Lignite-Derived Carbon Materials for Lithium-Ion Battery Anodes

DOE NETL Project DE-FE0031984

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College of Engineering and Mines

U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

April 2, 2024

Outline

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

Project Overview

- **Funding**

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

- **Project Performance Dates**
  - 1/20/21-6/30/24 (No-cost extension)
- **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)

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Project Overview

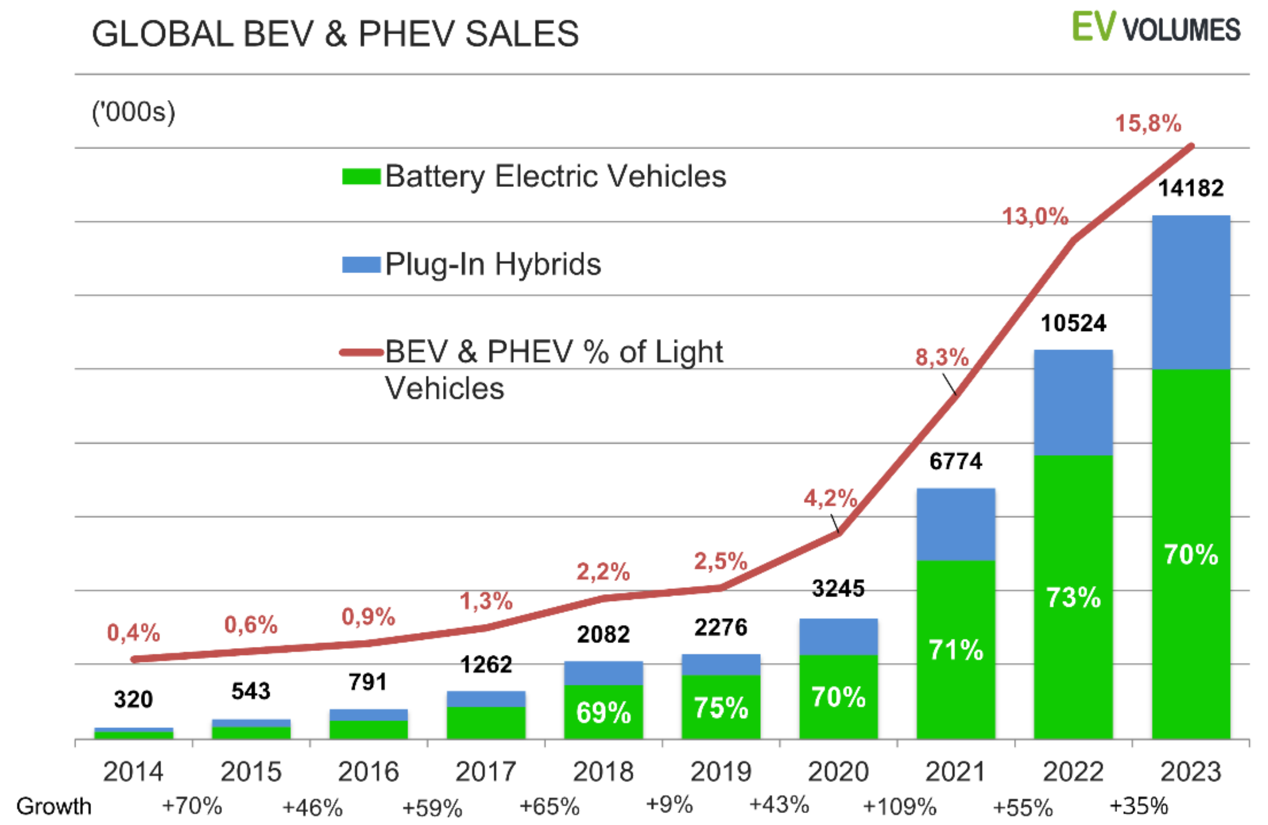
Project lead

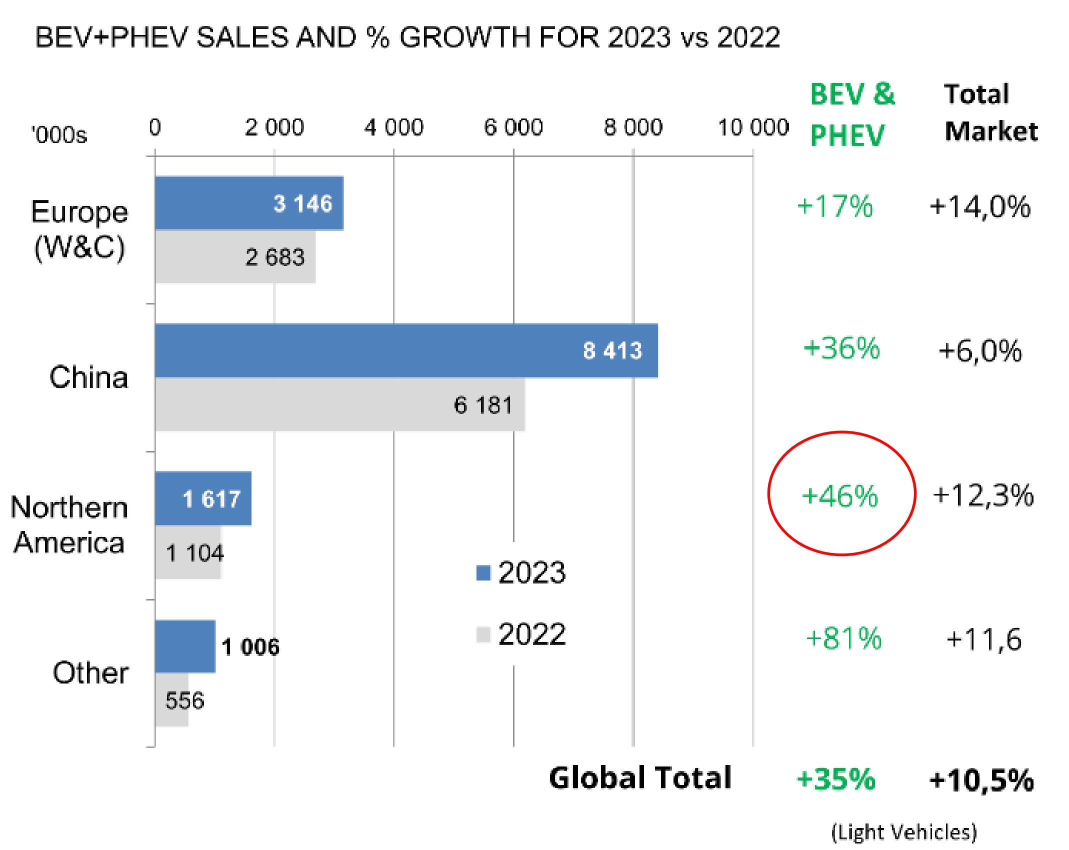
- Daniel Laudal (**PD**) & Xiaodong Hou (**PI**) (UND College of Engineering & Mines Research Institute)

Project Sponsor Representatives

- Bret Hakey (DOE NETL, successor to Michael A. Fasouletos)
- Mike Holmes (Lignite Research Council)
- Gerard Goven (North American Coal Corp)
- Dave Barry (AmeriCarbon)
- Yong Hou (Clean Republic LLC)

