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
• 1st 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

Voltage (V) vs. Li/Li^+

Cathode (Li_{1-x}MO_2)
Electrolyte oxidation

Cell Voltage = V_{Cathode} - V_{Anode}

Electrolyte reduction

Anode (Li_xC_6)
Lithium deposition

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

Coulombic Efficiency

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

- 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
  – Pet coke supply shortages foreseen
  – Graphite requires high purity needle pet coke, 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
Graphite From Biomass

CO₂

Bio-char

Bio-oil

Graphite (99.9% C)

$
Graphite From Biomass
Graphite From Biomass

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

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)

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Lignite Impurities

ND - 17% dry ash
MS - 27% dry ash
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