Low-Temperature Production of Battery Grade Graphite from Coal with Recovery and Reuse of the Catalyst

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Disclaimer

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Outline

NETL's Catalytic Graphitization Process

- Catalytic Conversion of Coal to Graphite
  - Optimization of Catalytic Graphitization
  - Catalytic Conversion of Different Coal Ranks
- Improving Material Quality to Produce Battery Grade Graphite
  - General Requirements for Battery Grade Graphite
  - Remove Mineral Matter & Fe Catalyst
  - Physical Processing
- Recovery/Recycling Fe Catalyst & HCl Recycling
- Elemental Analysis
- Summary

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Catalytic Conversion of Coal to Graphite

Conventional Graphitization

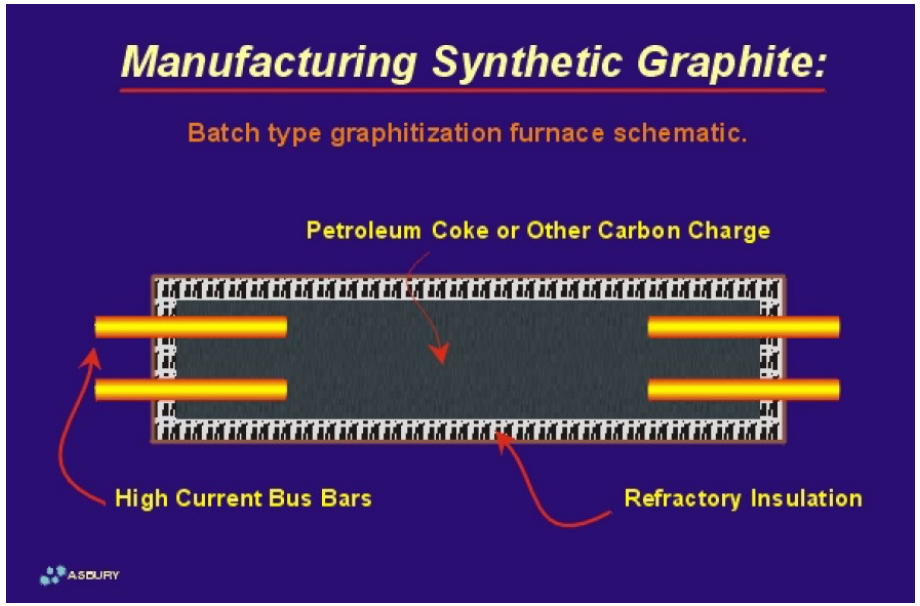
- Invented accidentally by Edward Goodrich Acheson in 1890s:

  $3C\ (coke) + SiO_2 \rightarrow SiC + 2CO(g)$ T = ~2000 °C

  $SiC \rightarrow C(graphite) + Si(g)$ T = ~4200 °C

- Current process:

  C (petroleum coke or coal tar) → C (graphite) T = ~3000 °C, 1–3 weeks



Schematic image of an Acheson type furnace
(https://asbury.com/media/1225/syntheticgraphiteparti.pdf)

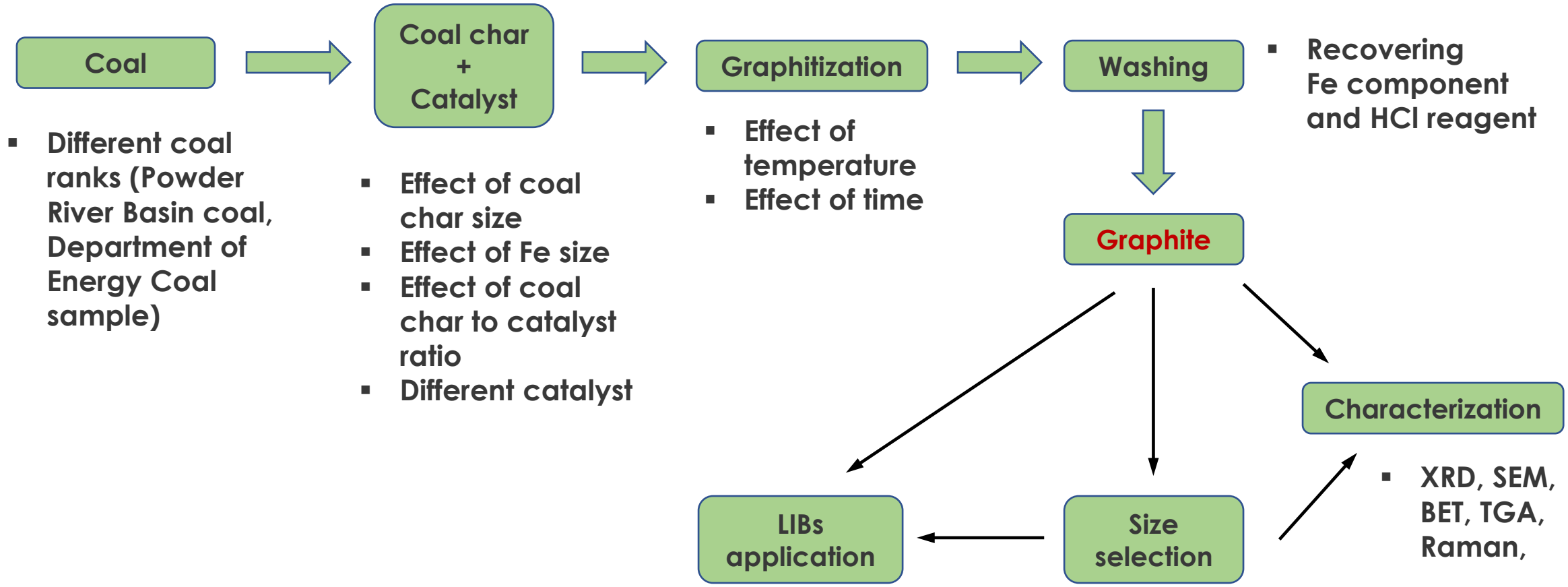
Raw coal → Catalytic Graphitization Process

T = >1500 °C, > 3 hours

"Battery-grade graphite"

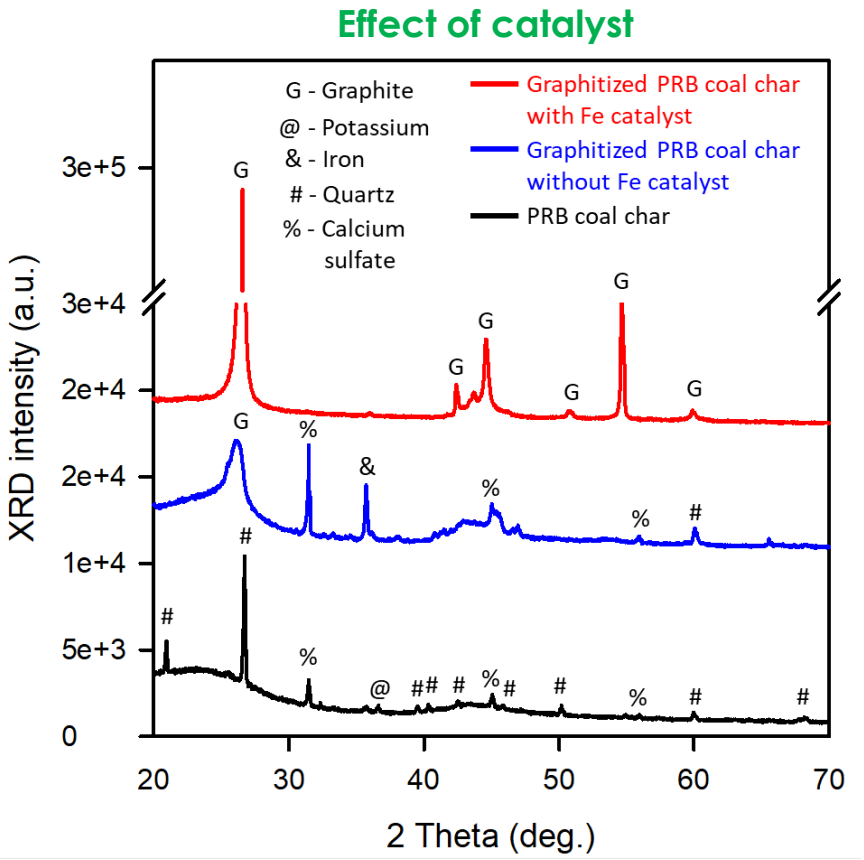
Catalytic Conversion of Coal to Graphite

