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

NETL Advanced Coal Processing Project Review Meeting
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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
- 1^{st} cycle Coulombic efficiency > 85%
- Production goal > 5 g/h
- Lithium-ion cell cycle life > 100 cycles

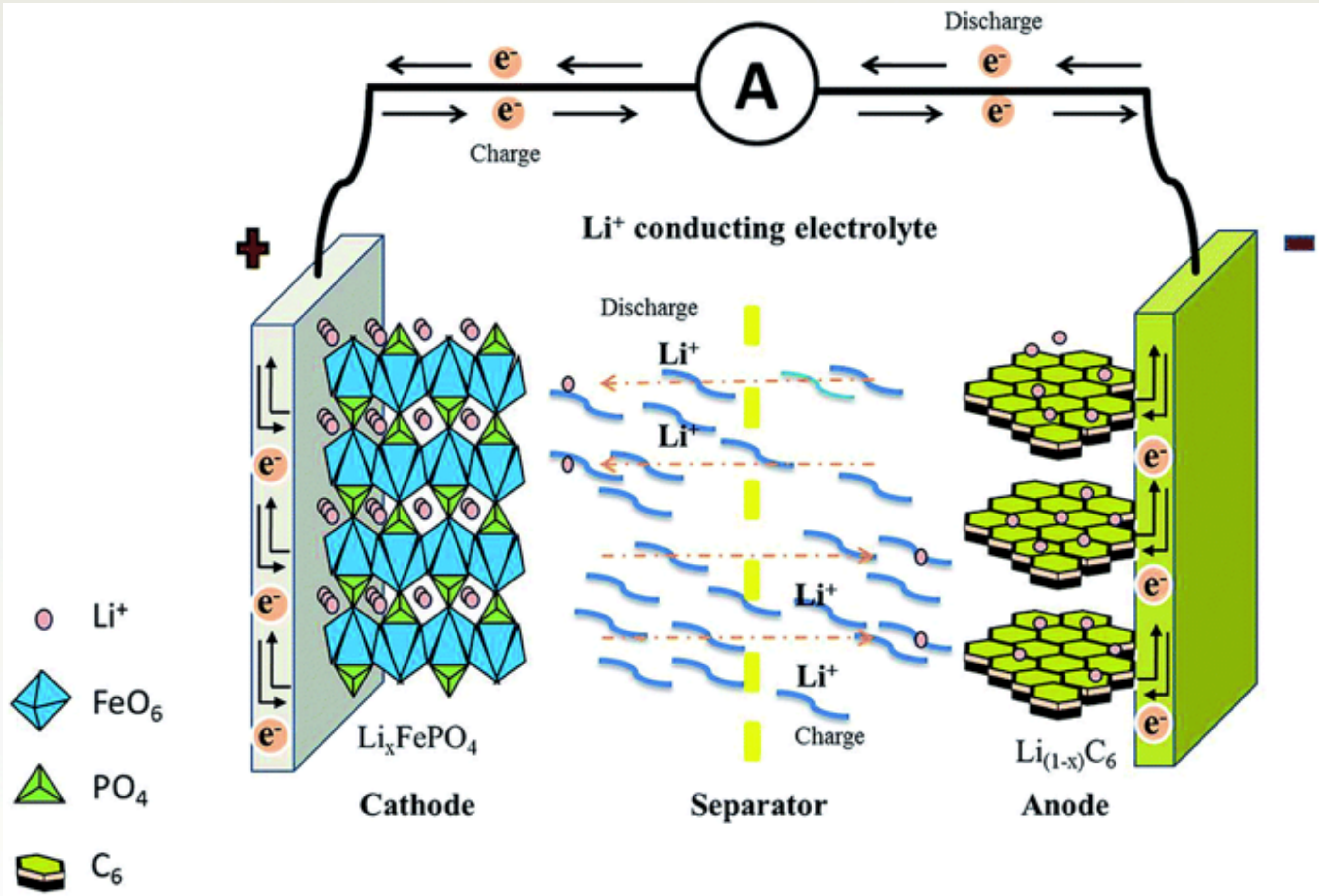
Validation

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

Technology Benchmarking

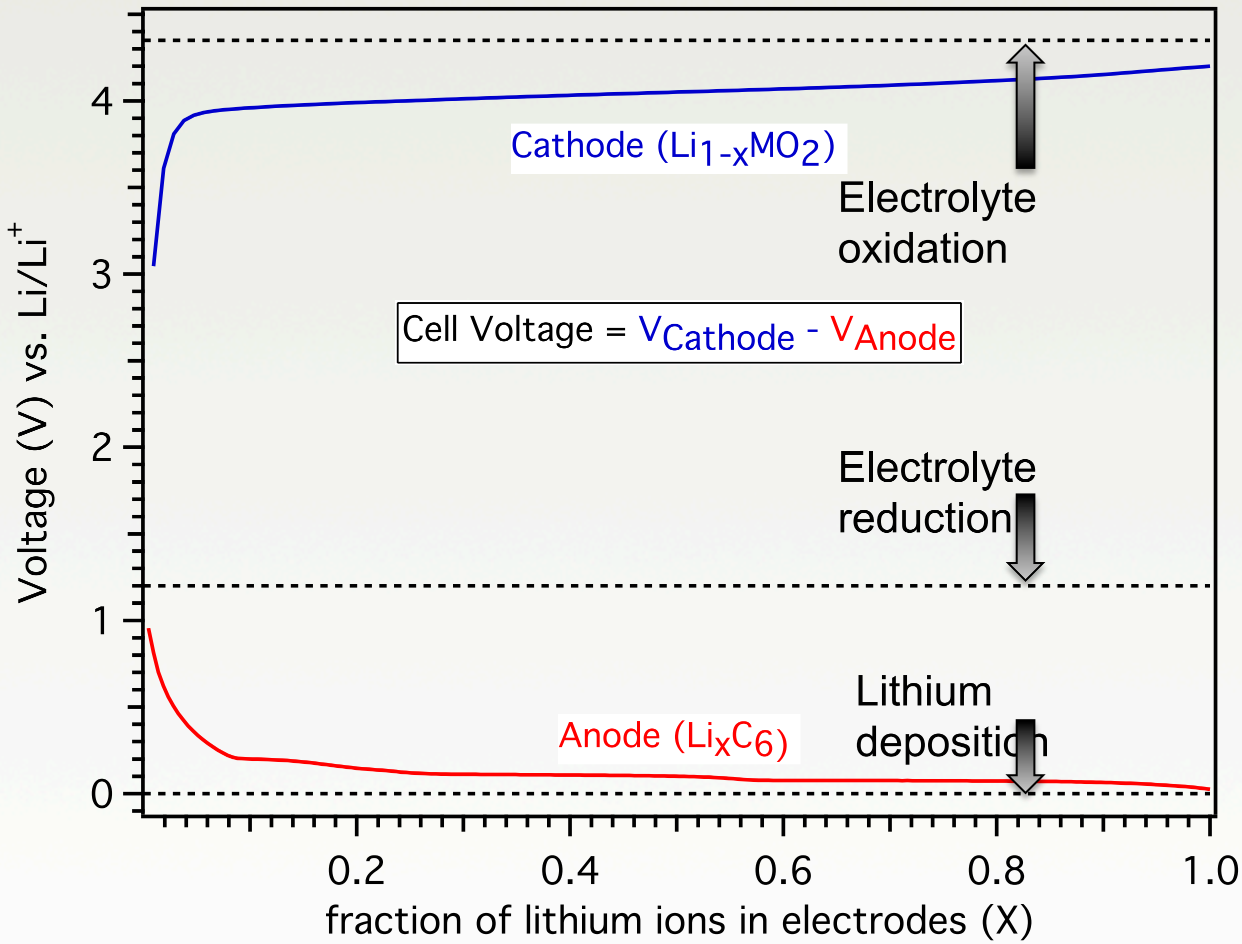
- Li-ion batteries require very high quality graphite (expensive)
- Natural flake graphite purified to lithium ion battery grade (~99+% C, coated “potato”): $14,870/ton
- Synthetic graphite: $18,000/ton

