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Energy & Environmental Research Center (EERC)

Advanced Processing of Coal and Coal Waste to Produce Graphite for Fast–Charging Lithium–ion Battery Anode

DE-FE0032139

U.S. Department of Energy

National Energy Technology Laboratory

2024 Resource Sustainability Project Review Meeting

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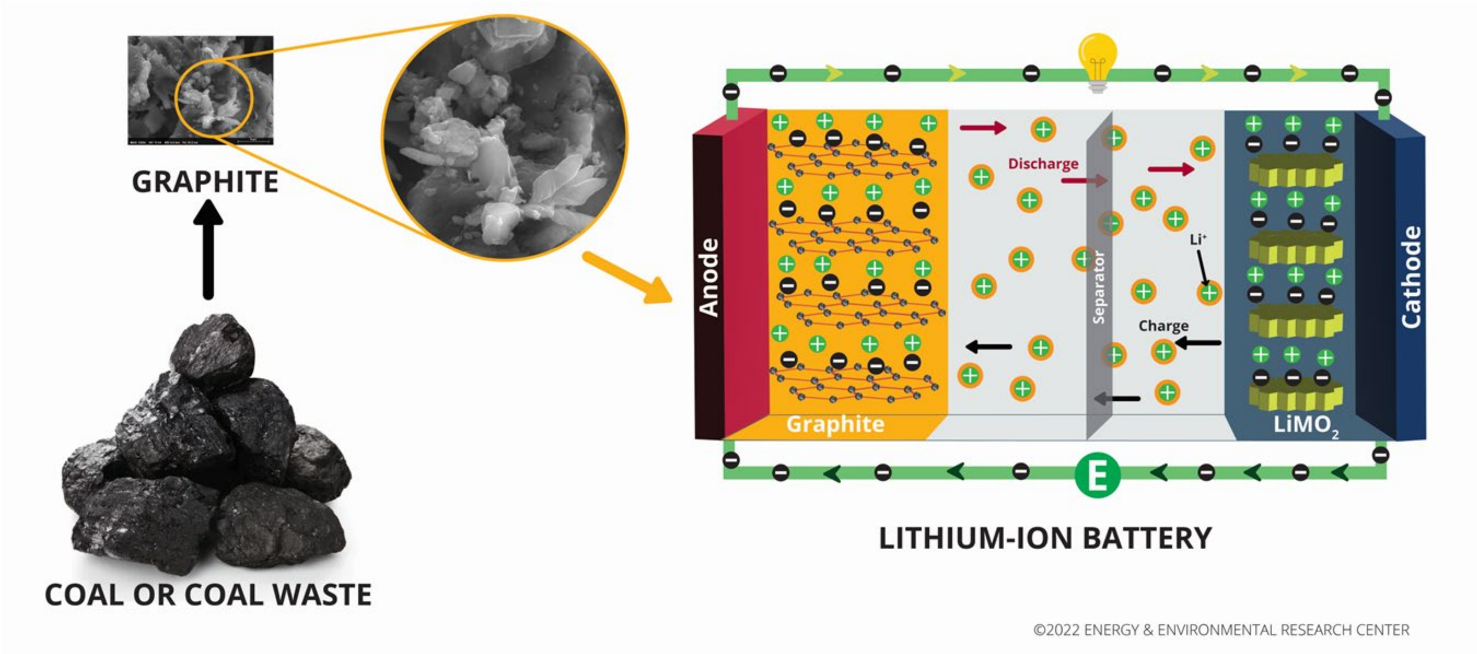
Project Overview: Objective and Duration

The overall objective is to:

- Validate an approach to make high-quality graphite from ND lignite and lignite coal waste
- Fabricate and test a fast-chargeable lithium-ion battery anode prototype

Project Duration: 36 months



Project Overview: Funding and Partners

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY **$1,000,000**

Lignite Energy Council **$500,000**

NORTH AMERICAN COAL **$45,000**

Total Funding = $1,545,000

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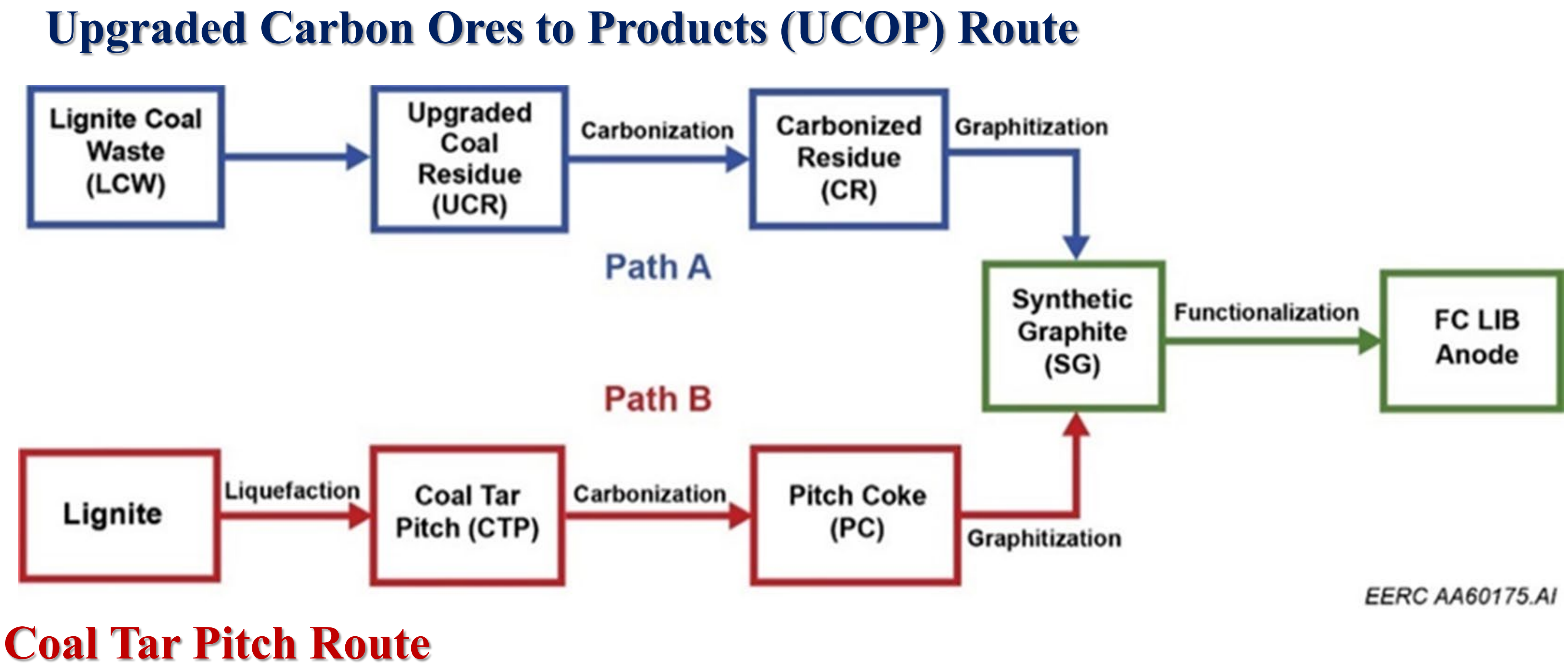
Technical Approach



Project Task Structure

- Task 1 – Project Management, Planning, and Reporting
- Task 2 – Coal Upgrading
- Task 3 – Coal-Derived Tar Pitch
- Task 4 – Carbonization
  - Task 4.1 – Upgraded Coal Carbonization
  - Task 4.2 – Coal Tar Pitch carbonization
- Task 5 – Graphitization
- Task 6 Production and Testing of LIB anode Prototype
  - Task 6.1 – Functionalization of Coal-Derived Graphite
  - Task 6.2 Electrochemical Performance Testing
- Task 7 – Economic Feasibility Analysis

