Conversion of Coal to Li-ion Battery Grade “Potato” Graphite

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Michael J. Wagner

Department of Chemistry

The George Washington University

Washington, DC

U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

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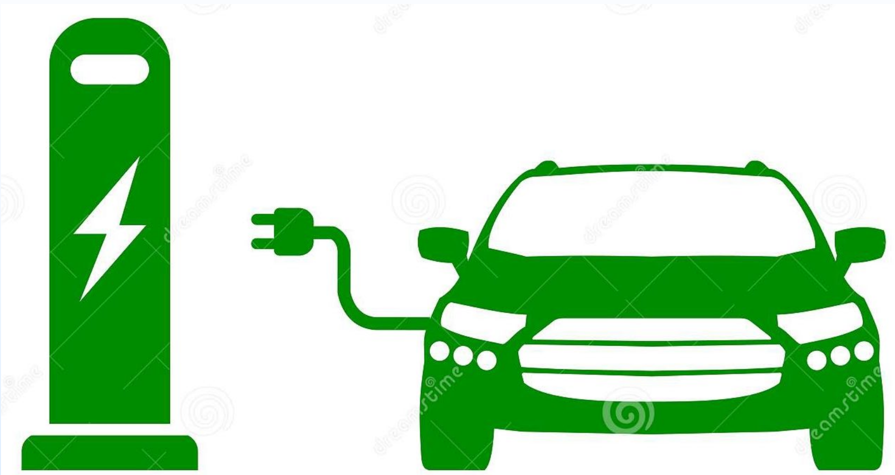
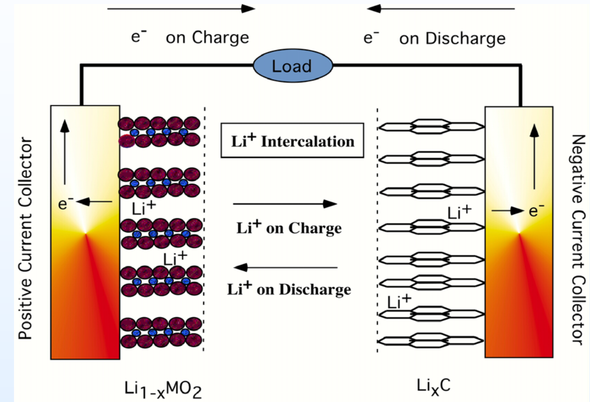
Project Overview

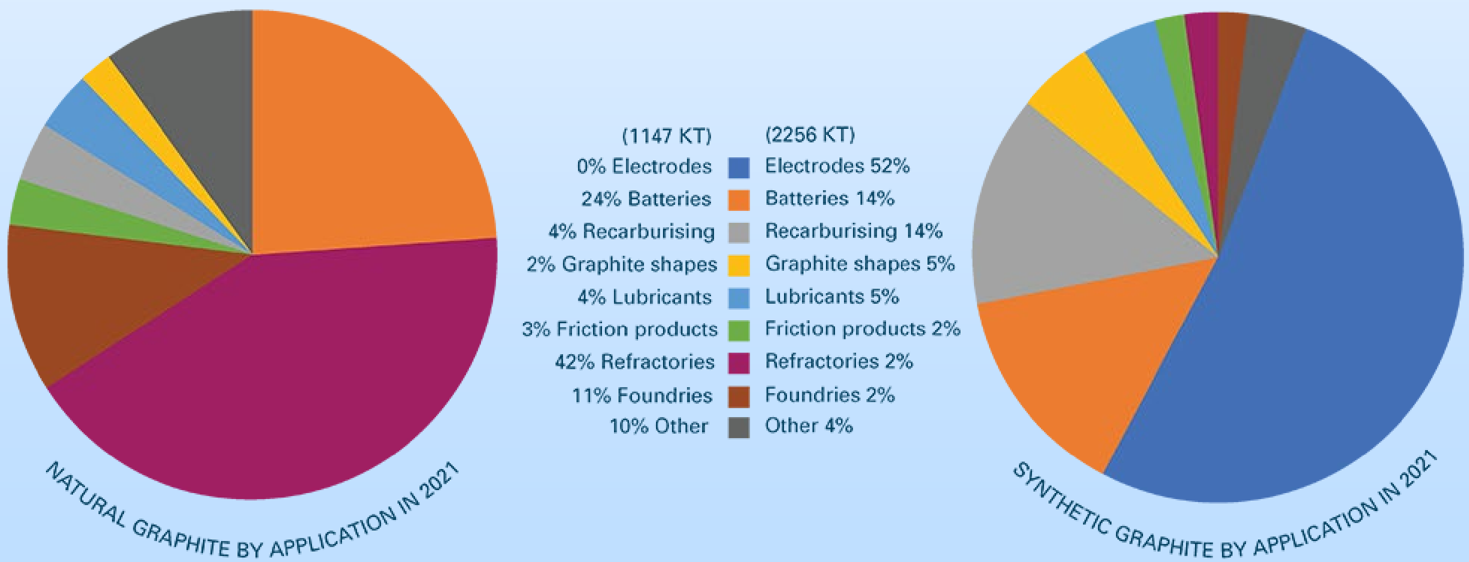
- Funding ($748,720 DOE & $200,310 Cost Share)
- 9/1/2019 to 8/31/2024
- George Washington University
- Overall Project Objective – Develop scalable method to convert low value coal to high value graphite (~ 1000 fold increase in value)

Graphite – Strategic Mineral



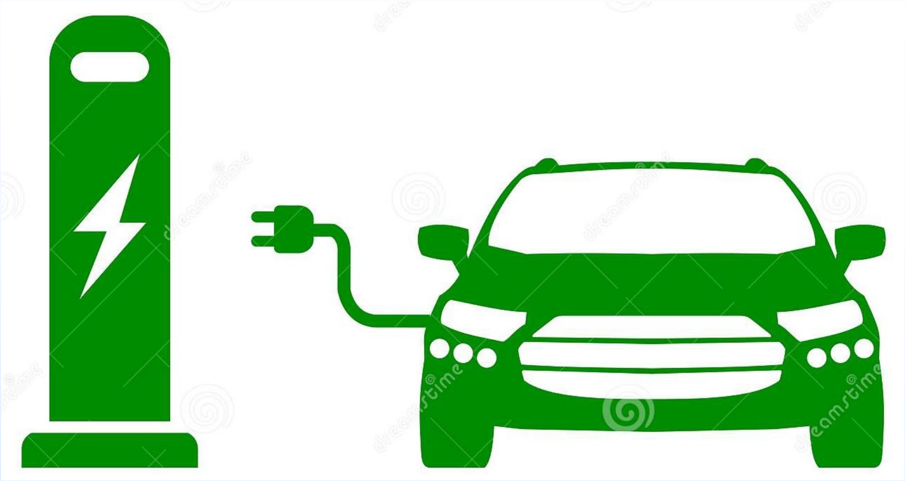


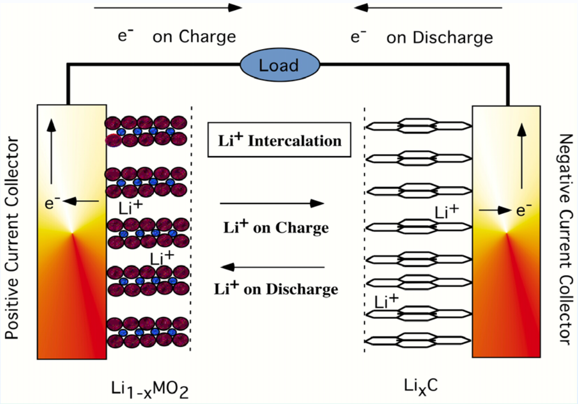
Adapted from: Sivakkumar, S. R.; Nerkar, J. Y.; Pandolfo, A. G., Rate capability of graphite materials as negative electrodes in lithium-ion capacitors. Electrochimica Acta 55, (9), 3330-3335.



source: Wood MacKenzie, 2022

Graphite – Shortage Coming (Here?)





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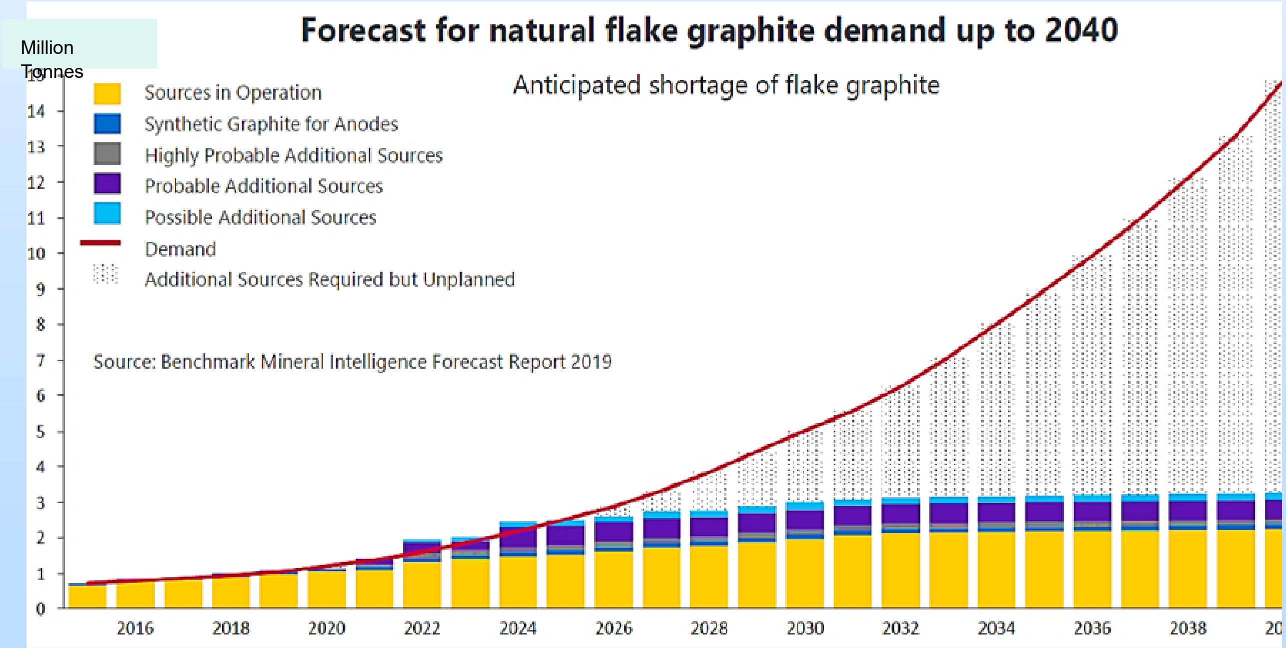
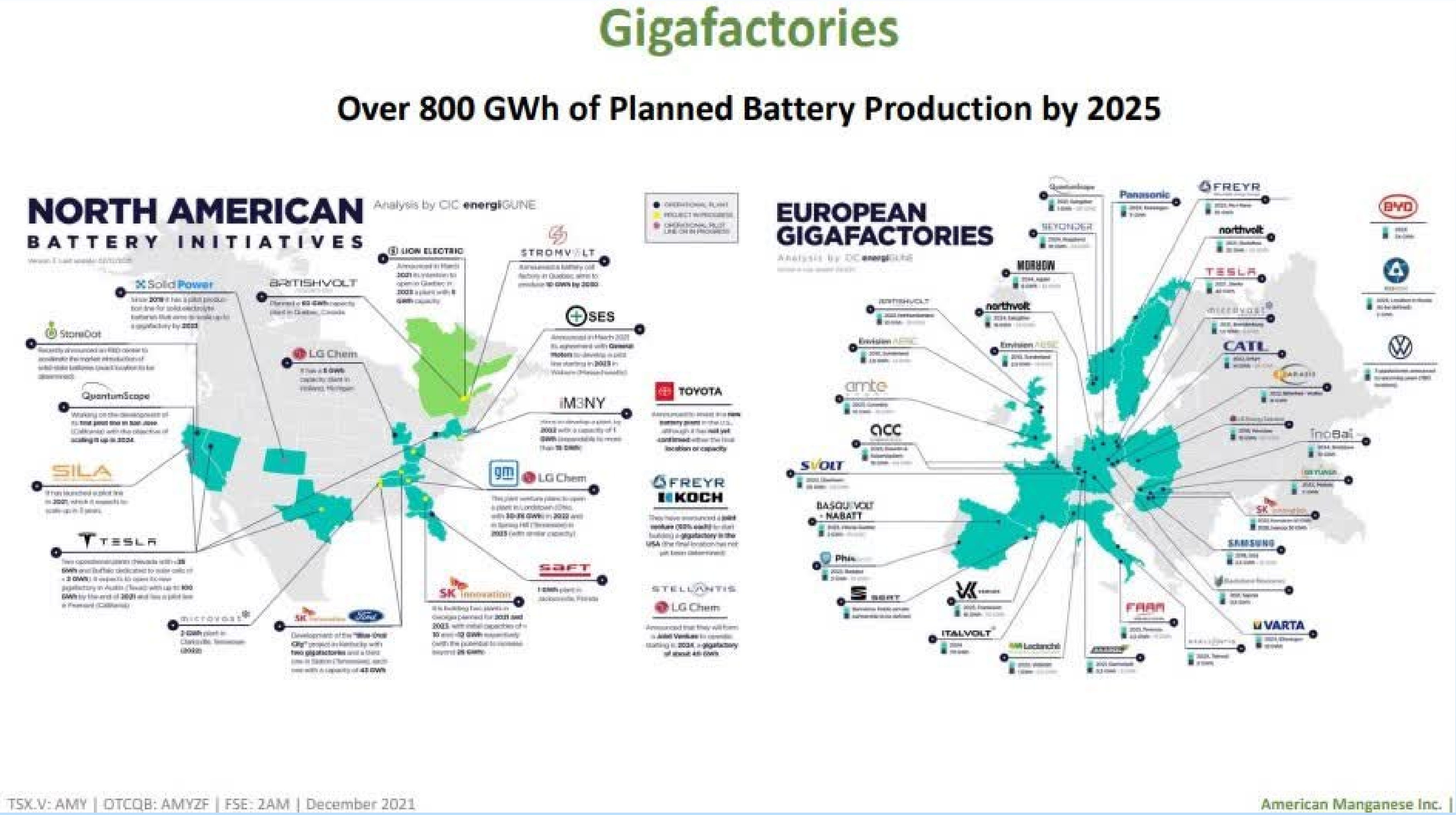
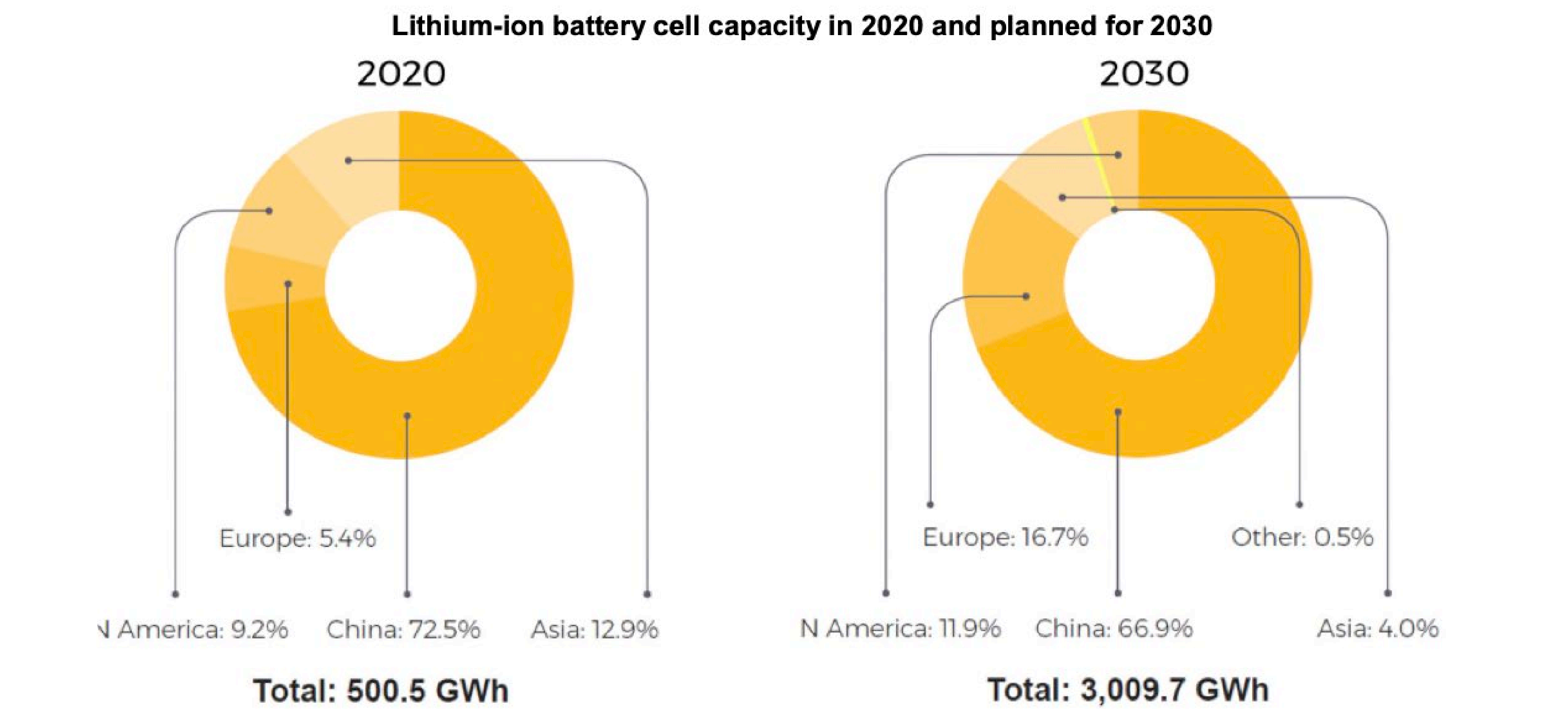


Tesla Li-ion Battery Gigafactory

Gigafactory Proliferation

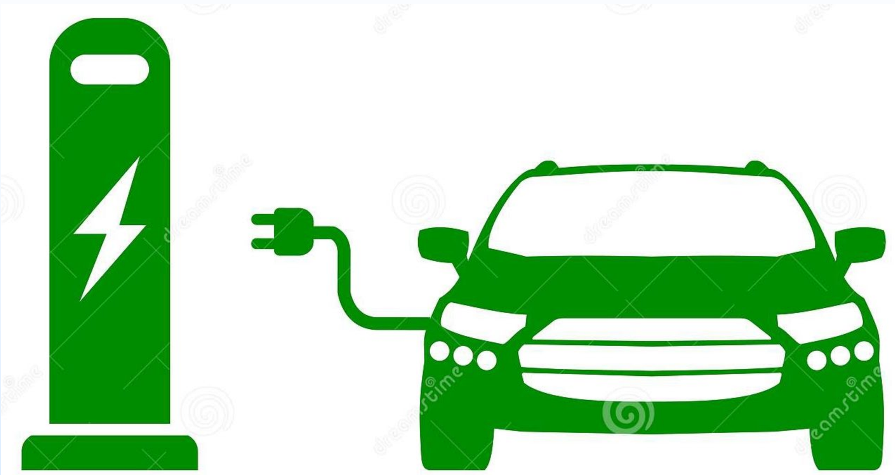


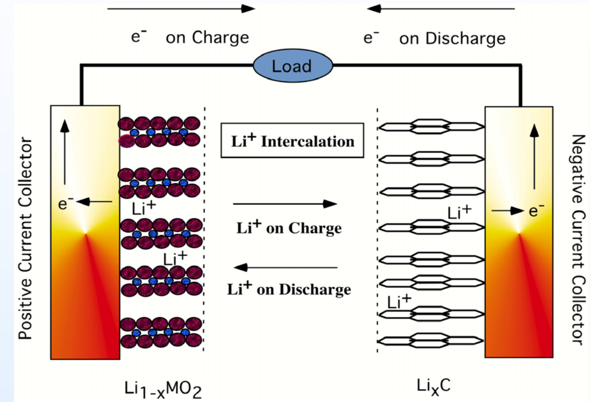
Li-ion Battery Market



Source: Benchmark Mineral Intelligence.

