4.62	4.58	4.97
Carbon	79.02	79.47	86.19
Nitrogen	1.57	1.58	1.71
Sulfur	0.98	0.99	1.07
Oxyen	6.06	5.59	6.06
Ash	7.75	7.79	0.00

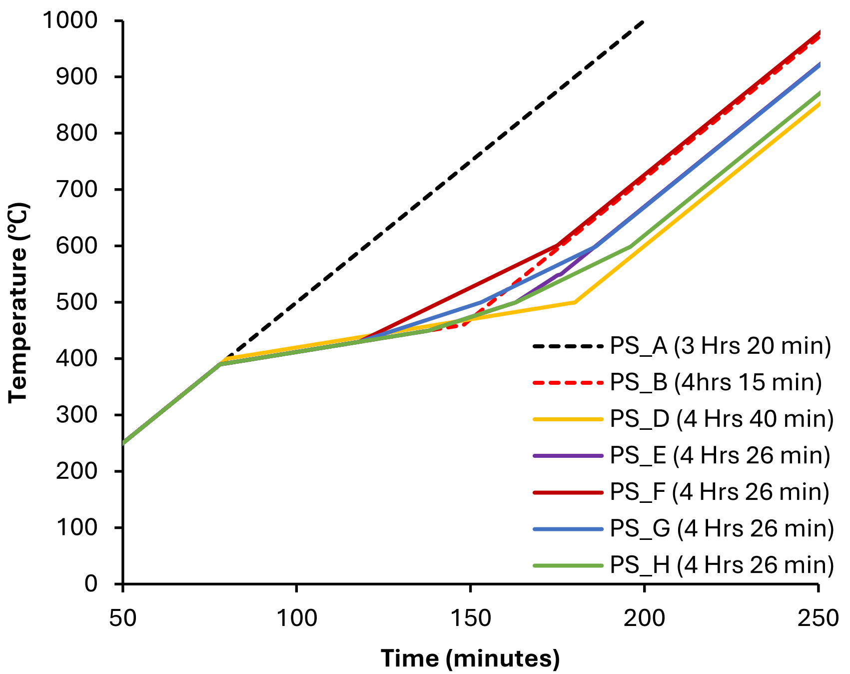
Extrusion

White Forest - Green Foam - Ultimate/Proximate Analysis (%)			
Proximate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Moisture	1.24	0.00	0.00
Ash	9.51	9.63	0.00
Volatile Matter	21.78	22.05	24.40
Fixed Carbon	67.47	68.32	75.60
Ultimate Analysis	**As Received**	**Dry**	**Dry Ash-Free**
Hydrogen	4.56	4.48	4.95
Carbon	74.91	75.85	83.91
Nitrogen	1.63	1.65	1.83
Sulfur	1.19	1.20	1.33
Oxyen	8.20	7.19	7.96
Ash	9.51	9.63	0.00