Project Progress Updates

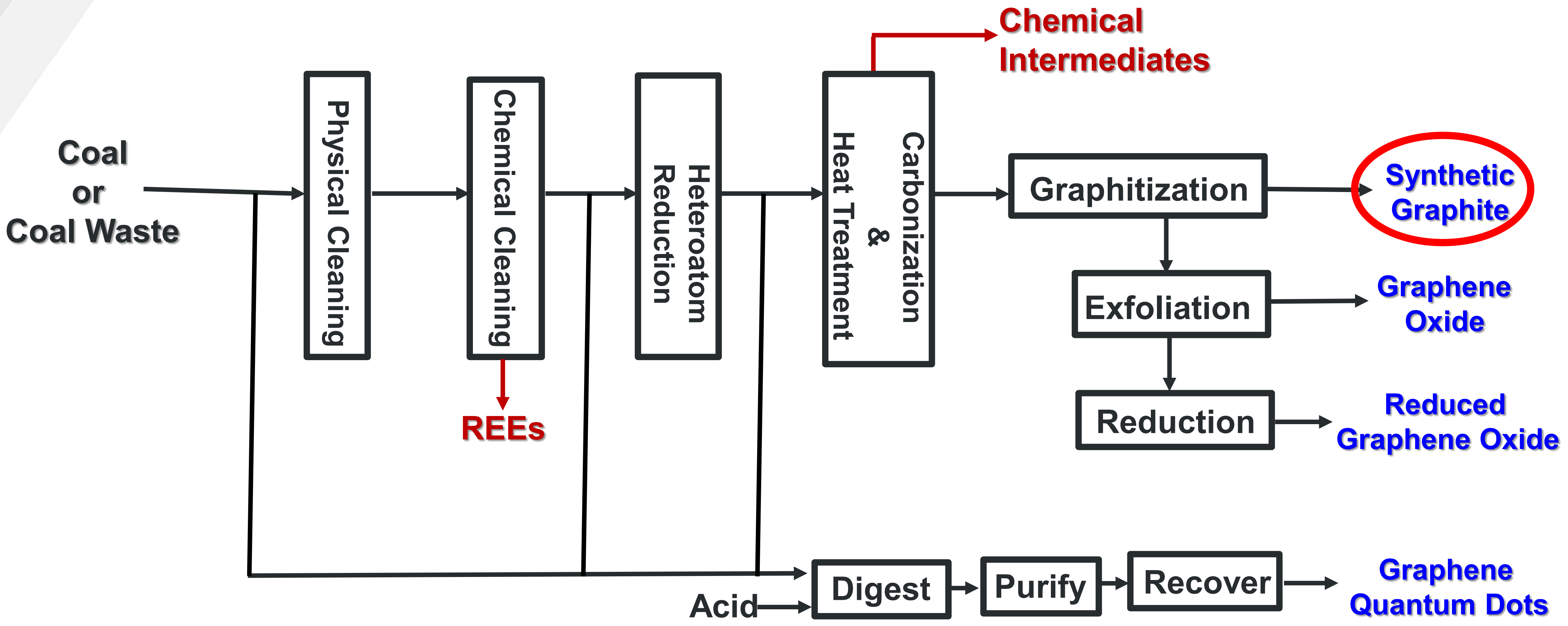
Milestones Updates

- **M1** – Coal upgrading **(Complete)** ✓
- **M2** – CTP **(Complete)** ✓
- **M3** – Upgraded coal carbonization **(Complete)** ✓
- **M4** – CTP carbonization **(Complete)** ✓
- **M5** – Graphitization **(70% complete)**
- **M6** – Graphite functionalization **(25% Complete)**
- **M7** – LIB anode testing **(25% Complete)**
- **M8** – Economic analysis **(Pending)**

Success Criteria Updates

- **BP1 (18 months)**
  - 3 lbs upgraded coal ✓
  - 1.5 lbs carbonized upgraded coal ✓
  - 0.5 lb of carbonized CTP ✓
  - 0.5–1 lb coal-derived graphite ✓
- **Go/no-go DP**
  - Up to 1 lb coal-derived graphite ✓
- **BP2 (18 months)**
  - LIB performance data
  - Economic analysis report

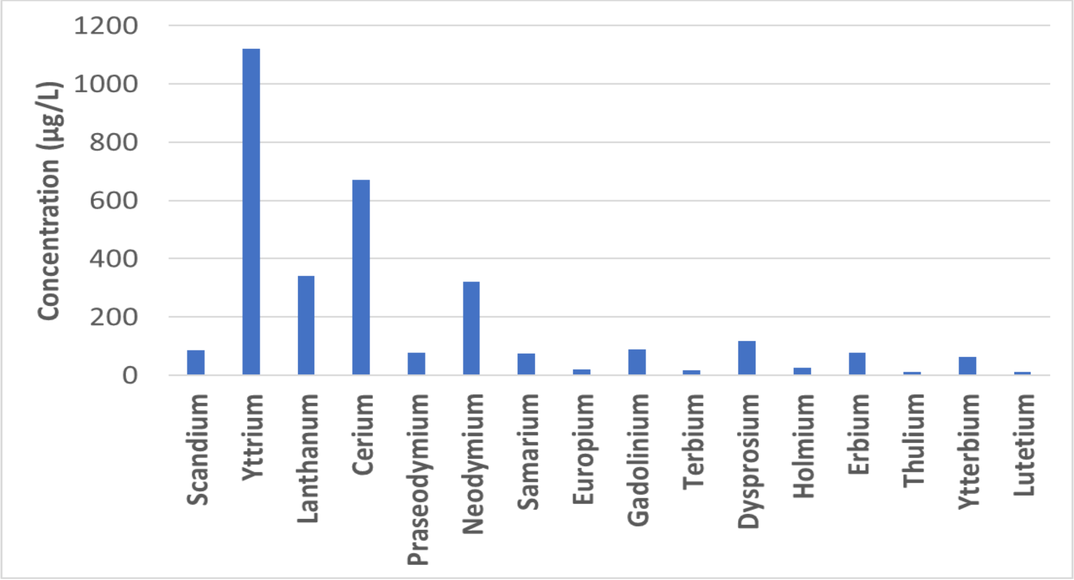
Upgraded Carbon Ores to Products (UCOP) Technology

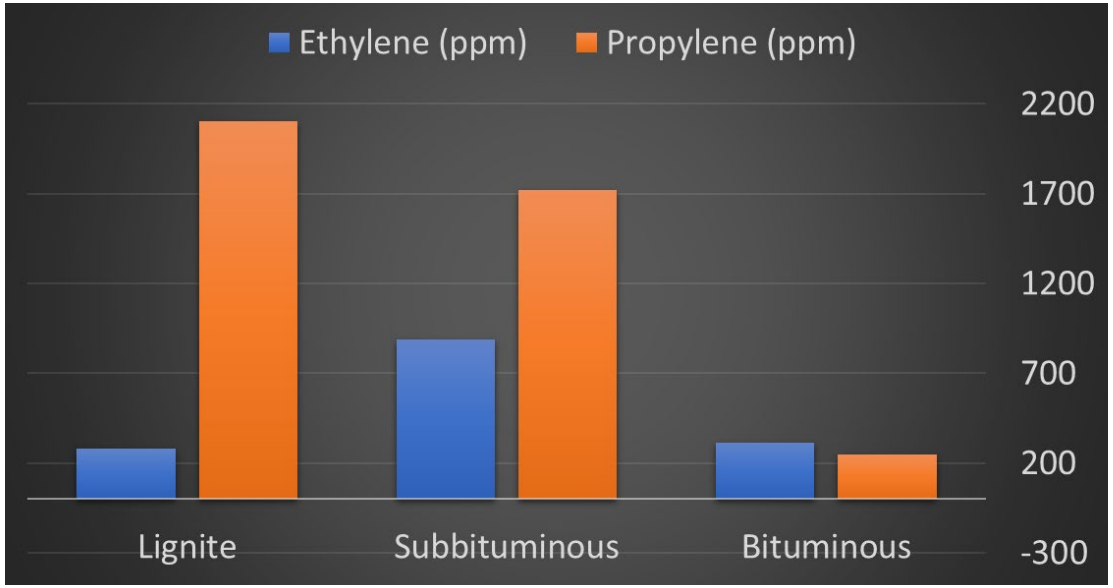


The UCOP Technology is applicable to all coal/coal wastes ranks

Technical and Economic Advantages of the UCOP Process

- Abundant Domestic Supply of Cheap Feedstock
- Low Environmental Impacts
- Lower Energy Consumption Compared to SOTA
- Economically Feasible at Scale
- Simple, Scalable Process
- Other Critical Byproducts:
    - REEs
    - Petrochemical Intermediates