Li-ion “Rocking Chair” Battery



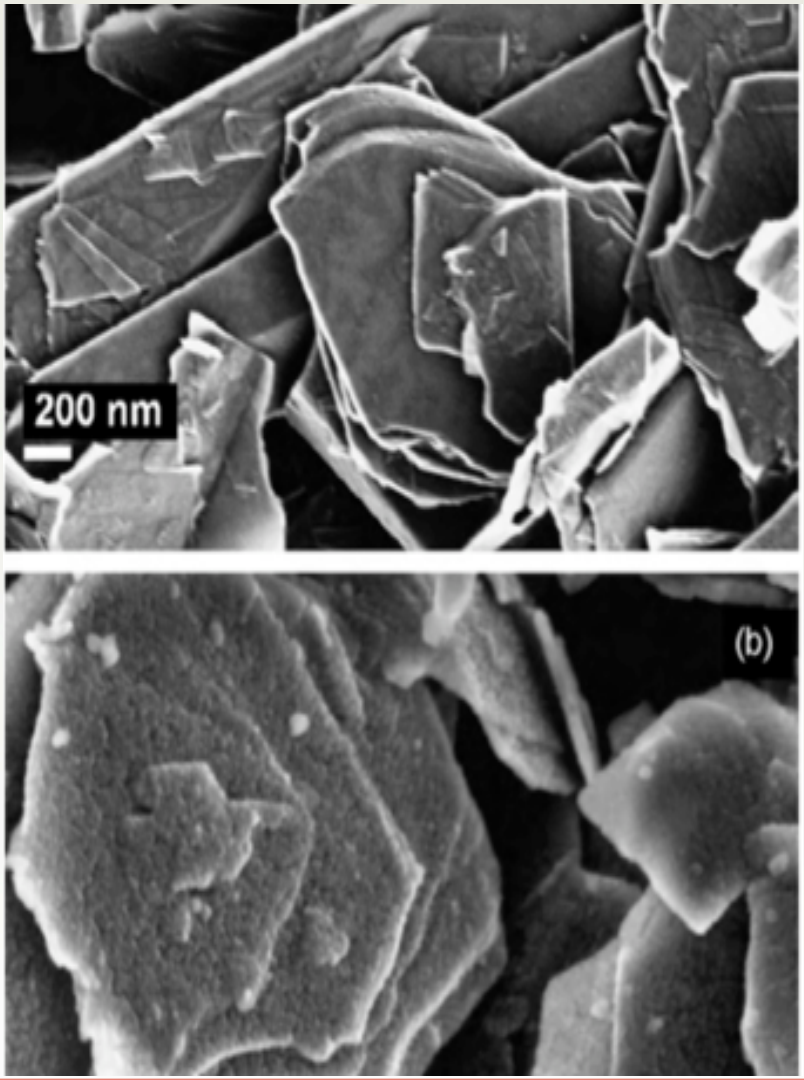
Zhang X. et al. *Polymer Reviews*. 2011, **51**, 239-264

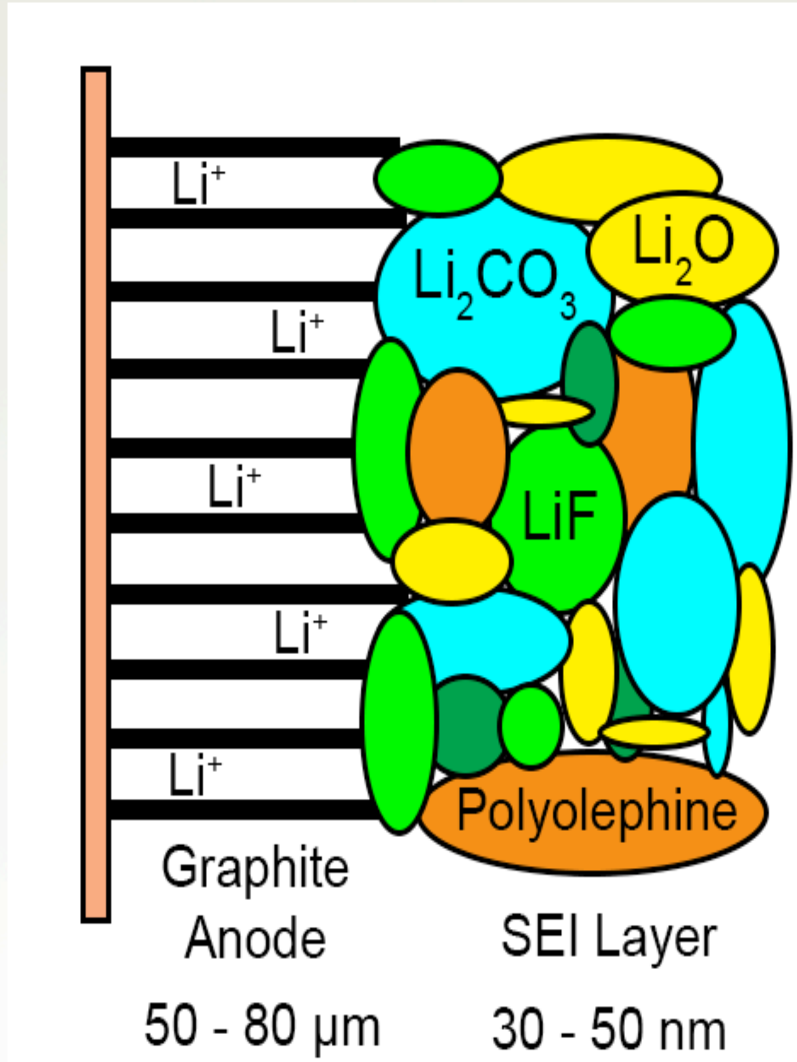
Li-ion Cells



4
3
2
1
0
Voltage (V) vs. Li/Li+
Cathode (Li1-xMO2)
Electrolyte oxidation
Cell Voltage = VCathode - VAnode
Electrolyte reduction
Lithium deposition
Anode (LixC6)
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

