Scale up Production of Graphite from Carbon Ore and Coal Refuse — FEAA157

2022 Resource Sustainability Annual Project Review Meeting

ORNL—Edgar Lara-Curzio, Frederic Vautard, Ercan Cakmak, Stephan Irle, GS Jung, Pilsun Yoo, Prashant Nagapurkar, Aparna Annamraju, Eric Wolfe,

UK-CAER — Rodney Andrews, Matthew Weisenberger, John Craddock, Vivian Edwards, Robert Pace, David Eaton, Asmund Vego, Kirk Norasak, George Frank, Christina Thompson, Michela Martinel

Penn State — Jonathan Mathews

October 2022

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

Activities funded by DOE's Fossil Energy and Carbon Management Program

Outline

- Project Objectives
- Background
- Approach
- Results
- Summary

Project Overview

- **Title**: Scale up Production of Graphite from Carbon Ore and Coal Refuse
- **Objective**: To develop and demonstrate processes for scaling up the production of graphite from carbon ore, coal refuse and waste streams associated with previous coal mining activities
- **Period of Performance**: December 2021 – November 2024
- **Project Managers**: Michael Fasouletos (NETL), Joe Stoffa (NETL), Ana Wendt (DOE-HQ)
- **Project Team**: ORNL and University of Kentucky, Pennsylvania State University.

Outline

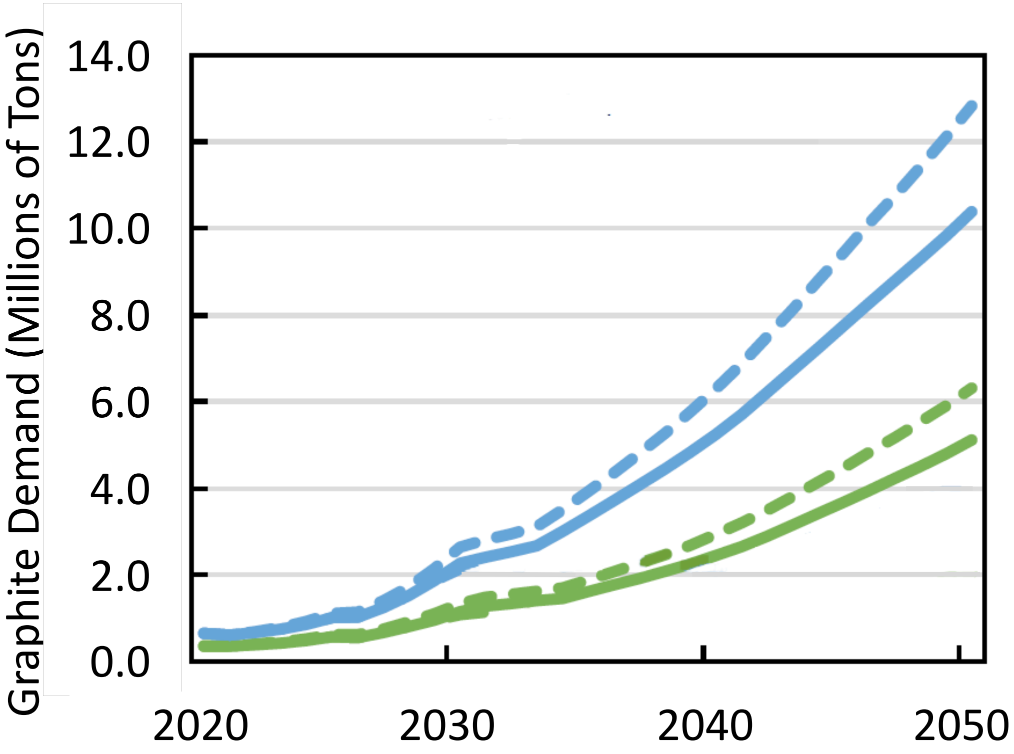
- Project Overview
- Background

Background: Demand for Graphite for Li-ion Batteries

The demand for graphite for anodes used in lithium-ion batteries needed for consumer electronics and electric vehicles is expected to grow significantly. Currently there are 88 battery megafactories in the world requiring 165,000 tons of graphite per year. According to various scenarios, more than 2.0 million tons-per-year will be needed by 2030 and more than 10 million tons-per-year by 2050.

International Energy Agency (IEA) scenarios:

- Stated Policies scenario, which incorporates existing government policies.
- Sustainable Development scenario, which is compatible with the climate goals of the Paris agreement and includes the target of reaching a 30% global sales share for EVs by 2030.



Nickel-Cobalt-(Manganese , Aluminum) cathodes

$LiFePO_4$ cathodes

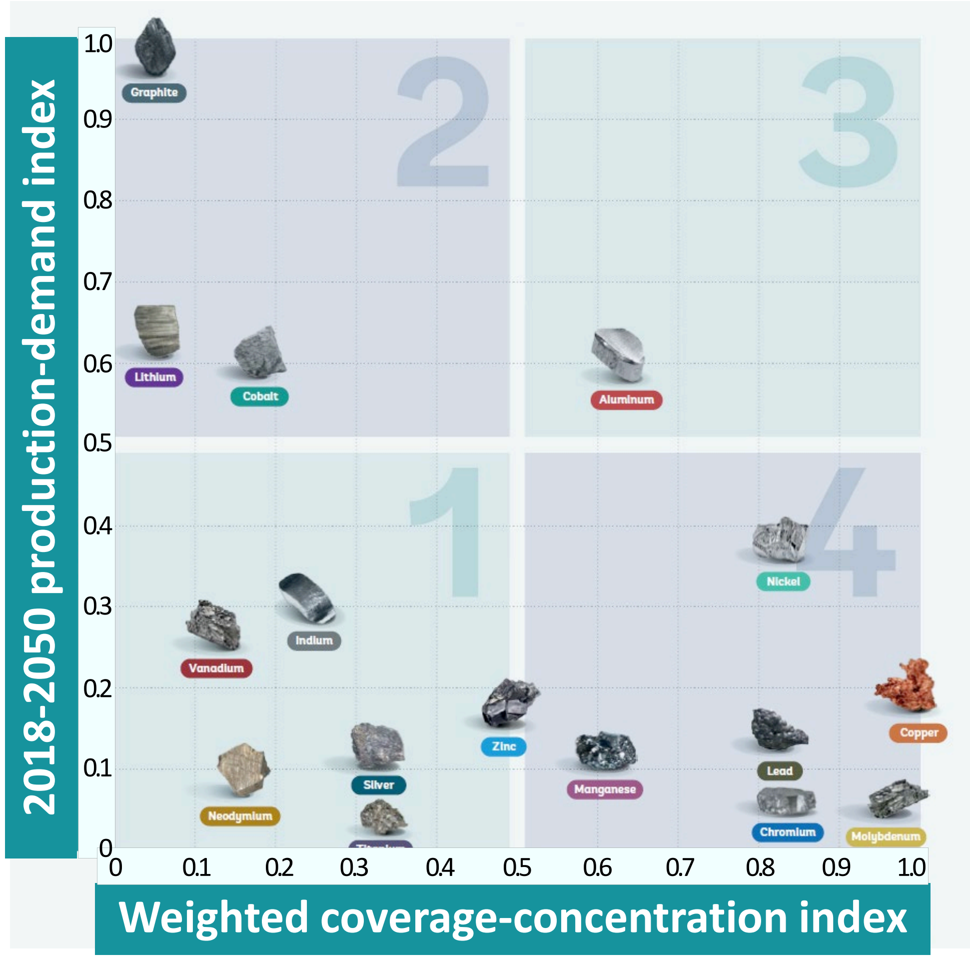
Xu, C., Dai, Q., Gaines, L., Hu, M., Tukker, A. and Steubing, B., 2020. Future material demand for automotive lithium-based batteries. *Communications Materials*, *1*(1), pp.1-10.

Background: Demand for Graphite for Li-ion Batteries (cont.)

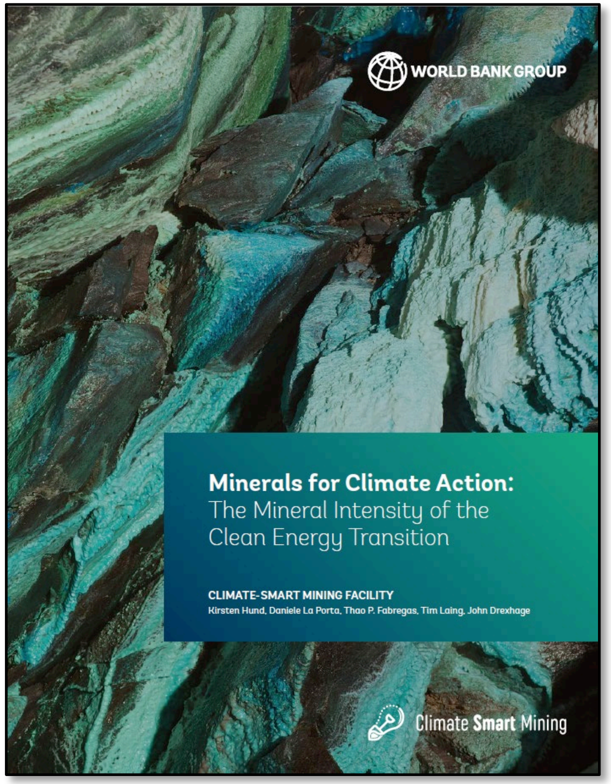
2018-2050 production-demand index: This index captures the scale to which production must scale up to meet demand from energy technologies. The index consists of two parts:

- Relative demand is captured by comparing 2050 demand from energy technologies to 2018 total production of the mineral. An index between 0 and 1 is then computed, with the mineral with highest relative demand, graphite, given a score of 1 and each other mineral given a score relative to graphite.
- Absolute demand is captured through the absolute level of demand in 2050 from energy technologies for each mineral. The mineral with the highest level (aluminum) is given a score of 1 and every other mineral is given a score between 0 and 1 relative to aluminum.

The two parts of the index are given an equal weight to compute an overall production-demand index.

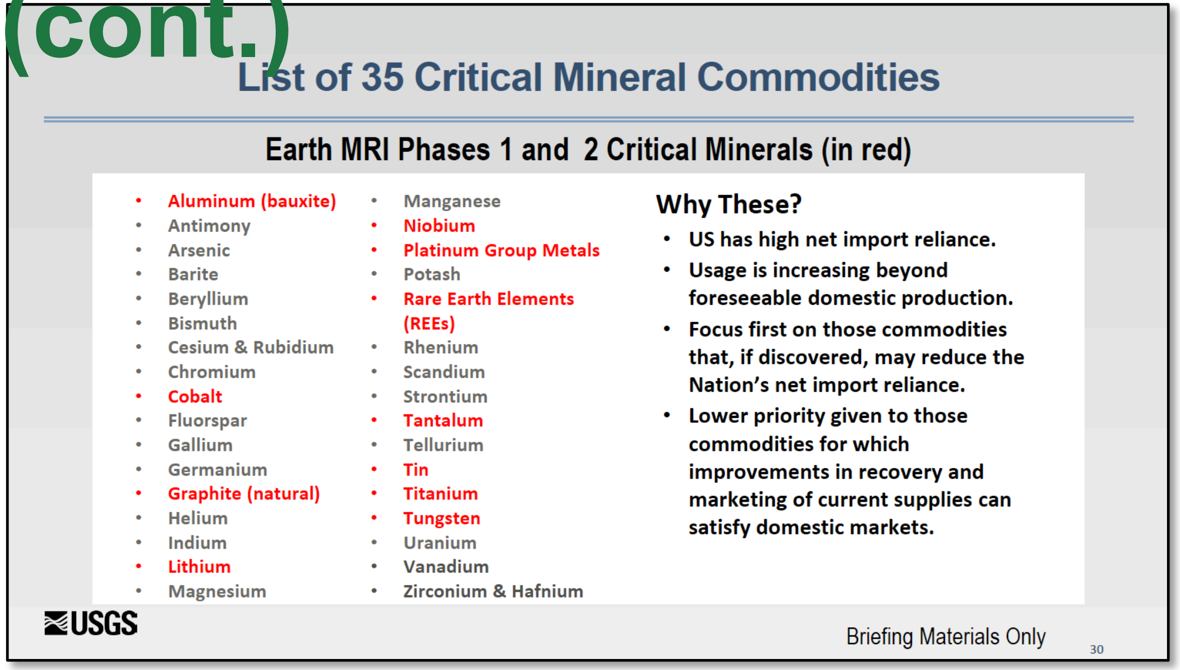


Weighted coverage-concentration index. This index captures how cross-cutting or concentrated in a few technologies the minerals are. A value for 1 is given for the most cross-cutting mineral, namely copper, with the scores for all other minerals relative to copper. The index is calculated on an equal weighting of : (1) the number of technologies that require one mineral, and (2) the share of demand for minerals that comes from a single technology.



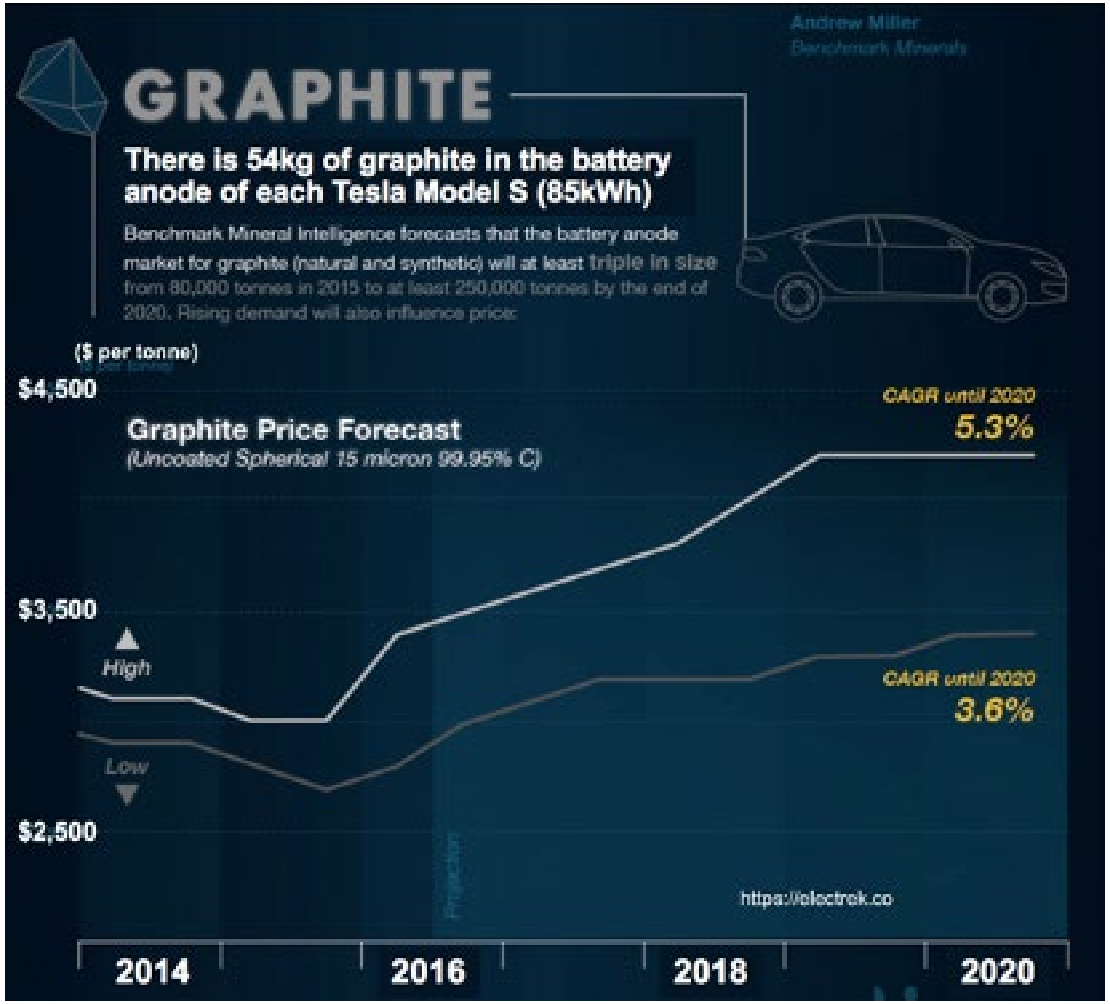
Under a 2-degree scenario (2DS), production of graphite, lithium, and cobalt will need to be significantly ramped up by more than 450% by 2050—from 2018 levels—to meet demand from energy storage technologies.

Background: Demand for Graphite for Li-ion Batteries (cont.)



The USGS has listed graphite as a critical mineral

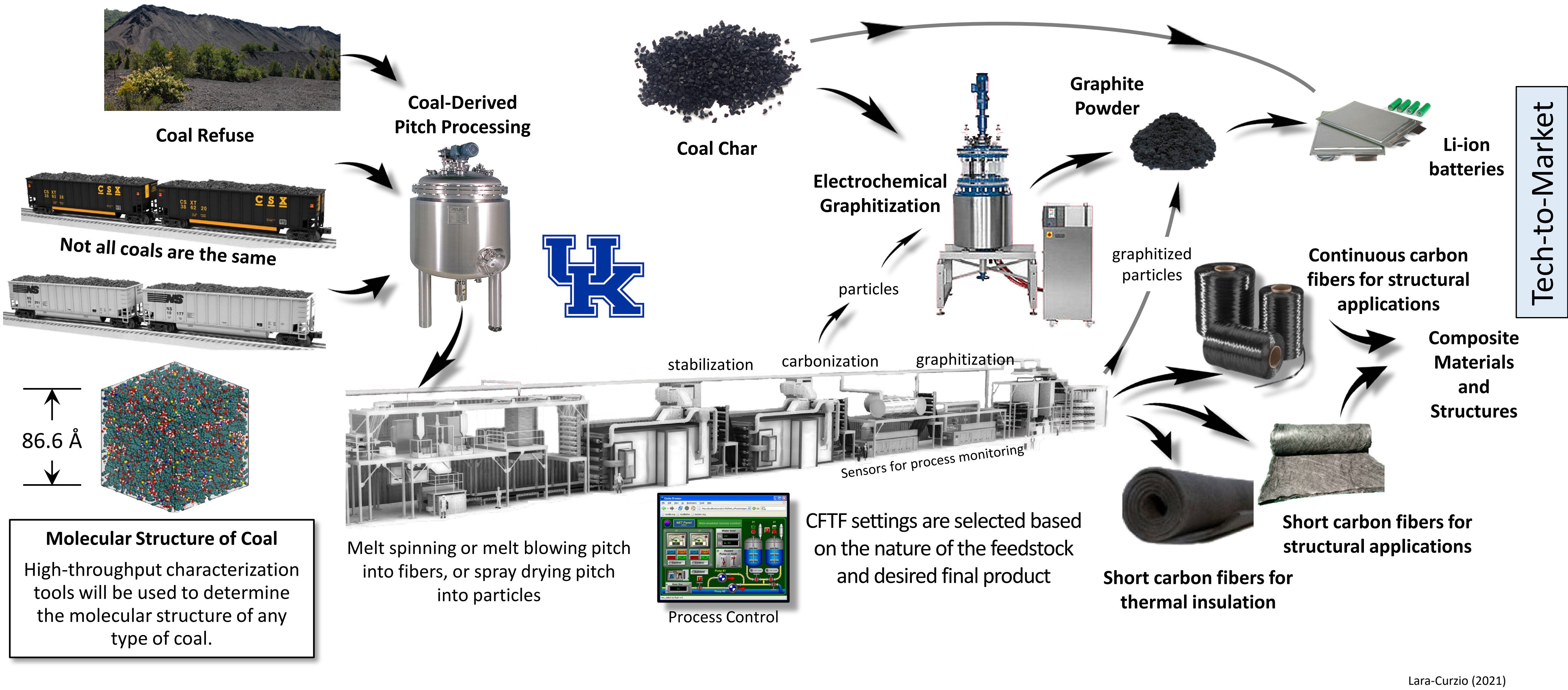
China is by far the largest producer of natural graphite, accounting for roughly two-thirds of world production. Only 4 percent of the world's natural graphite comes from North America, with no U.S. production in decades. Although natural graphite was not produced in the United States in 2016, about 98 U.S. firms, primarily in the Northeastern and Great Lakes regions, consumed graphite in various forms from imported sources for use in brake linings, foundry operations, lubricants, refractory applications, and steelmaking. Graphite's use in rechargeable batteries, as well as technologies under development (such as large-scale fuel-cell applications), could consume as much graphite as all other uses combined.