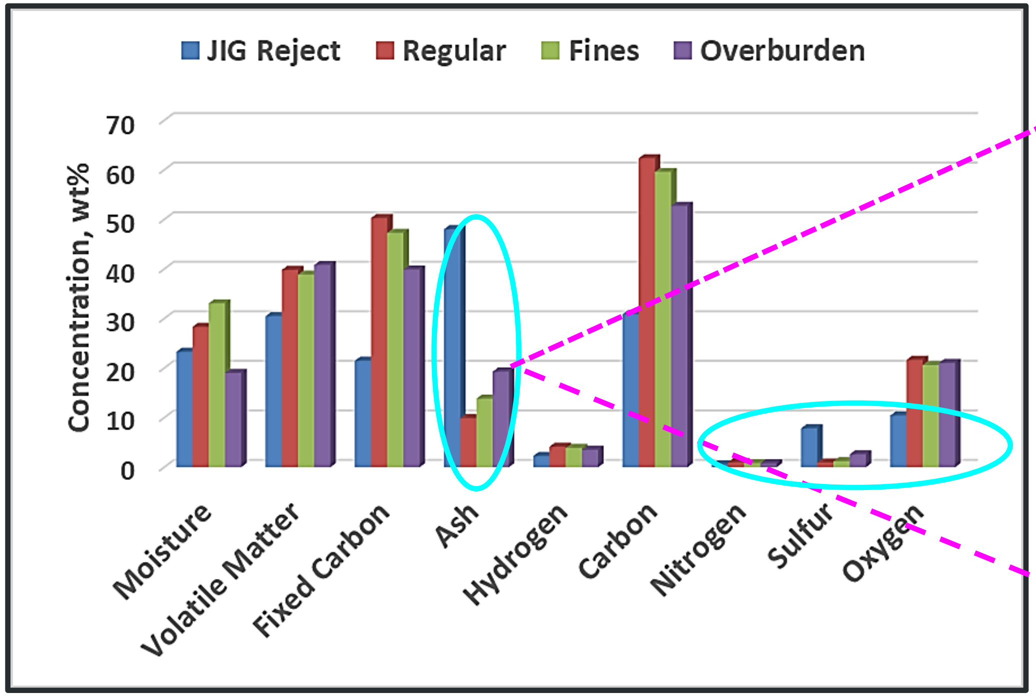


Current Results

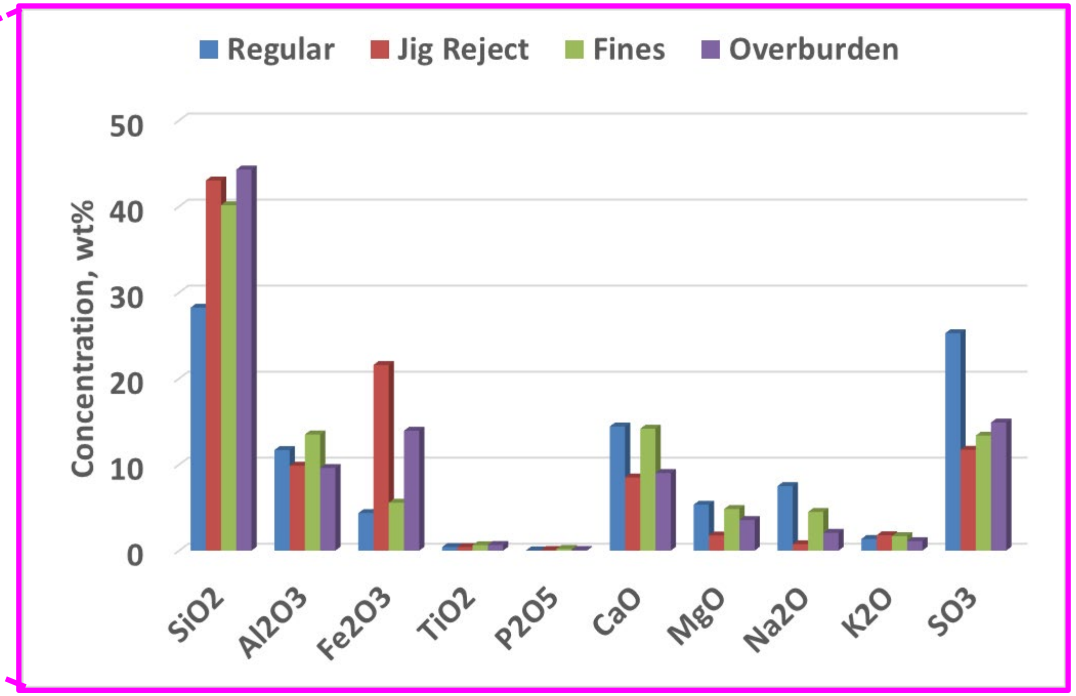
Analytical Characterization of Coal-Derived Graphite

- Scanning Electron Microscopy
  - **Graphite Microstructures**
- X-ray Diffraction
- X-ray Fluorescence
- Raman Spectroscopy
- Proximate/Ultimate Analyses
- ICP-MS