Graphite – Market Driven by Li-ion





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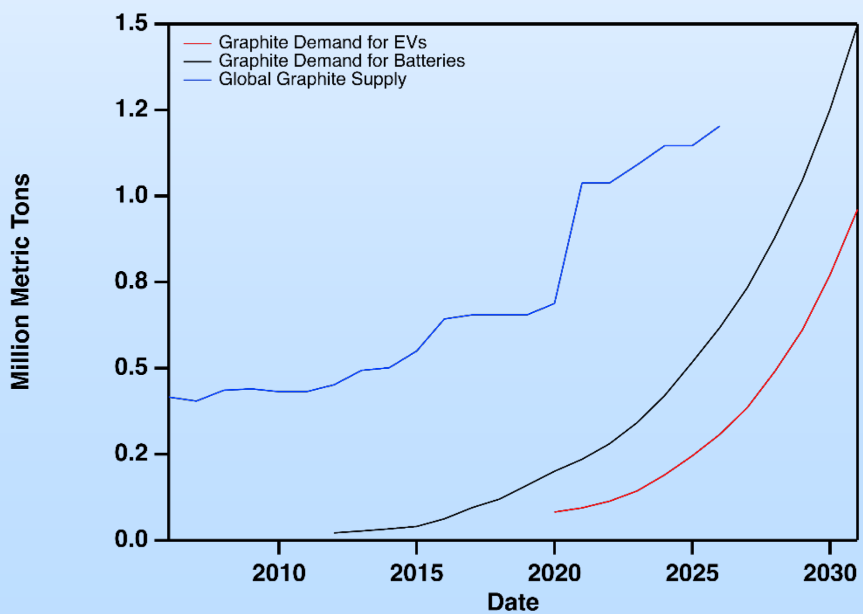
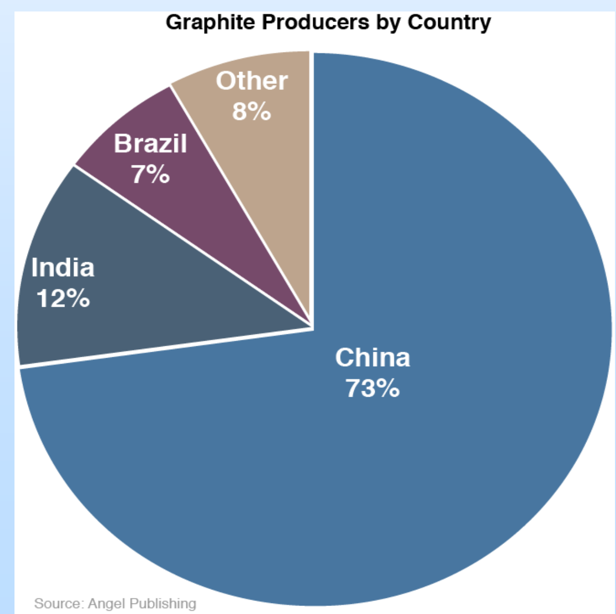
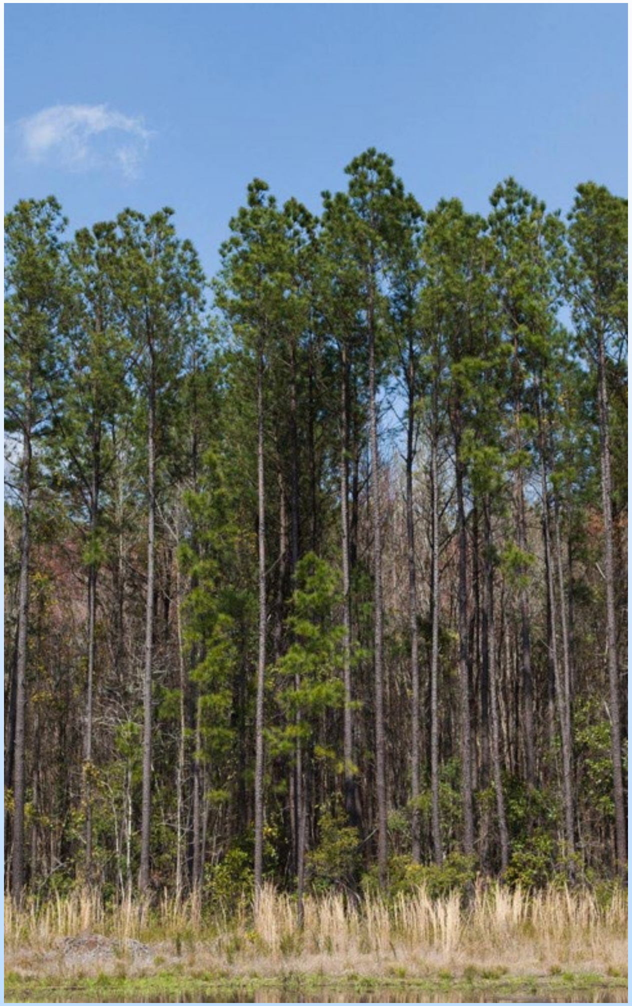


https://www.statista.com/statistics/719592/global-distribution-of-graphite-consumption-by-end-use/



US Carbon Resources

Agriculture

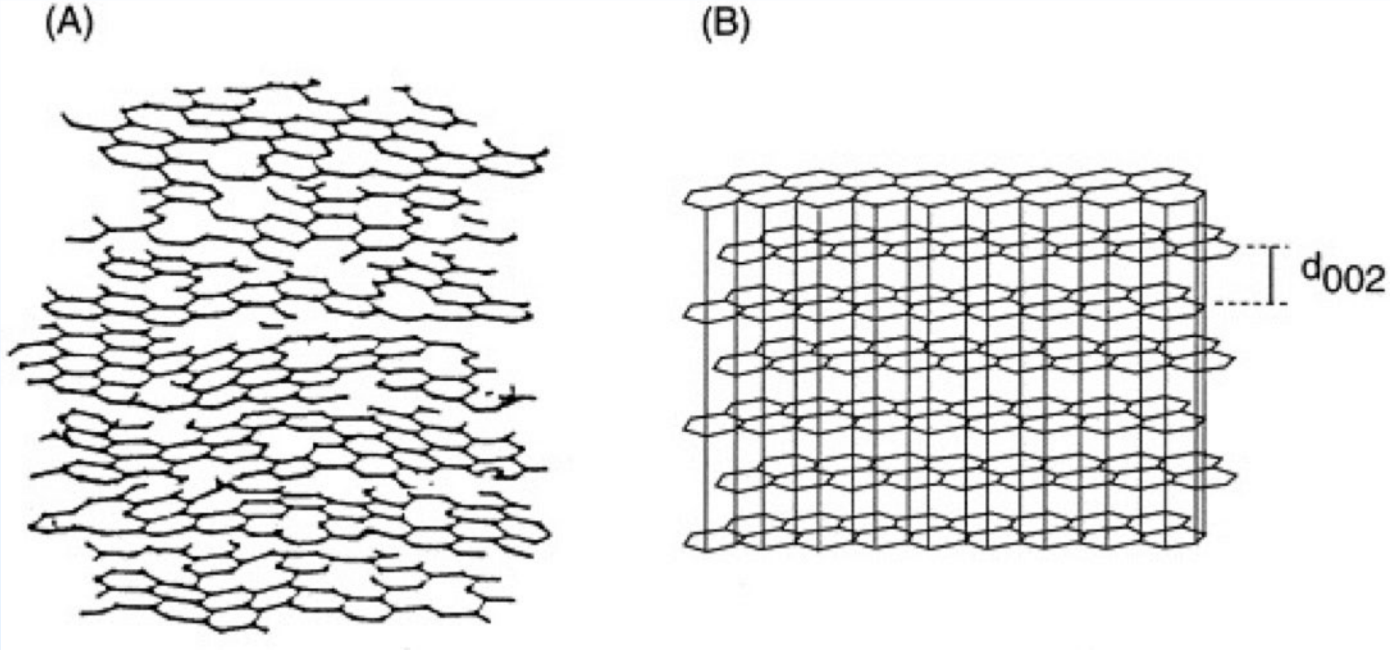


Forestry

US Carbon Resources

Coal

Hard Carbons & Graphite



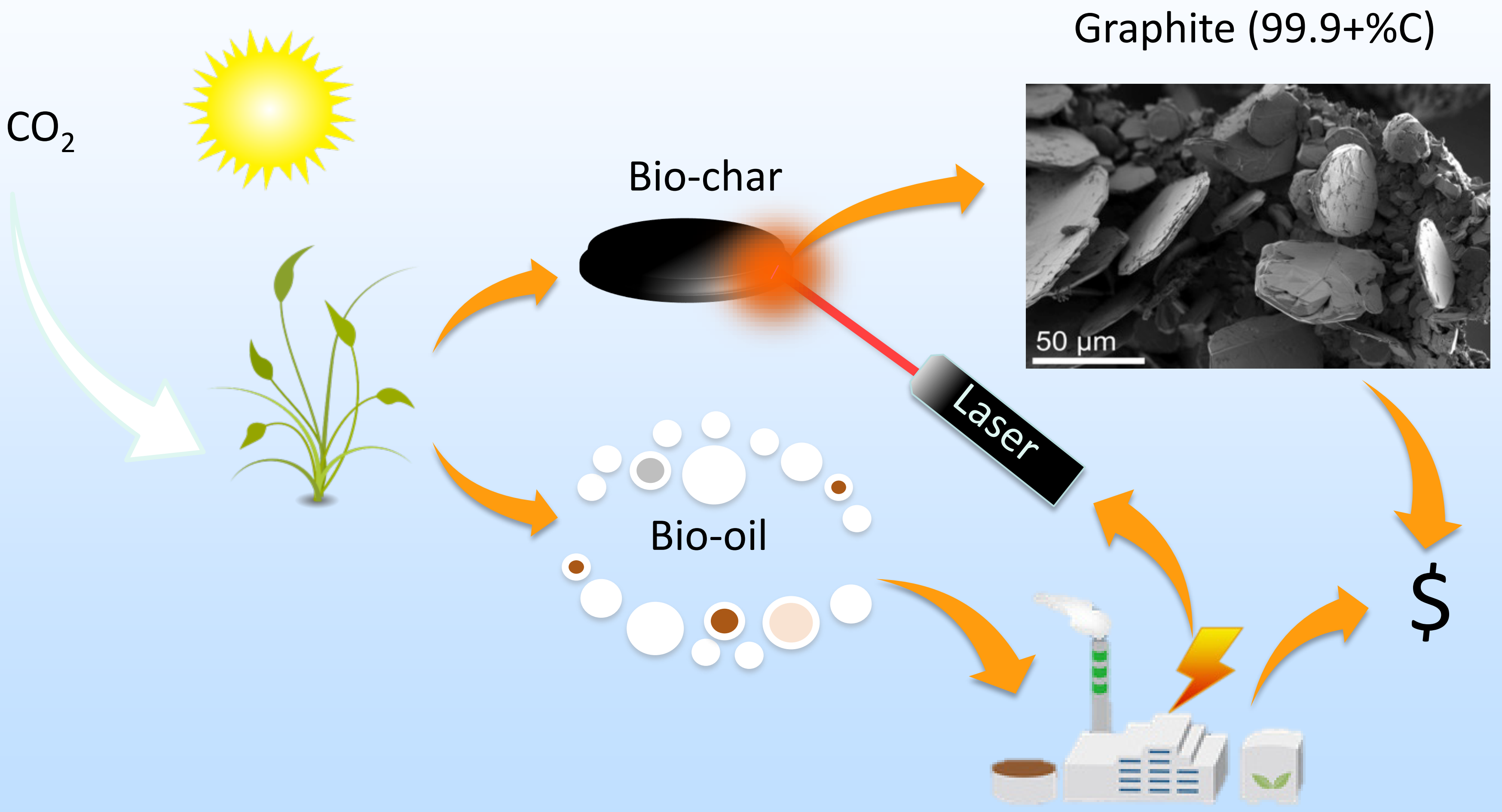
$D_{002} \geq 3.4$ Å

$D_{002} = 3.354$ Å

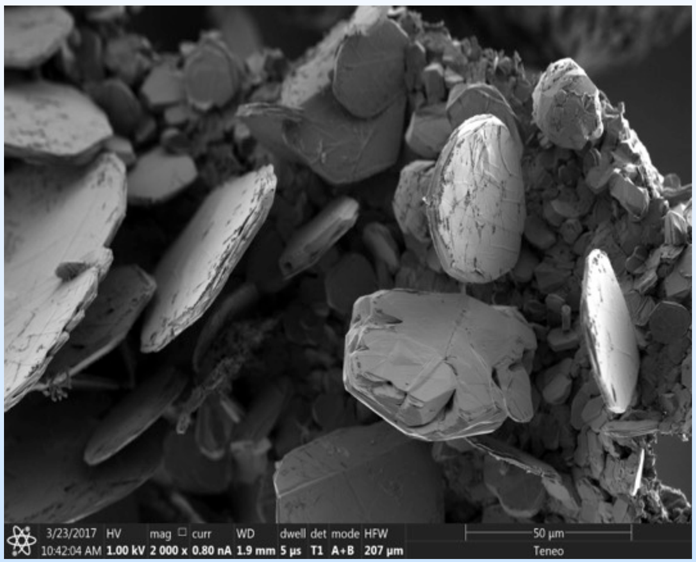
- Non-graphitizable
  - Biomass chars
  - Lignite & Anthracite
- Graphitizable
  - Coking carbons

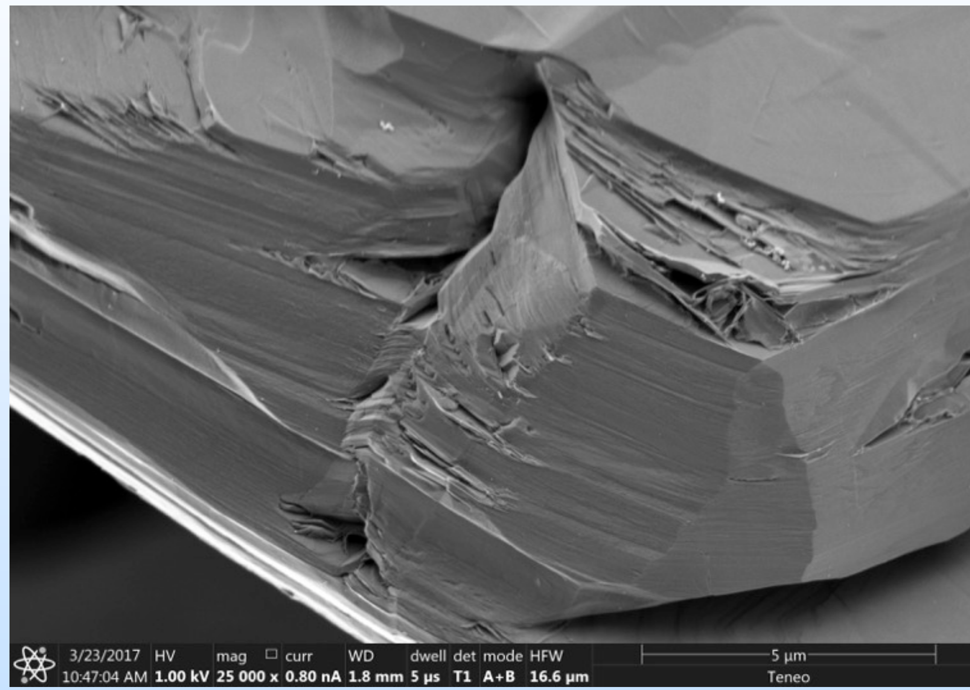
Bijan K. Miremad and Konrad Colbow, Sensors and Actuators B: Chemical,46, 1,1998,30-34

