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

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U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

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Project Overview

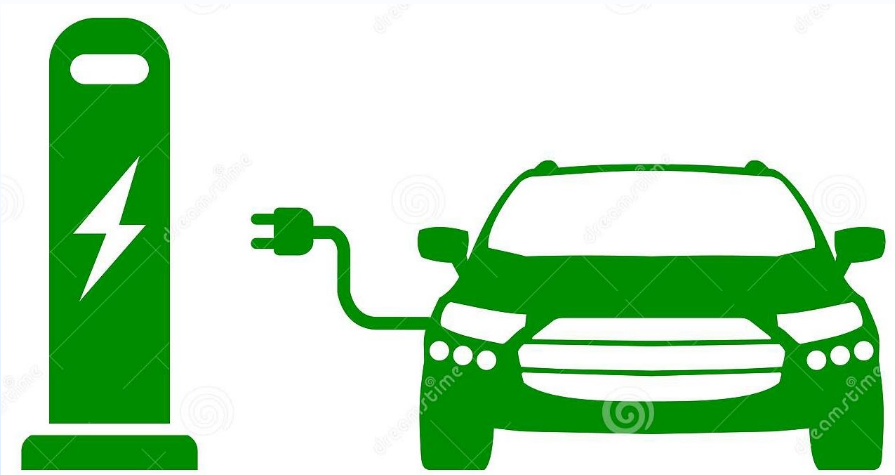
– Funding ($748,720 DOE & $200,310 Cost Share)

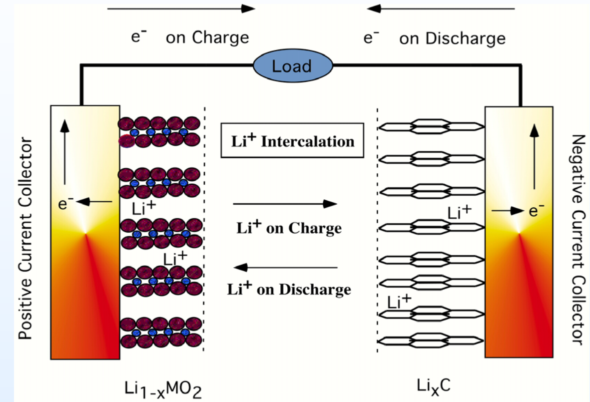
– 9/1/2019 to 8/31/2024

– George Washington University

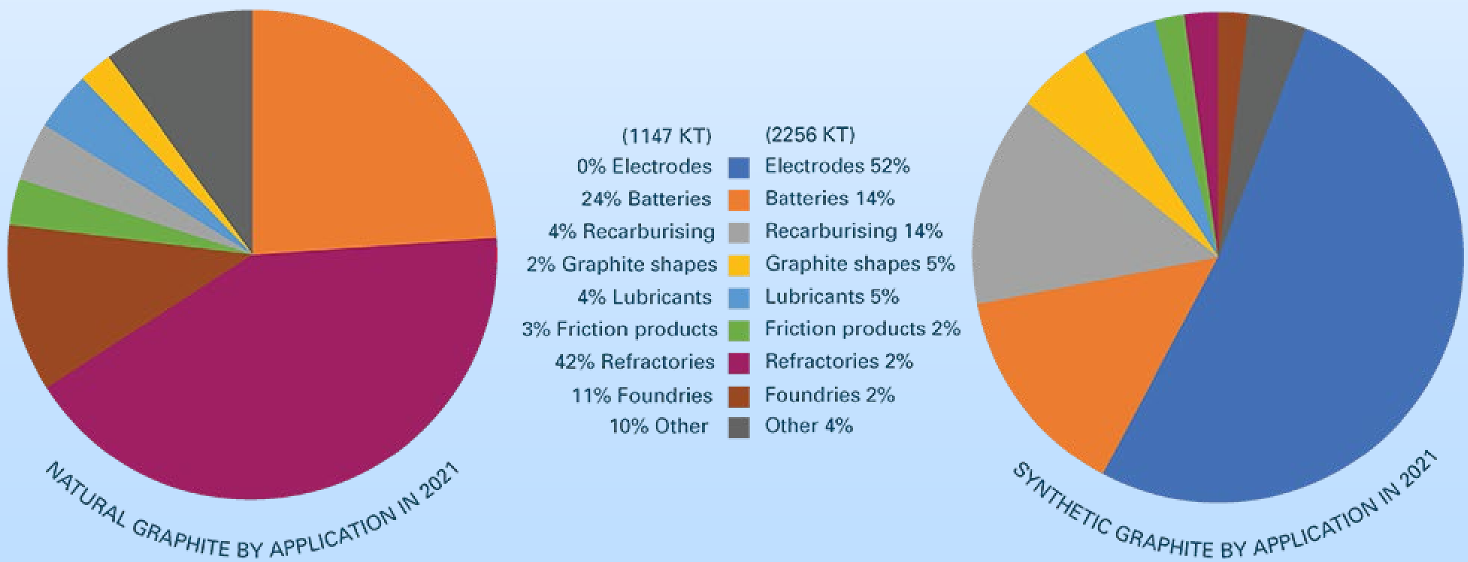
– Overall Project Objective – Develop scalable method to convert low value coal to high value graphite (~ 1000 fold increase in value)

Graphite – Strategic Mineral



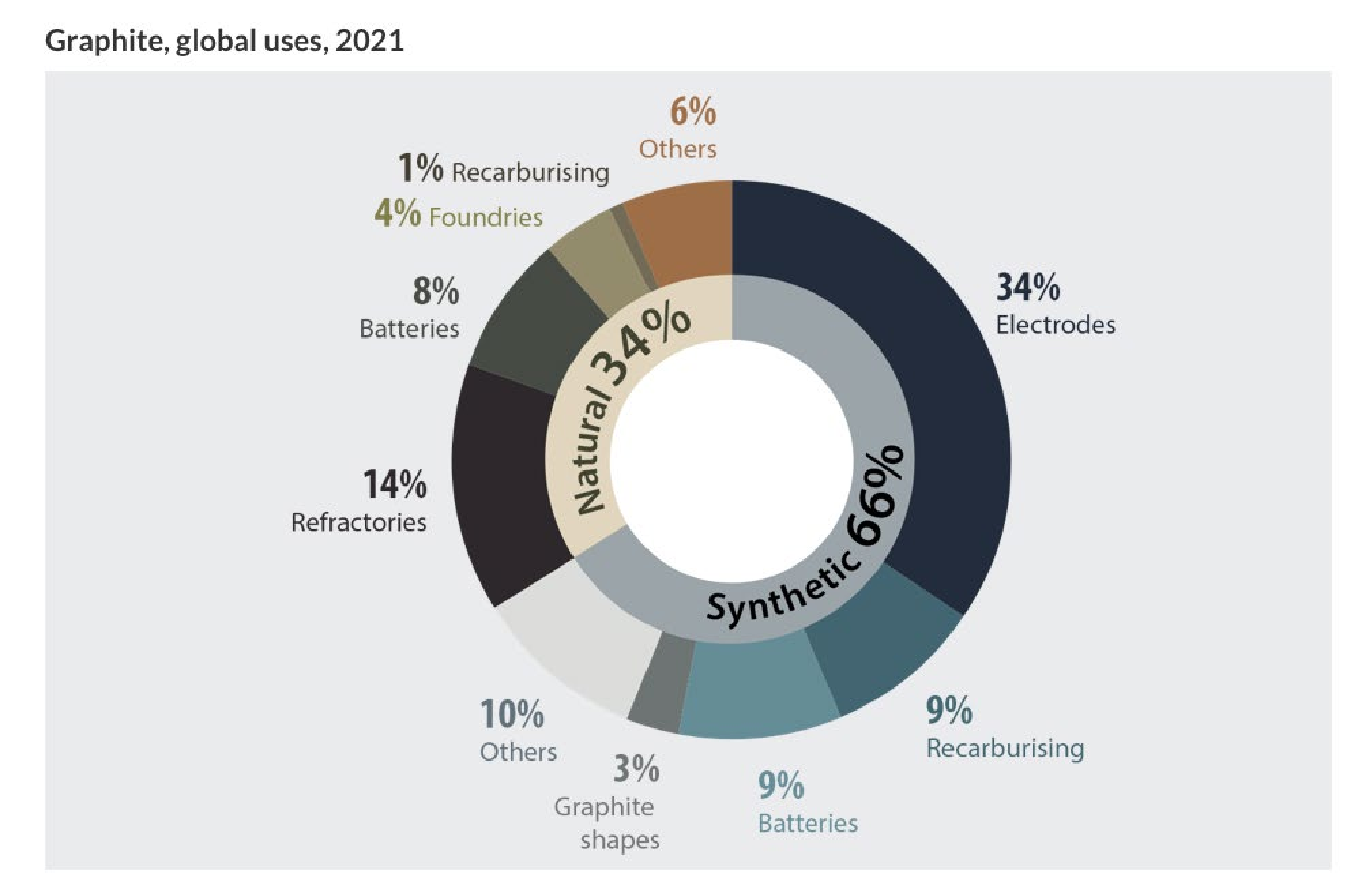


Adapted from: Sivakkumar, S. R.; Nerkar, J. Y.; Pandolfo, A. G., Rate capability of graphite materials as negative electrodes in lithium-ion capacitors. Electrochimica Acta 55, (9), 3330-3335.



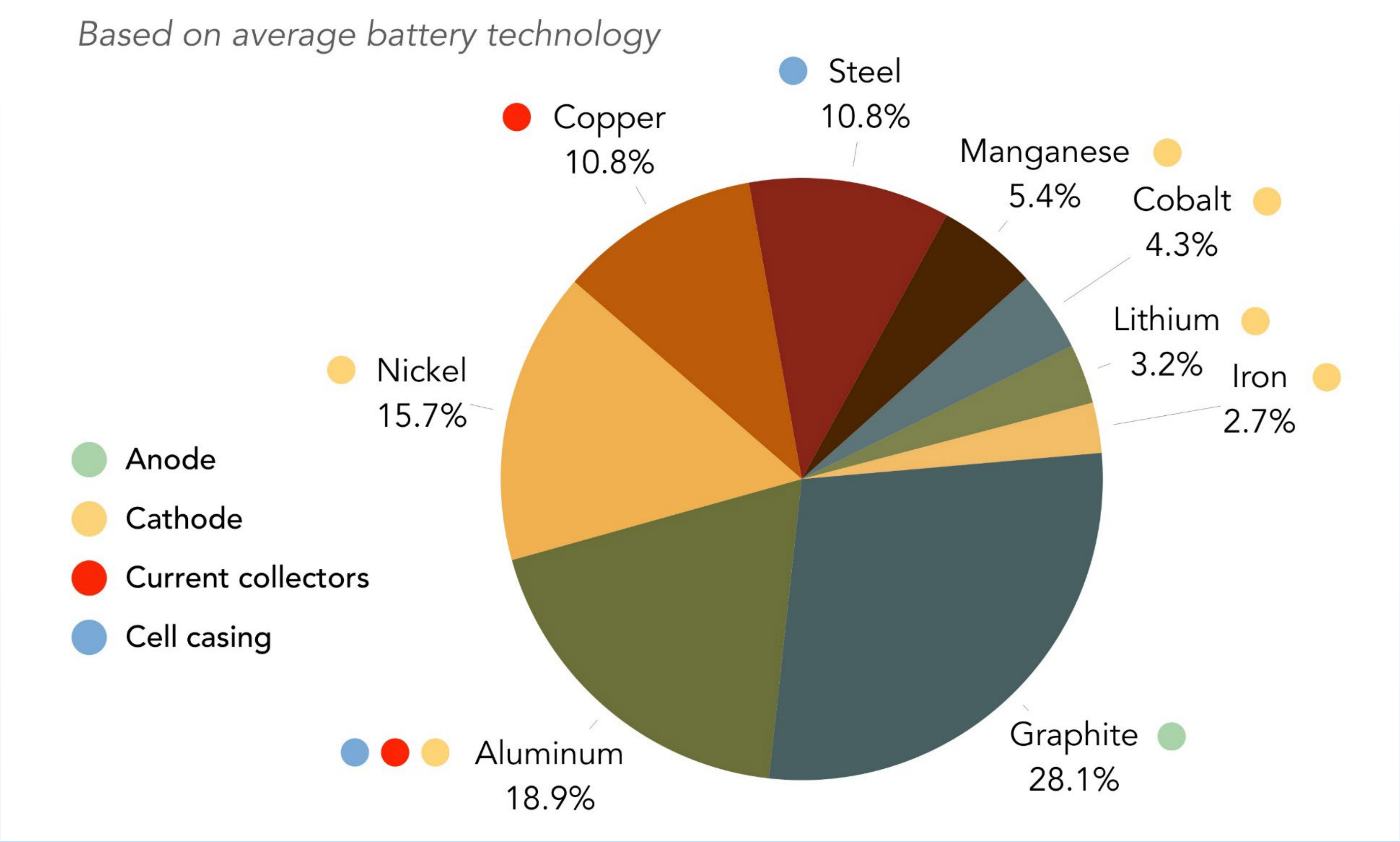
source: Wood MacKenzie, 2022

Graphite Market



~ 3.5 million tons/yr

Graphite – Li-ion Batteries

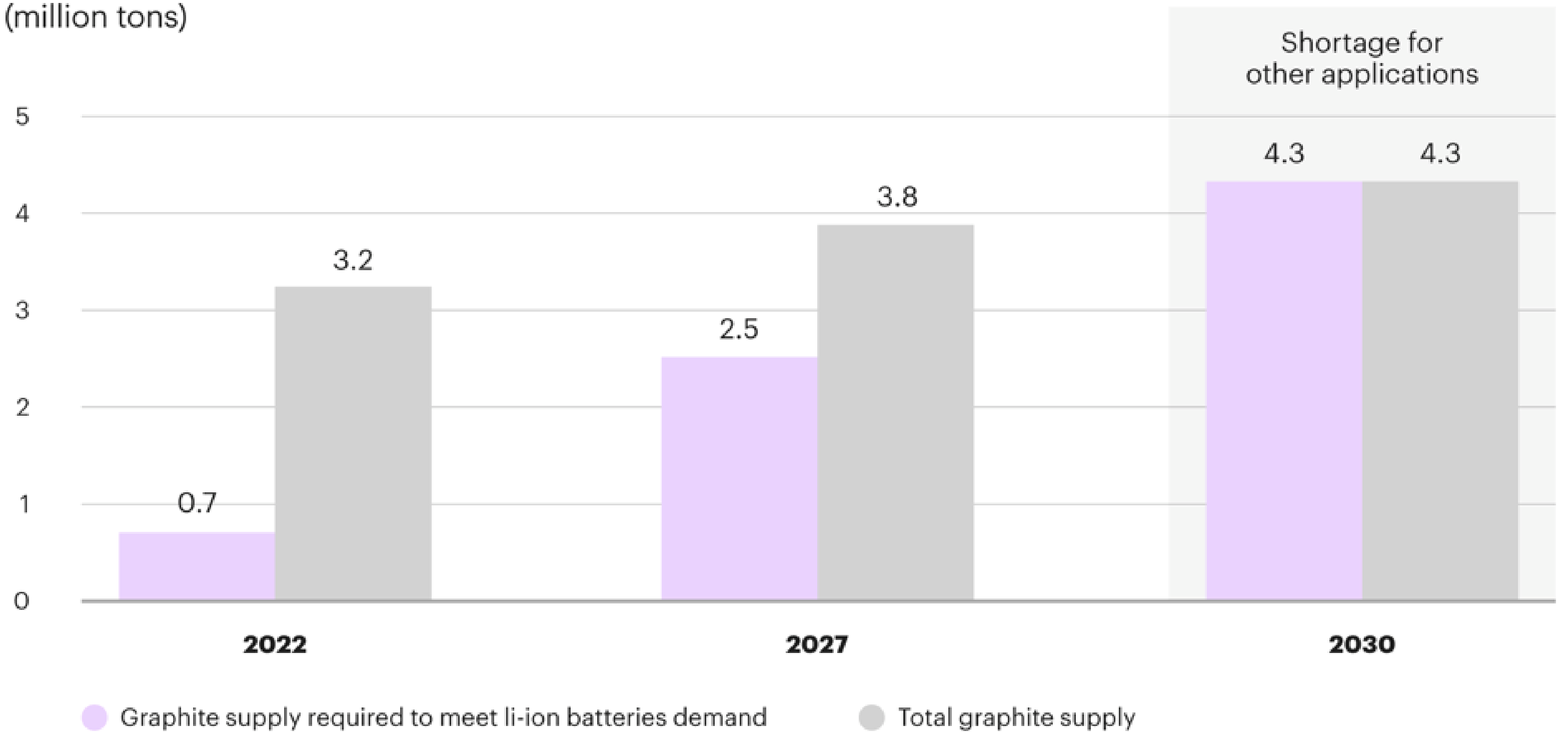


https://www-forbes-com.cdn.ampproject.org/c/s/www.forbes.com/sites/jimvinoski/2022/05/31/unless-we-get-serious-about-domestic-mining-americas-electrified-future-is-impossible/amp/

Graphite – Shortage Coming

Figure 1
EV demand will absorb all graphite output at current rate

Total graphite (natural + synthetic) demand–supply forecast
(million tons)

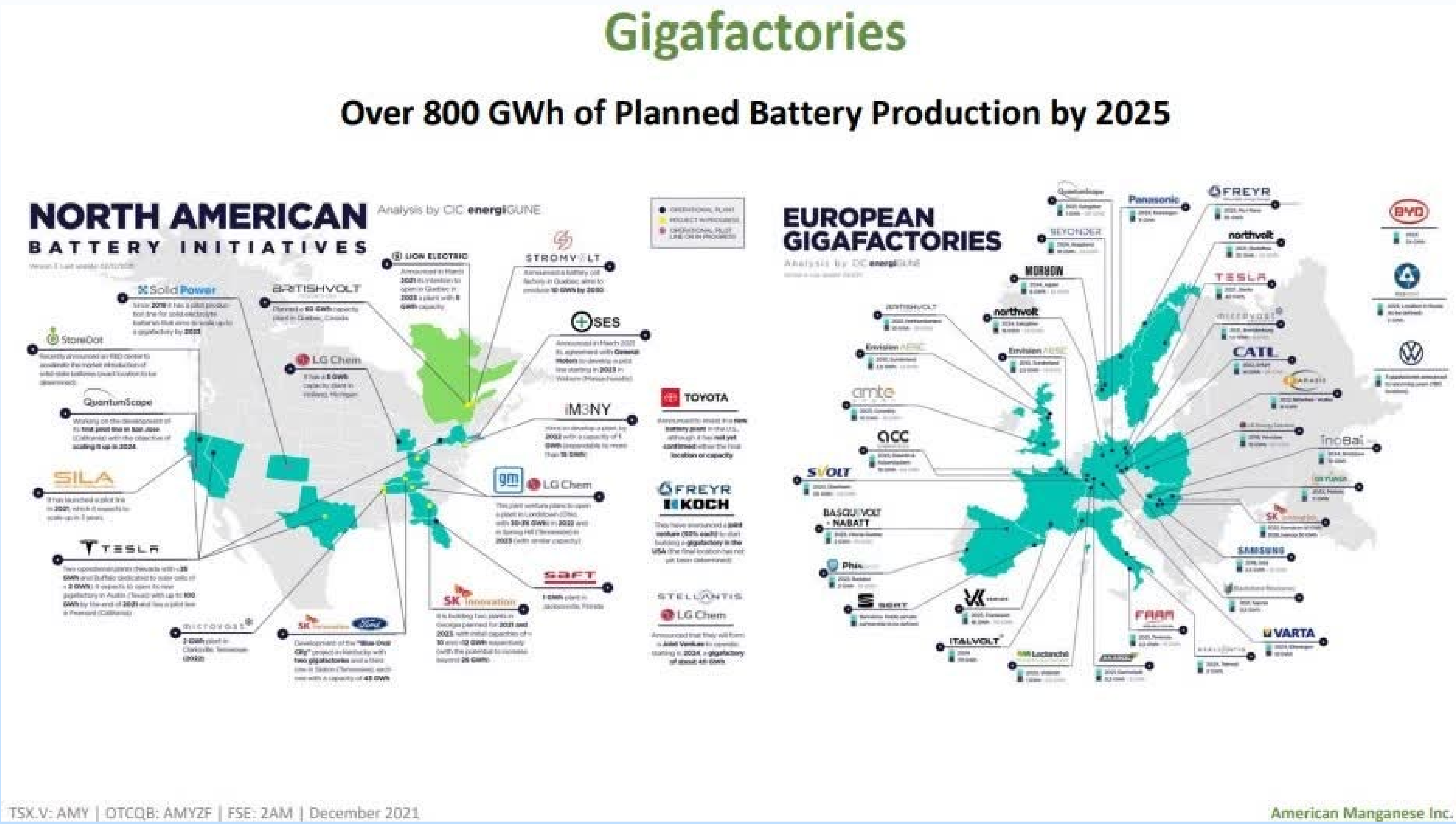


Sources: desktop research, expert interviews, supply from Allied Market Research, demand information from https://nmg.com/wp-content/uploads/2021/06/NMG-Graphite-101.pdf; Kearney analysis

