Lignite-Derived Carbon Materials for Lithium-Ion Battery Anodes

DOE NETL Project DE-FE0031984

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U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
October 25 - 27, 2022

Outline

- Project Overview
- Background: Lithium-ion Battery & Si Anode
- Technical Approach & Project Scope
- Progress and Current Status
- Future Plan
- Summary

Project Overview

- Funding

DOE Funds	Cost Share	Total Cost
$499,815	**$167,650**	$667,465
74.88%	**25.12%**	100%

- Overall Project Performance Dates
  - 1/20/21-1/19/23 (No-cost extension to 9/30/23)
- Goal

ND lignite → **Si/C Anodes for Li-ion Battery**

  - Production: Lab-scale (10g) to Bench-scale (1kg)
  - Superior battery performance vs Benchmark
  - Competitive price: $20/kg (vs $20-30 benchmark commercial anode)

Project Overview

Project lead

- Daniel Laudal (**PD**) & Xiaodong Hou (**PI**) (UND Institute for Energy Studies)

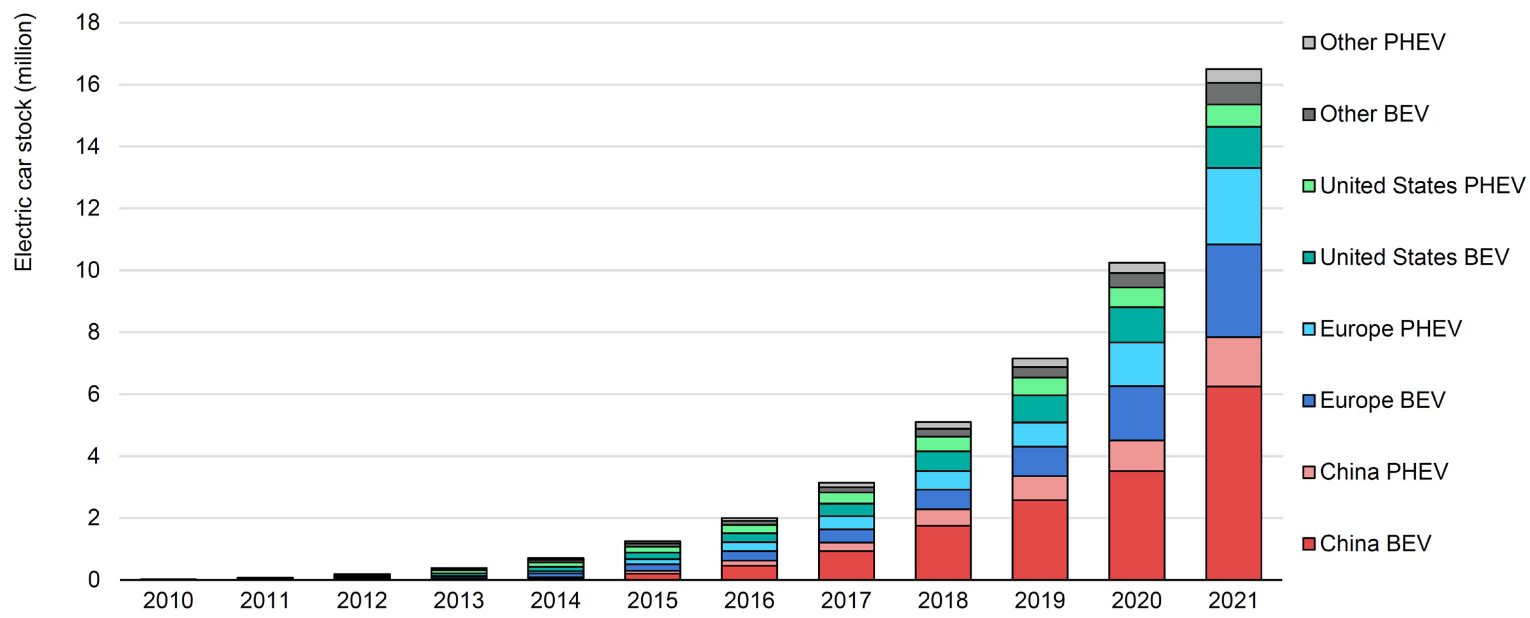
Project Sponsor Representatives

- Michael Fasouletos (DOE NETL)
- Mike Holmes (Lignite Research Council)
- Gerard Goven (North American Coal Corp)
- Yong Hou (Clean Republic LLC)

Background: EV & Li-ion Battery

Over 16.5 million electric cars were on the road in 2021, a tripling in just three years

Global electric car stock, 2010-2021



Notes: BEV = battery electric vehicle; PHEV = plug-in hybrid electric vehicle. Electric car stock in this figure refers to passenger light-duty vehicles.
"Other" includes Australia, Brazil, Canada, Chile, India, Japan, Korea, Malaysia, Mexico, New Zealand, South Africa and Thailand. Europe in this figure includes the EU27, Norway, Iceland, Switzerland and United Kingdom.
Sources: IEA analysis based on country submissions, complemented by ACEA; CAAM; EAFO; EV Volumes; Marklines.

A turning point - 5% Market Penetration Q1 2022!