Graphite and Bio-oil Co-production

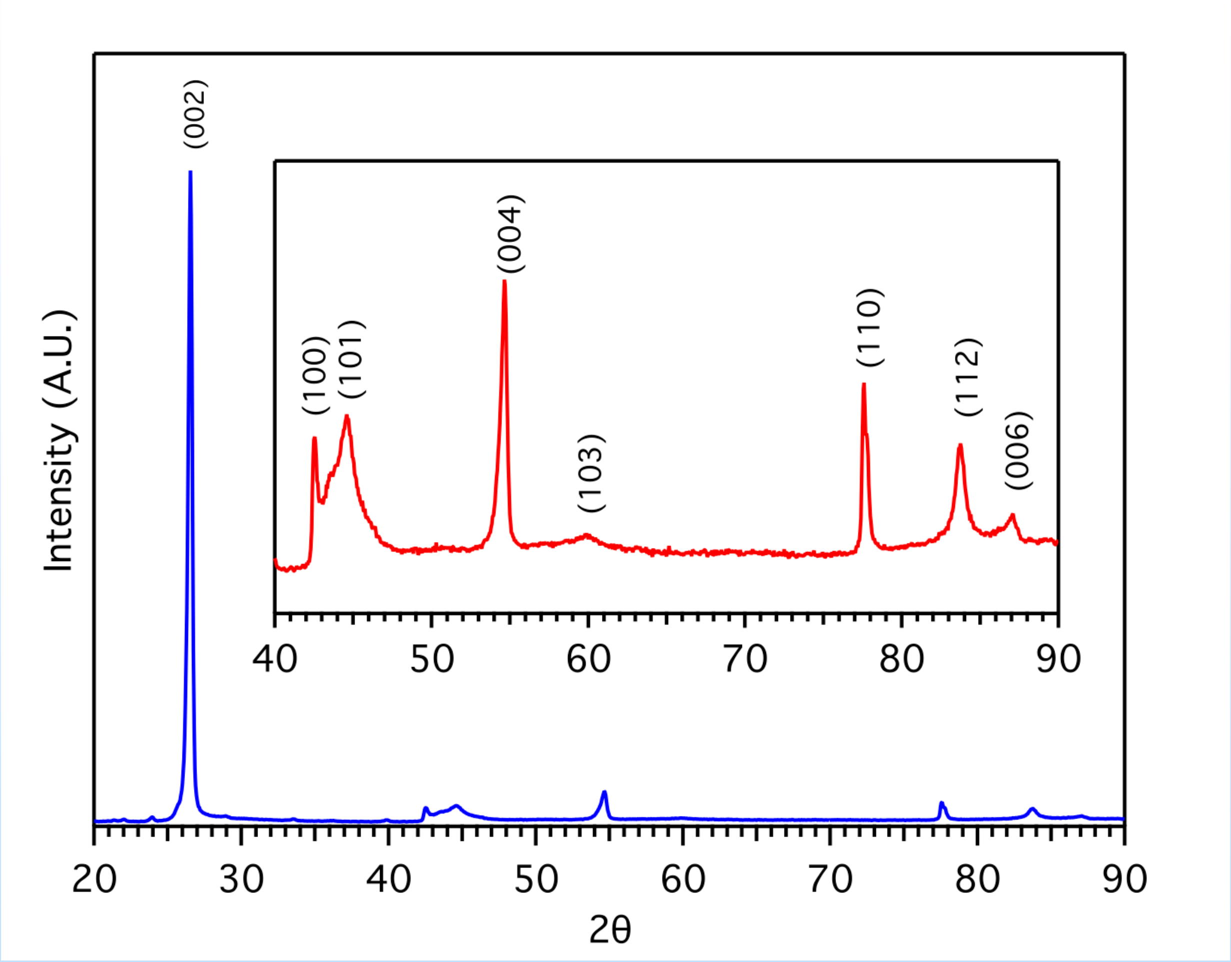


Flake Graphite from Biomass





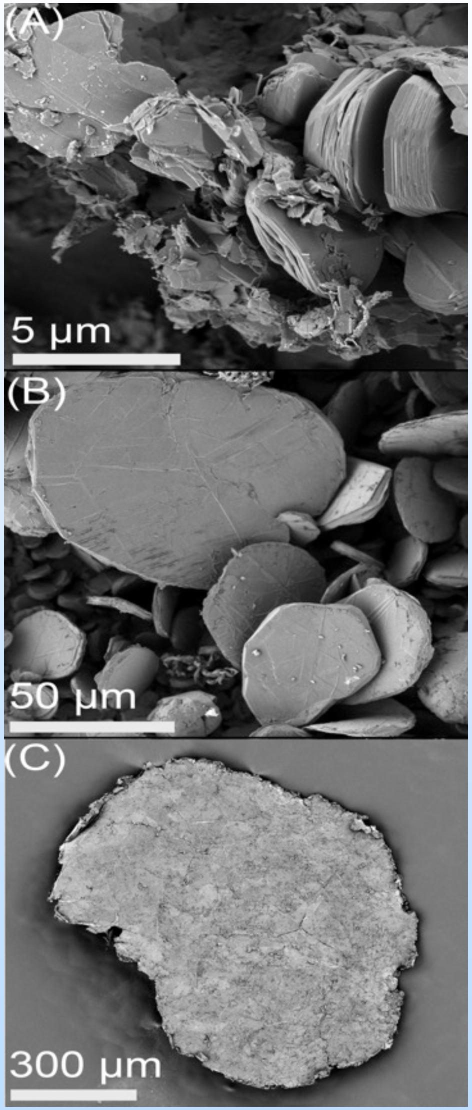
Flake Graphite from Biomass



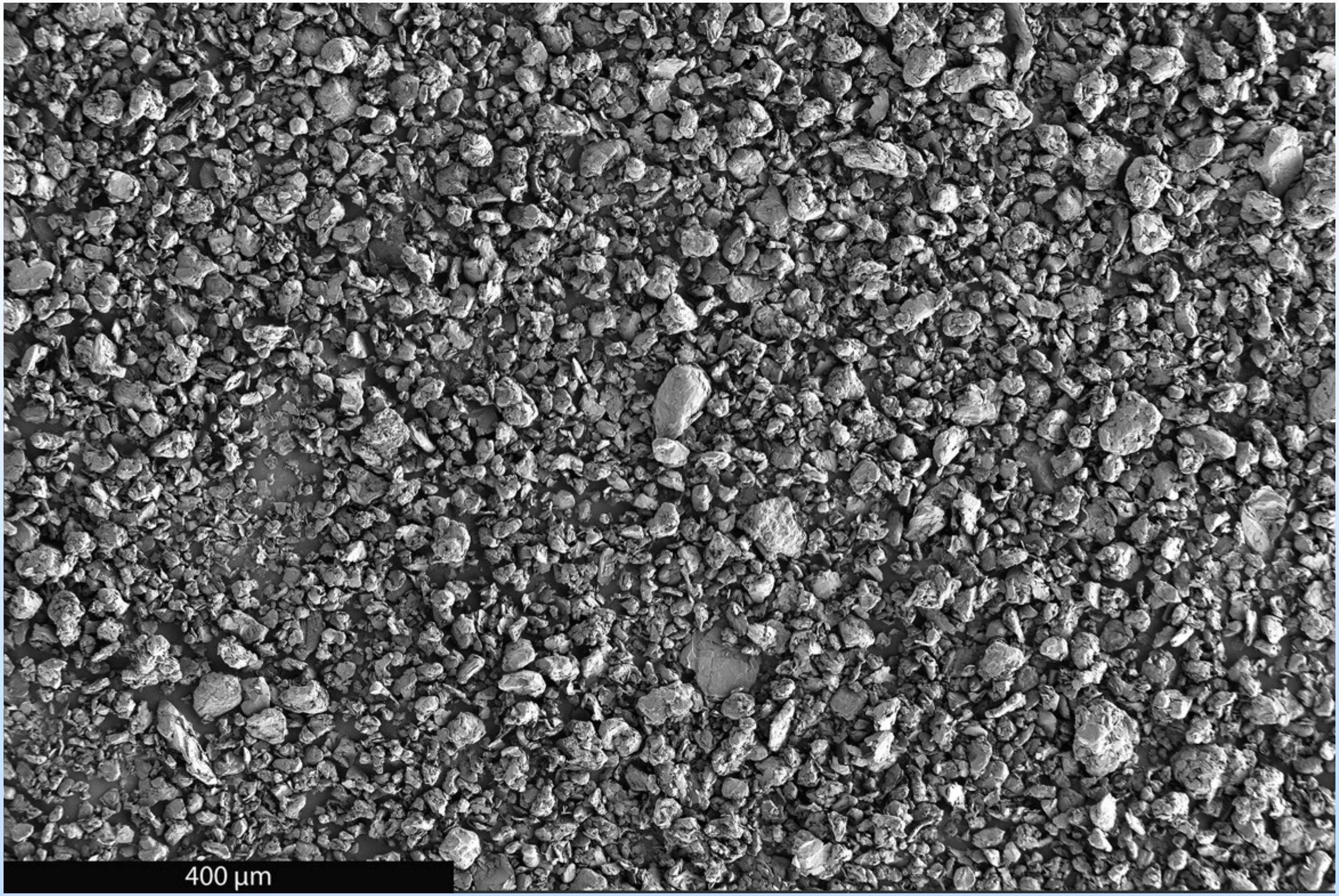
D_{002} = 3.3546(5) Å I_D/I_G Ratio < 0.04 > 99.95% C

Flake Graphite from Biomass

- ~ 5 µm Fe
- 0.60 mm Fe
- 1 – 2 mm Fe

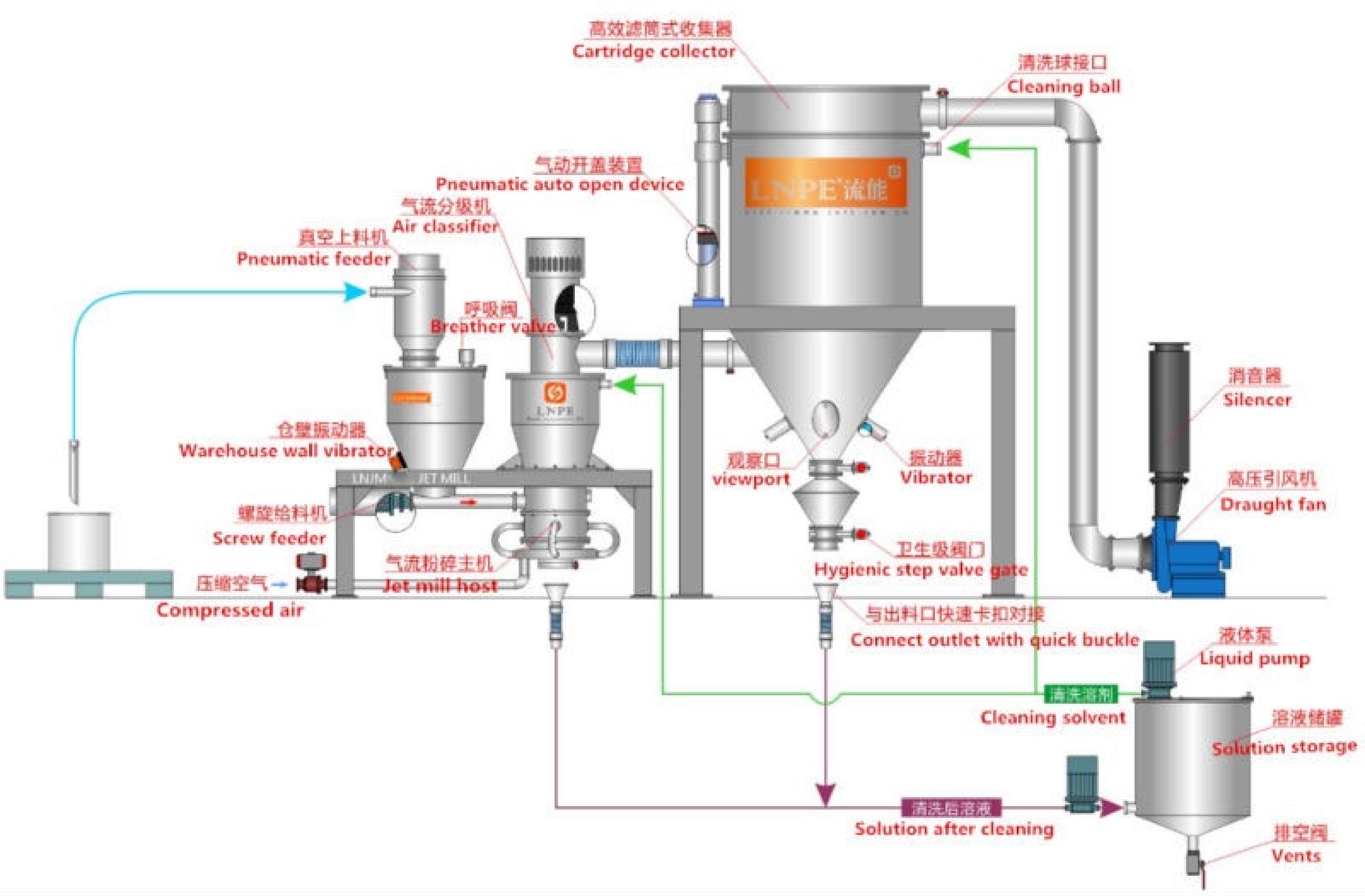


Commercial Li-ion Graphite



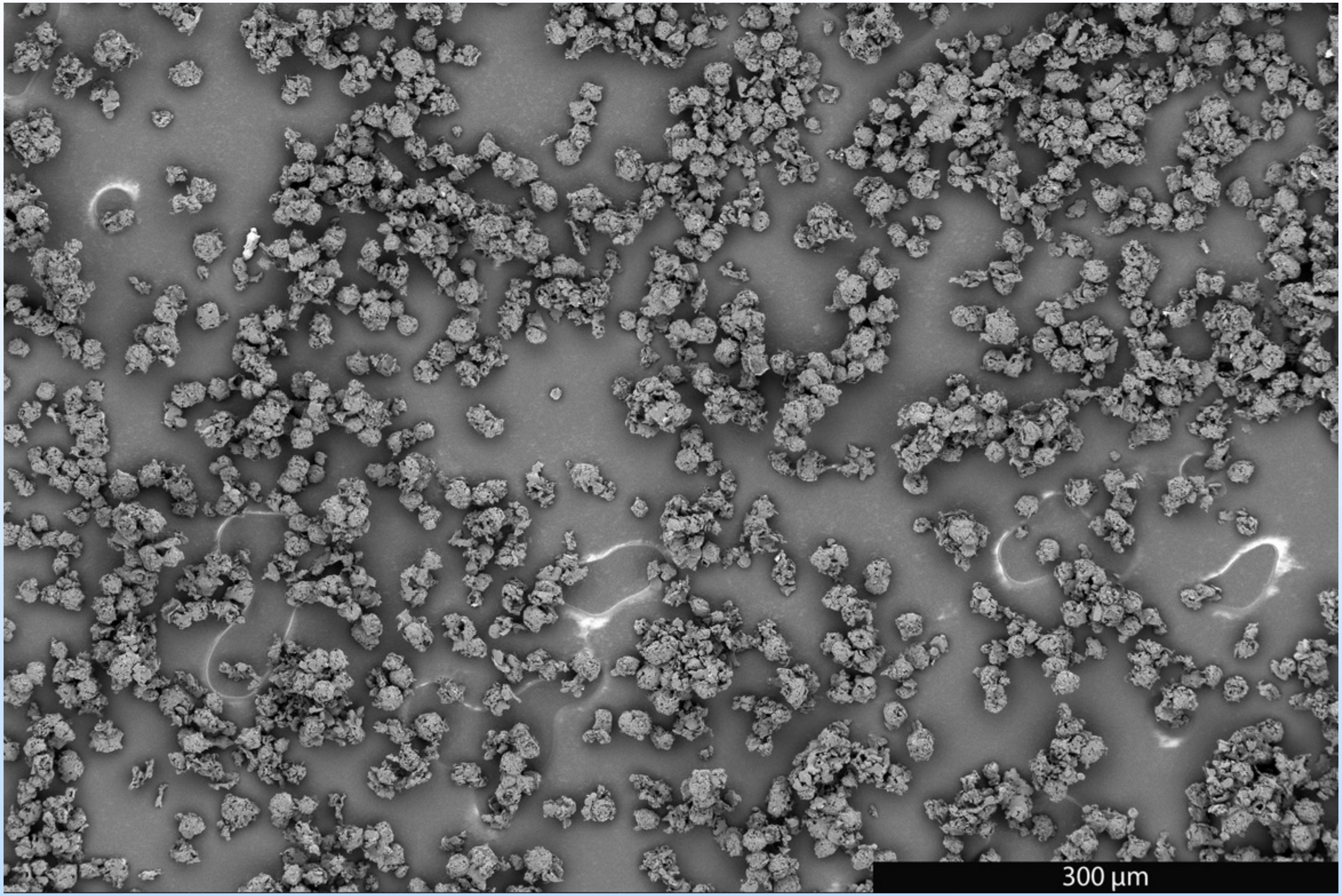
Hitachi MagE3 Shaped (milled) Li-ion Graphite