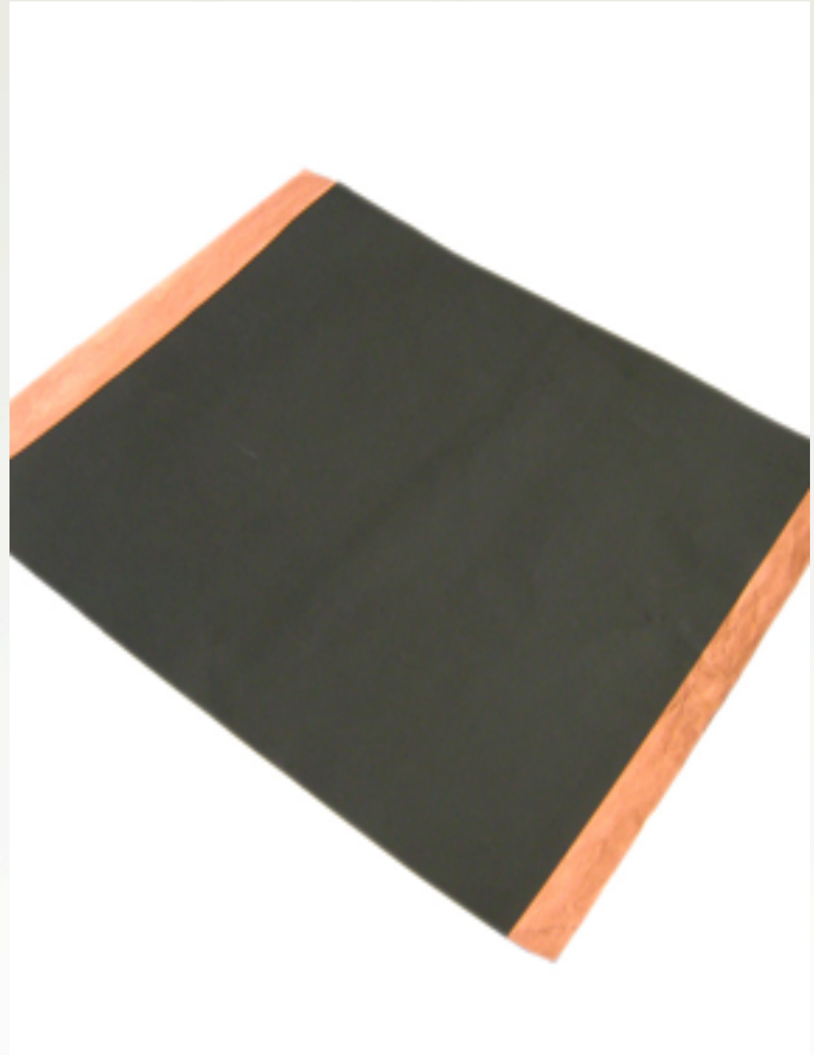
Coulombic Efficiency

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

- Loss of lithium from cathode
- Loss of electrolyte

Graphite – Commercial Li-ion Anodes

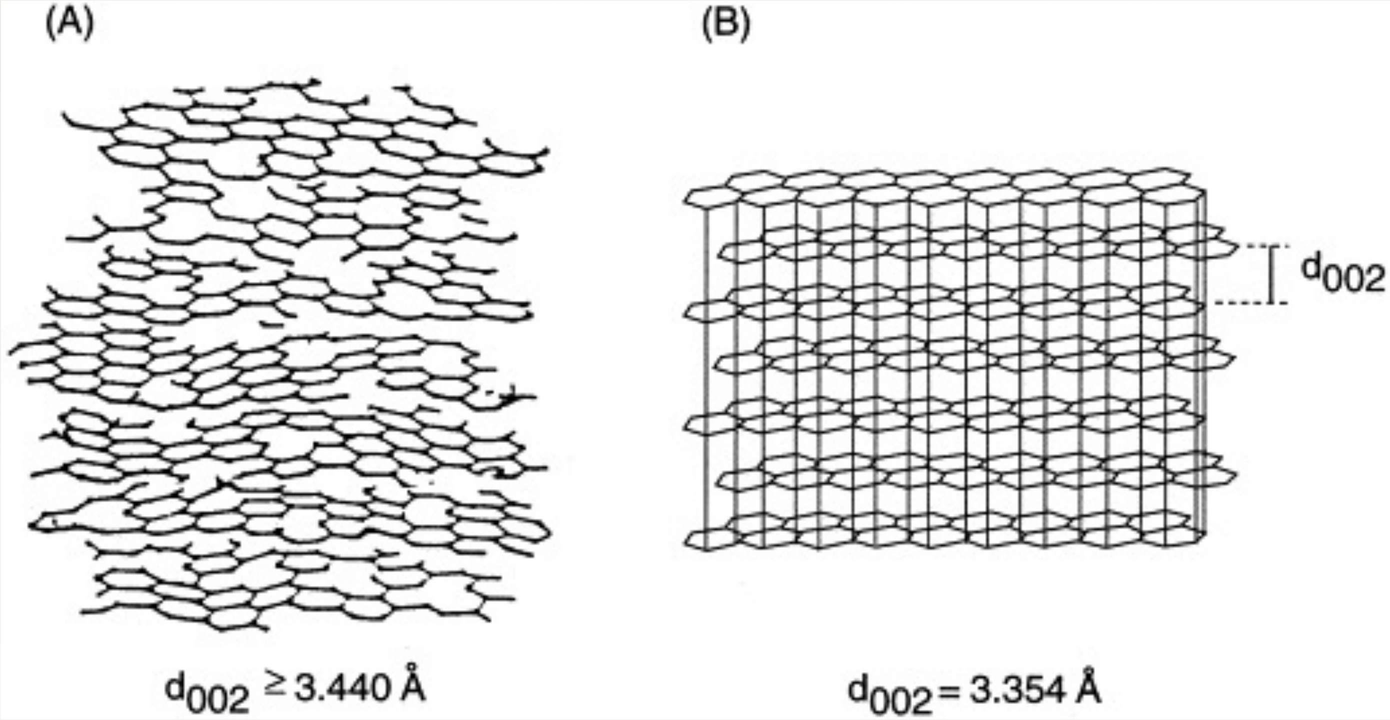
- Abundant and scalable
- Stable
- Safe & compatible
- Energy Dense
  - 372 mAh/g
  - 837 mAh/cm^3
- Long cycle life
- Cost
  - 15% of total battery cost
- High coulombic efficiency
  - >90% first cycle
  - Low surface area
- Entrenched technology



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

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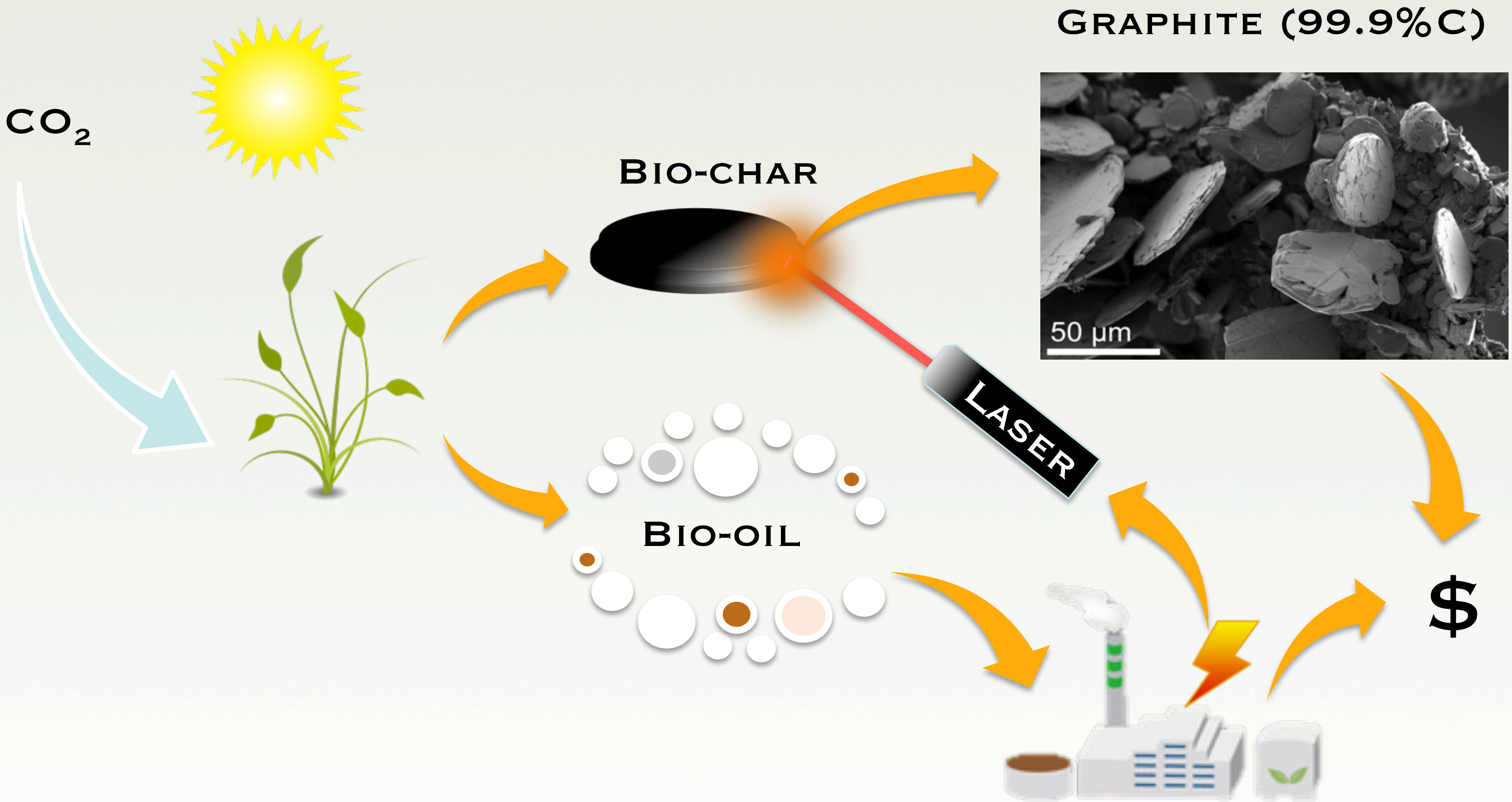
Graphite From Biomass