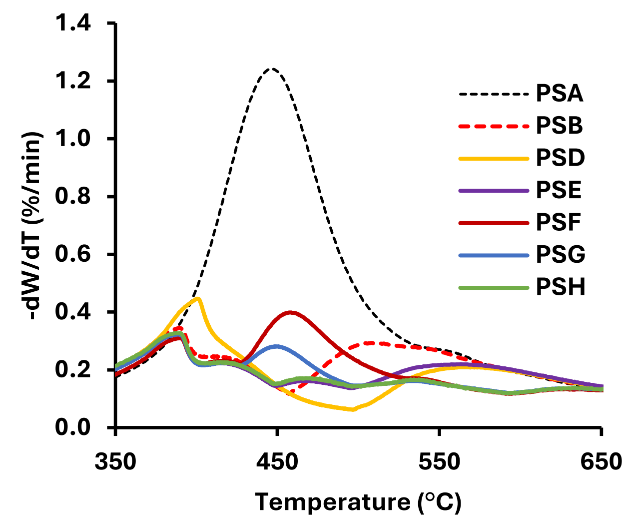
Carbon Foam Extrusion



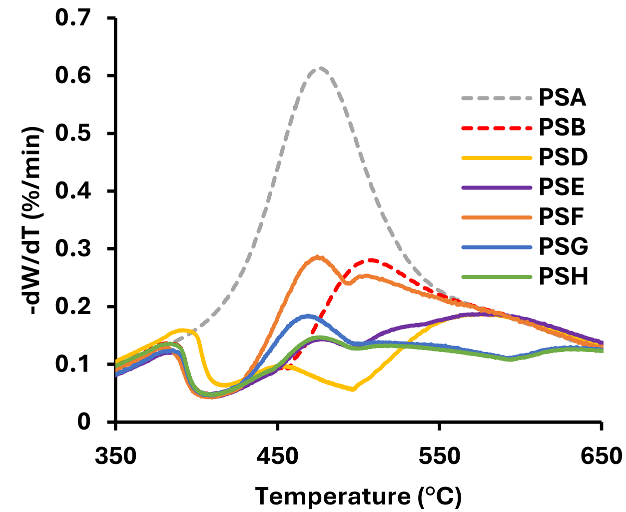
Carbon Foam Extrusion



Pyrolysis Schedules

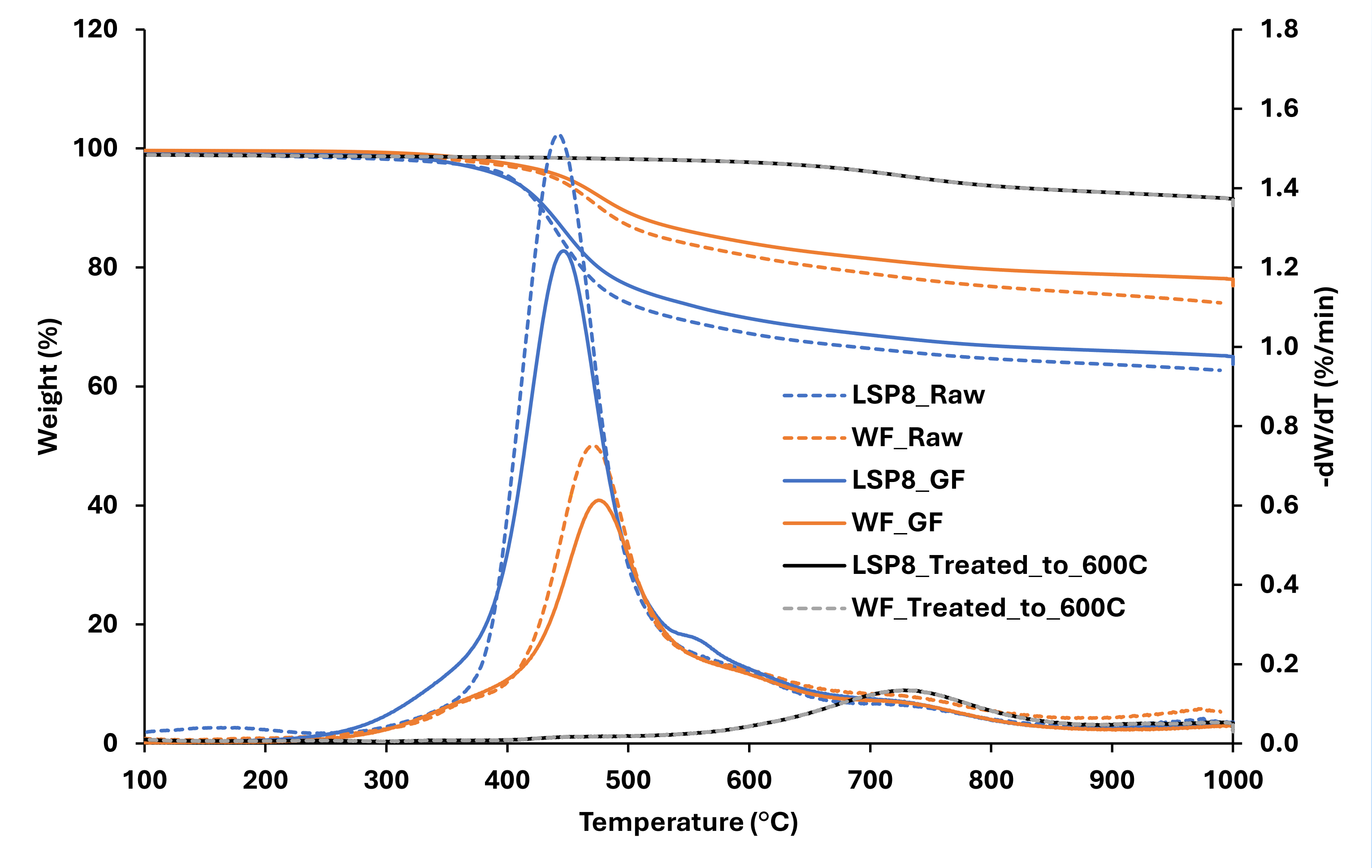


P8 DTG Curves

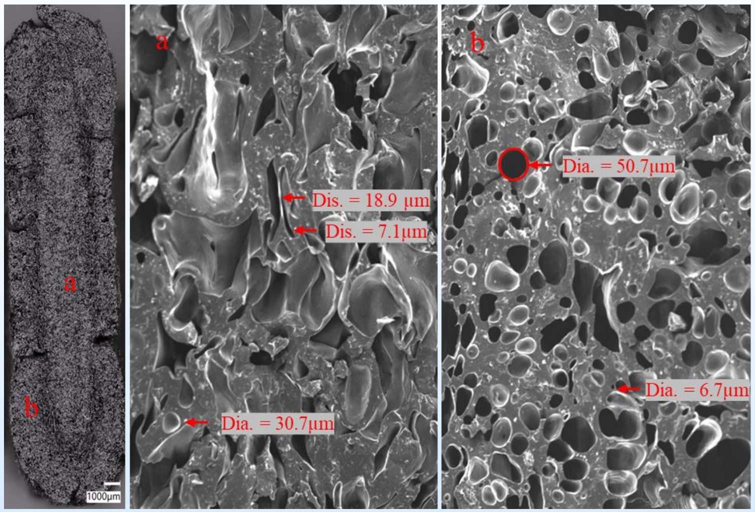