Conventional Graphite Shaping



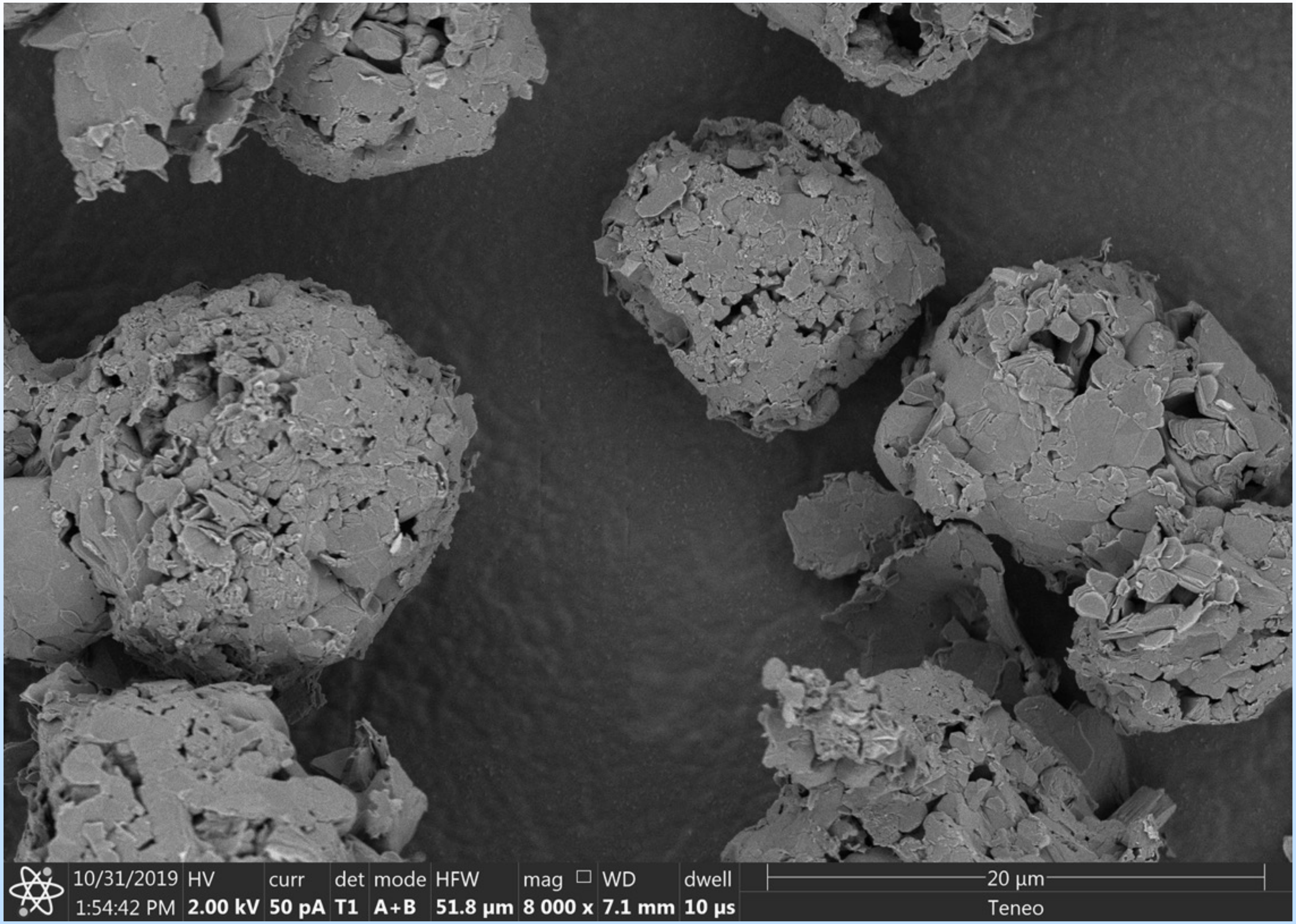
Graphite is brittle – 70% loss

Shaped by Design



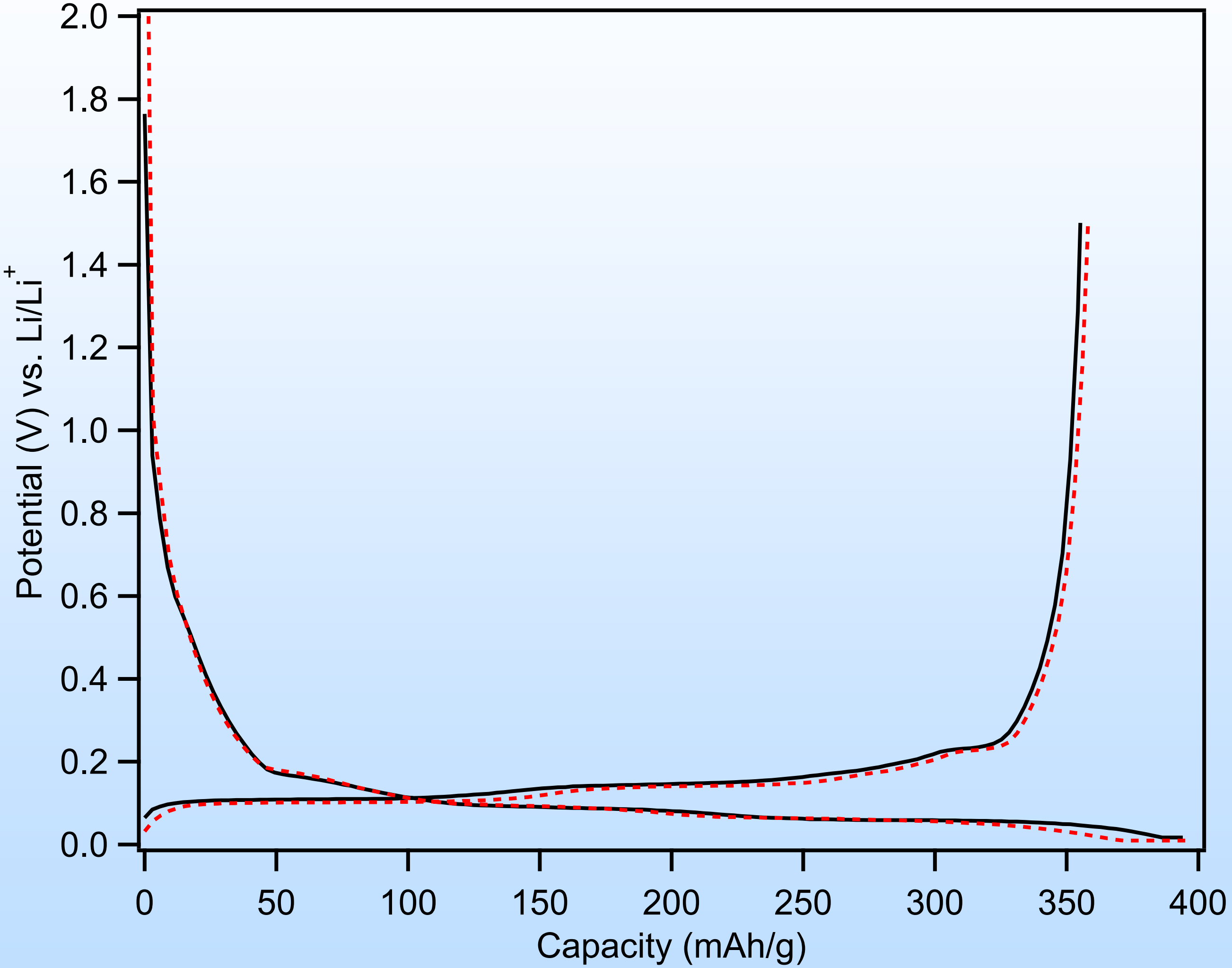
Optimize flake & potato size independently - no graphite loss

Shaped by Design



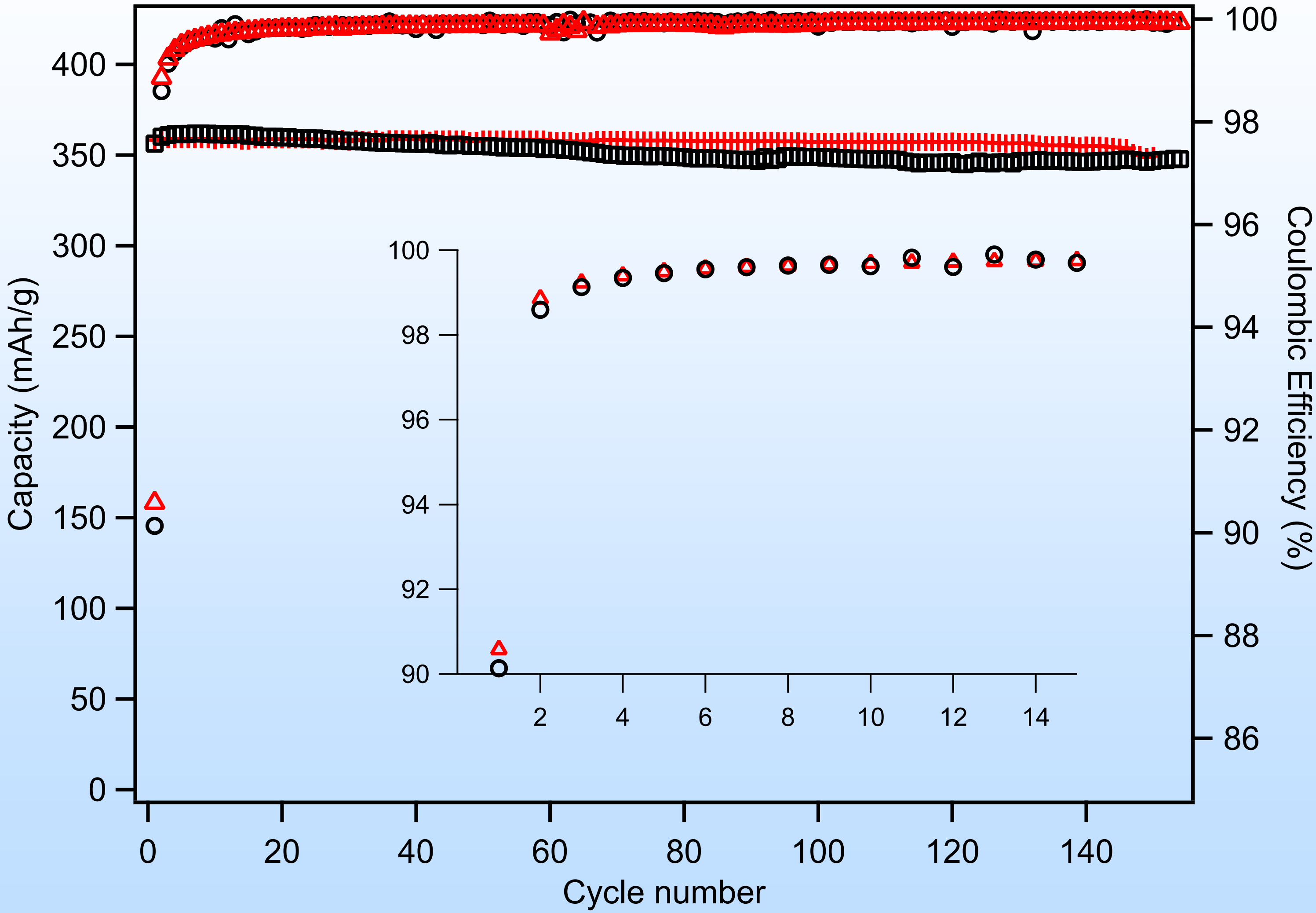
Surface area: 3.08 m^2/g (8% larger than MagE3 2.83 m^2/g)

Rational Design of Graphite



sBCG (solid black) and Hitachi MagE3 (dashed red).

Rational Design of Graphite

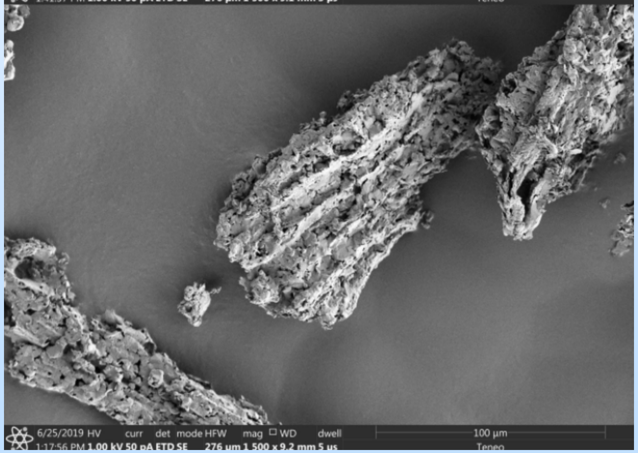


sBCG (black) and Hitachi MagE3 (red).

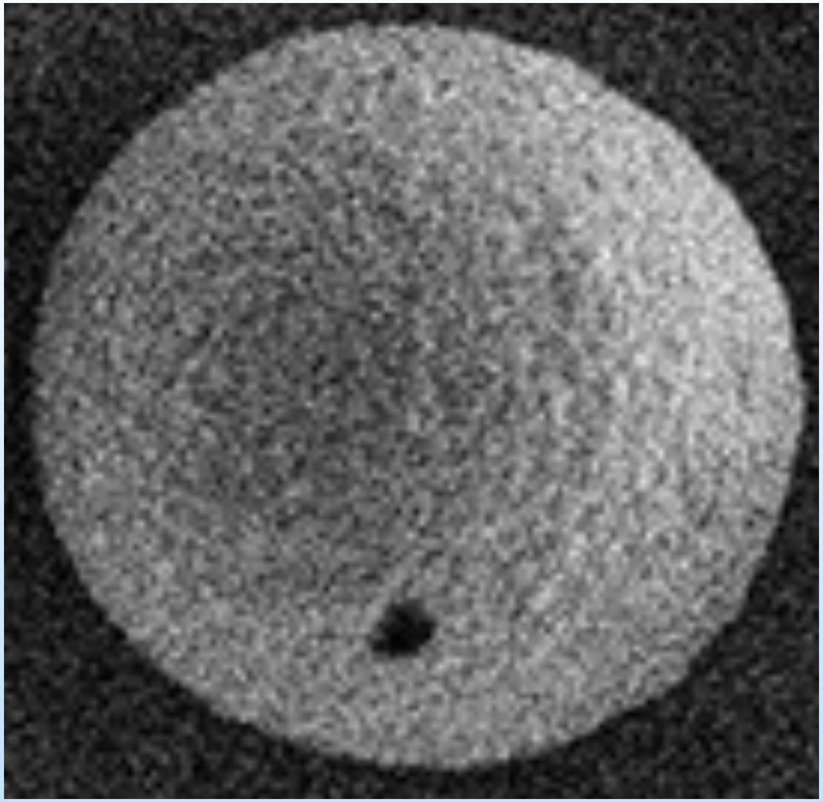
Graphite from Biomass

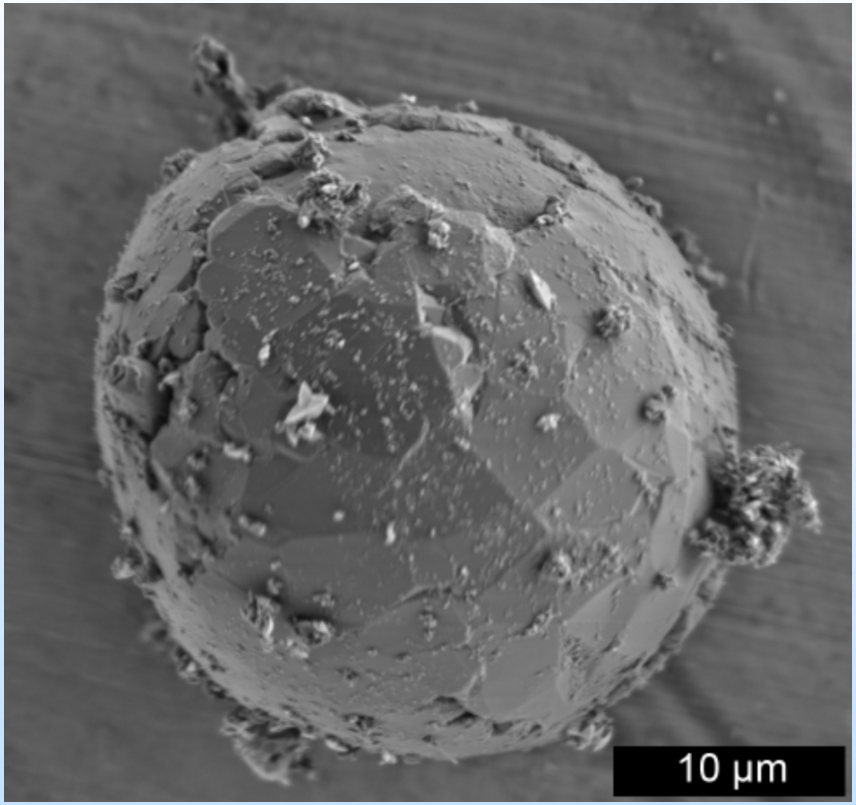
- Wood Char

- Graphite



Graphite from Biomass



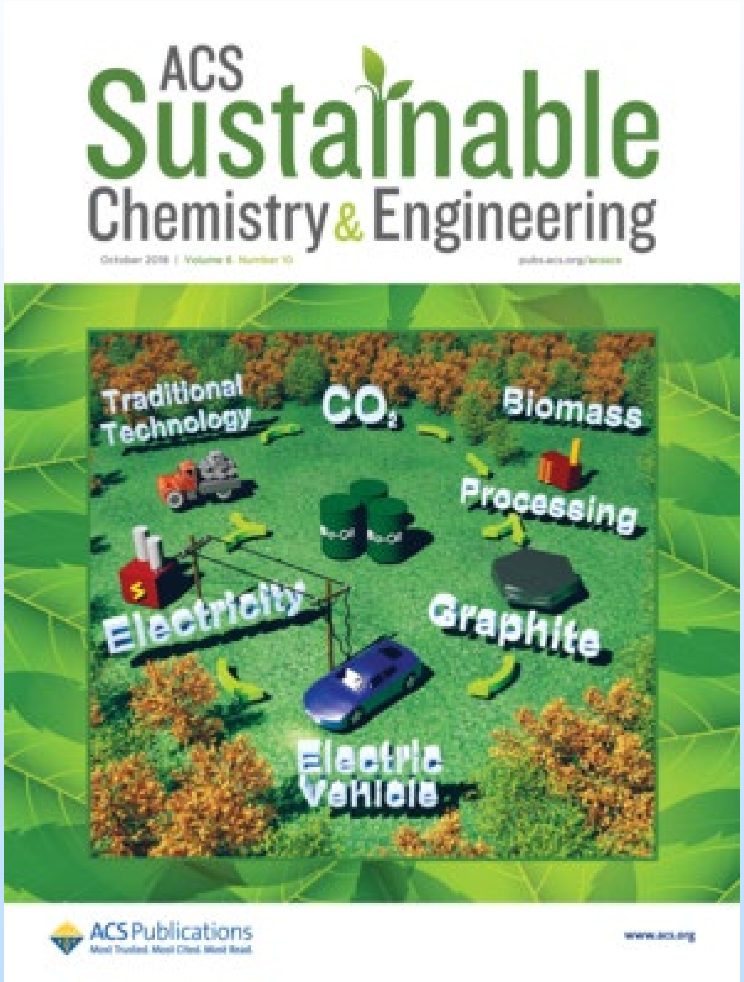


Algae

Graphite

Graphite from Biomass

- High Yield (95.7%, >0.4 kg/kWh)
- High Purity (> 99.95% carbon)
- High crystallinity
- Shape/size control
- High capacity (350 – 370 mAh/g)
- Energy Production Exceeds Input
- Market disruptively inexpensive?