NETL's Catalytic Graphitization Process

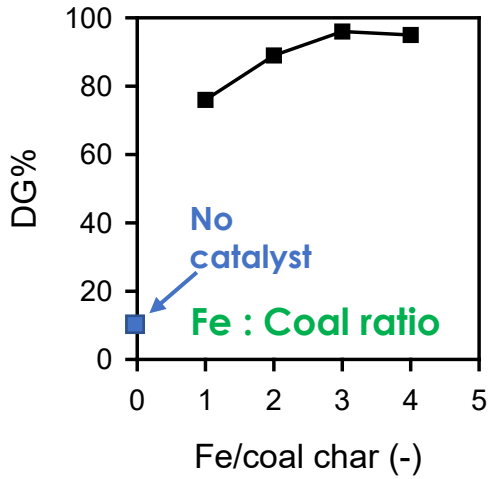


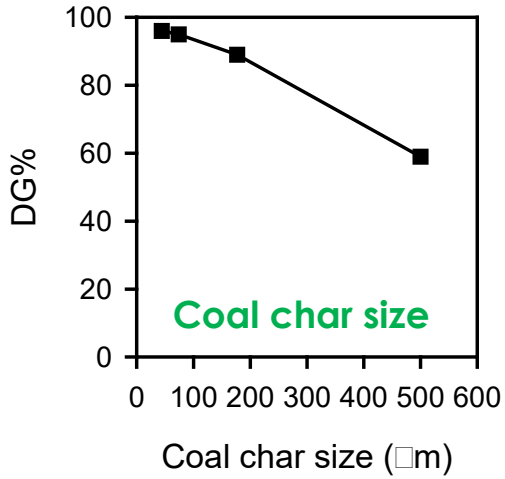
Catalytic Conversion of Coal to Graphite

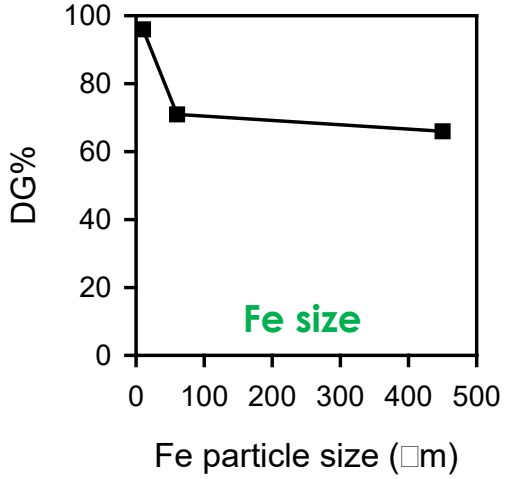
Optimization of Catalytic Graphitization