WF DTG Curves

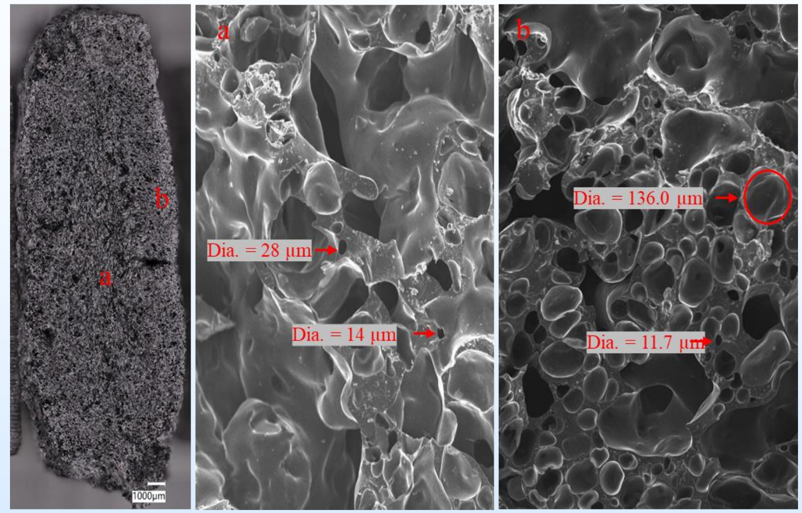
Carbon Foam Extrusion-Thermal Stability



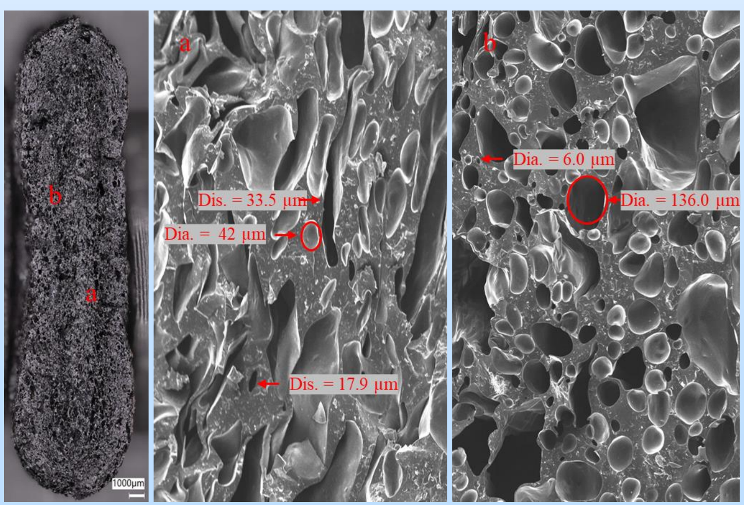
Carbon Foam Extrusion



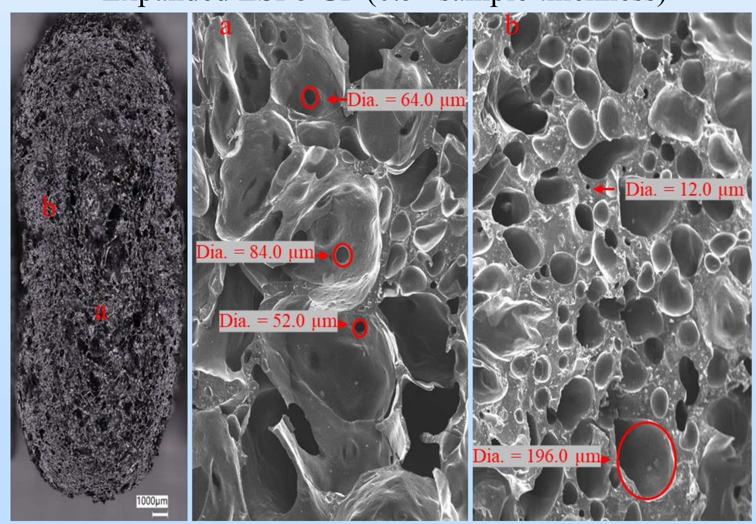