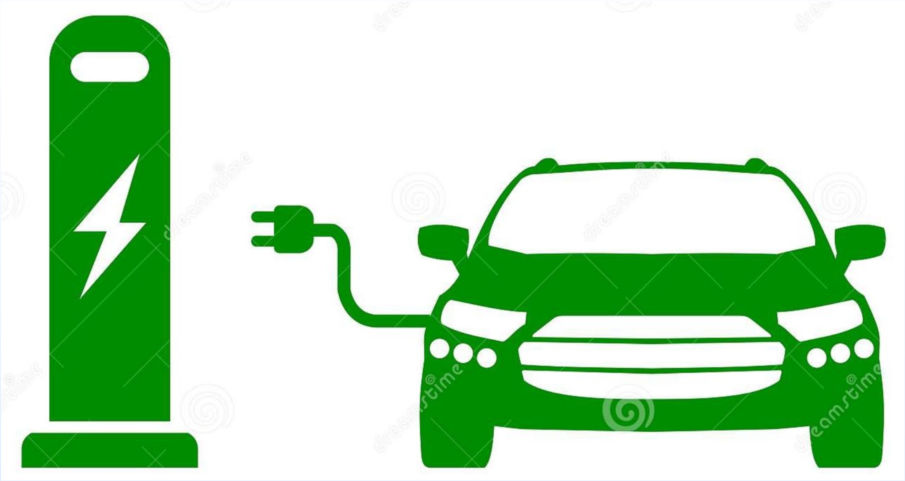
1.2 million ton shortfall by 2030

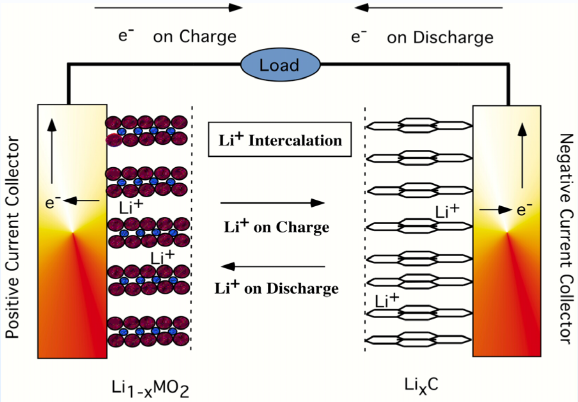
Tesla Li-ion Battery Gigafactory

Gigafactory Proliferation



Graphite – Market Driven by Li-ion





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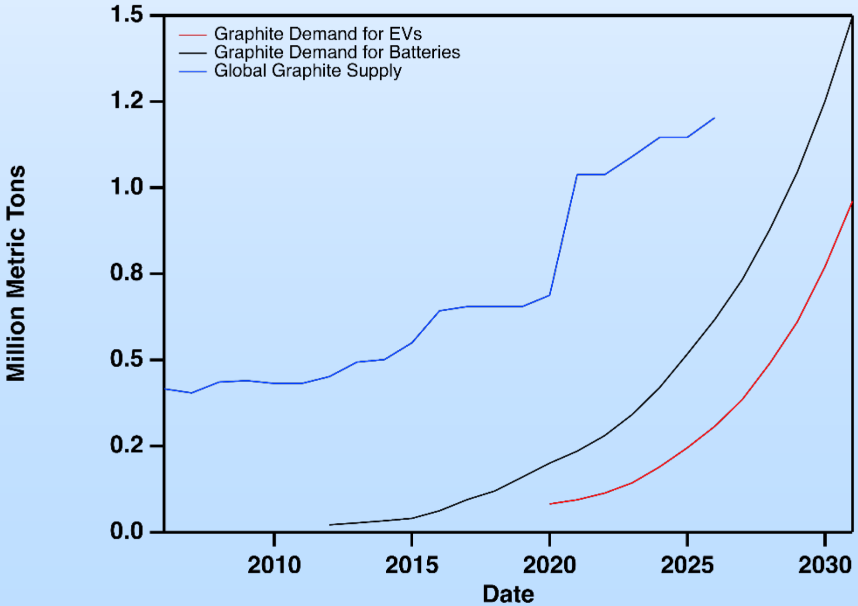
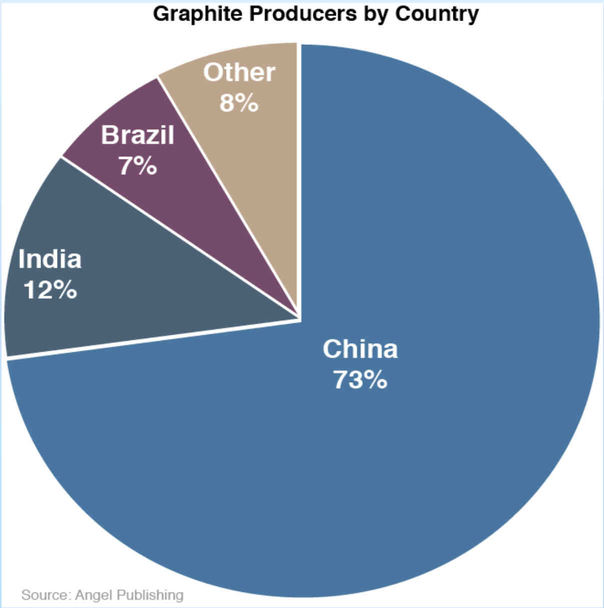
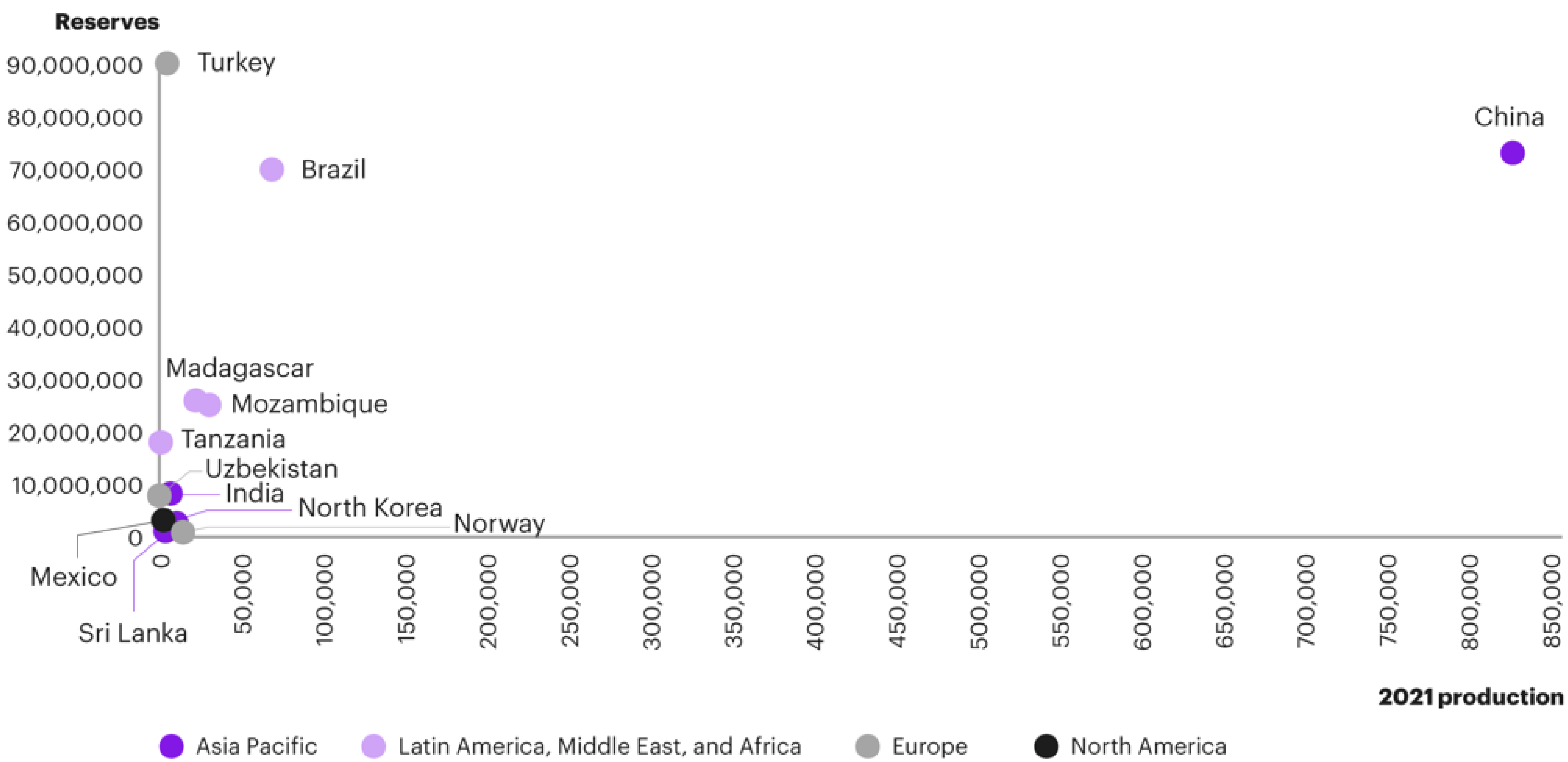


https://www.statista.com/statistics/719592/global-distribution-of-graphite-consumption-by-end-use/



Graphite Production

There is extreme reliance on China, which provides about three-quarters of the world's supply of both natural and synthetic graphite



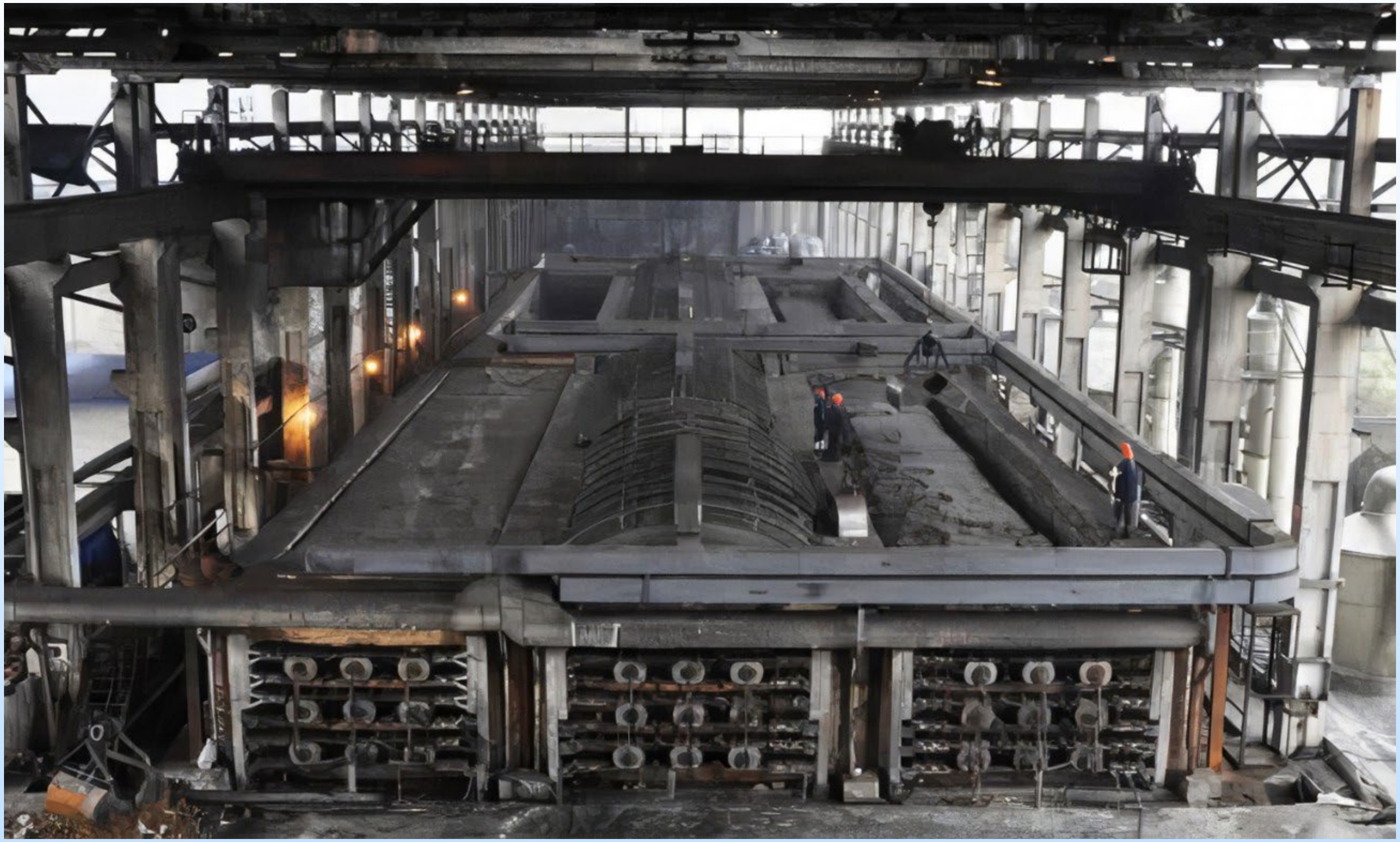
Sources: https://pubs.usgs.gov/periodicals/mcs2022/mcs2022-graphite.pdf; Kearney analysis

GRAPHITE: EXISTING SUPPLY & PRODUCTION

Properties Needed for Battery Grade Graphite

- Purity (>99.95%C)
- Appropriate Crystallite Size (<10μm)
- High Crystallinity
- Appropriate Shape (Spherical, ~ 20 μm)
- Low Surface Area (< 4 m^2/g)

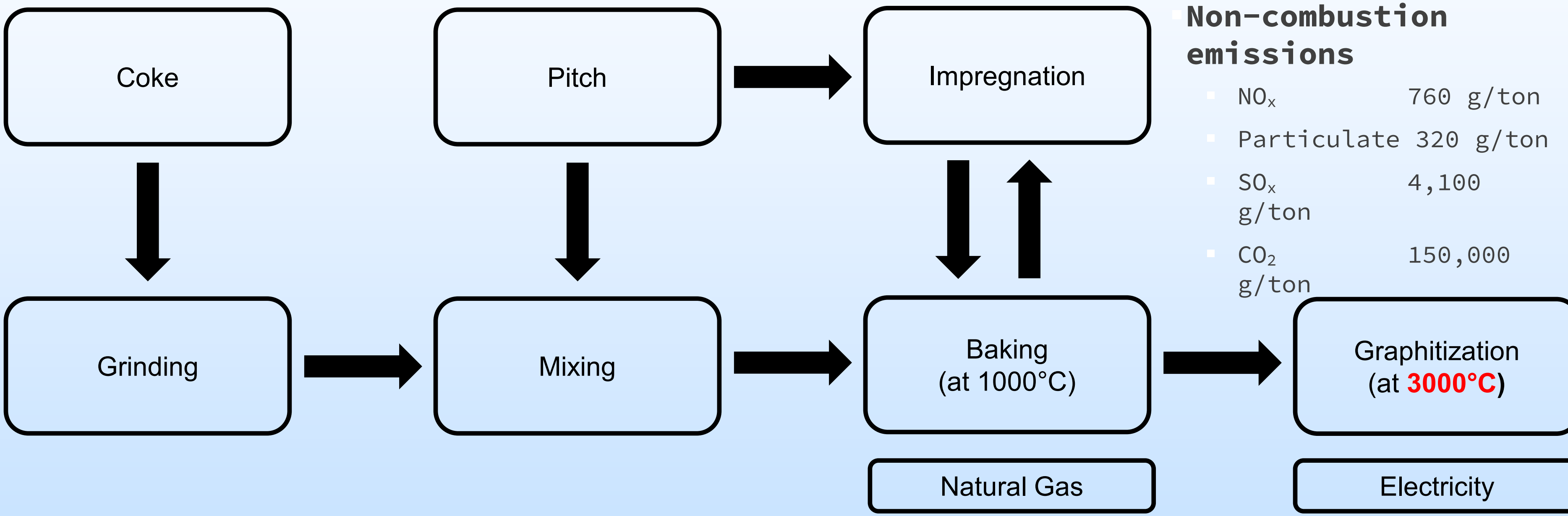
Graphite Supply - Artificial



https://th.bing.com/th/id/R.6006b425cbeb07069549e83bffdd5f61?rik=sjpAk5o4OdNsIg&pid=ImgRaw&r=0&sres=1&sresct=1

Graphite Supply - Artificial

Fossil Fuel Based Precursors



Non-combustion emissions

- NO_x 760 g/ton
- Particulate 320 g/ton
- SO_x 4,100 g/ton
- CO_2 150,000 g/ton

Weeks of Heating

Material and Energy Flow in the Production of Cathode and Anode Materials for Lithium Ion Batteries (ANL ESD 14/10REV),J. B. Dunn, C. James, L. Gaines, K. Gallagher, Q, Dai, and J. C. Kelly
Argonne National Laboratory

Graphite Supply - Mining

https://geology.com/minerals/graphite.shtml

Graphite Supply - Mining

https://www.washingtonpost.com/graphics/business/batteries/graphite-mining-pollution-in-china/

Graphite Supply - Mining

http://www.indmin.com/events/download.ashx/document/speaker/8431/a0ID000000X0j4uMAB/Presentation

Graphite Supply - Mining

http://www.china.org.cn/environment/2014-04/28/content_32224052.htm

Graphite Supply – Mining Purification

- Graphite Ore
  - <20%C
- Crushing and Grinding
  - 30%C
- Froth Flocculation
  - 50%C
- Acid Leaching
  - 60%C
- Alkaline Roasting
  - 80%C
- Beneficiation
  - 90%C
- HF Acid Leaching
  - 95%C
- Starting Graphite Material
  - 95%C Flake Concentrate

Micronization & Spheroidization

95%C Lg Flake → Micronization → Spheroid Formation → Chemical Purification → 99.95%C Spherical Graphite

Chemical Purification

- HF
- H_2SO_4

Graphite Brittle – 70% loss

High Crystallinity

- Re-Graphitization and defect repair at high temperature
- Coating to Lower Surface Area

https://jjrorwxhinrnlm5p-static.micyjz.com/cloud/liBpmKrnlpSRnjqponjrip/Super-large-graphitization-furnace-logo.jpg

DOMESTIC GRAPHITE MINING

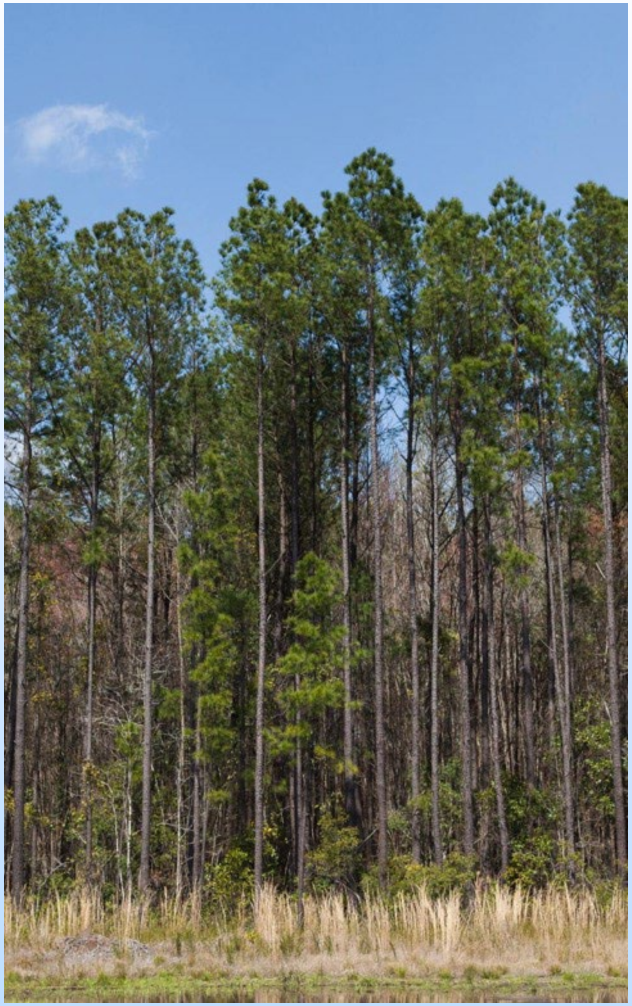
North American Graphite Mining

- Last Mined in US in 1990
- 100% imported
- Some mines coming
  - Graphite One (Alaska) – 60,000 tons/y
  - COOSA (Alabama) – 8,050 tons/y
- Canada (Northern Graphite)