Background: EV & Li-ion Battery





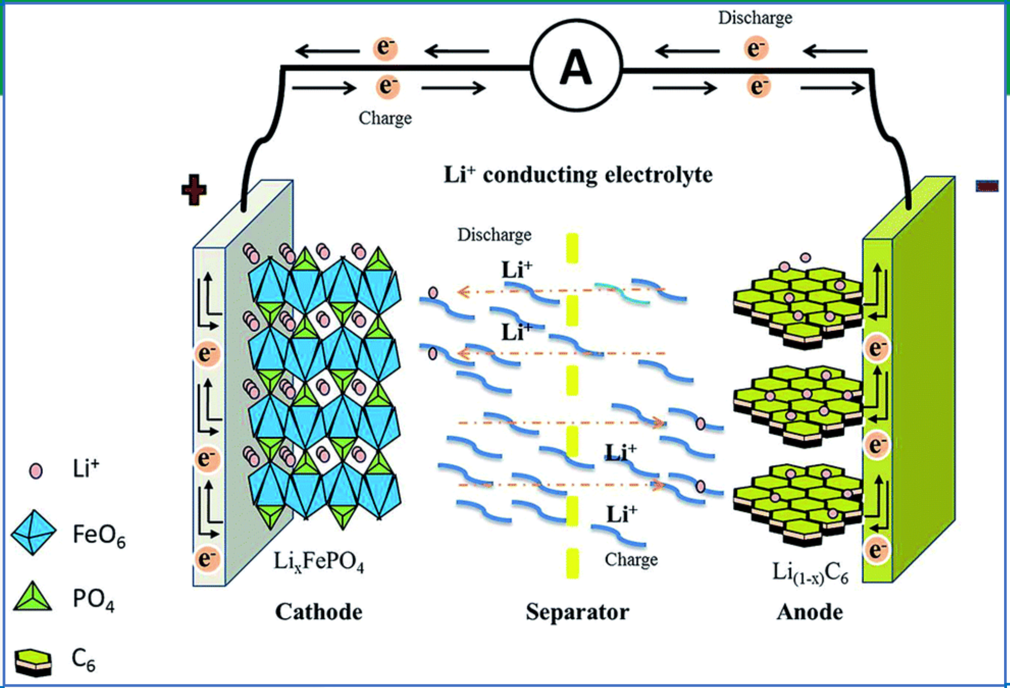
Source: https://www.ev-volumes.com/

Battery supply constraints!

Background: Li-ion Battery (LIB)

Capacity

Cycle Life



Safety

Cost

Cathode (40-50%)
Anode (5-7%)
Separator (5%)
Electrolyte (5%)