Outline

- Project Overview
- Background
- Approach

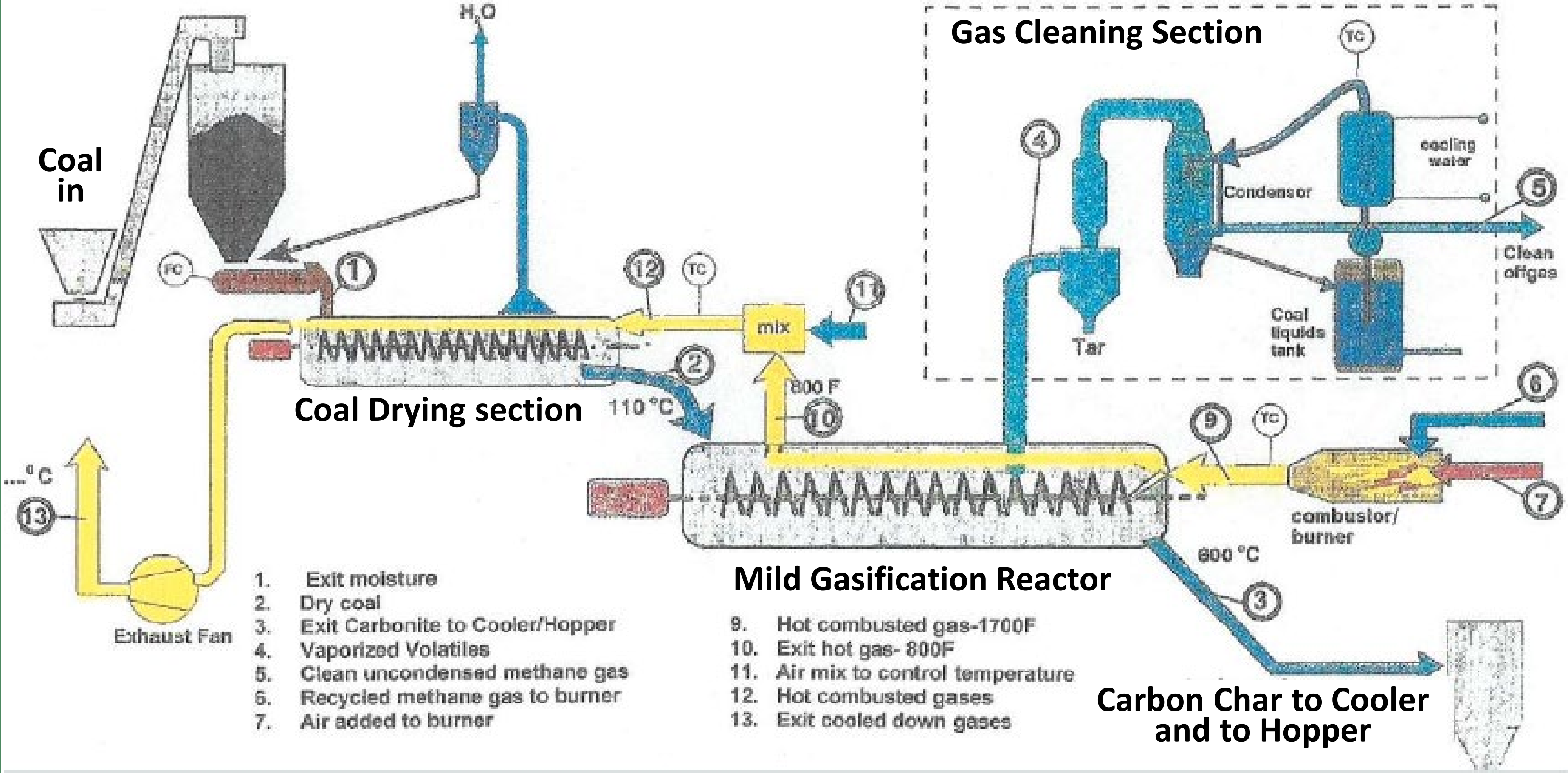
Carbon Ore and Coal Refuse-to-Products at ORNL's Carbon Fiber Technology Facility

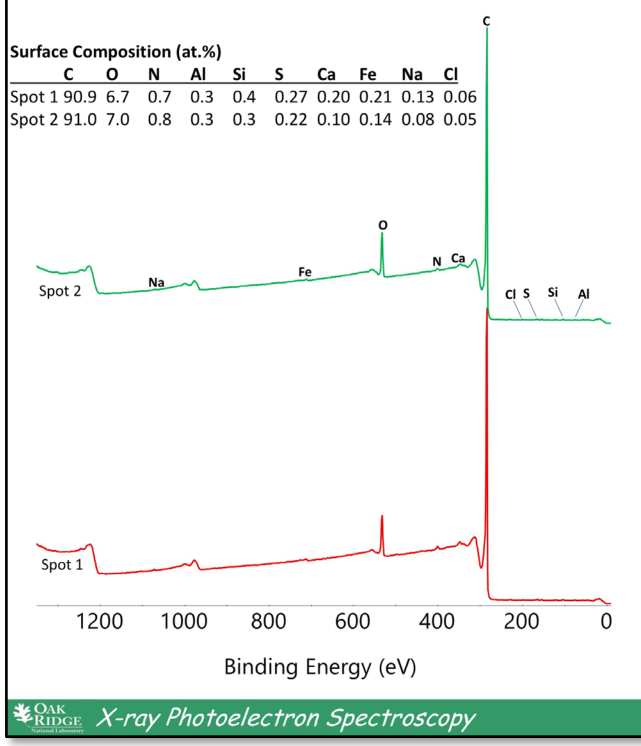


Coal Char by Mild Gasification — Carbon Technology Co

Coal ➡ Carbon Char

CTC'S Mild Gasification Process Converting Coal into Carbon Char, Coal Oil Liquids and Synthetic Non-Condensable Gas





Surface Composition (at.%)

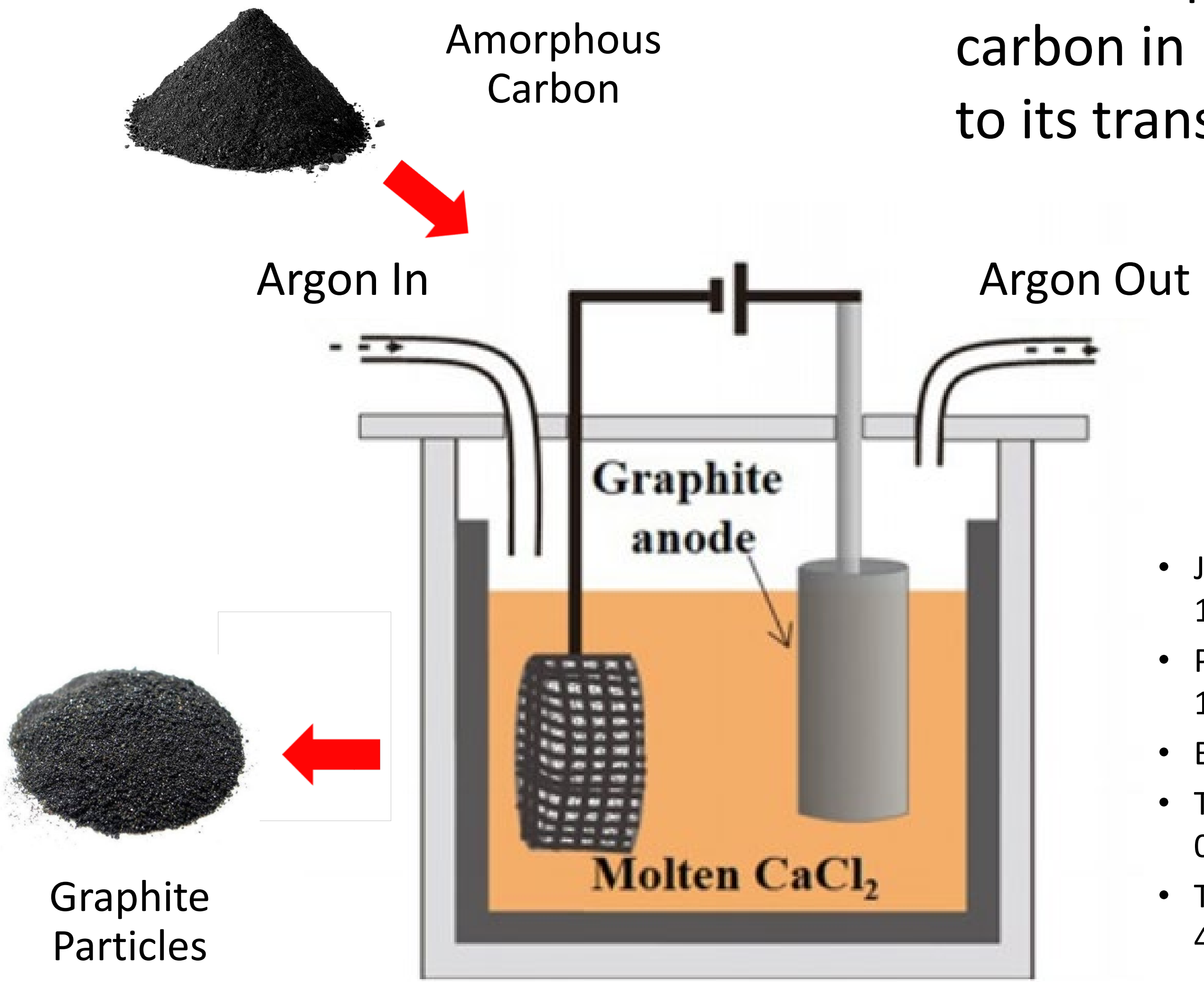
	C	O	N	Al	Si	S	Ca	Fe	Na	Cl
Spot 1	90.9	6.7	0.7	0.3	0.4	0.27	0.20	0.21	0.13	0.06
Spot 2	91.0	7.0	0.8	0.3	0.3	0.22	0.10	0.14	0.08	0.05

Blue Gem Coal Char

Carbon Technology Co. LLC
Bristol, Virginia

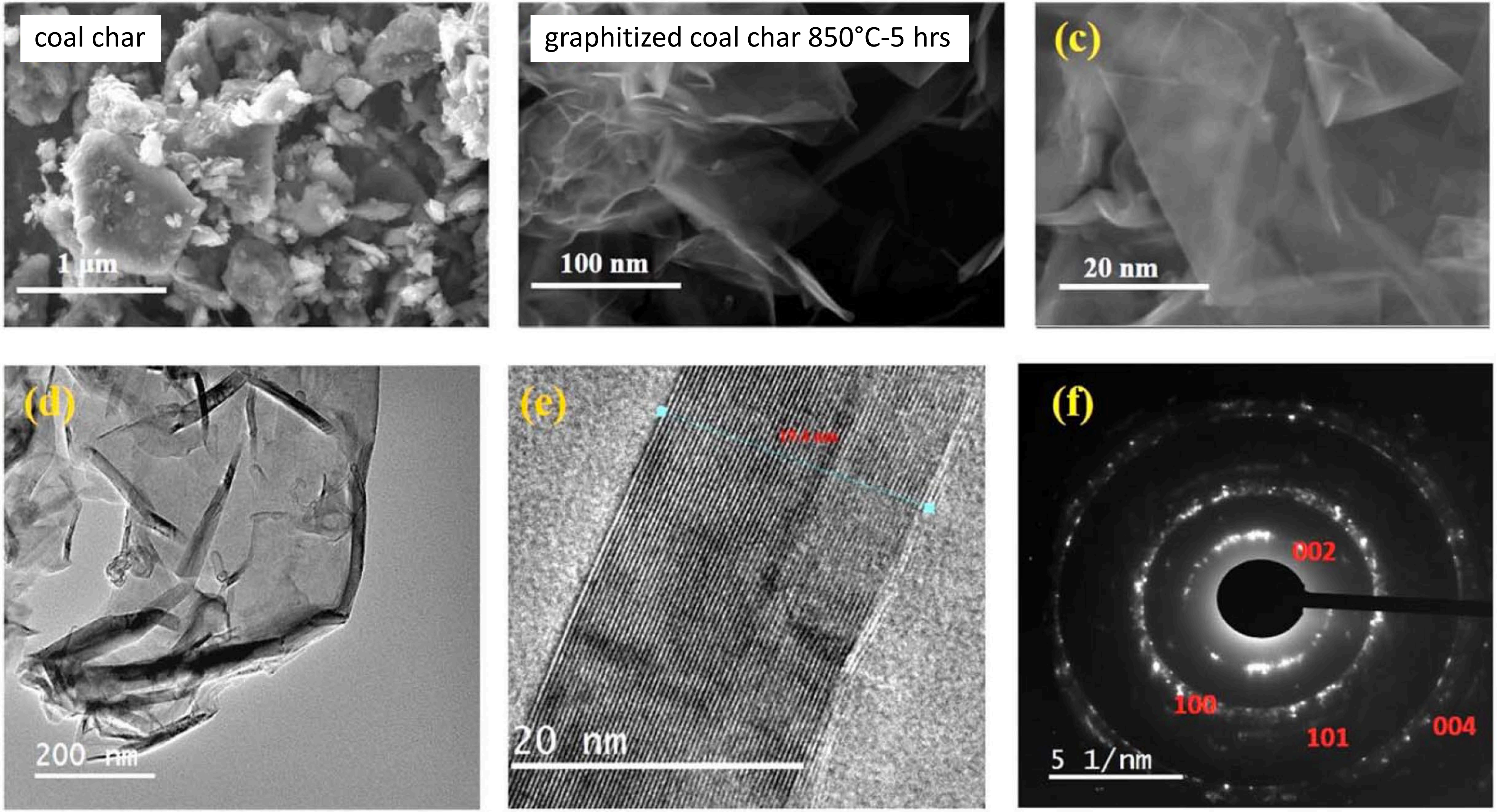
Electrochemical Graphitization

Cathodic polarization of amorphous carbon in molten $MgCl_2$ at ~850°C leads to its transformation into graphite.

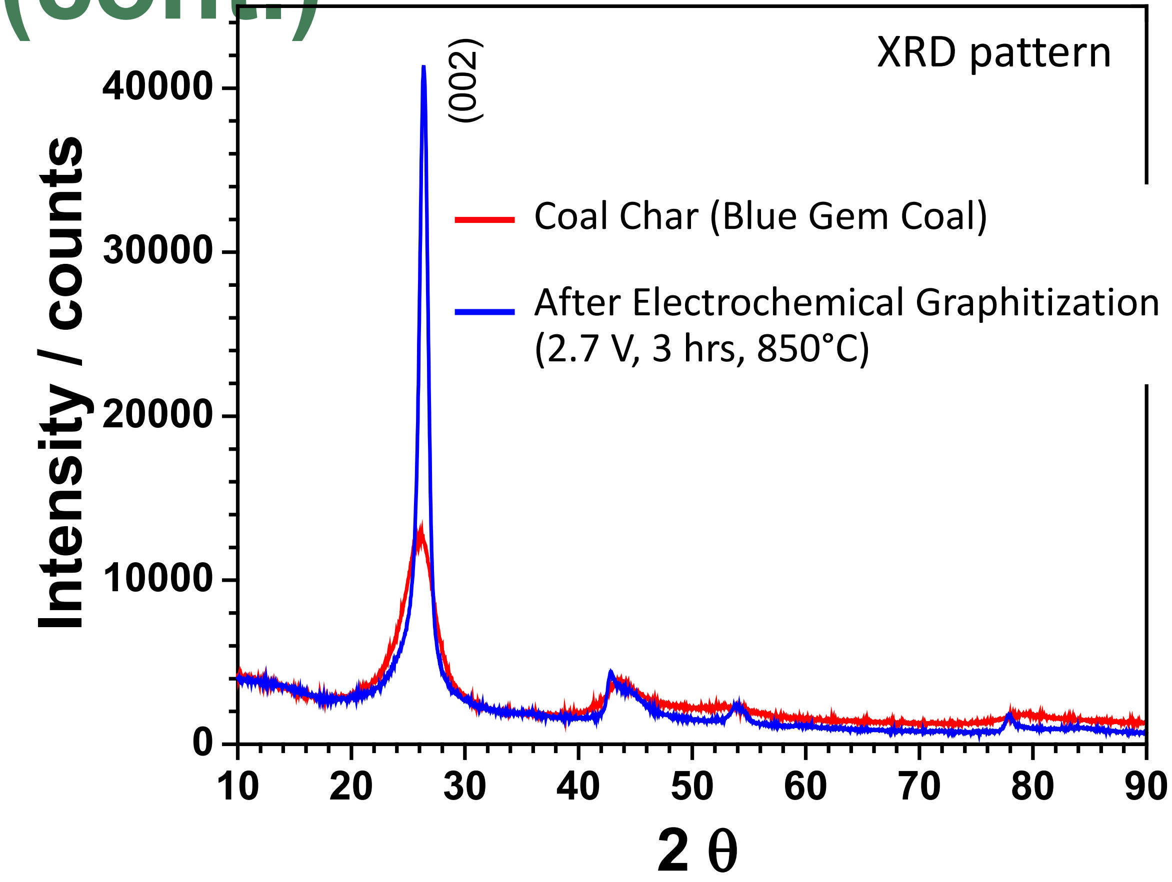


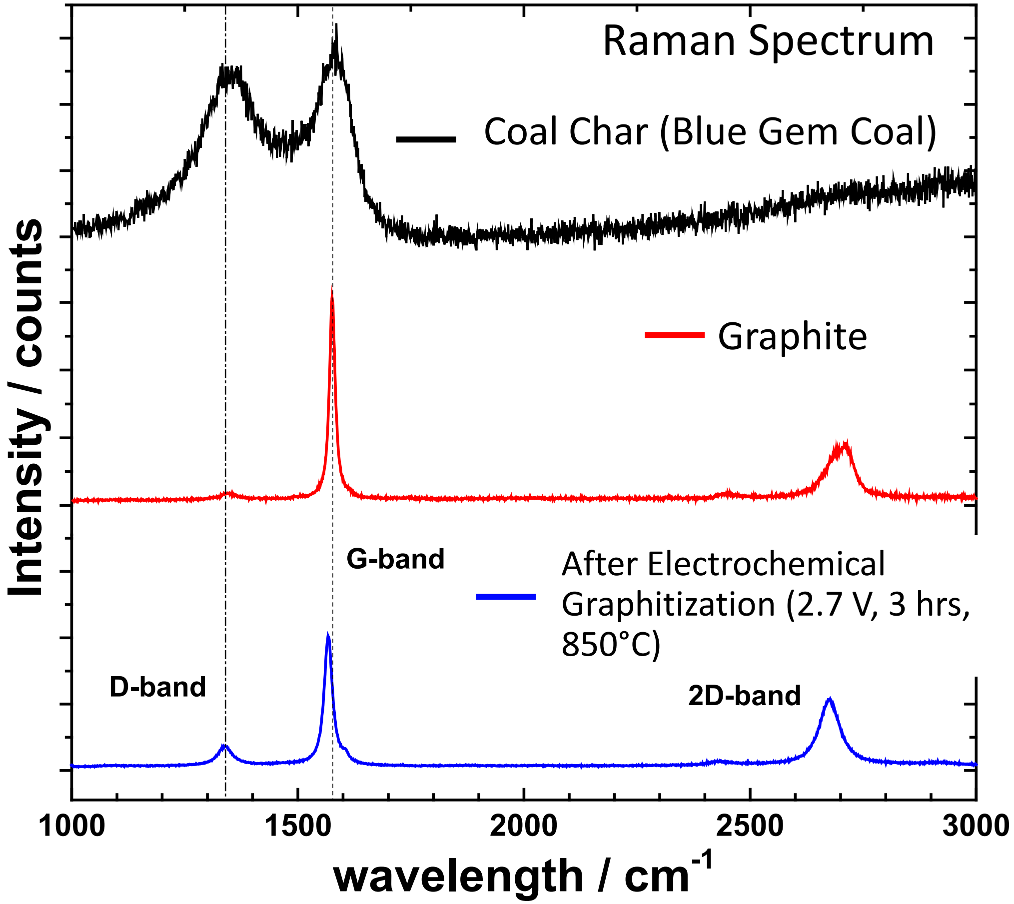
- Jin, X. B.; He, R.; Dai, S. *Chem.-Eur. J.* **2017**, *23*, 11455-11459
- Peng et. al., *Angew. Chem. Int. Ed.* **2017**, *56*, 1751-1755
- Bagri et. al., *Chem. Commun.* **2020**, *56*, 2783-2786
- Thapaliya et. al., *J Electrochem. Soc.* **2021**, *168*, 046504
- Thapaliya et. al., *ACS Appl. Mater. Interfaces* **2021**, *13*, 4393-4401

Electrochemical Graphitization of Coal Char



Electrochemical Graphitization of Coal Char (cont.)

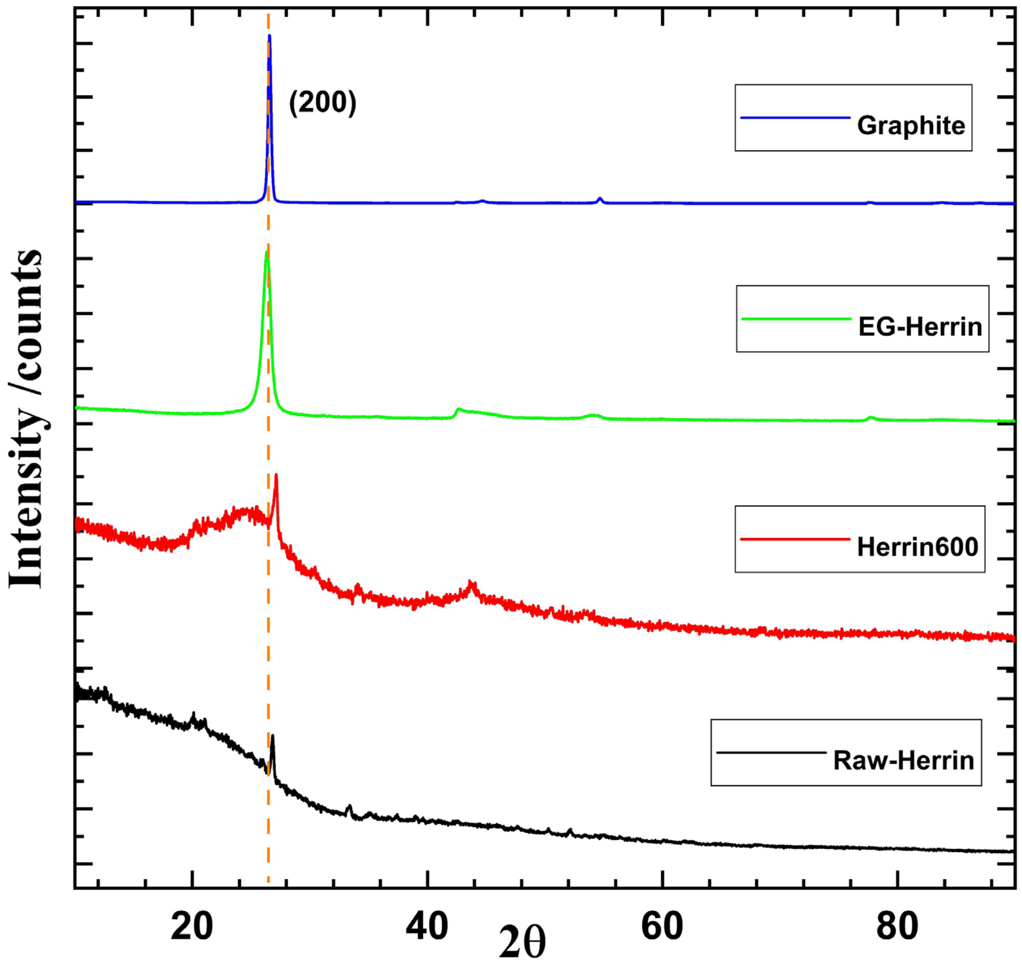




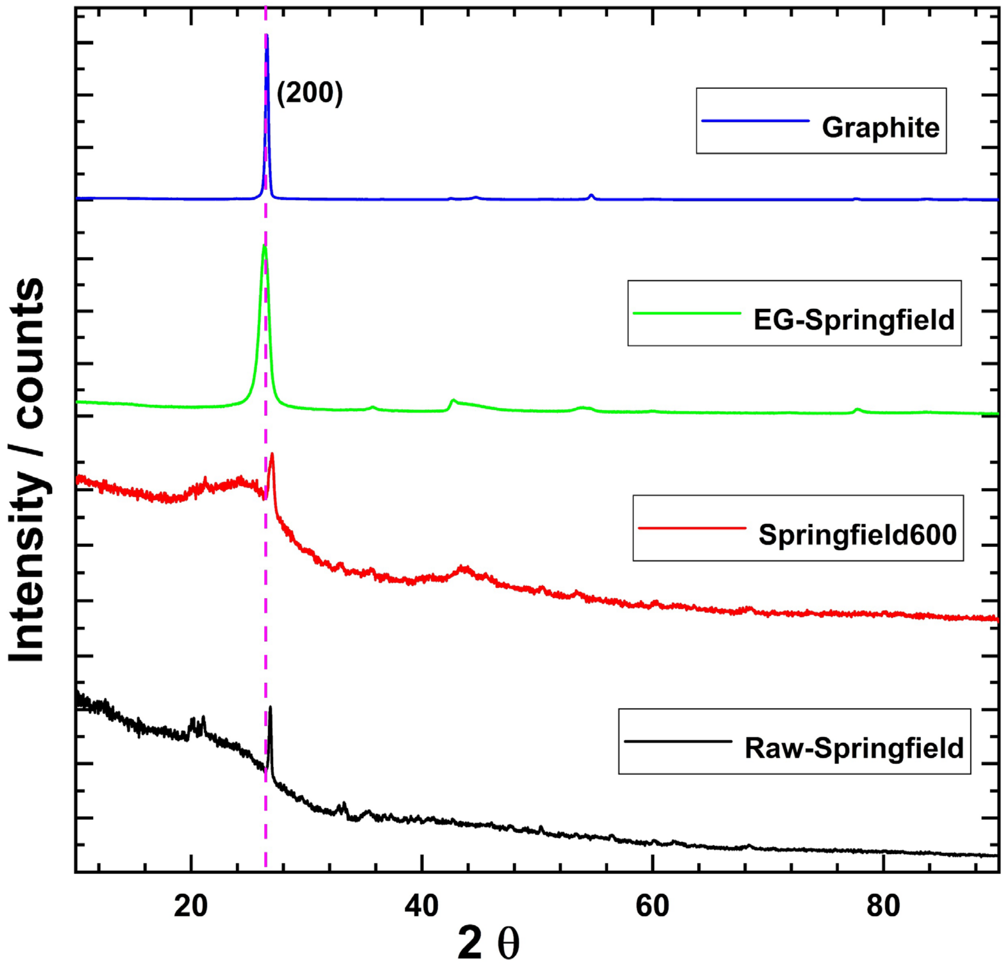
- XRD and Raman spectroscopy data confirmed successful graphitization.
  - Increased (002) peak intensity in XRD pattern
  - Low I_D/I_G ratio in Raman spectrum