GRAPHITE SYNTHESIS

US Carbon Resources

Agriculture

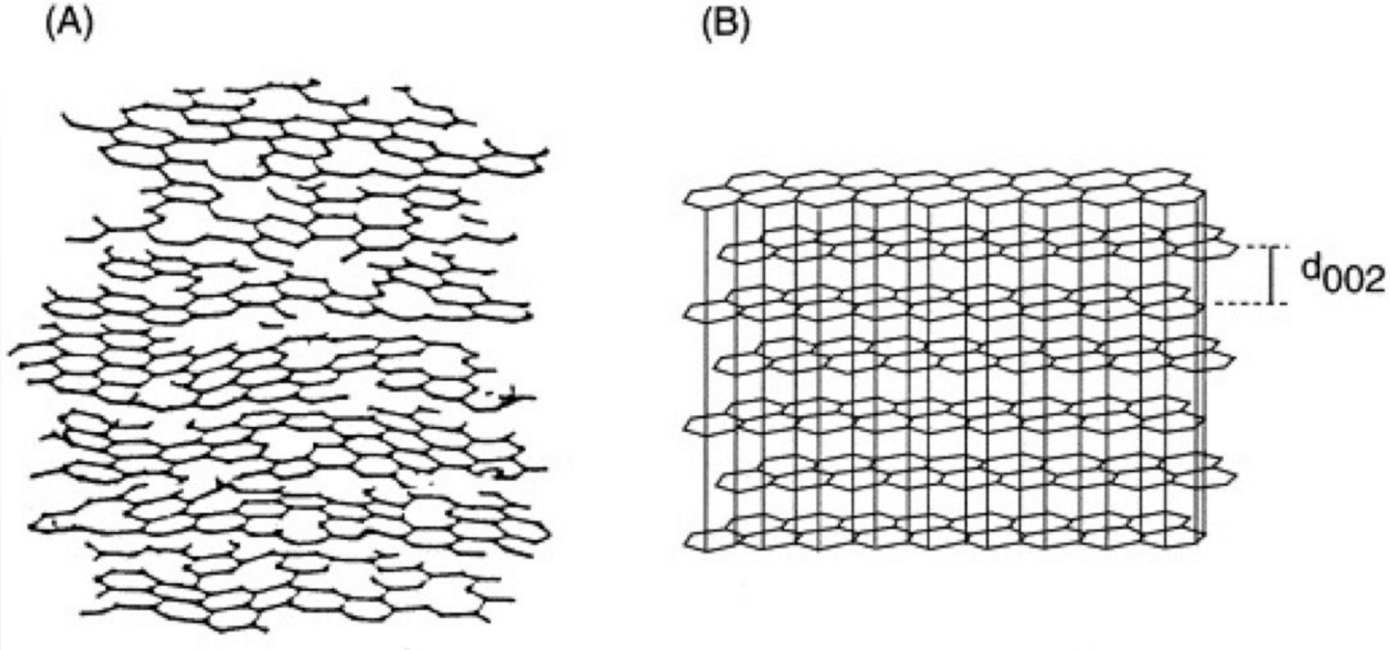


Forestry

US Carbon Resources

Coal

Hard Carbons & Graphite



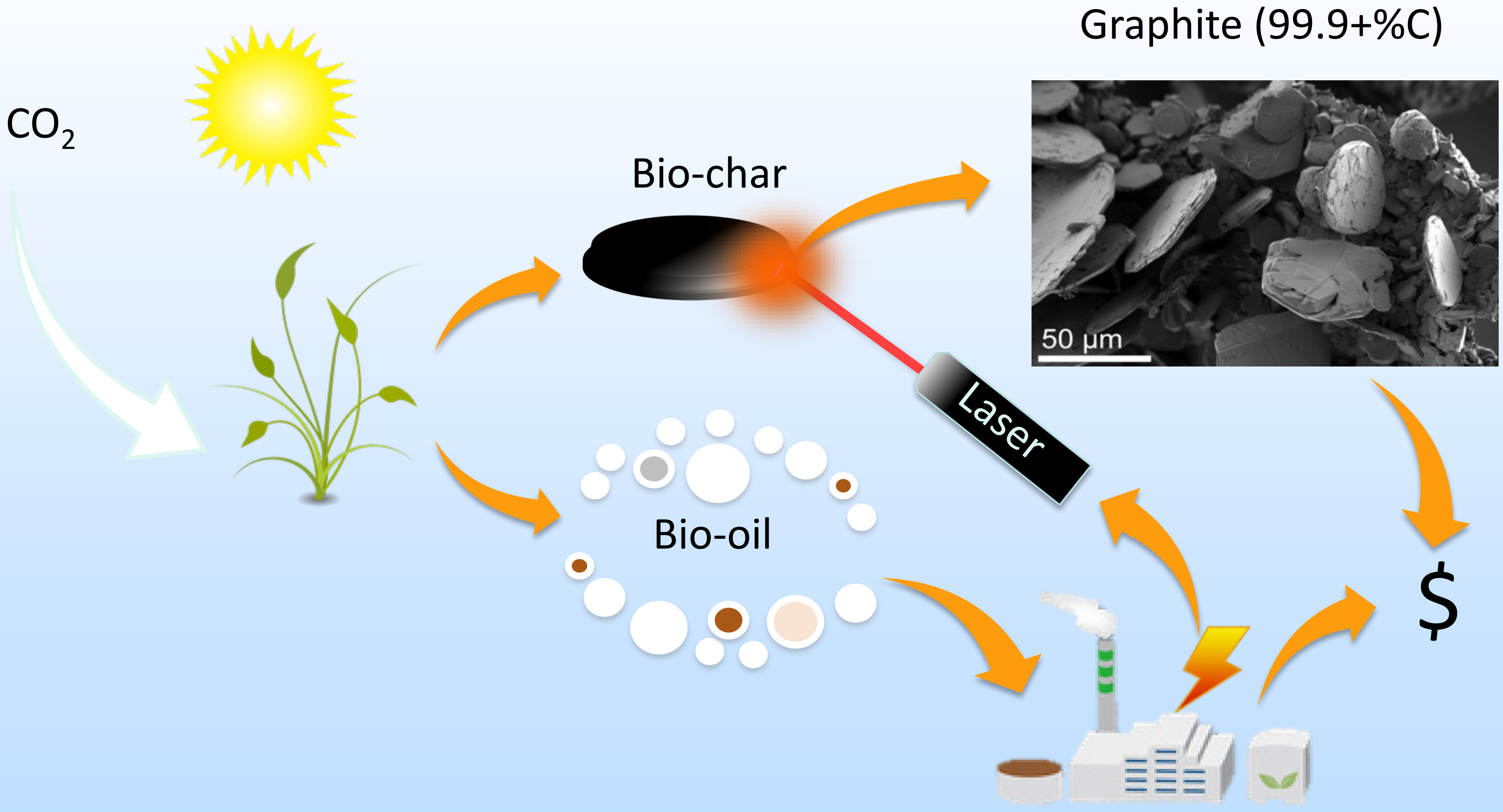
$D_{002} \geq 3.4$ Å

$D_{002} = 3.354$ Å

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

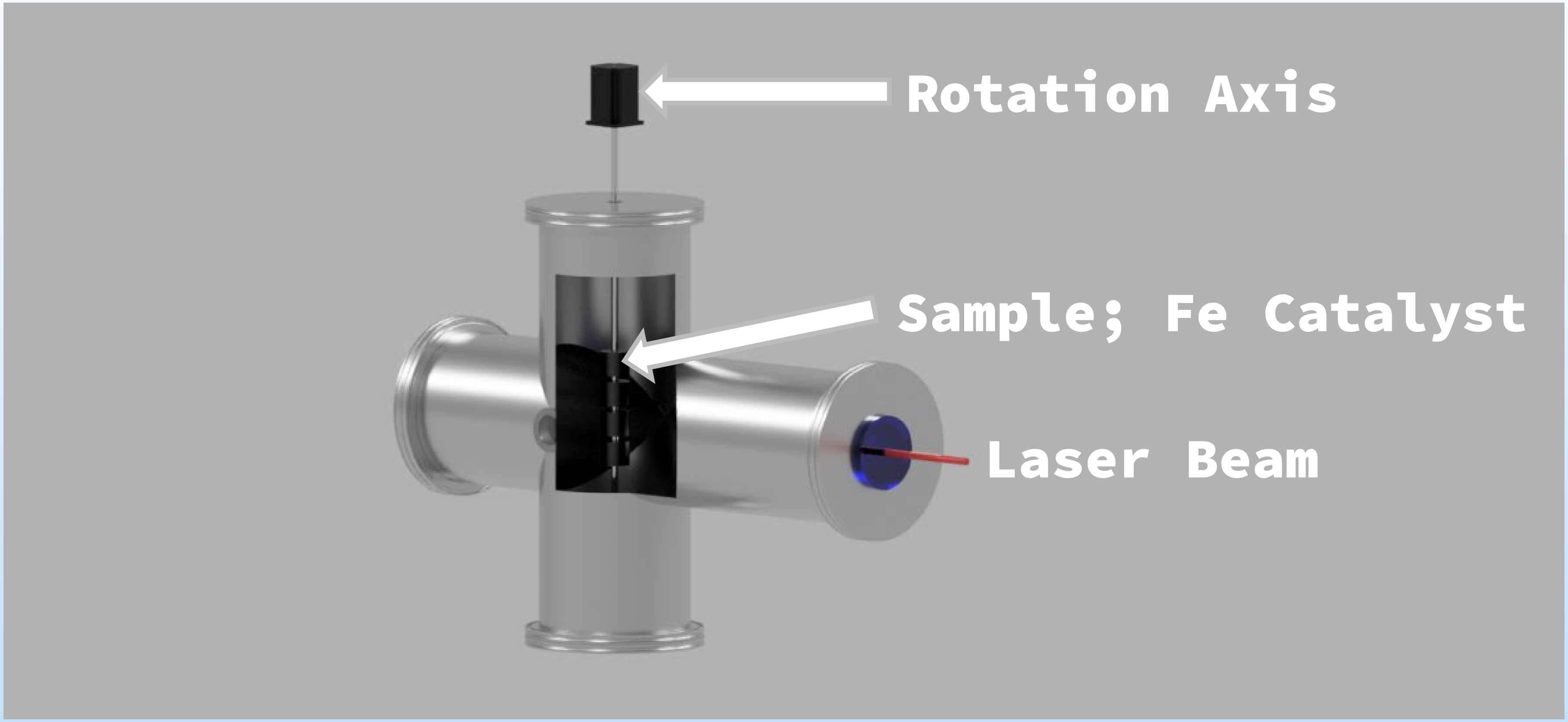
Bijan K. Miremad and Konrad Colbow, Sensors and Actuators B: Chemical,46, 1,1998,30-34