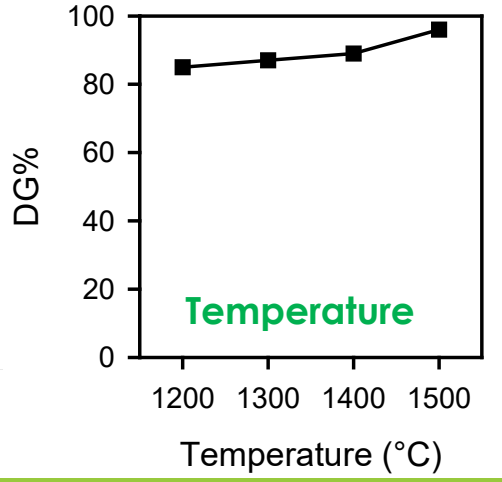


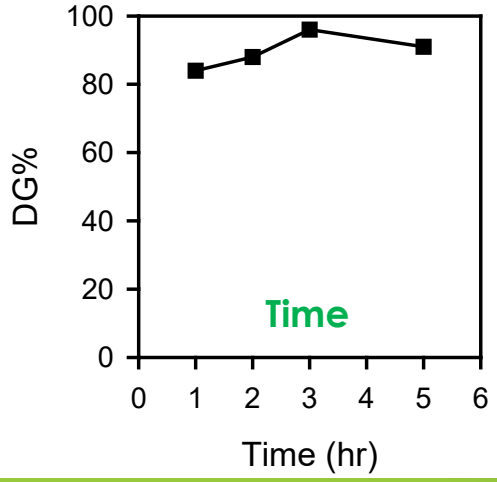
DG% = degree of graphitization

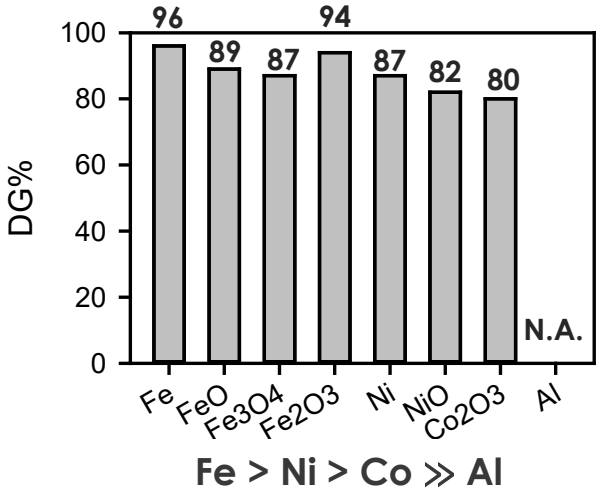








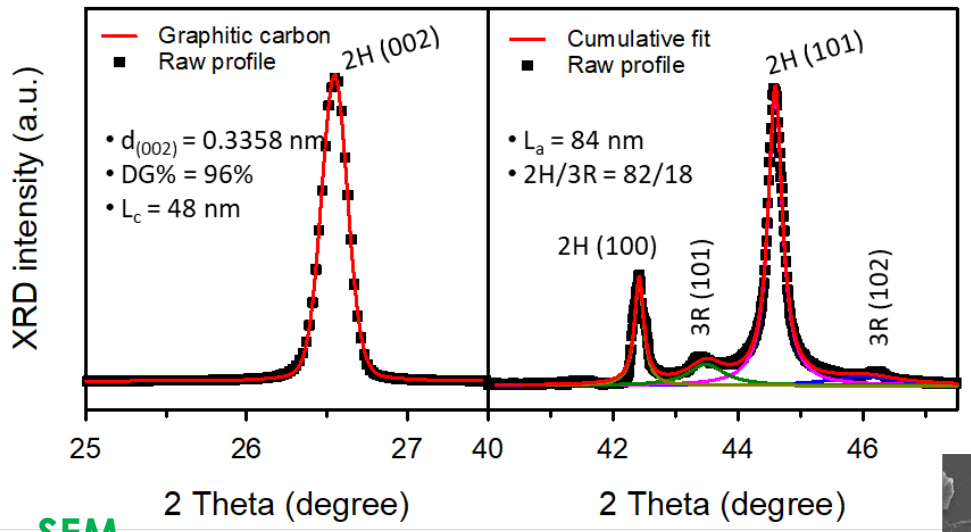




Catalytic Conversion of Coal to Graphite

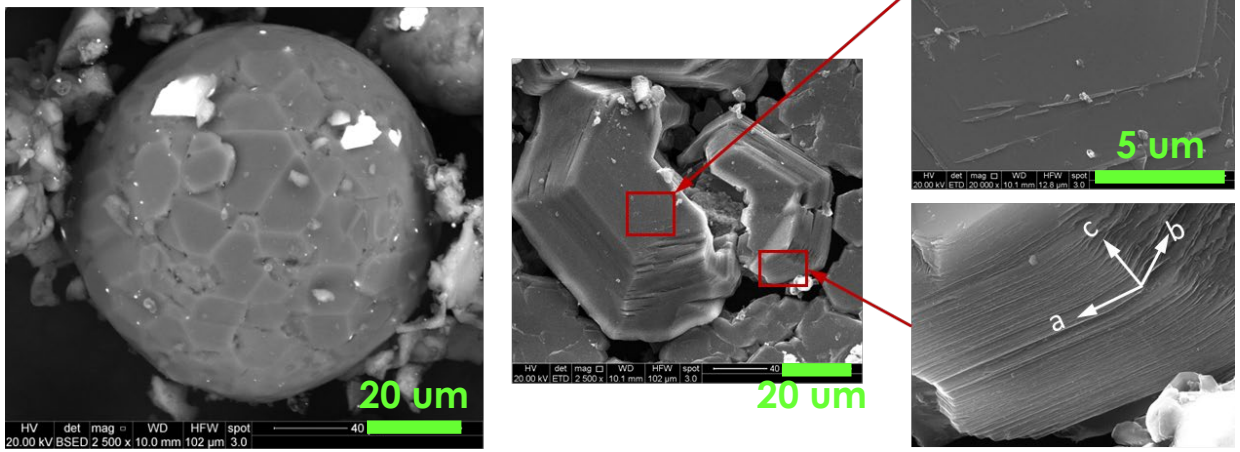
NETL's Best Graphite

XRD

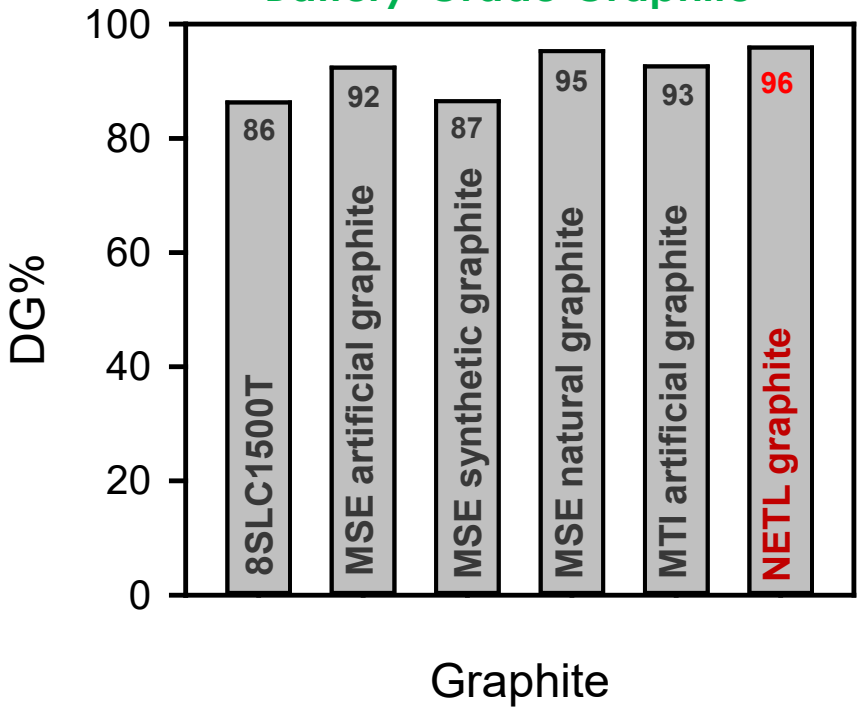


- Surface Area ≈ 5 m^2/g
- Ash < 0.1 wt.%

SEM



Comparison with Commercial Battery-Grade Graphite

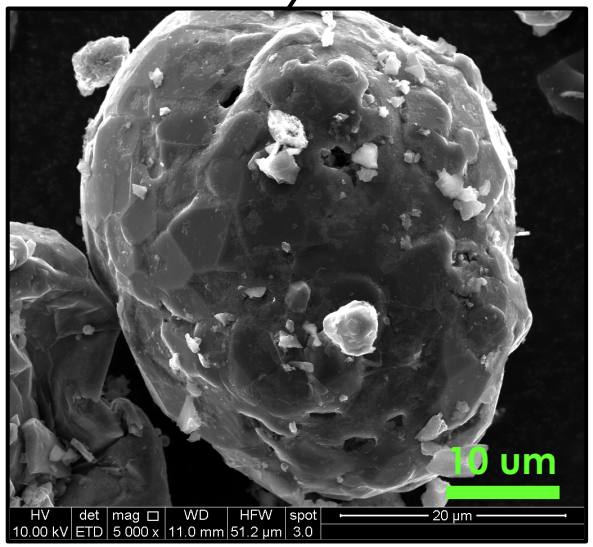


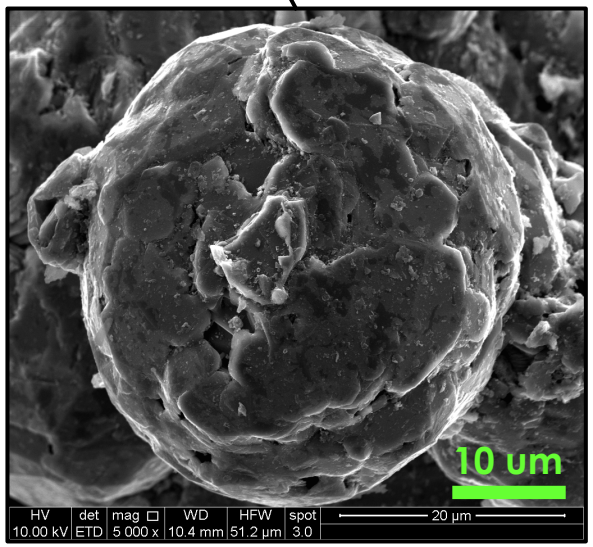
Catalytic Conversion of Coal to Graphite

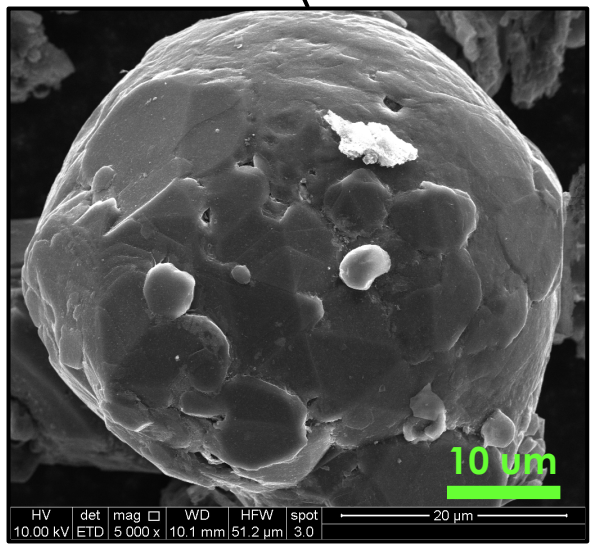
Catalytic Conversion of Different Coal Ranks