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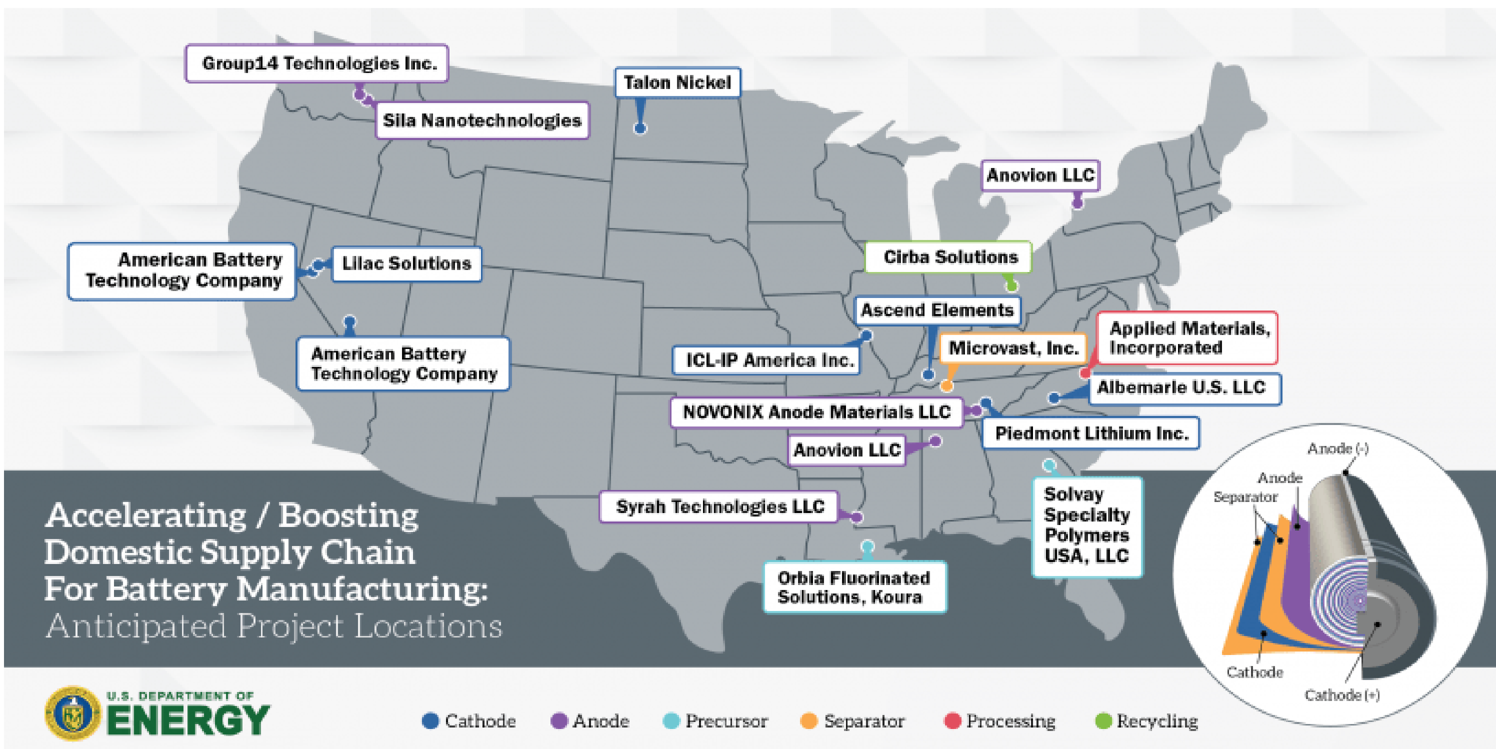
Background: Battery Materials Capacity Gap In US

Department of Energy

Biden-Harris Administration Awards $2.8 Billion to Supercharge U.S. Manufacturing of Batteries for Electric Vehicles and Electric Grid

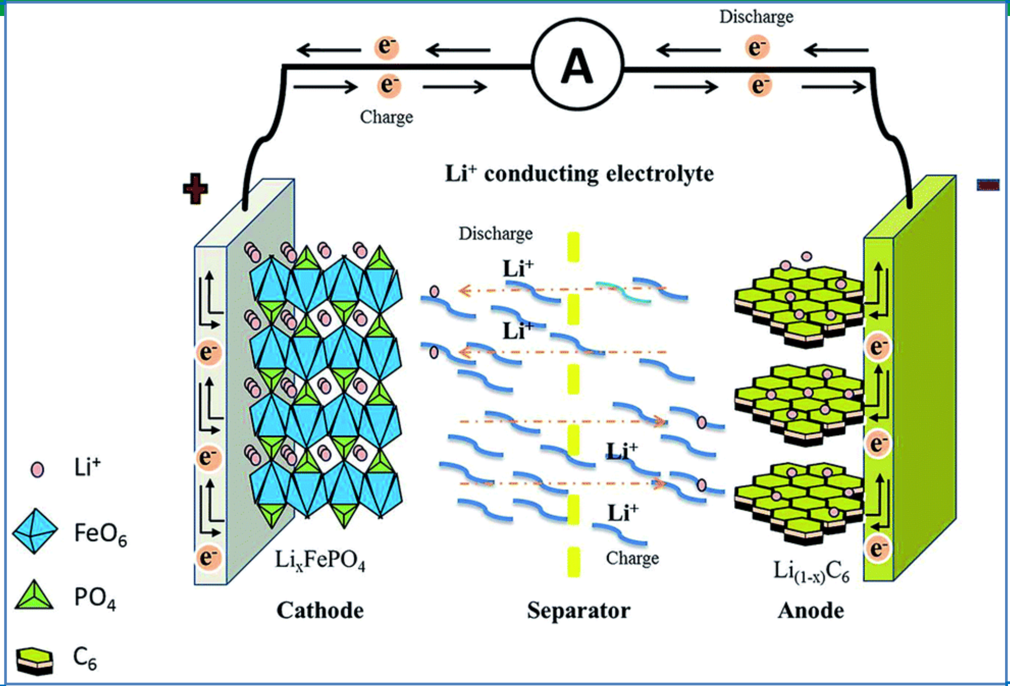
OCTOBER 19, 2022



Background: Li-ion Battery (LIB)

Capacity

Cycle Life



Safety

Cost

Cathode (30%)
Anode (10%)
Separator (5%)
Electrolyte (5%)