Graphite and Bio-oil Co-production

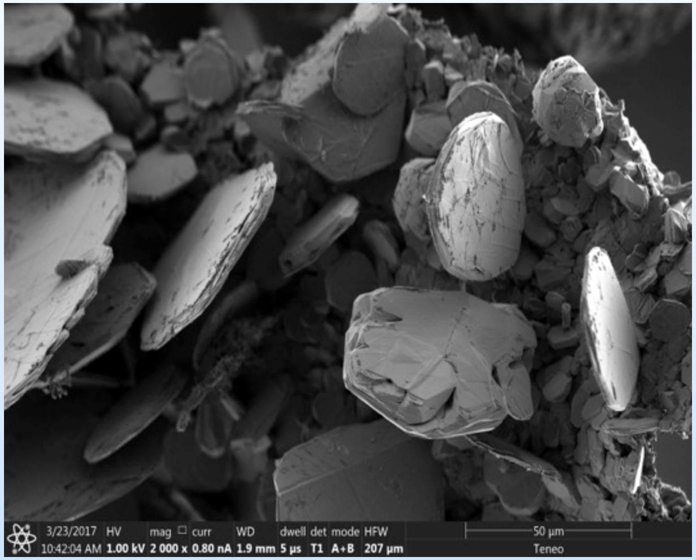


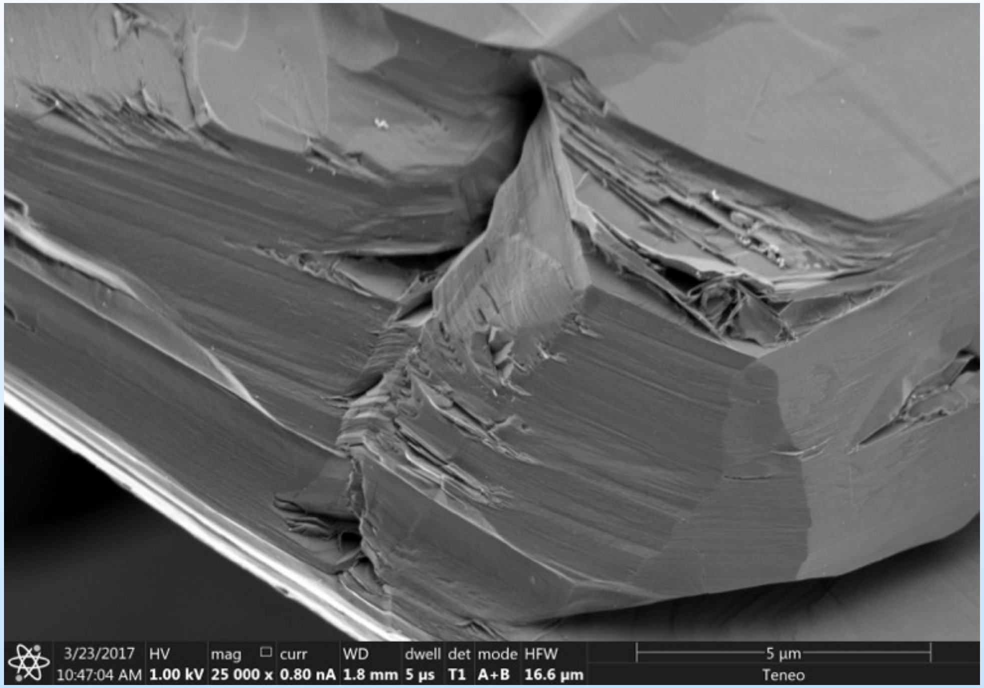
Pellet production

Graphite Laser Synthesis



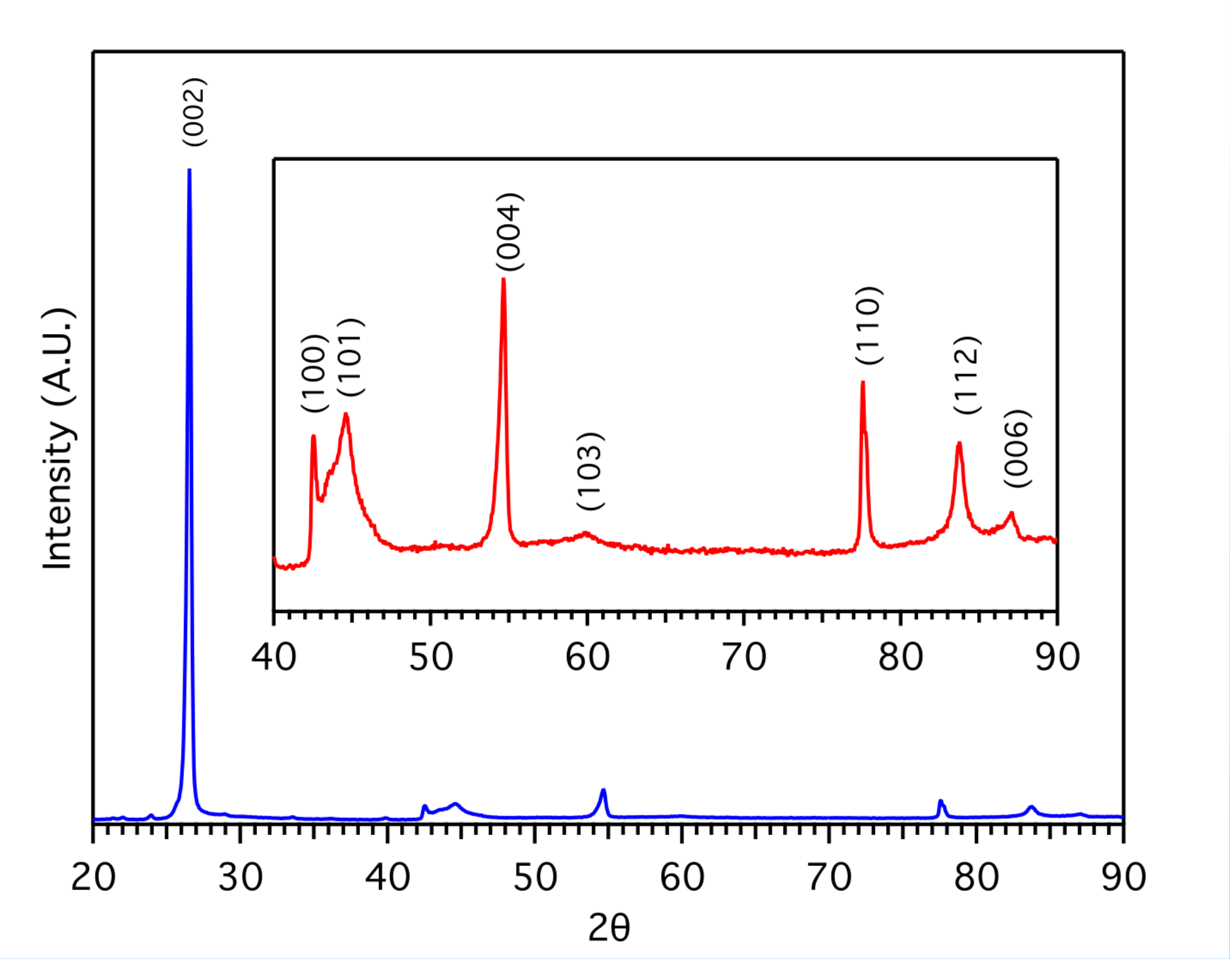
Flake Graphite from Biomass





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

Flake Graphite from Biomass



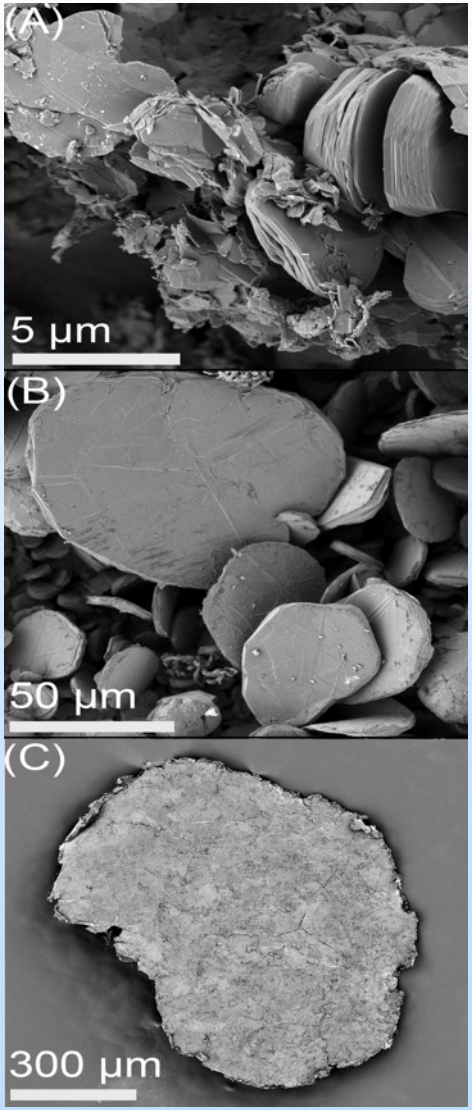
D_{002} = 3.3546(5) Å

I_D/I_G Ratio < 0.04

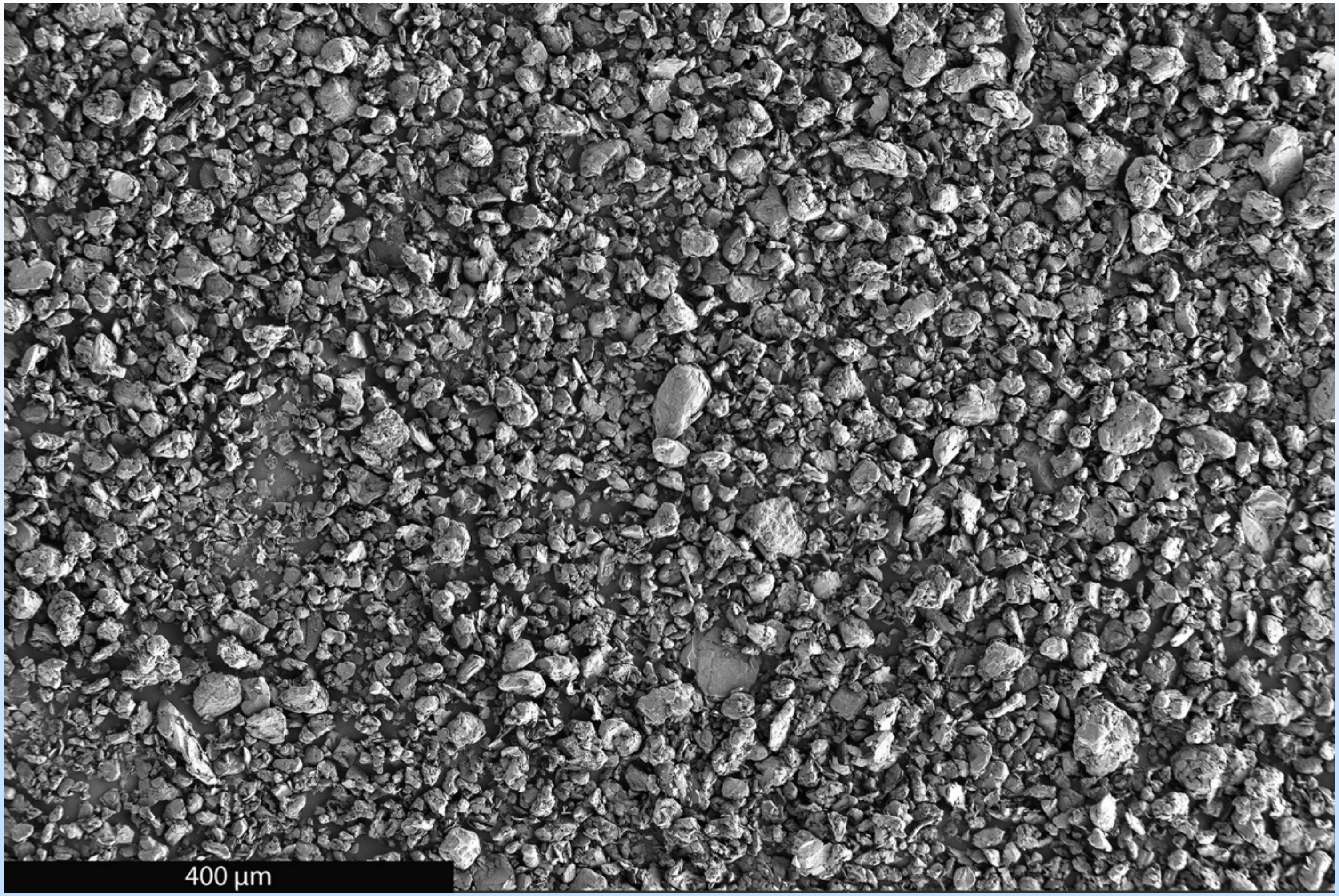
> 99.95% C

Flake Graphite from Biomass

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

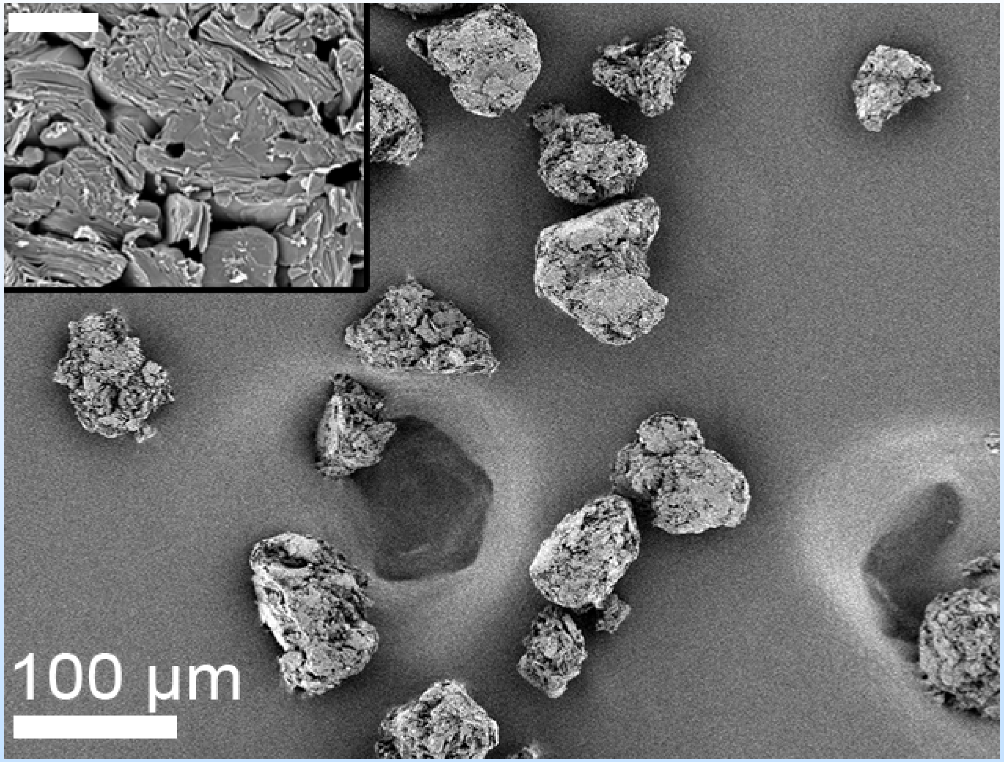


Commercial Li-ion Graphite



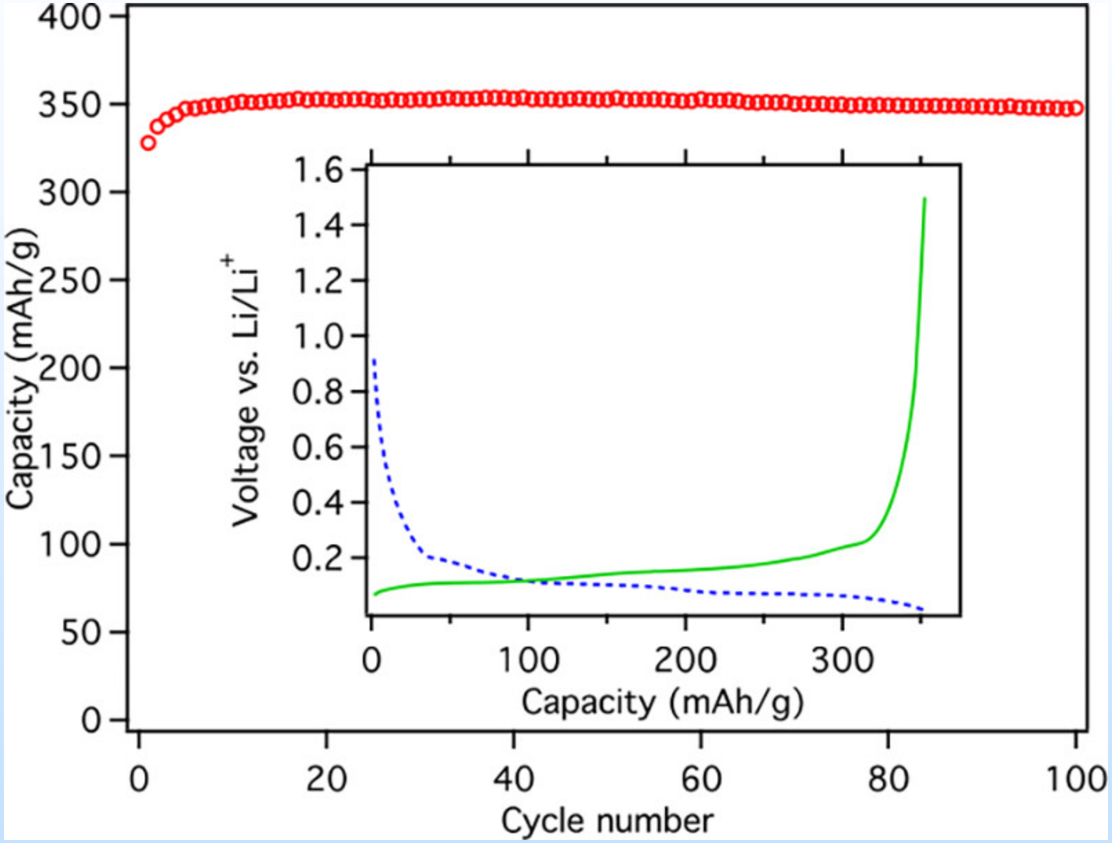
Hitachi MagE3 Shaped (milled) Li-ion Graphite

Spherical Graphite from Biomass



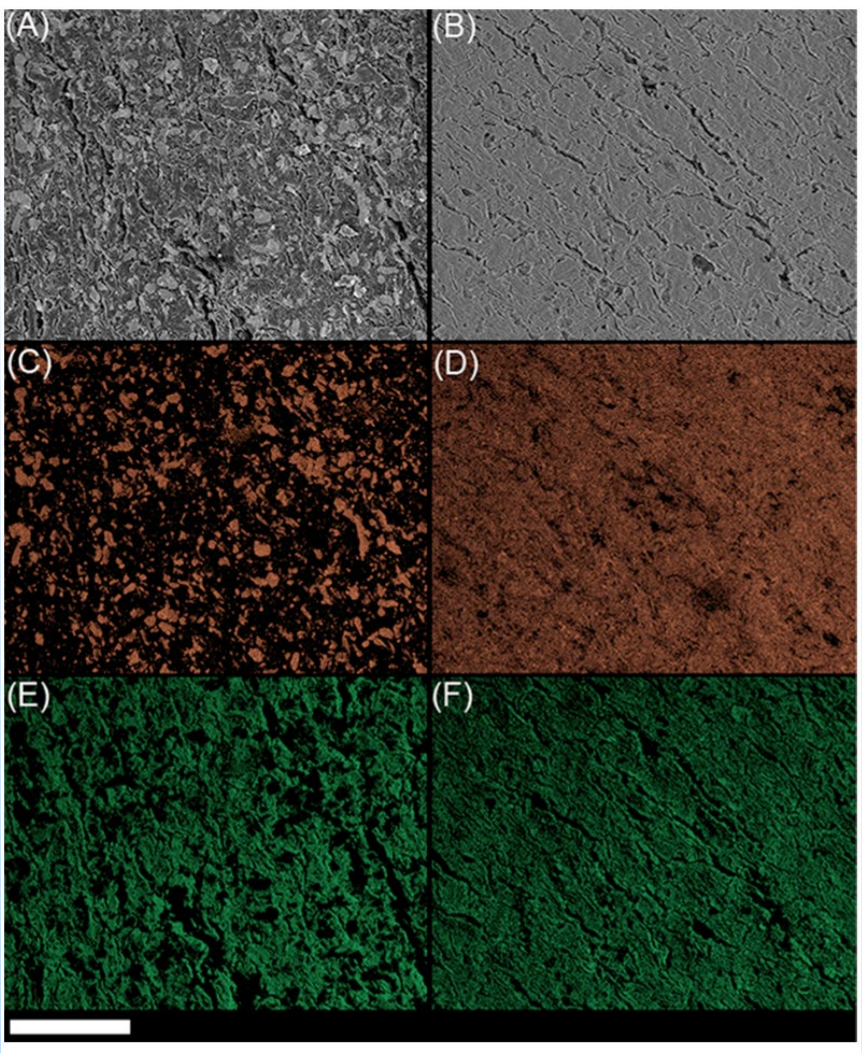
~ 10 m^2/g

Cycling Performance



84% First Cycle Coulombic Efficiency (CE)

SEM – Fe & C



SEM

EDX (Fe)

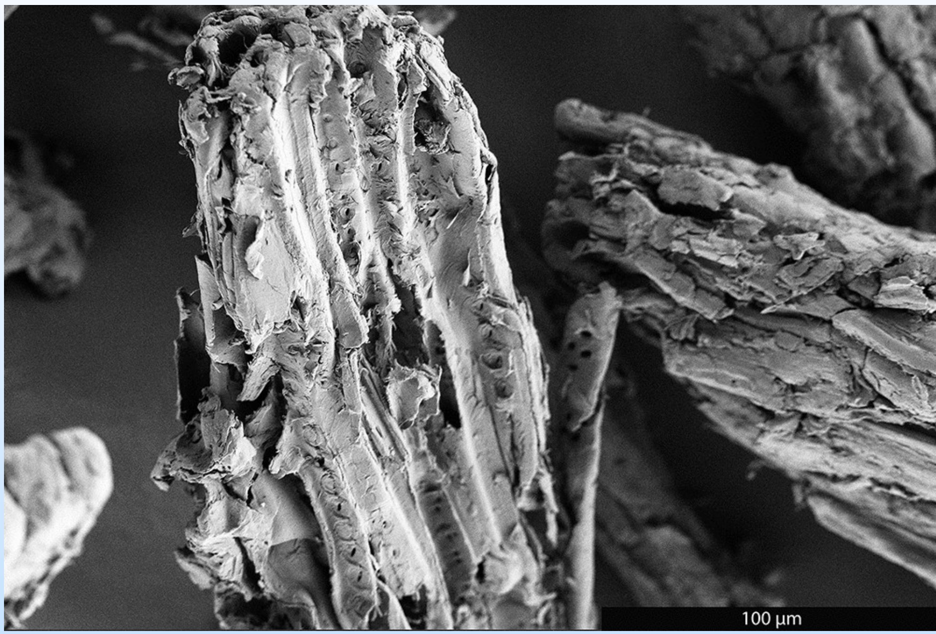
EDX (C)

500 µm

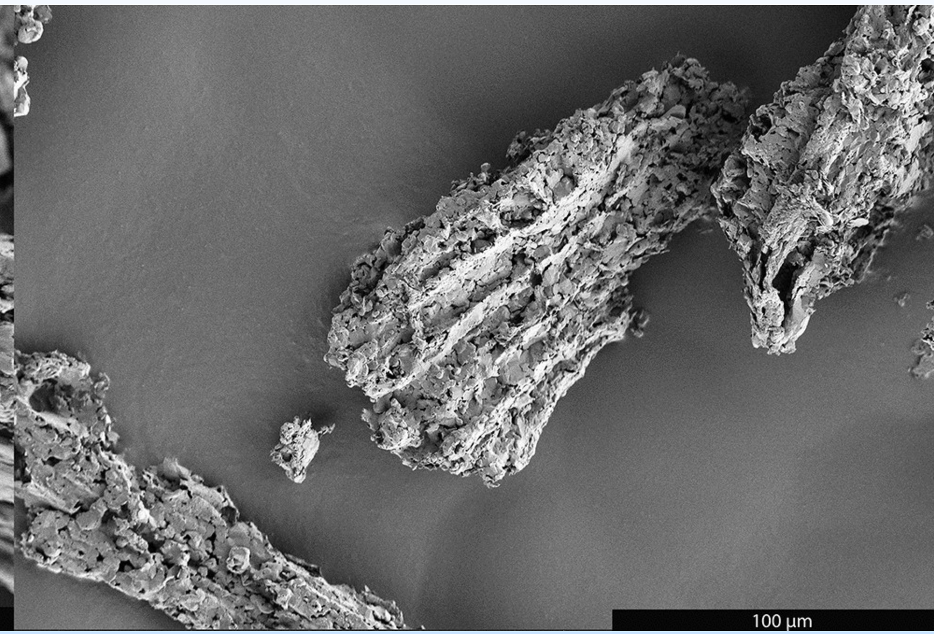
before after

https://doi.org/10.1038/s41598-022-11853-x

Wood Before and After Graphitization



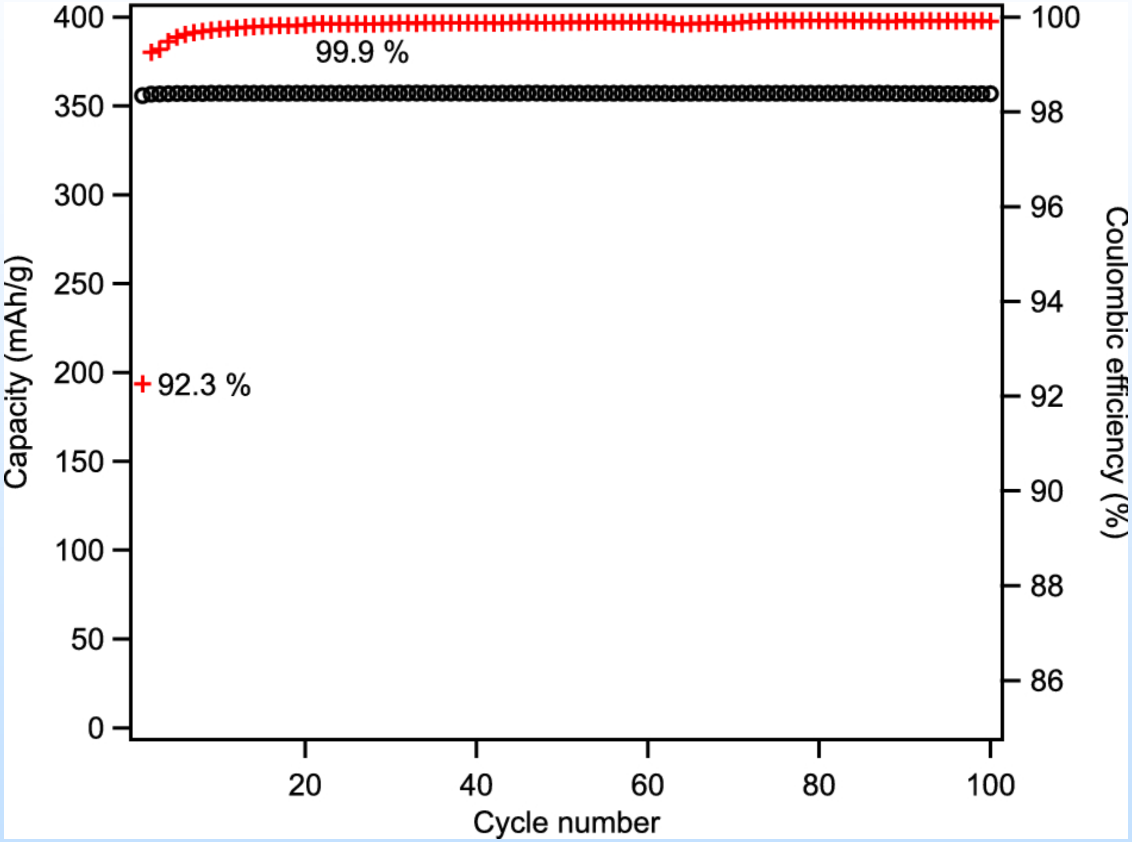
Wood Char



Graphite

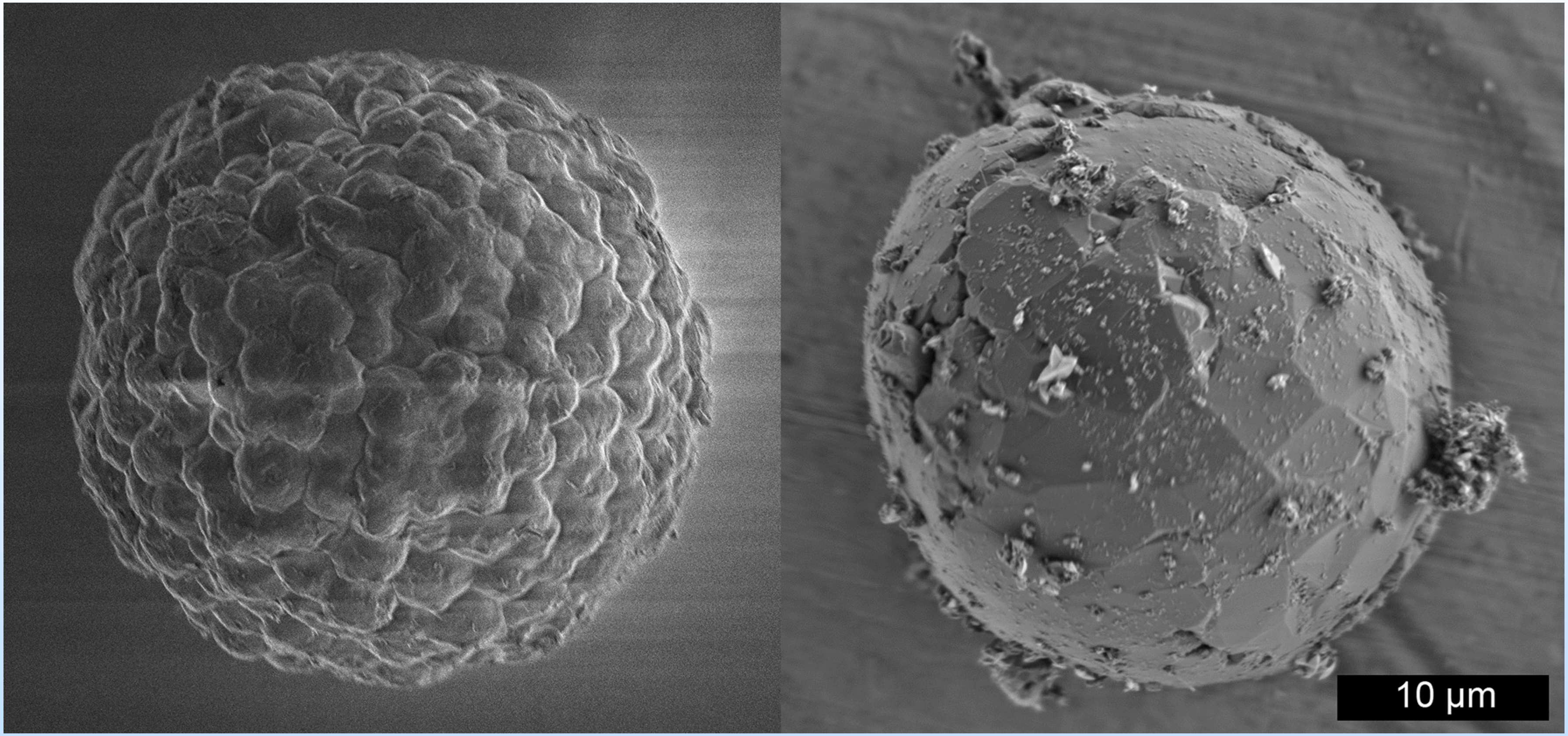
https://doi.org/10.1038/s41598-022-11853-x