>60% cost of LIB

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

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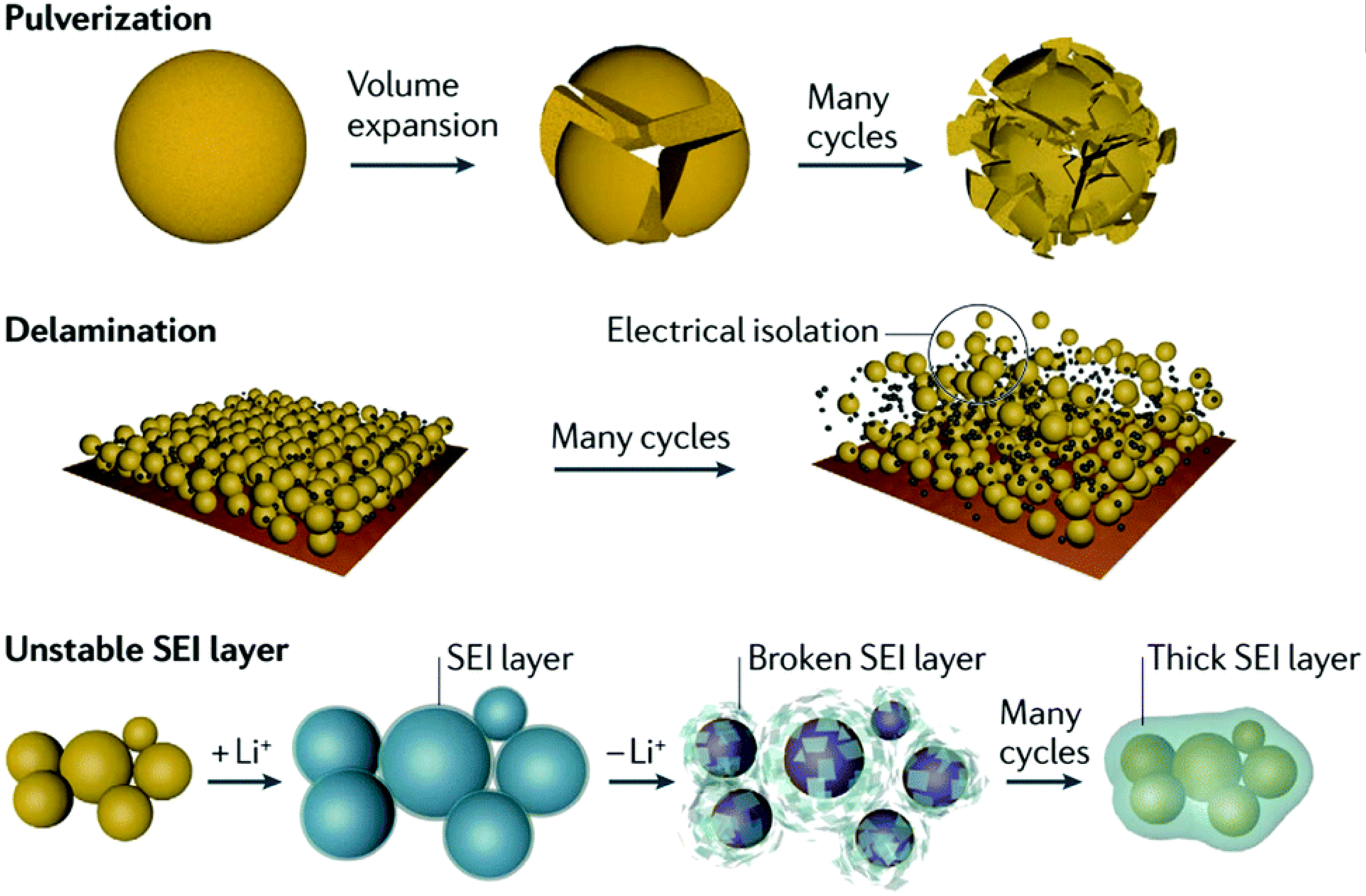
Background: Anodes for LIB

	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	$2.2-8.8 ($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



Why ICE (1st cycle/initial columbic efficiency) matters?

- ICE= Q_{dis}/Q_{ch} *100%
- ICE=85%, 15% Li loss
- $(99.5\%)^{100}$ = 60%

Solutions:

1. **Nano-Si**
2. **Si/C**

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

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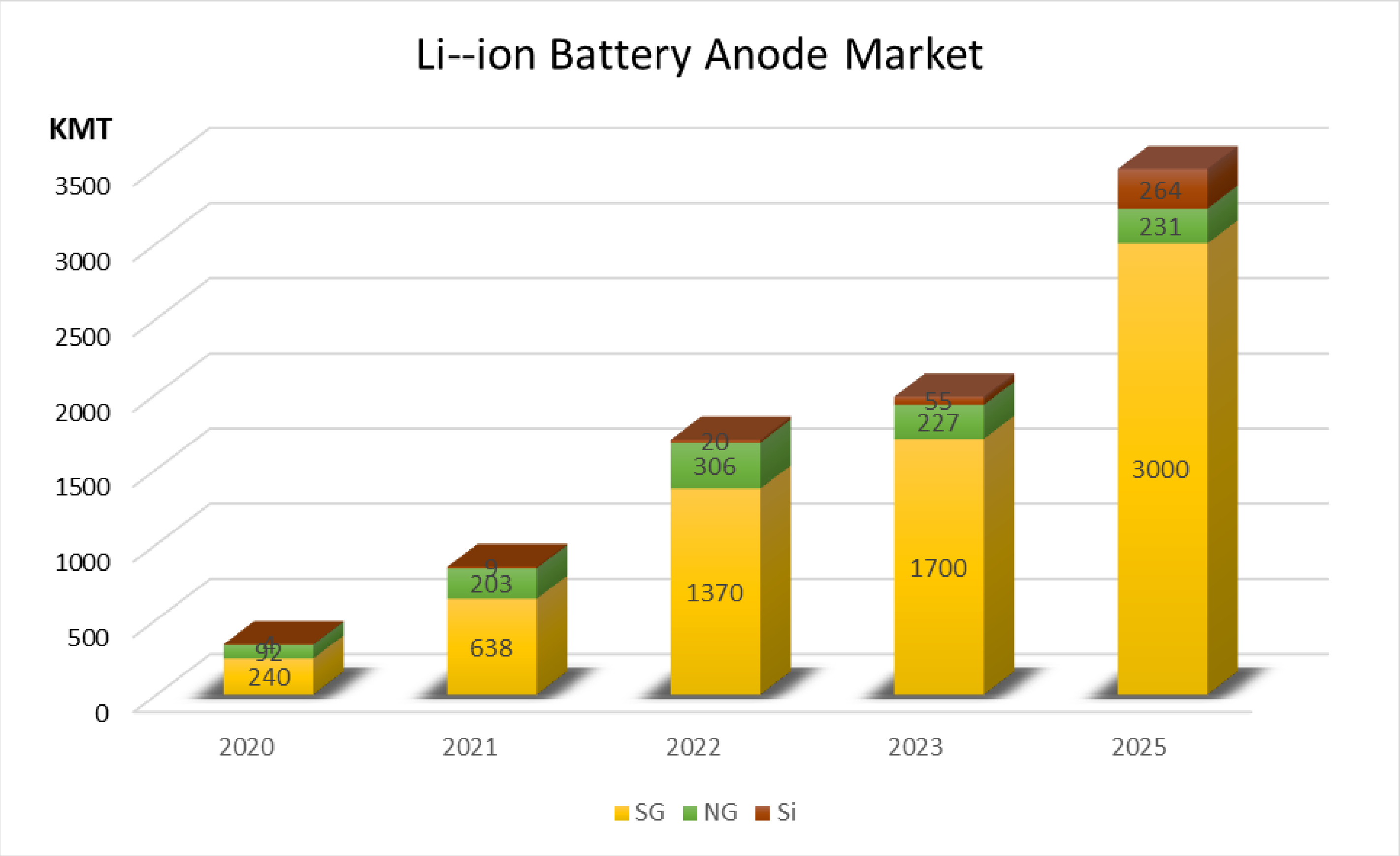
Background: Anode Market Size Forecast