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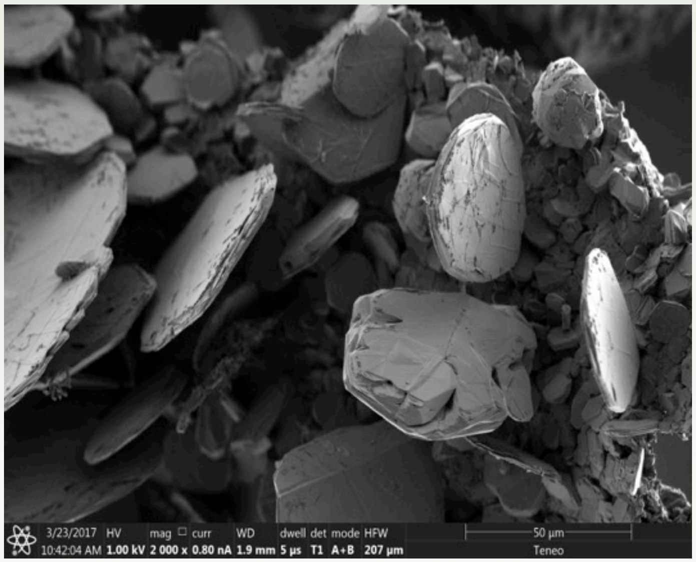
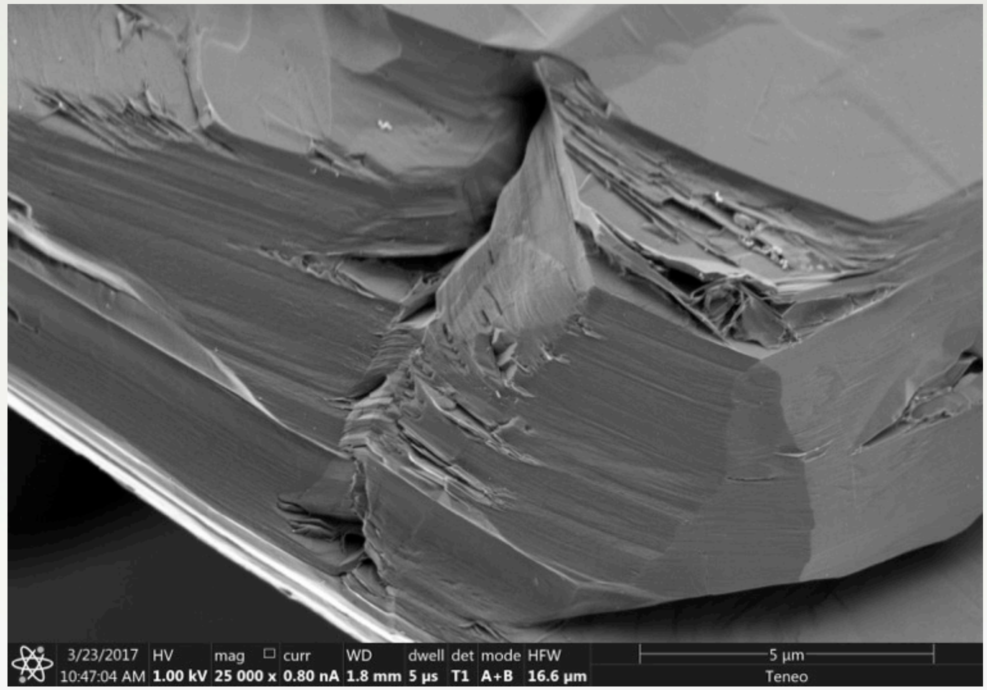
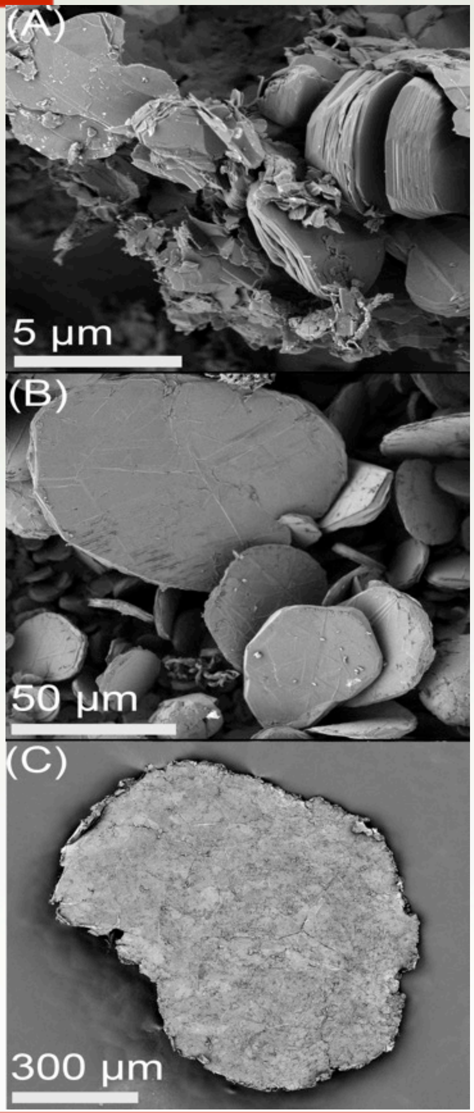
Graphite From Biomass





Graphite From Biomass

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



Potato Graphite

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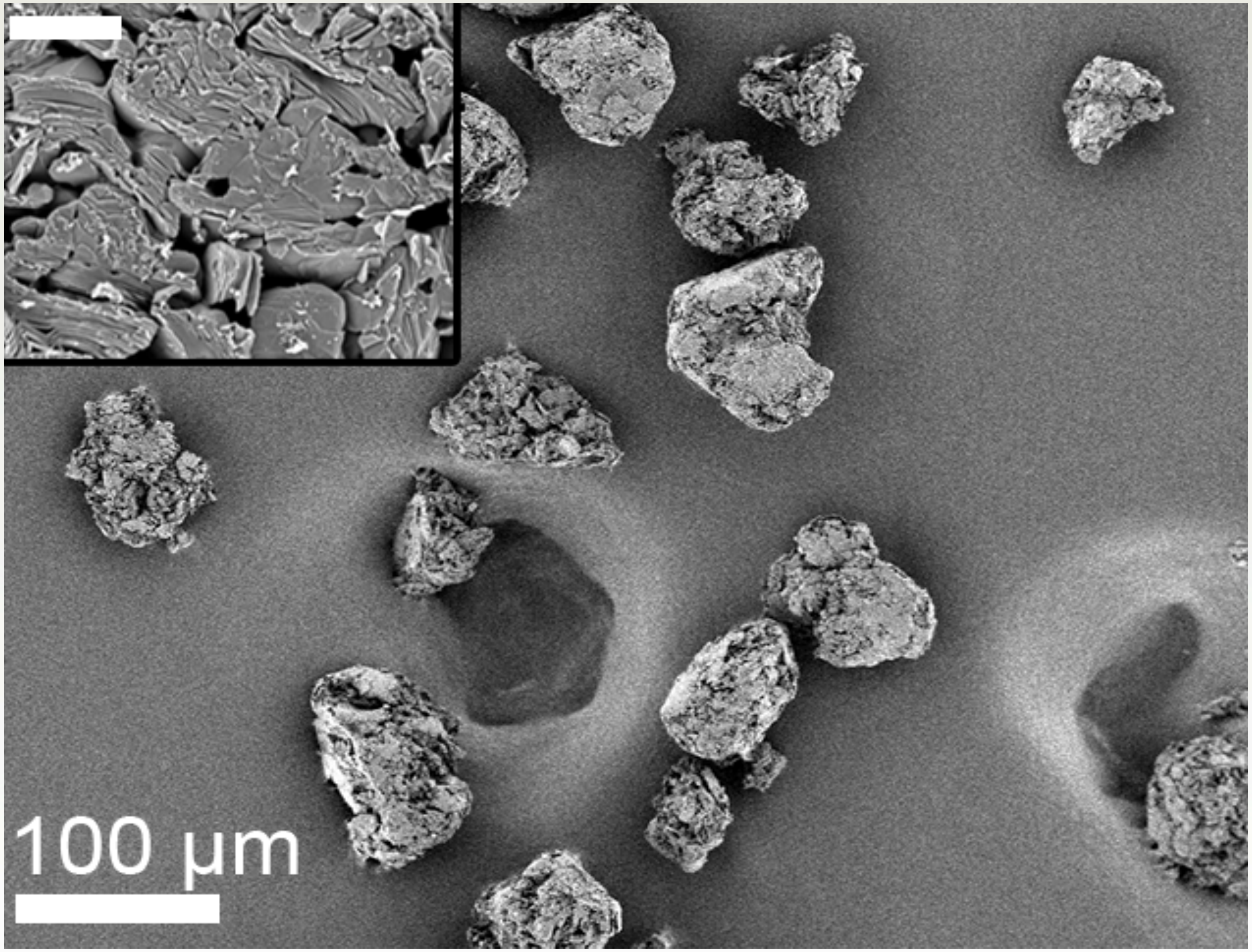