Electrochemical Graphitization of Different Coal Chars

Herrin Coal



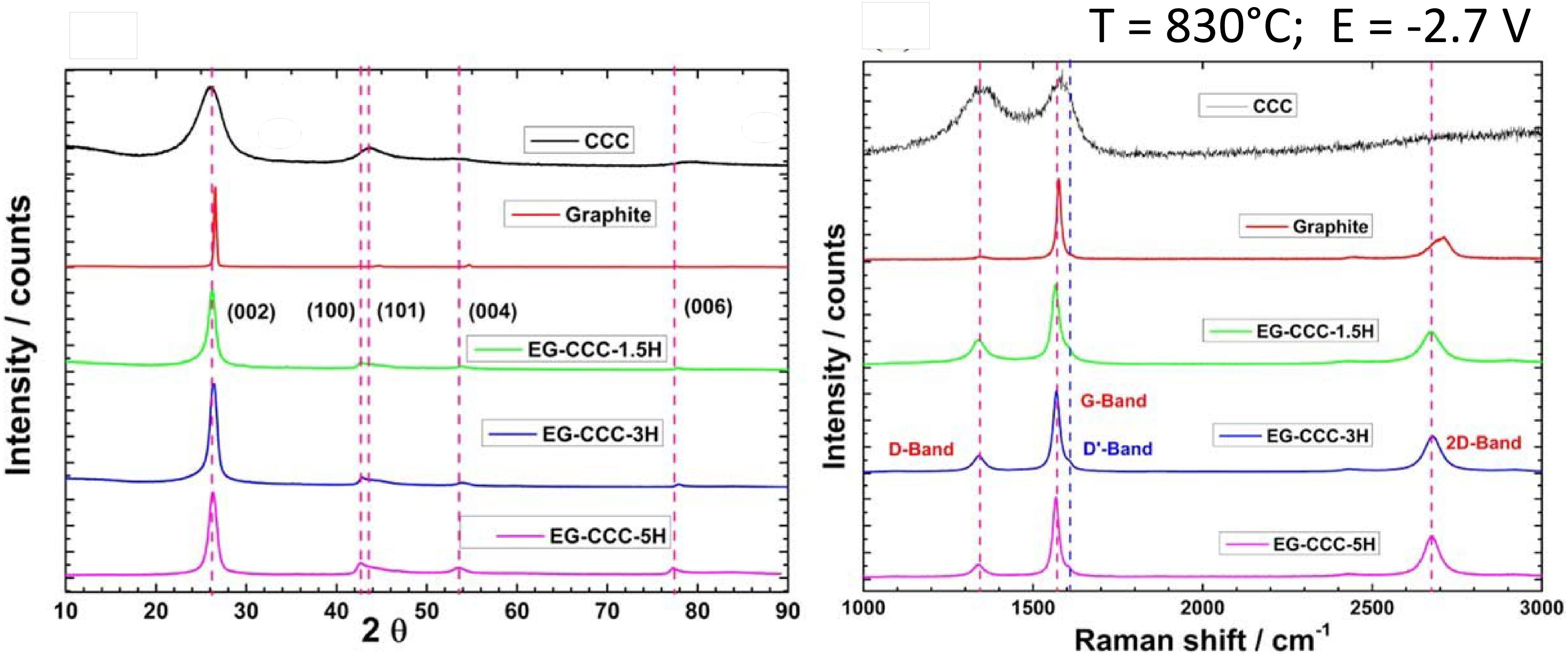
Springfield Coal



XRD patterns of raw-coal, of chars obtained by mild gasification (600°C for 6 hours), and electrochemically-graphitized chars at: -2.7 V, 850°C for 4 hours.

Low-Temperature Electrochemical Graphitization

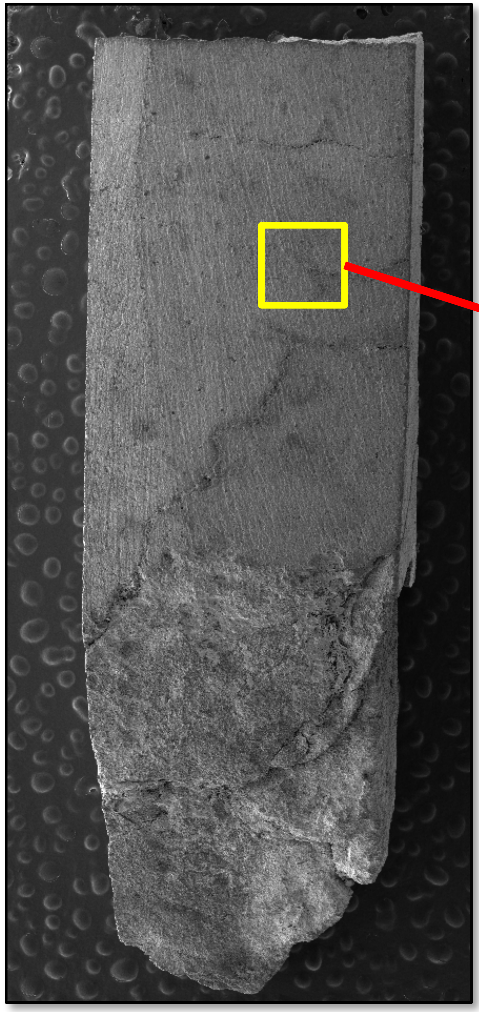
T = 830°C; E = -2.7 V

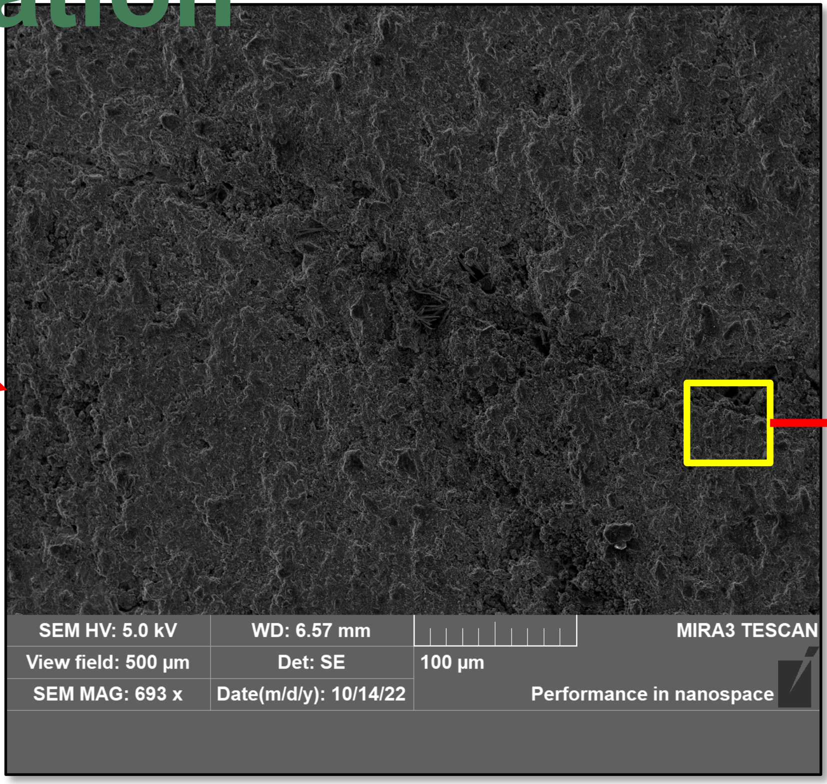


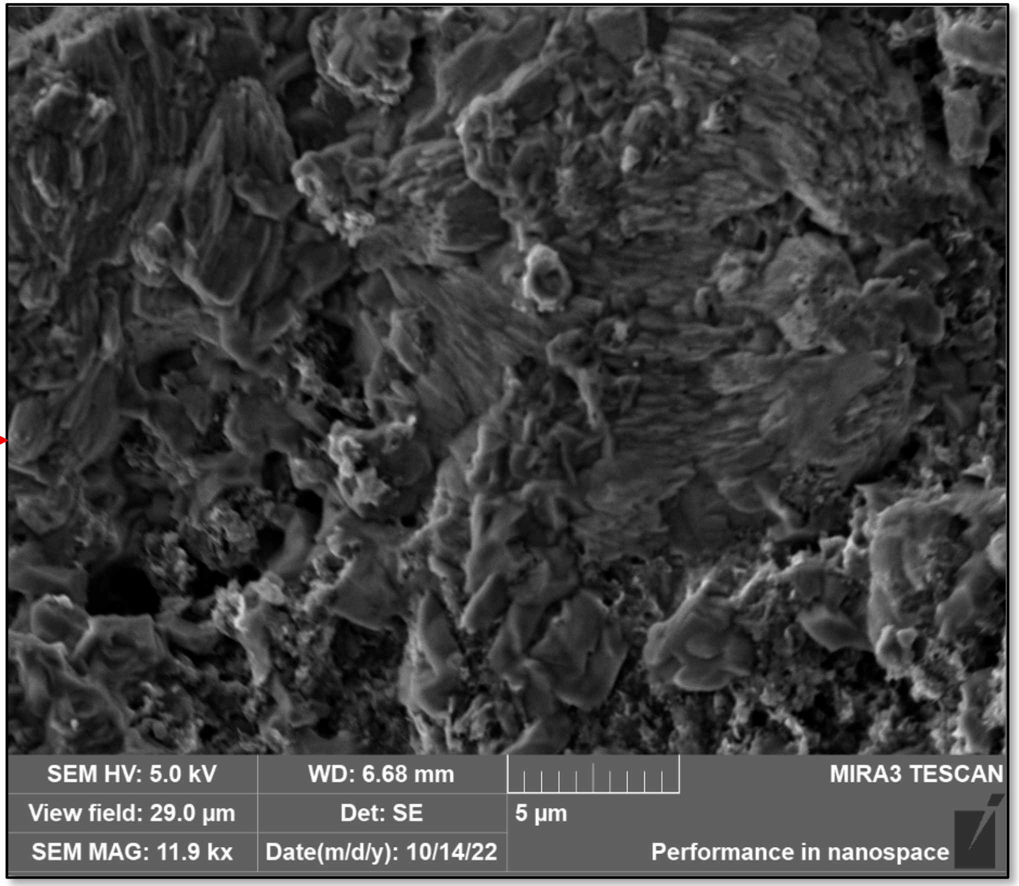
(left) XRD patterns (right) Raman spectra of coal char and electrochemically graphitized coal char (EG-CCC) as a function of time. Blue Gem Coal

OAK RIDGE National Laboratory

Low-Temperature Electrochemical Graphitization



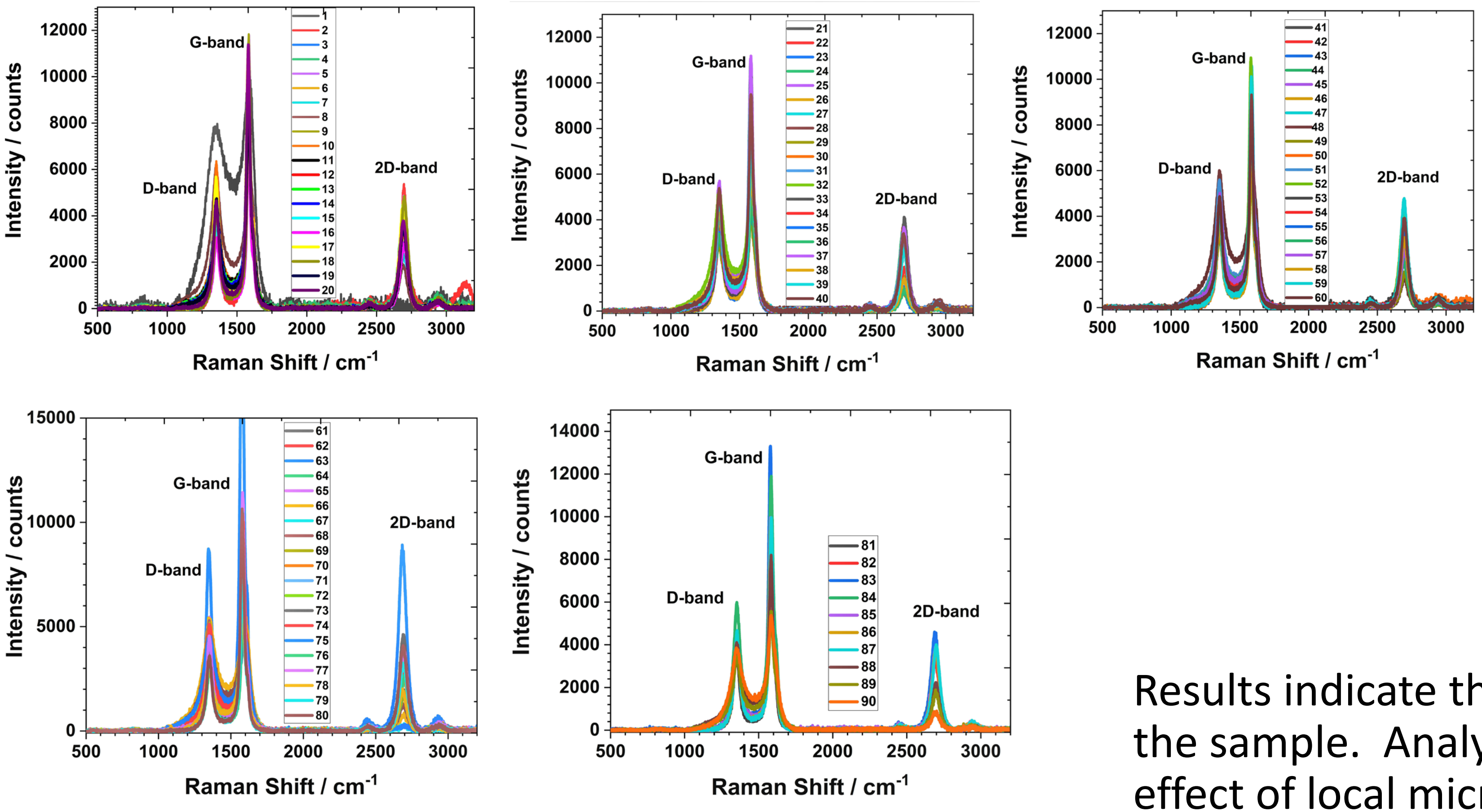


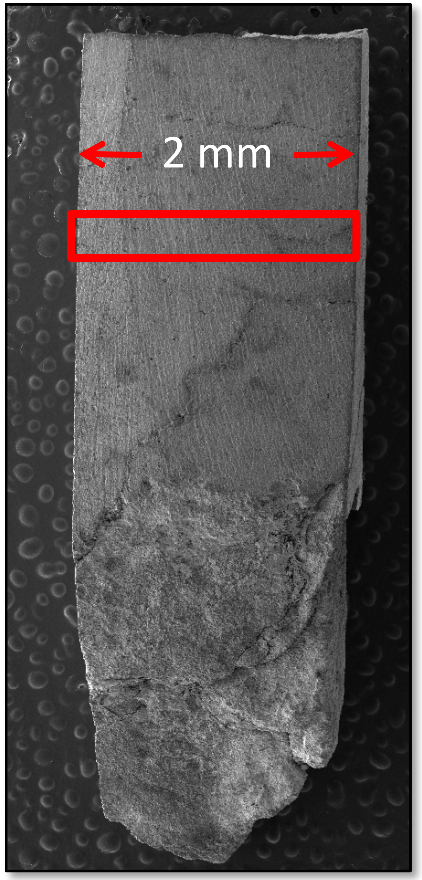


Assembly of cold-pressed coal char particles after electrochemical graphitization:
-2.7 V, 3 hours, 850°C.

Low-Temperature Electrochemical Graphitization

90 Raman spectra were obtained across the width of the sample (assembly of cold-pressed coal char particles)

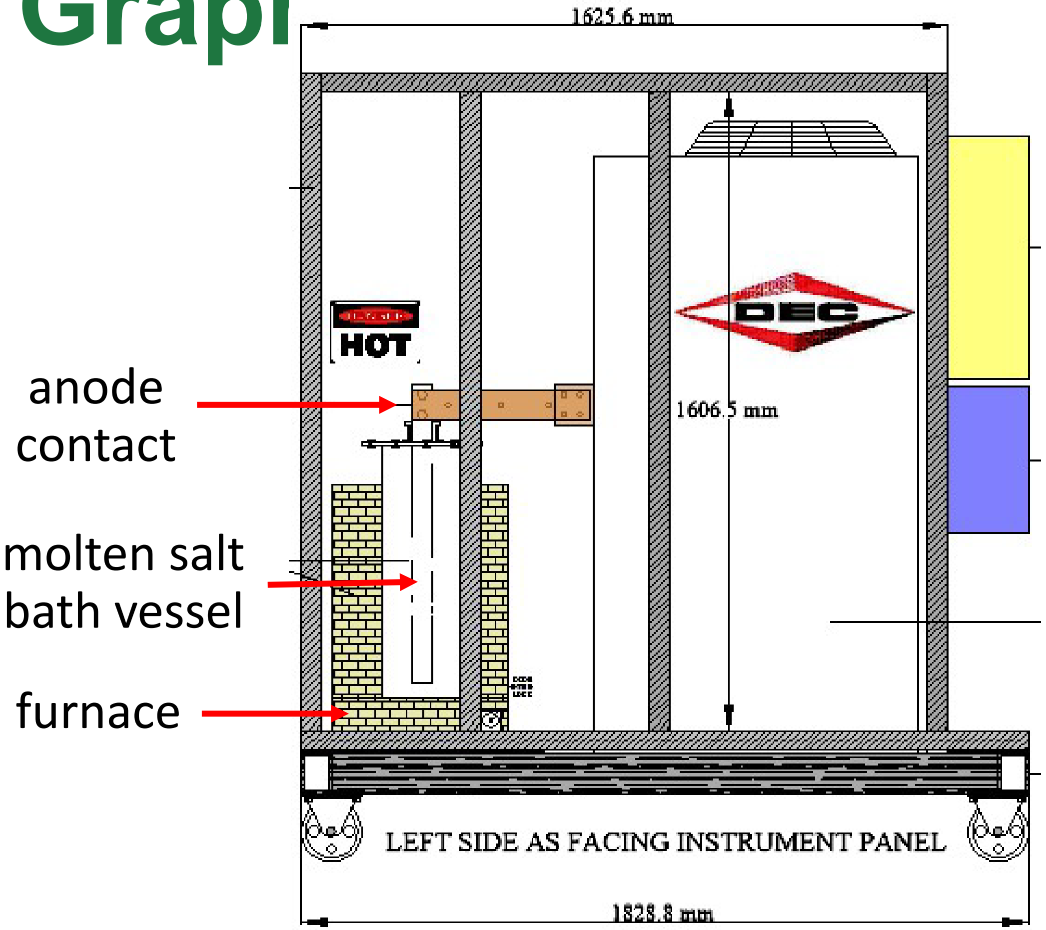




Results indicate that graphitization occurred across the sample. Analysis is in progress to correlate effect of local microstructure on graphitization.