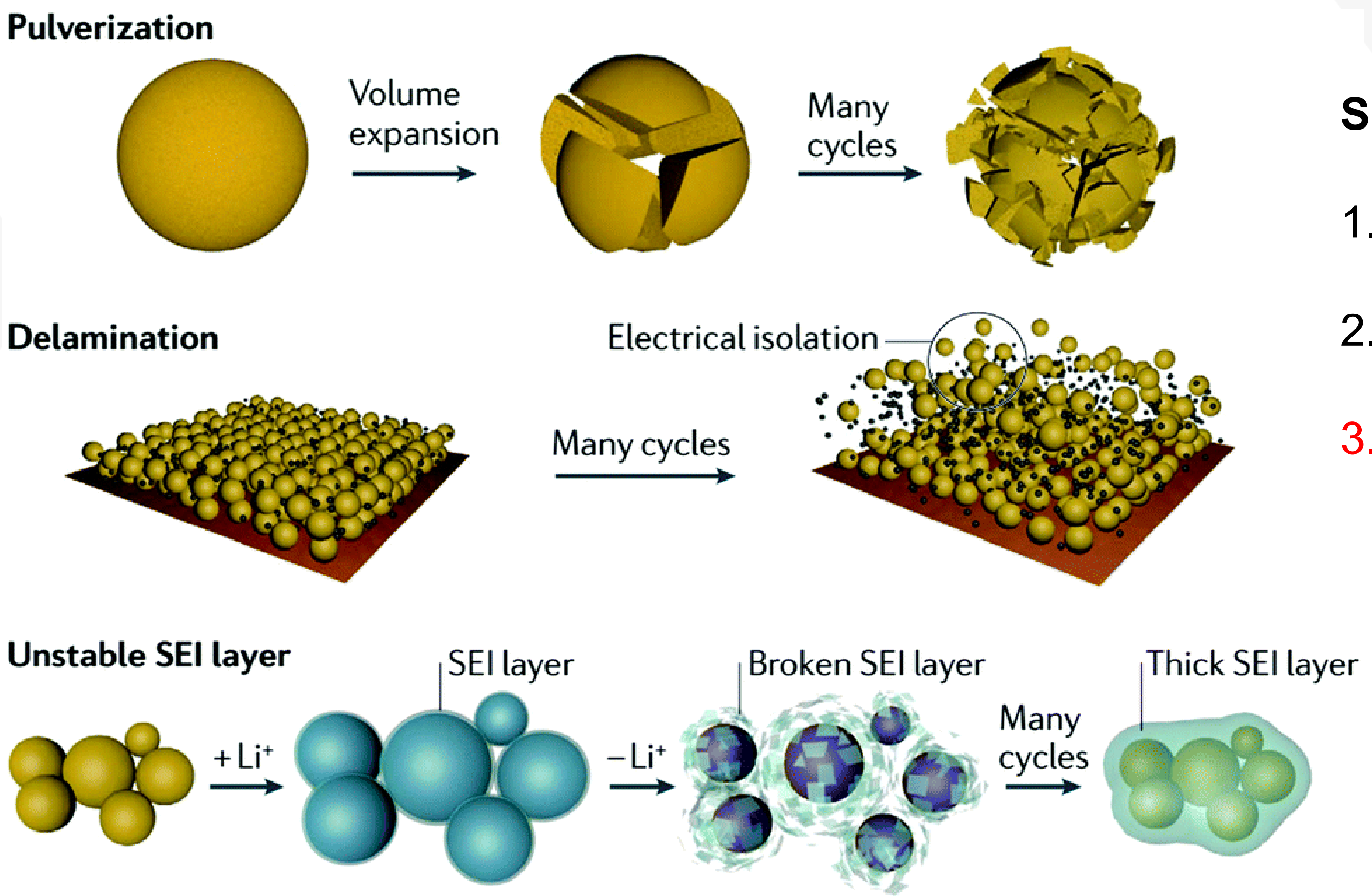
>50% cost of LIB

Energy Environ. Sci., 2014,**7**, 3857-3886

Background: Anodes for LIB

	Graphite	Si
Capacity	372 mAh/g	3600-4200 mAh/g
Cycle life (80% Retention)	>1000	<300
Mechanism	$Li + 6C = LiC_6$	$15Li + 4Si = Li_{15}Si_4$ $22Li + 5Si = Li_{22}Si_5$
Cost	$10-15/kg	≥$65/kg
Other Key Issues	Poor low-T performance & rate capability	Low conductivity & low ICE, >300% volume change

Background: Problems with Si-Anode



Solutions:

1. Nano-Si
2. Si Alloy
3. Si/C

Mater. Chem. Front., 2017,**1**, 1691-1708

Background: Anode Market Size Forecast

2025 vs (2020)

Solid Products	Market Volume (kilo-ton)	Annual Growth (%)	Market Value ($Billion)	Coal Utilized (million tons)
Anodes	1500 (400)	40	20	3.5
Synthetic Graphite	650 (240)	20	6.5	2
Si–C Anodes	500 (<20) 33% (<5%)	130	10	1.5

Background: Anode Materials Capacity Gap in US

	Share of Graphite Capacity (tons tpa, % Share)		
	Total Installed	In Construction	Planned New (2030)
US	4K, 0.3%	2K, 0.15%	150K, 2.9%
Asia	1.6M, 94.4%	1.4M, 99.4%	4.6M, 91.7%

One EV needs average 100kg graphite

Biden's goal of 50% EV sales by 2030 needs 15M*50%*0.1=750K (80%)