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"Potato" Graphite from Biomass

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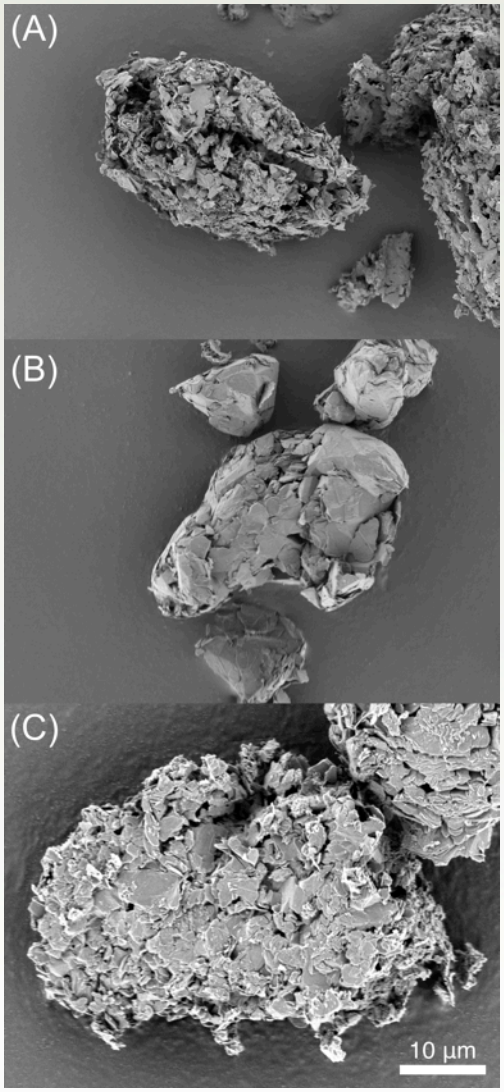
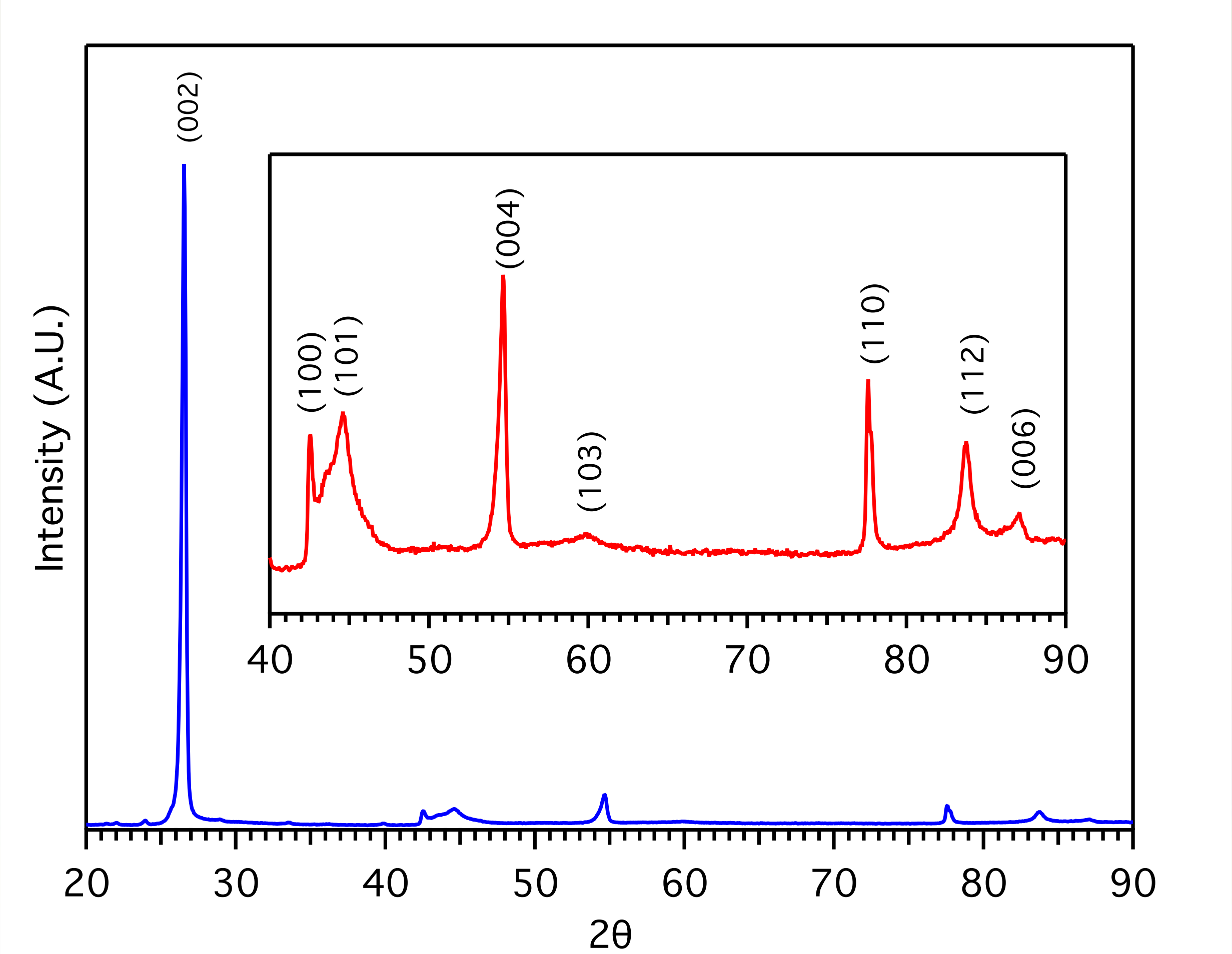
Graphite From Biomass