Analysis of Coal and Coal Wastes Feedstocks



Proximate & Ultimate Analysis



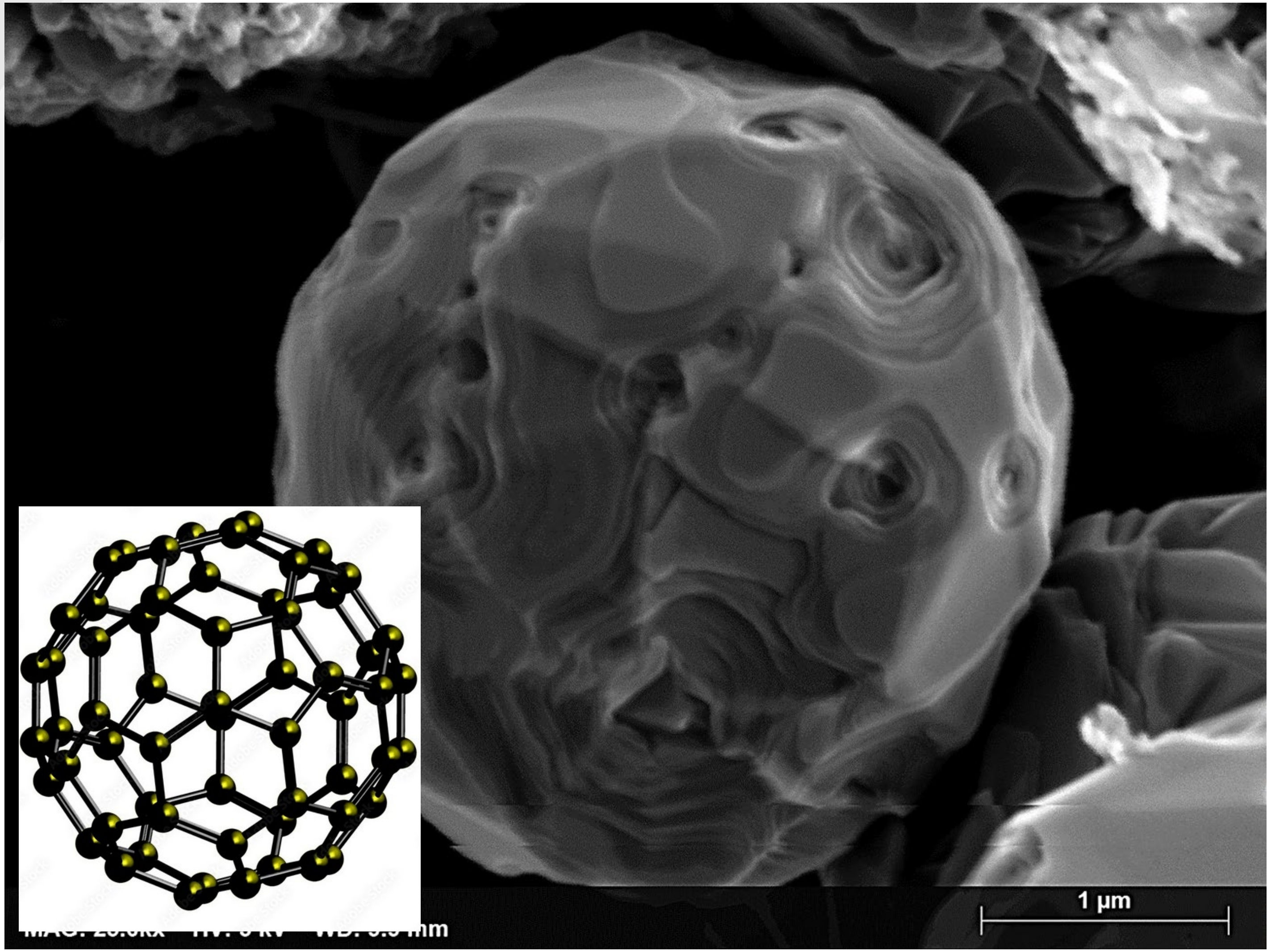
XRF Analysis

Coal and Coal Wastes Ash Removal

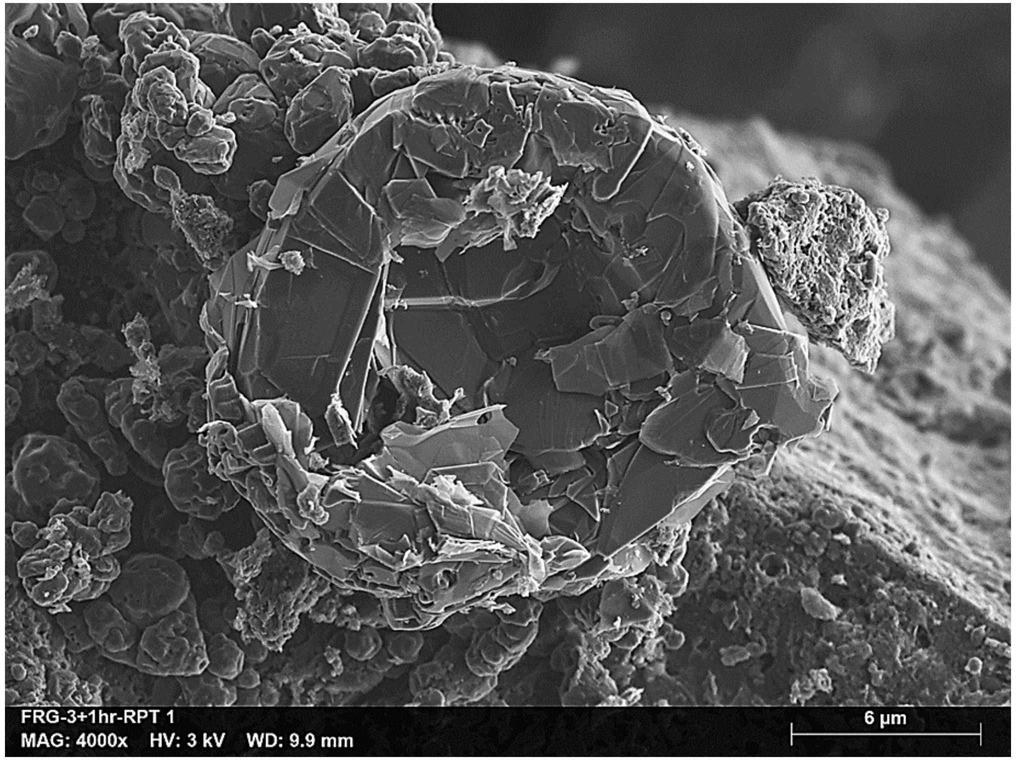
Coal Type	Raw Coal Ash (wt%)	Clean Coal Ash (wt%)	Ash Reduction (%)
Regular	9.90	5.63	43.1
Fines	13.85	7.54	45.6
Overburden	19.30	4.43	77.0
Jig Reject	**49.0**	**2.90**	**94.1**