LSP8 compressed GF (0.25" sample thickness)



Expanded LSP8 GF (0.5” sample thickness)



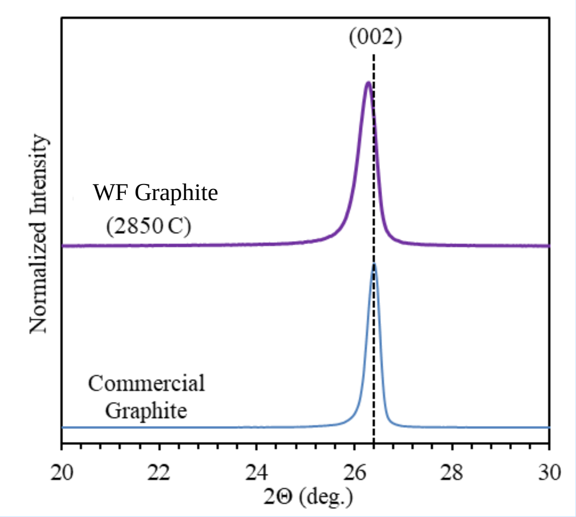
WF compressed GF (0.25" sample thickness)

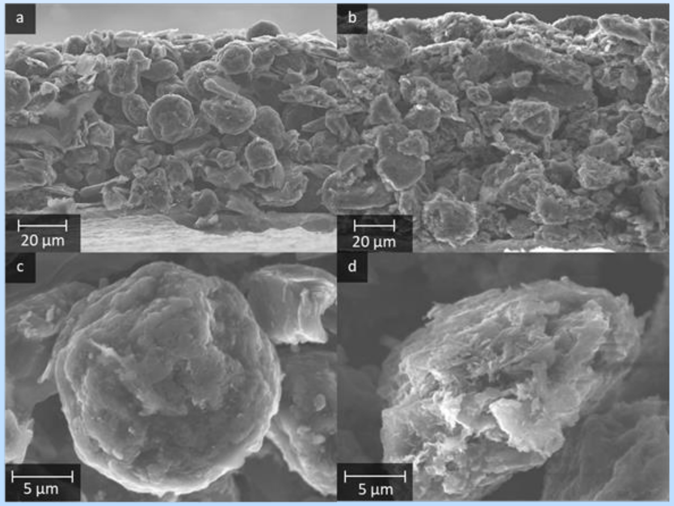


Expanded WF GF (0.5” sample thickness)