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

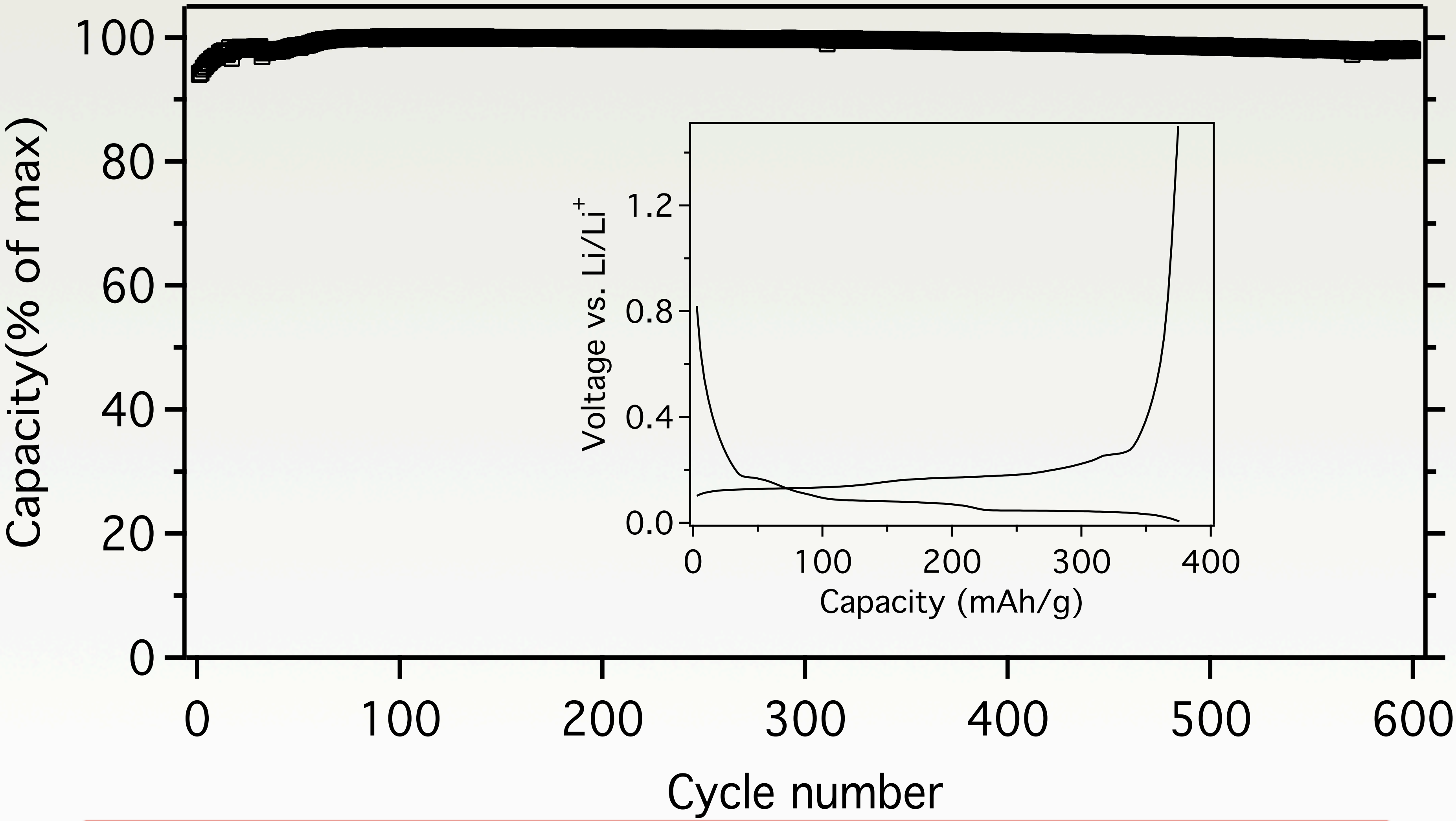


X-ray Diffraction



Nearly as crystalline as Sri Lanka lump graphite

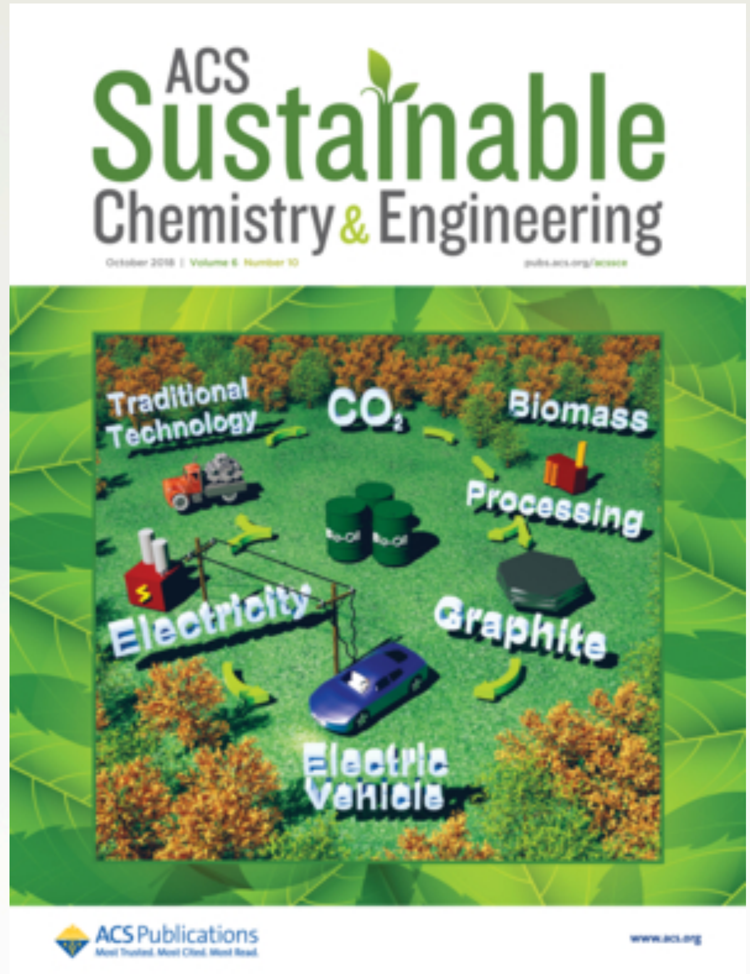
Biomass-graphite Li-ion Performance



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

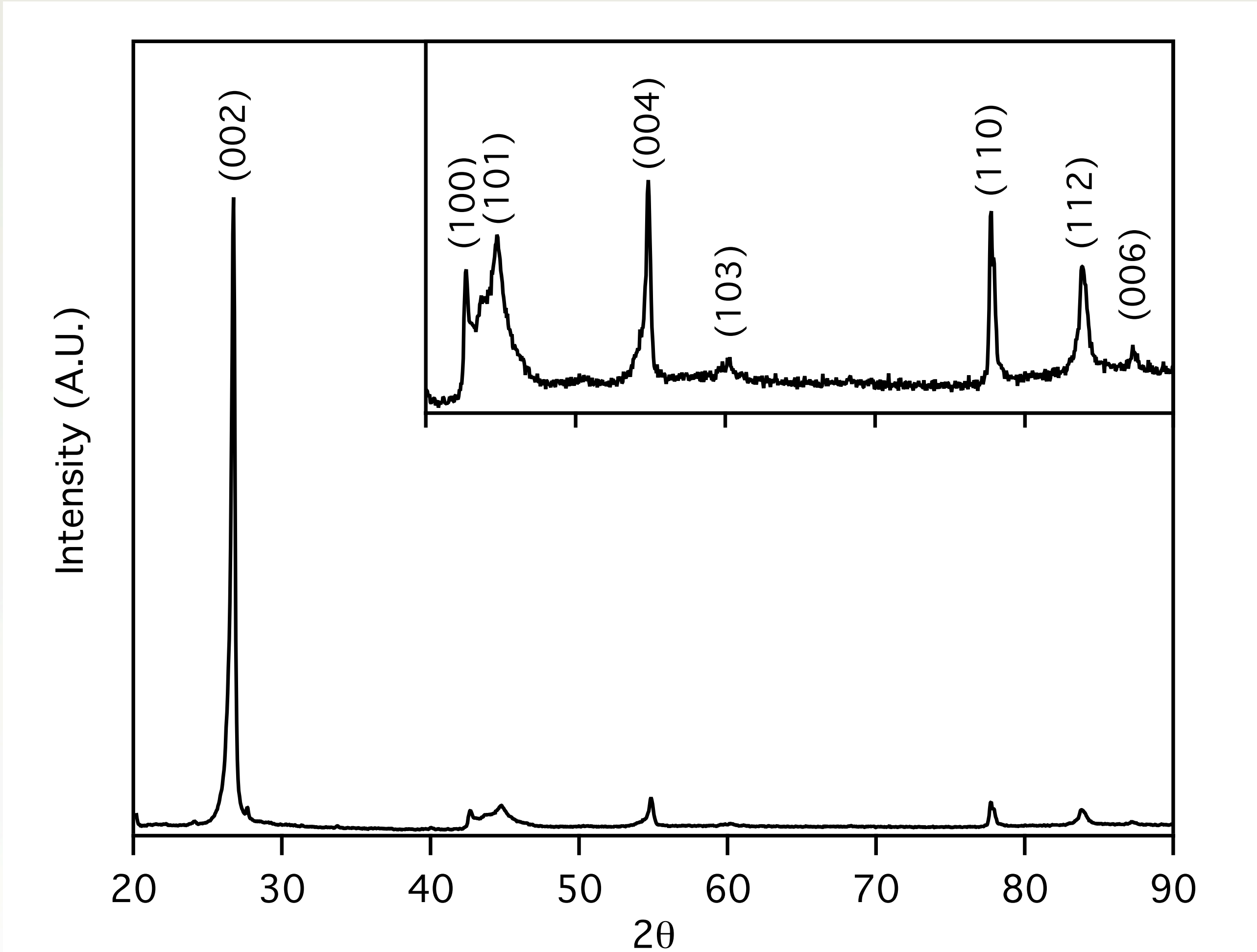
Feedstock

- ❑ 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
  - None of the Mississippi graphitize
- 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