OAK RIDGE National Laboratory

Scaling up — Electrochemical Grapl



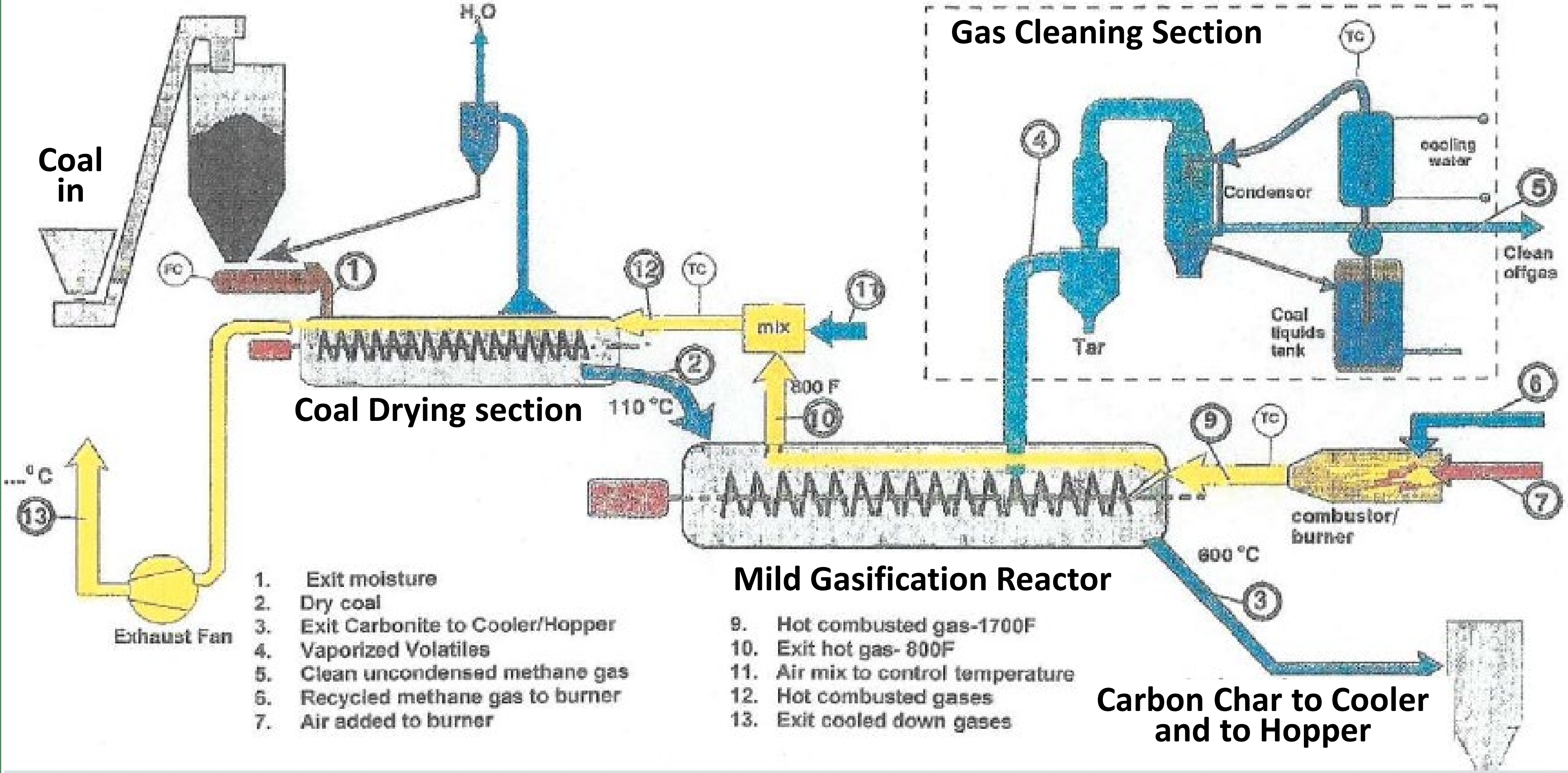
A system is being assembled to produce kilogram-quantities of graphite per batch.

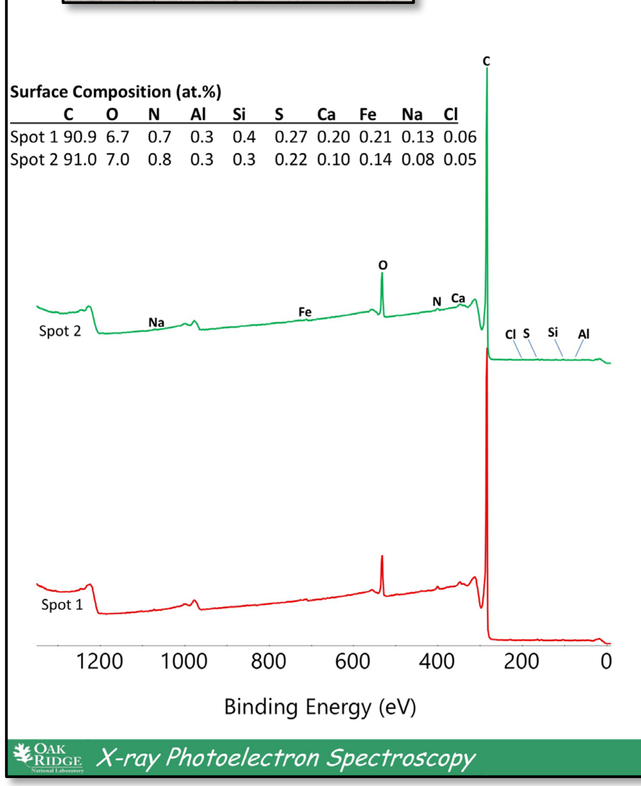
OAK RIDGE National Laboratory

Coal Char by Mild Gasification — Carbon Technology Co

Coal ➡ Carbon Char

CTC'S Mild Gasification Process Converting Coal into Carbon Char, Coal Oil Liquids and Synthetic Non-Condensable Gas



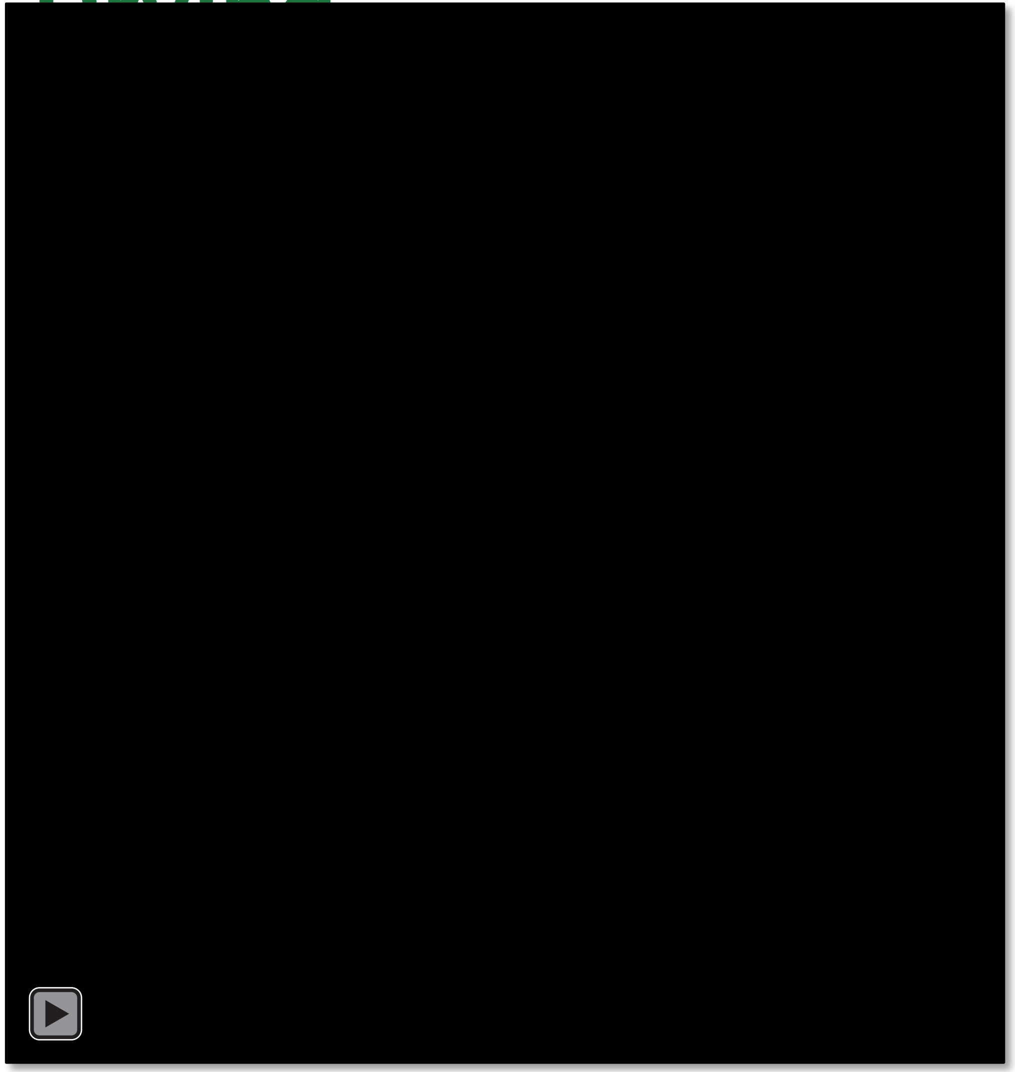


	C	O	N	Al	Si	S	Ca	Fe	Na	Cl
Spot 1	90.9	6.7	0.7	0.3	0.4	0.27	0.20	0.21	0.13	0.06
Spot 2	91.0	7.0	0.8	0.3	0.3	0.22	0.10	0.14	0.08	0.05

Blue Gem Coal Char

Carbon Technology Co. LLC
Bristol, Virginia

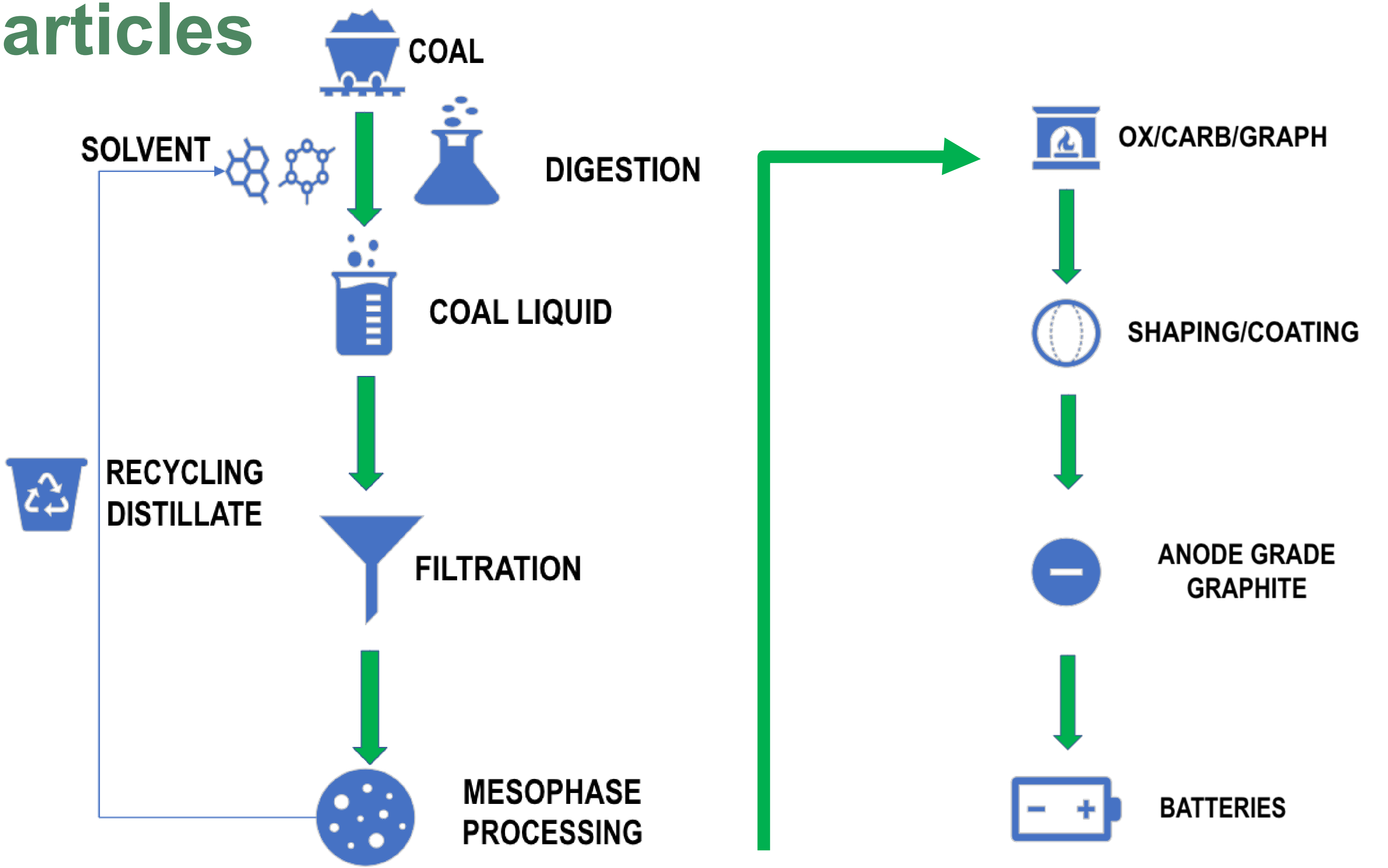
Production of spherical carbon particles by Spray Drying



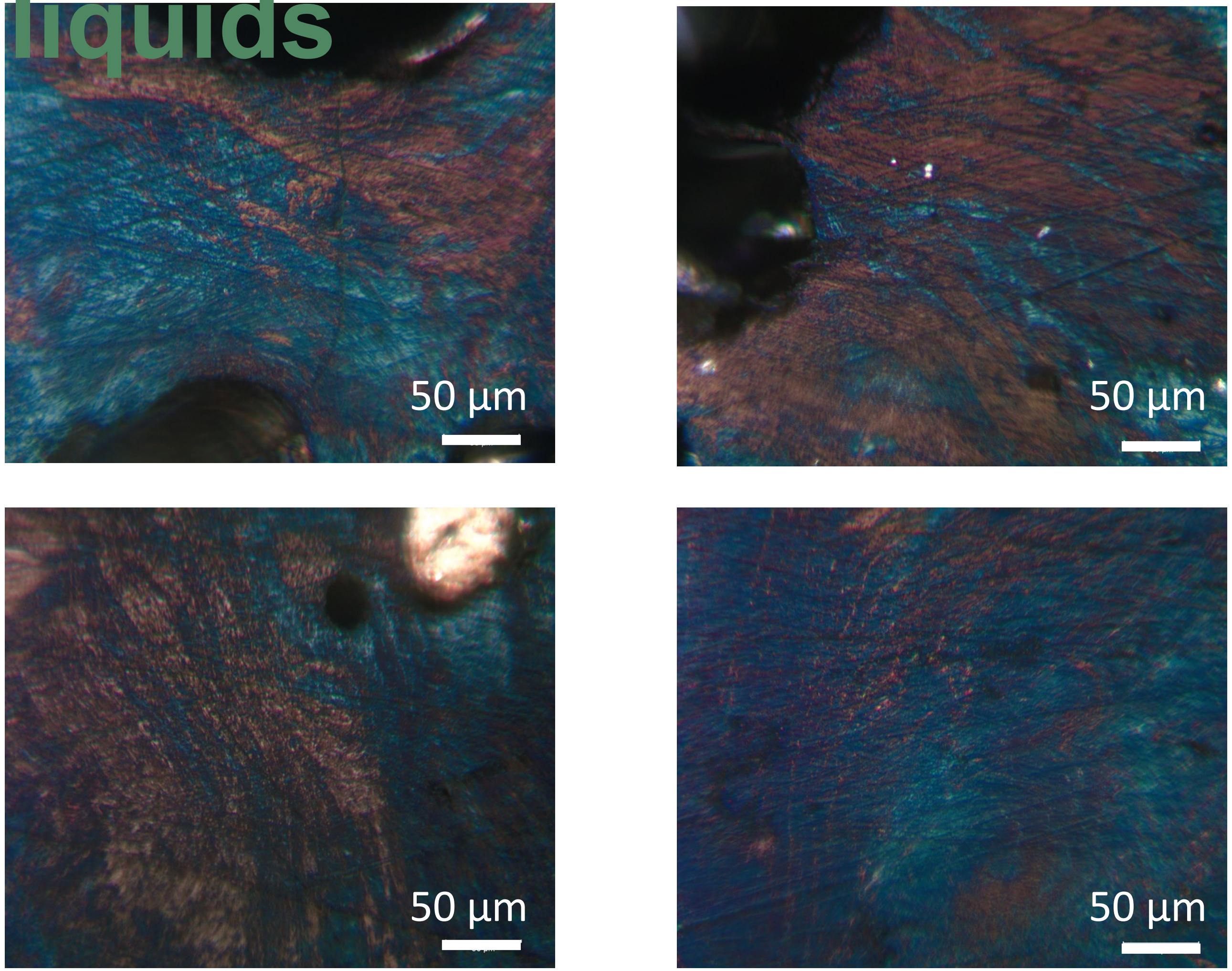
Solid carbon particles are used as feedstock for electrochemical graphitization.

Process enables control of particle size distribution

Alternative Route for Manufacturing of Graphite Particles



Mesophase (Graphite Precursor) from coal liquids



SFDO2(13)-M173

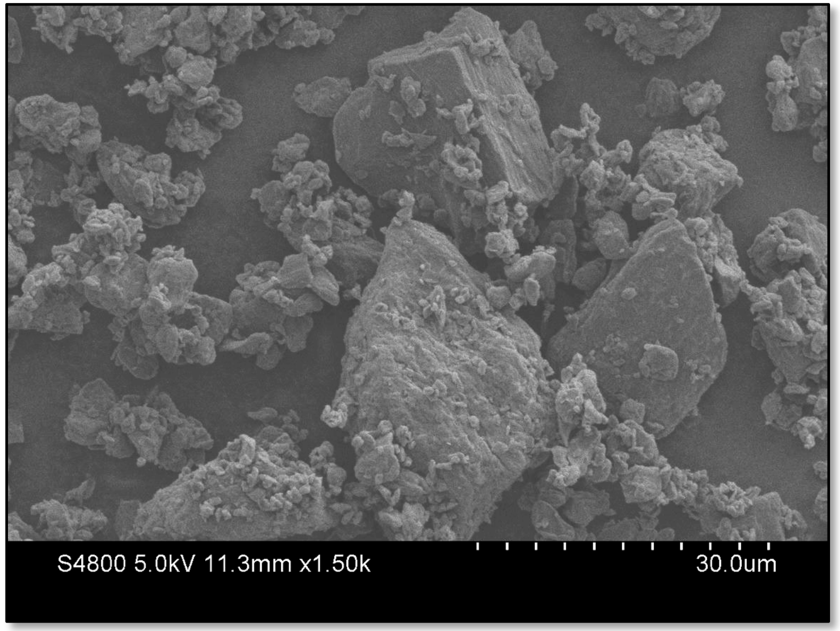
Springfield Coal/Decant Oil 410°C, ~240 min

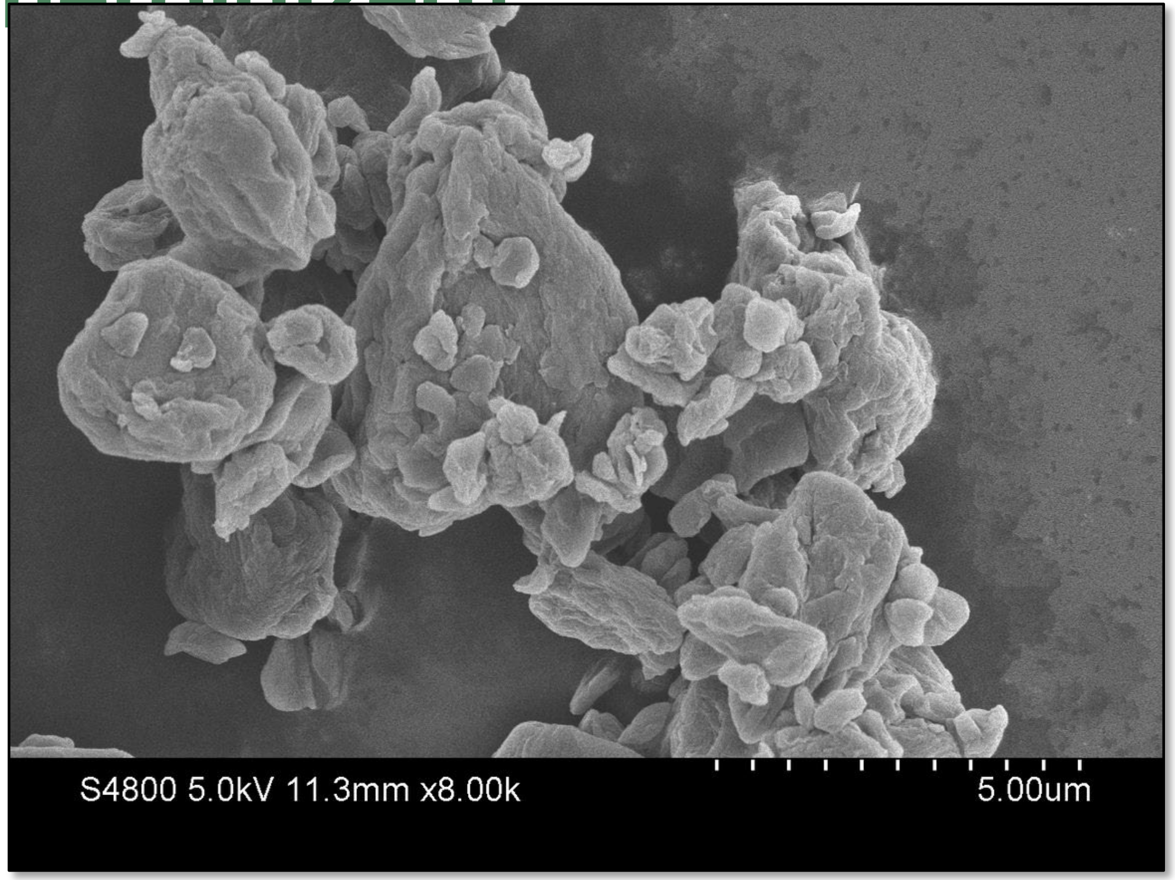
- T_{sp}: 388 °C
- Mesophase count: 100%

- M173 was powdered via ball mill and sieved to < 200 mesh before oxidation.
- **Oxidation Profile:** 120 °C to 310 °C
- **Carbonization/Graphitization Profile:** 900 °C then 2400 °C

Step	Yield
Oxidation	108.7%
Carb/Graph	51.1%
Final	55.5%

SEM images of Graphitized Mesophase from Coal Liquid (not spheroidized)





