DE-FE0031797- Conversion of Coal to Li-ion Battery Grade "Potato" Graphite

NETL Advanced Coal Processing Project Review Meeting
April 27, 2021

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Project Description & Objectives

Purpose of Project

- Develop method to convert low value coal to high value graphite (~ 1000 fold increase in value)
- Successful research and commercialization would
  - open a new, very large market for coal
  - provide domestic production of a “Strategic and Critical Mineral” essential for clean energy EV transportation
  - Create American jobs

Driving question – “Can coal be economically transformed to high purity, high value, Li-ion grade graphite?”

Benchmarking

- Direct performance comparison to commercial Li-ion battery grade graphite
- Economic modeling for comparison to market pricing

Project Description & Objectives

Current Project Status – All Year 1 goals met

- Graphite yield goal > 0.20 kg/kWh
- 1st cycle Coulombic efficiency > 85%
- Production goal > 5 g/h
- Lithium-ion cell cycle life > 100 cycles

Validation

- Collaboration with Dr. Wenquan Lu (Argonne National Laboratory) for independent validation of candidate materials

Technology Benchmarking

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- Li-ion batteries require very high quality graphite (expensive)
- Natural flake graphite purified to lithium ion battery grade (~99+% C, coated "potato"): $14,870/ton
- Synthetic graphite: $18,000/ton

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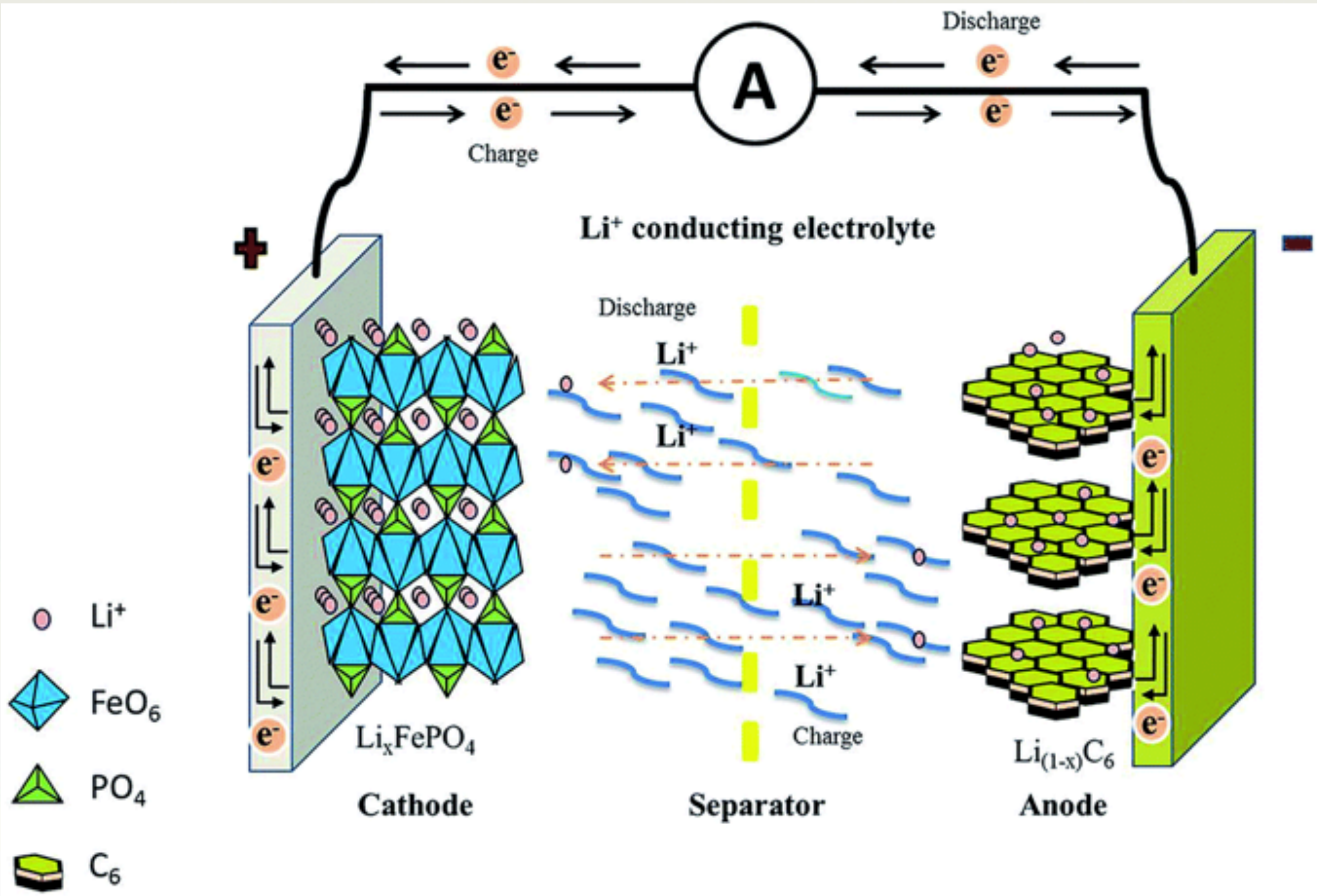
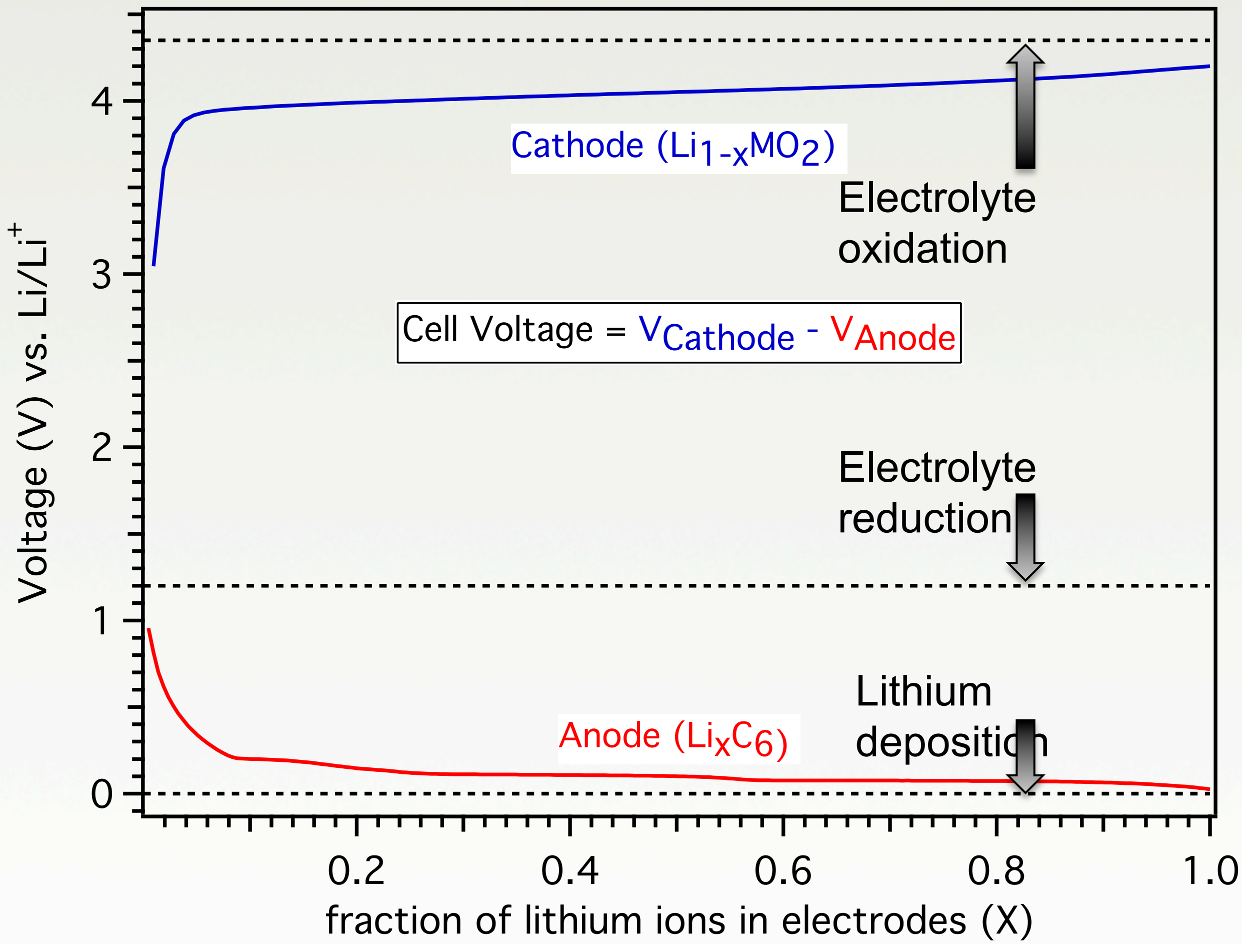
Li-ion "Rocking Chair" Battery



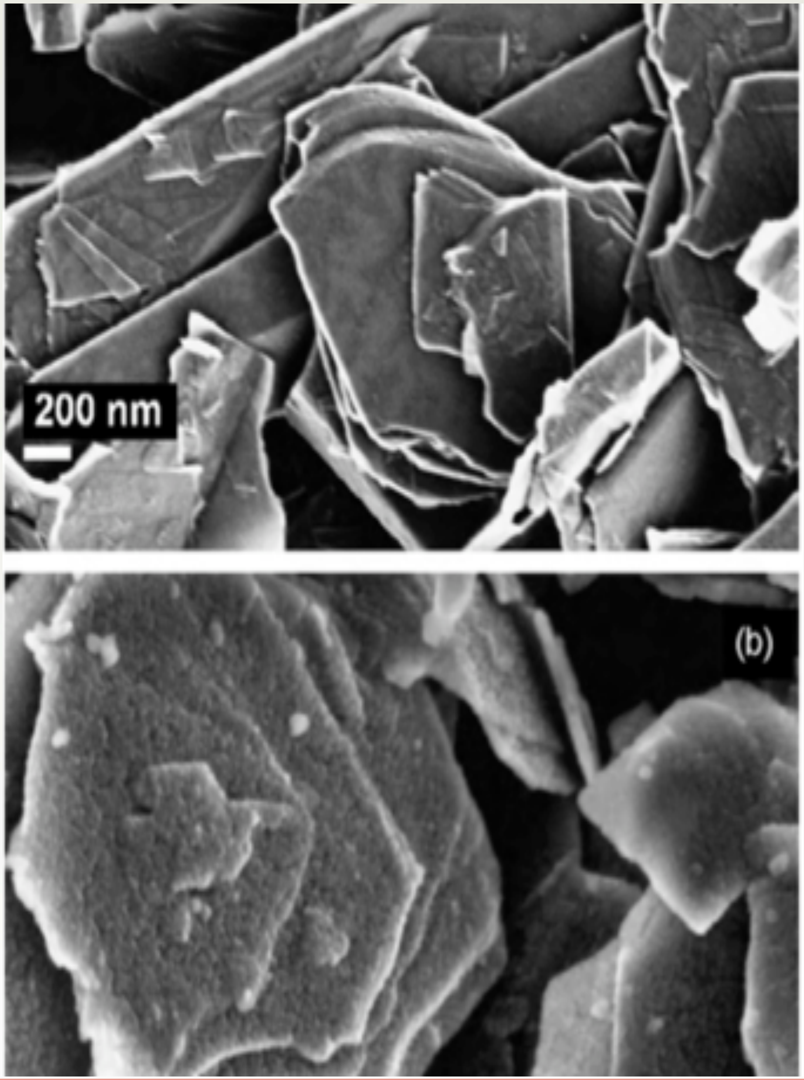
Zhang X. et al. *Polymer Reviews*. 2011, **51**, 239-264

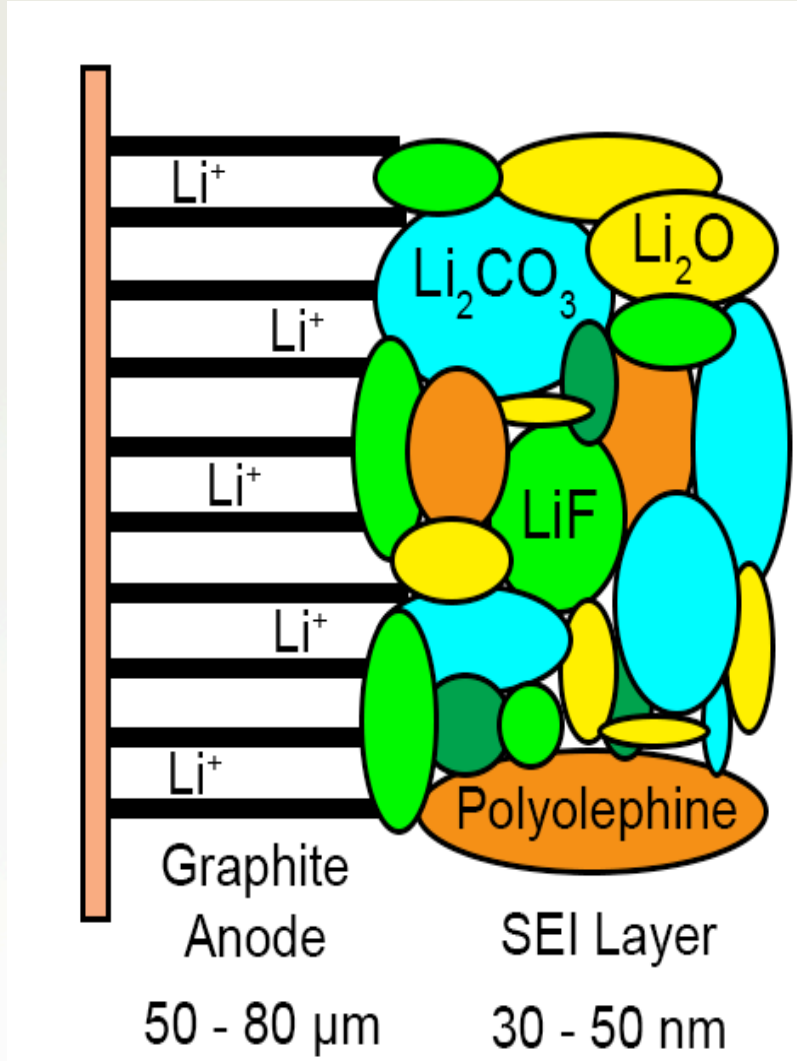
Li-ion Cells



Cathode ($Li_{1-x}MO_2$)
Electrolyte oxidation
Cell Voltage = $V_{Cathode}$ - V_{Anode}
Electrolyte reduction
Lithium deposition
Anode (Li_xC_6)
Voltage (V) vs. Li/Li+
0
1
2
3
4
0.2
0.4
0.6
0.8
1.0
fraction of lithium ions in electrodes (X)