Coal-Derived Graphite

Metric	MCMB (Commercial)	White Forest	Pitt No.8	Itmann	Anthracite
D-spacing (002) [Å]	3.389±0.006	3.396±0.001	3.389±0.005	3.384±0.002	3.384±0.001
L_c (002) [nm]	26.2±7.6	18.7±0.2	17.0±1.3	24.4±0.5	23.7±0.6
L_a (002) [nm]	85.9±7.9	67.4±1.8	63.3±8.4	80.6±3.7	75.9±2.6
Degree of Graphitization [%]	60±7	51±1	59.9±0.2	64.9±0.1	65.2±0.0
Surface Area [m^2/g]	1.35±0.06	7.34±0.29	-	-	-
D50 [µm]	18	26	-	-	-
I_D:I_G Ratio	0.97	0.78	-	-	-





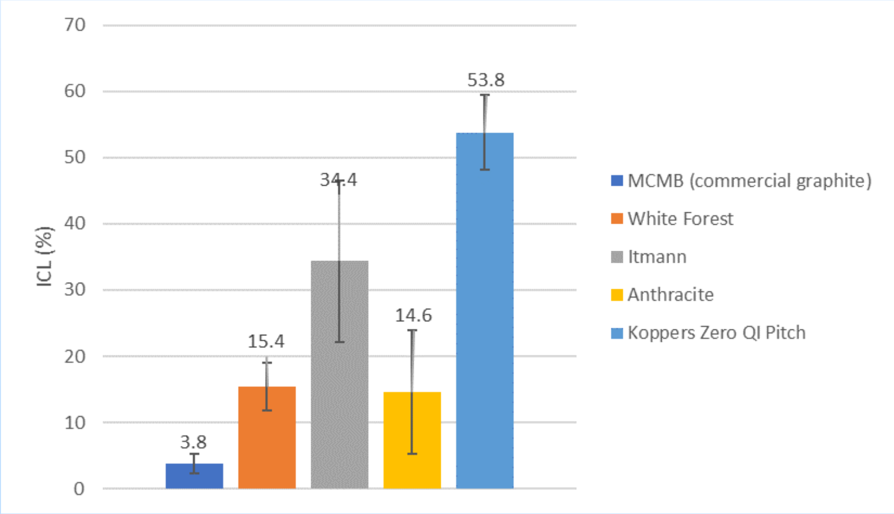
Coal-Derived Graphite

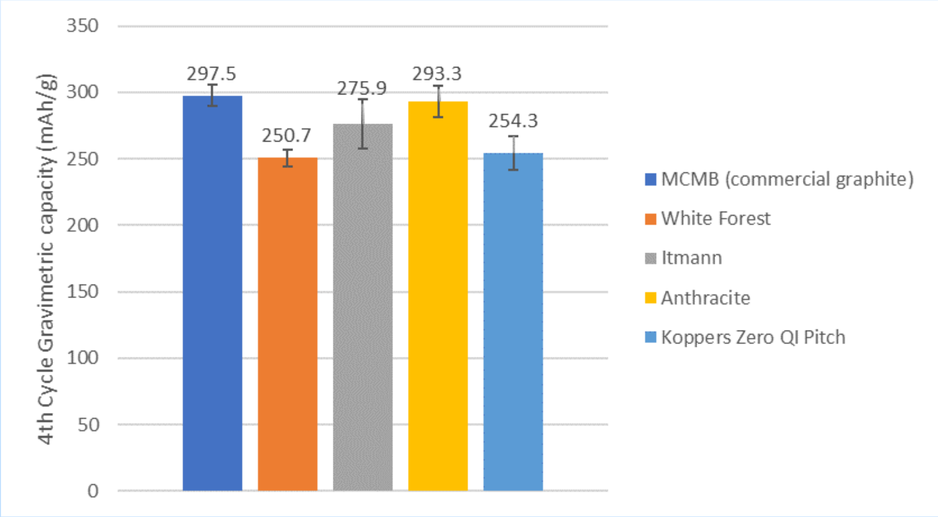
- Generally, graphitized White Forest coal has lower concentrations of trace elements than the raw coal (exceptions include B, Br, Si, and Ca)
- Graphitized White Forest coal also has lower concentrations than the commercial MCMB graphite (excepting Br)