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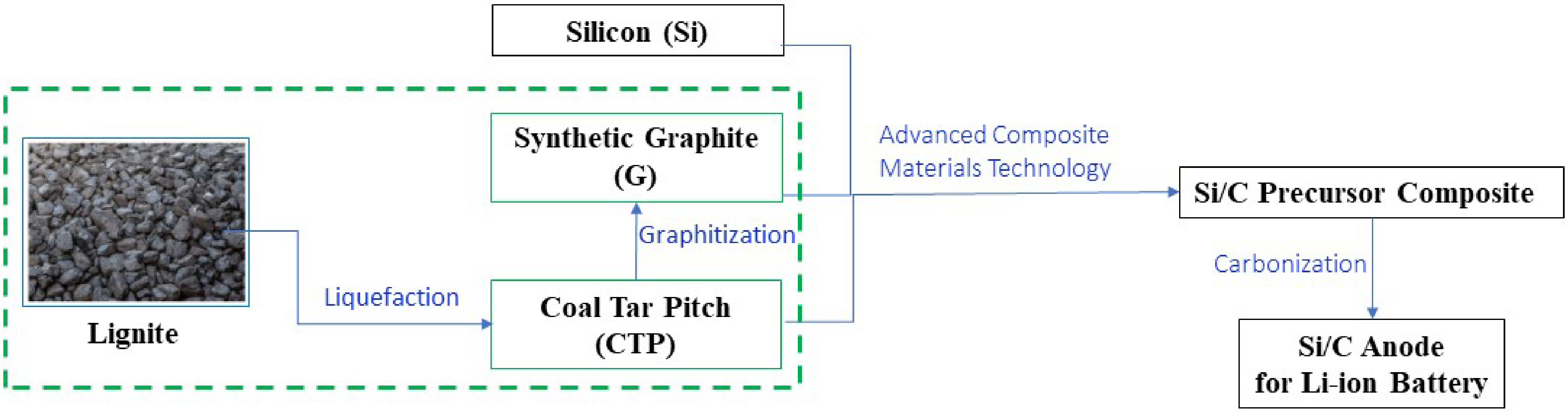
Technical Approach



Advantages:

- ✓ High performance
  - Reversible capacity
  - Initial Columbic efficiency
  - Cycling life
- ✓ Low-cost
  - Micro-size Si sources
  - Coal-derived feedstock

Challenges:

- ✓ Homogeneity ?
  - Si evenly distributed in Carbon matrix

Success Criteria

Performance Attribute	Performance Requirement	Reference Materials (S450-2A)
Reversible Capacity (mAh/g)	540	450
Initial Columbic Efficiency (ICE)	>90	90
Cycling Life (@80% capacity retention)	500	300
Cost ($/ton)	11,060	16,530

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Scope of Work

- Task 1 – Project Management and Planning (90% completed)
- Task 2 – Analysis of Lignite-derived carbon Feedstock (100% completed)
- Task 3 – Development of Si-C anode (100% completed)
    - Subtask 3.1 Preparation of Si/graphite/CTP composite precursor
    - Subtask 3.2 Preparation of Si/C anodes
    - Subtask 3.3 Electrochemical performance Testing
- Task 4 – Bench-scale Test (30% completed)
- Task 5 – Techno-Economic Analysis of Integrated Process (25% completed)

Progress & Current Status- Feedstock Analysis

Lignite-derived CTP Feedstock

- Softening point (SP)
- Coking Value
- Chemical composition & Ash
- Graphitization Yield

Coal Tar Pitch (CTP)

- Low softening point (< 75℃)
- Medium softening point (85 ℃ - 95℃)
- High softening point (>95℃)

High SP (ND lignite) | Low SP | Medium SP

Coke samples

Progress & Current Status- Feedstock Analysis

CTP Source	Softening Point (℃)	Coking value %	Graphitization Yield	Ash	C	H	N	S	O
Commercial CTP-1	< 75 ℃	20.6%	--	0.64	79.80	6.08	<0.20	<0.01	13.27
CommercialCTP-2	85 ℃ - 95 ℃	27.1%	--	0.33	81.98	6.59	0.98	0.17	9.95
CommercialCTP-3	> 95 ℃	36.8%	93.4%	0.25	68.60	6.33	1.28	0.08	23.47
ND lignite CTP-0	> 95 ℃	49.4%	--	4.38	87.41	4.15	1.18	0.67	2.20
ND lignite CTP-1	102℃	28.1%	92.0%	1.05	88.65	5.61	1.00	0.66	3.03
ND lignite CTP-2	> 95 ℃	27.6%	93.7%	1.98	85.40	6.34	0.77	0.51	4.92
ND lignite CTP-3	> 95 ℃	30.9%	89.4%	--	--	--	--	--	--
ND lignite CTP-1-G	--	--	--	--	>99.3	<0.5	<0.2	<.0.01	<0.01

- Total seven CTP has been analyzed (more are ongoing)
- High C, C/H ratio, very low O
- Slightly high ash, higher S