Solid Electrolyte Interface





Verma P. et al. *Electrochimica Acta*. 2010. **55,** 6332–6341

Coulombic Efficiency

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$$CE = \frac{Q_{out}}{Q_{in}} * 100$$

- Loss of lithium from cathode
- Loss of electrolyte

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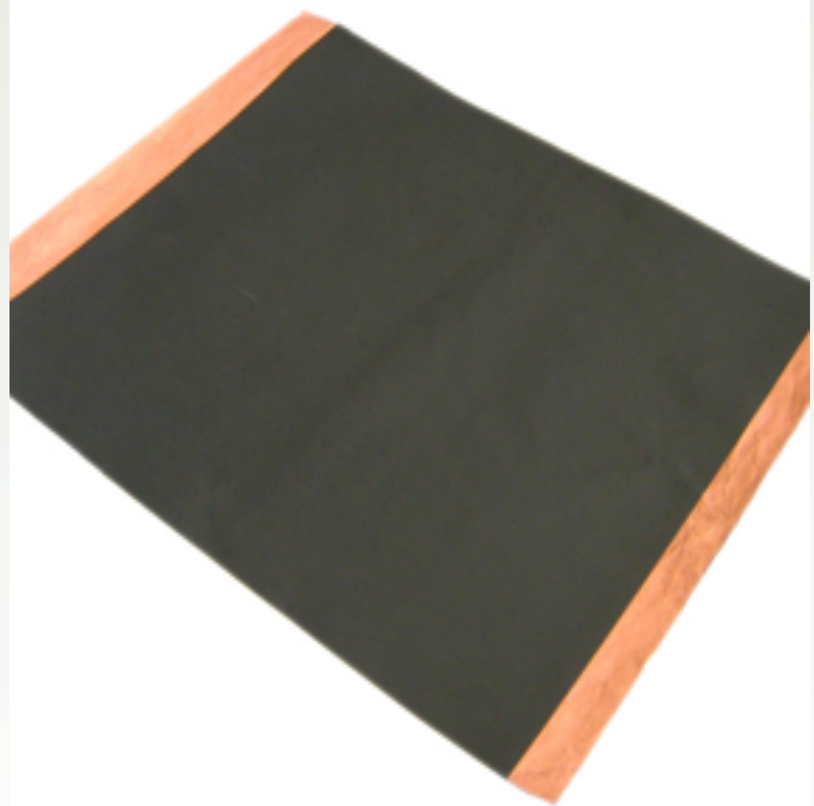
Graphite – Commercial Li-ion Anodes

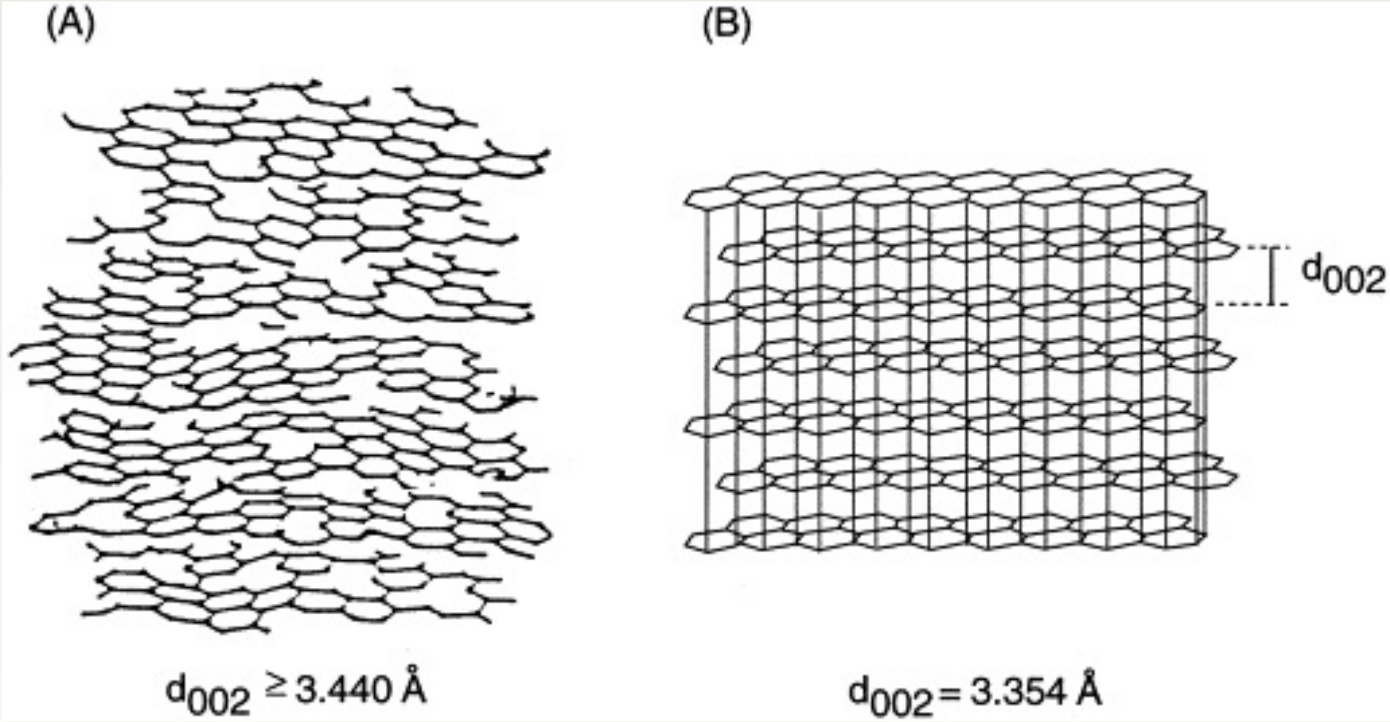
- Abundant and scalable
- Stable
- Safe & compatible
- Energy Dense
  - 372 mAh/g
  - 837 mAh/cm^3
- Long cycle life
- Cost
  - 15% of total battery cost
- High coulombic efficiency
  - >90% first cycle
  - Low surface area
- Entrenched technology



Graphite Supply Constraints

- Significant graphite supply shortages are predicted
  - Graphite prices have tripled in the past 10 years and production has been flat as the major producers appear to be near their limit of flake graphite production.
- Natural graphite
  - China (supplier of 65% of world's natural graphite production) has shut down ~200 flake graphite mines in response to environmental concerns
- Synthetic graphite
  - Petcoke supply shortages foreseen
  - Graphite requires high purity needle petcoke, available from only a fraction of the supply of crude oil
- ***Li-ion battery cell production expected to quadruple to 1.3 TWh by 2030.***

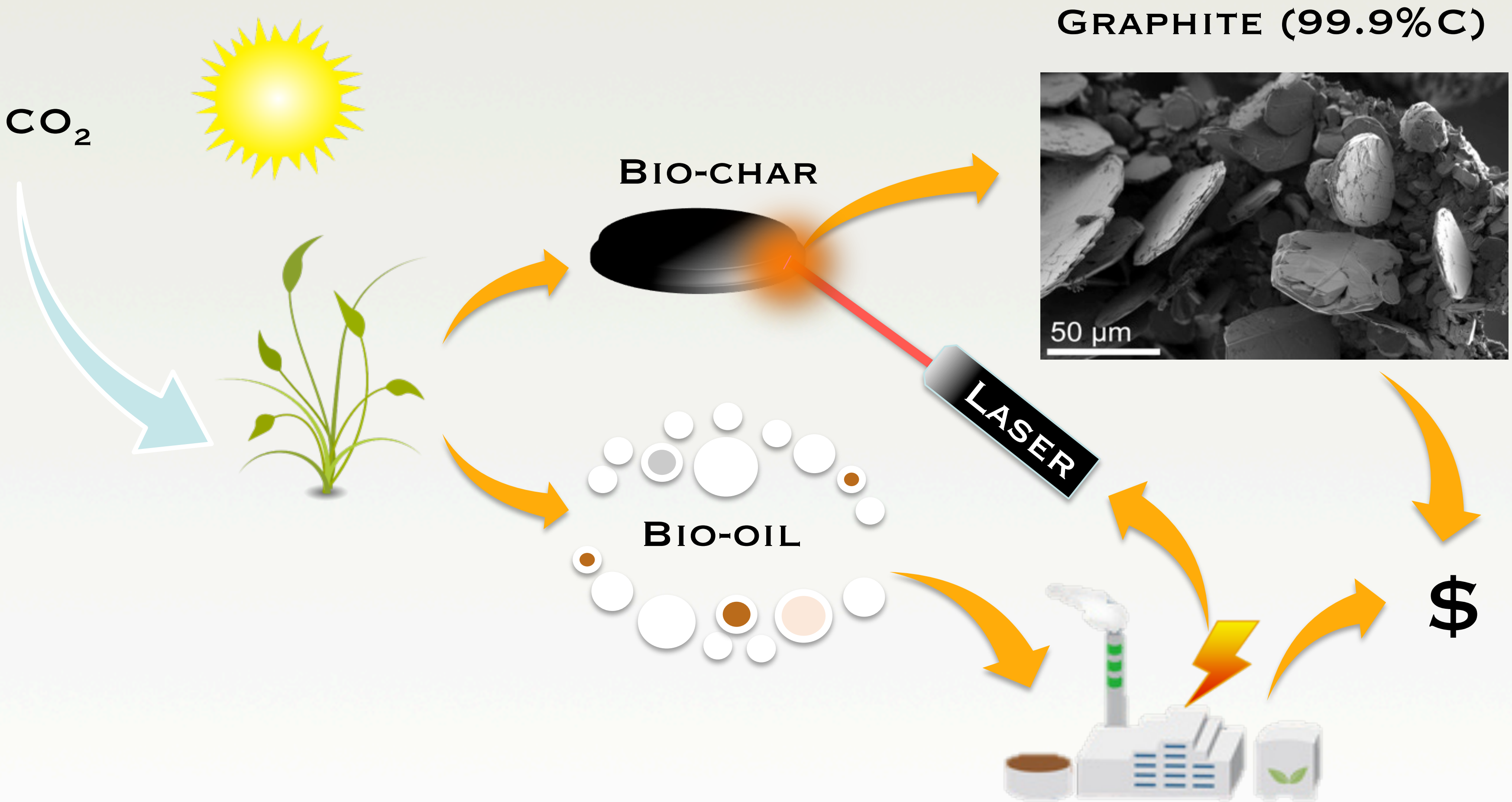
Non-graphitizable Carbons



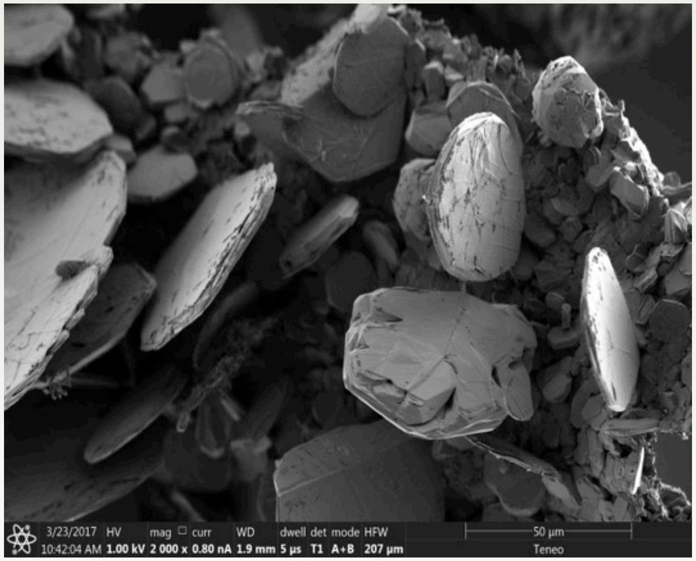
- Non-graphitizable
  - Biomass chars
  - Lignite & Anthracite
- Graphitizable
  - Coking carbons