2400°C

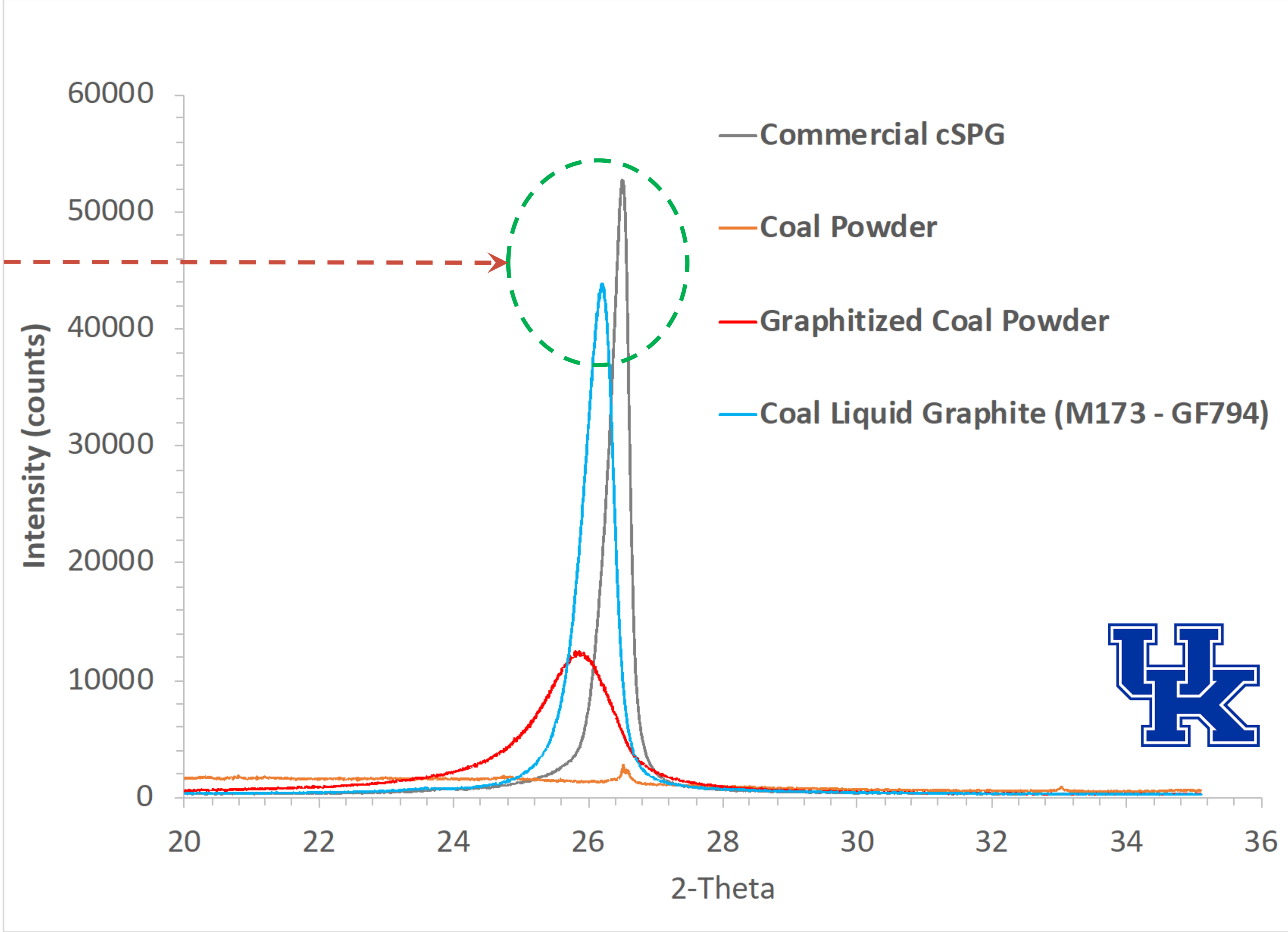
M173

Oak Ridge National Laboratory

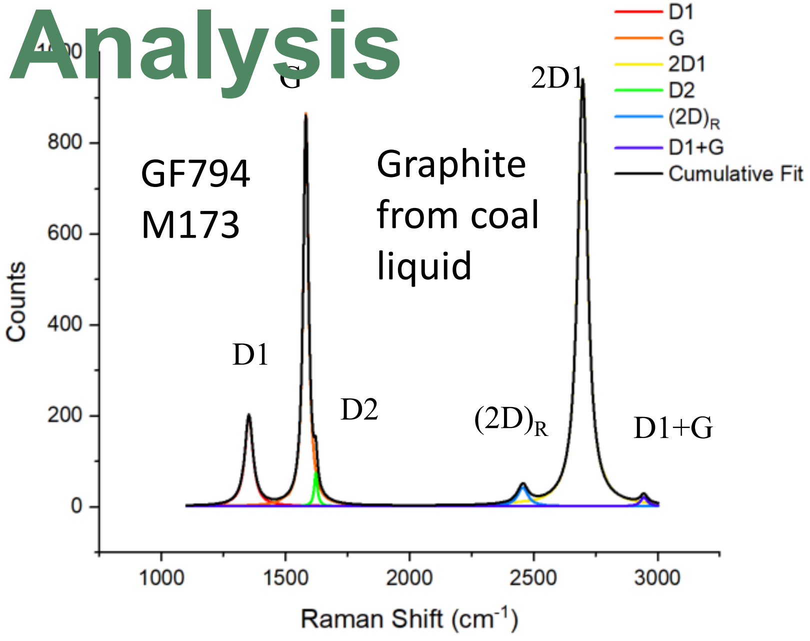
Graphitized Mesophase from Coal Liquid — XRD Results

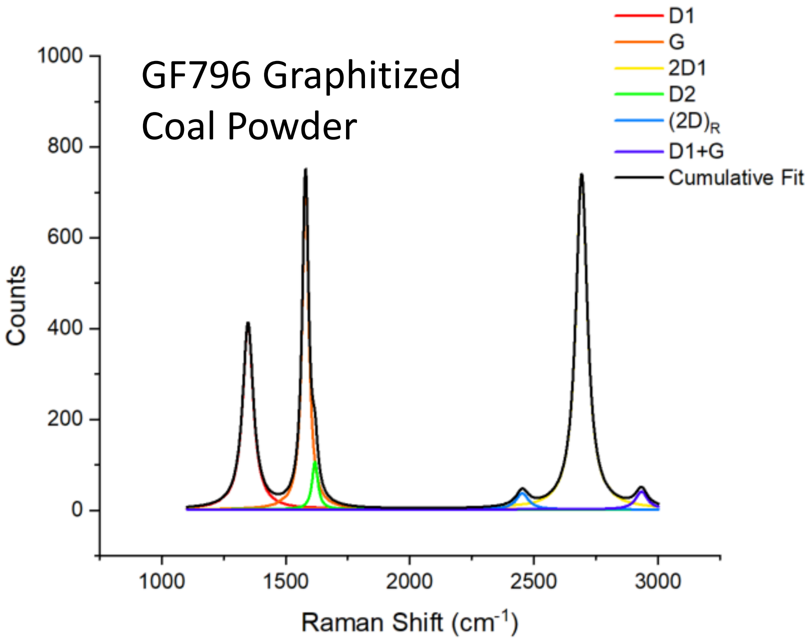
Graphitization of coal powders does not generate a well-formed graphite crystal

Graphite stemming from the coal-liquid-derived mesophase compares favorably with a commercial (coated) spherical graphite, after a heat treatment at 2400 °C.



Graphitized Mesophase from Coal Liquid — Raman Analysis





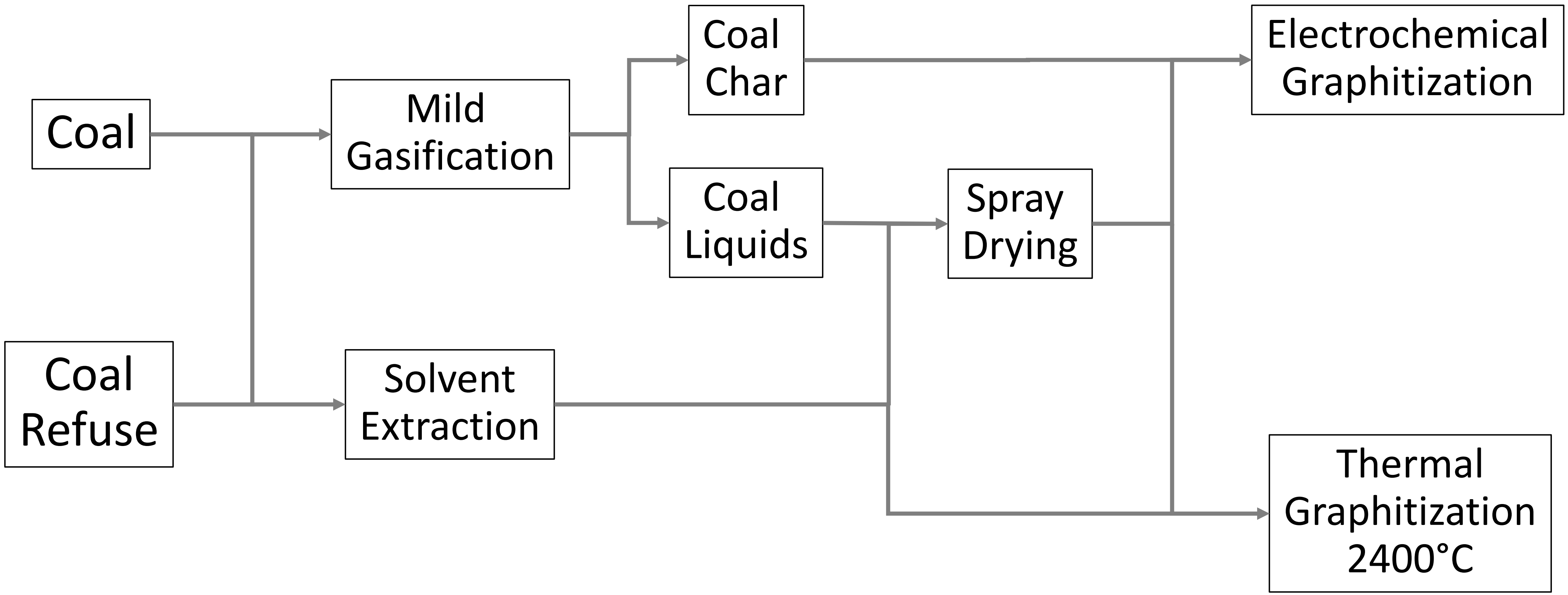
	I_{D1}/I_G	A_{D1}/A_G	G-FWHM
GF794 M173 Graphite-mesophase	0.23	0.36	25
GF796 Graphite - Coal Powder	0.55	0.91	31

Graphitized mesophase pitch (GF794 M173) compared to graphitized coal (GF796)

- Increased order evident with reduction in I_{D1}/I_G
- A_{D1}/A_G and G-FWHM decrease with metamorphism, which is commonly used in characterizing the increasing structural order
- For most coal derived graphites, the A_{D1}/A_G values are between 0.85 and 1.70[1]
- G-FWHM less than 30.3 cm^{-1} is classified as a graphite, while a G-FWHM greater than greater than 30.3 cm^{-1} is classified as a semi-graphite[2]
- Emergence of 2D1 and D1+G peaks indicate stacking along the c-axis
- The $(2D)_R$ peaks indicates the formation of a large aromatic ring system

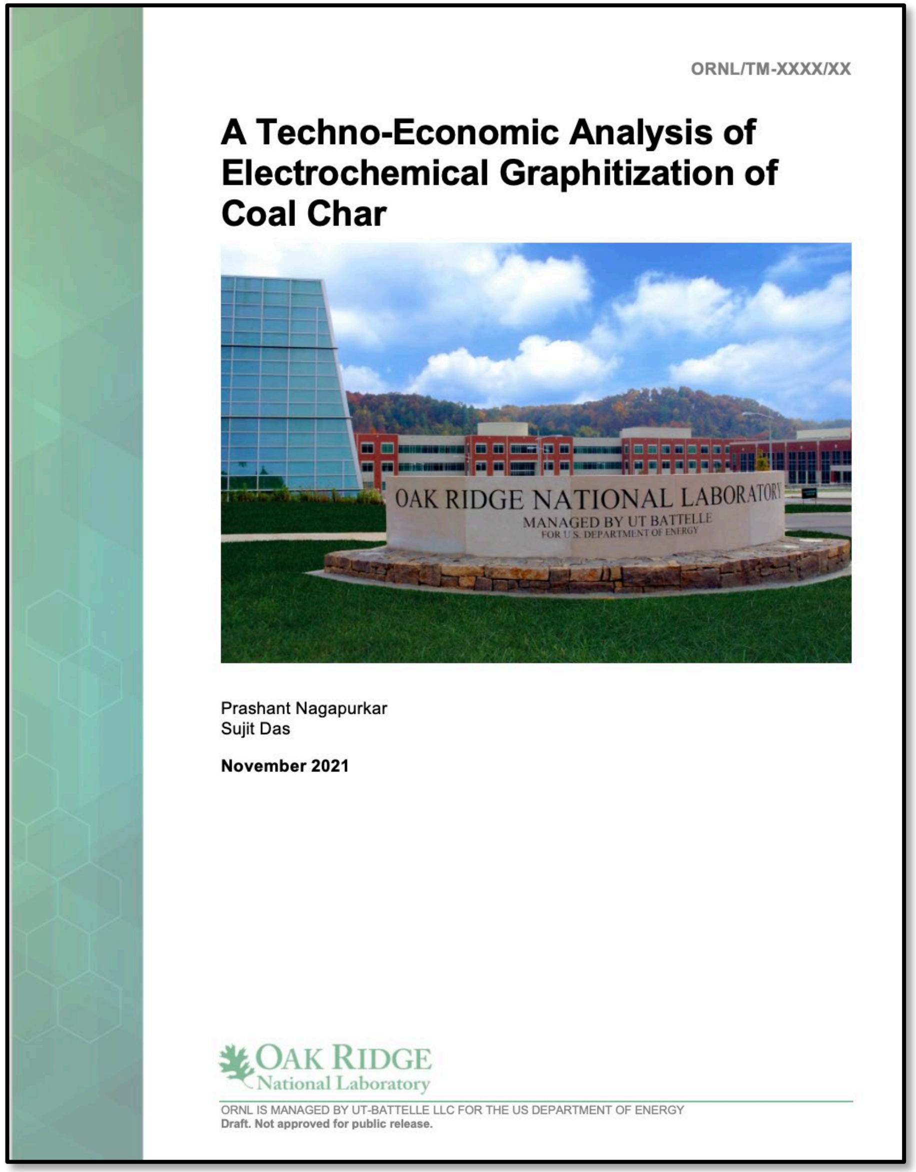
[1]Yuan, L., et al. *Energy Fuels* **2021,** 35, (3), 2335-2346.
[2]Zhang, S., et al. *Carbon* **2020,** 157, 714-723.

Different routes to graphite



Techno-Economic and Life-Cycle Analyses

Technical, economic, and environmental analyses are being formulated to assess the market viability of graphite derived from carbon ore and coal refuse for lithium-ion batteries.


ORNL/TM-XXXX/XX

A Techno-Economic Analysis of Electrochemical Graphitization of Coal Char

Prashant Nagapurkar
Sujit Das

November 2021

OAK RIDGE National Laboratory

ORNL IS MANAGED BY UT-BATTELLE LLC FOR THE US DEPARTMENT OF ENERGY
Draft. Not approved for public release.

Technology-to-Market

- One objective of this project is to advance the commercial viability of graphite obtained from carbon ore and coal refuse, including the development of strategies to maximize the chances of commercialization.
- Workshops will be organized to disseminate the results from this project and to engage stakeholders, including Lithium-ion battery manufacturers and OEMs to explore technology transfer and commercialization opportunities.

Summary

- A process is being developed to scale up the electrochemical graphitization of carbons from different sources.
- Mild gasification of coal and coal refuse can be used to produce high-carbon-content char and coal liquids.
- Spray drying is being used to obtain carbon particles with controllable particle size distribution from coal liquids and mesophase.
- Graphite particles have been obtained by heat treating mesophase obtained by solvent extraction at 2400°C.
- A technoeconomic analysis is being formulated to identify the most cost-effective route for producing graphite for lithium-ion batteries

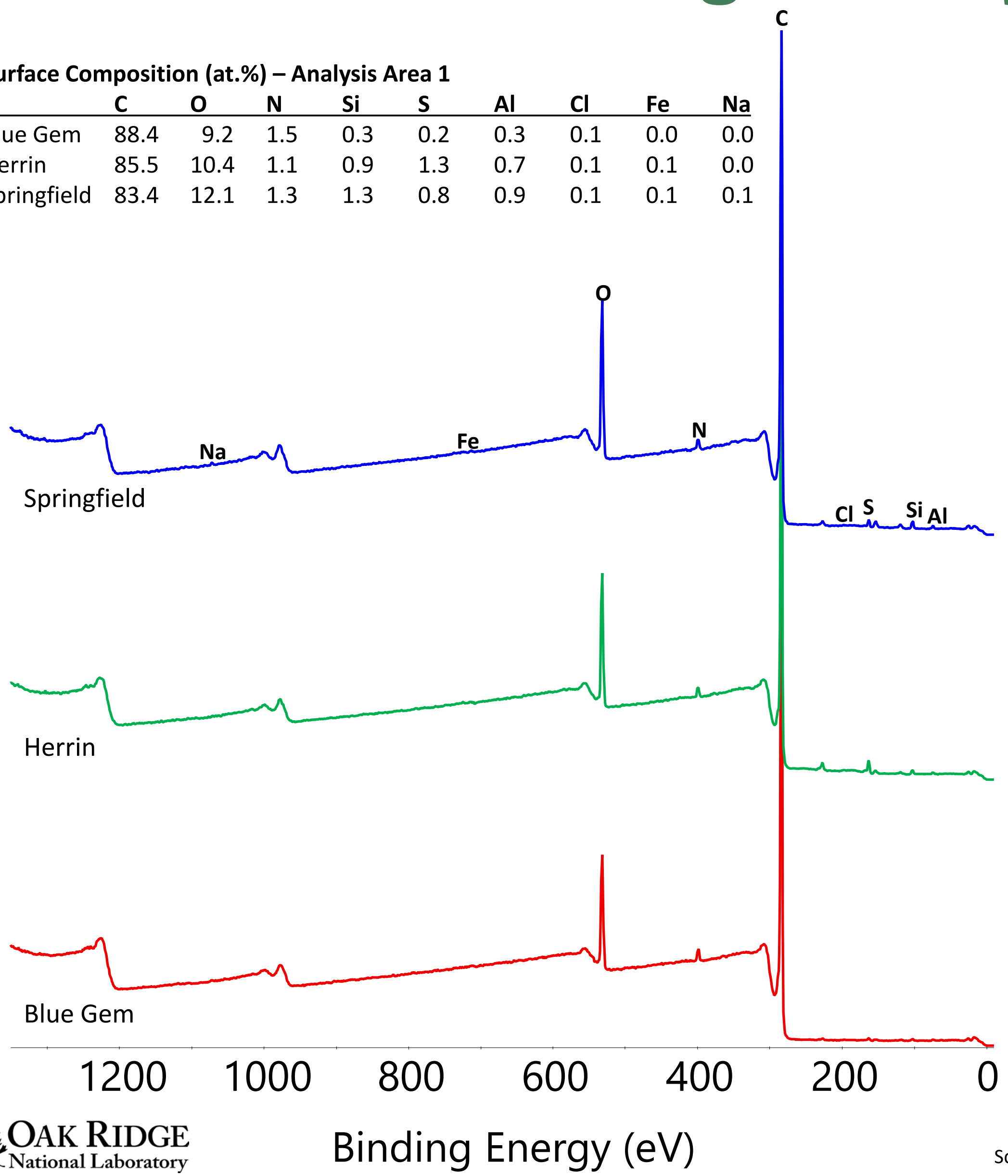
Questions?

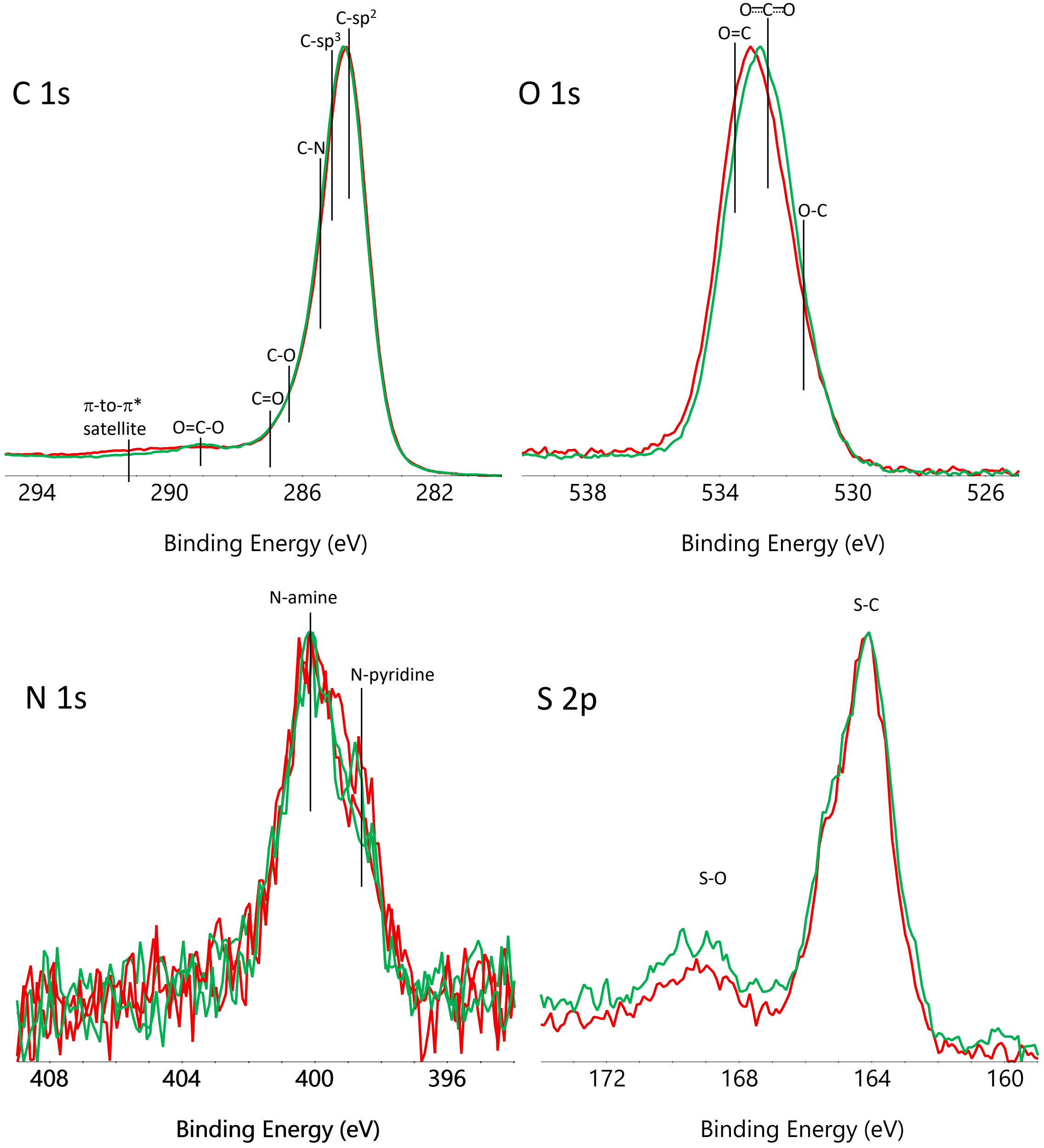
Additional Slides

XPS data provides elemental quantification as well as quantification of organically b