Croissant Graphite

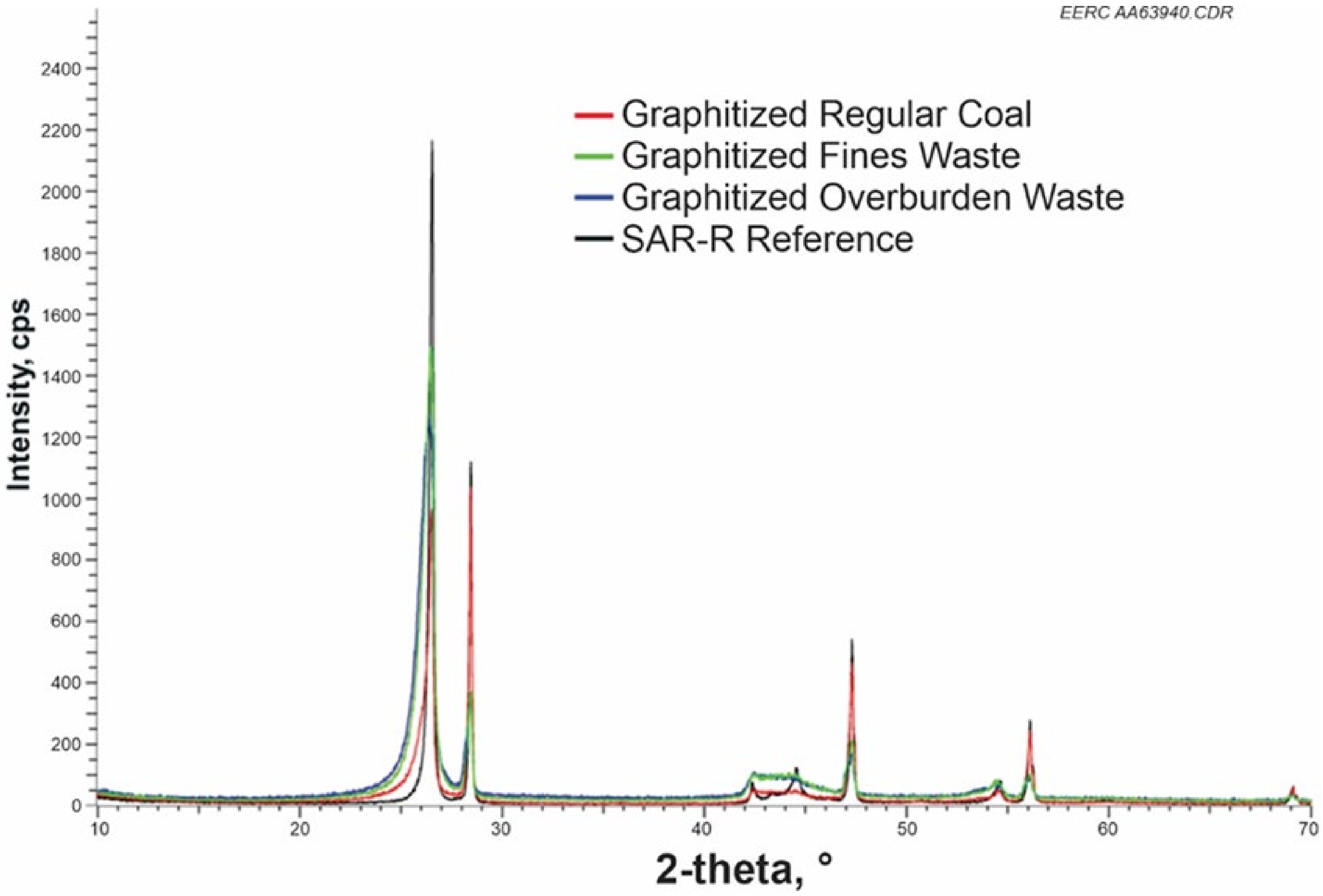
Graphulerenite



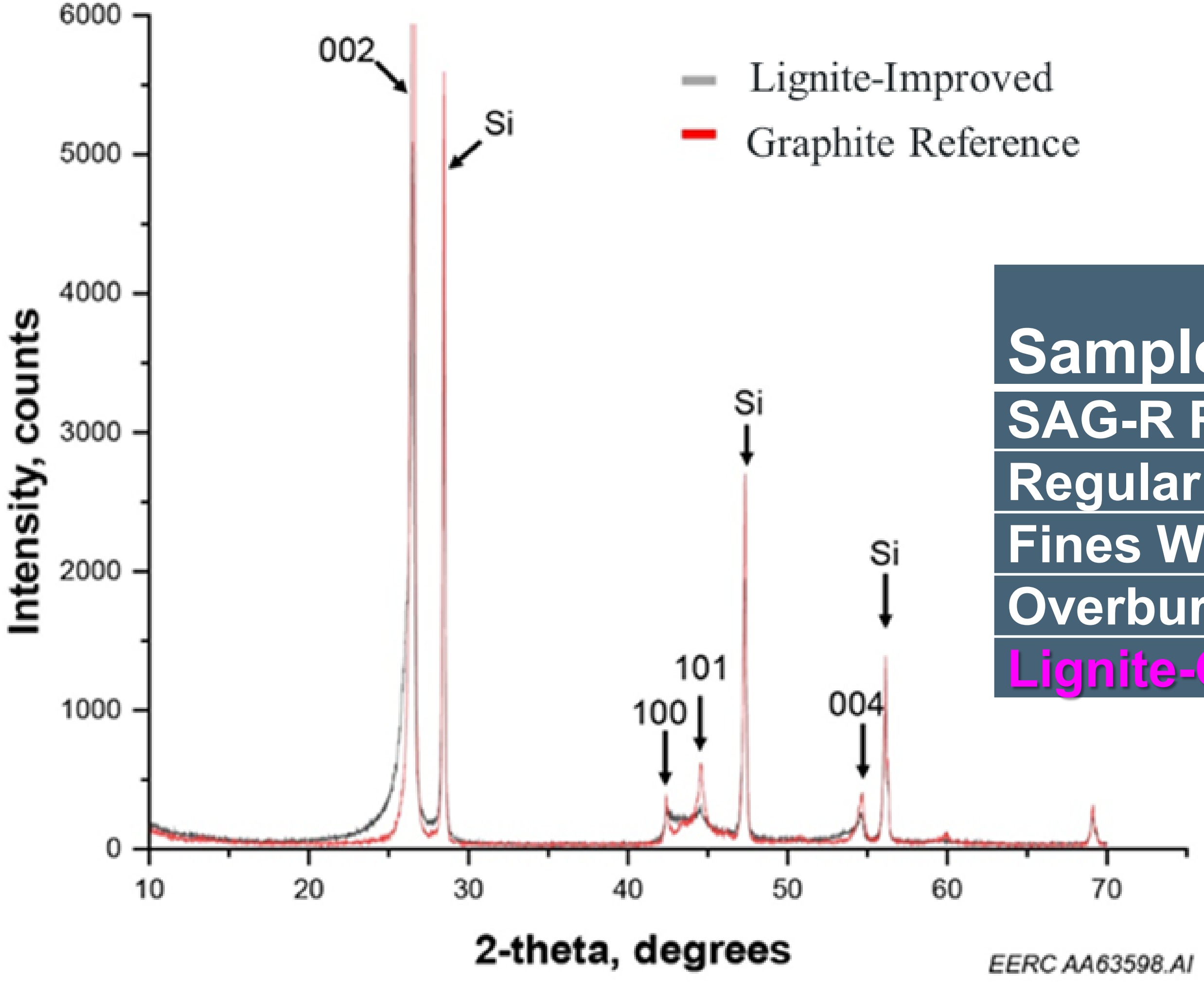
Cross-Section View



XRD Analysis of Coal/Coal Waste Derived Graphite

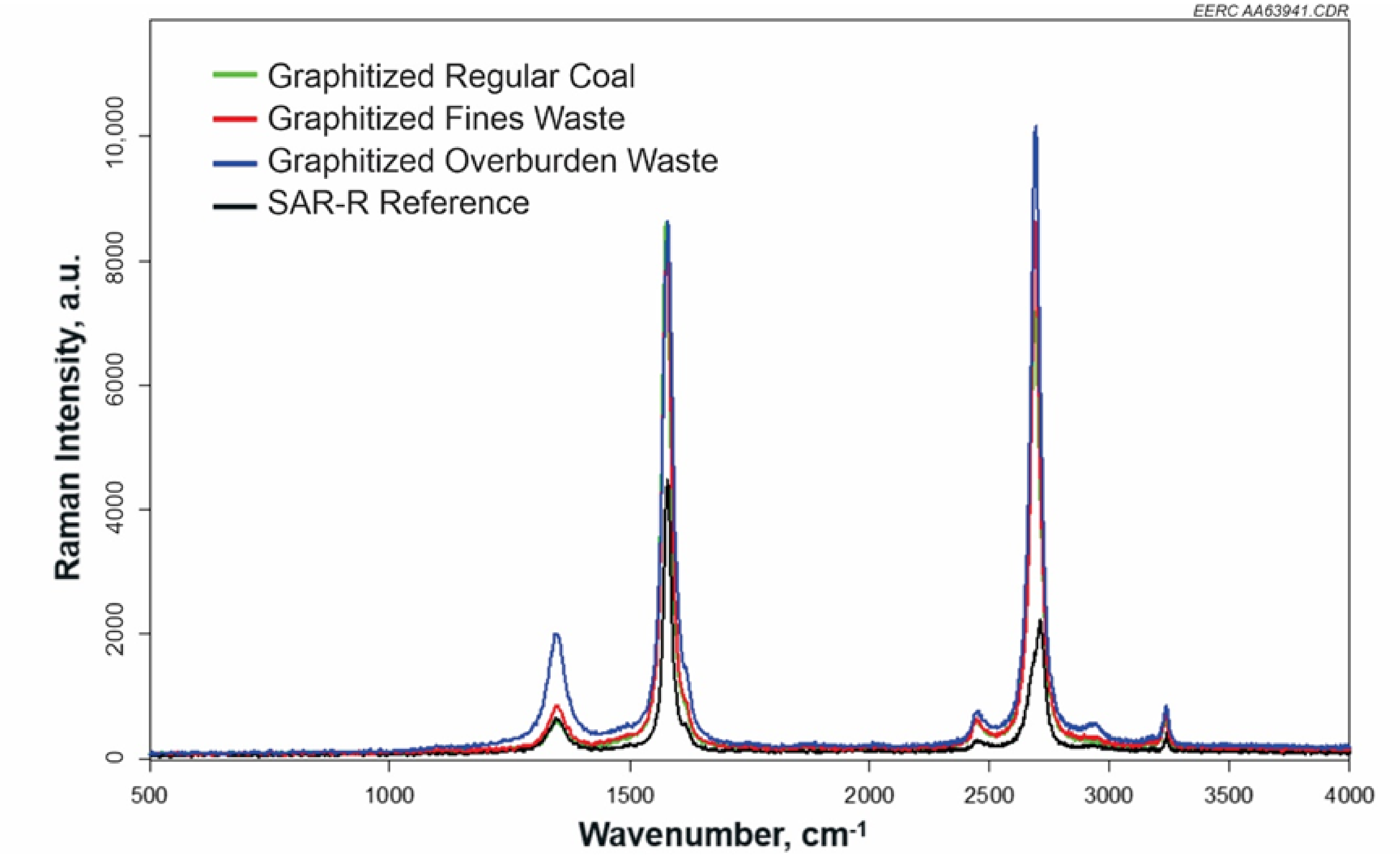


Optimized Lignite-Derived Graphite



Sample	2-Theta (°)	d-spacing (Ǻ)	DoG (%)
SAG-R Reference	26.56	0.3356	97.71
Regular Coal	26.50	0.3363	89.03
Fines Waste	26.35	0.3382	67.31
Overburden Waste	26.41	0.3374	76.53
Lignite-Optimized	**26.54**	**0.3358**	**95.25**

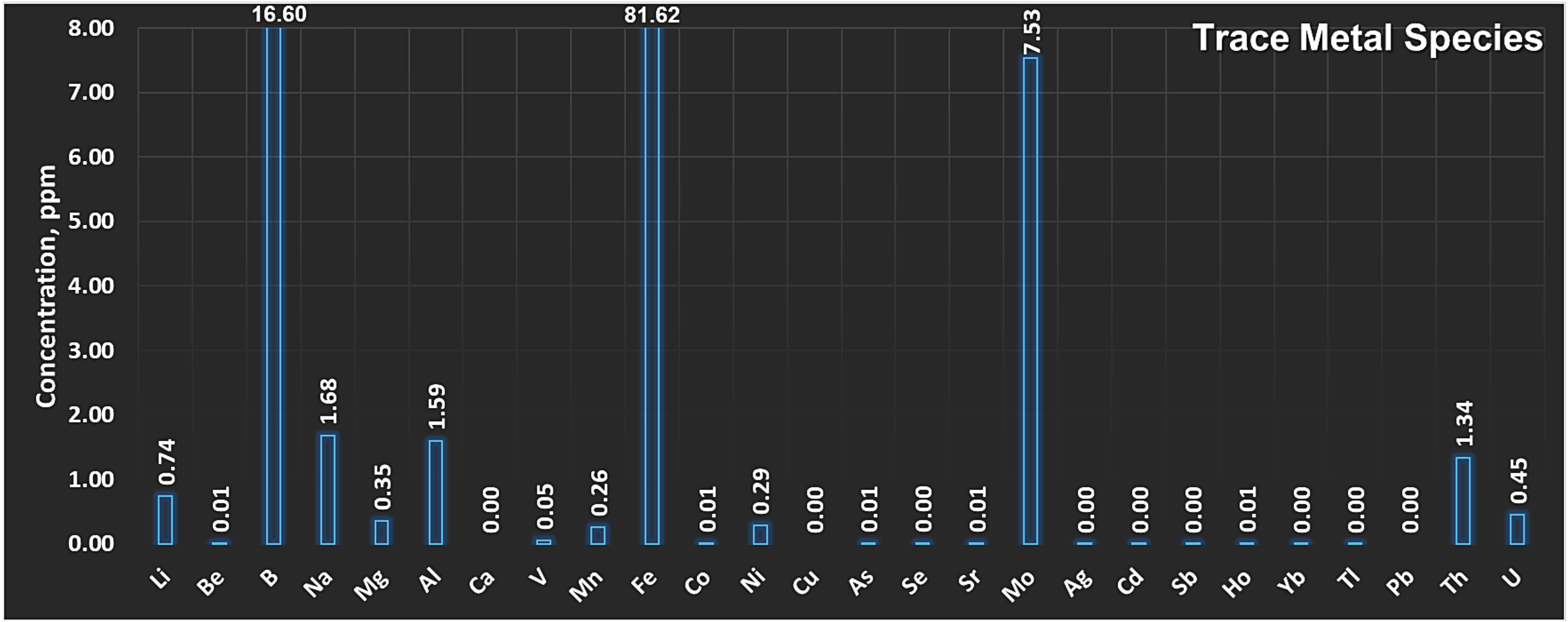
Raman Spectroscopy Analysis



Coal-Derived Graphite Purity

Property	Coal-Derived Graphite	Commercial Graphite
Carbon Purity (%)	~99.98	≥99.95
Ash (wt%)	~0.013	<0.2
Moisture (%)	~0.011	<0.01

Trace Metals Species



UCOP Process Summary and Next Steps