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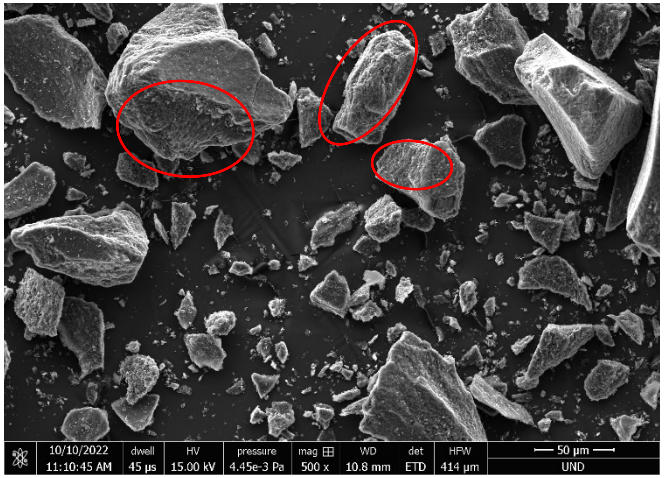
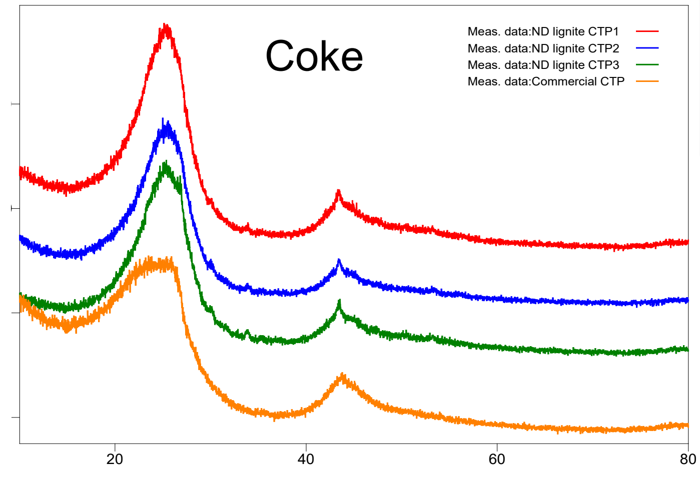
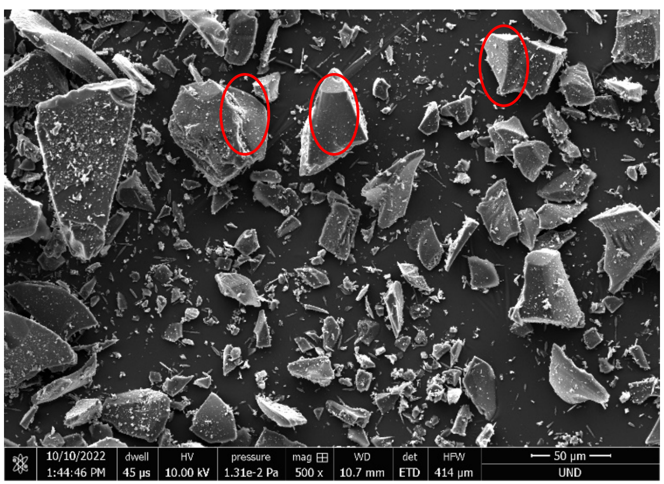
Progress & Current Status-Feedstock Analysis

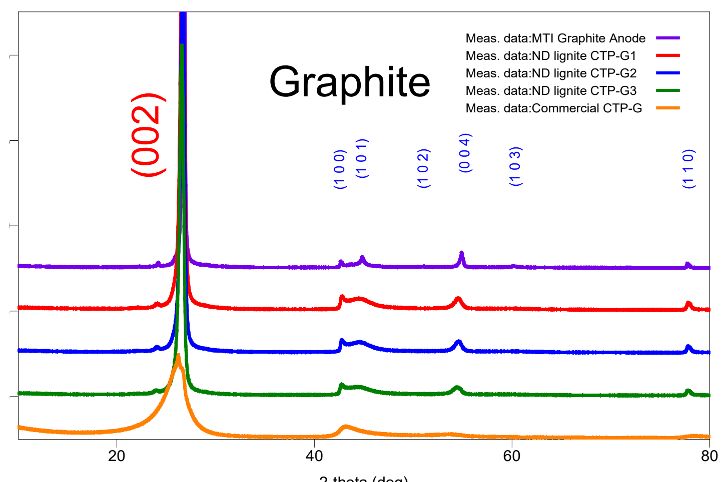
ND lignite CTP-G





Commercial CTP-G





*Optimized pattern is displayed.

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Progress & Current Status- Si/G/CTP Precursor Composite Development

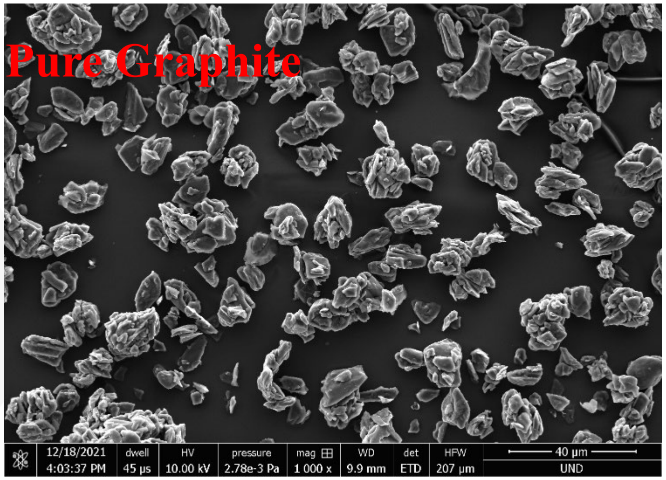
- One typical low SP and high SP CTP with low ash were selected
- Composite preparation approach: wet chemistry + mechanical force

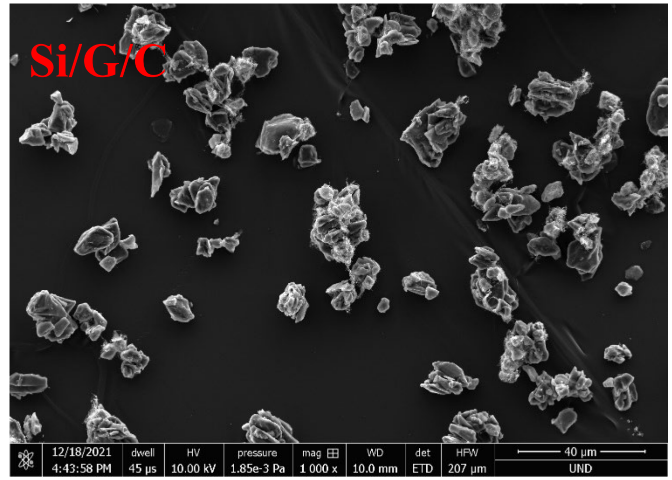
CTP	Primary Approach	Secondary Approach
Low SP	Wet chemistry	Mechanical force
High SP	Mechanical force	Wet chemistry