Species (mg/kg or ppm)	**Raw Coal (White Forest)**	**Graphitized Coal (White Forest)**	**Commercial Graphite (MCMB)**
Mercury	0.189	<0.010	<0.010
Selenium	2.0	<1.0	<1.0
Thallium	<0.151	<1.96	<1.97
Antimony	3.27	<9.81	<9.86
Tin	<0.755	<9.81	<9.86
Uranium	2.43	<0.98	1.13
Beryllium	2.43	<0.0981	1.23
Thorium	2.70	<0.98	1.58
Molybdenum	4.06	<1.96	3.89
Cobalt	7.95	1.13	4.39
Arsenic	7.27	2.65	4.44
Lead	8.76	<1.96	5.57
Lithium	11.7	<0.981	6.46
Zinc	16.2	<0.981	9.22
Nickel	22.6	3.53	14.7
Boron	5.74	11.8	15.5
Strontium	26.9	2.8	20.8
Copper	47.9	2.11	23.0
Chromium	23.0	10.0	24.4
Barium	38.9	3.58	28.4
Fluorine	50	24	31
Manganese	58.1	10.2	52.4
Vanadium	69.9	8.58	66.4
Bromine	155	543	467
Silicon	434	433	833
Calcium	650	849	2820
Iron	3490	897	3500

Coin Cell Data

- Low initial capacity loss (ICL) and high gravimetric capacity are desired
- MCMB (commercial graphite) has lowest ICL and highest 4th cycle gravimetric capacity
- White Forest and Anthracite coal-derived graphites have similar ICLs and are closet to the commercial graphite
- Anthracite has the highest gravimetric capacity of the coal-derived graphites.



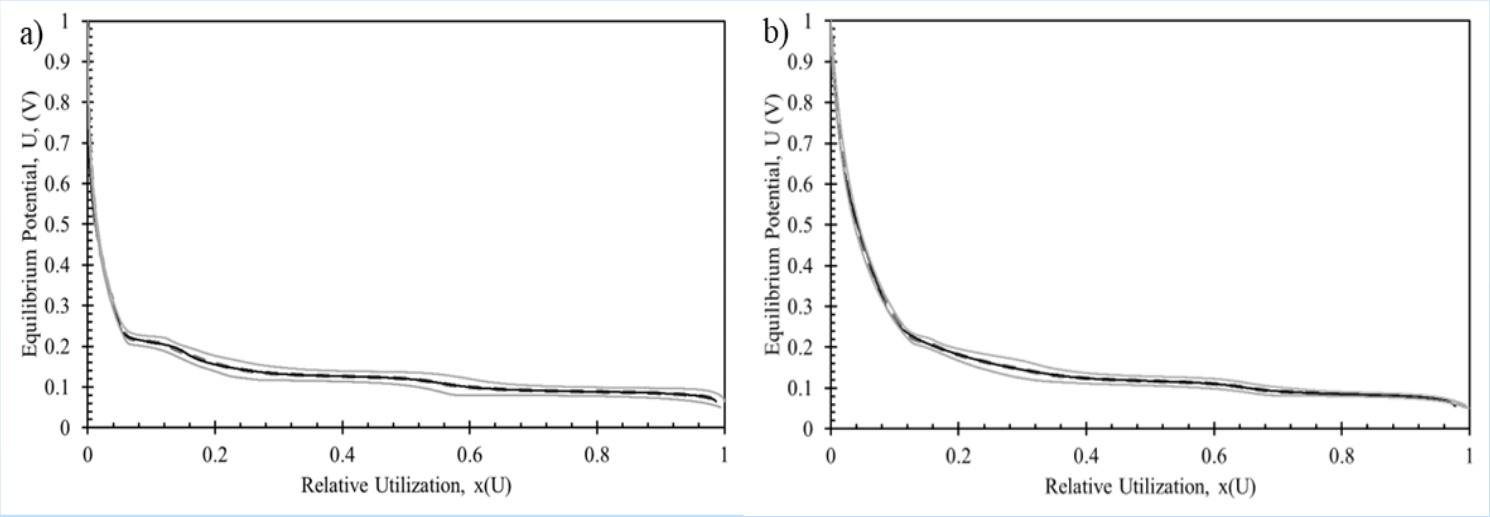


Left: Initial capacity loss for commercial and coal-derived graphites
Right: 4th cycle gravimetric capacity for commercial and coal-derived graphites

MSMR Modeling

Application of the Multi-Species, Multi-Reaction (MSMR) Model

- MSMR approach treats thermodynamics of individual stages or galleries in intercalations processes – works on pseudo-equilibrium (very low scan rate) data
- Has been applied to graphite and several positive electrode materials
- This project applies the MSMR model to coal-derived graphite for the first time
- Results have been presented at Electrochemical Society meetings and published as open-access in Journal of the Electrochemical Society