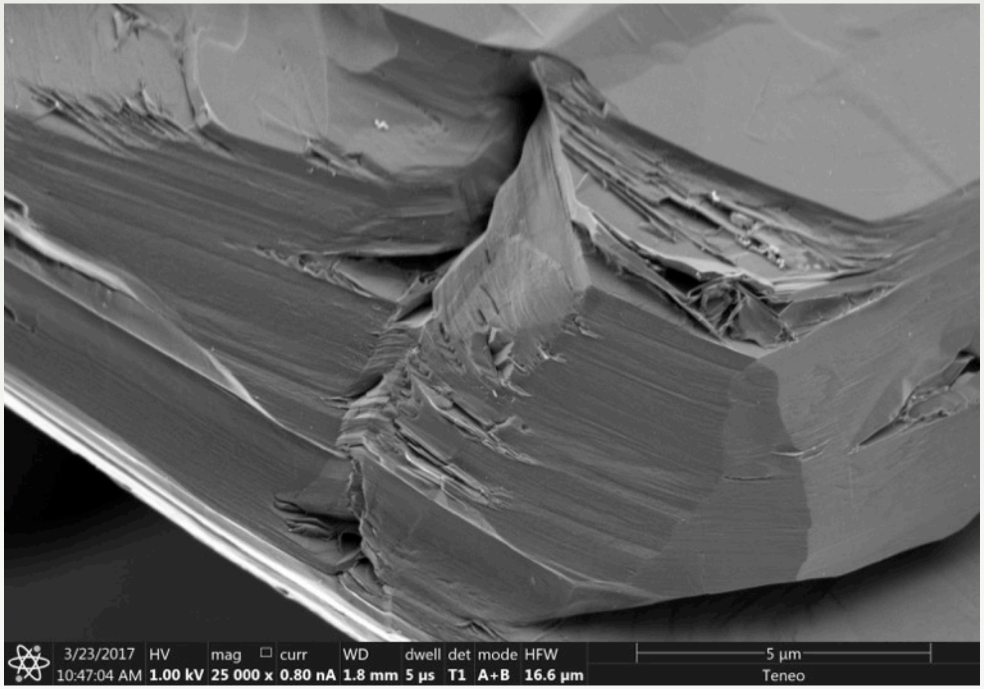
Bijan K. Miremad and Konrad Colbow, Sensors and Actuators B: Chemical,46, 1,1998,30-34