Coal vs Biomass

Advantages (Lignite)

- Cheaper
  - ~ 6.7 fold decrease
- Supply Chain
- Co-products

Disadvantages (Lignite)

- ❑ Impurities
- ❑ Not carbon neutral?

https://www.wesa.fm/post/new-coal-mine-opening-pennsylvania-trump-thank#stream/0

Technical Approach/Project Scope

1) Explore the ability of our (batch) method to graphitize a variety of coal feedstocks.

2) Determine coal properties conducive to graphitization at high yield. Raise yield to economically viable levels.

3) Characterize products chemical purity, crystallinity, morphology and electrochemical properties. Improve properties to Li-ion battery grade.

4) Transition from batch to continuous processing maintaining high yield and favorable properties.

Success Criteria

1) Convert lignite to graphite with at or in excess of 0.3 kg graphite/kWh laser output power efficiency.

2) Attain better than 90% first cycle Coulombic efficiency and in excess of 340 mAh/g with batteries employing lignite-derived graphite as the Li ion storage material.

3) Produce graphite from lignite at a rate that exceeds 25 g/h of laser irradiation.

4) Demonstrate 500 or more charge/discharge cycles to end of life, defined as 80% of initial reversible capacity, with a battery employing lignite-derived graphite as the Li ion storage material.

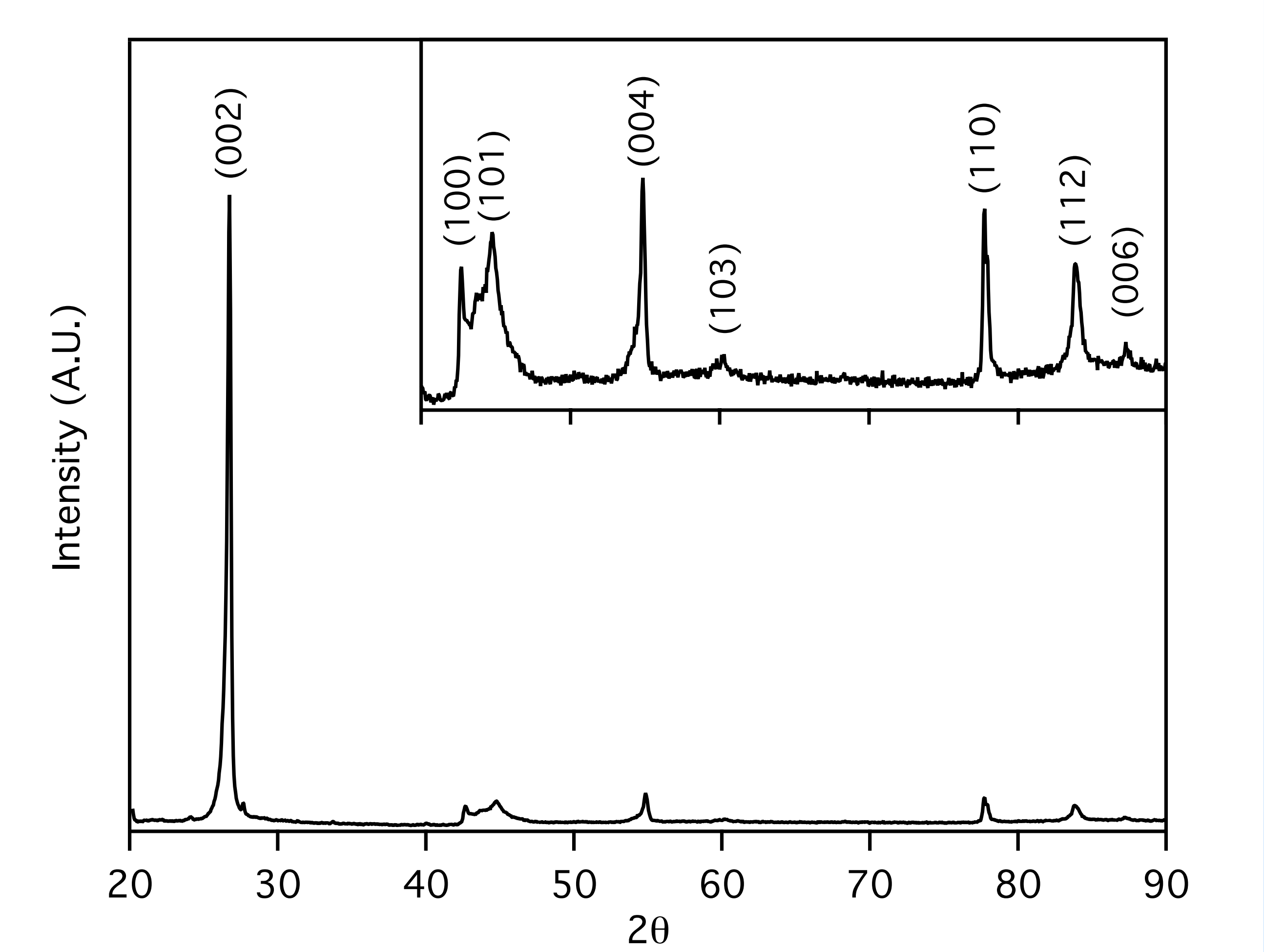
Project Feedstock

- 18 lignite samples
  - Multiple kg each
  - Impurity profiles vary
  - Macerals vary
  - Cut variety
- North Dakota lignite (high Na/Ca)
- Mississippi lignite − (high mineral)
- Bituminous & antharcite

Coal Graphitization

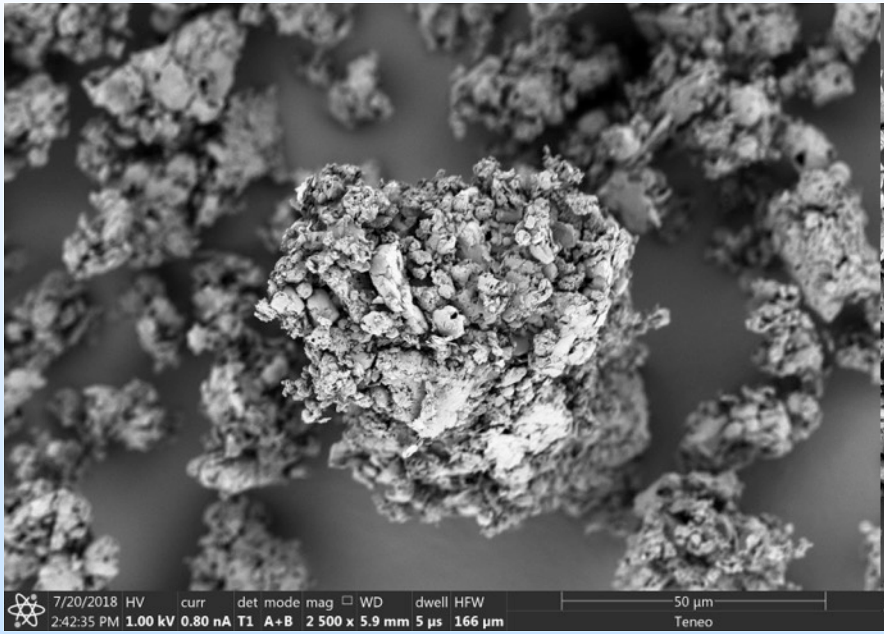
- Lignite
  - All of the North Dakota samples graphitize
  - Mississippi samples graphitize with low yield (25 – 33% at 200 W laser power)
- Bituminous sample does not graphitize – despite it being a “graphitizable carbon”
- Anthracite sample does not graphitize