CAGR:
Si: 64.5%
SG: 20%
NG: 17.1%

Price in 3/2024 ($/MT):
Si: $17,000-$123,000
SG: $2,200-8,800
NG: $3,300-7,215

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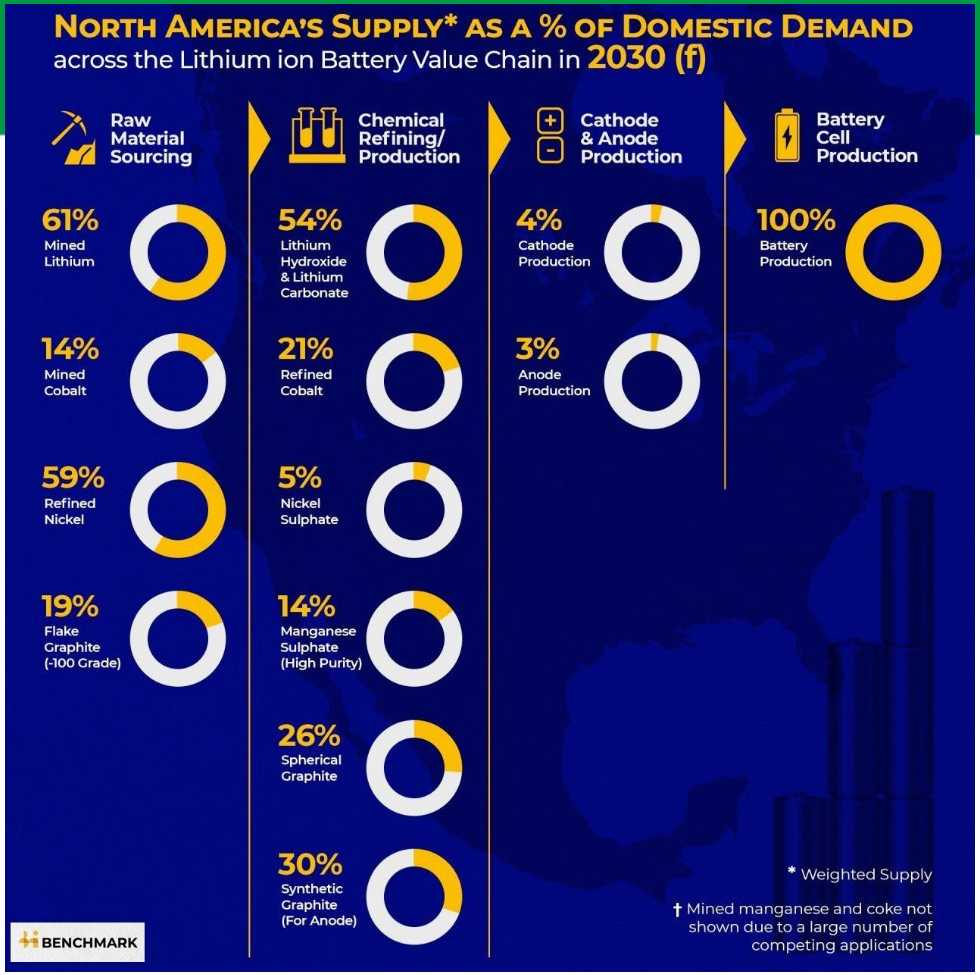
Background: Anode Supply Gap in US

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%

Given one EV needs average 100kg graphite

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



https://www.carbonscape.com/latest-news/freedom-from-the-chain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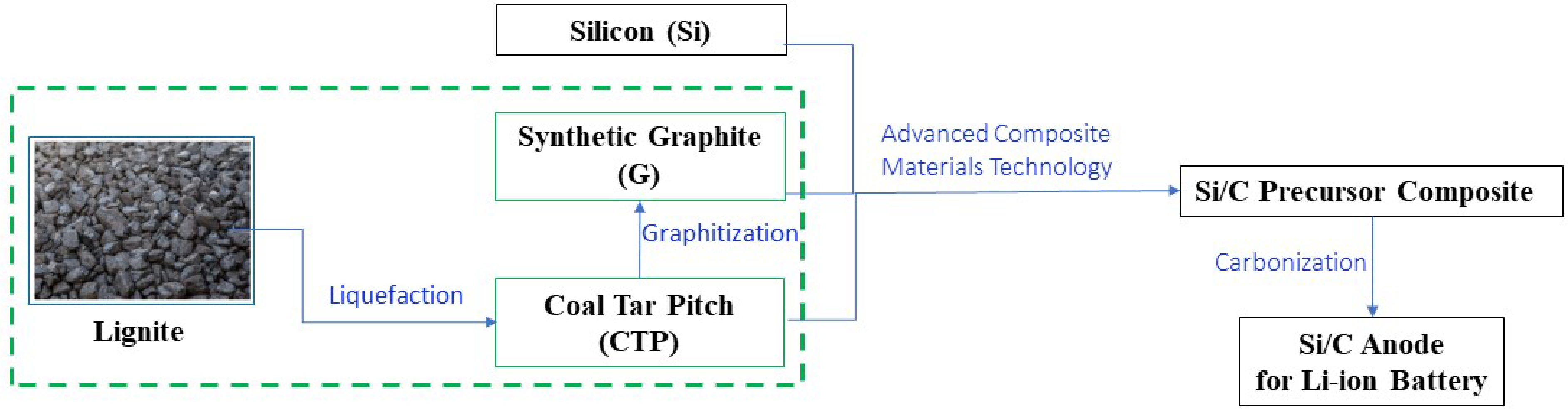
Economics