Graphite From Biomass



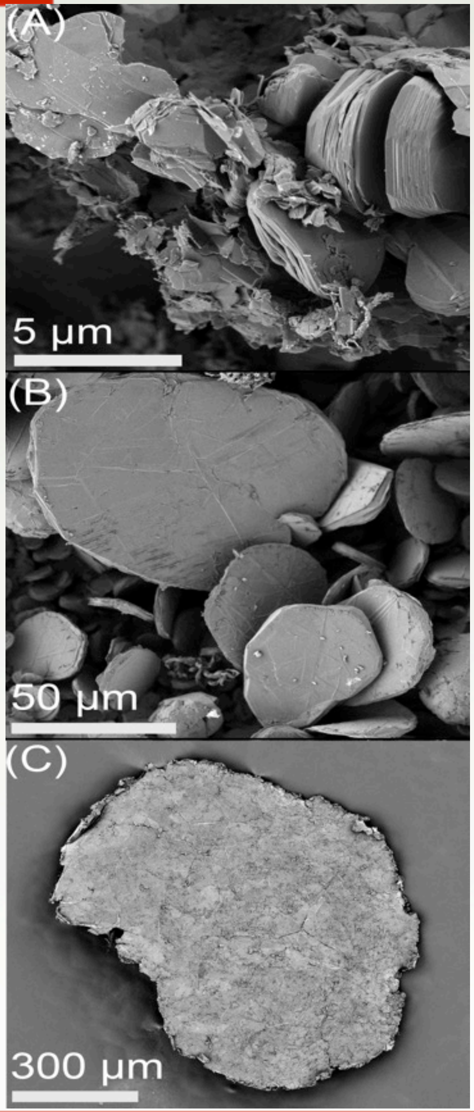
Graphite From Biomass



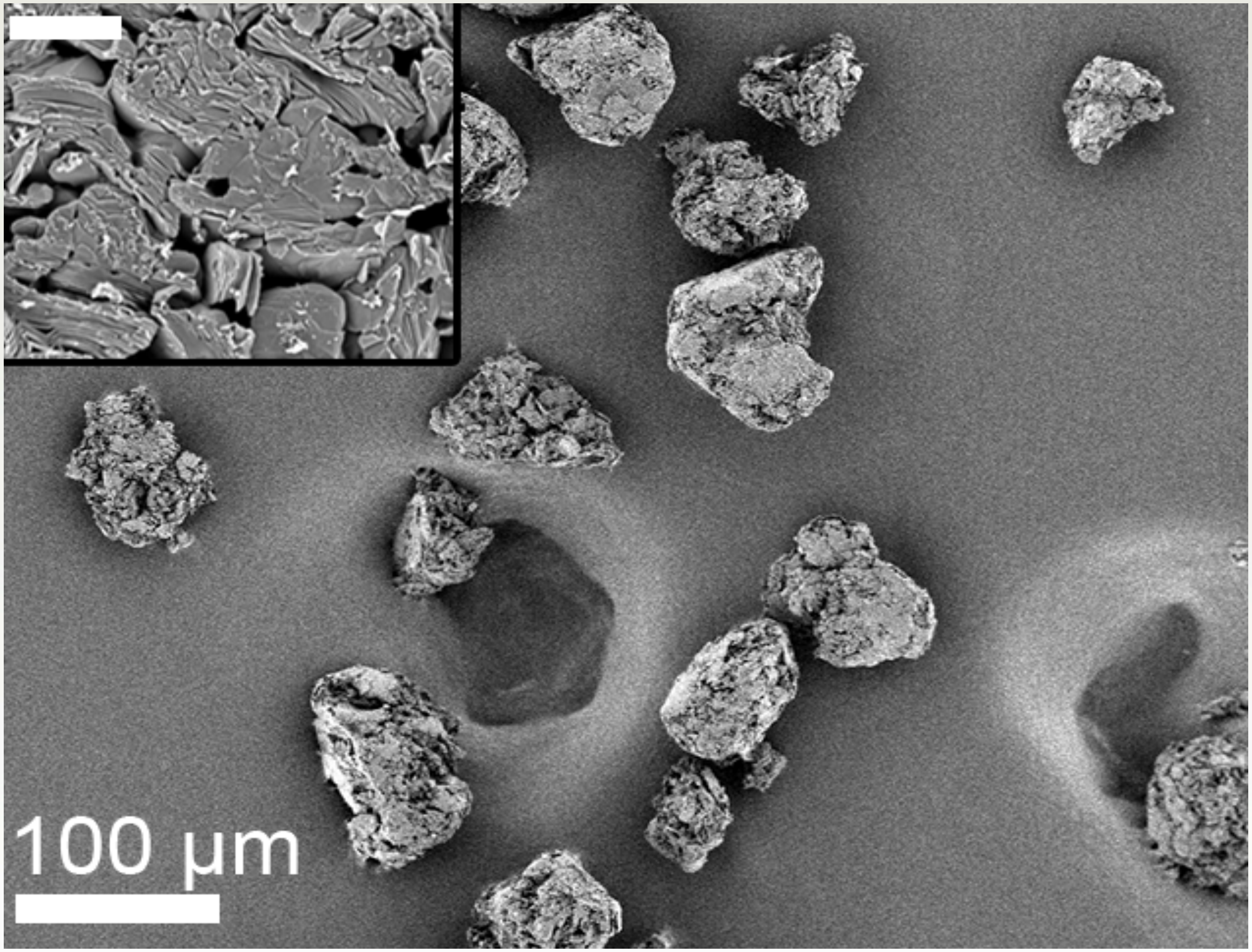


Graphite From Biomass

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



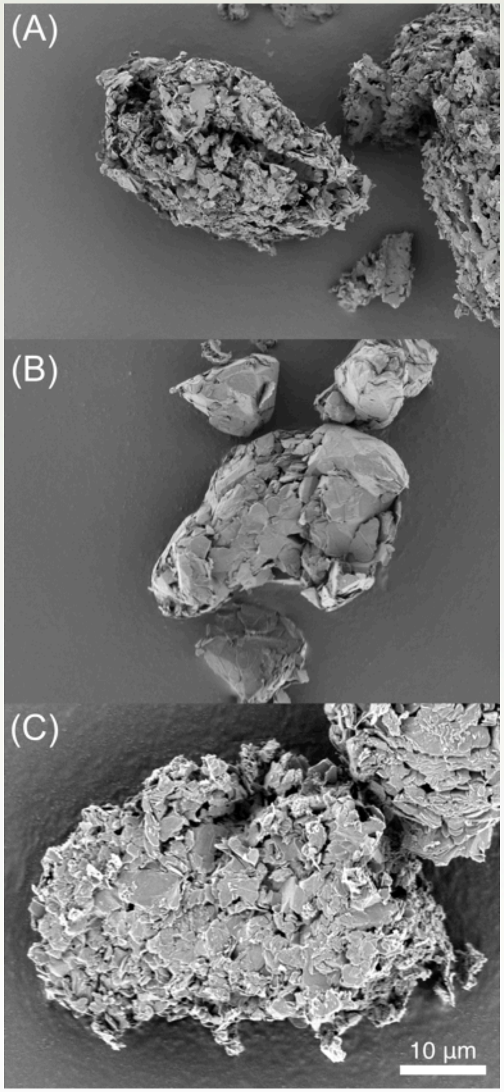
Potato Graphite



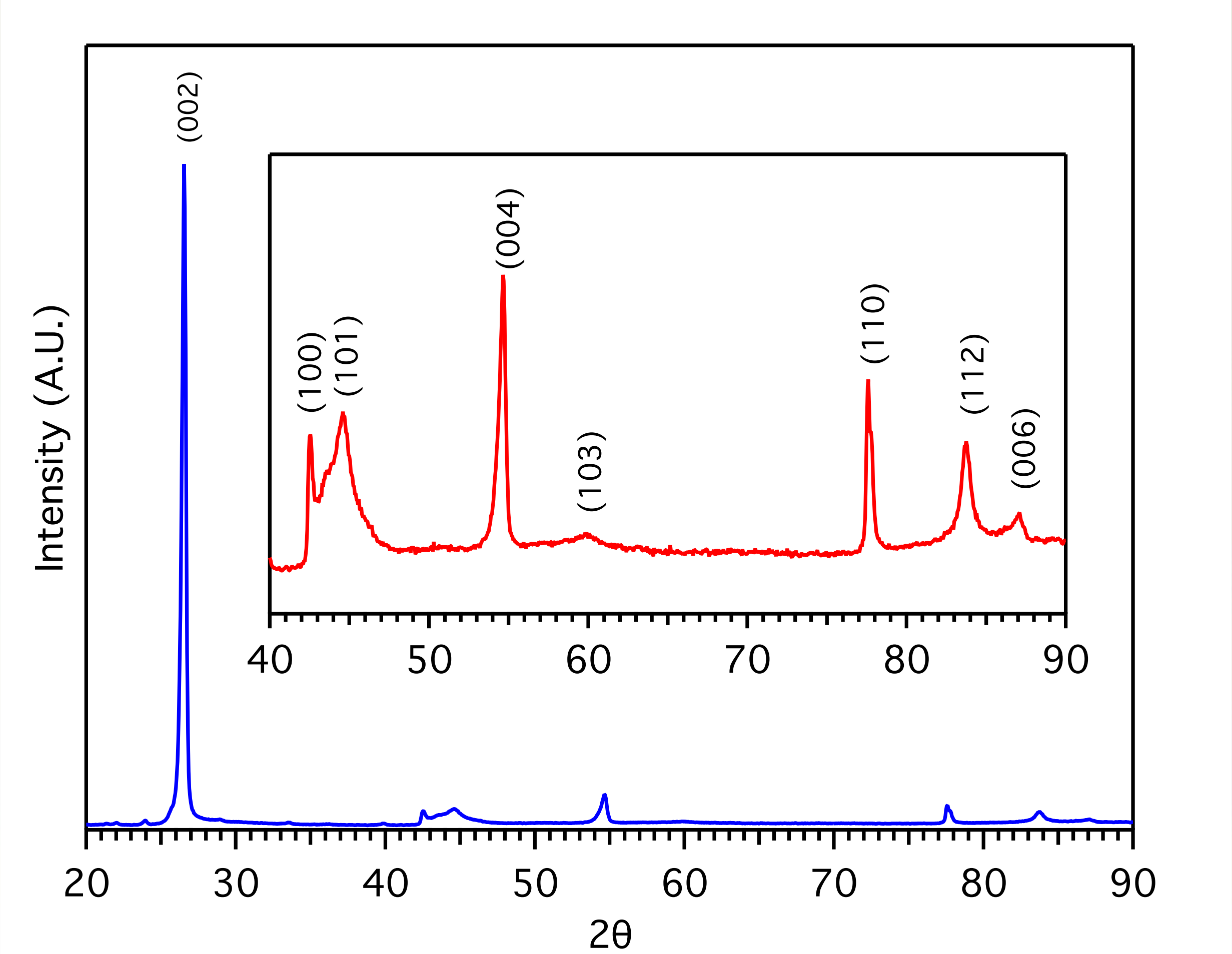
“Potato” Graphite from Biomass

Graphite From Biomass

- ~ 5 μm Fe
- Hitachi MagE3
- ~ 5 μm Co

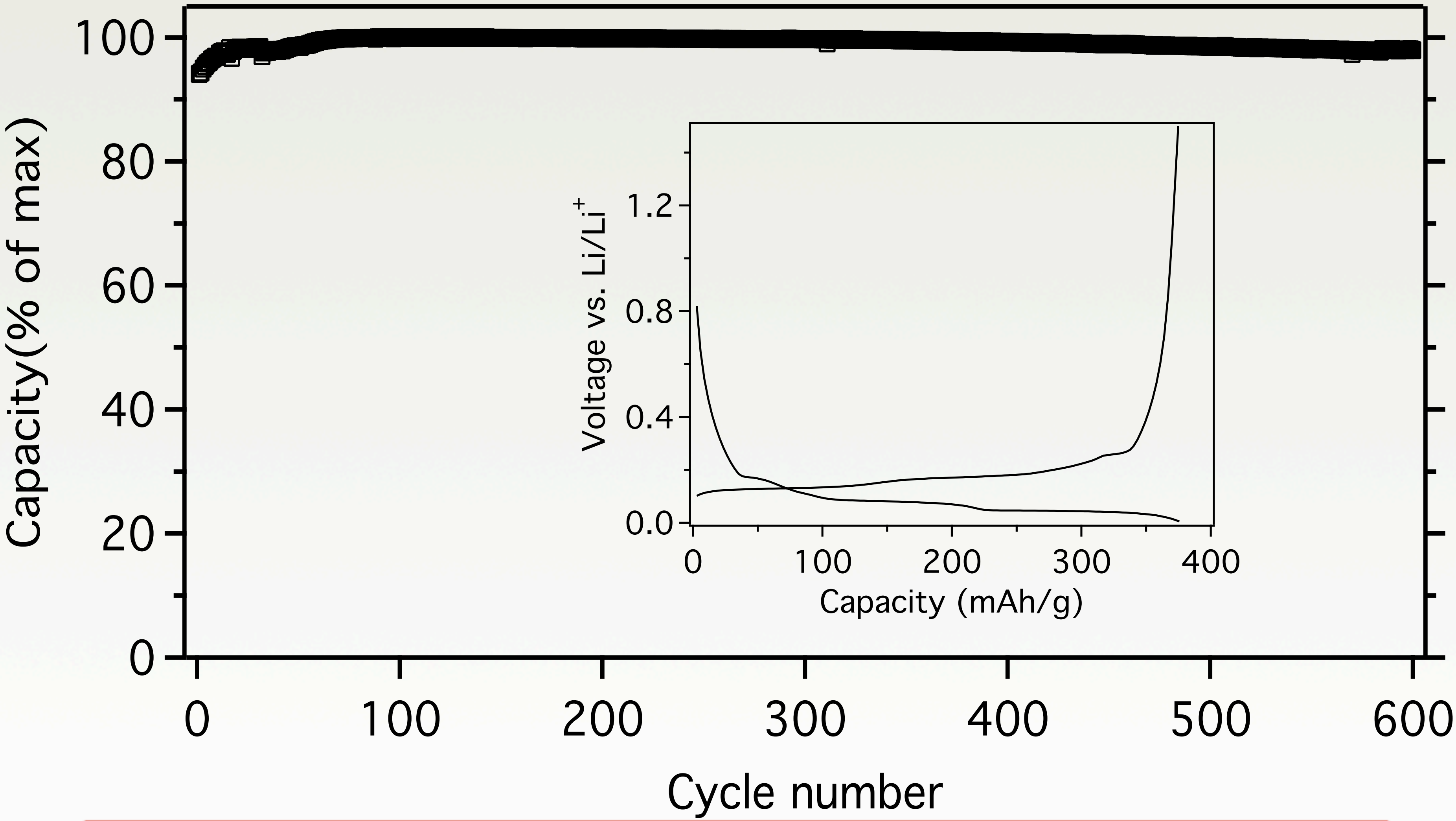


X-ray Diffraction



Nearly as crystalline as Sri Lanka lump graphite

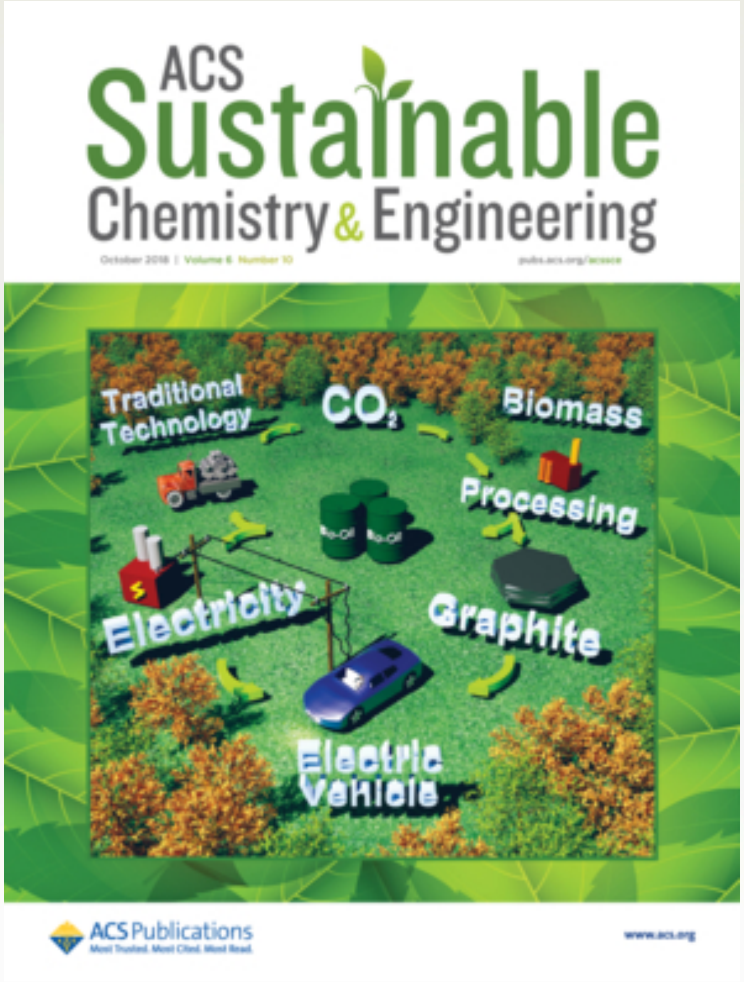
Biomass-graphite Li-ion Performance



Excellent capacity retention > 350 mAh/g

Graphitizing Non-Graphitizable Carbons

- Fe metal catalyst
- High Yield (95.7%, 0.25 kg/kWh)
- High Purity (> 99.95% carbon)
- High crystallinity
- High capacity (350 – 370 mAh/g)
- “Green” Chemistry
- Energy Production Exceeds Input
- Inexpensive



Coal

- **Derived from biomass**