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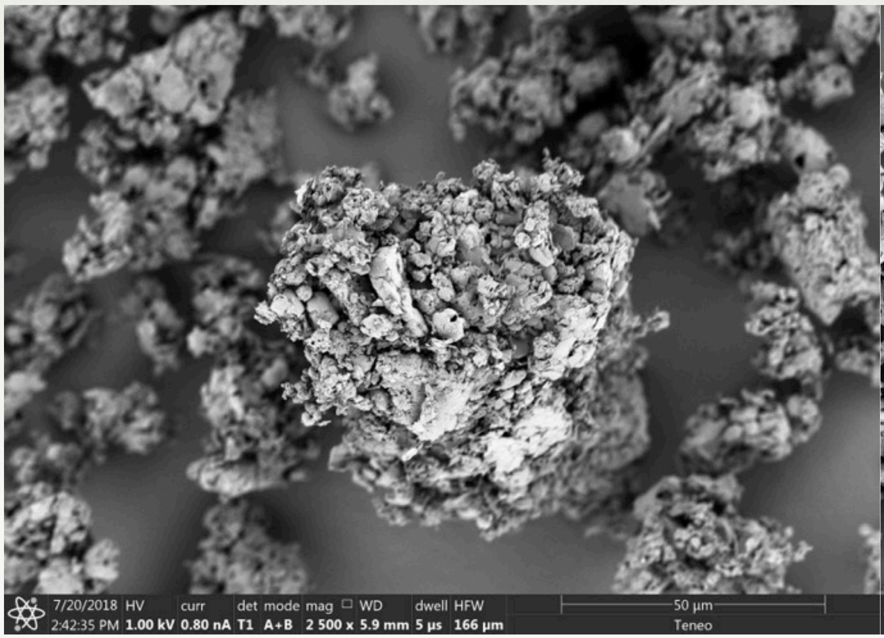

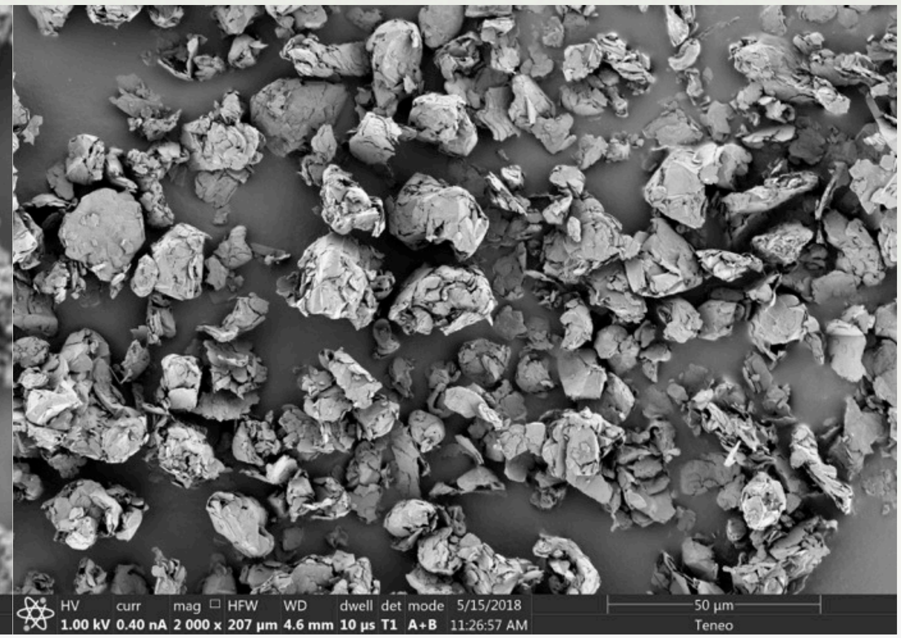

Graphite from Lignite

Hitachi MagE3 Graphite

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ND Lignite Graphite – Li-ion Battery

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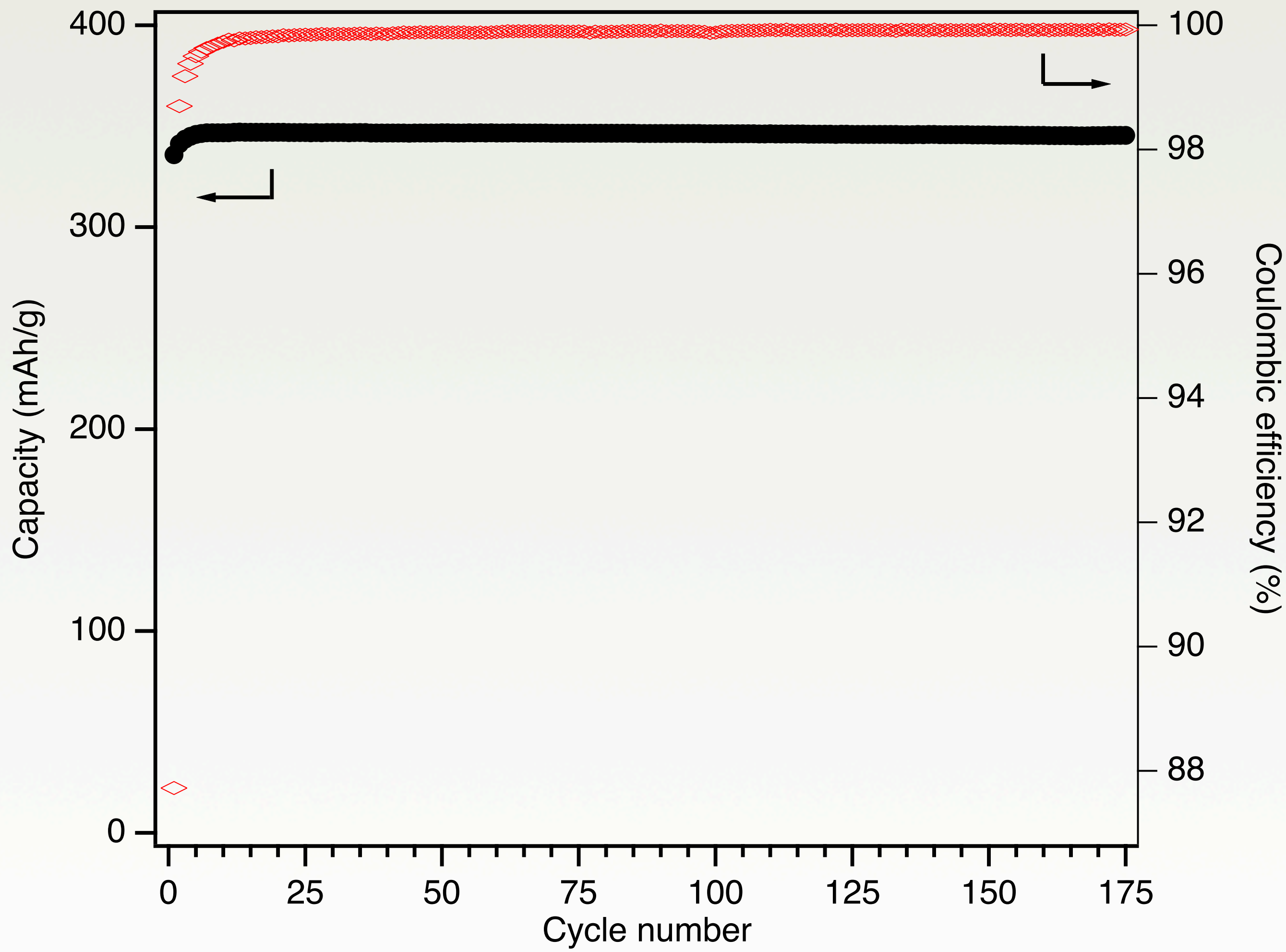