China Tightens Export Controls on Battery-Making Graphite

- Beijing includes some types of graphite in export control list
- Move comes after US tightened rules to keep chips out of China

By Bloomberg News
October 19, 2023 at 10:52 PM CDT

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

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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

Scope of Work

- Task 1 – Project Management and Planning (95% 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 (95% completed)
- Task 5 – Techno-Economic Analysis of Integrated Process (100% completed)

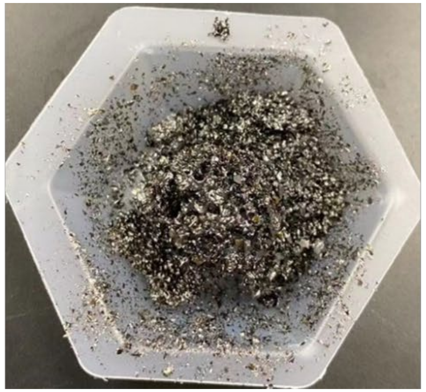
Feedstock Analysis

Lignite-derived CTP Feedstock

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

Coke samples

High SP (ND lignite)



Low SP

Medium SP

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

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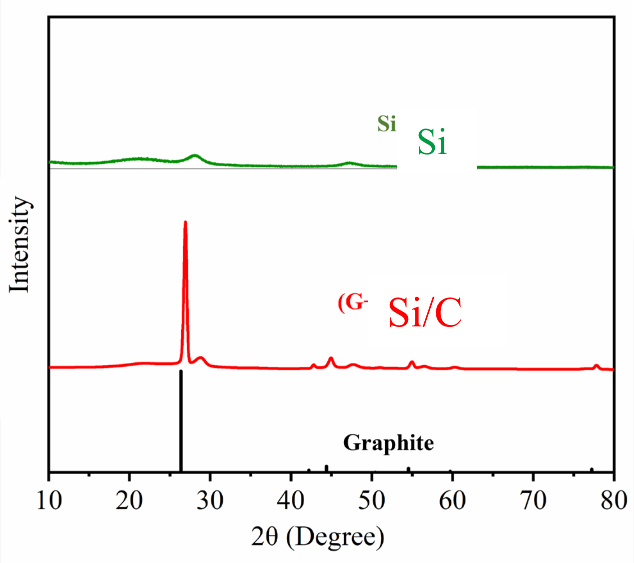
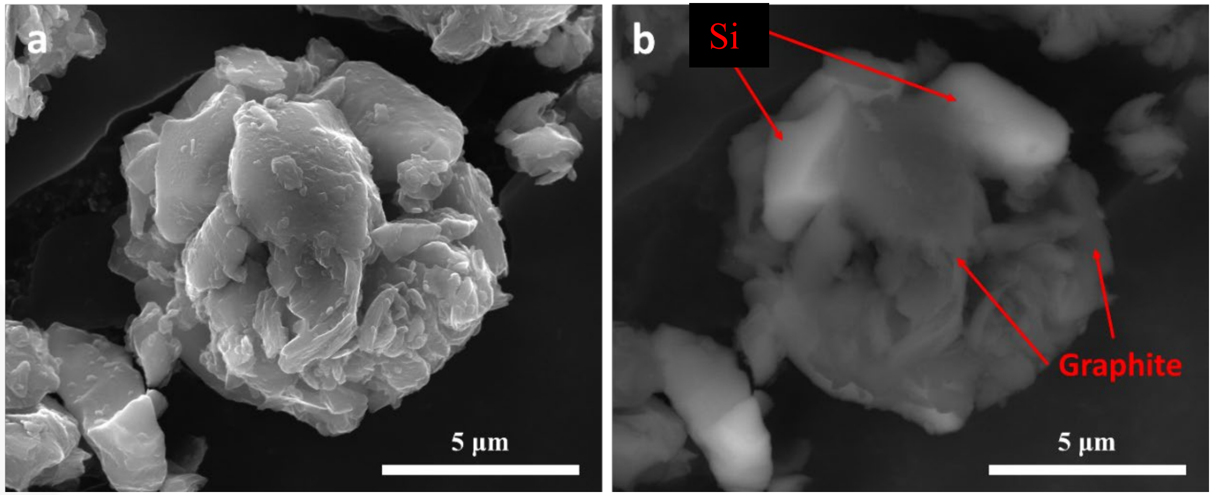
Si/C Composite Development