Cycling Performance



https://doi.org/10.1038/s41598-022-11853-x

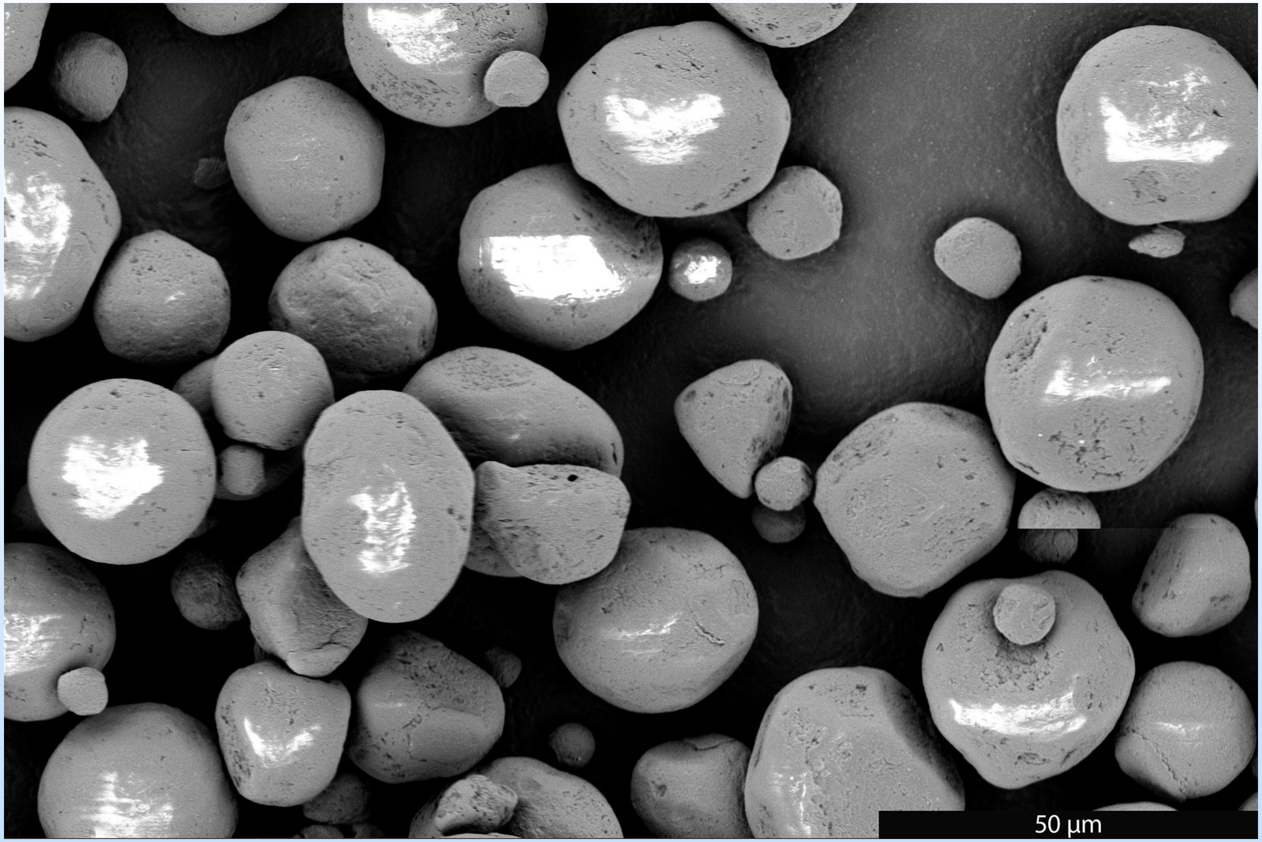
Graphite from Spherical Algae



https://doi.org/10.1038/s41598-022-11853-x

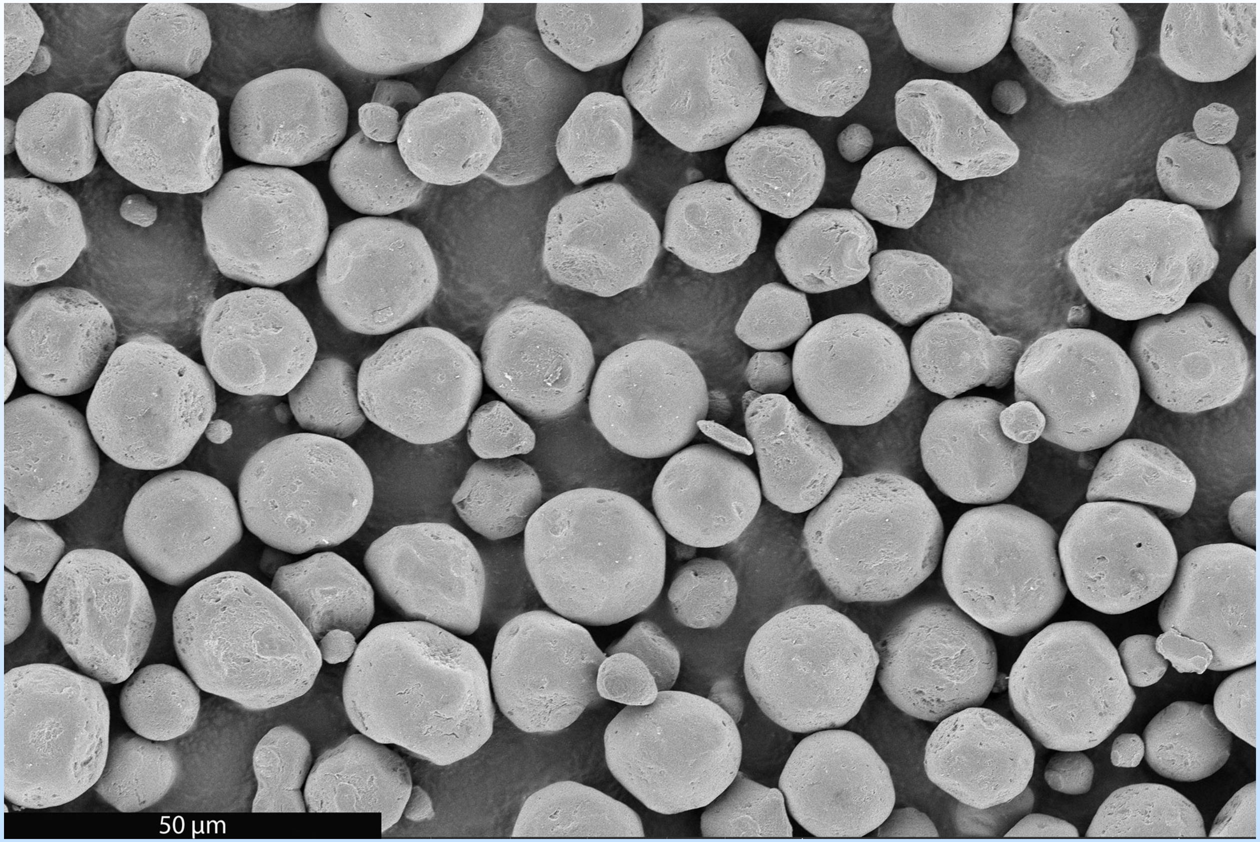
RATIONAL SYNTHESIS OF SHAPED GRAPHITE

Cellulose Spheroids



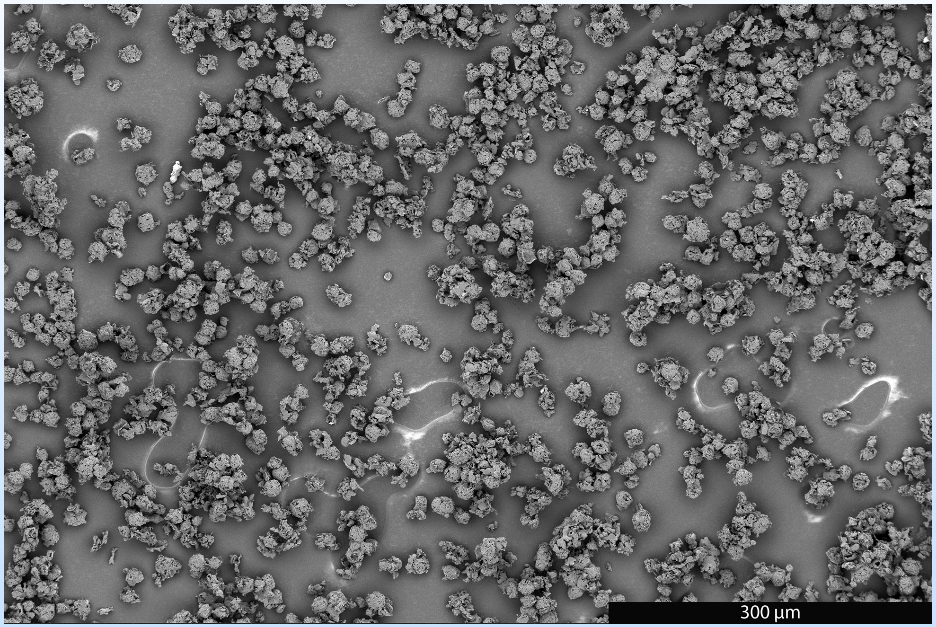
https://doi.org/10.1038/s41598-022-11853-x

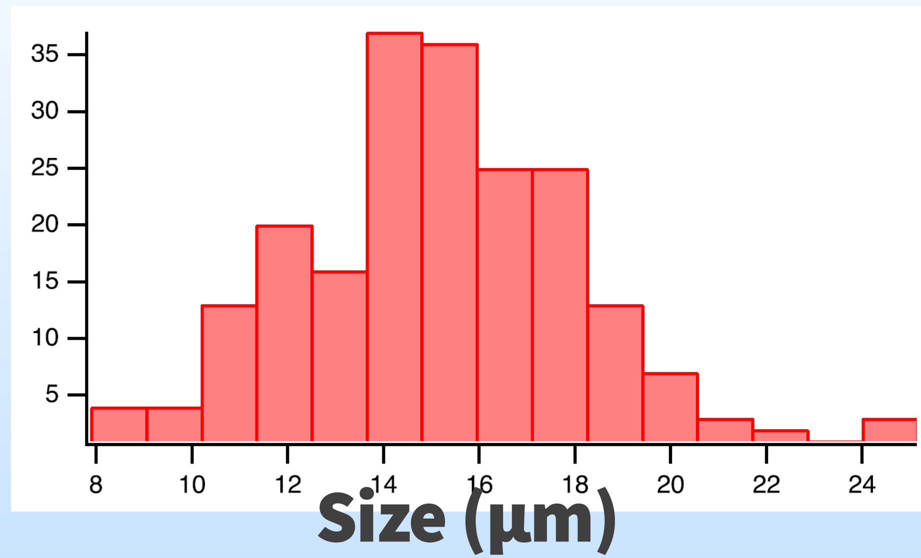
Cellulose Spheroid Char



https://doi.org/10.1038/s41598-022-11853-x

Spherical By Design

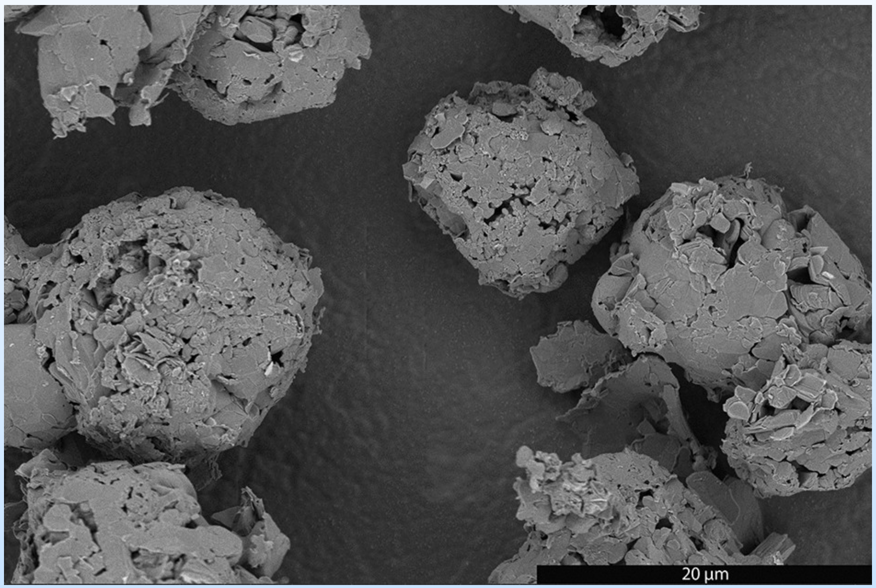




https://doi.org/10.1038/s41598-022-11853-x

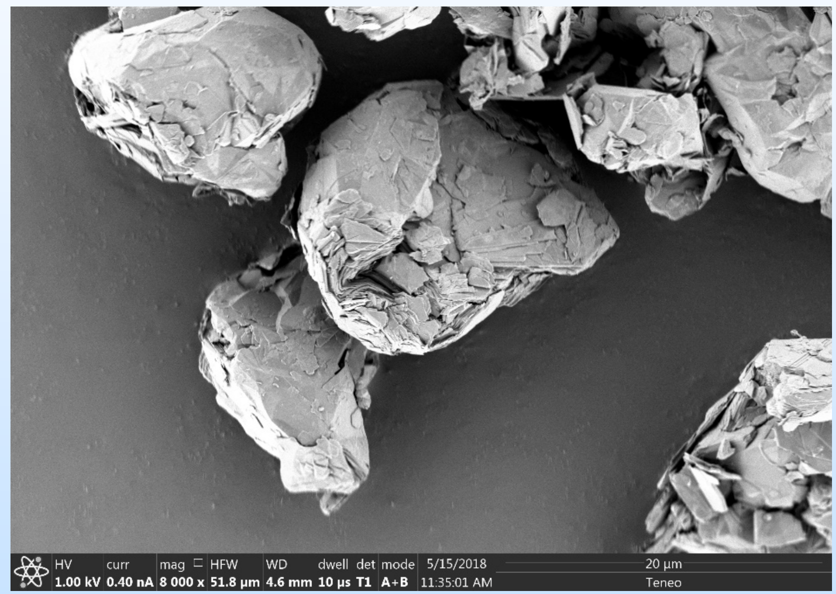
Spherical By Design

Biomass Graphite



3.08 m^2/g

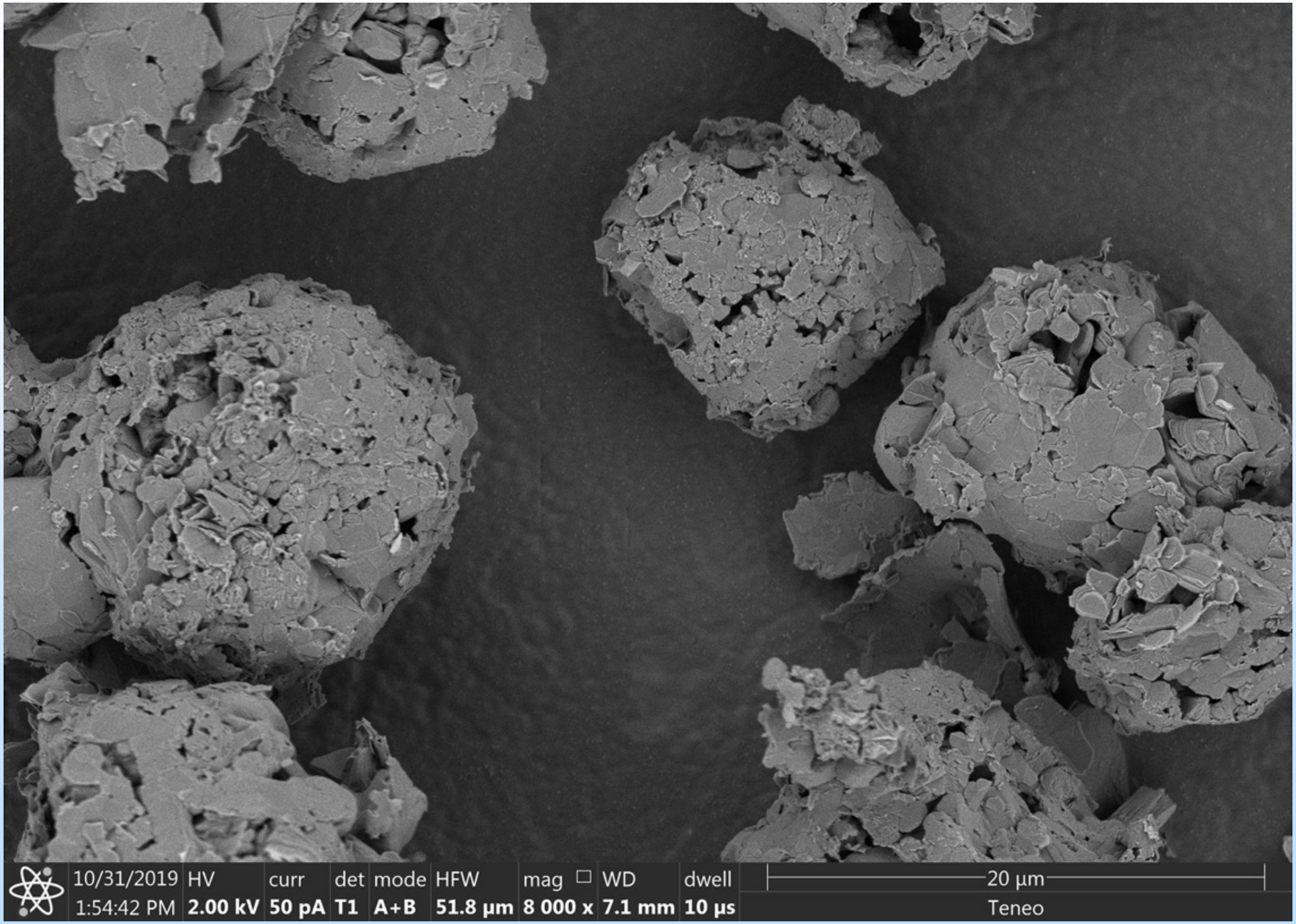
Hitachi MAGE3



2.83 m^2/g

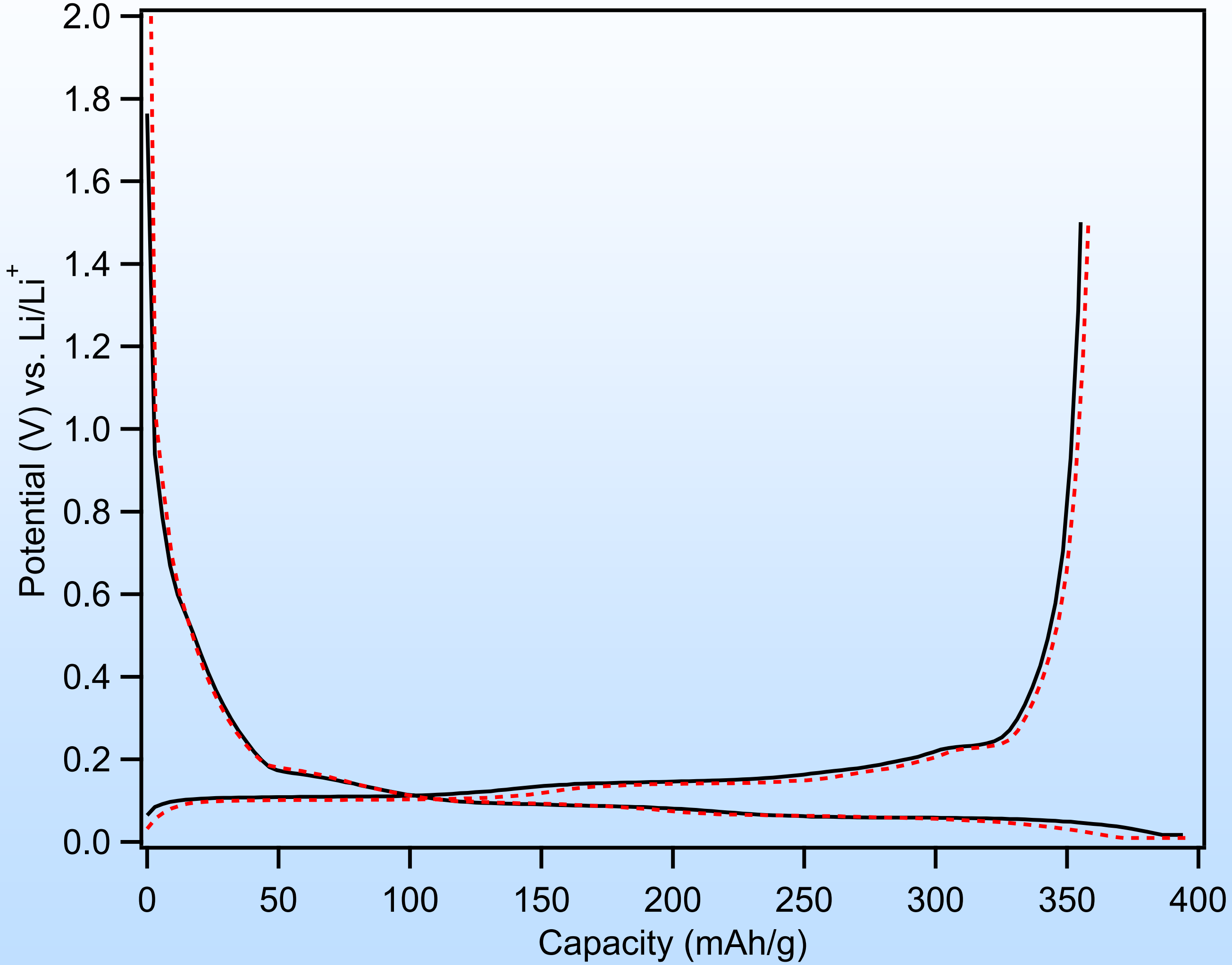
https://doi.org/10.1038/s41598-022-11853-x