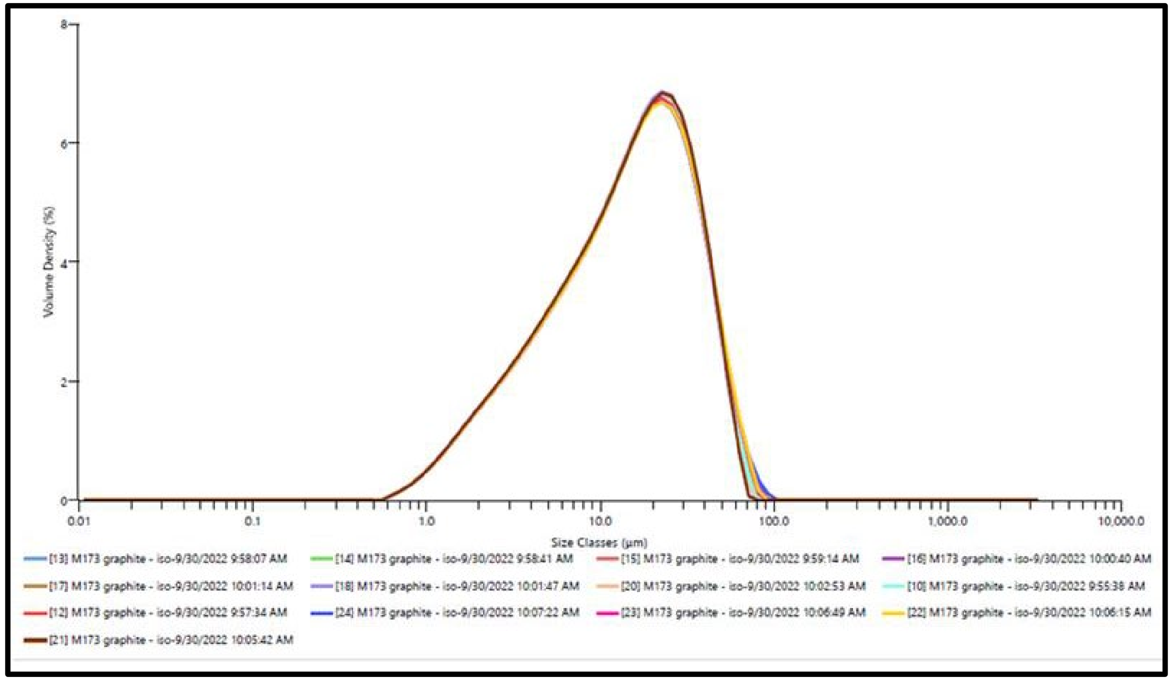
Surface Composition (at.%) – Analysis Area 1

	C	O	N	Si	S	Al	Cl	Fe	Na
Blue Gem	88.4	9.2	1.5	0.3	0.2	0.3	0.1	0.0	0.0
Herrin	85.5	10.4	1.1	0.9	1.3	0.7	0.1	0.1	0.0
Springfield	83.4	12.1	1.3	1.3	0.8	0.9	0.1	0.1	0.1





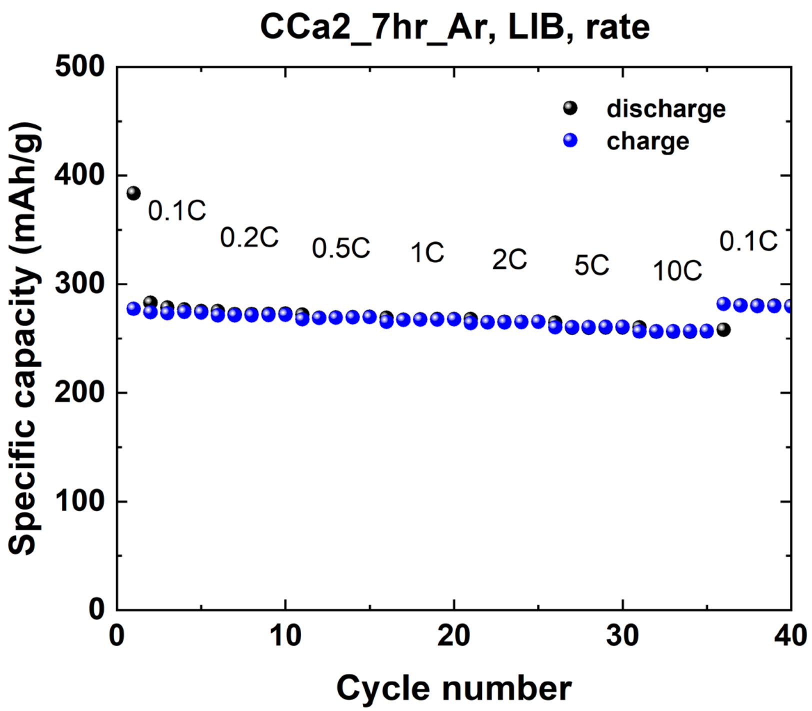
Size Distribution of Graphitized Mesophase Particles from Coal Liquid

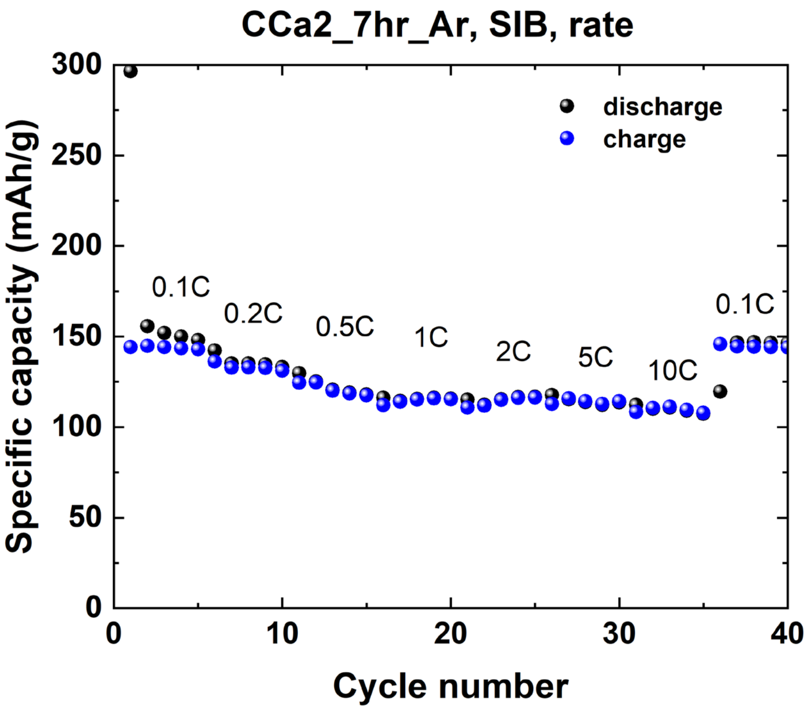


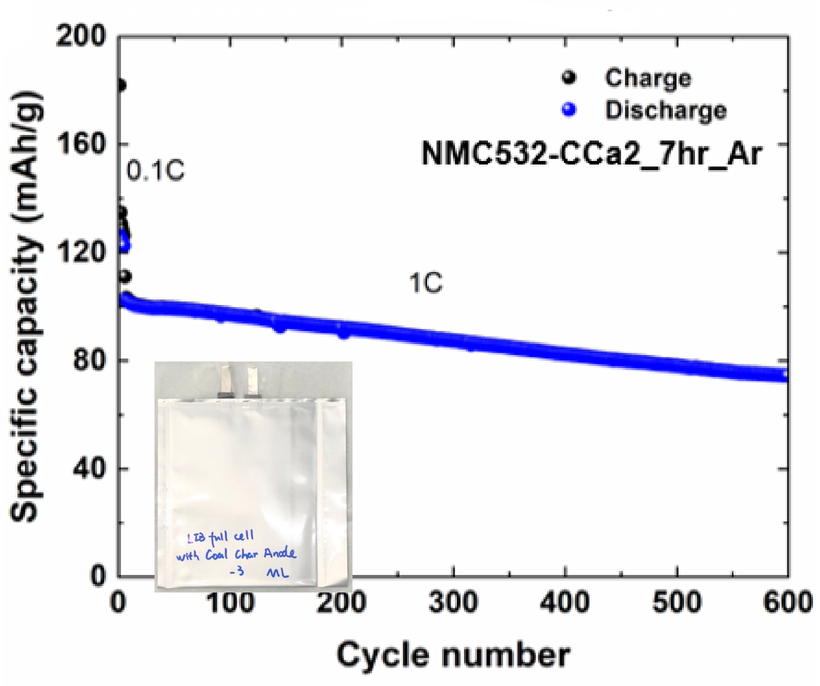
	Record Number	Sample Name	Dx (10) (μm)	Dx (50) (μm)	Dx (90) (μm)
	13	M173 graphite - iso	2.95	14.8	39.6
	14	M173 graphite - iso	2.95	14.7	39.2
	15	M173 graphite - iso	2.93	14.6	38.5
	16	M173 graphite - iso	2.94	14.7	39.6
	17	M173 graphite - iso	2.92	14.5	37.8
	18	M173 graphite - iso	2.92	14.5	37.9
	20	M173 graphite - iso	2.93	14.5	38.4
	10	M173 graphite - iso	2.94	14.6	38.9
	12	M173 graphite - iso	2.96	14.8	39.5
	24	M173 graphite - iso	2.95	14.8	40.0
	23	M173 graphite - iso	2.95	14.8	39.7
	22	M173 graphite - iso	2.95	14.8	39.9
	21	M173 graphite - iso	2.93	14.5	38.0
Mean			**2.94**	**14.7**	**39.0**
1xStd Dev			**0.0129**	**0.115**	**0.784**
1xRSD (%)			**0.438**	**0.785**	**2.01**

OAK RIDGE National Laboratory

Electrochemical Performance of Acid-Treated

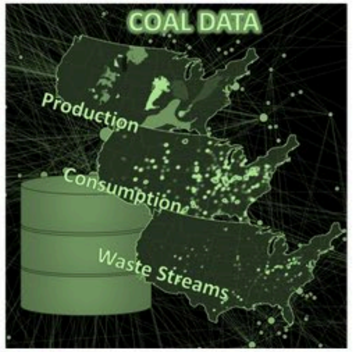






- Ar-annealed, HNO_3 treated coal char exhibited excellent rate performance in lithium-ion batteries, and improved capacities at high rate for sodium-ion batteries.
- Full cell powered by Ar-annealed, HNO_3 treated coal char anode and NMC532 cathode exhibited good cycling @ 1C with 73.2% capacity retention over 500 cycles.

Data Management



ACD Coal Materials Resources

American Coal Database (ACD) is a database under dev at NETL to support coal...

Favorite

EDX Workspaces

eXtremeMAT Consortium - IP Council

The objective of the eXtremeMAT consortium (XMAT) is to develop...

Favorite

EDX Workspaces

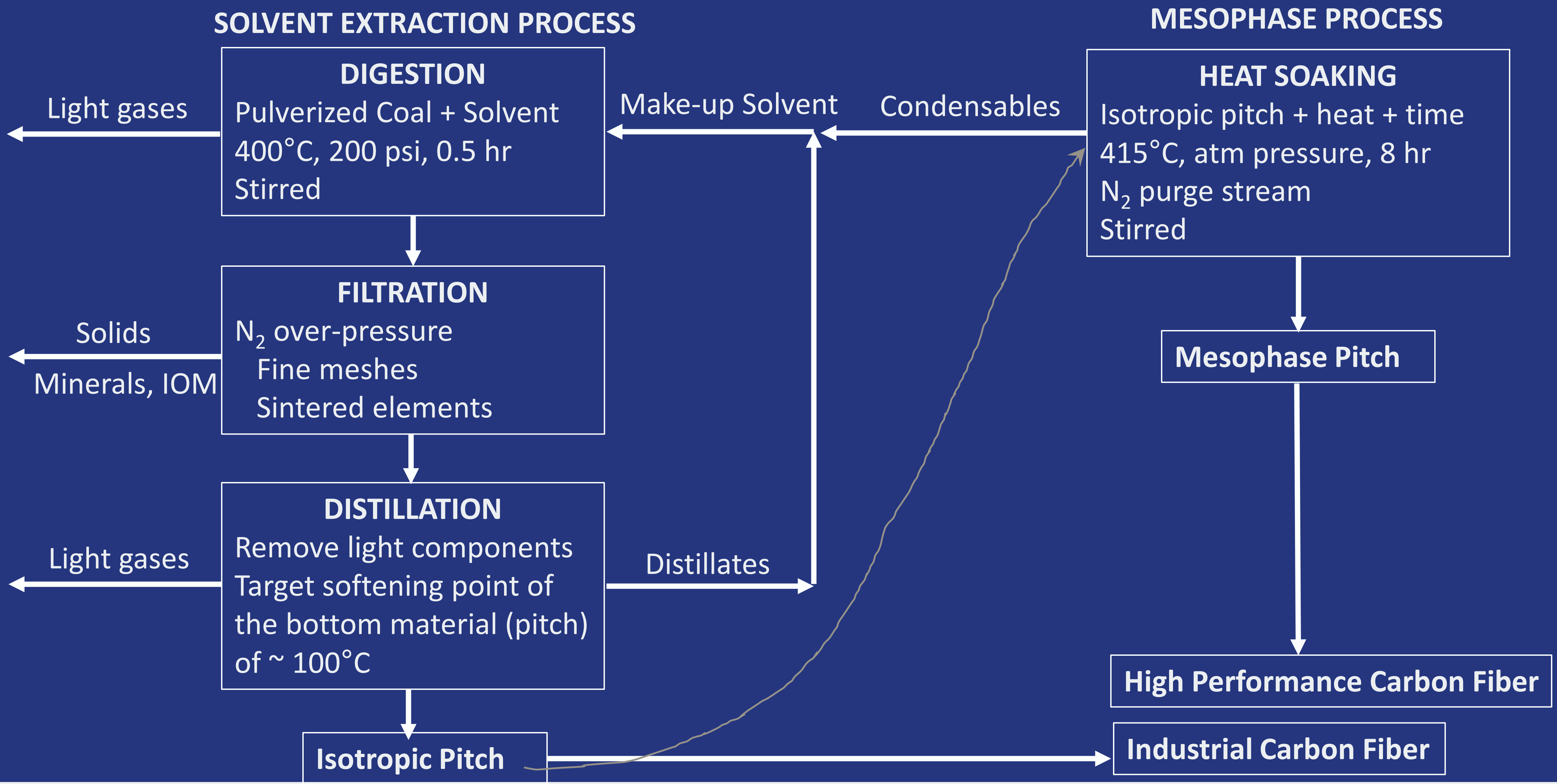
NETL-ORNL Coal data share

Workspace to share coal data between NETL and ORNL

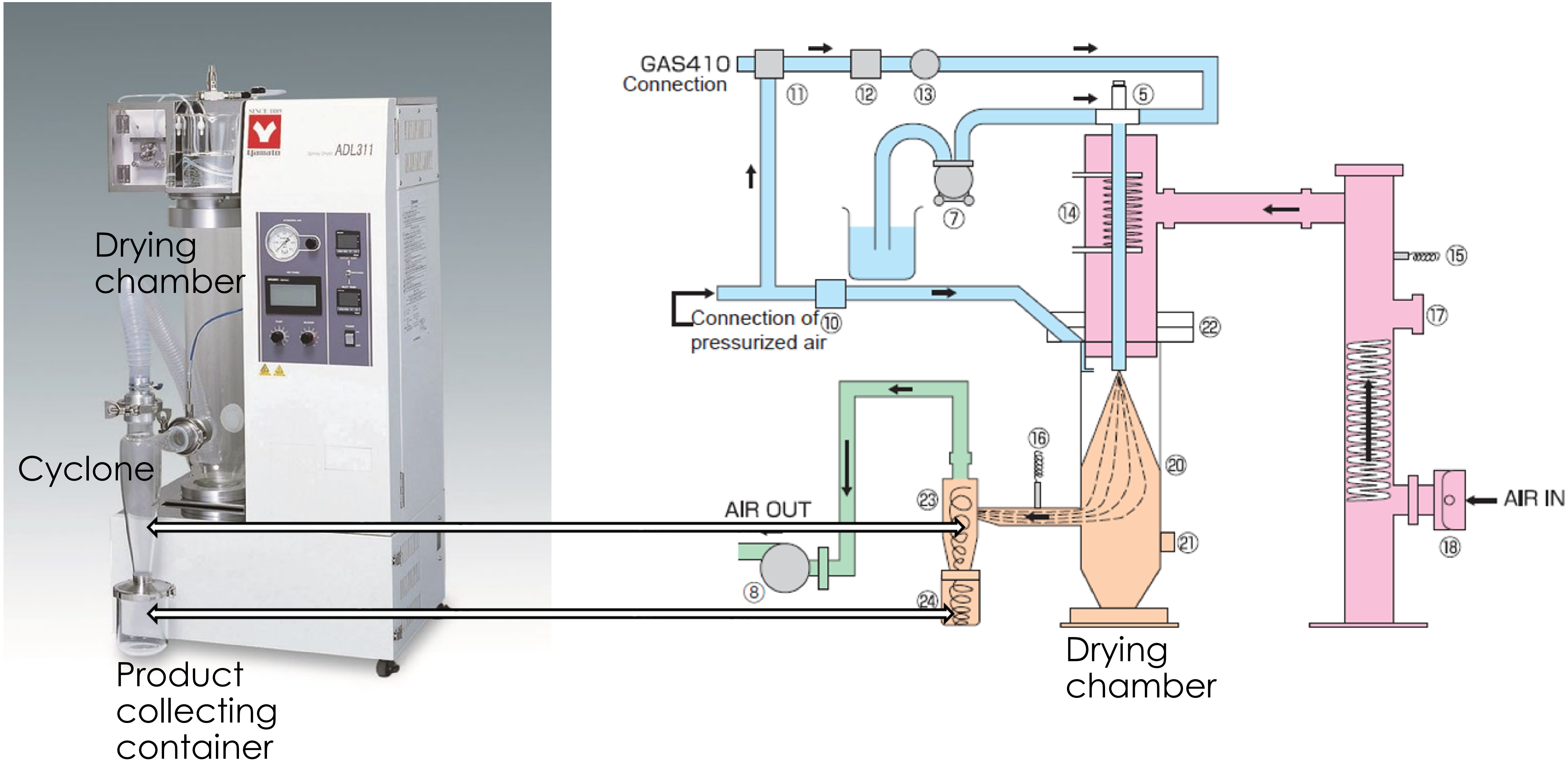
Favorite

EDX will be the repository for all data generated in this project

Overview – COAL & PITCH Processing

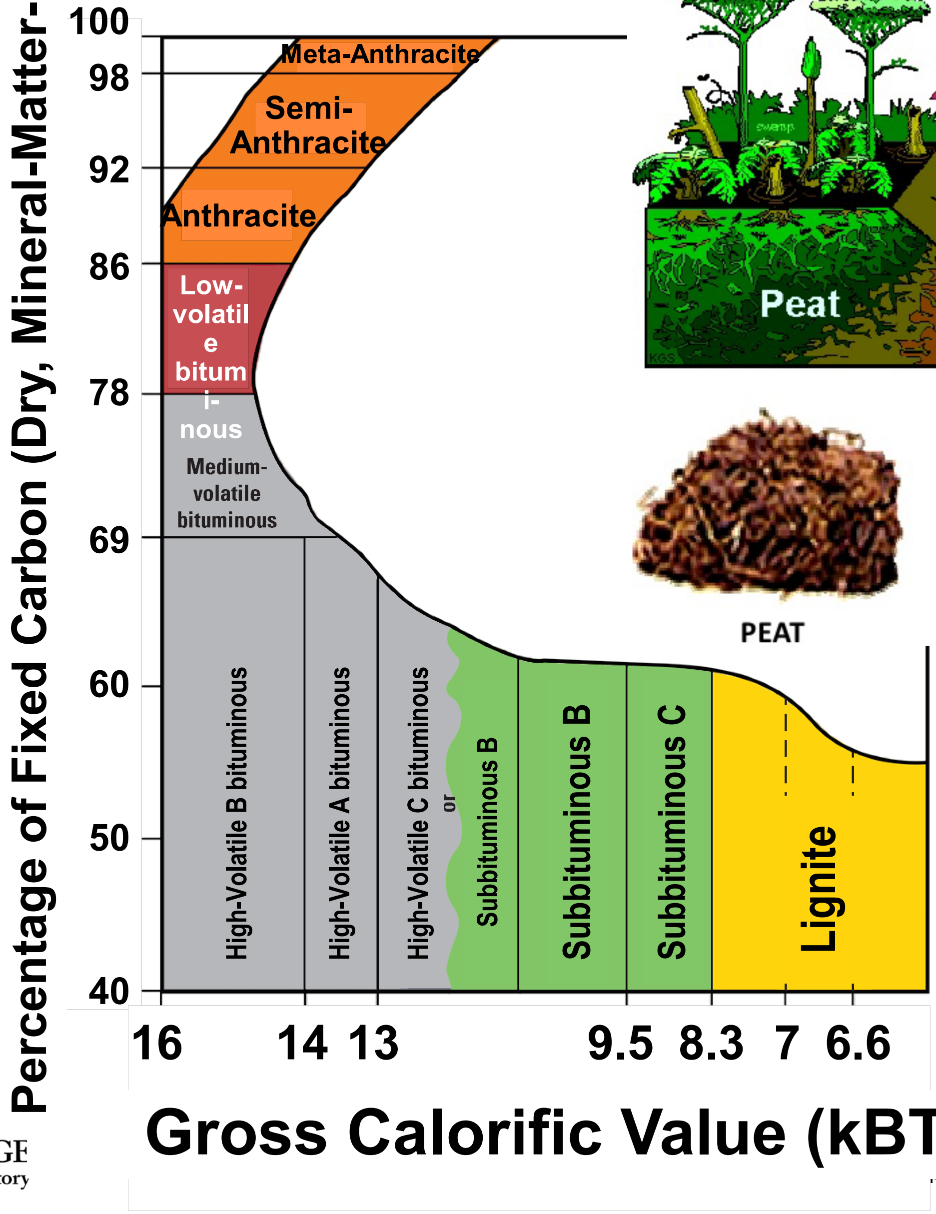


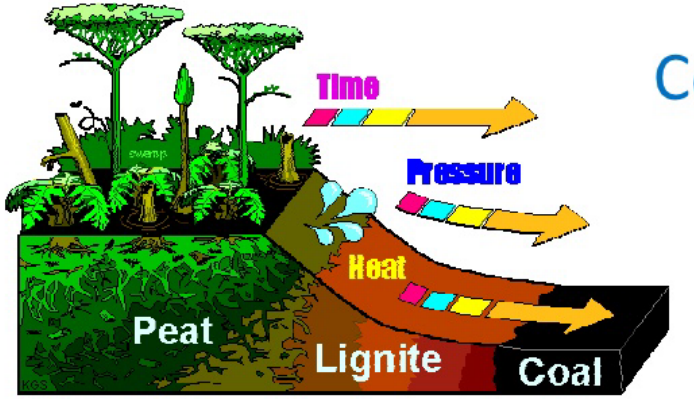
Spray drying unit GAS410



Scale up Production of Graphite from Carbon Ore and Coal Refuse — FEAA157. October 2022

Not all coals are the same!





