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

NETL Advanced Coal Processing Project Review Meeting
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Michael J. Wagner
Department of Chemistry
The George Washington University
Washington, DC
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\textsuperscript{st} 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

- 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

Cell Voltage = $V_{\text{Cathode}} - V_{\text{Anode}}$

Cathode ($\text{Li}_{1-x}\text{MO}_2$)

Electrolyte oxidation

Electrolyte reduction

Anode ($\text{Li}_x\text{C}_6$)

Lithium deposition

Voltage (V) vs. Li/Li$^+$

Fraction of lithium ions in electrodes (X)
Solid Electrolyte Interface

Coulombic Efficiency

\[ CE = \frac{Q_{out}}{Q_{in}} \times 100 \]

- 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/cm³
- 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

CO₂

Bio-char

Bio-oil

Graphite (99.9%C)

50 µm

$
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 & Accomplishments
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 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% +
  - 1st cycle 88% (low)
- Purity
  - 99% (low)
ND Graphite Purification

The graph shows the X-ray diffraction patterns of HF purified product and unpurified product. The peaks indicate the crystalline structure of graphite. The red line represents the HF purified product, and the blue line represents the unpurified product. The intensity is measured in arbitrary units (A.U.) and the 2-Theta value is the angle at which the peak occurs.
ND Graphite Purification

- **KOH Purified (Microwave)**
- **KOH Purified (Room Temperature)**
- **HF Purified**
- **Unpurified**
ND vs MS Coal

Intensity (a.u.)

2θ

10 20 30 40 50 60 70 80 90 100 110

m2002p; ND Coal
m2009p; MI Coal
ND vs MS Coal

![Graph comparing ND and MS Coal products](image.png)
Lignite Impurities

- ND - 17% dry ash
- MS - 27% dry ash
ND vs MS Elemental Analysis

Concentration (ppm)

Element

ND Coal
m2002 Product
MI Coal
m2009 Product

0 10 20 30 40 50 60 70 80 90 100

Al B Ca Er Fe Ge Ir K Mg Na S Si Sr Th Zn
Coal Char Average Pore Diameter

- ND
- MS
- BIT
- ANTH

Pore Diameter (nm)
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 (CO₂ 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