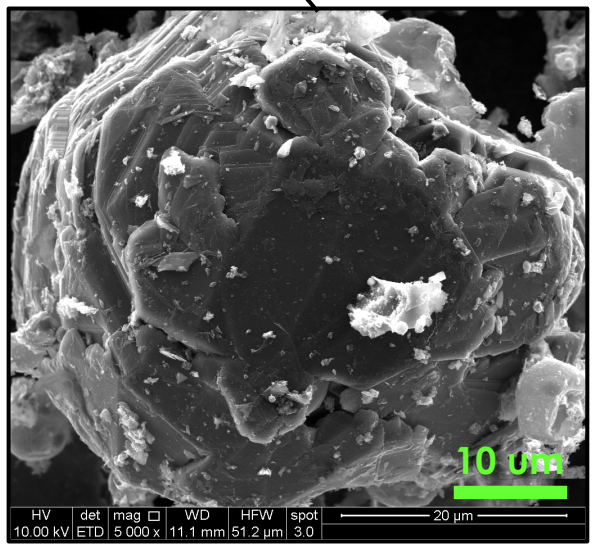
https://www.uky.edu/KGS/coal/coal-rank.php

Peat	Low-rank coal					Medium-rank coal					High-rank coal			Method for determining rank (dmmf) (U.S. ASTM)
	Lignite		Sub-bituminous			Bituminous					Anthracitic			
	B	A	C	B	A	high volatile C	high volatile B	high volatile A	medium volatile	low volatile	Semi-anthracite	Anthracite	Meta-anthracite	









Catalytic Conversion of Coal to Graphite

Catalytic Conversion of Different Coal Ranks

Coal rank (ASTM rank)	Anthracite (an)	Bituminous (hvAb)	Sub-Bituminous (subB)		Sub-Bituminous (subC)		Lignite (ligA)		Commercial Graphite	
Sample	DECS-21	DECS-32	DECS-9	DECS-26	DECS-8	DECS-39	DECS-11	DECS-25	Natural graphite	Artificial graphite
Seam	Lykens Valley #2	Stockton-Lewiston	Dietz	Wyodak	Smith-Roland	Anderson/ Canyon	Beulah	Pust	MSE supplies	MTI corporation
County, State	Columbia, PA	Kanawha, WV	Bighorn, MT	Campbell, WY	Campbell, WY	Campbell, WY	Mercer, ND	Richland, MT		
Char Yield (%)	92.3	70.3	43.8	39.4	38.9	39.5	38.1	36.0	-	-
Ash (wt%)[a]	3.02	4.11	0.415	0.095	0.67	0.888	1.67	3.86	<0.1	0.53
DG (%)[b]	83	81	**91**	**96**	**95**	**91**	**91**	88	95	93
$d_{(002)}$ (nm)[b]	0.33683	0.33712	0.33620	0.33577	0.33585	0.33622	0.33622	0.336413	0.33581	0.33604
Lc (nm)[b]	47	39	46	48	44	47	43	45	45	41
La (nm)[b]	25	47	77	84	33	73	53	58	85	39
Nc (-)[b]	140	114	136	143	132	139	128	133	135	122
2H/3R (%)[b]	62/38	57/43	62/38	82/18	64/36	70/30	51/49	57/43	81/18	81/19
S_{BET} (m^2/g)[c]	9.48	24.14	5.34	5.40	7.50	5.60	13.54	7.90	2.26	2.48

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  - **Physical Processing**
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Improving Material Quality to Produce Battery Grade Graphite

General Requirements for Battery-Grade Graphite

High-Quality Graphite for Battery Application

Low ash (< 0.1%)

- High-Purity for Max. Li ion loading (theoretical specific capacity of graphite is 372 mAh/g)

Flake graphite (micrometer sizes)

- Highly crystalline flake graphite is essential for high-grade commercial Li-ion grade graphite

Particle morphology (potato)

- Decreasing Coulombic losses, and a high packing efficiency, increasing volumetric and areal capacity

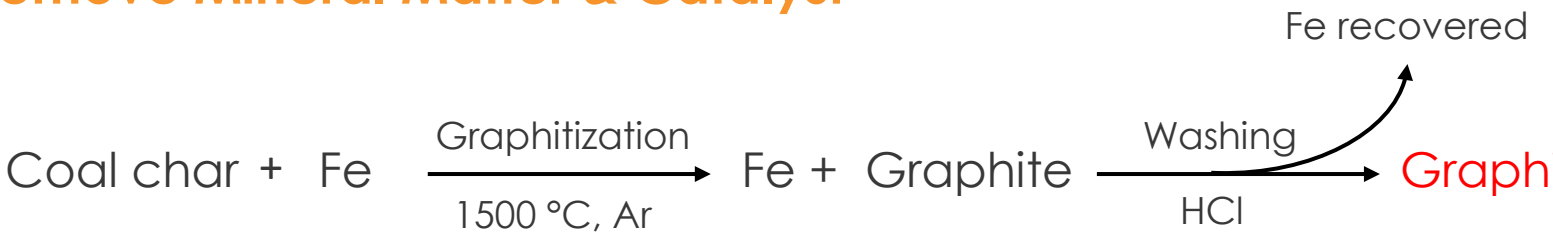
Low surface area (< 5 m^2/g)

- Mitigate the SEI formation, mitigate irreversible capacity

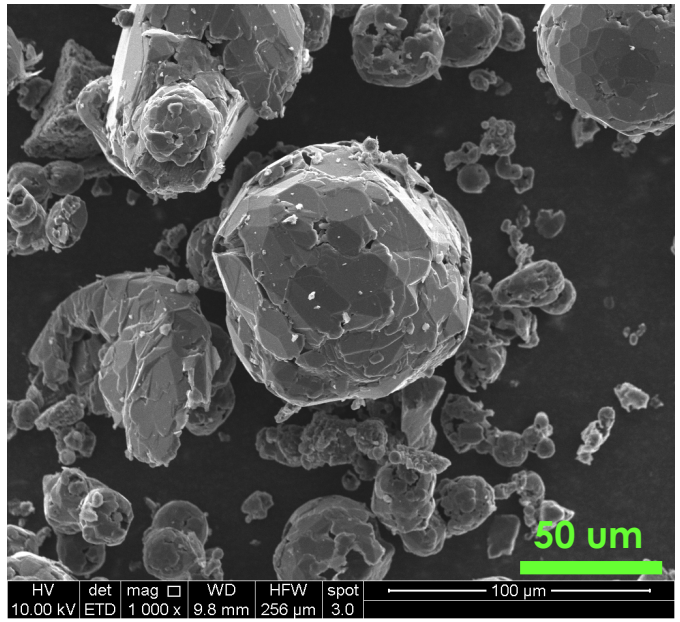
Natural graphite after physical processing