Graphite From ND Lignite

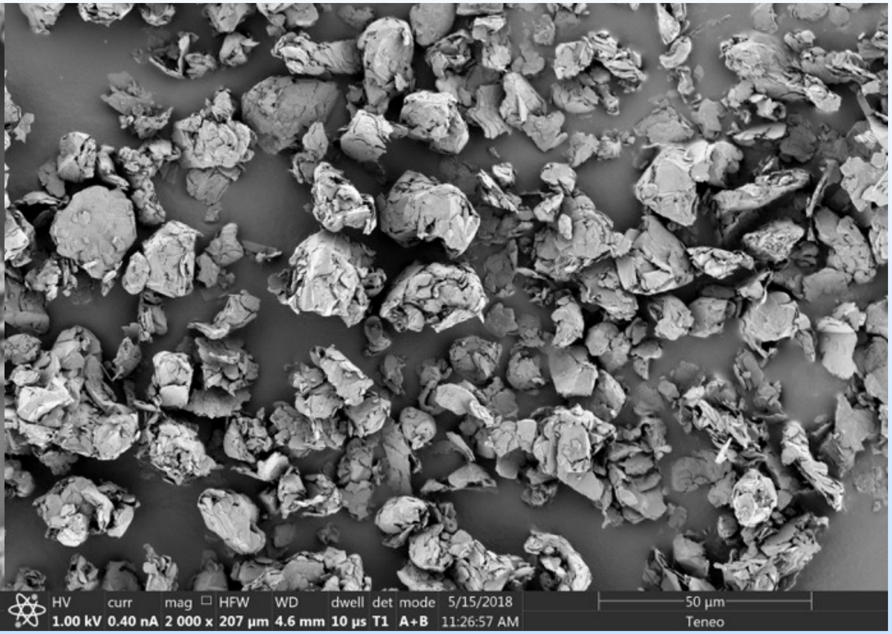


Highly Crystalline Graphite from Lignite

Shaped Graphite From ND Lignite

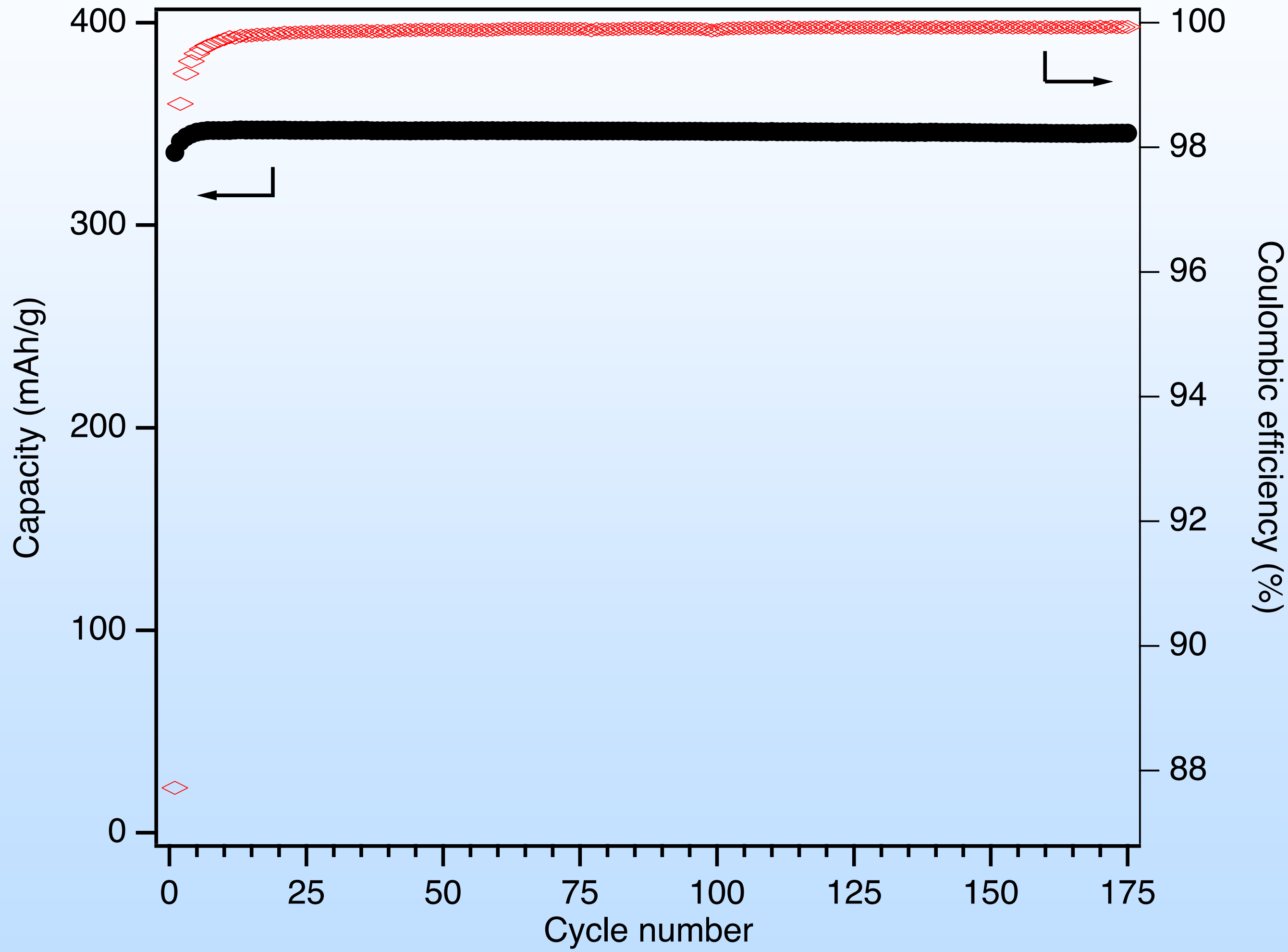


Graphite from Lignite



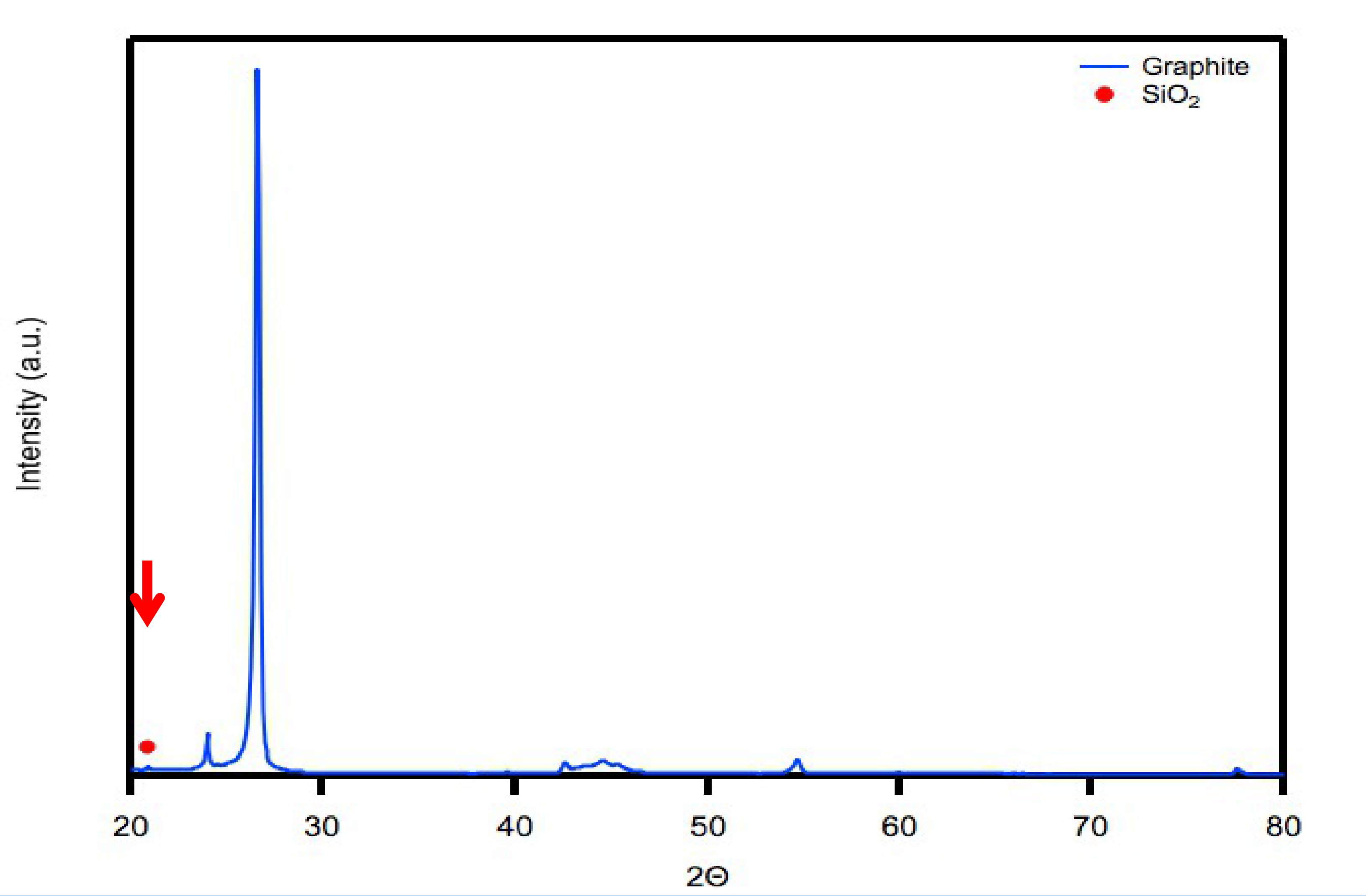
Hitachi MagE3 Graphite

ND Lignite Graphite – Li-ion

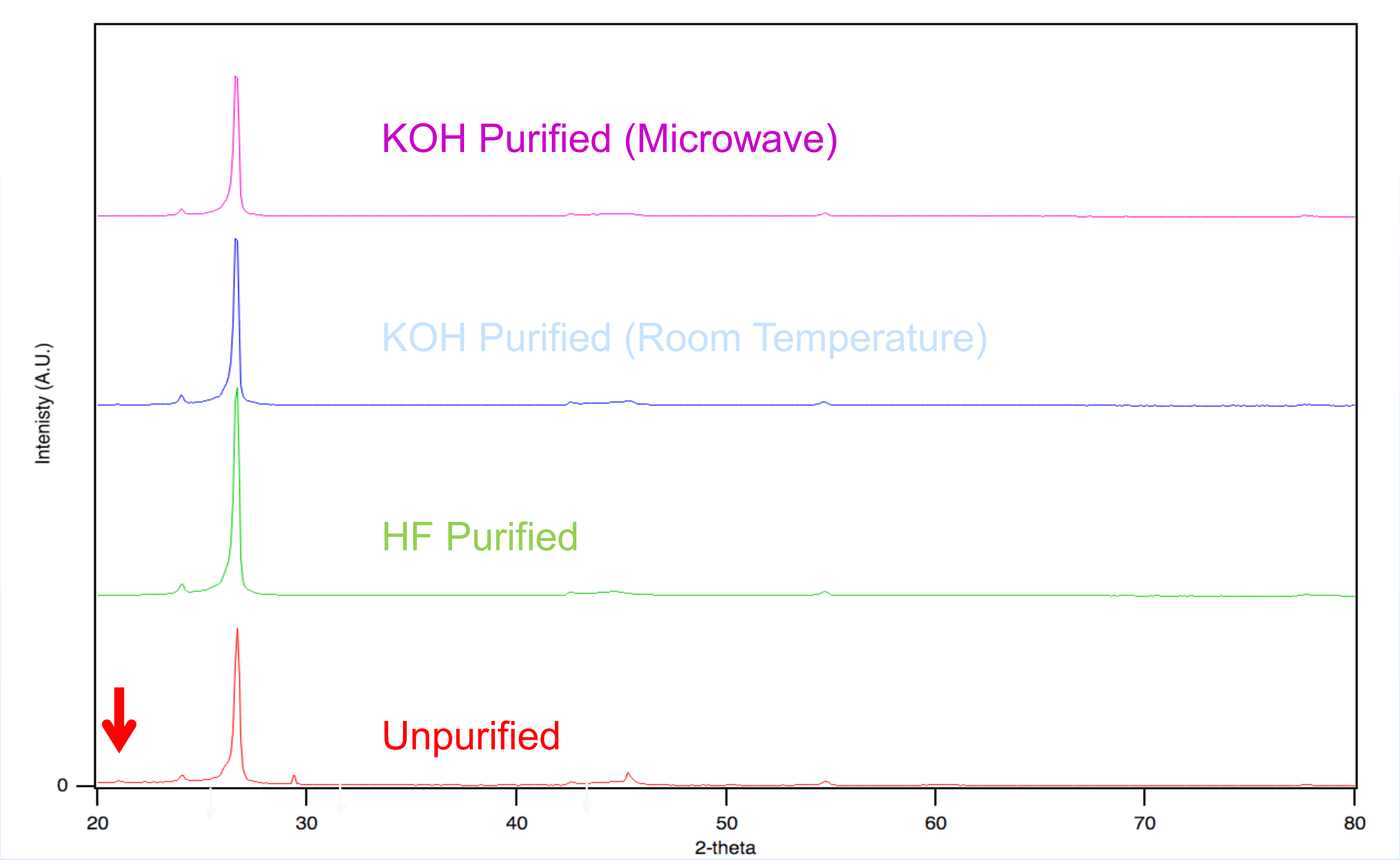


347 mAh/g, > 88% 1st Cycle CE

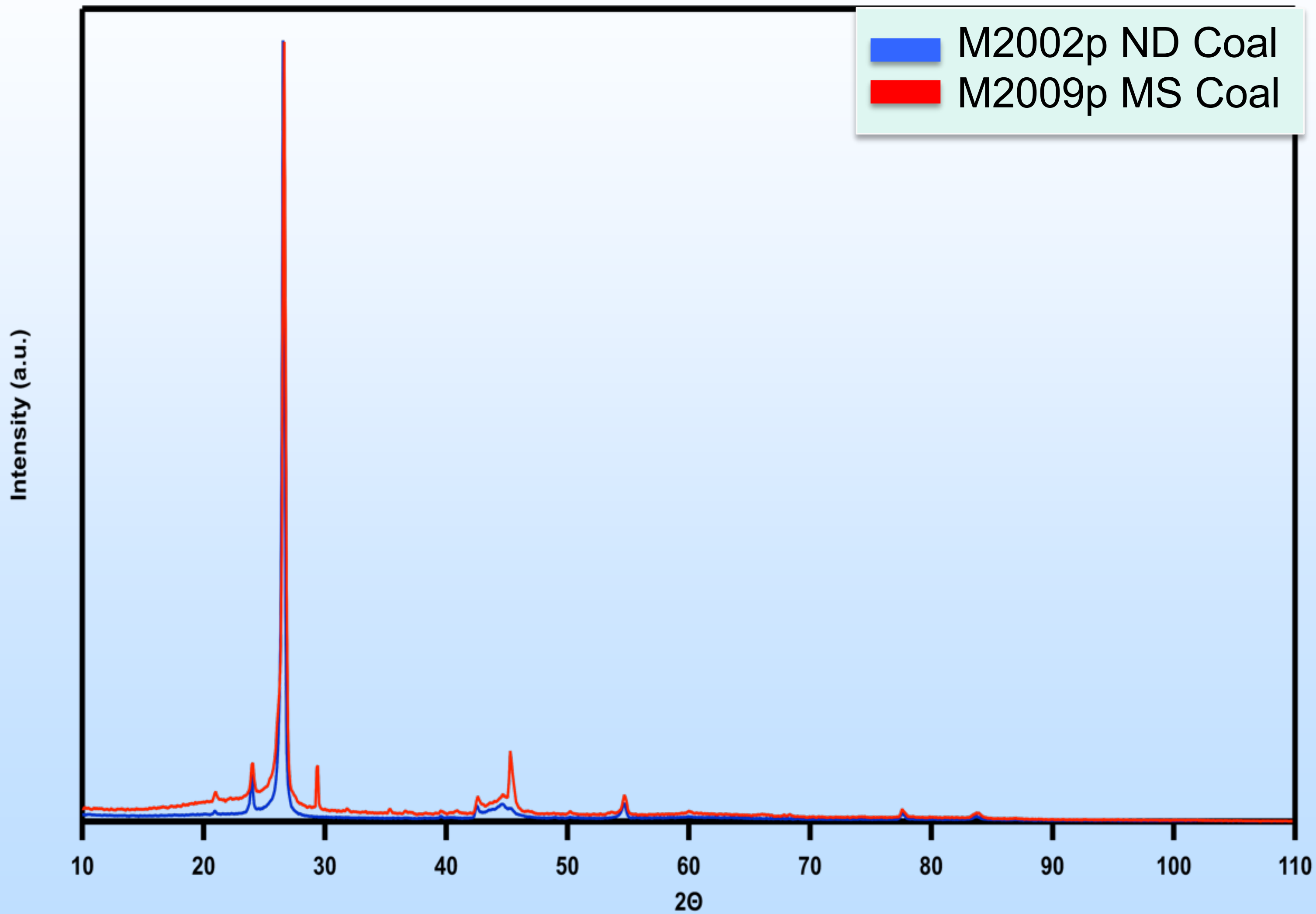
ND Lignite Graphite – SiO_2



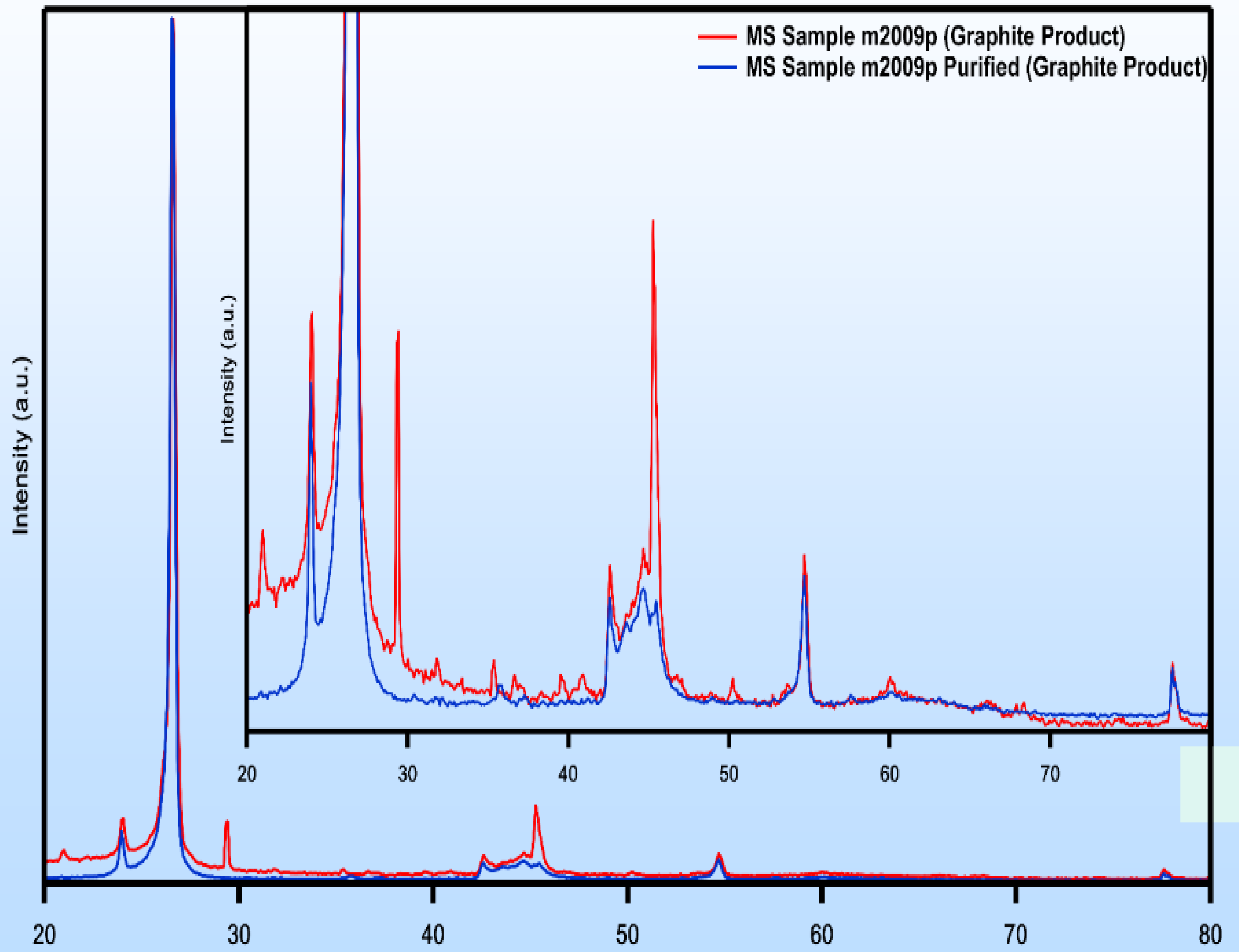