- Intensive Design of Experiment (DoE) optimizing the feedstock and process parameters
- An optimal procedure was developed for each CTP

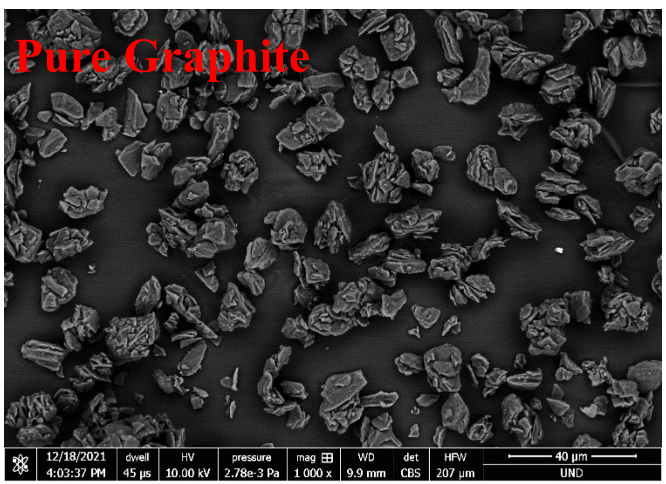
Progress & Current Status- Si/G/C Precursor Composite Development

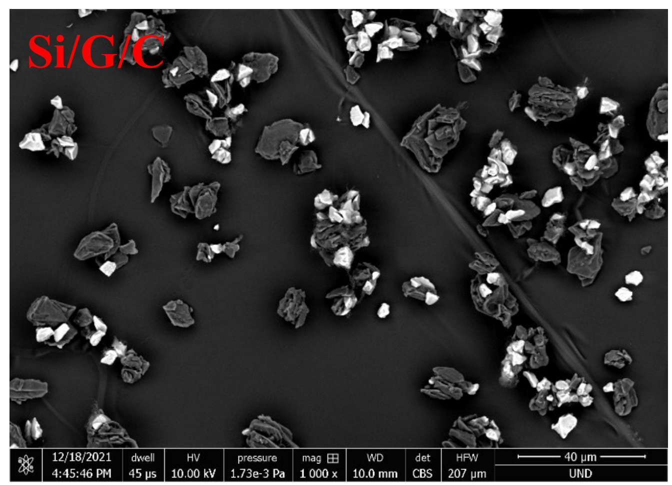
SE





BSE

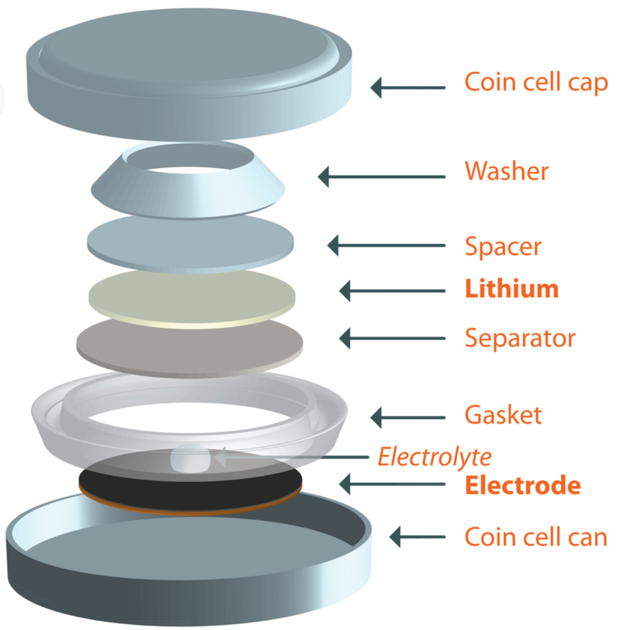




- Si/C: ~20/80
- C: >99% Coal-derived
- Si well dispersed
- No graphite agglomeration