Improving Material Quality to Produce Battery Grade Graphite

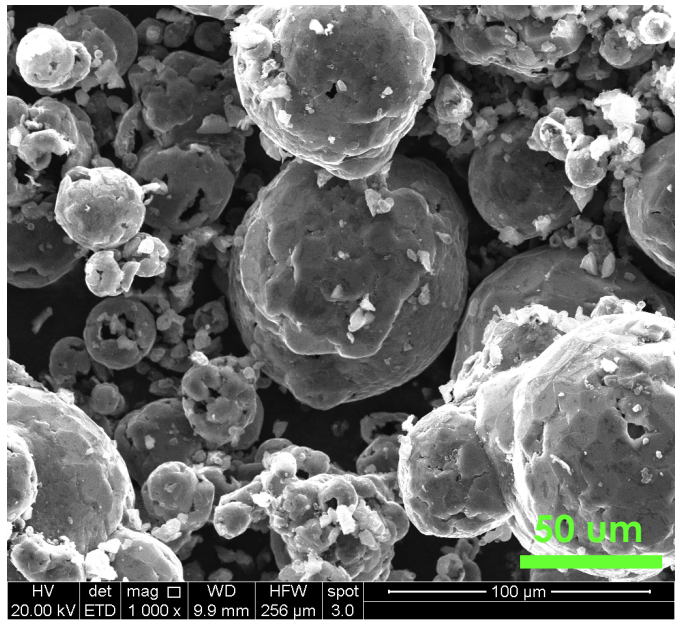
Remove Mineral Matter & Catalyst

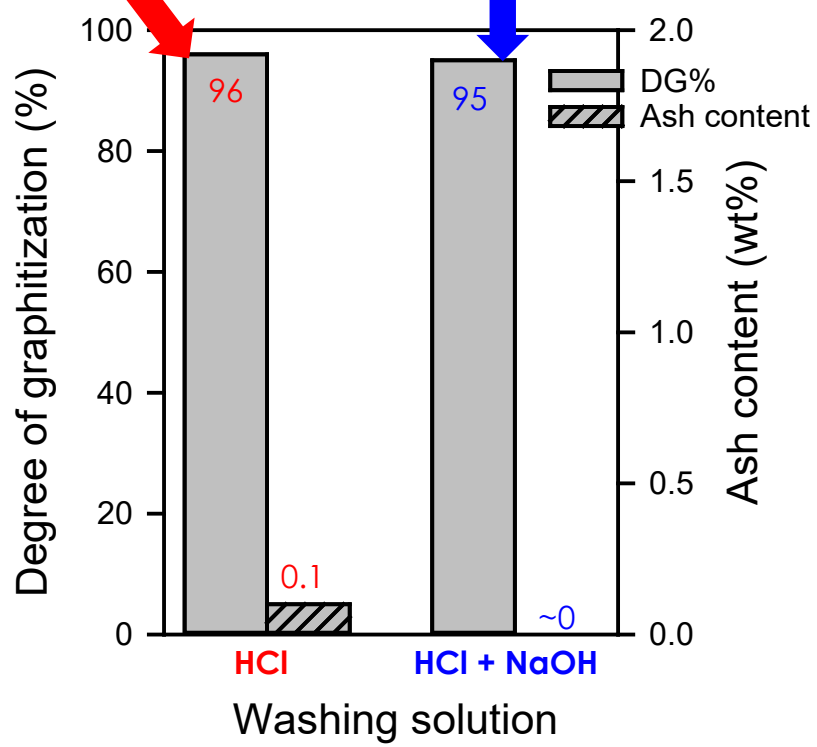


HCl



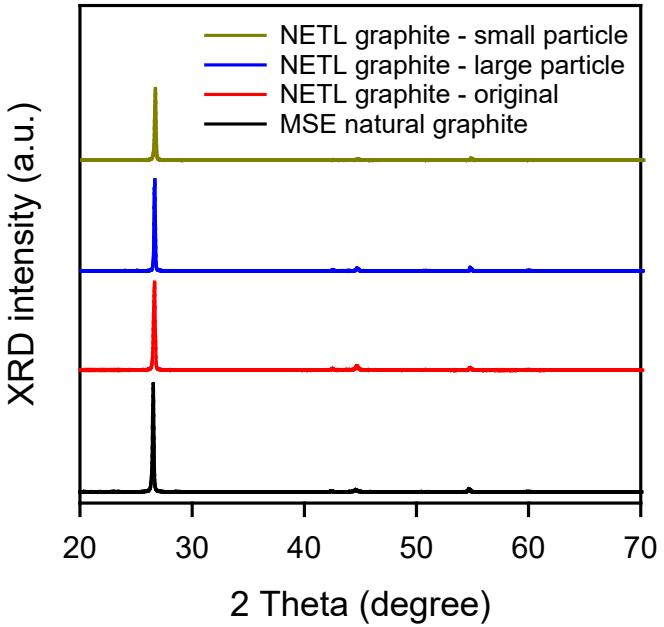
HCl & NaOH

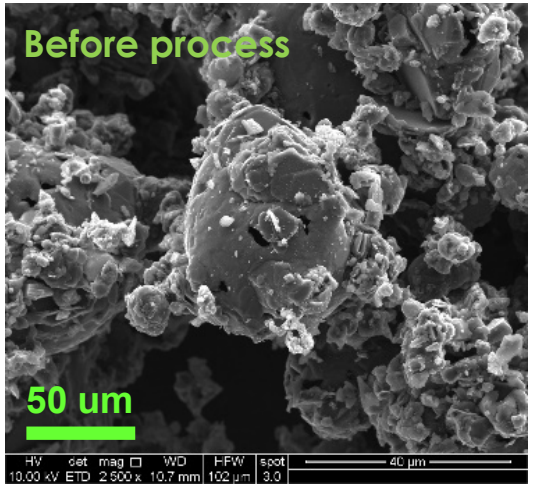


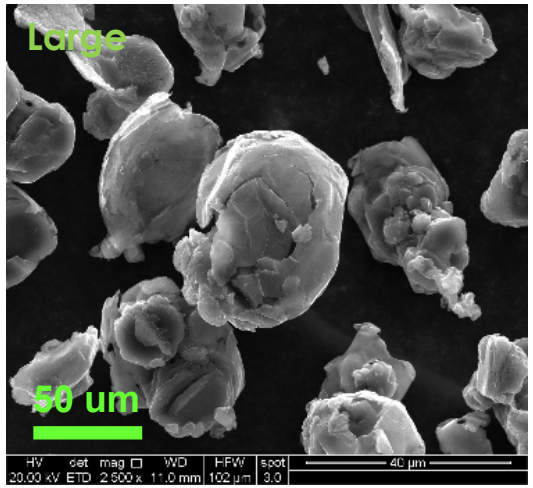


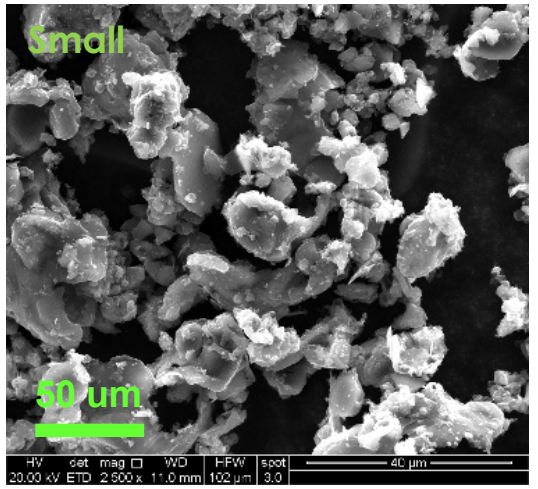
Improving Material Quality to Produce Battery Grade Graphite