- **Summary**
  - High-quality graphite can be made from coals and coal wastes using the UCOP process.
  - Preprocessing conditions are key to achieve high quality and observed new graphite microstructures.
  - Additional post-graphitization processing is needed to optimize performance.

- **Next Steps**
  - Continue to fine-tune graphitization conditions
  - Graphite properties characterization

Coal Tar Pitch (CTP) Process

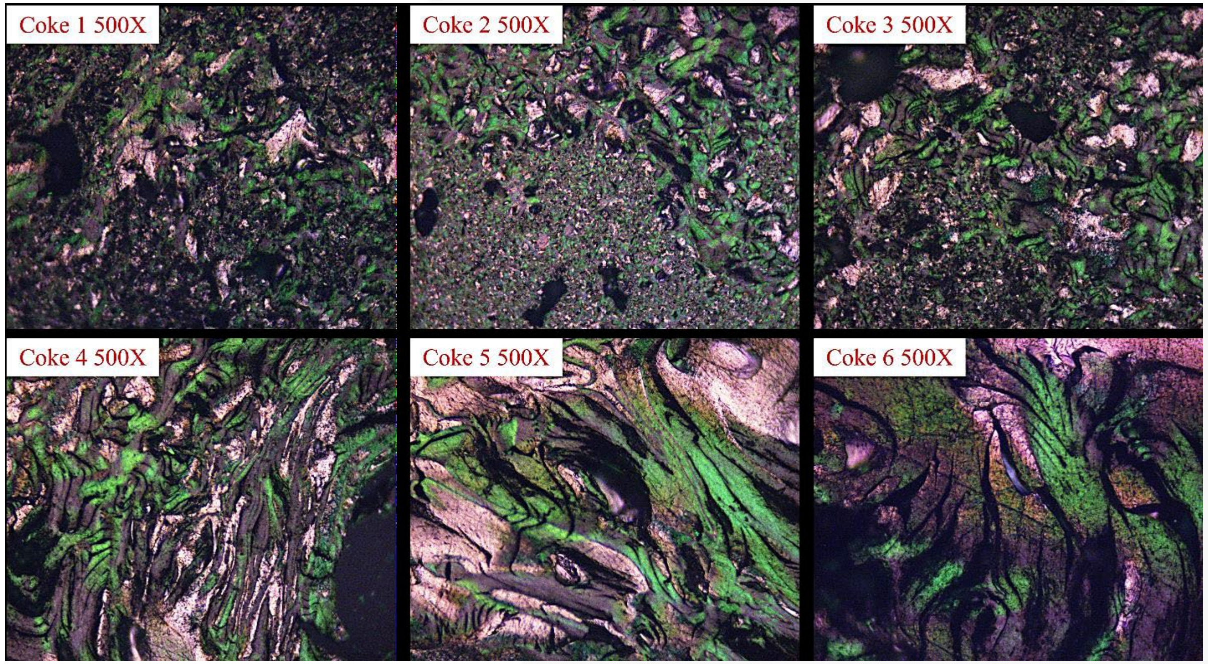
CTP Coking and Carbonization

Coke	Name	Softening Point °C	Optical Property	Quinoline Insoluble
1	M-CTP-Mid	Medium	Mesophase	Low
2	I-CTP-Mid	Medium	Isophase	High
3	I-CTP-Low	Low	Isophase	Low
4	M-CTP-High	High	Mesophase	High
5	Refined CTP-1	Low	/	Extremely low
6	Refined CTP-2	Low	/	Extremely low