Progress & Current Status- Si/C Anode Development

Li-ion Battery Fabrication and Testing



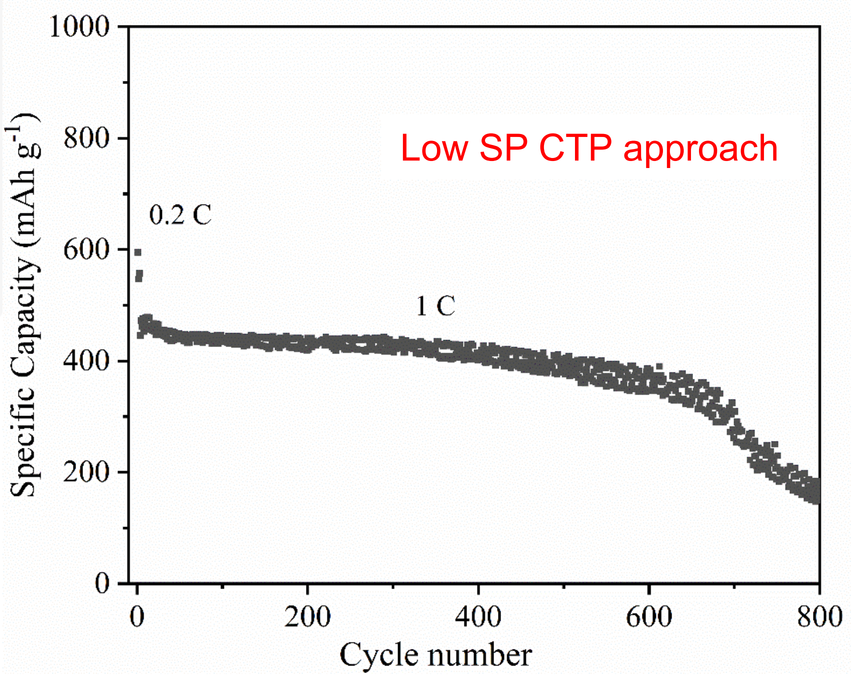
Coin cell configuration

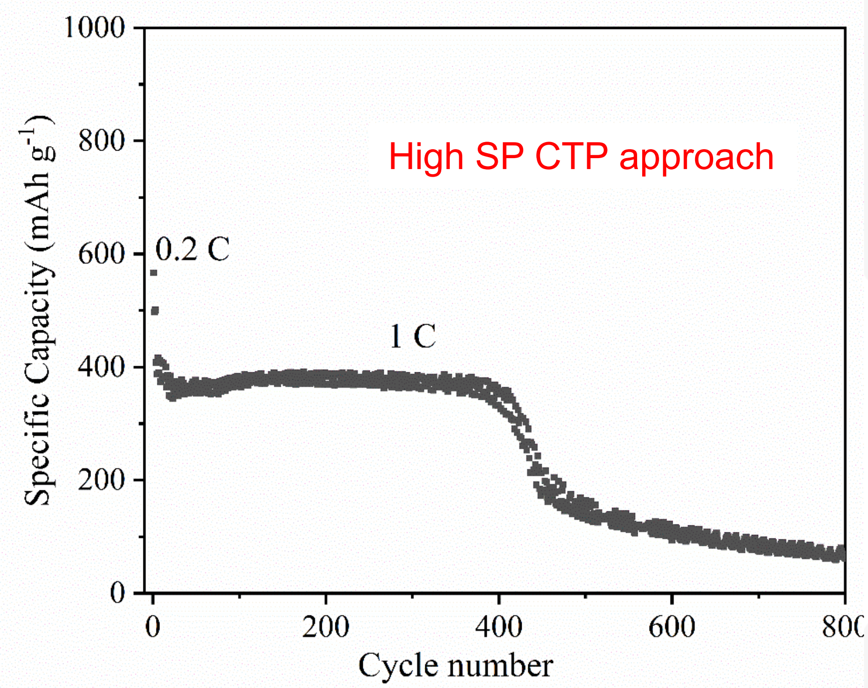
Glove Box

Coin-cell Tester

Progress & Current Status- Si/C Anode Development

Battery Testing Results





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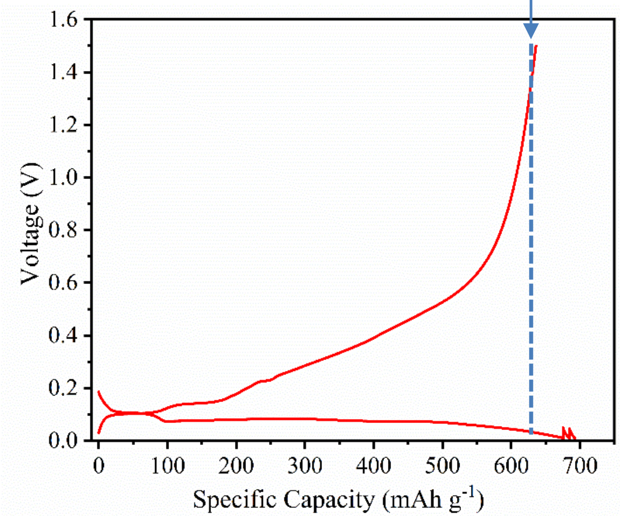
Progress & Current Status- Si/C Anode Development

Performance Attribute	Performance Requirement	Reference Materials (S450-2A)	Low SP CTP Approach	High SP CTP Approach
Reversible Capacity (mAh/g)	540	450	595	550
Initial Columbic Efficiency (ICE)	>90	90	82	85
Cycling Life (@ 80% capacity retention)	500	300	650	410
Cost ($/ton)	11,060	16,530		

- **Pre-lithiation to increase ICE:**
  - 91% (6 mins)
  - 95% (12 mins)



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Future Plan

- Optimize the pre-lithiation process and complete testing the pre-lithiated samples
- Continue the bench-scale sample preparation
- Fabricate and test larger cells
- Complete the Tech-economic analysis

Outreach and Workforce Development Efforts or Achievement

- **Outreach**
  - IES is helping a ND coal community to cope with the clean energy transition
  - Build a strong partnership with NACoal and its partner CTP producer
- **Workforce development**
  - One postdoc
  - 3 graduates
  - 3 under graduates