Physical Processing







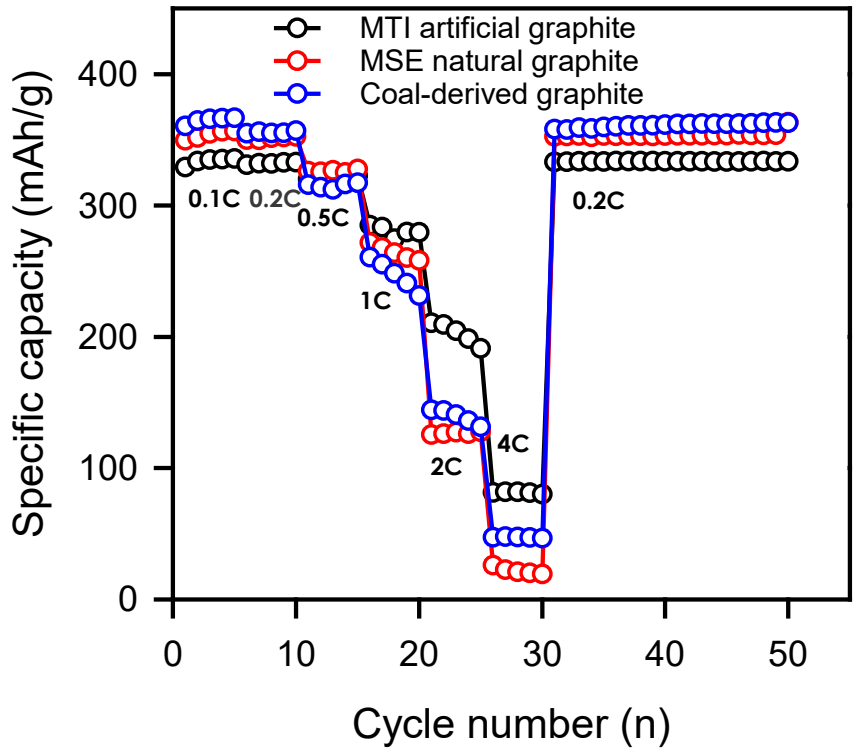


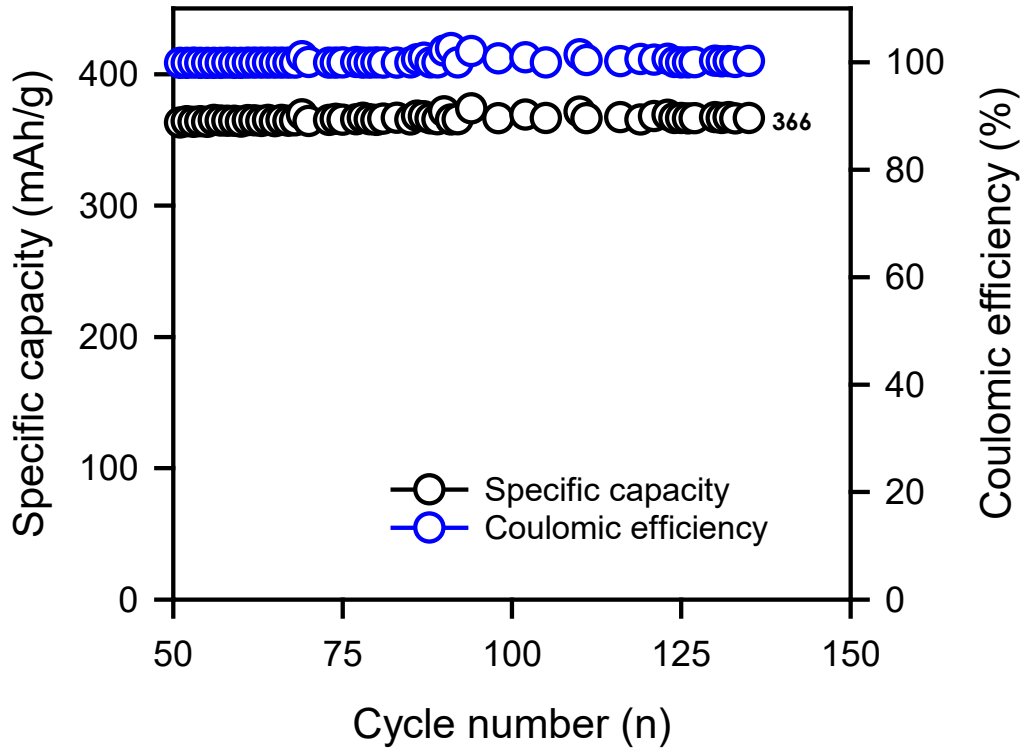
	Commercial Natural Graphite	NETL Graphite Original	NETL Graphite Large (80 wt.%)	NETL Graphite Small (20 wt.%)
Ash (wt.%)	0.1	0.095	~0	0.46
Surface area (m^2/g)	1.38	5.4	3.4	23.0
DG%	95	96	96	93

Improving Material Quality to Produce Battery Grade Graphite

LIBs Testing Performance

Graphite	NETL Graphite	MSE Natural Graphite	MTI Synthetic Graphite
First discharge capacity (mAh/g)	340	349	329
First discharge efficiency (%)	82	74	74





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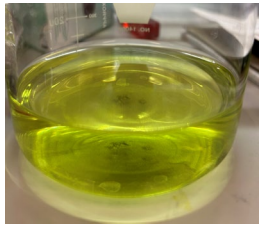
Recovery/Recycling Fe Catalyst & HCl Recycling

Recovery/Recycling Fe Component

Fe_2O_3 + Fe + Coal char $\xrightarrow[Ar]{1500\ °C,\ 3\ hr}$ Fe + Graphite

Fe + Graphite $\xrightarrow{2M\ HCl}$ $FeCl_x$ + HCl + Graphite $\xrightarrow[\text{Filtered}]{\text{Sample}}$ $FeCl_x$ (aq) + HCl

Solid Graphite Recovered



$FeCl_x$ (aq) + HCl $\xrightarrow[\text{Distillation}]{\text{Hydrolytic}}$ **Fe_2O_3 (s) + HCl**

Fe_2O_3

Recovery >95%

Hydrolytic Distillation

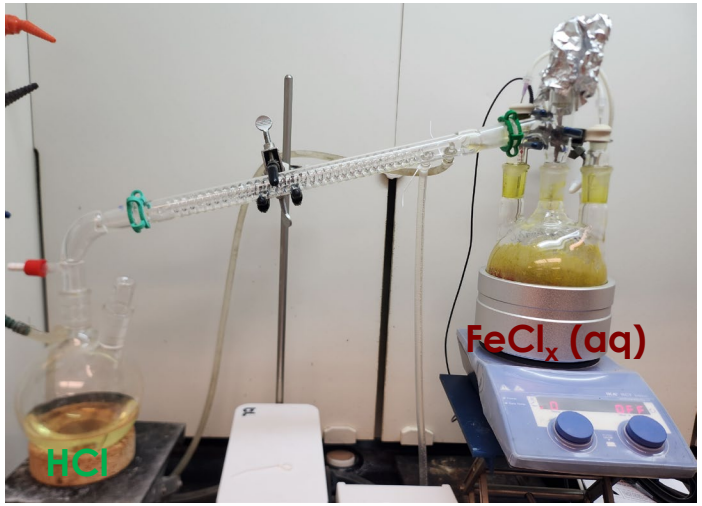
$FeCl_3 \cdot xH_2O$ (l) $\longrightarrow$ $FeCl_3 \cdot 2H_2O$ (l) + (x-2) H_2O (g)

$FeCl_3 \cdot 2H_2O$ (l) $\longrightarrow$ $FeOCl \cdot H_2O$ (s or l) + 2 HCl (g)

$FeOCl \cdot H_2O$ (s or l) $\longrightarrow$ HCl (g) + FeOOH (s)