ND Lignite Graphite – Purification



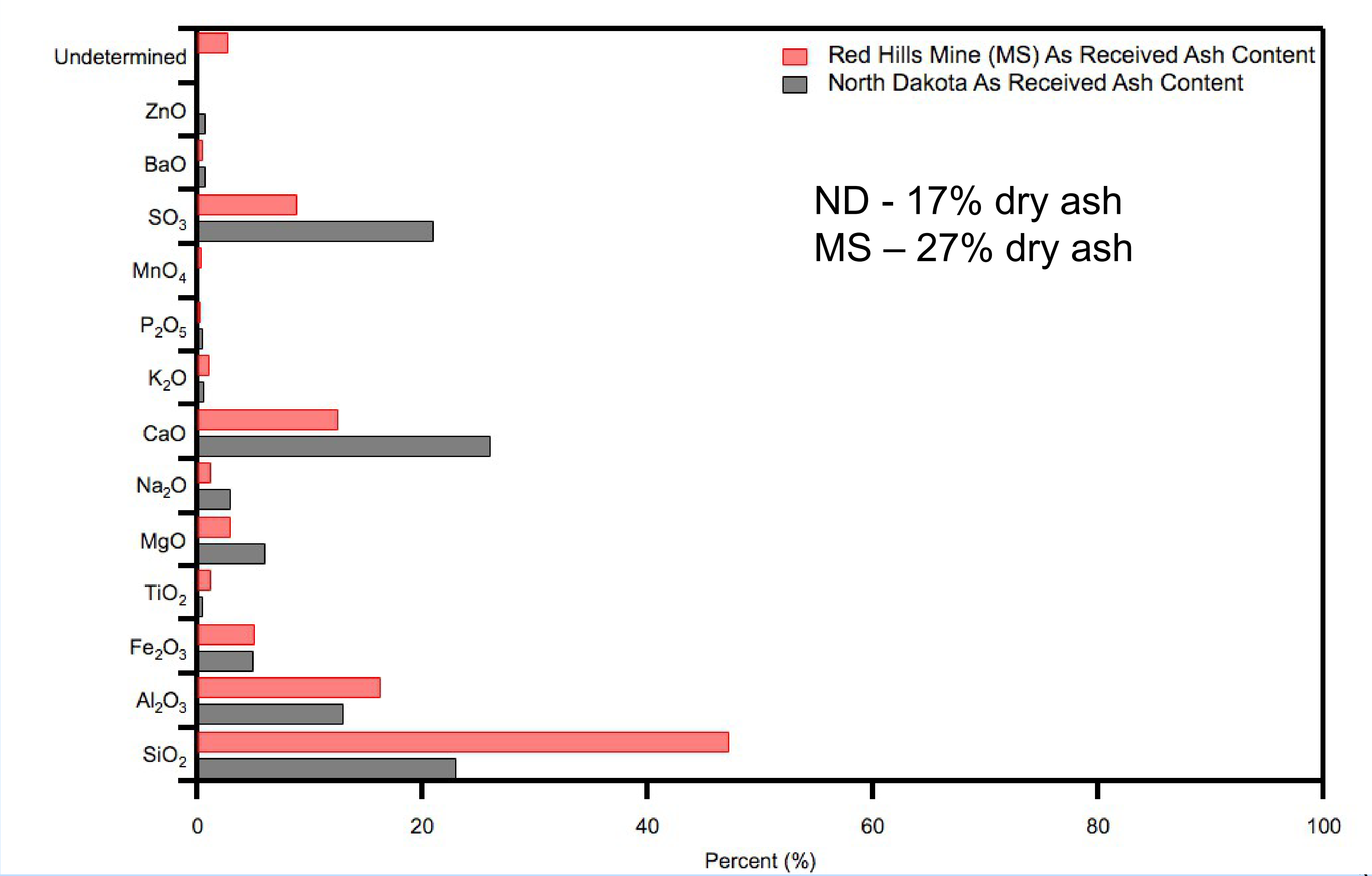
ND vs MS Lignite Graphite



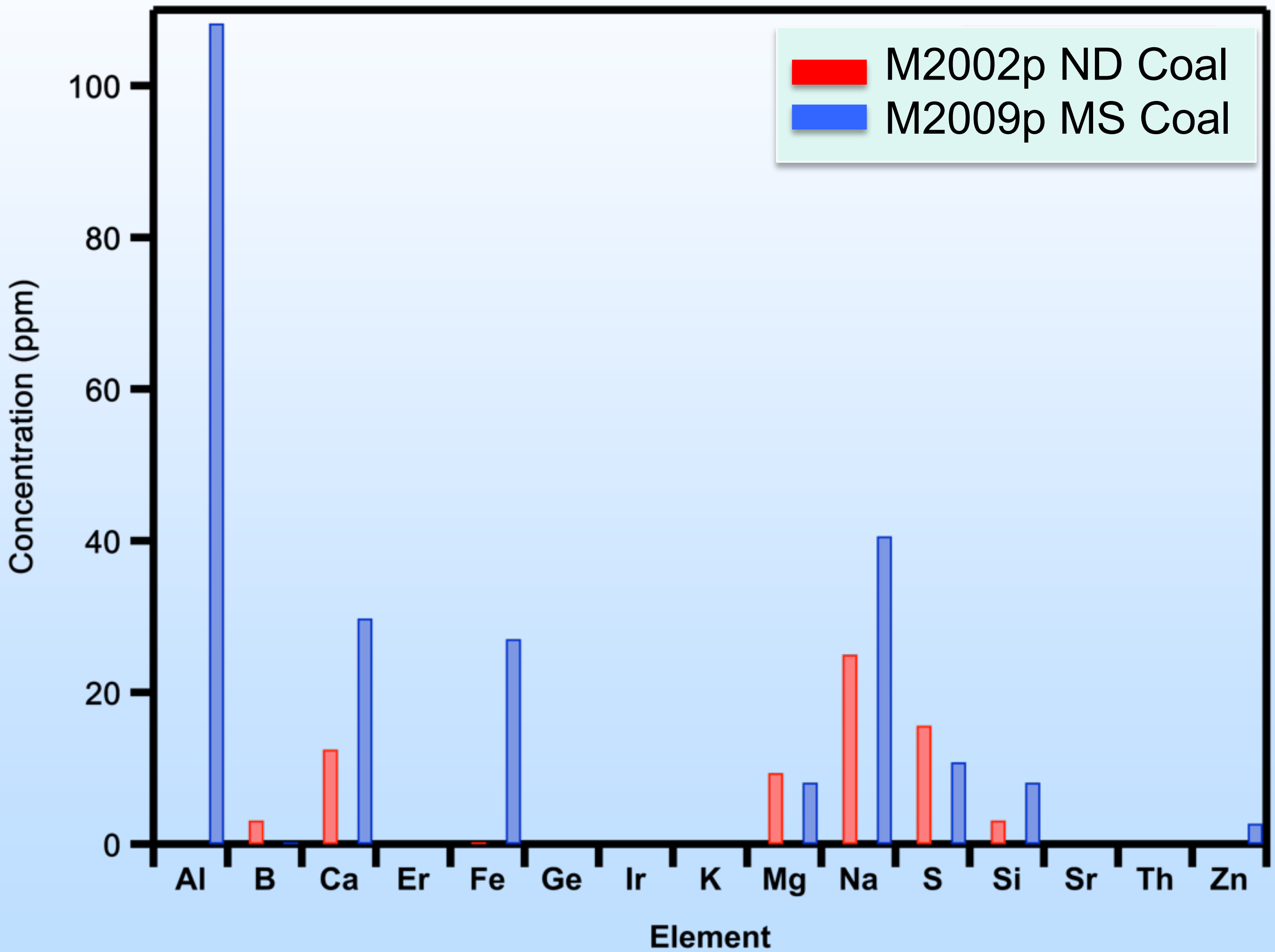
MS Lignite Graphite – Purification



Lignite Impurities – As Received



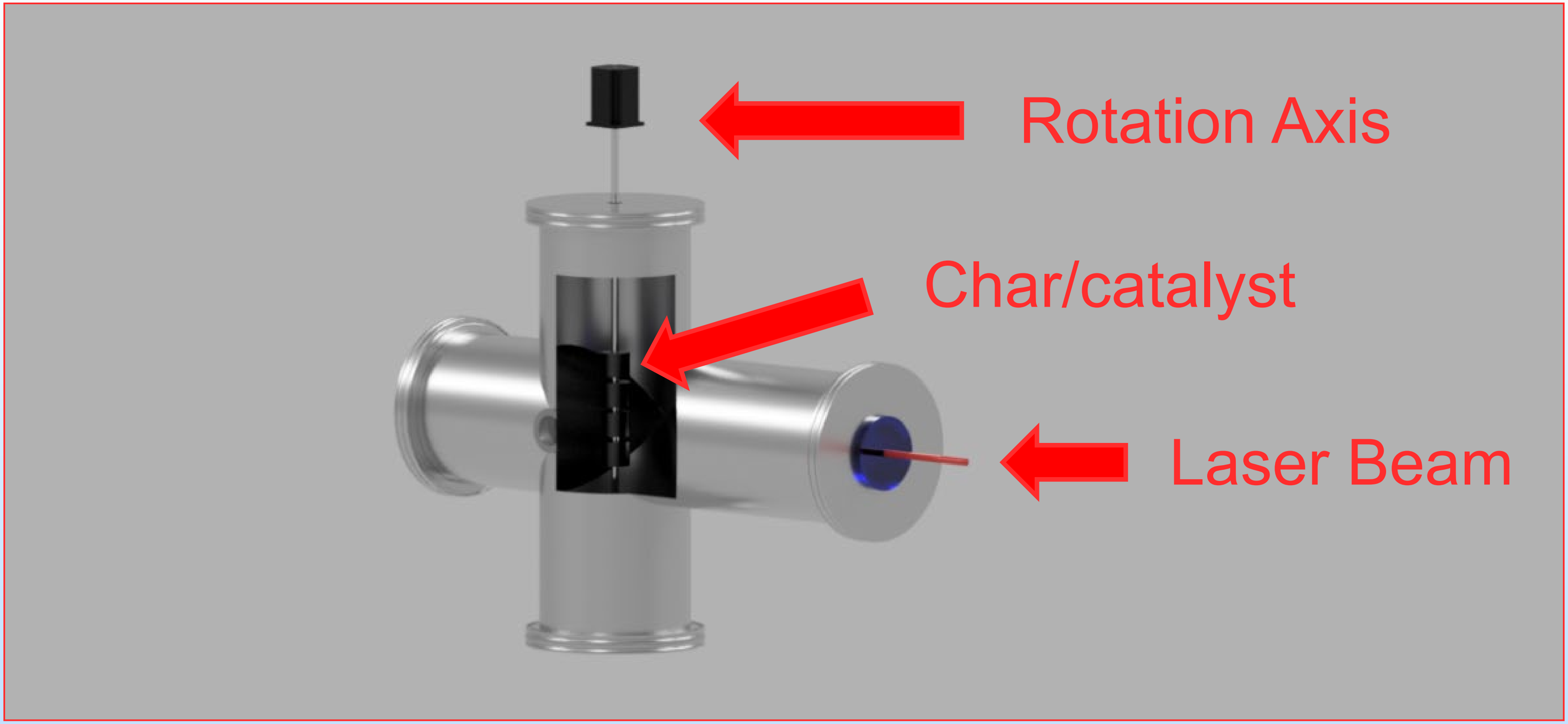
ND vs MS Product Analysis



Continuous Processing

Batch Process – Sample Prep

Batch Process – Sample Prep

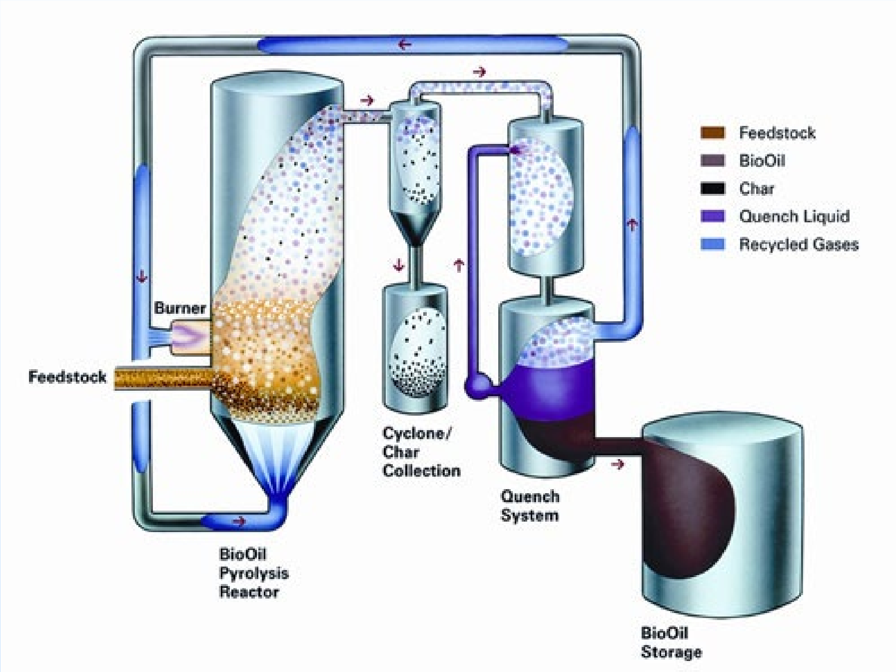


20 mm dia char/catalyst pellet 1 full 5 – 50 s rotation @ 200 W laser power

Batch Process (gram scale)