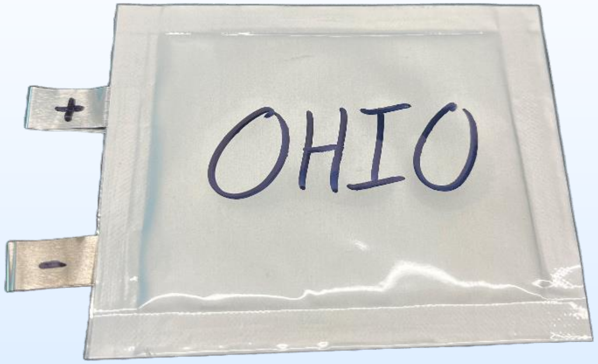
Left: MSMR applied to commercial graphite.
Right: MSMR applied to coal-derived graphite.

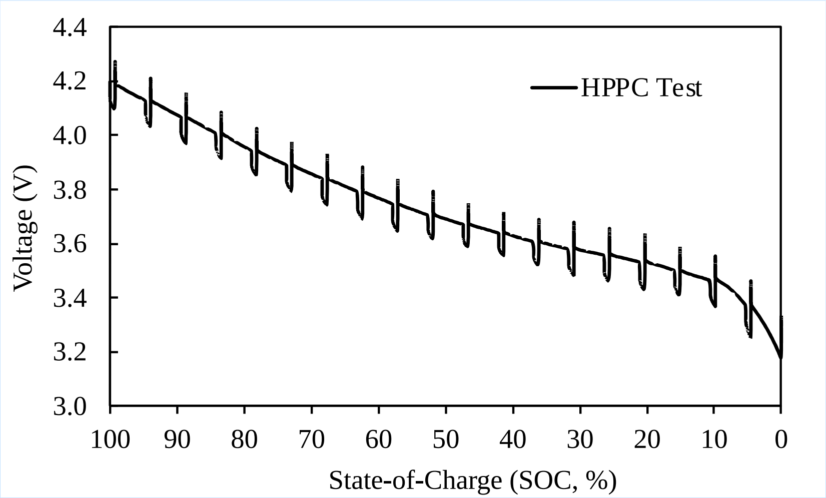
Abigail Paul et al 2024 J. Electrochem. Soc. 171 023501

Pouch Cell Development

~70 mAh single layer pouch cells (4 x 6 cm^2) prepared at University of Michigan Battery Lab

- 35X the capacity of the coin cells
- > 1 kg of graphitized coal produced to develop full cells
- Pouch cell format is more similar to target EV battery cells and reduces internal resistance
- Coal-derived graphite anodes and NMC 811 cathodes
- Testing underway to characterize ageing and high-rate performance (HPPC tests)





Future Work

- Carbon Foam Extrusion
  - Scale extrusion to 1-inch die
  - Assess mechanical, thermal, and electrical properties
- Coal-derived graphite production
  - Build improved pouch cells with the most promising materials tested in coin cells (only materials with large quantities available were used for the initial pouch cell development)
- Pouch Cell Testing
  - Ageing and HPPC (rate/kinetics)
  - Kinetic/diffusion parameters will be extracted for virtual scale-up/modeling

Outreach and Workforce Development Efforts or Achievements

- Outreach –
  - ECS Presentations
  - Provide a bulleted list of community outreach efforts or achievements.
- Workforce Development
  - Graduate student training
  - Undergraduate student training

Summary Slide

- Continuous extrusion of coal and waste coal into graphitizable precursor material demonstrated with coal and waste coals
- Graphite materials derived from coal, waste coal, and coal pitches have been synthesized
- Coal-derived graphite incorporated into coin and pouch cells
- MSMR modeling used to characterize coal-derived graphite thermodynamic properties

Acknowledgments

- Ohio University: Abigail Paul, Caleb Gula, Kody Wolfe PhD, Yahya Al-Majali PhD, John Staser PhD
- CONSOL Innovations: Rudolph Olson III PhD, Eric Shereda, and Natasha Smith PhD
- Koppers: Carl Mueller
- Americarbon: Dave Berry
- General Motors: Taylor Garrick PhD and Jeffrey Lowe PhD