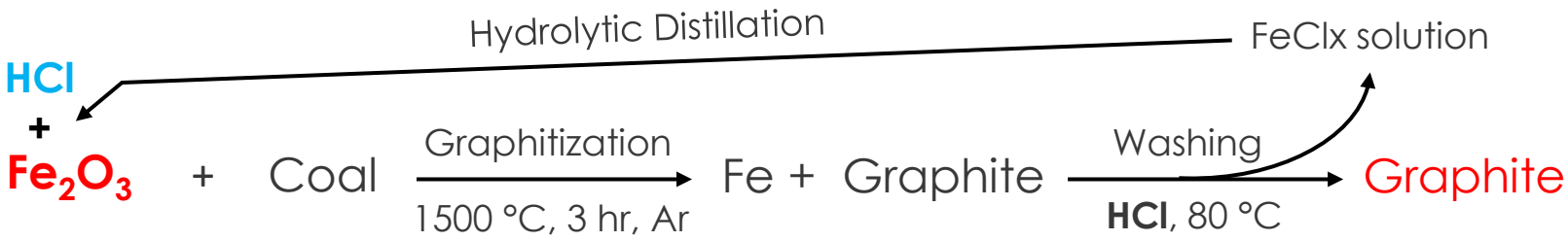
2 FeOOH (s) $\longrightarrow$ Fe_2O_3(s) + H_2O (g)