Spherical By Design



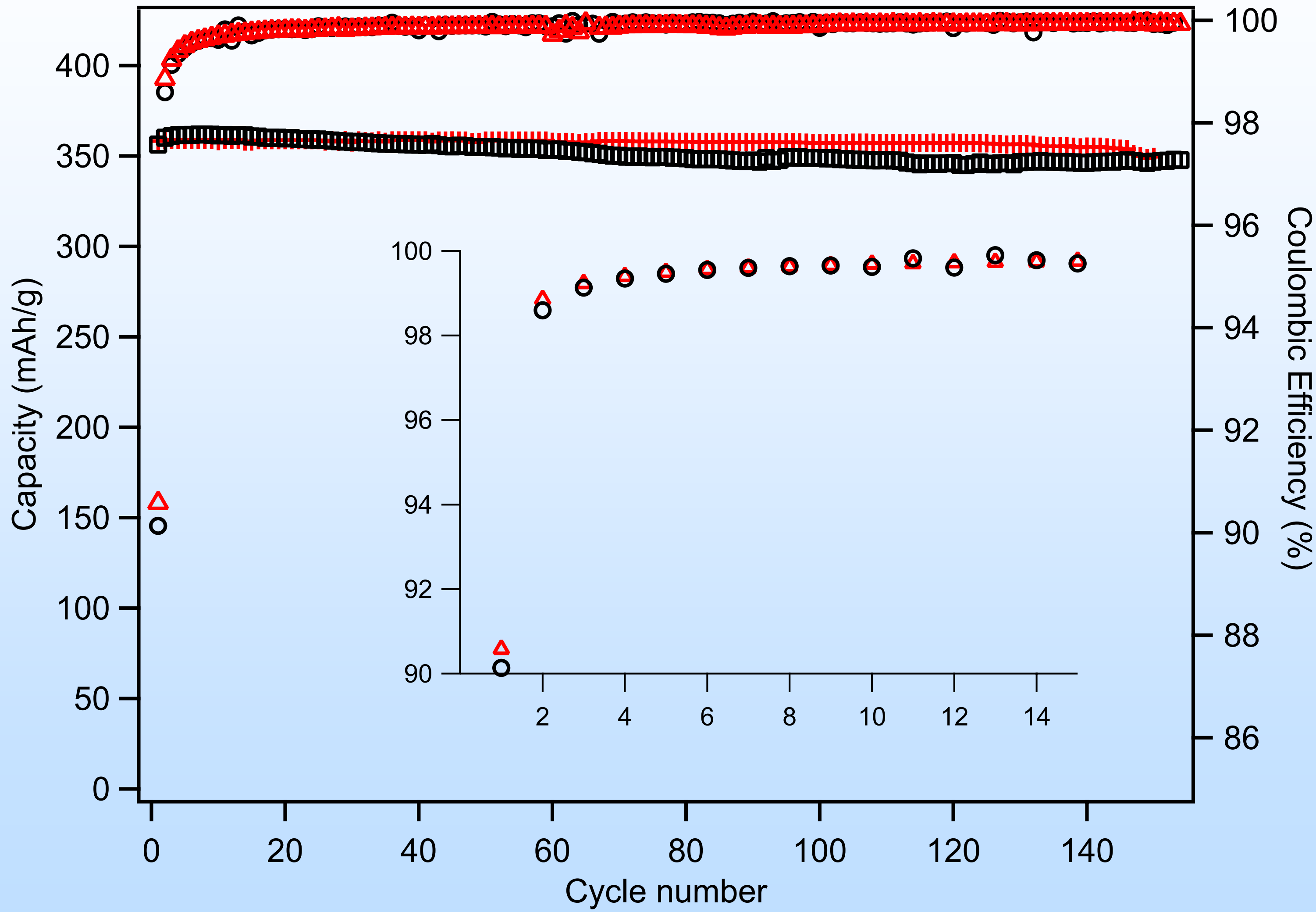
Surface area: 3.08 m^2/g (8% larger than MagE3 2.83 m^2/g)

Rational Design of Graphite



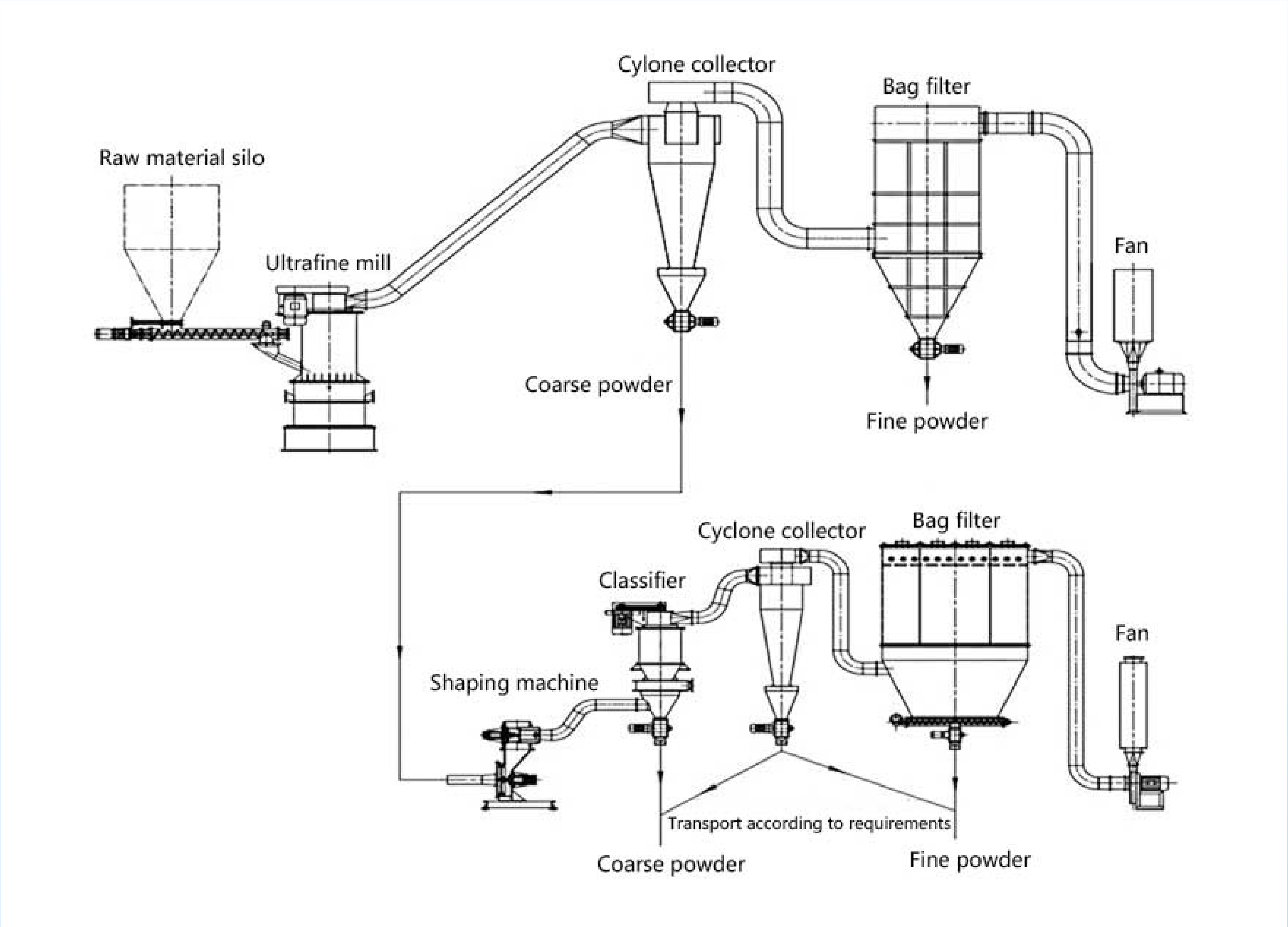
sBCG (solid black) and Hitachi MagE3 (dashed red).

Rational Design of Graphite



sBCG (black) and Hitachi MagE3 (red).

Conventional Graphite Shaping



Graphite is brittle – 70% loss

https://lithium.alpapowder.com/processing-technology/graphite-anode-materials-processing-technology/

Coal vs Biomass

Advantages (Lignite)

- Cheaper
  ~ 6.7 fold decrease
- Supply Chain
- Minimize Transportation
- 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.

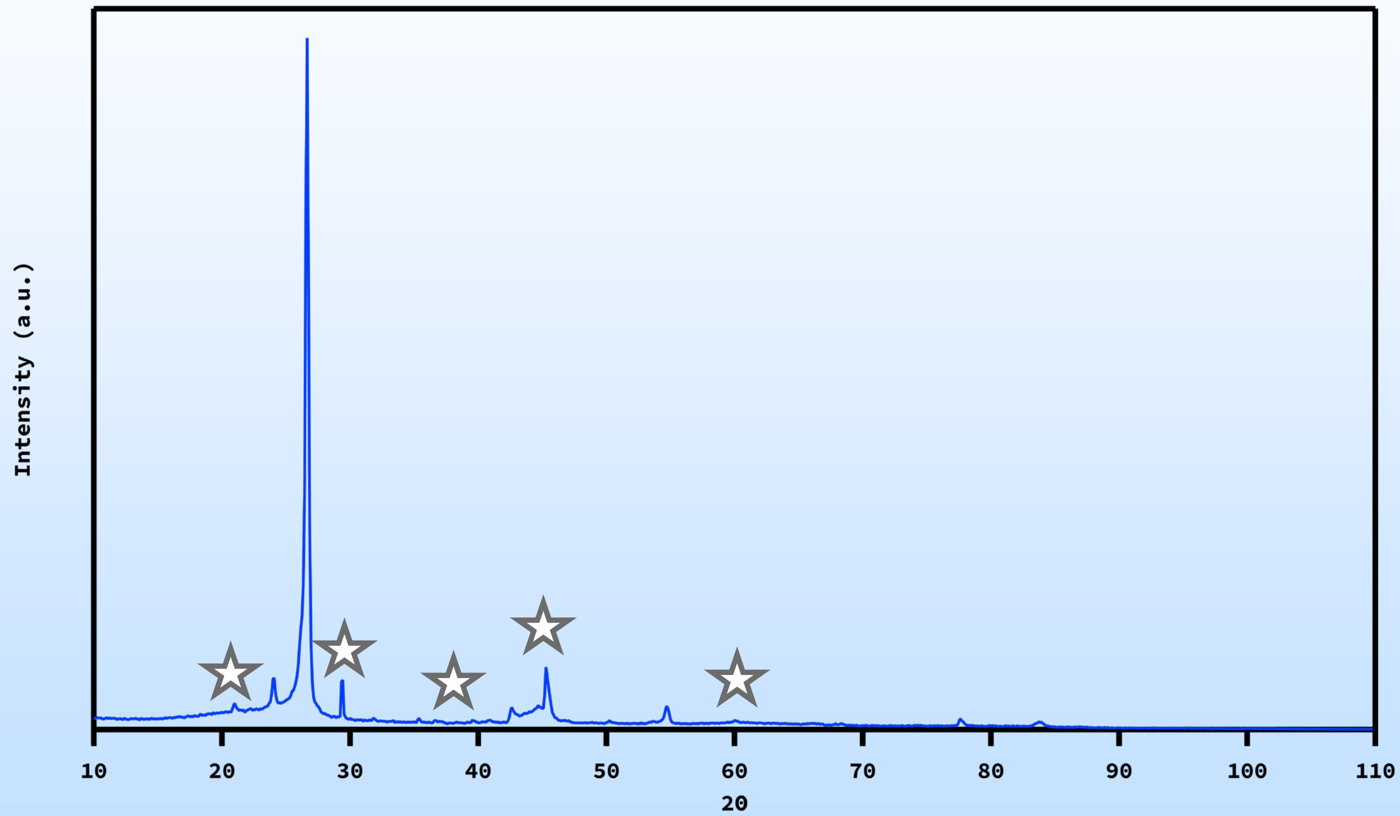
3) Produce graphite from lignite at a rate that exceeds 25 g/h of laser irradiation.

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.