- Over 10 CTPs supplied by AmeriCarbon with optical property (isophase and mesophase), Softening point, and Quinoline insoluble content, refined and unrefined treatment, have been tested for graphite production (6 examples listed in the table).
- The coking conditions, including temperatures, pressure, time, and carbonization temperatures in the coking and carbonization process have been optimized.
- The yield from CTP to Coke varies from 40% to 80%.
  - High softening point pitch has a higher coke yield
  - Refined pitches has lower yield

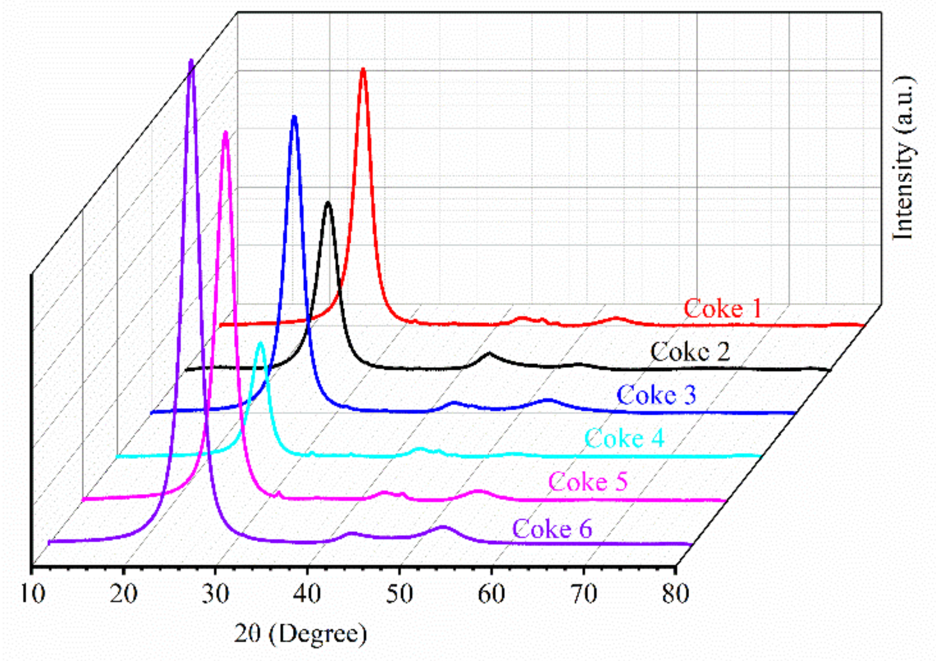
CTP Coking and Carbonization

Polarized optical images of cokes



- Cokes (1, 2, 3, 4) from unrefined CTPs display dominant mosaic structures
- Cokes (2 and 3) from Isophase CTPs have higher portion of fine mosaic than coke (1 and 4) from mesophase CTPs. Coke 2 has the highest portions of fine mosaic. Coke 4 has the lowest proportion of fine mosaic
- Cokes (5 and 6) from refined CTPs present flow structures, representing ordered carbon layer stack