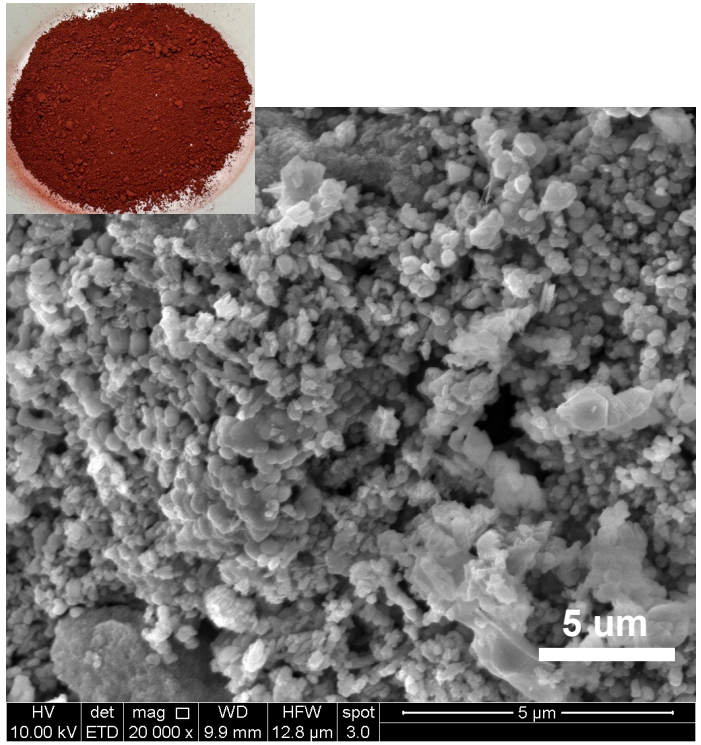
FeOCl

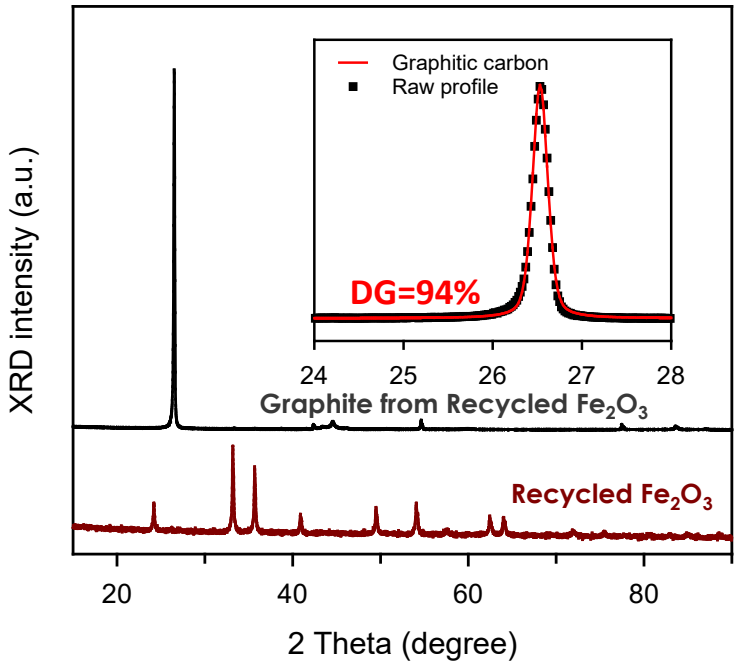


Recovery/Recycling Fe Catalyst & HCl Recycling

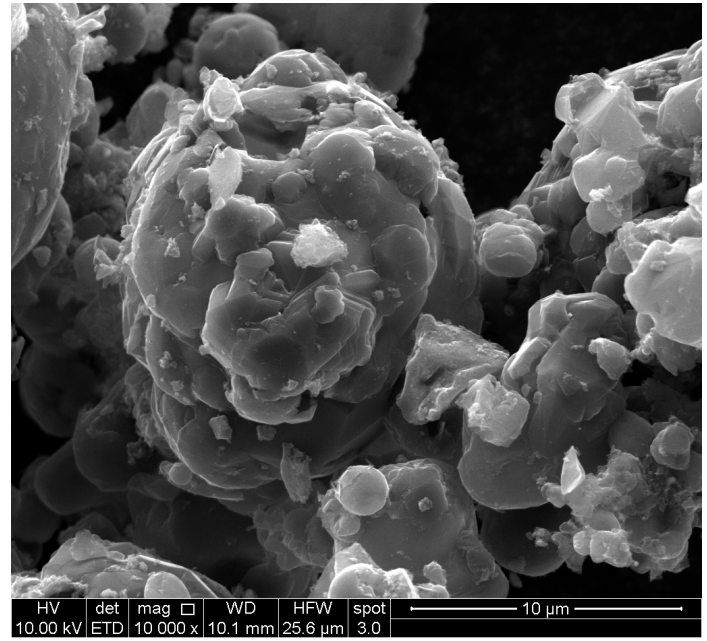
Recovery/Recycling Fe Component





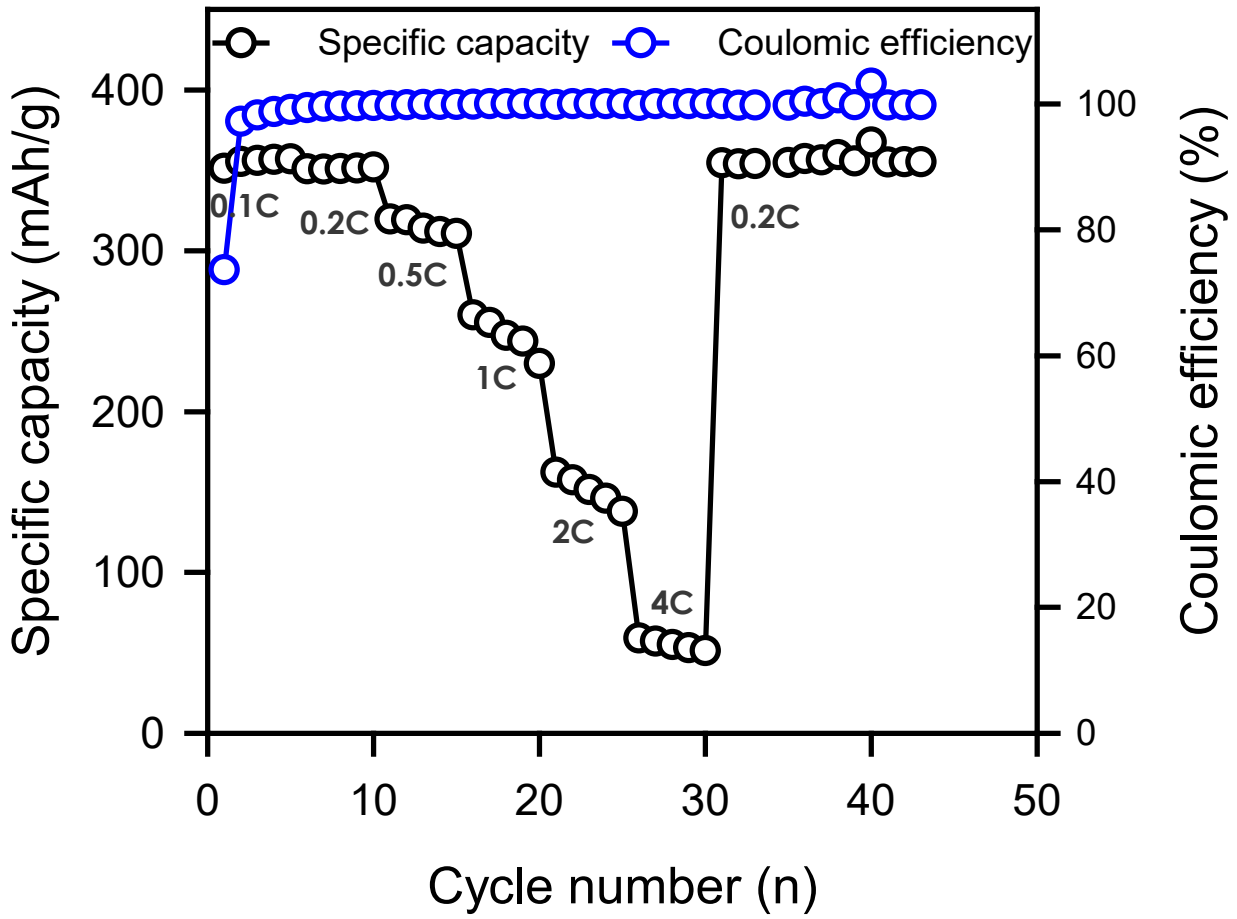


- Surface area ≈ 8.4 m^2/g
- Ash ≈ 0 wt.%



Recovery/Recycling Fe Catalyst & HCl Recycling

LIBs Testing Performance



Graphite	NETL Graphite by Fresh Catalyst	NETL Graphite by Recycled Fe_2O_3 and HCl
DG%	96	94
Ash (wt.%)	<0.095	~0
Surface area (m^2/g)	5.4	8.4
First discharge capacity at 0.1 C (mAh/g)	340	351
First charge capacity at 0.1 C (mAh/g)	415	476
Initial Coulombic efficiency (%)	82	74
50^{th} discharge at 0.2C (mAg/h)	357	355
50^{th} CE (%)	99.8	99.8

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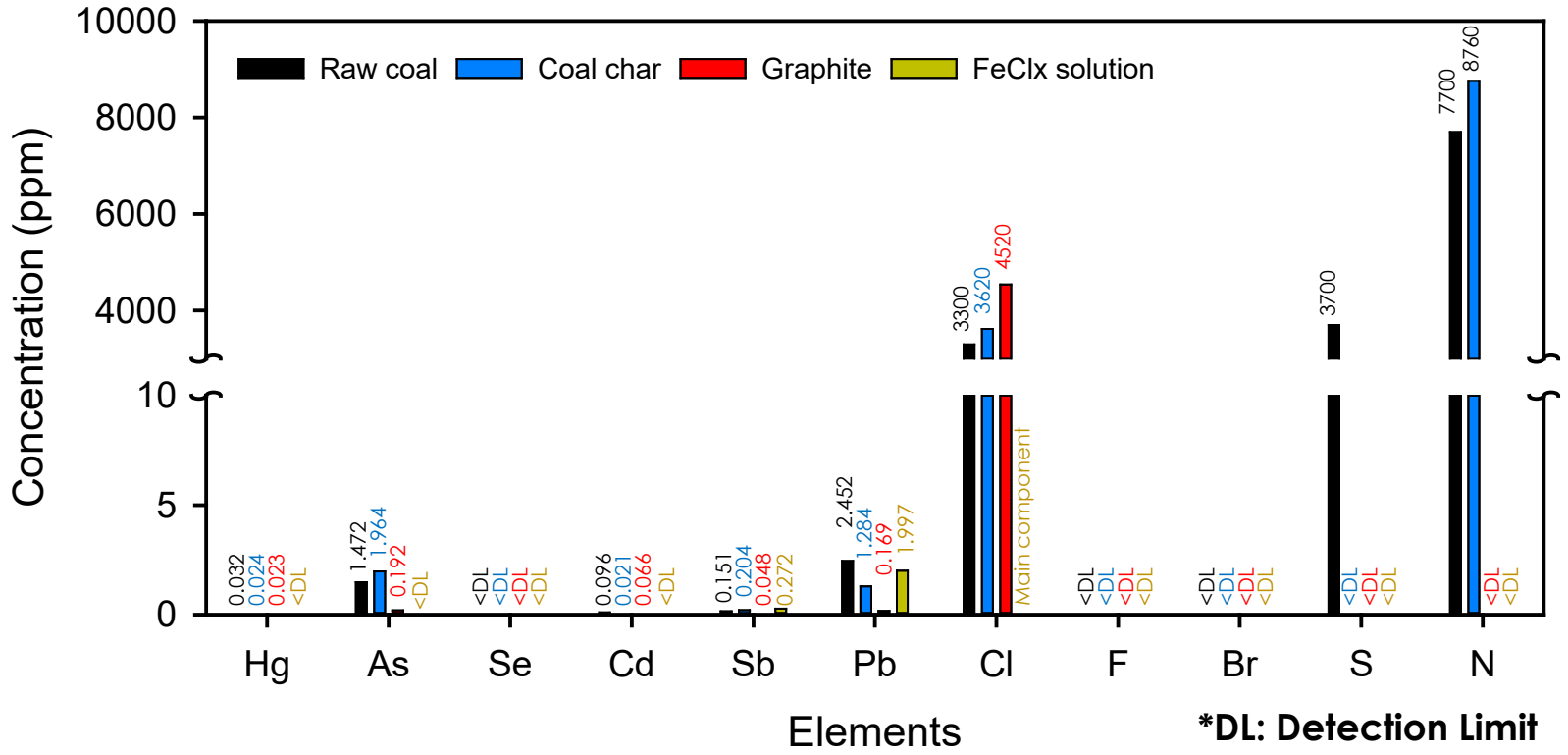
Elemental Analysis

Elements of Interest ("Bad actors")

Coal (S) → Charred, 900 °C, Ar → **Coal Char (S)** → Graphitized with Fe, 1500 °C, Ar → Graphite as synthesized (S) → Washed, 2M HCl → **Graphite after washing (S)**

→ ***FeClx solution (L)**



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Summary and Next Steps

Catalytic Conversion of Coal to Graphite

- Summary
  - Investigated a series of experiments for the catalytic graphitization process with coal, where the size of Fe particles, the ratio of catalyst to coal sample, and graphitization temperatures/times were varied to optimize the synthetic process of coal-derived graphite, as well as different coal ranks.
  - Successfully demonstrated catalytic graphitization of coal with degree of graphitization of >95% and highly crystalline graphite powder, comparable or higher than numerous commercial battery-grade graphite on the market.
  - Investigated a washing procedure and physical processing that additionally improves the quality of graphite.
  - Demonstrated the recycling process of Fe component and HCl reagent and reused them as sustainable resources in graphitization process.
  - Fabricated LIBs with NETL's best graphite as an anode electrode material, and the testing electrochemical performance was benchmarked against commercial battery-grade graphite.

Acknowledgments

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Thank you!