Coal – Stages of Formation

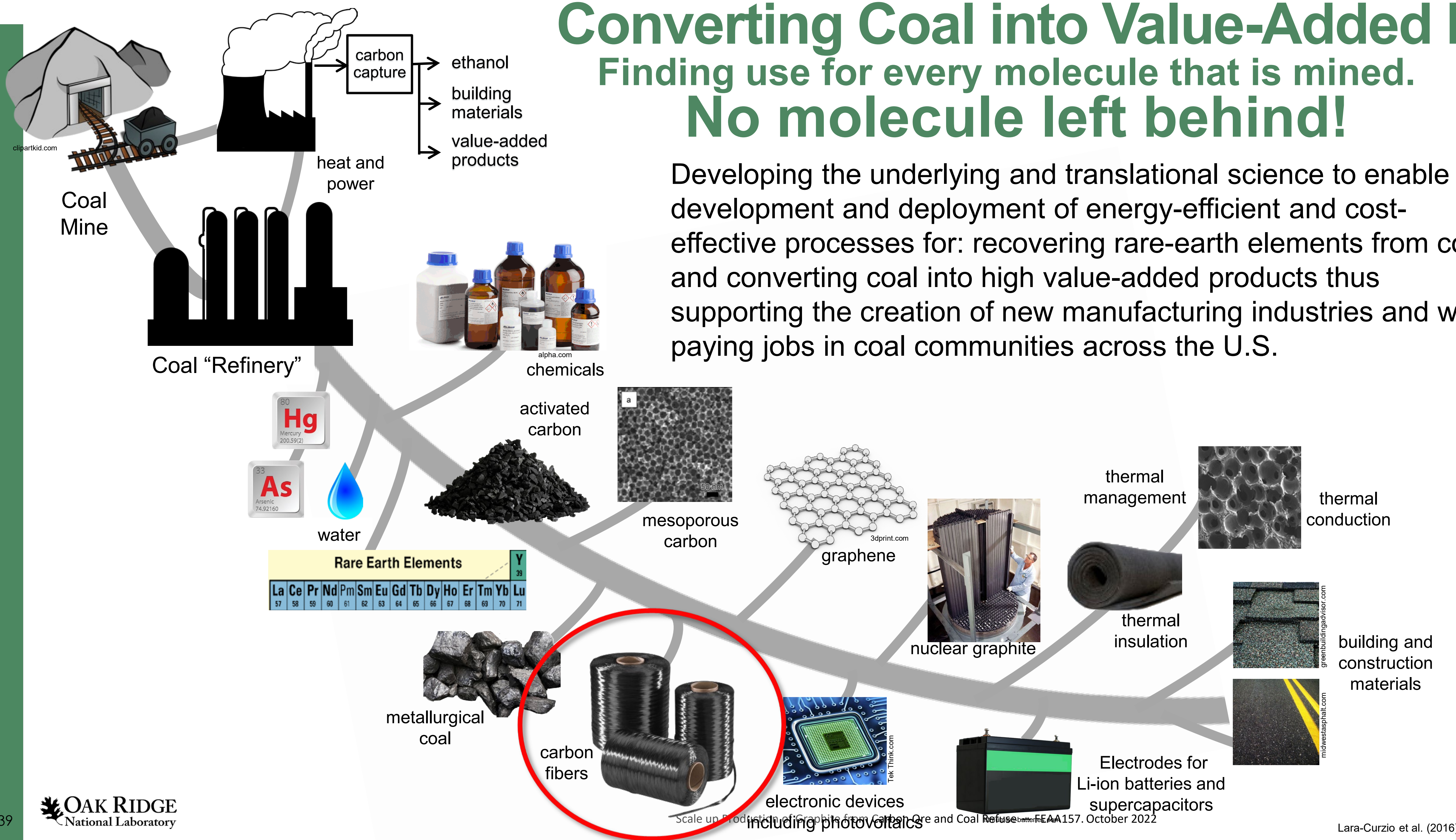
Fossil Fuels. Energy Information Association

Converting Coal into Value-Added Pro

Finding use for every molecule that is mined.

No molecule left behind!

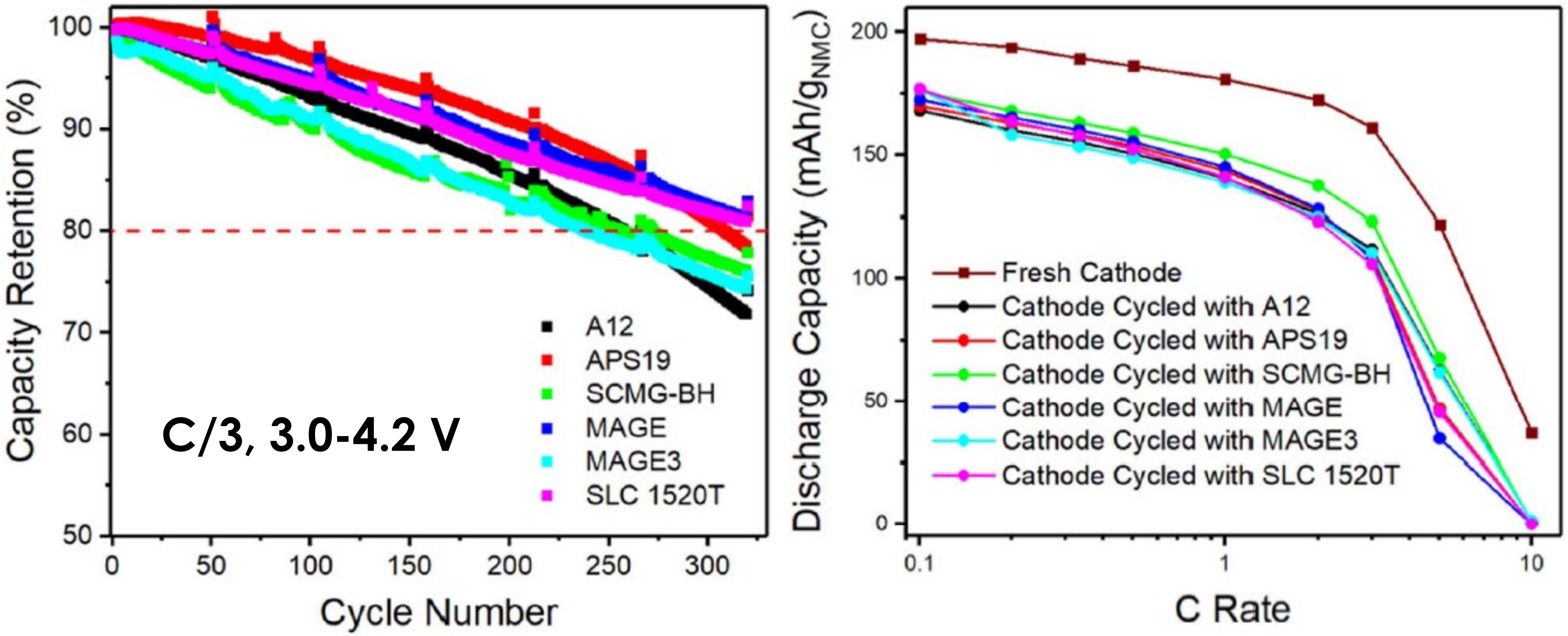
Developing the underlying and translational science to enable the development and deployment of energy-efficient and cost-effective processes for: recovering rare-earth elements from coal and converting coal into high value-added products thus supporting the creation of new manufacturing industries and well-paying jobs in coal communities across the U.S.



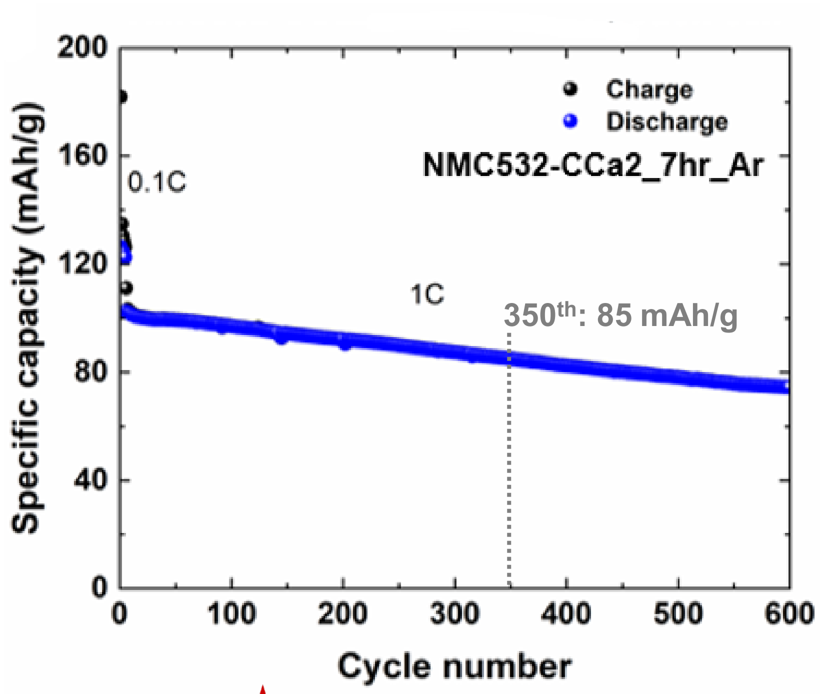
Lara-Curzio et al. (2016)

Conventional Graphite Anode in LIBs as a Comparison

- Different types of graphite against NMC811 in LIB full cells (capacity normalized to cathode mass):



J. Electrochem. Soc., 2018, 165 (9) A1837-A1845.



★ Coal anode (our work)

- Initial capacity (graphite anode) at 1C charge/discharge rate: ~ 140 mAh/g.
- Assuming 80% capacity retention over 350 cycles, estimated discharge capacity (graphite anode) at 350th cycle: ~ 112 mAh/g.
- Notice: the specific capacity of NMC532 is lower than NMC811.

Demand for Graphite for Li-ion (cont.)

Press Release

Electric Vehicle Companies Could Have a Massive Graphite Supply Problem

Published: March 25, 2021 at 9:30 a.m. ET

0

The MarketWatch News Department was not involved in the creation of this content.

Mar 25, 2021 (Bays
electric vehicles fro
Motors (NYSE:GM)
increasing the need
as Ceylon Graphite
(OTC:GPHOF), and
graphite is an essen
batteries using in e

investor intel the stock source

Trending Markets More

HOME » MARKET OPINION » MARKET ANALYSIS INTEL

The coming tsunami of electric car demand will need many more anode megafactories and graphite

MATTHEW BOHLSEN | APRIL 29, 2019 | 2 COMMENTS

Most investors don't yet understand the tsunami of electric car demand that is just around the corner. Bloomberg New Energy Finance forecasts that by 2020 there will be over 289 different models of electric cars. Just recently Bloomberg has revised their targets now saying the same as I have said for the past 3 years. Bloomberg now says by 2022 electric cars will become price competitive with conventional cars. Previously they said by 2025. Even Volkswagen predicts that EVs will go mainstream in 2022.

Volume 4
Number 11
November 2020
Pages 5363–5870

Sustainable Energy & Fuels

Interdisciplinary research for the development of sustainable energy technologies

rsc.li/sustainable-energy

ISSN 2398-4902

ROYAL SOCIETY OF CHEMISTRY

REVIEW ARTICLE
Zhen Chen, Dominic Bresser *et al.*
The success story of graphite as a lithium-ion anode material – fundamentals, remaining challenges, and recent developments including silicon (oxide) composites

COMMUNICATIONS MATERIALS

ARTICLE
https://doi.org/10.1038/s43246-020-00095-x OPEN
Check for updates

Future material demand for automotive lithium-based batteries

Chengjian Xu[1,3], Qiang Dai[2], Linda Gaines[2], Mingming Hu[1], Arnold Tukker[1] & Bernhard Steubing[1,3]

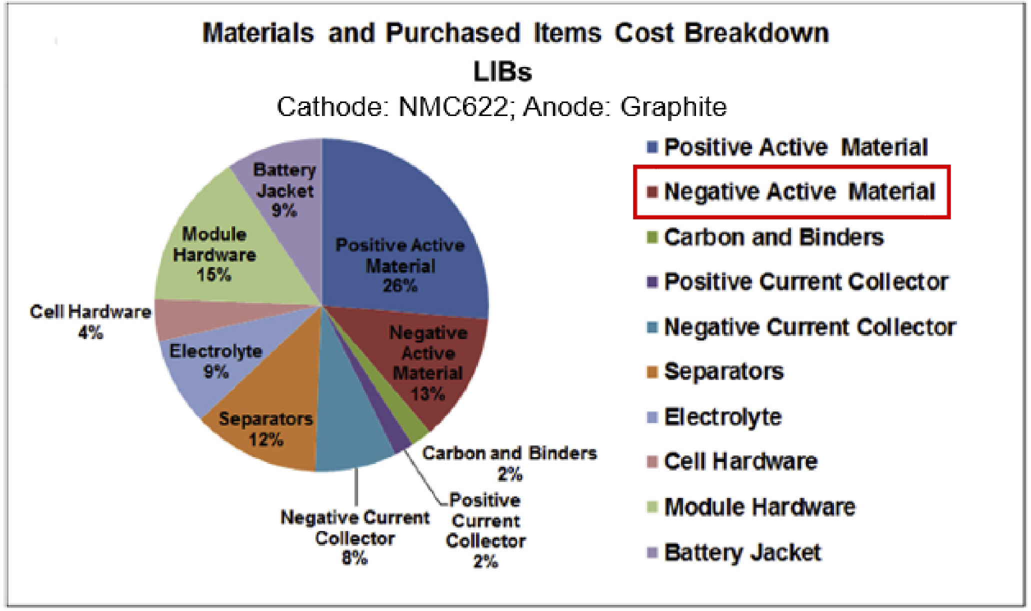
The world is shifting to electric vehicles to mitigate climate change. Here, we quantify the future demand for key battery materials, considering potential electric vehicle fleet and battery chemistry developments as well as second-use and recycling of electric vehicle batteries. We find that in a lithium nickel cobalt manganese oxide dominated battery scenario, demand is estimated to increase by factors of 18–20 for lithium, 17–19 for cobalt, 28–31 for nickel, and 15–20 for most other materials from 2020 to 2050, requiring a drastic expansion of lithium, cobalt, and nickel supply chains and likely additional resource discovery. However, uncertainties are large. Key factors are the development of the electric vehicles fleet and battery capacity requirements per vehicle. If other battery chemistries were used at large scale, e.g. lithium iron phosphate or novel lithium-sulphur or lithium-air batteries, the demand for cobalt and nickel would be substantially smaller. Closed-loop recycling plays a minor, but increasingly important role for reducing primary material demand until 2050, however, advances in recycling are necessary to economically recover battery-grade materials from end-of-life batteries. Second-use of electric vehicles batteries further delays recycling potentials.

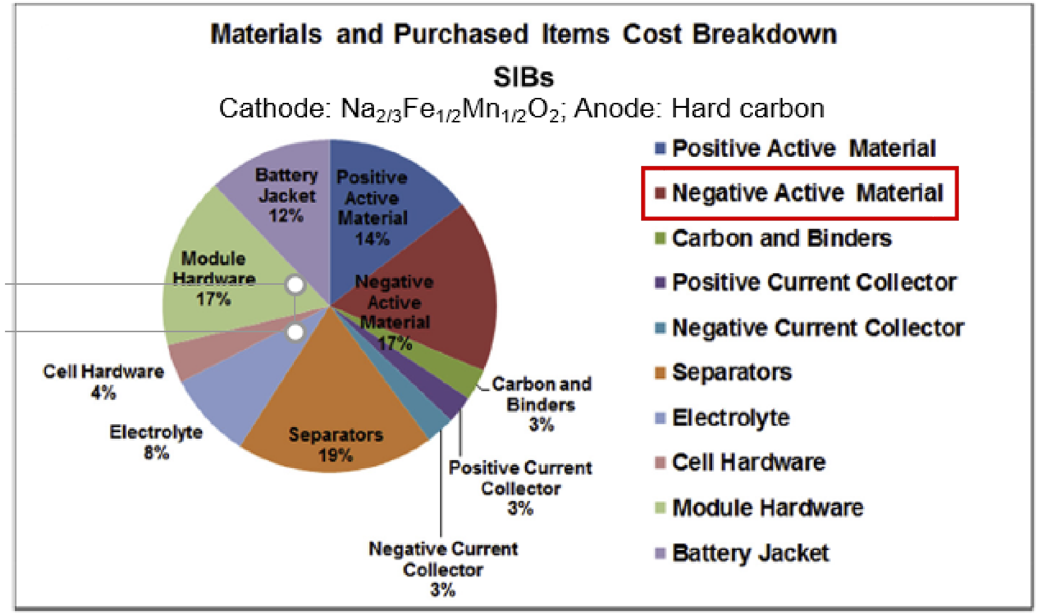
[1]Institute of Environmental Sciences (CML), Leiden University, 2300 RA Leiden, The Netherlands. [2]ReCell Center, Argonne National Laboratory, Lemont, IL, USA. [3]These authors contributed equally: Chengjian Xu, Bernhard Steubing. email: b.steubing@cml.leidenuniv.nl

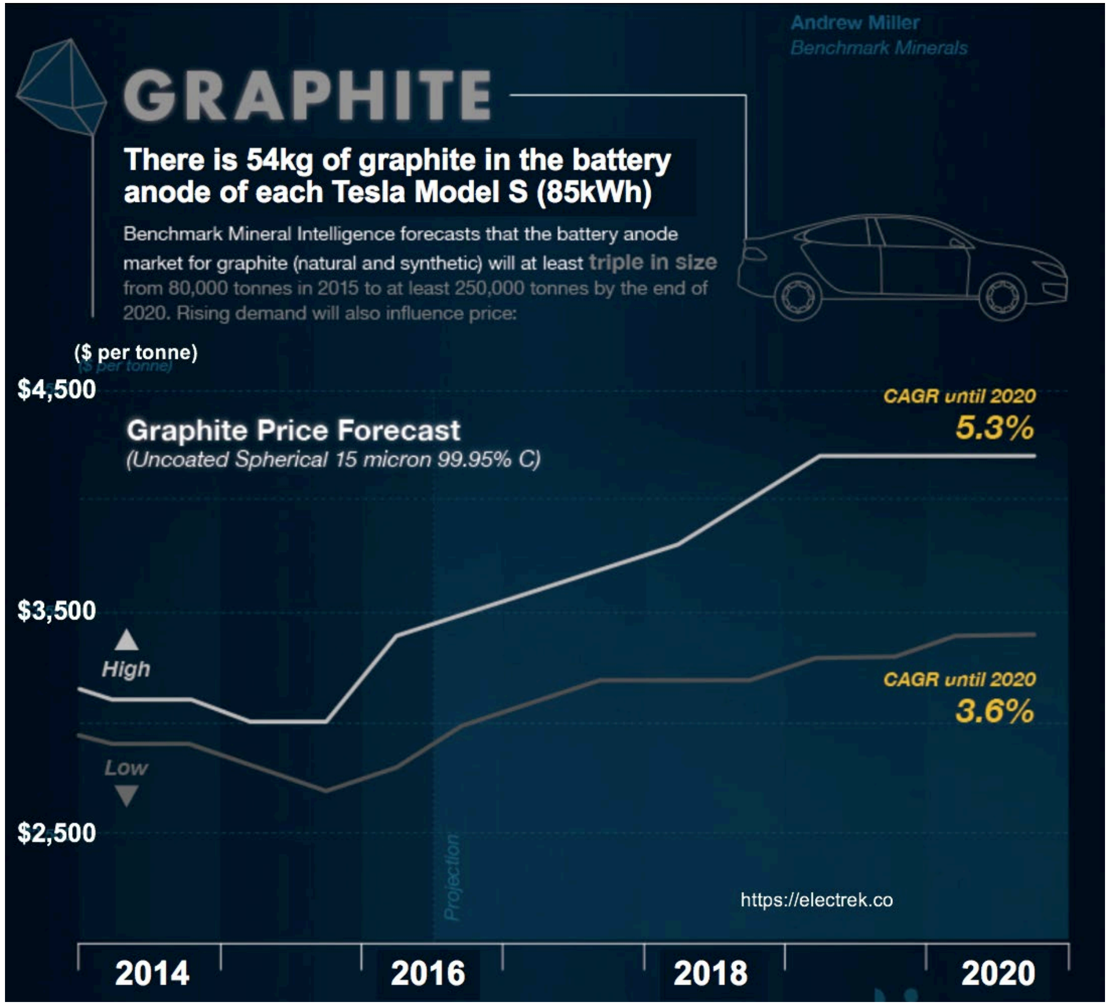
COMMUNICATIONS MATERIALS | (2020)1:99 | https://doi.org/10.1038/s43246-020-00095-x | www.nature.com/commsmat 1

Cost Perspective in Batterie

	Negative active materials cost percentage
Li-ion Batteries (LIBs)	13%
Na-ion Batteries (SIBs)	17%





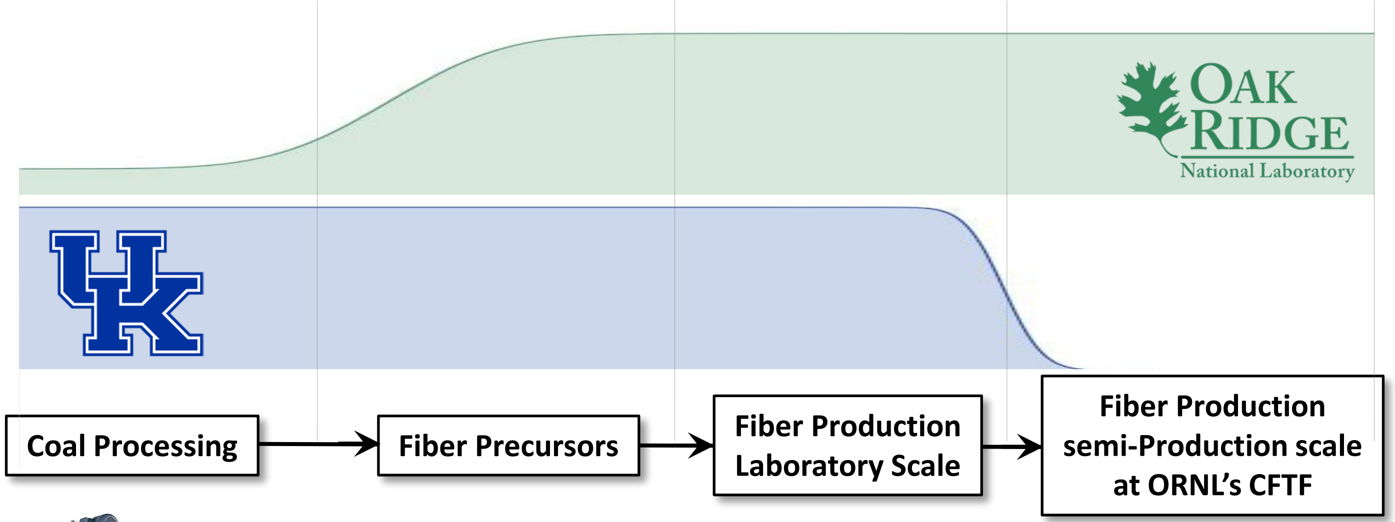


Energy Storage Materials 25 (2020) 520–536.