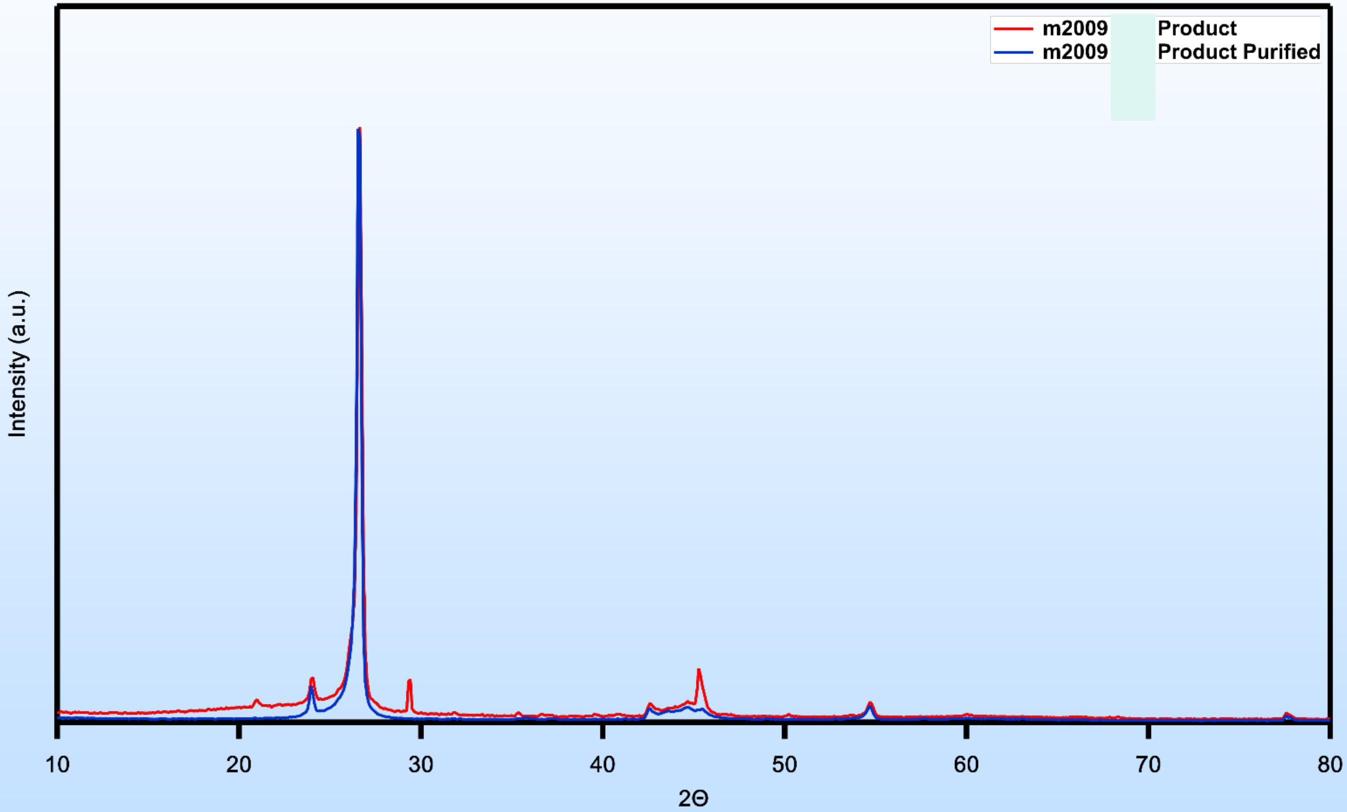
Project Feedstock

- 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

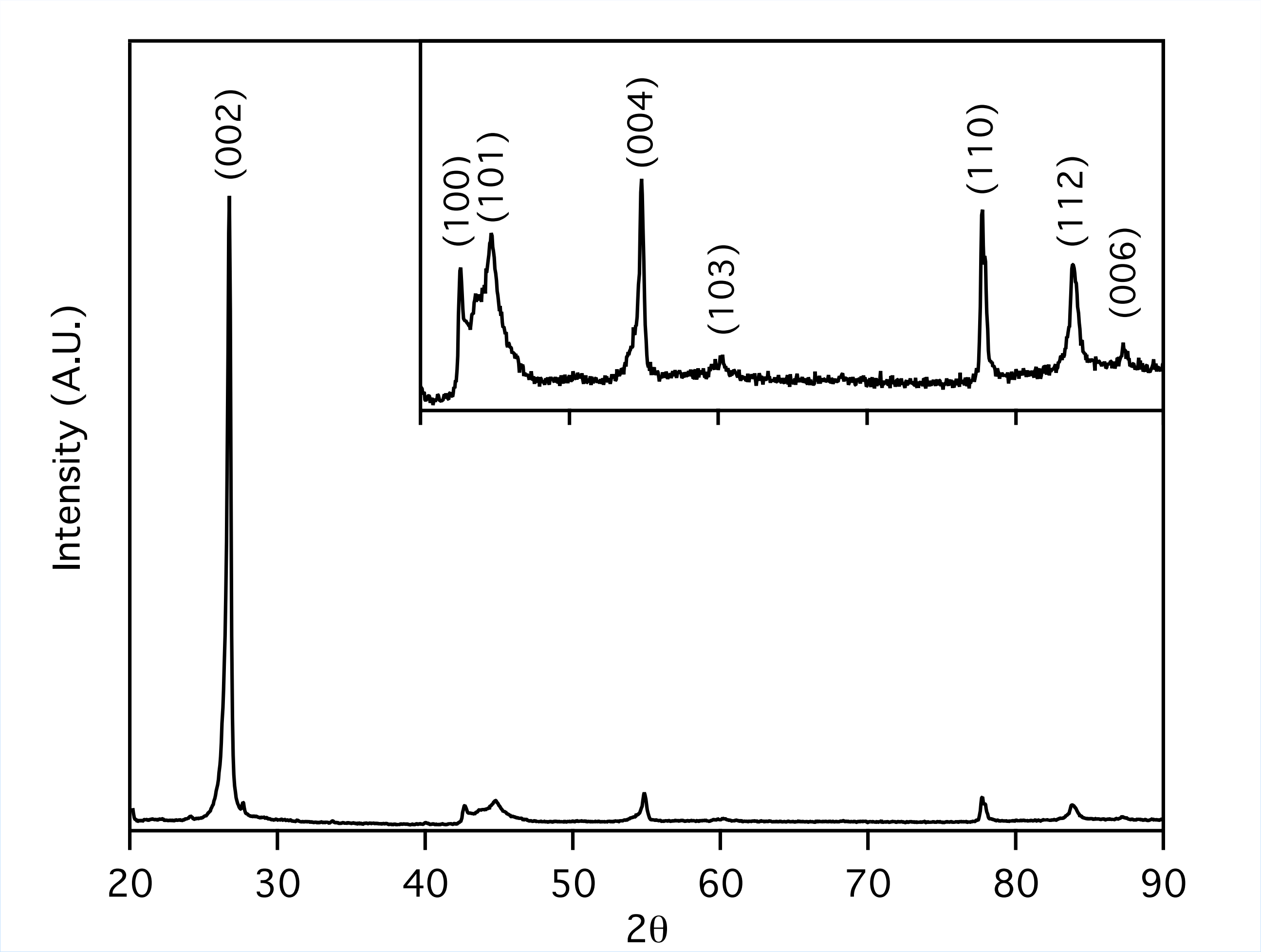
XRD MS Coal Graphite



Purification of MS Coal Graphite



Graphite From ND Lignite



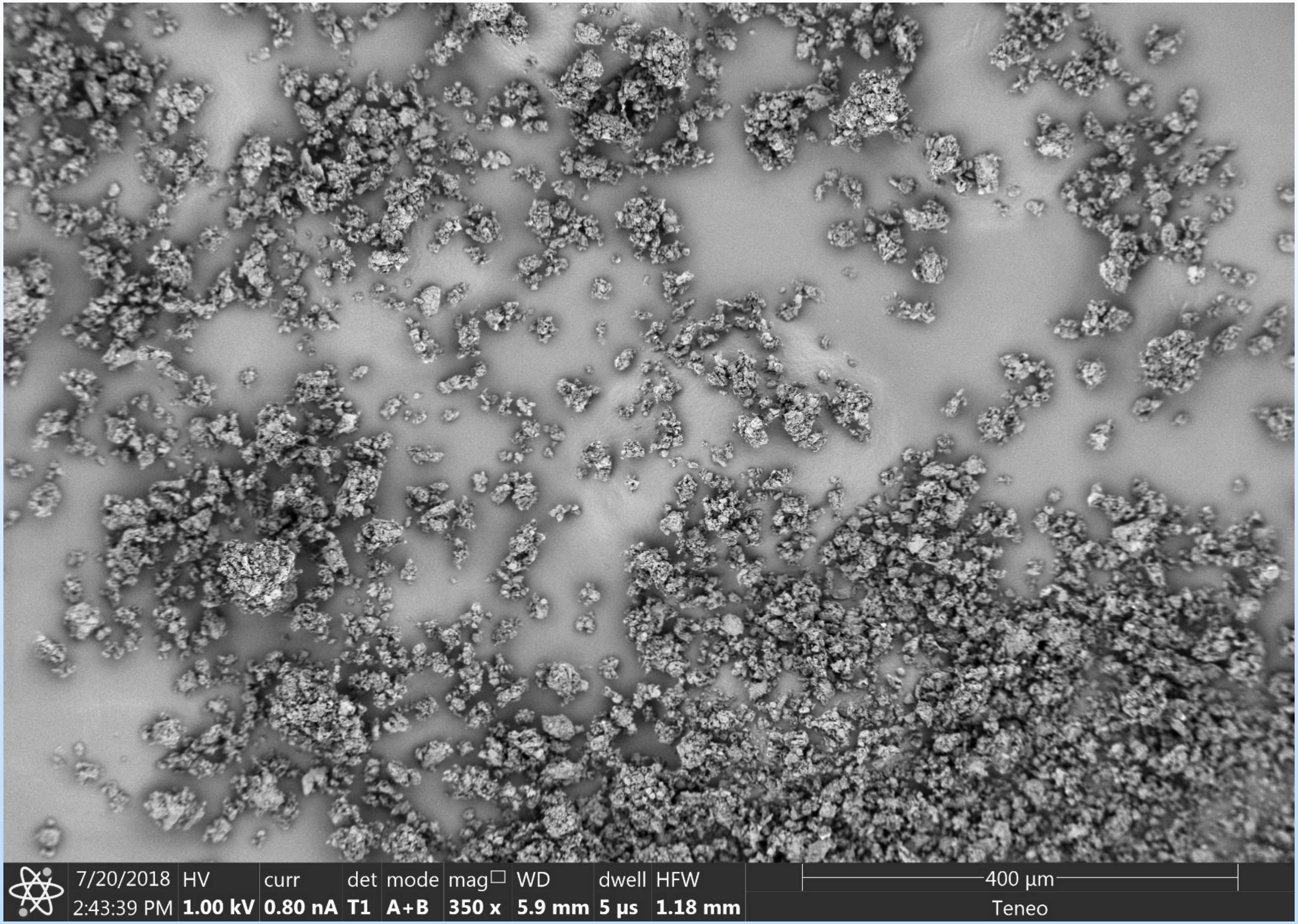
Highly Crystalline Graphite from Lignite

Coal Graphitization

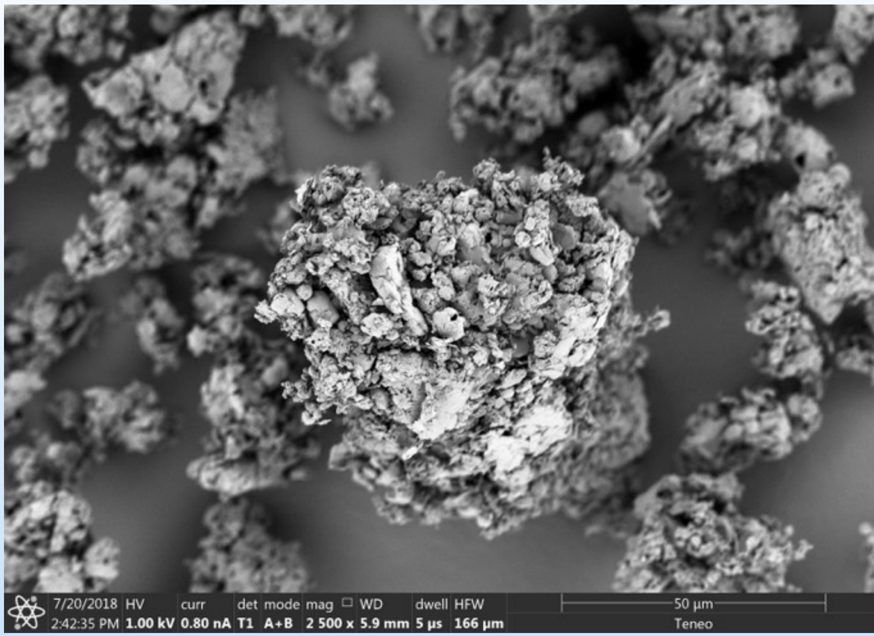
- Lignite
  - All of the North Dakota samples graphitize
  - Mississippi samples graphitize with low yield (25 – 33% at 200 W laser power)
- Bituminous sample does not graphitize – despite it being a "graphitizable carbon"
- Anthracite sample does not graphitize

Shaping

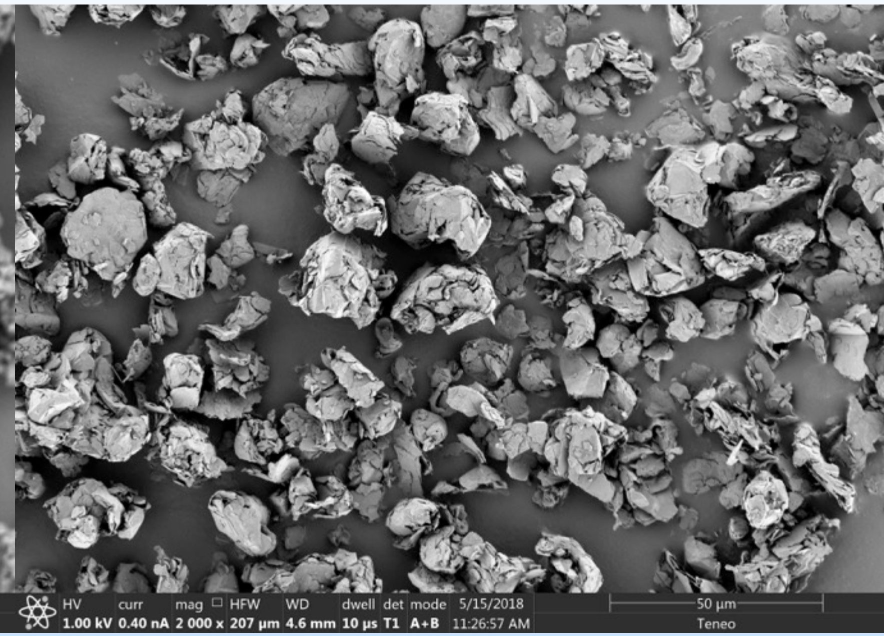
Spherical Lignite Graphite



Shaped Graphite From ND Lignite

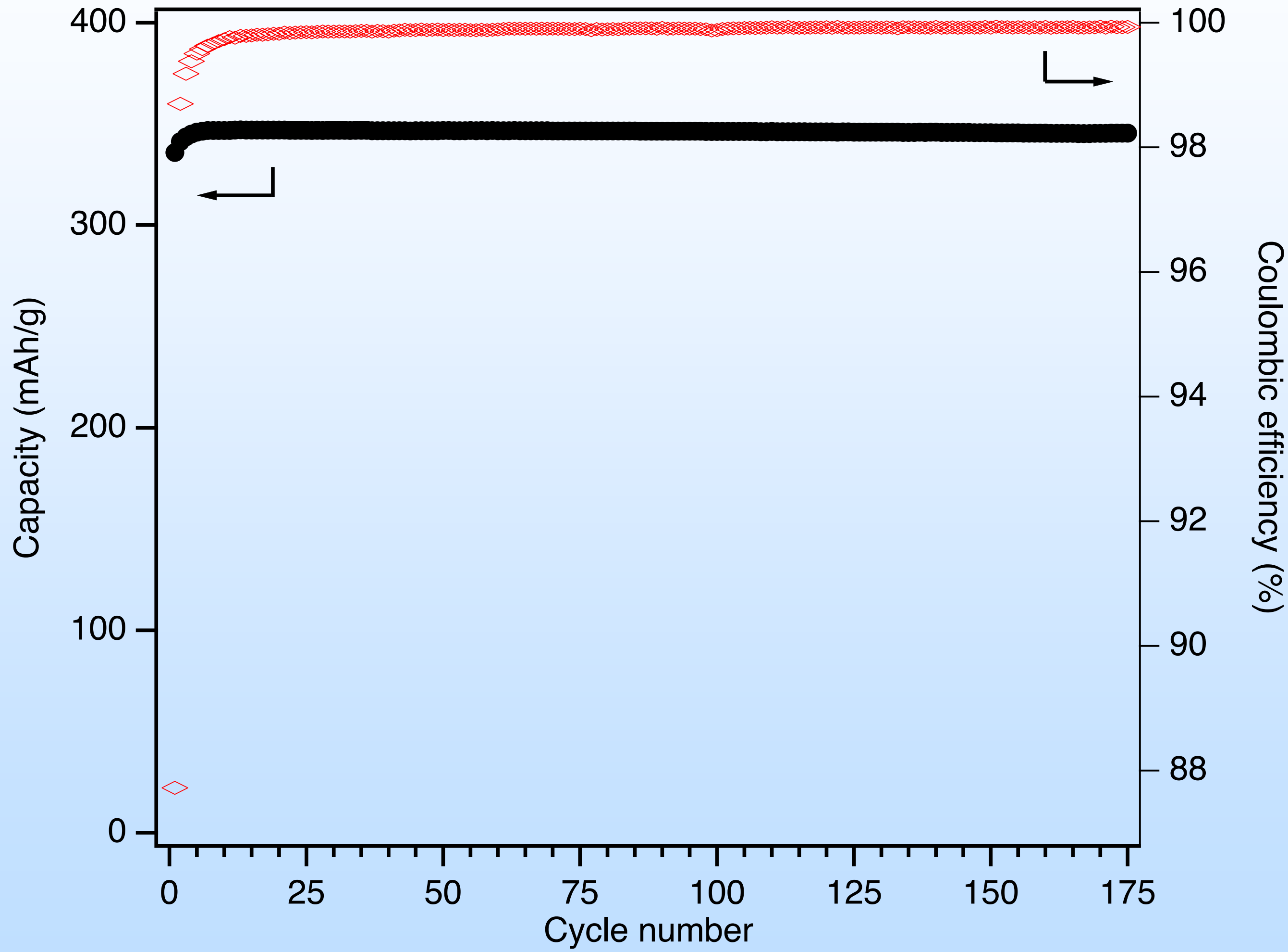


Graphite from Lignite



Hitachi MagE3 Graphite

ND Lignite Graphite – Li-ion

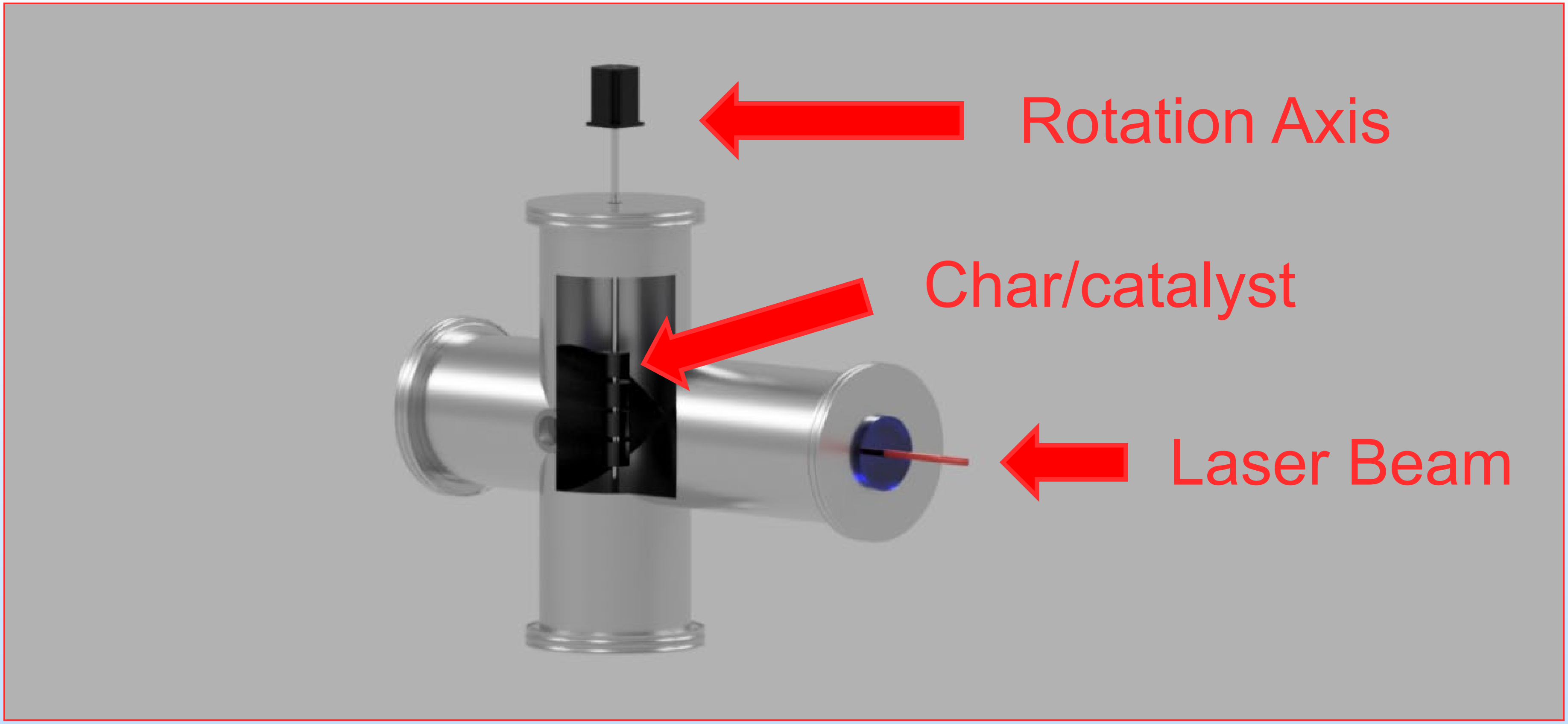


347 mAh/g, 88% 1st Cycle CE

Continuous Processing

Batch Process – Sample Prep

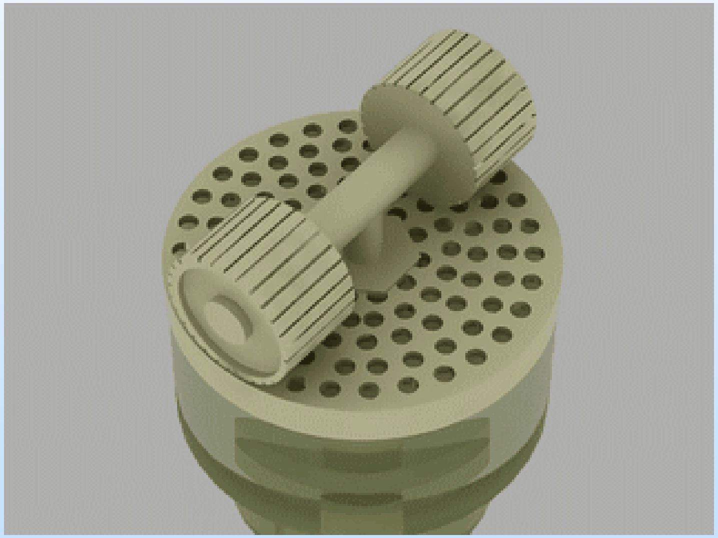
Batch Process – Sample Prep



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

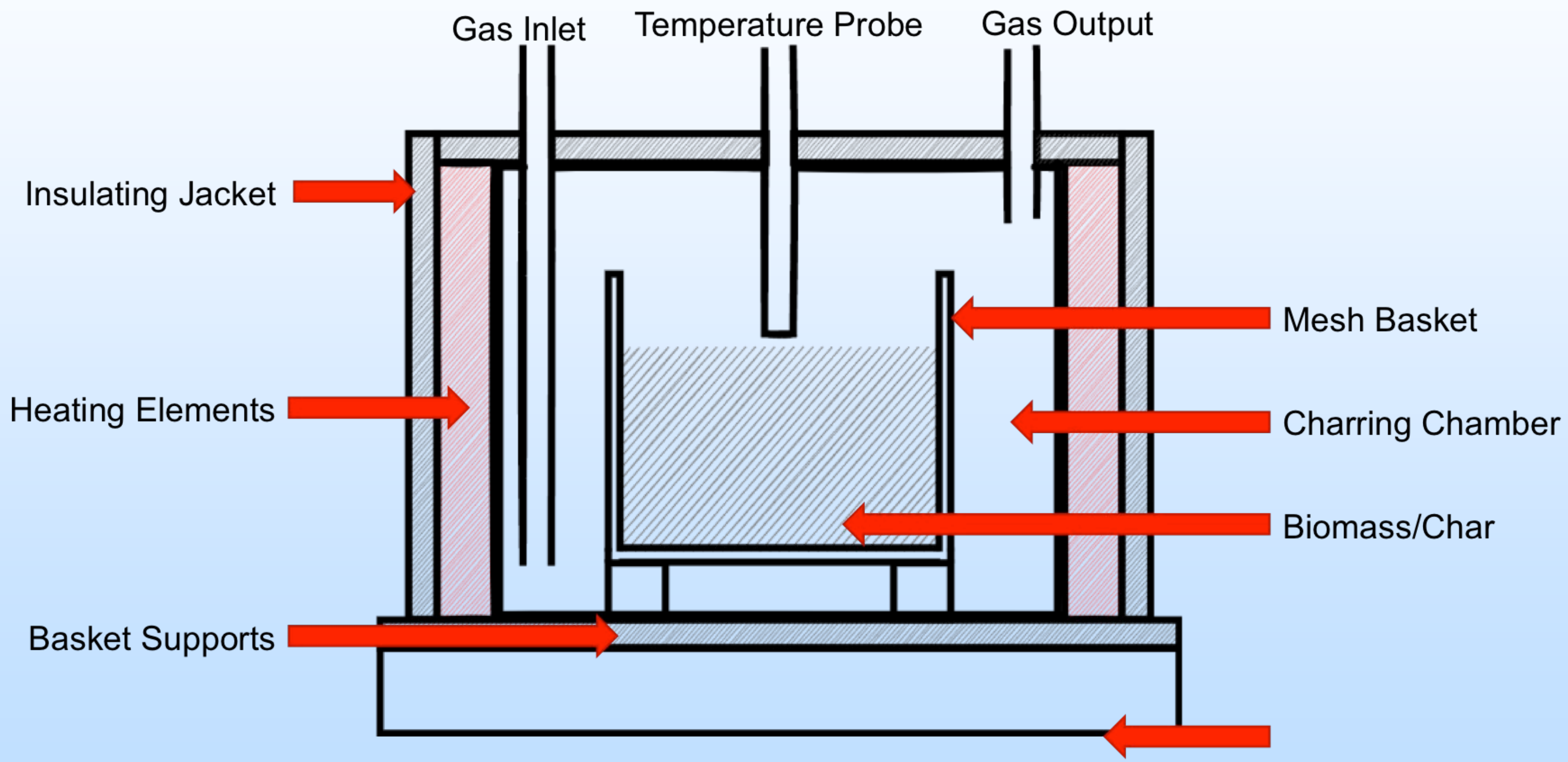
Batch Process (gram scale)