Summary

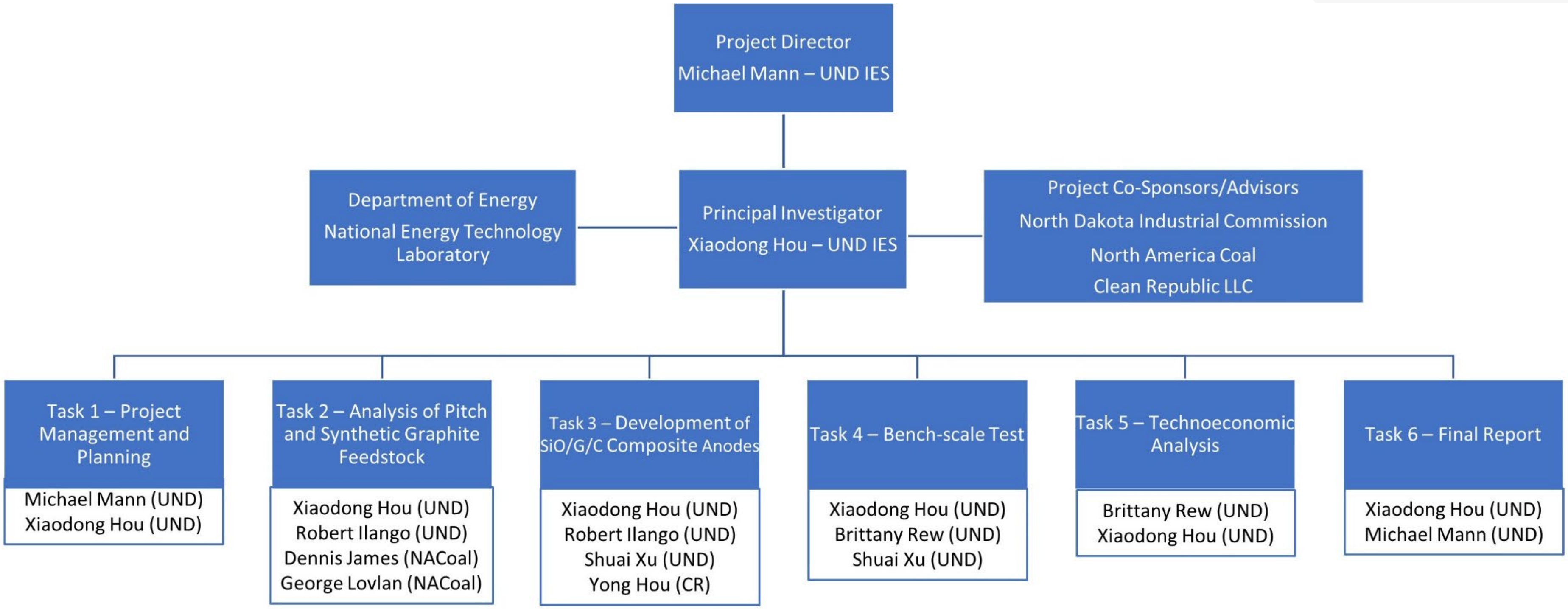
- Si/C anode was successfully developed using ND lignite CTP feedstock. The synthetic process is SP dependent.
- Coin-cells battery performance results are better than commercial refences, and close to our targets
- The battery performance needs to be tested on larger cells

Acknowledgement

- **Sponsors**

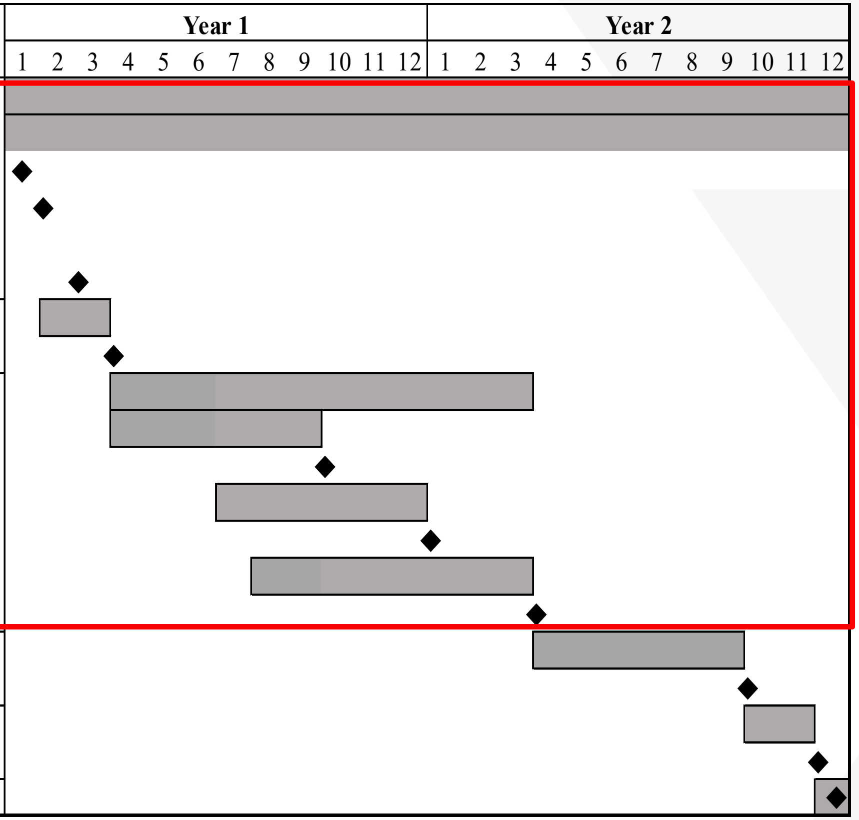
- **Students**
    - Shuai Xu
    - Xin Zhang
    - Molly Rayhorn

Organizational Chart



Gantt Chart

ID	Task Name	Start	Finish
1	**Task 1 - Project Management and Planning**	1/1/21	12/31/22
	Subtask 1.1 - Project Management Plan	1/1/21	1/31/21
	Milestone A		
	Milestone B		
	Subtask 1.2 - Technology Maturation Plan	2/1/21	2/28/21
	Milestone C		
2	**Task 2 - Analysis of Pitch and Synthetic Graphite Feedstock**	1/15/21	3/31/21
	Milestone D		
3	**Task 3 - Development of SiO/G/C Composite Anodes**	4/1/21	3/31/22
3.1	*Subtask 3.1 - Preparation of SiO/G/CTP Porous Microspheres*	4/1/21	9/30/21
	Milestone E		
3.2	*Subtask 3.2 - Preparation of SiO/G/C Composite Anodes*	7/1/21	12/31/21
	Milestone F		
3.3	*Subtask 3.3 - Electrochemical Performance Testing*	8/1/21	3/31/22
	Milestone G		
4	**Task 4 - Bench-scale Test**	4/1/22	9/30/22
	Milestone H		
5	**Task 5 - Techno-Economic Analysis**	10/1/22	11/30/22
	Milestone I		
6	**Task 6 - Final Report** (Milestone G)		12/31/22



Background: Li-ion Battery (LIB)