- Lignite (25 – 30% C)
- Subbituminous (35 – 40% C)
- Bituminous (45 – 86% C)
- Anthracite (86 – 97% C)

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

Coal vs Biomass

Advantages (Lignite)

- Cheaper
  - ~ 6.7 fold decrease
- Supply Chain

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

Project Status
&
Accomplishiments

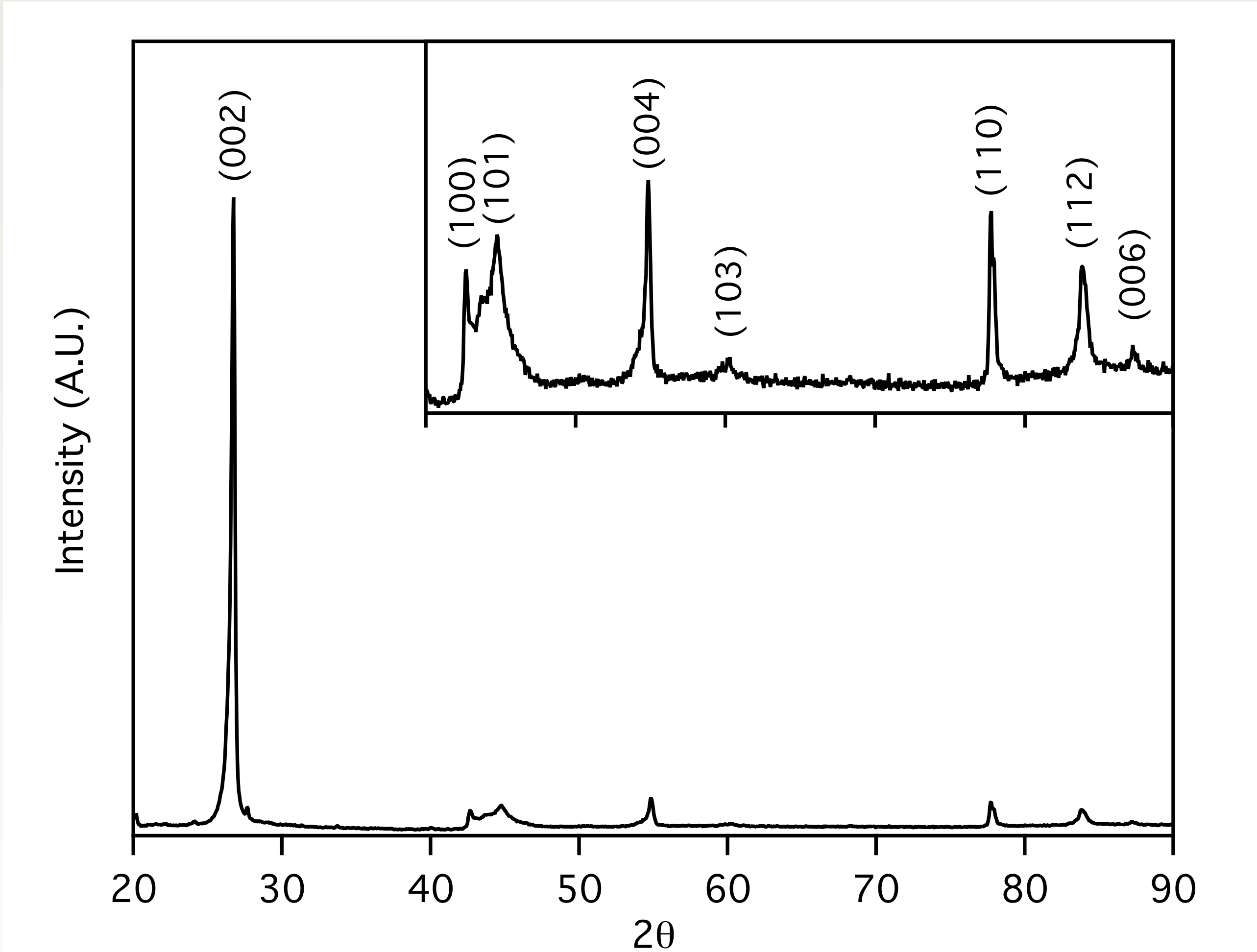
Feedstock

- 16 lignite samples
  - Multiple kg each
  - Impurity profiles vary
  - Macerals vary
- North Dakota lignite (high Na/Ca)
- Mississippi lignite – (high mineral)
- Bituminous & antharcite

Preliminary Findings

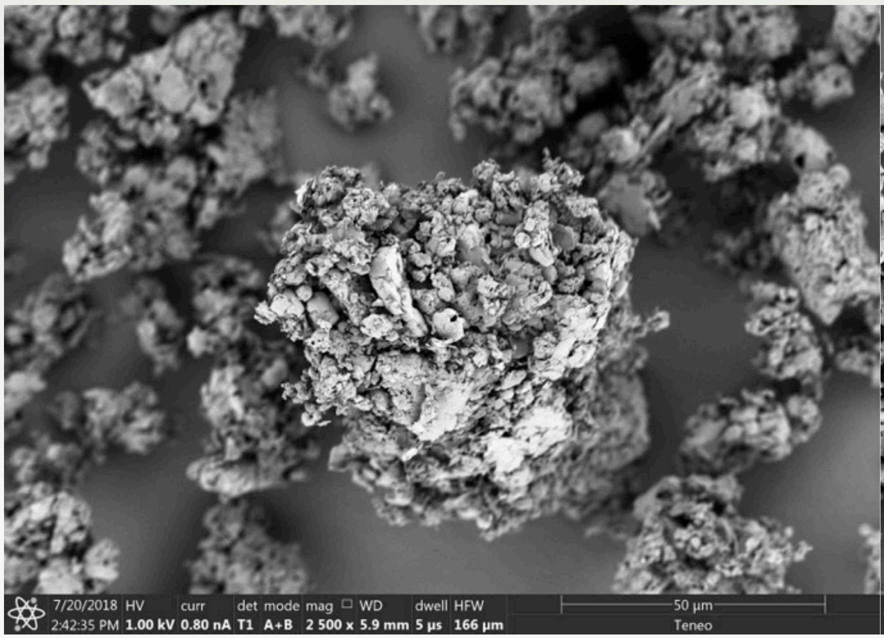
- Lignite
  - All of the North Dakota samples graphitize
  - Mississippi samples graphitize with low yield (25 – 33% at 200 W laser power)
- Bituminous sample does not graphitize – despite it being a “graphitizable carbon”
- Anthracite sample does not graphitize