Agricultural Pelletizer (kg scale)

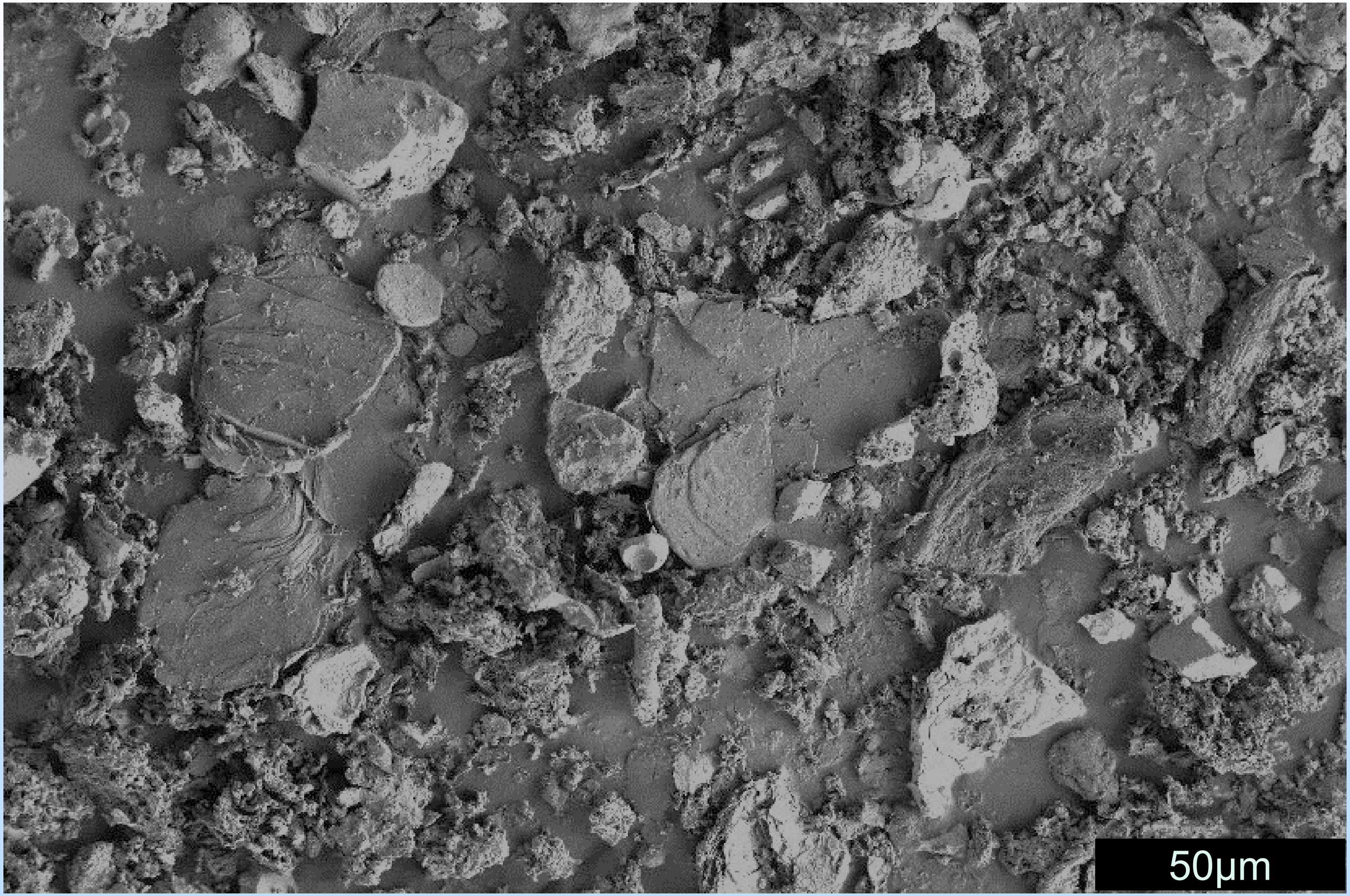


https://www.smallpelletmachine.com/product/electric-pellet-mill/azsplm400-electric-pellet-machine/

Charring (kg scale)

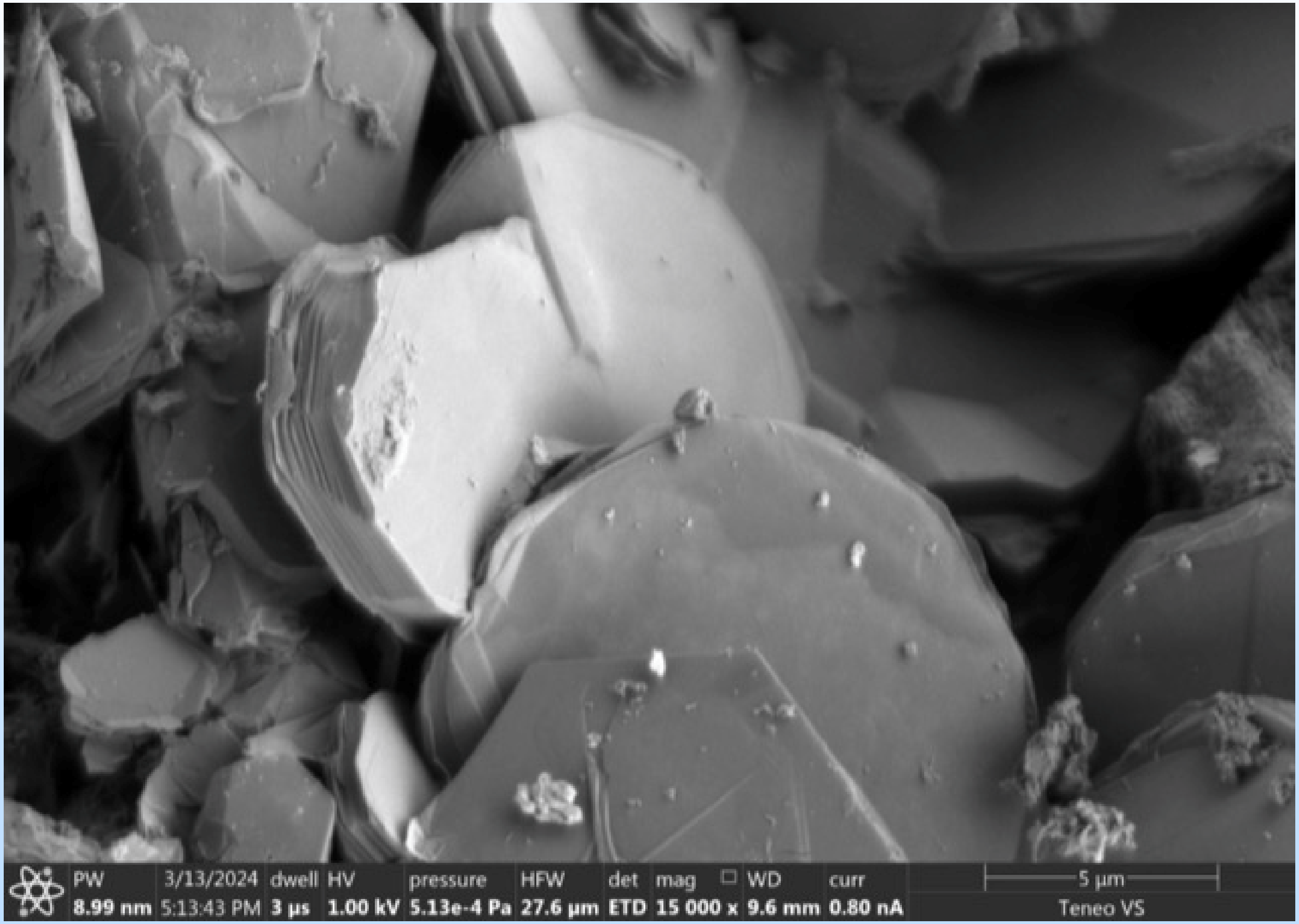


Continuous Synthesis - Graphite



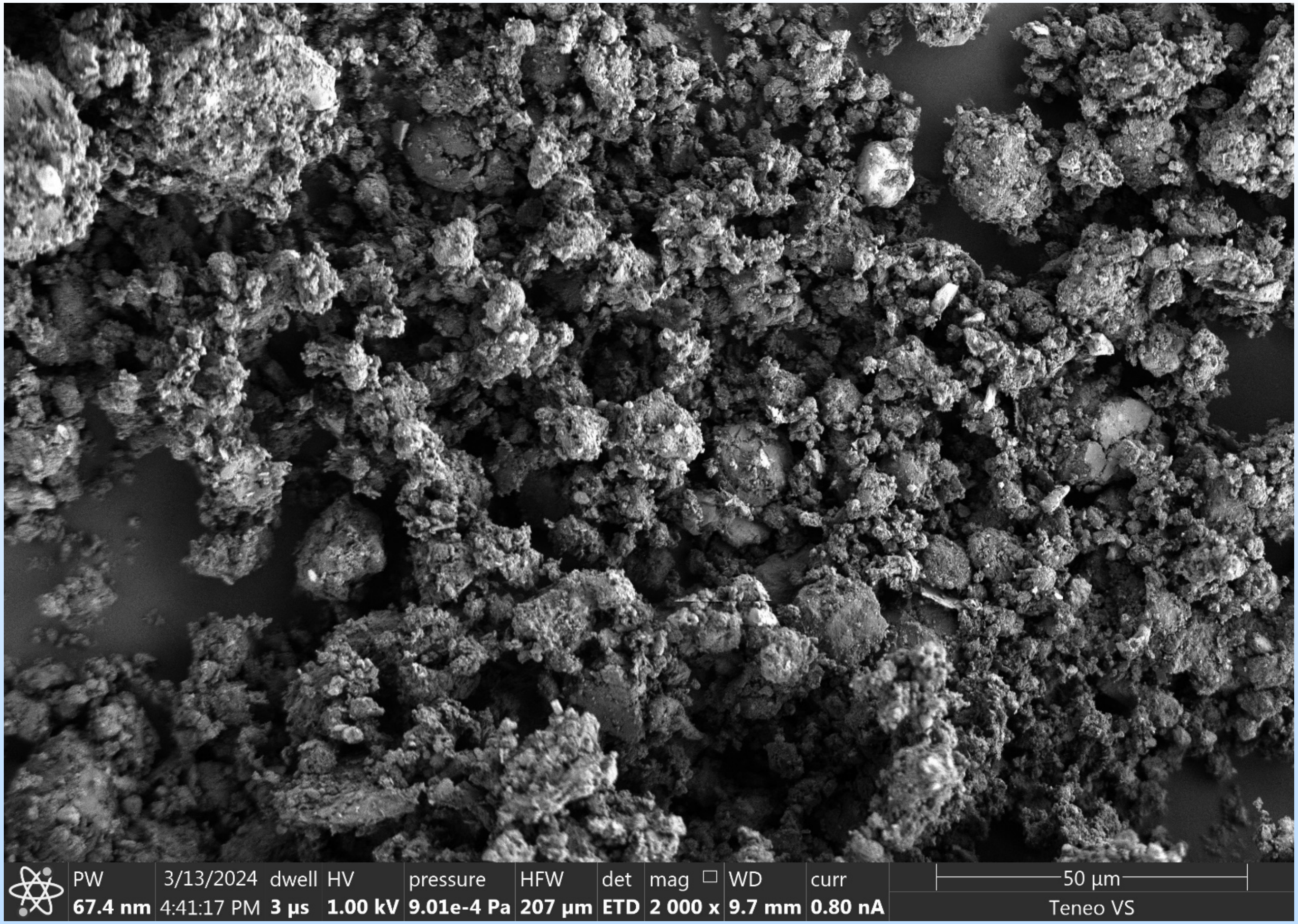
Mk1 - Works – But inconsistent/jamming

Continuous Synthesis - Graphite



Mk2 - Works Well – Flake Graphite

Continuous Synthesis - Graphite



Mk2 - Works Well – Shaped Graphite

Laser Pyrolysis Chamber

- After a number of designs, we now have a system that can operate continuously
- ~ 0.6 kg/h @ 1 kW
- Minimal modifications to adapt to 12 kW fiber laser for > 60 ton/y commercial
- Estimated cost ~ $900/ton

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.

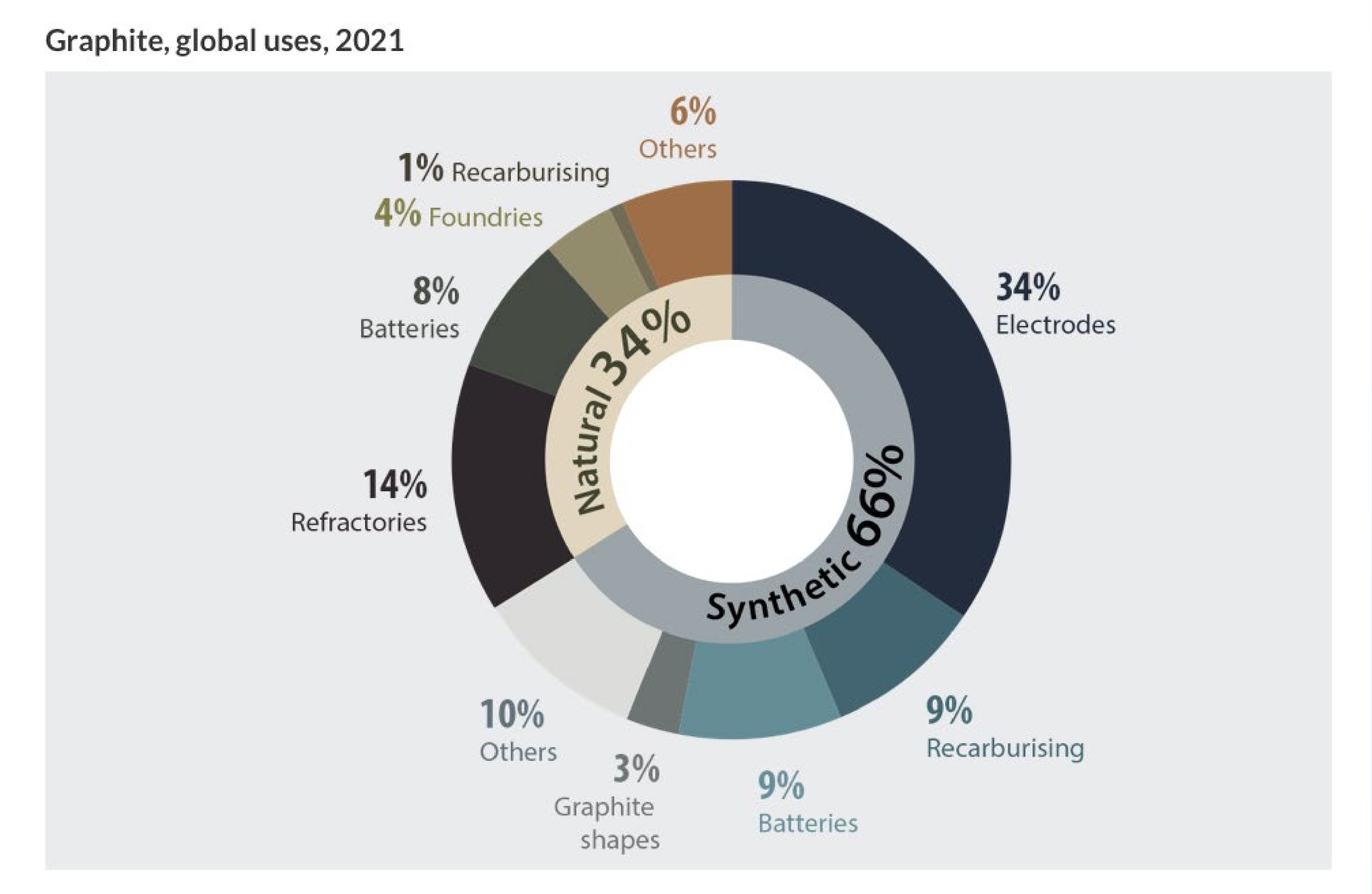
3) Produce graphite from lignite at a rate that exceeds 25 g/h of laser irradiation.

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.

Plans for future development/ commercialization

- Production scale reactor module
  - Small space requirements (in lab)
  - 60 ton/year Continuous Operation
  - Modular Production Line Deployment
    - Low risk direct lab to production module
    - Sized to Readily Available Industrial Lasers
    - Scale by module addition
- Pilot
- Production

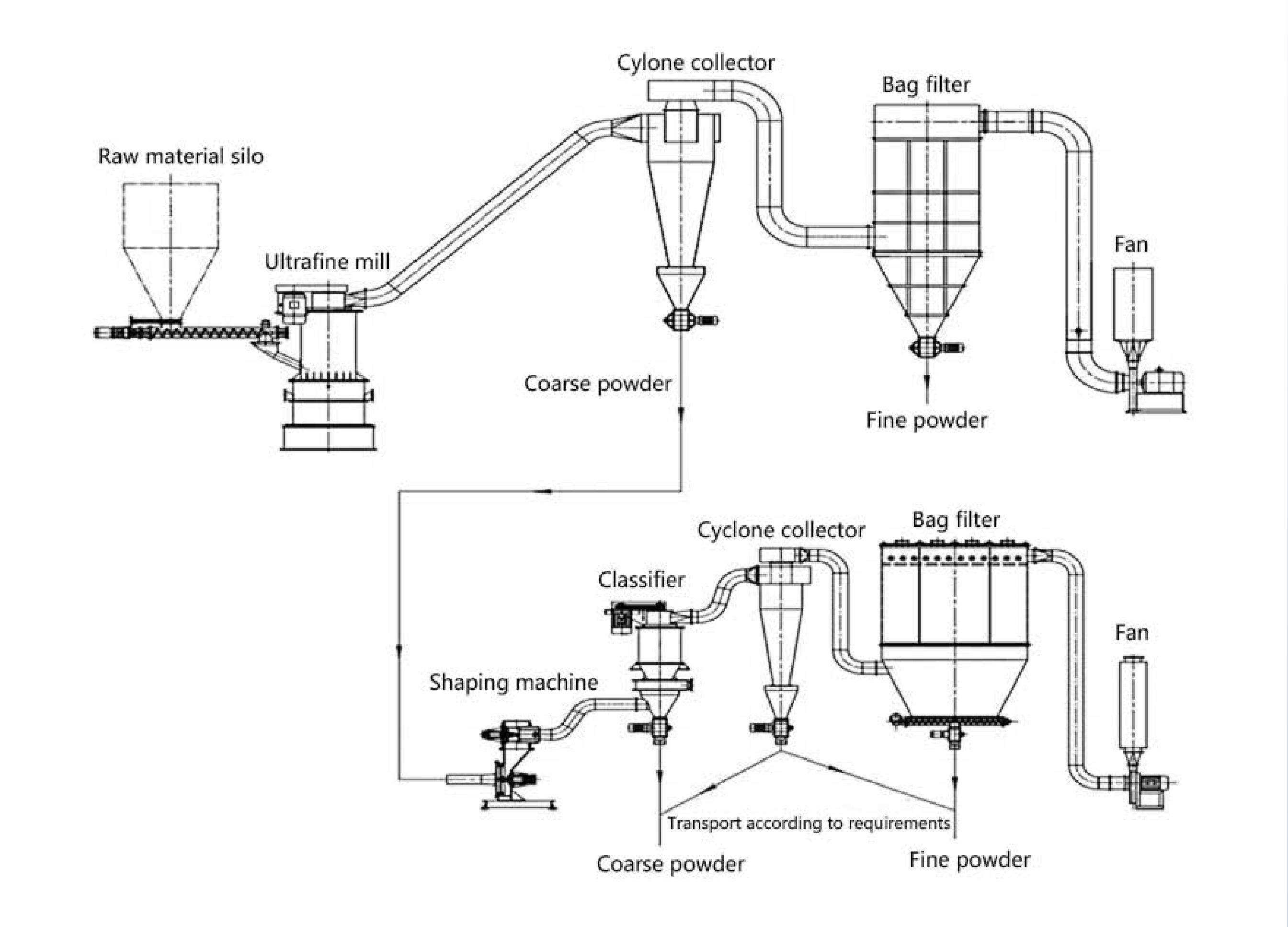
Graphite Market



~ 3.5 million tons/yr

Natural Resources Canada

Lignite/Char Shaping



Shaping of inexpensive starting material

https://lithium.alpapowder.com/processing-technology/graphite-anode-materials-processing-technology/

Commercialization Plans

- Developing Partnerships to Commercialize
- Moving to pilot scale with partner and with successful pilot, production

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 commercially viable
- Continuous graphitization demonstrated

Appendix

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.