Mixing → Com-paction → Char-ring → Laser Pyroly-sis → Purifi-cation

Bio-oil/Biochar Production



Biomass Charring

ENSYN

Fulcrum BIOENERGY

SIERRA ENERGY

KARR ECO-FRIENDLY SOLUTIONS

ExxonMobil

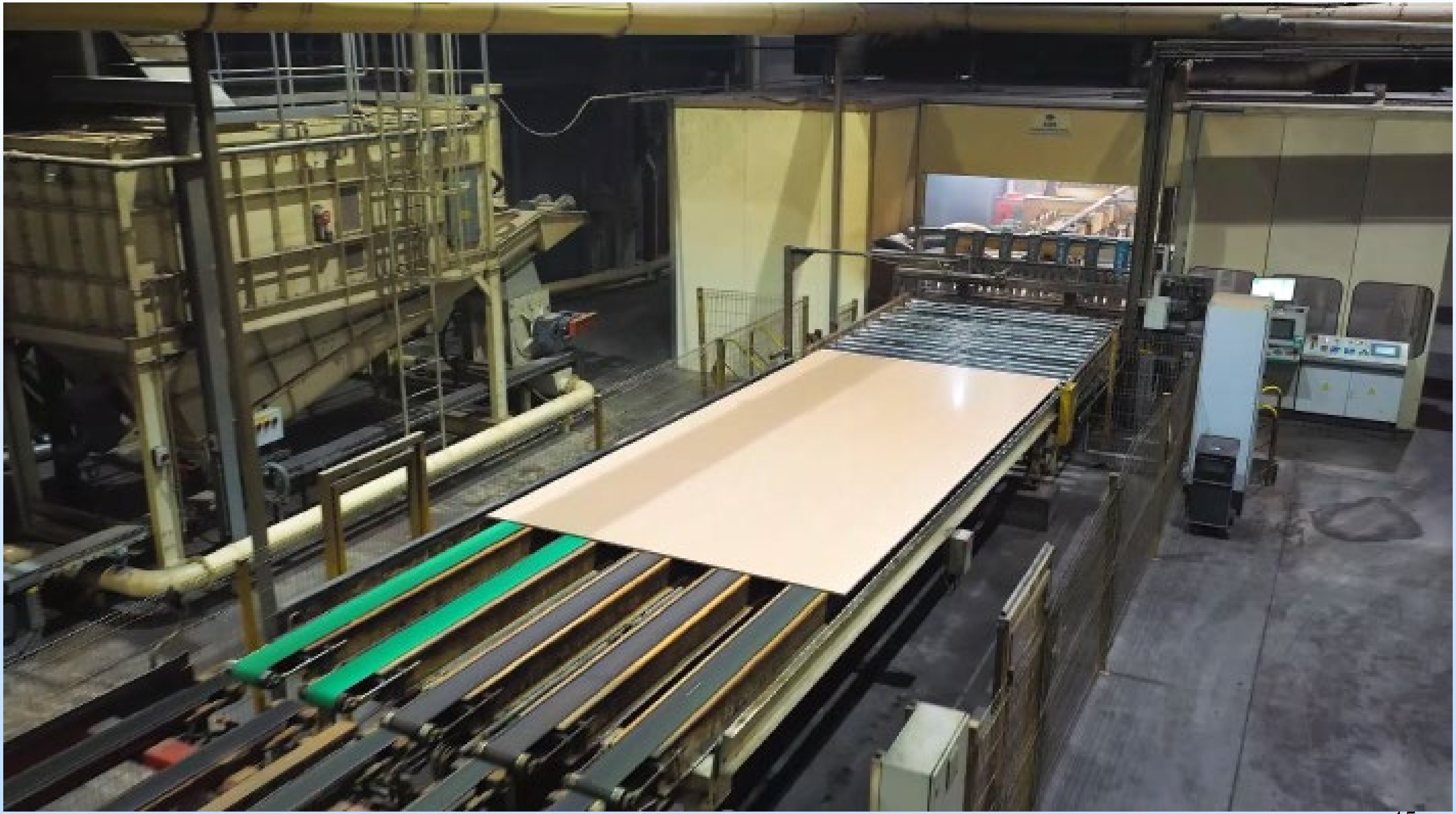
IOGEN CORPORATION

Chevron

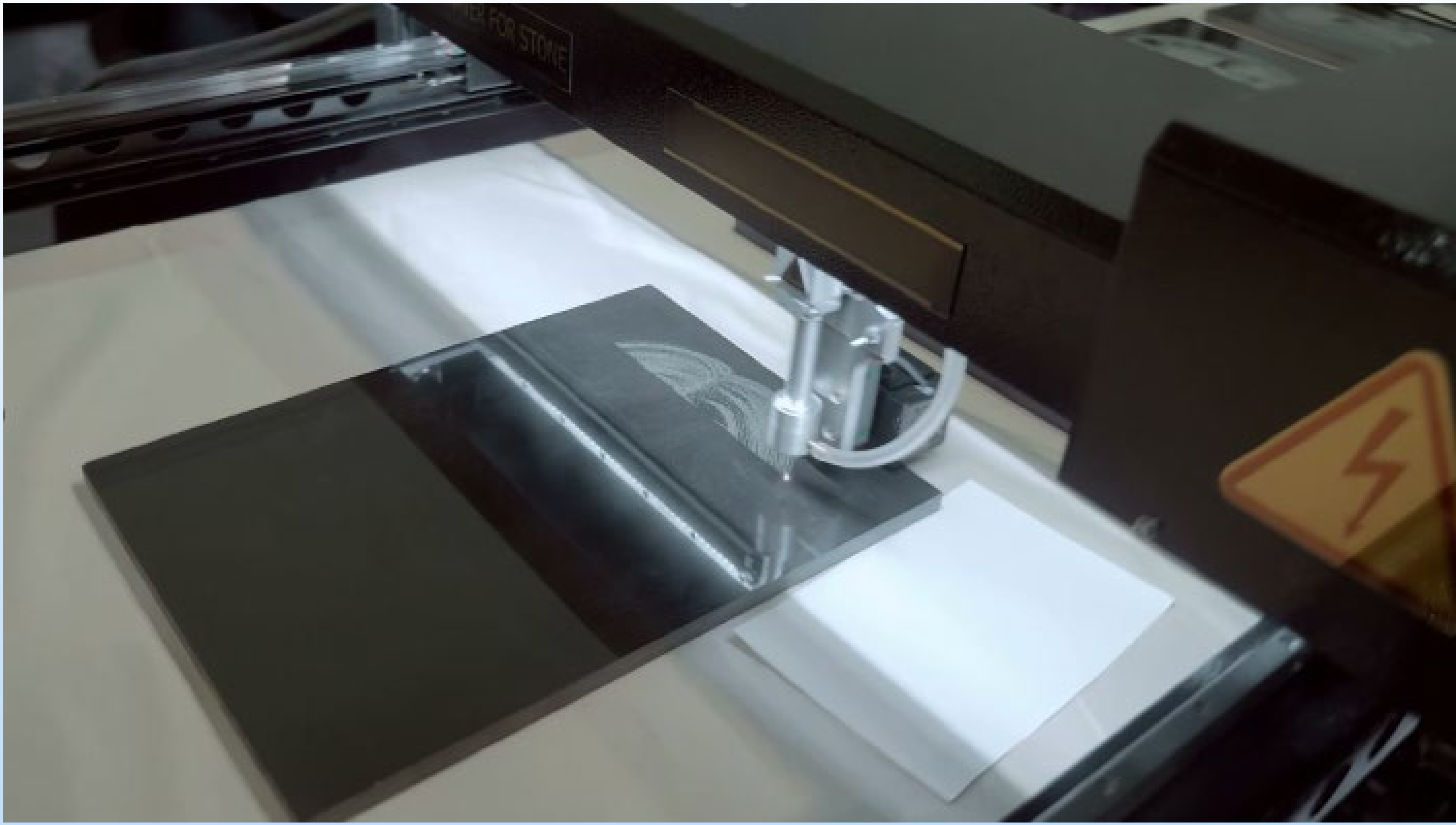
Sapphire Energy

sundrop fuels

Hard Board

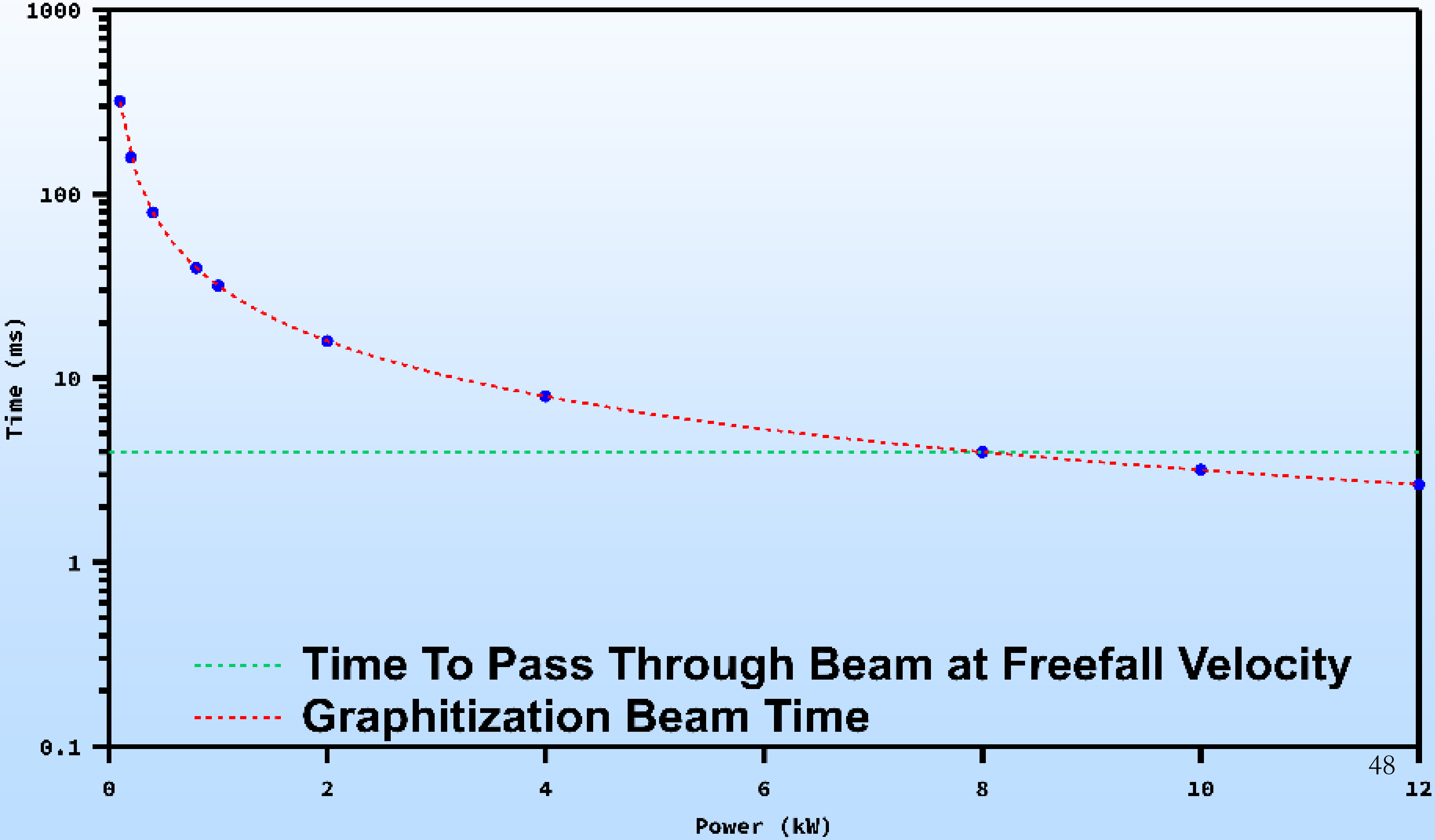


Raster Laser



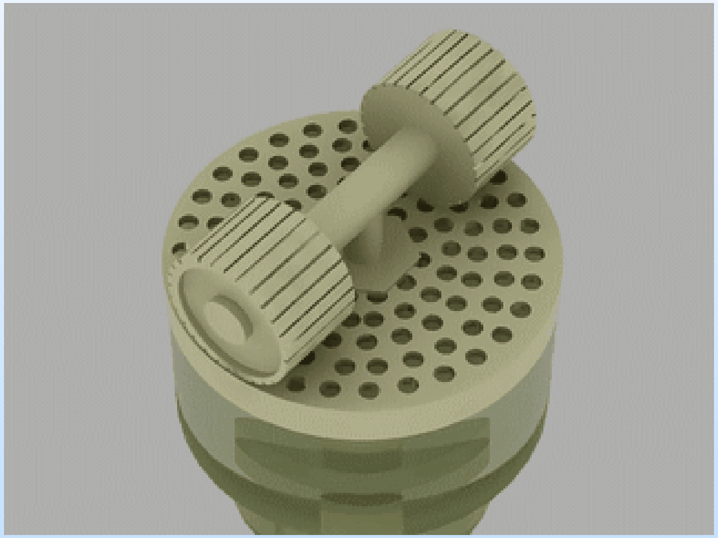
Pellets

Freefall Processing



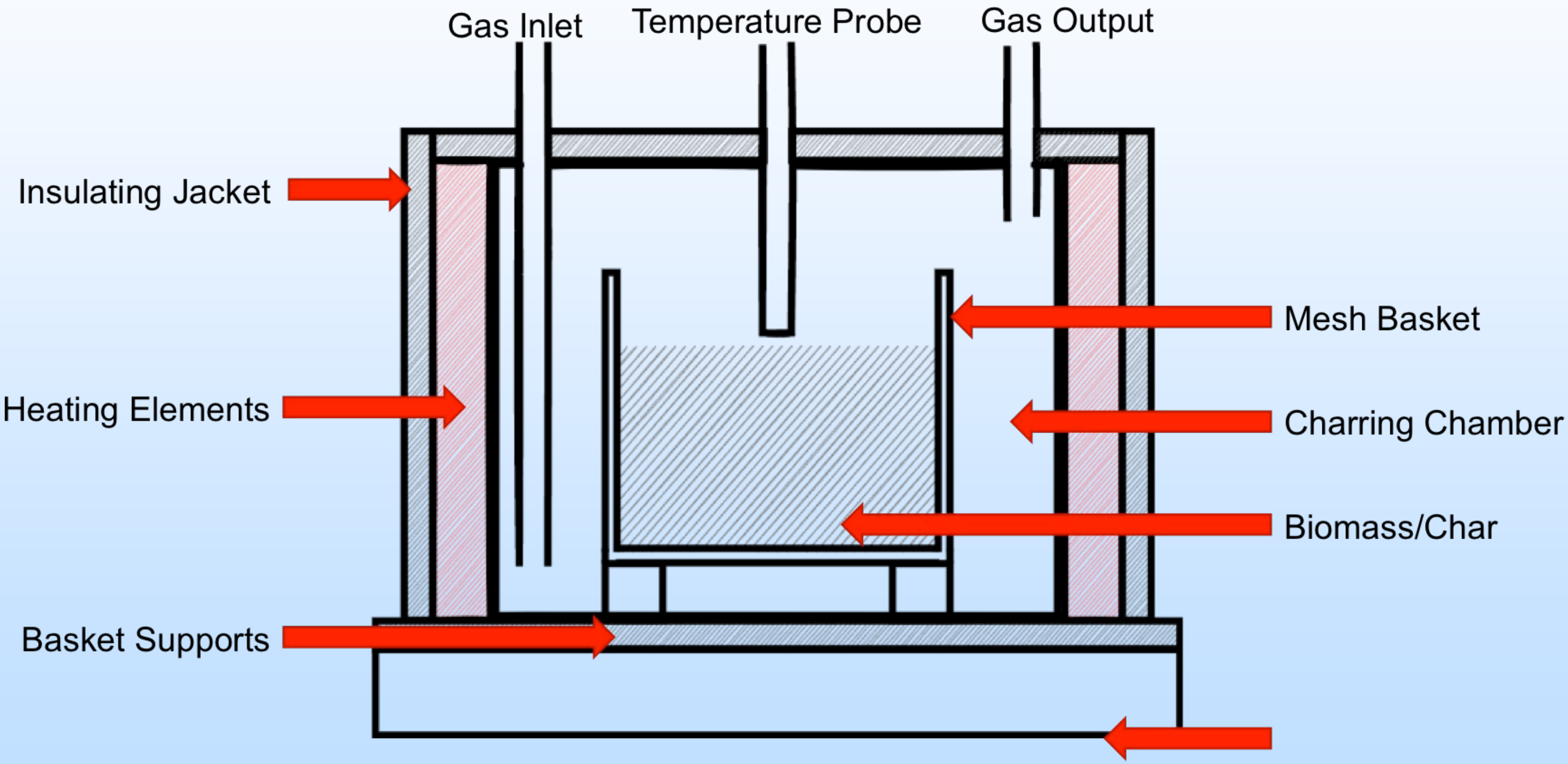
Batch Process (gram scale)

Agricultural Pelletizer (kg scale)



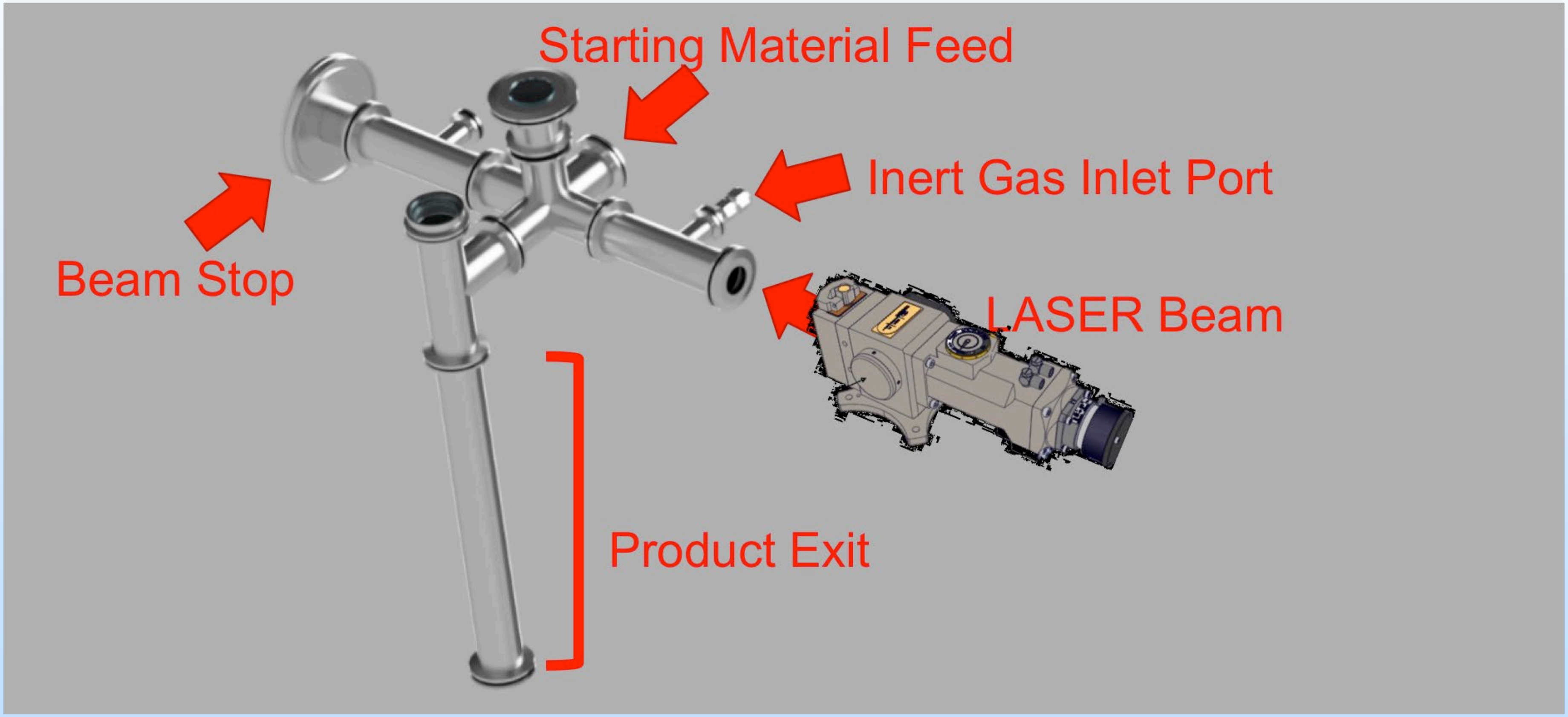
https://www.smallpelletm...

Charring (kg scale)

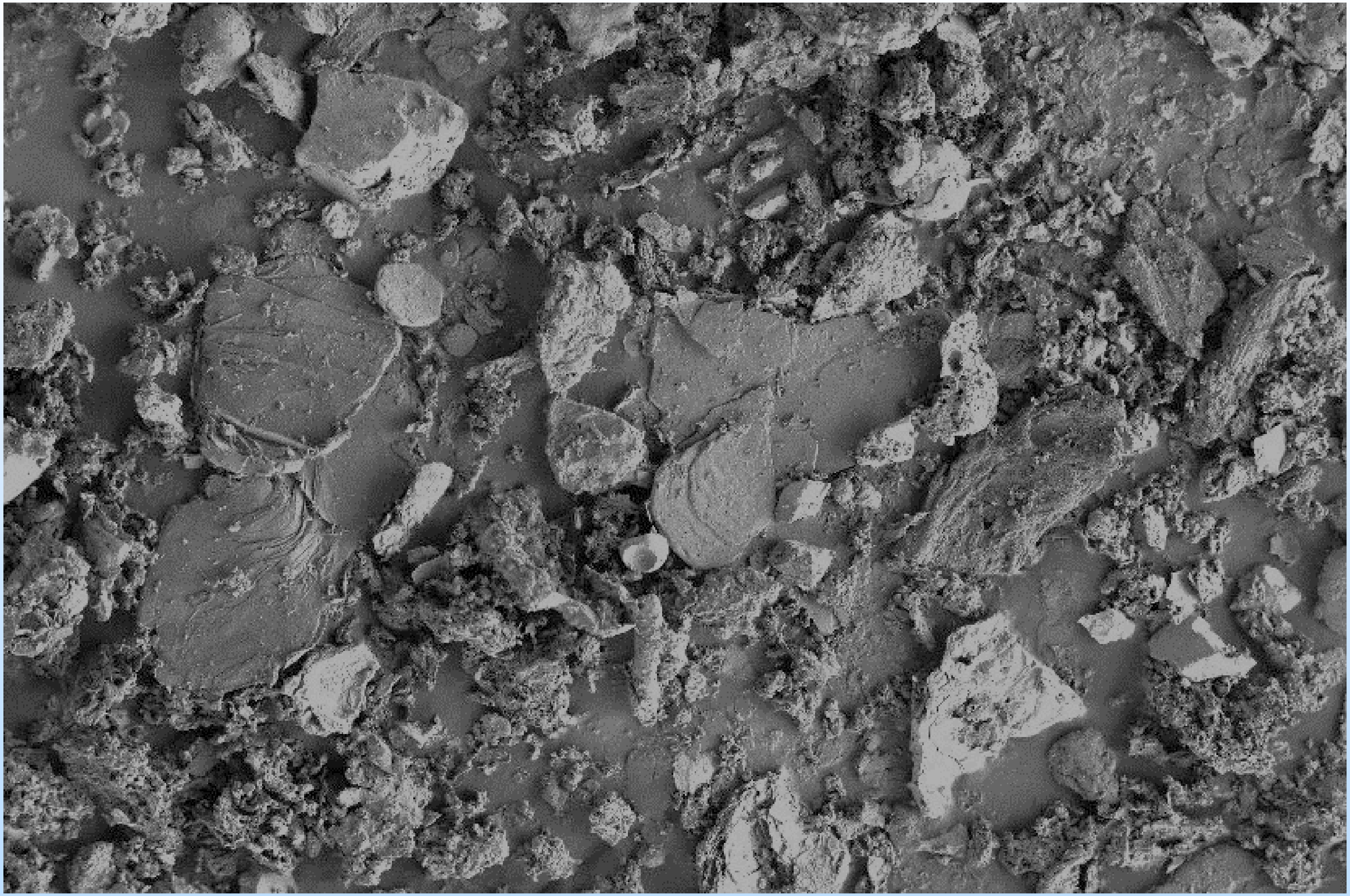


Vibratory Pellet Feed

Laser Pyrolysis Chamber



Continuous Synthesis - Graphite



Plans for future development/ commercialization

- Optimizing composition & processing (mixing, forming, composition & charring)
- Optimize residence time, laser power, wavelength
- Optimize flake & potato size
- Demonstrate continuous production of Li-ion grade graphite at optimal yield
- Demonstrate long cycle life with optimized graphite

Commercialization Plans

Developing collaborative relationships to move to demonstration/pilot scale with success in this project

Summary

- Successfully produced graphite from lignite, but not bituminous or anthracite.
- ND sourced lignite yields high grade ‘potato” or flake graphite
- Li-ion battery performance near but not equal to that of commercial graphite
- Mineral content likely source of low yield of graphite from MS lignite.
- Continuous graphitization demonstrated

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Organization Chart

- The project team consists of the PI and his graduate students working in his laboratory and shared institutional facilities at the George Washington University. The vast majority of the coal samples have been provided by North American Coal as a collaborative contribution.

Project Timeline

Task Name	Assigned Resources	Year 1				Year 2			
		Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Task 1.0 Project Management and Planning	PI								
Task 2.0 - Improve Yield - Achieved									
Milestone 3 (> 0.30 kg/kWh Graphite Yield)	N/A								
Task 3.0 - Improve 1st Cycle Coulombic Efficiency									
Task 3.1 - Optimize "Potato" Size and Porosity	Grad. Student 1								
Milestone 2 (> 88% 1st Cycle Coulombic Eff.)									
Milestone 3 (> 90% 1st Cycle Coulombic Eff.)									
Task 3.2 - Increase Purity	Grad. Student 2								
Milestone 3 (> 90% 1st Cycle Coulombic Eff.)									
Task 4.0 - Transition to Continuous Processing	Grad. Student 3								
Milestone 3 (> 25 g/h Graphite Production)									
Task 5.0 - Demonstrate Long-Term Cycling	Graduate Students								
Milestone 2 (Li-ion cell life > 250 cycles)									
Milestone 3 (Li-ion cell life > 500 cycles)									
Task 6.0 - Economic Modeling	PI								

Note: This project timeline is truncated and accounts for the final two years of the project period of performance. Year 1 = 09/01/2022 – 08/31/2023 and Year 2 = 09/01/2023 – 08/31/2024.