Graphite From ND Lignite

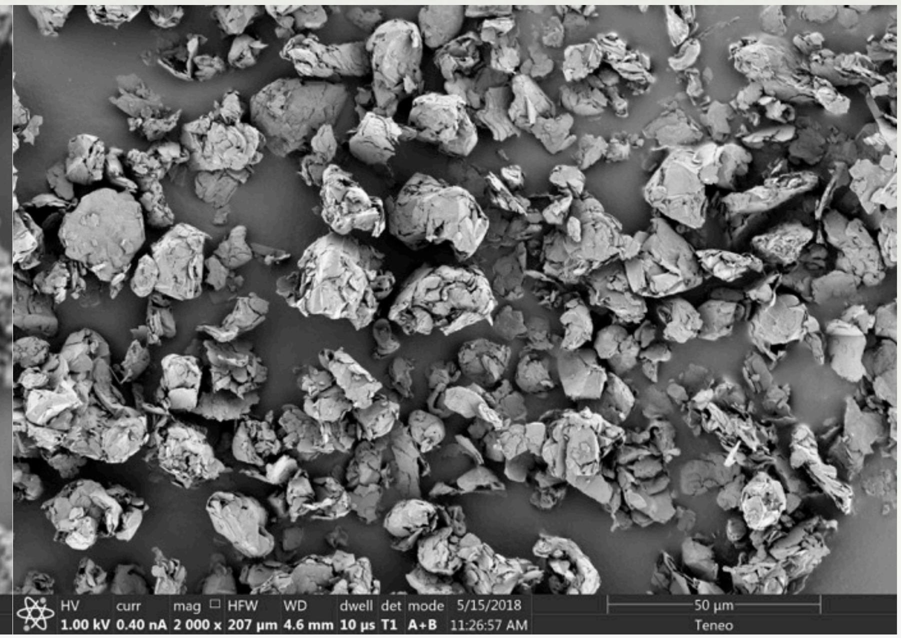


Highly Crystalline Graphite from Lignite

Graphite From ND Lignite - Potato

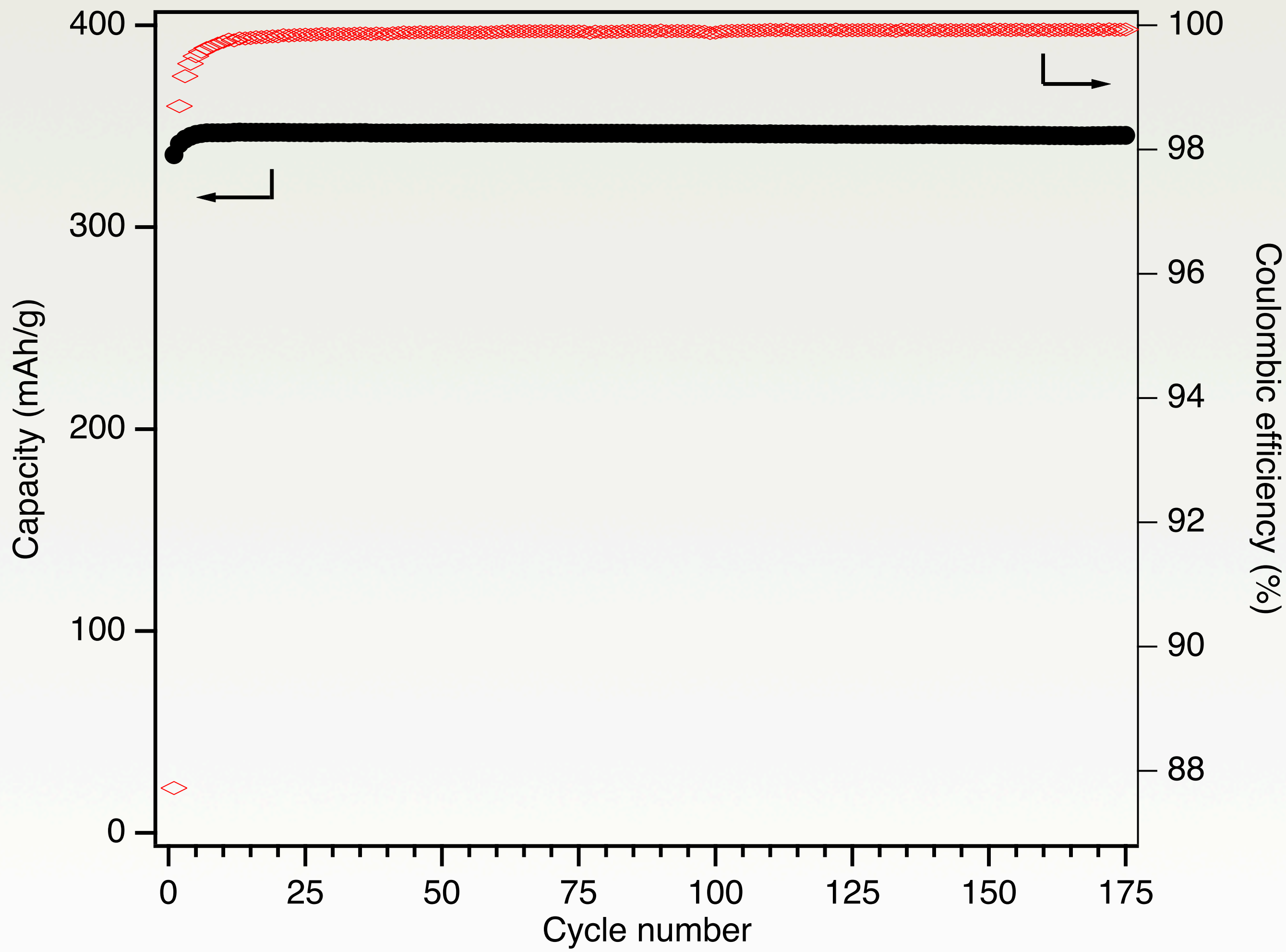


Graphite from Lignite



Hitachi MagE3 Graphite

ND Lignite Graphite – Li-ion Battery



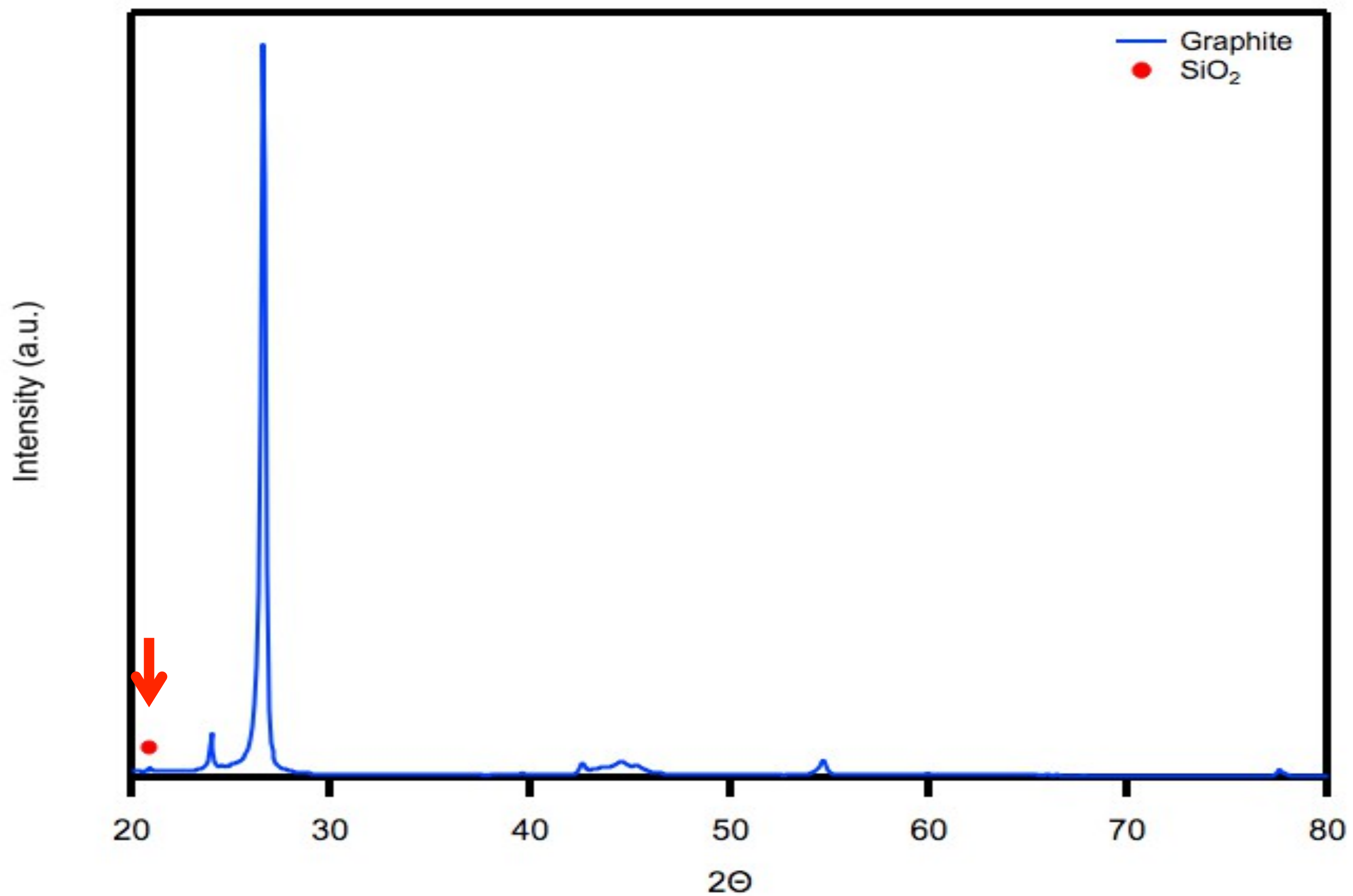
347 mAh/g, 88% 1st Cycle CE

Graphite from Coal - Performance

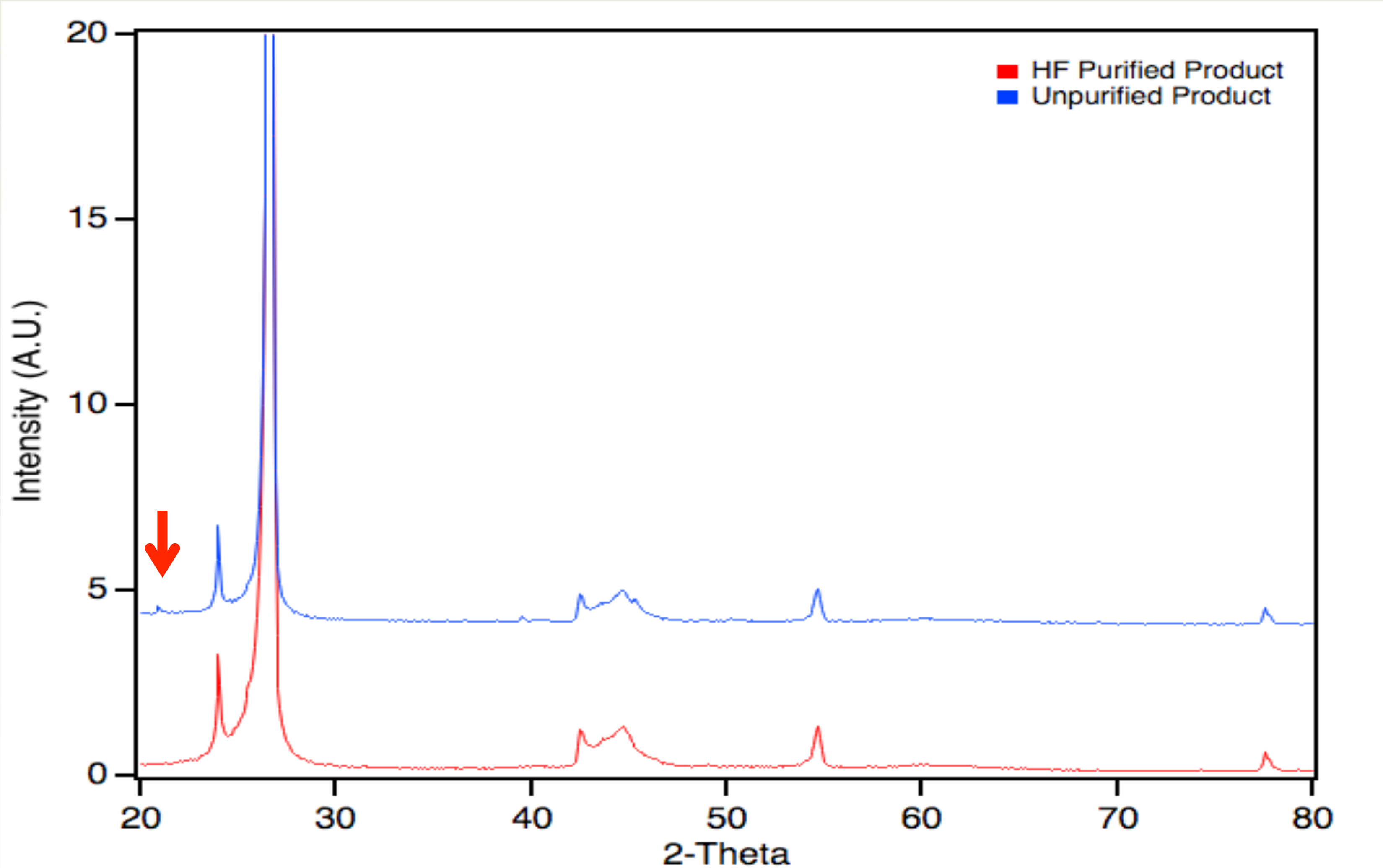
- Commercially viable capacity (347 mAh/g)
- Good capacity retention Coulombic efficiency
  - Long term 99.9% +
  - 1^{st} cycle 88% (low)
- Purity
  - 99% (low)