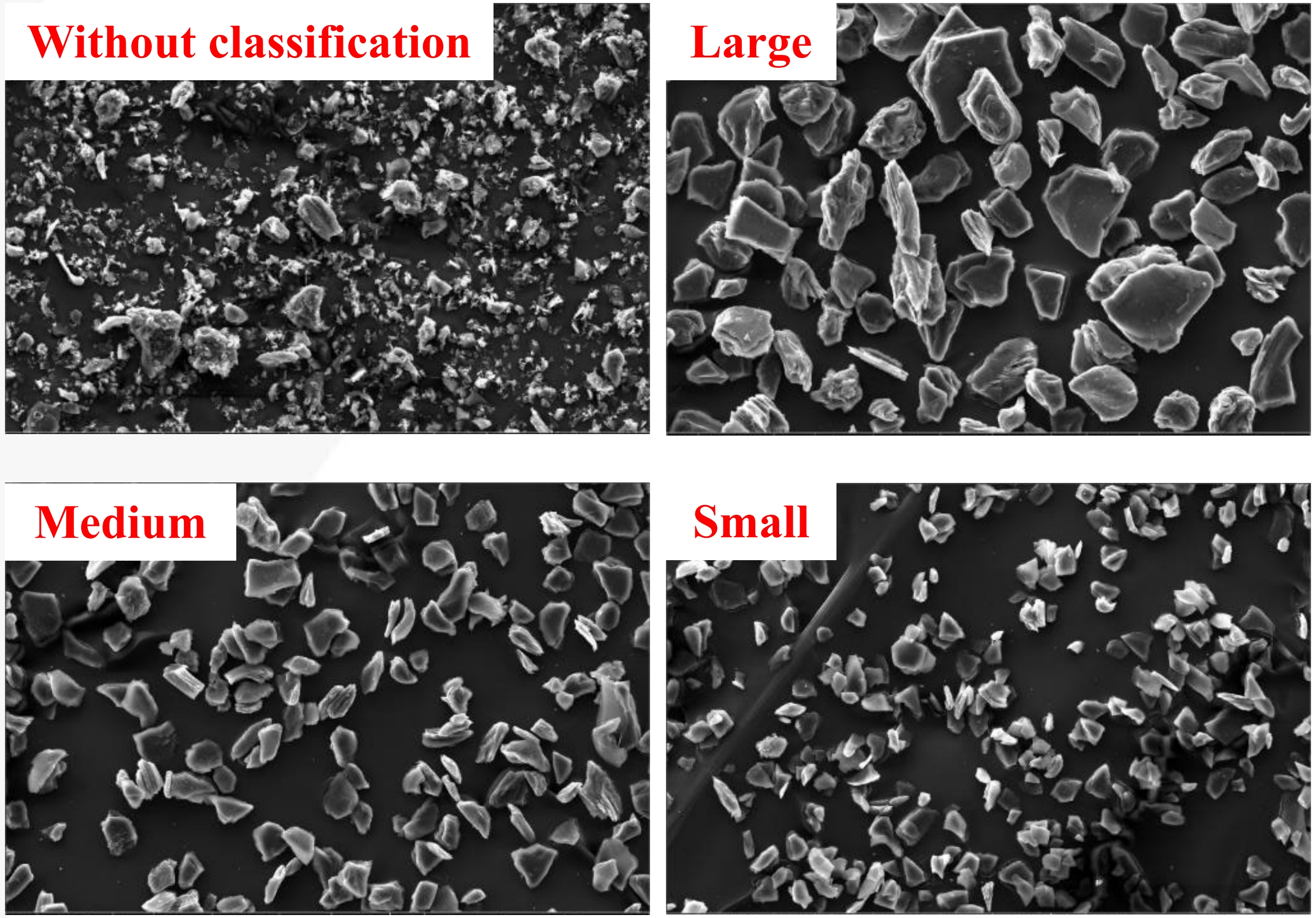
XRD patterns of cokes



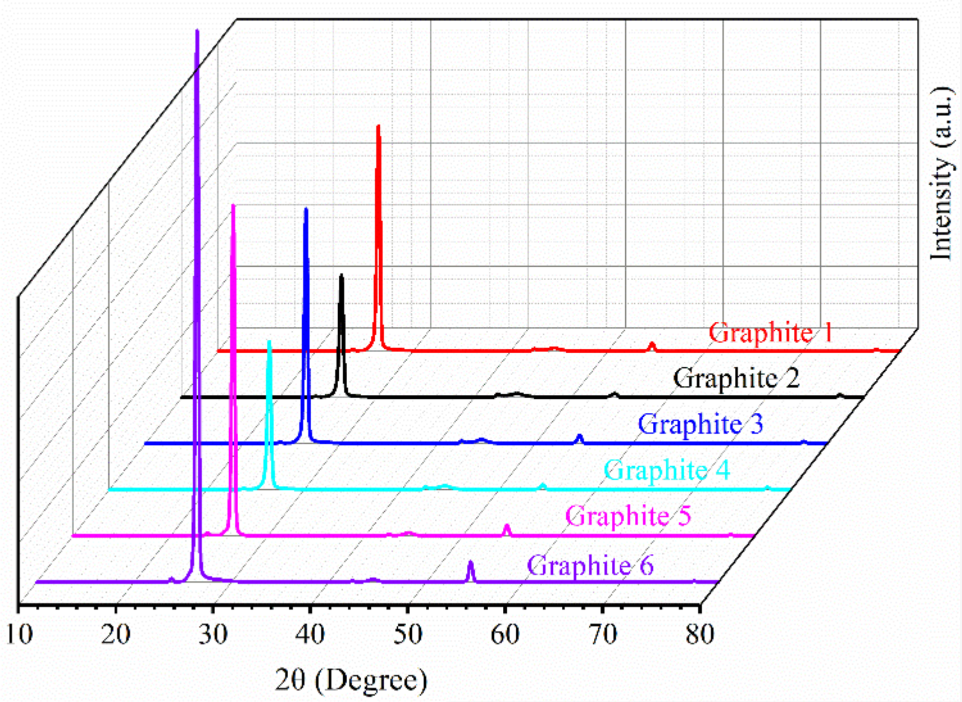
- All cokes present the featured XRD patterns belonging to graphite.
- Cokes 5 and 6 from refined CTPs display sharper (002) peaks than the rest, indicating a well-stacked carbon arrangement.

Functionalization: Particle Size Classification

- The coke samples were pulverized, and size-classified to enhance the battery performance.
- Nano-sized ash and submicron small particles removed to minimize surface area.
- Coke powder was classified into three groups belong to particle size range: large, medium, and small.



Graphitization Process



Samples	d_{002} (nm)	La (nm)	Lc (nm)	G (%)
Graphite 1	0.3364	57.53	22.54	88.0
Graphite 2	0.3374	51.92	18.21	76.5
Graphite 3	0.3363	57.85	22.11	89.4
Graphite 4	0.3367	53.94	19.73	84.9
Graphite 5	0.3365	62.91	24.38	86.8
Graphite 6	0.3363	65.28	24.53	89.4
Commercial Graphite	0.3364	41.91	21.64	86.7

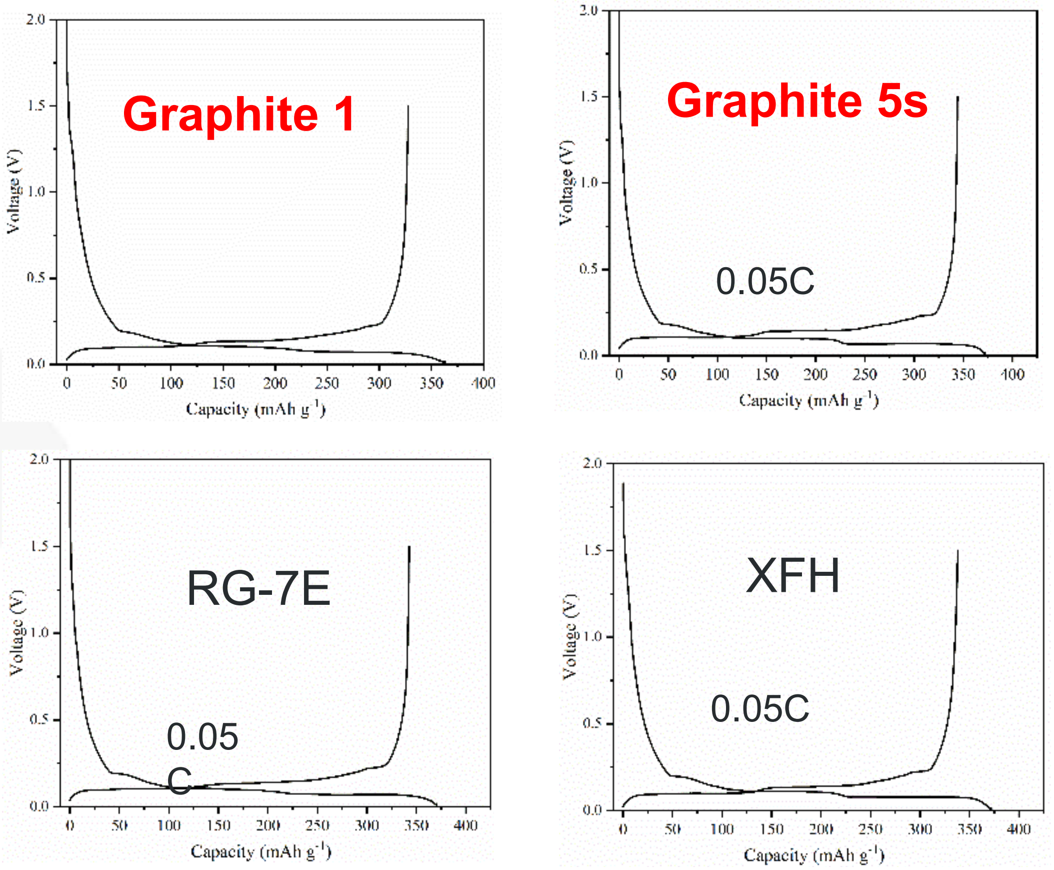
- The coke-to-graphite yield ranges from 90% to 98%. And the overall CTP-to-graphite yield ranges from 40 to 70%. High softening point CTP has higher graphite yield.
- All six samples present characteristic graphite XRD patterns: (002), (100), (101), and (004).
- All sample except graphite 2 have a graphitization degree, close or better than our commercial reference
- The order of the factors impacting the graphite quality: Impurities (Quinoline Insolubles) > Optical property > SP

Battery Testing Results

Samples	Initial charge capacity mAh/g	Initial discharge capacity mAh/g	ICE/ %
Our graphite: Graphite 1	338	363	90.2
Our graphite: Graphite 5s	344	372	92.4
Ref 1: coal-derived graphite: RG-7E	342	370	92.4
Ref 2: high-rate graphite: XFH	338	372	90.8

- Coin cells were assembled for battery testing
- Graphite 1 and 5s presents similar charge-discharge profiles to the commercial references
- Graphite 1 and 5s presents similar or better charge-discharge capacities and ICE than the commercial reference
- Rate and cycle performance testing is ongoing

Charge/discharge Profiles



Summary

	Units	Graphite (Commercial Graphite)	Coal Derived Graphite	Results
Target Graphite Grade	-	Fine grain	Fine grain	Fine grain
Flake/Particle Size	µm	10-25	10-25	Size adjustable (5-45)
Carbon Content	%	>99.8	>99.8	--
Ash Content	%	<0.05	<0.05	<0.03 (Total metal by ICP)
Surface area	m^2/g	0-10	0-10	--
Tap Density	g/cm^3	0.8 (1.05-1.2)	>0.8	1.1-1.2
Pressing Density	g/cm^3	1.5-1.7	>1.5	--
Initial Specific Capacity	mAh/g	>345	>345	>370
Initial Columbic Efficiency	%	>90	>90	>92
Capacity retention at 1C	%	30	80	--
Capacity Retention at 2C	%	10	50	--

Next Steps

- Graphite functionalization

Morphology control and surface modifications to the cokes/graphite will be conducted to improve fast-charging capability.

- Electrochemical performance tests

More rate and cycle performance characterizations in coin cells and cylinder cells will be conducted to evaluate the graphite.