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347 mAh/g, 88% 1st Cycle CE

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Graphite from Coal - Performance

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

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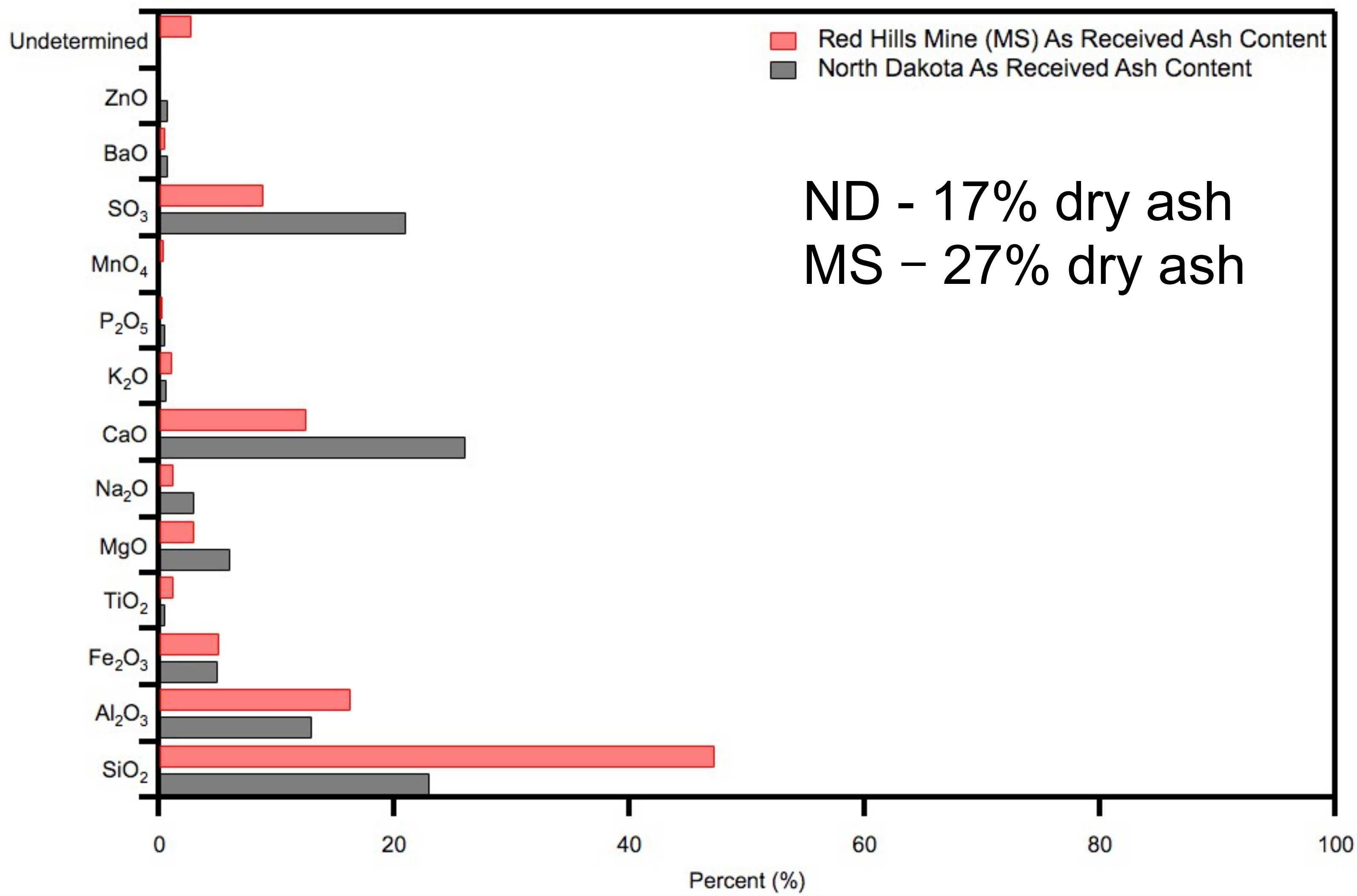
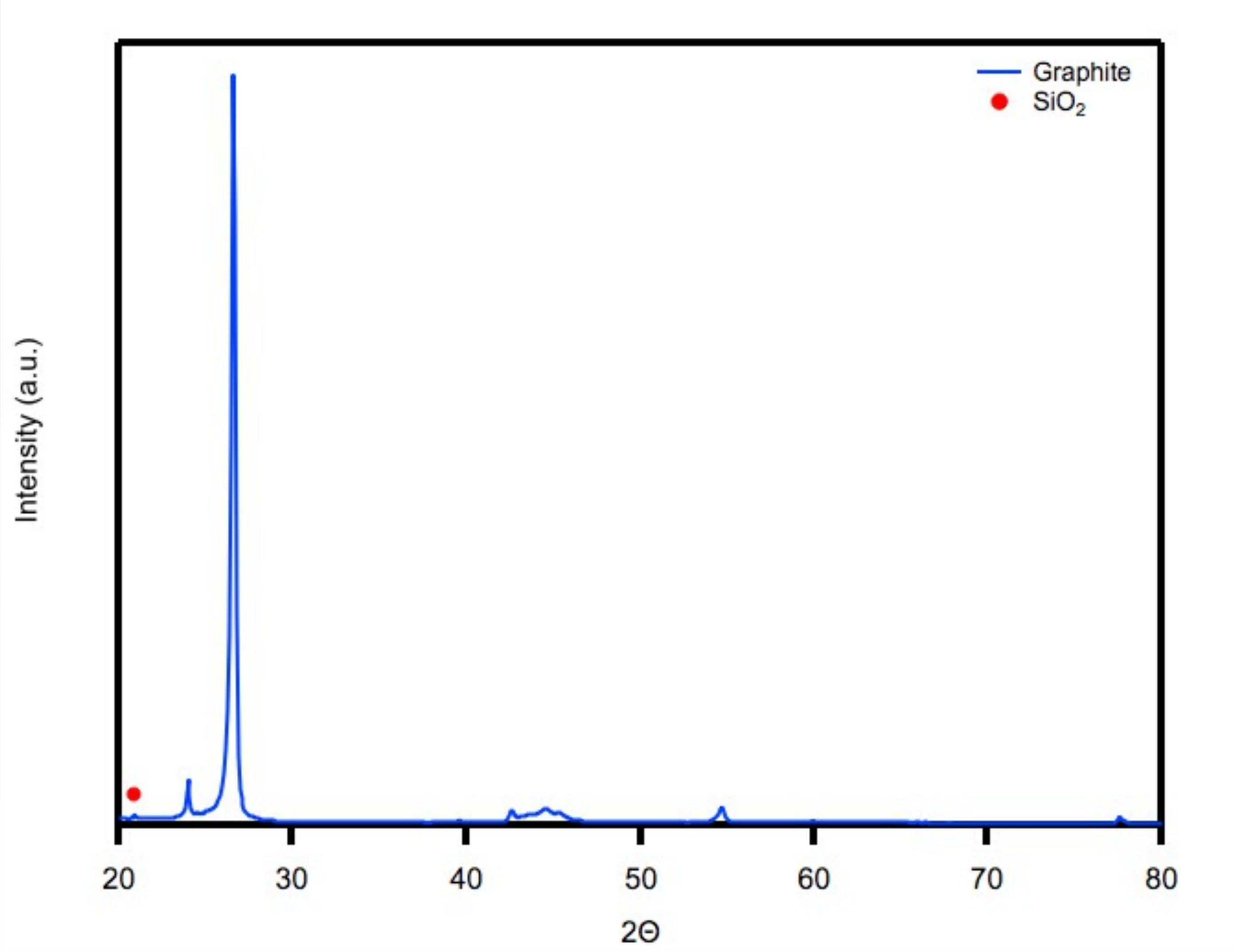
Lignite Impurities



ND Graphite Impurities



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 failure to graphitize MS lignite
- Limited char porosity likely source of failure to graphitize bituminous coal and anthracite

Next Steps

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