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

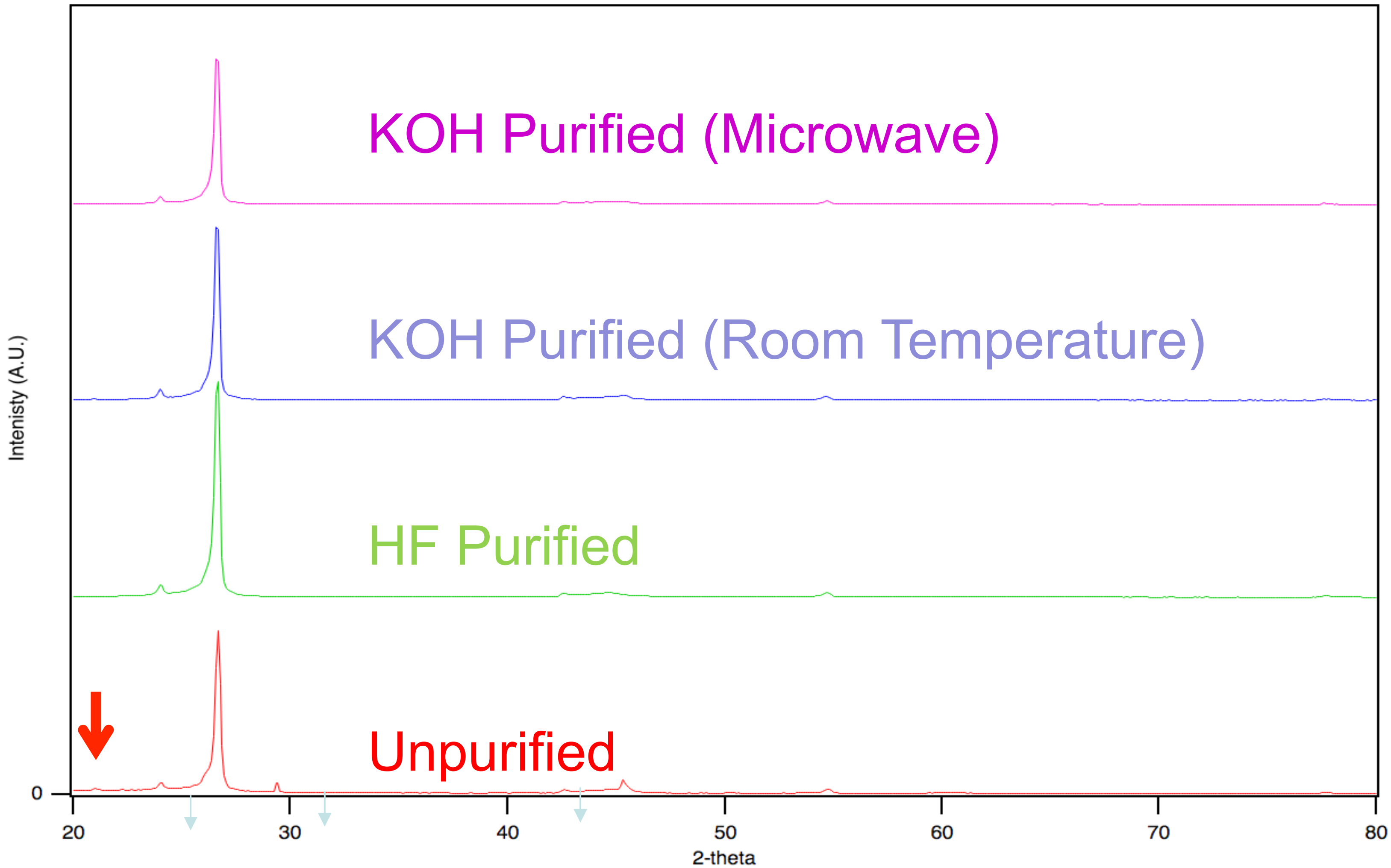
ND Graphite - SiO_2



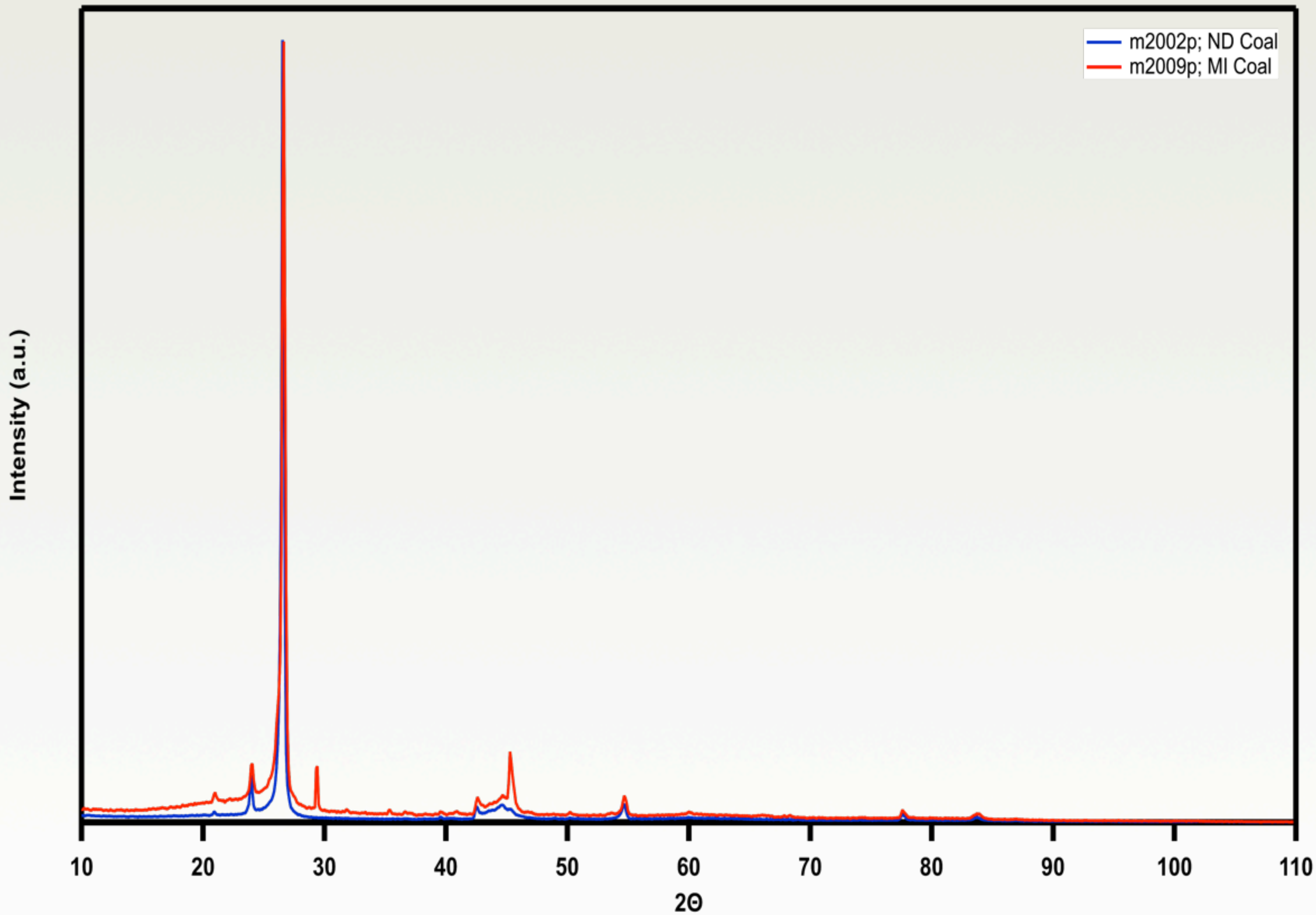
ND Graphite Purification



ND Graphite Purification

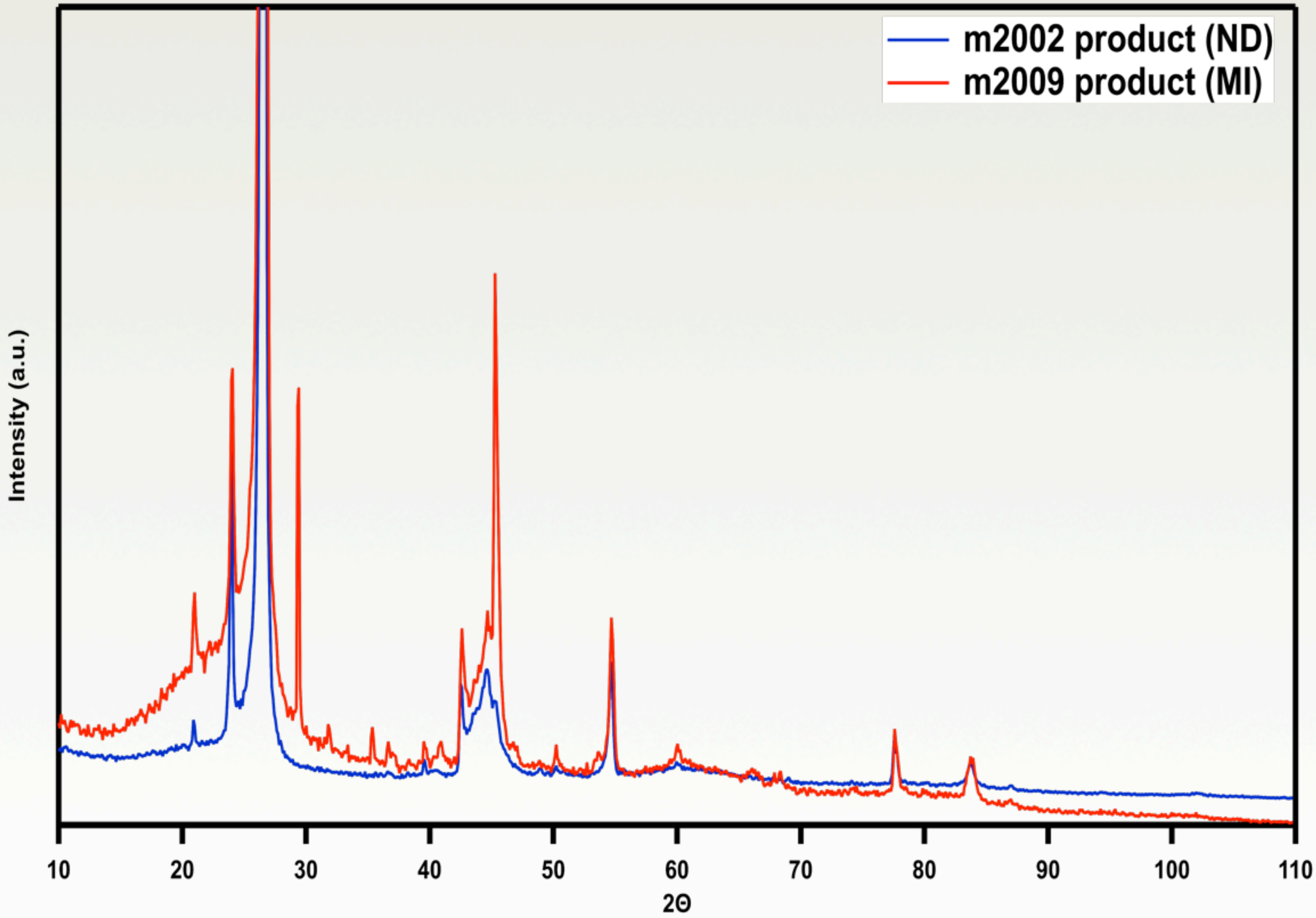


ND vs MS Coal



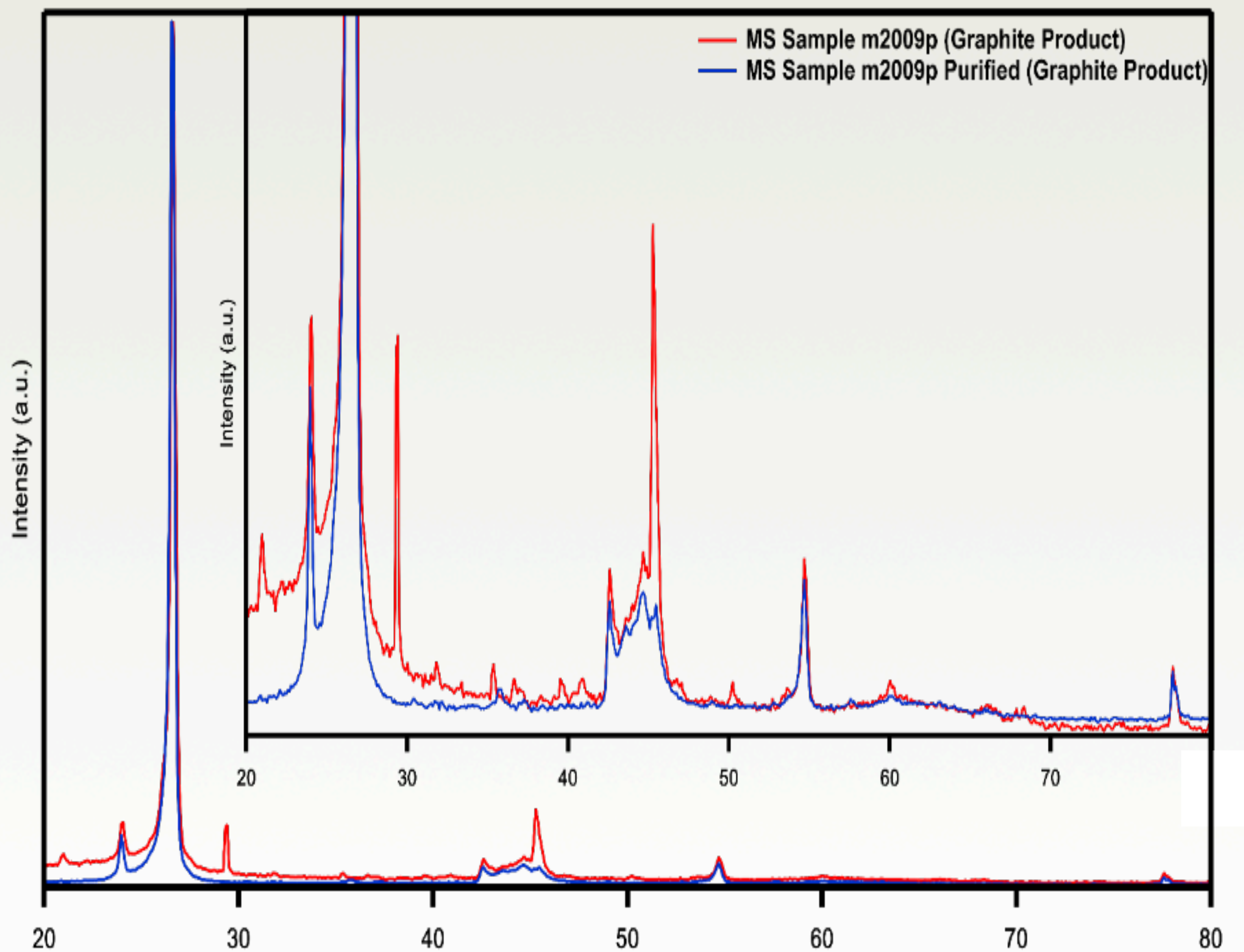
m2002p; ND Coal
m2009p; MI Coal
Intensity (a.u.)
10
20
30
40
50
60
70
80
90
100
110
2Θ

ND vs MS Coal

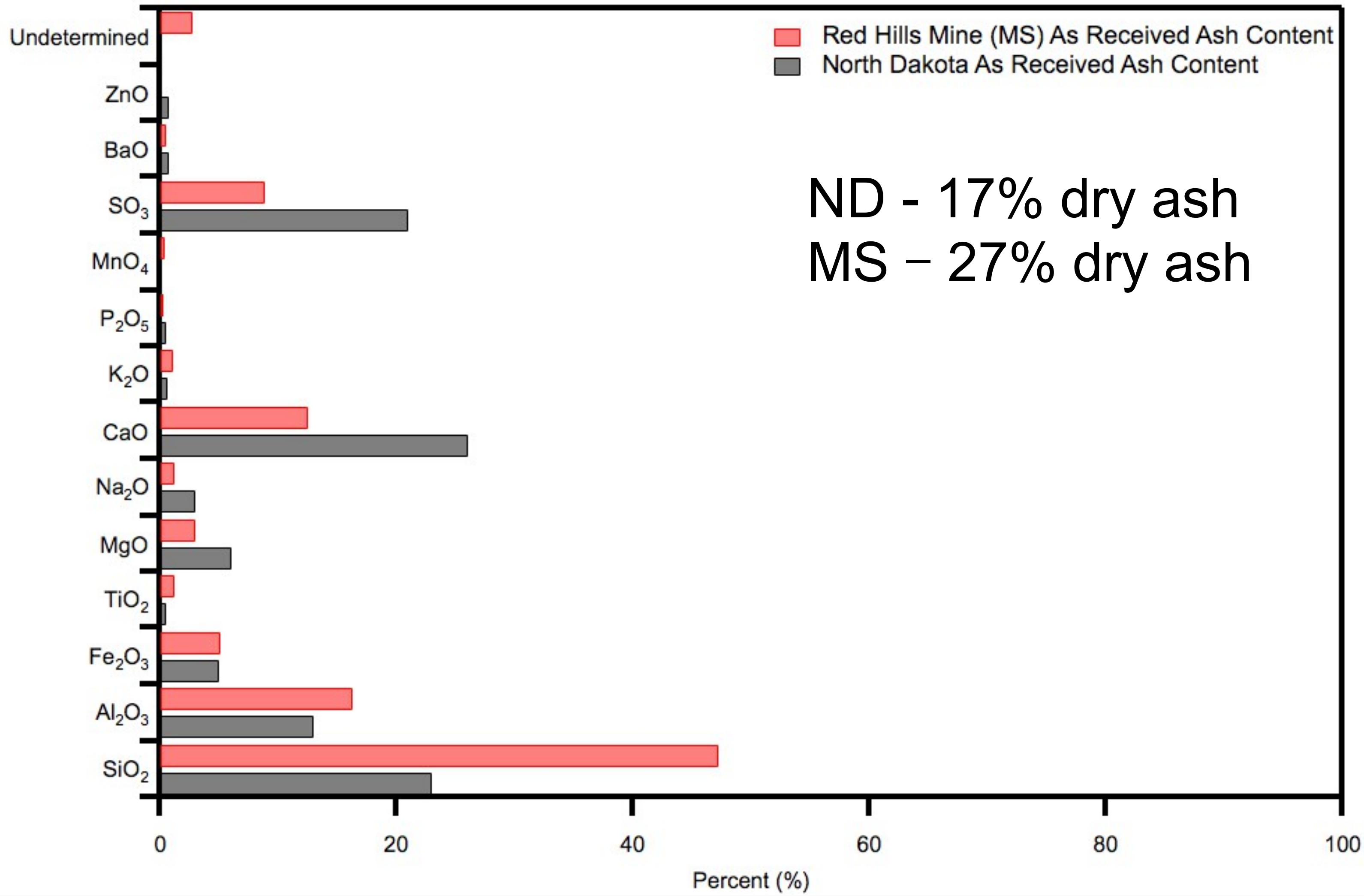


m2002 product (ND)
m2009 product (MI)
Intensity (a.u.)
10
20
30
40
50
60
70
80
90
100
110
2Θ