The ORNL-UK Partnership to Develop Coal-Derived Carbon Fibers | A Perfect Match

Together, ORNL and UK bring **complementary and unparalleled capabilities** in fundamental science and translational research and development, with particular expertise in:

- coal processing
- separation science and technology
- carbon science & technology
- computational chemistry and high-performance computing
- advanced characterization
- advanced manufacturing



Continuous carbon fibers for structural applications

Composite Materials and Structures

Short carbon fibers for structural applications

Short carbon fibers for thermal insulation

Not all coals are the same

Objective: To develop scalable, efficient, cost-effective, and environmentally sustainable processes for manufacturing low-cost coal-derived carbon fibers with tunable physical and mechanical properties. A key element of this project is scaling fiber production from the laboratory benchtop level up to semi-production scale at ORNL's Carbon Fiber Technology Facility.

This project will demonstrate a clear path for competitive industrialization of coal-derived carbon fibers and composites for a wide range of applications.

Project Initiated in 2020

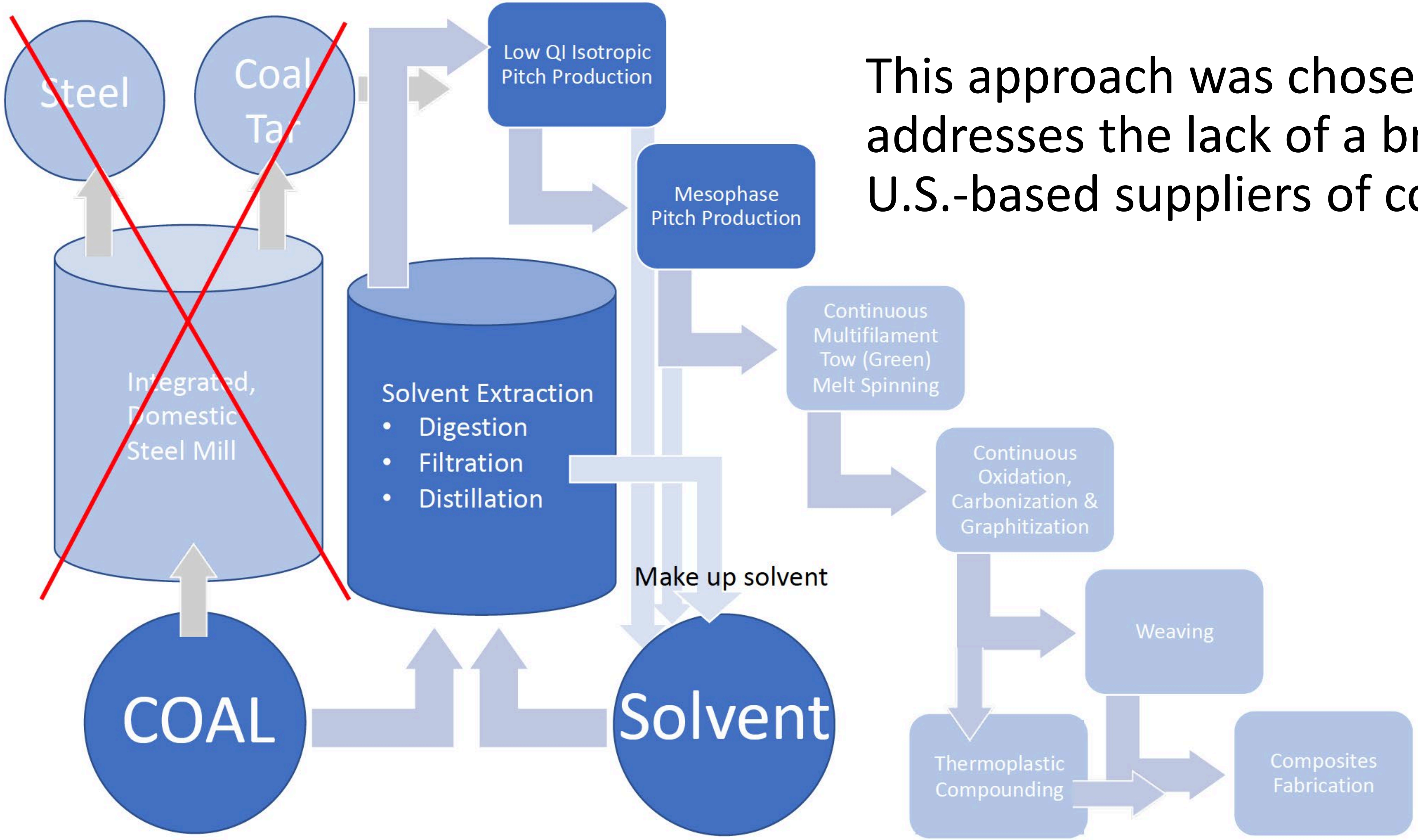
Lara-Curzio et al. (April 2020)

ORNL’s Carbon Fiber Technology Facility (

Established in 2013, the CFTF is the Department of Energy’s only designated user facility for carbon fiber innovation.

- 42,000 sq. ft. facility
- 390 ft. long processing line, capable of custom unit operation configuration
- Up to 25 tons per year

Advanced Coal Processing at the University of K



This approach was chosen because it addresses the lack of a broad base of U.S.-based suppliers of coal tar pitch.

Life Cycle and Technoeconomic Analyses of Coal-Derived Carbon Fiber Manufacturing

Raw Coal
$0.03/kg
$21B

Metallurgical Coal
$0.15/kg
$51B

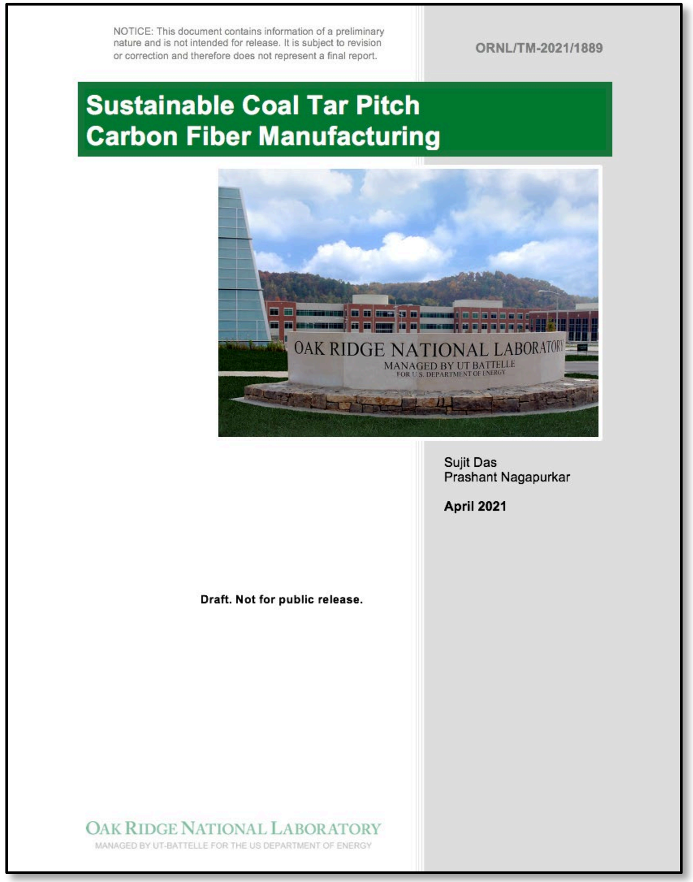
Coke
$0.25/kg
$2.9B

Coal Tar
$0.40/kg
$0.24B

Coal Tar Pitch
$0.70/kg
$0.2B

Mesophase Coal Tar Pitch Precursor
$3.30/kg
$0.8B

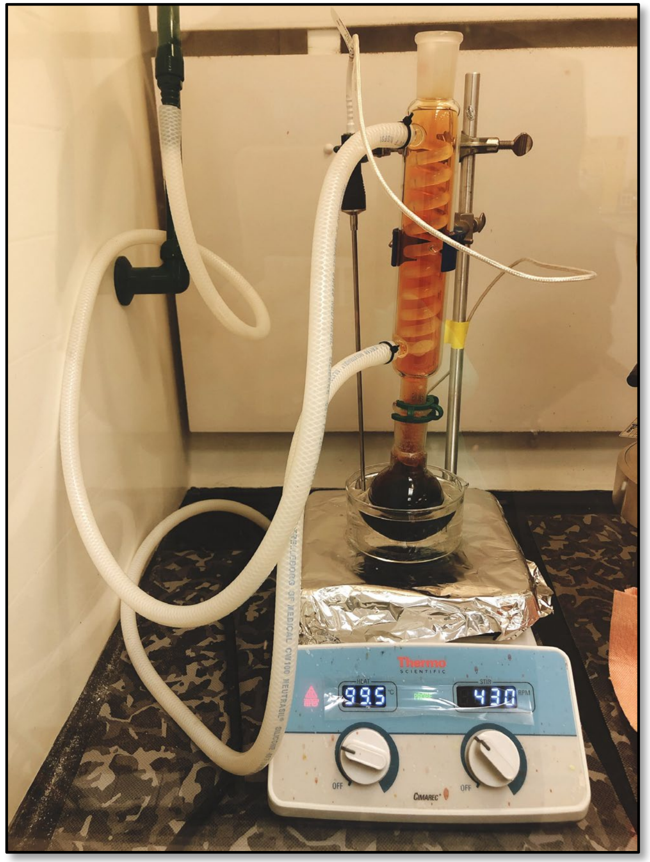
Pitch Carbon Fiber
$11.00/kg
$1.9B

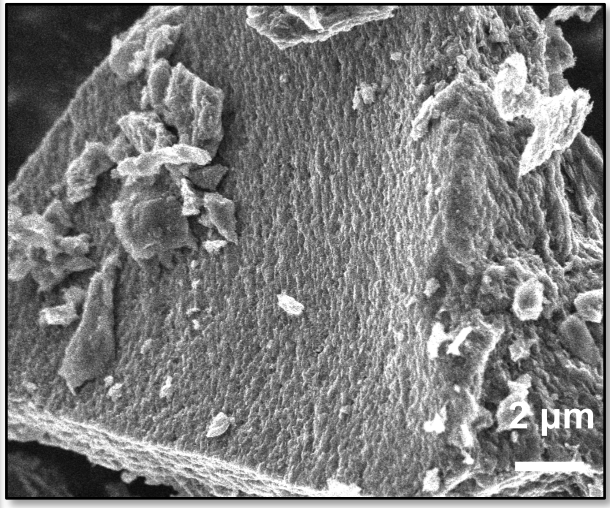


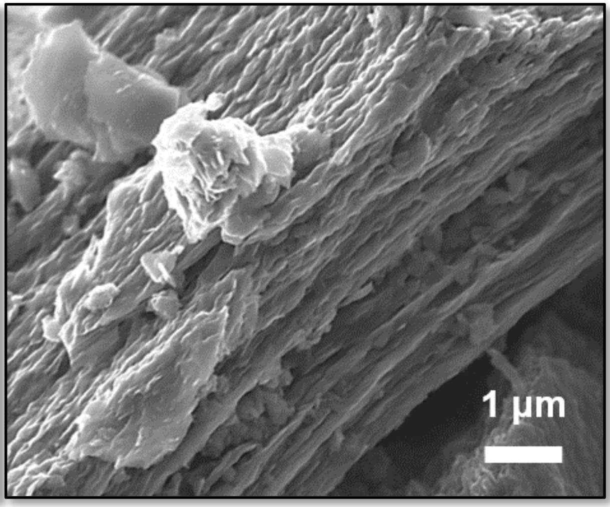
If there is no pre oxidation, the powder coalesces into a single piece during carbonization and graphitization

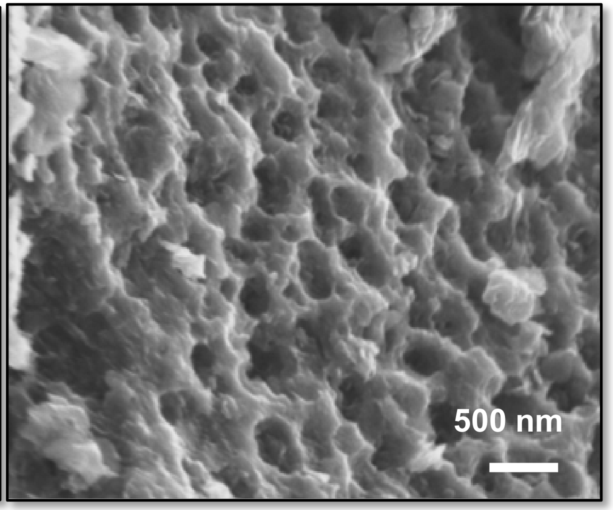
NHO_3 Treatment of Coal Char

Acid-reflux system (100°C)







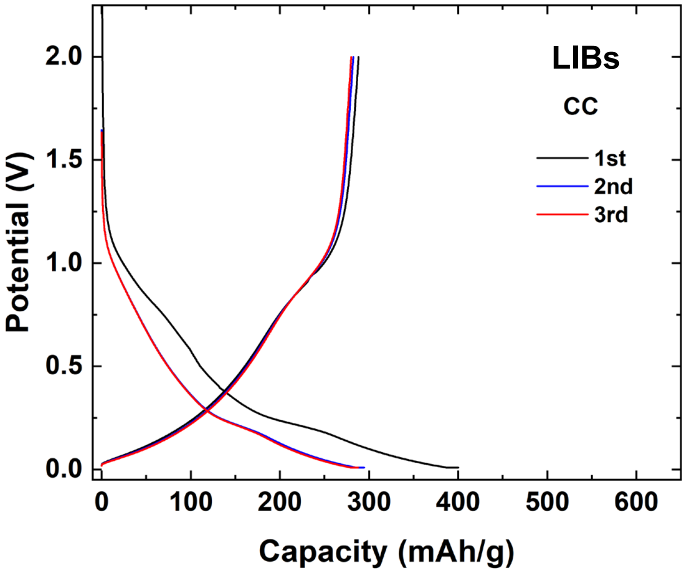


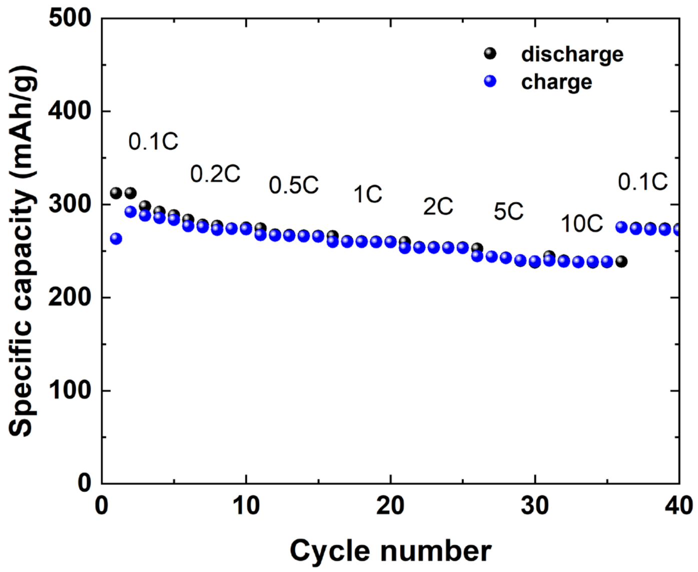
SEM of nitric acid-treated coal char:

- Porous surface with uniformly distributed nanopores
- Layered structure

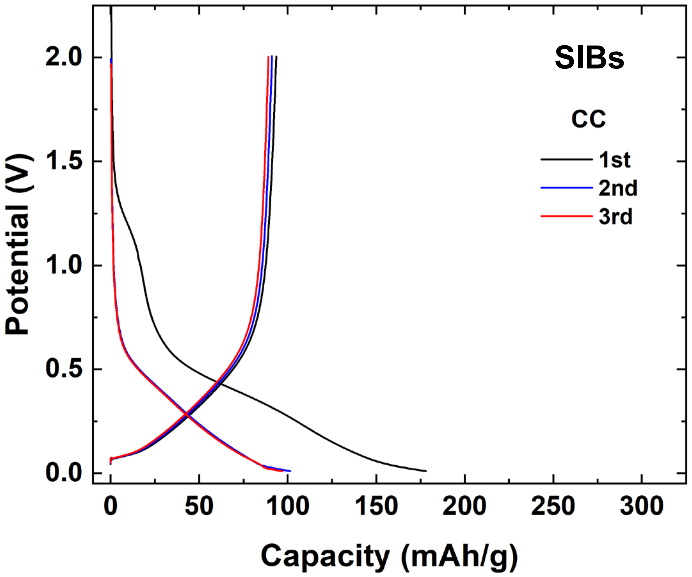
Electrochemical Performance of as-Received Coal Char

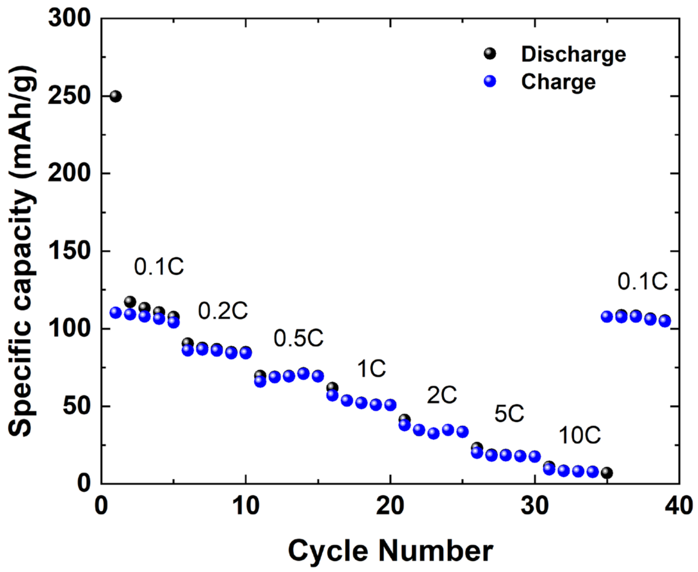
Li-ion battery half cell



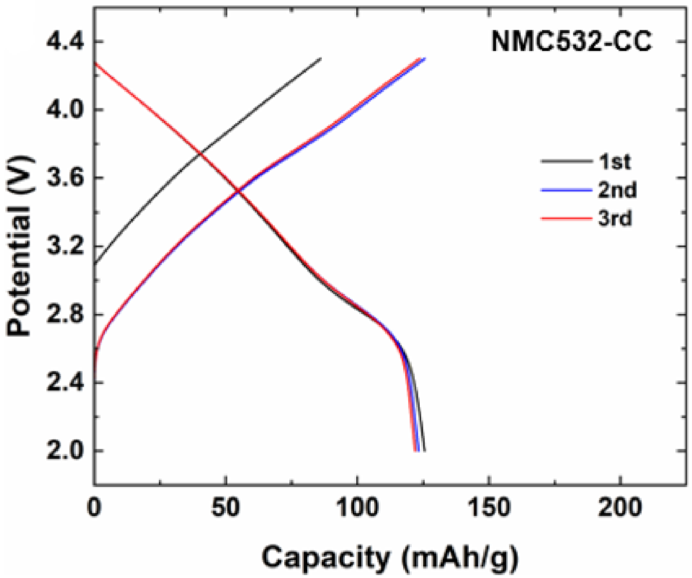


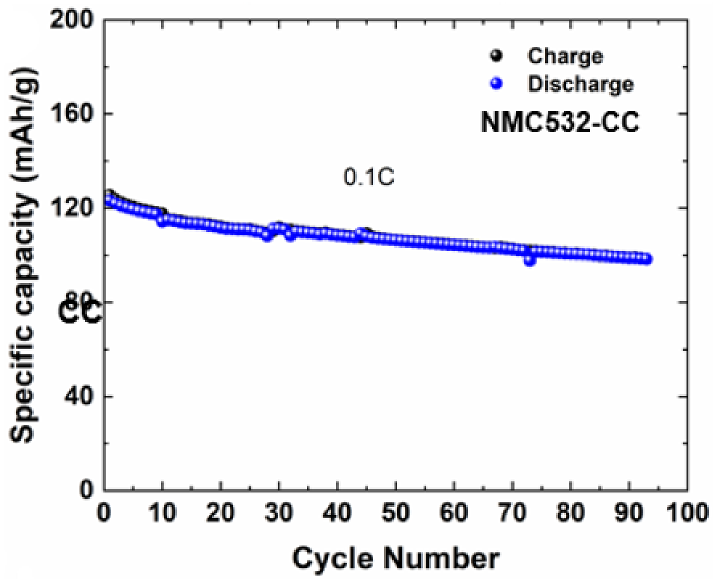
Na-ion battery half cell





Li-ion battery full cell (pouch)





OAK RIDGE National Laboratory

Manufacture of spherical carbon particles by Spray Drying

Coal liquids, a byproduct from mild gasification of coals and coal refuse, are being used as feedstock for manufacturing carbonaceous spheres

Inlet temperature: 170 to 200°C
Outlet temperature: 70 to 80°C

Control of particle size distribution

OAK RIDGE National Laboratory

Lower Chinese graphite production could mean higher batte

China has steadily been forcing producers of graphite — a material commonly used in smartphone and laptop batteries — to close in response to rising pollution, as mining companies fail to improve the conditions of local land and water resources.

Why it matters: Batteries account for roughly 30% of the global demand for graphite, and China produces 70% of the world's graphite supply.

As demand for the material continues to grow, battery prices may rise, which would impede progress toward the $100 per kilowatt hour lithium-ion target that many companies, including Tesla and BMW, are looking to achieve.

Background: The expanding electric vehicle market has been a major contributor to the global rise in graphite demand.

Axios. March 1, 2019