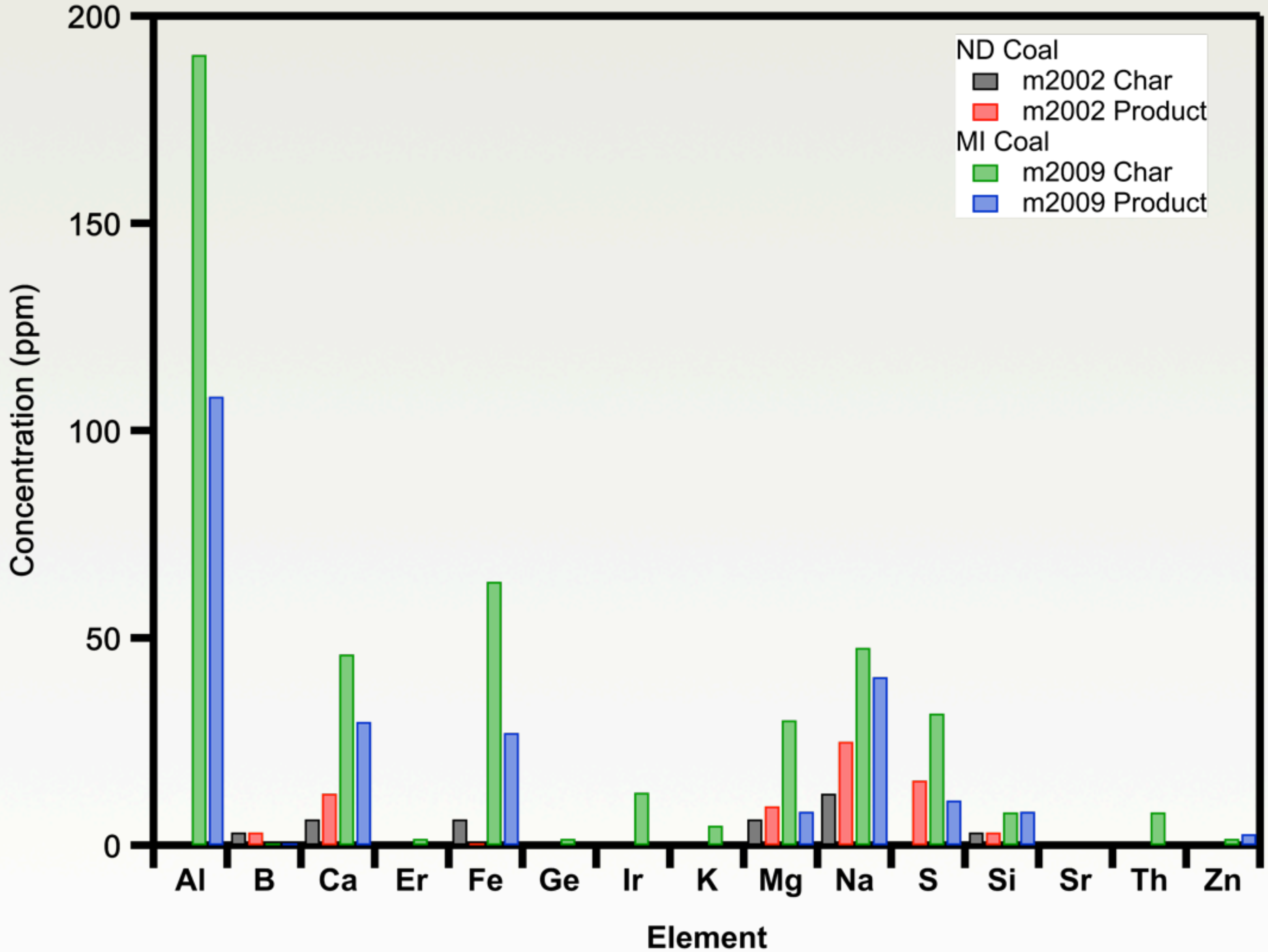
MS Graphite Purification



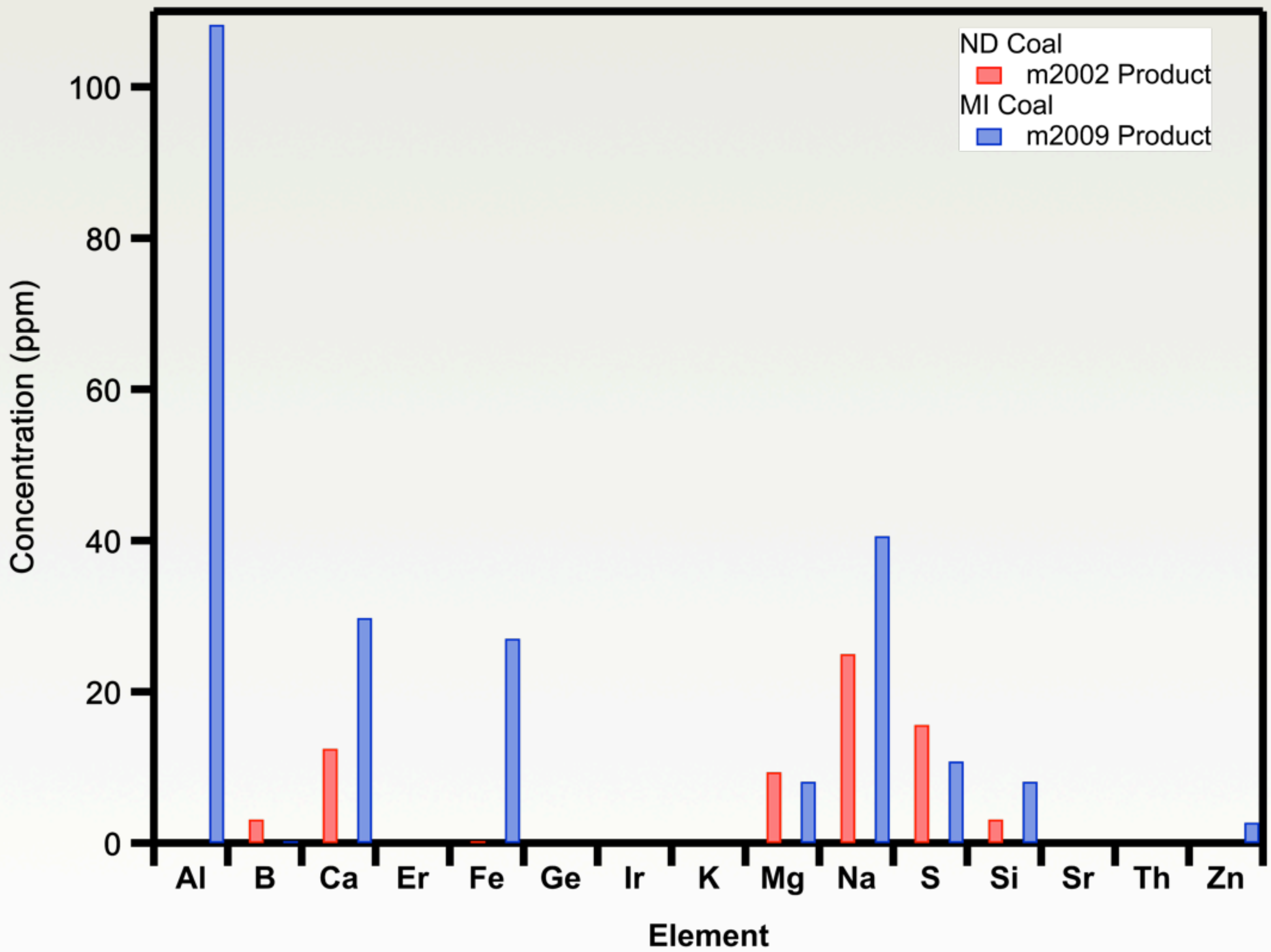
Lignite Impurities



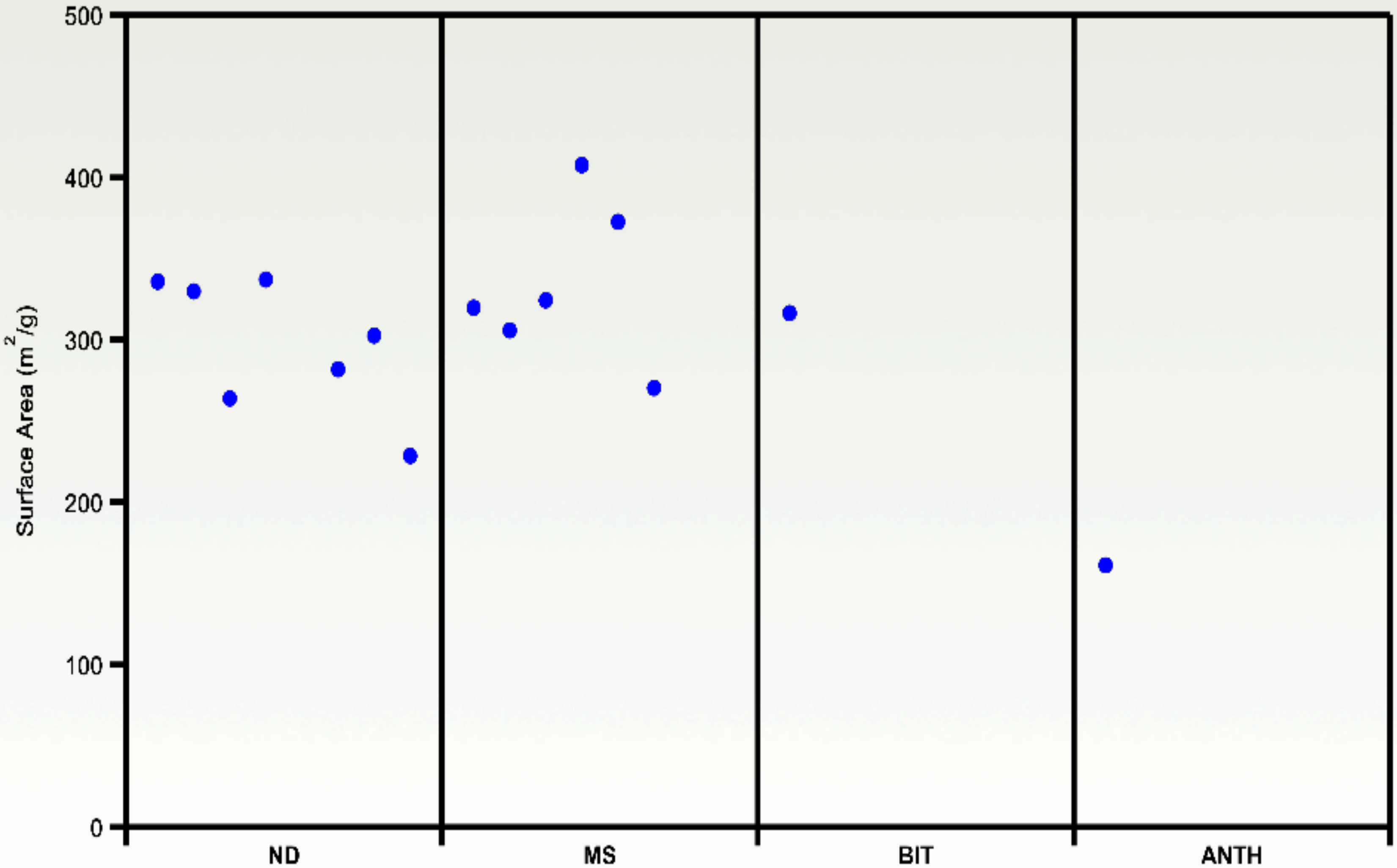
ND vs MS Elemental Analysis



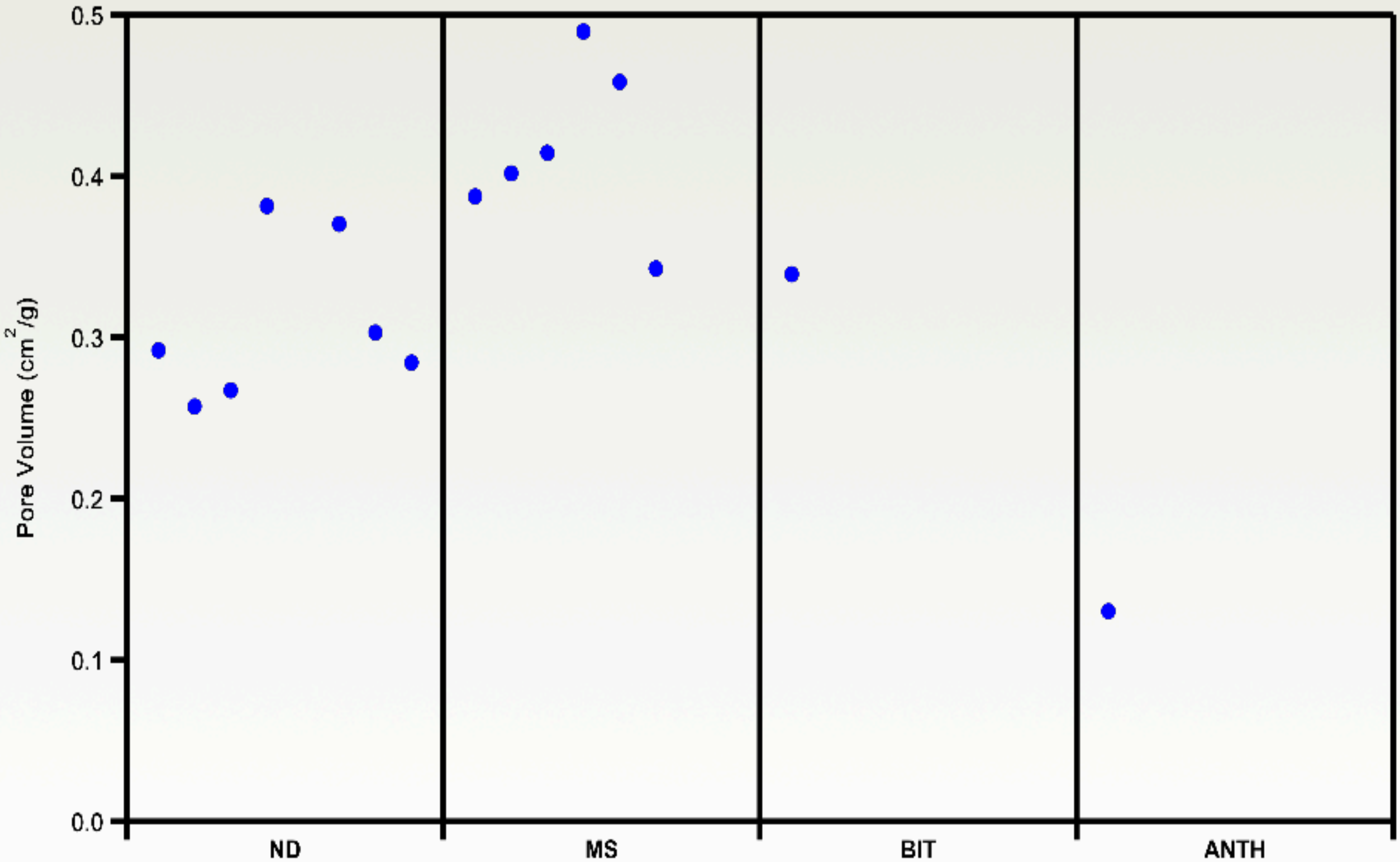
ND vs MS Elemental Analysis



Coal Char Surface Area



Coal Pore Volume



Coal Char Average Pore Diameter

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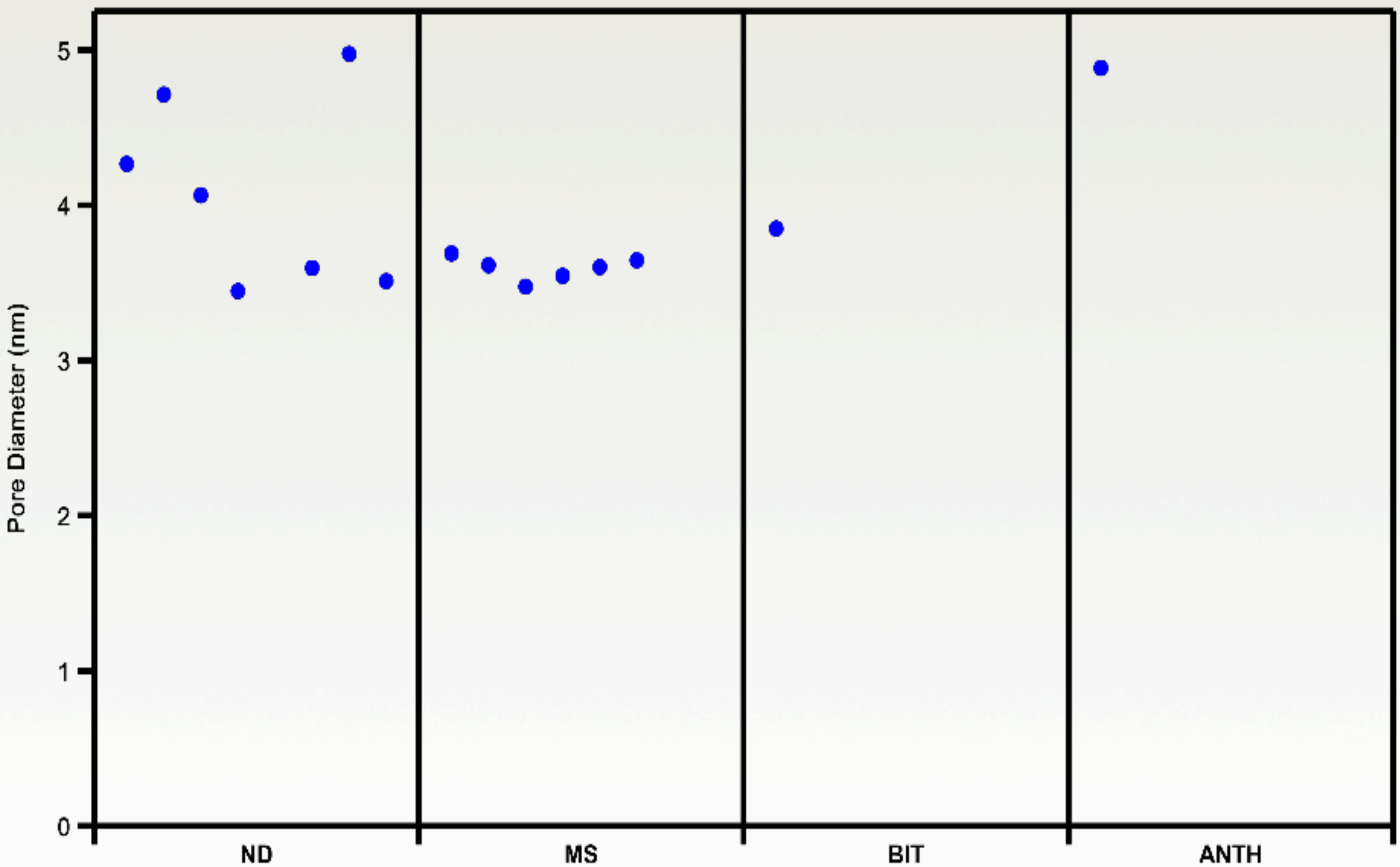

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Concluding Remarks

- Successfully produced high grade graphite from ND sourced lignite
- 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
- Purification of graphite possible

Next Steps

- Investigate differences in feedstock graphitization
  - Lignite – ND vs MS (lignite/char purification)
  - Bituminous/Anthracite (CO_2 porosity)
- Improve purity
- Investigate potential yield
- Optimizing composition & processing (mixing, forming,composition & charring)
- Optimize residence time, laser power, wavelength
- Optimize flake & potato size
- Translate from batch to continuous production