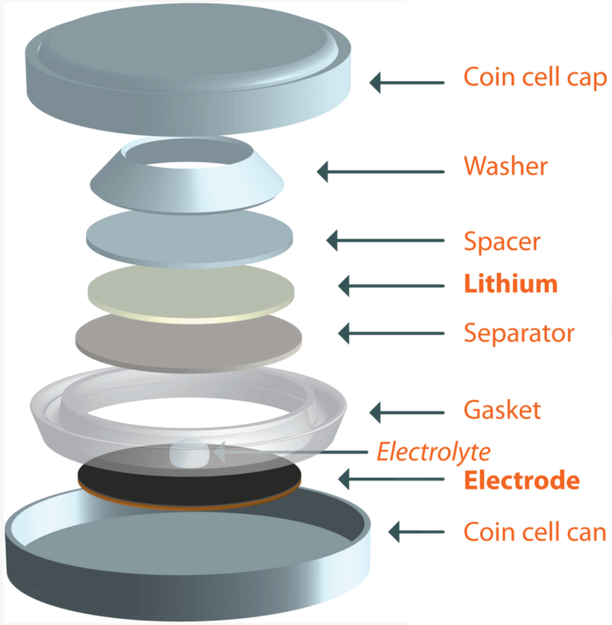


XRD clearly demonstrate the composition of the Si/C composite

SEM demonstrate the designed structure that Si and graphite particles are bonded by carbon (pitch binder after calcination) in a secondary particle.

Si/C Anode Battery Testing – Coin Cell

Coin-cell Li-ion Battery Fabrication and Testing



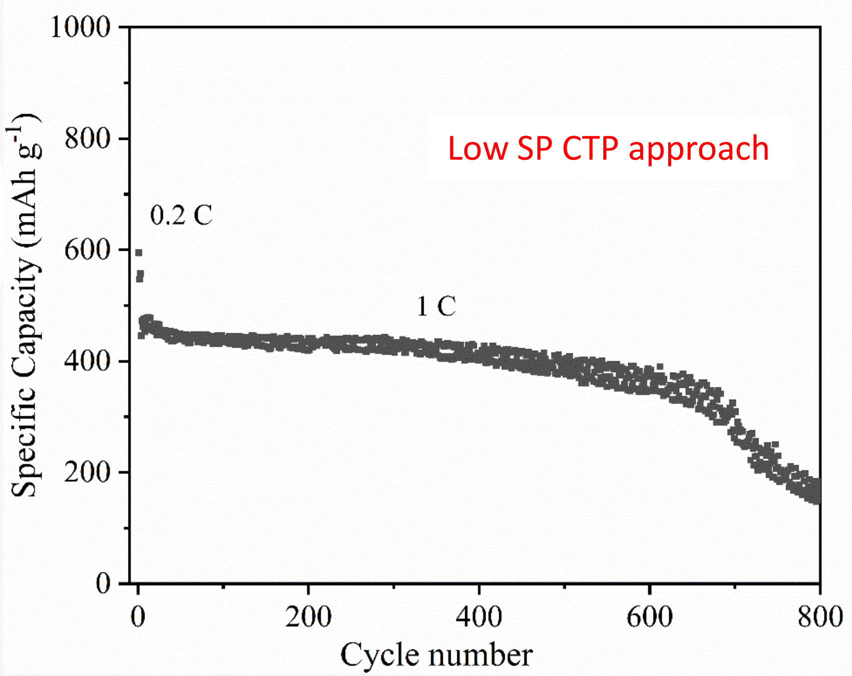
Coin cell configuration

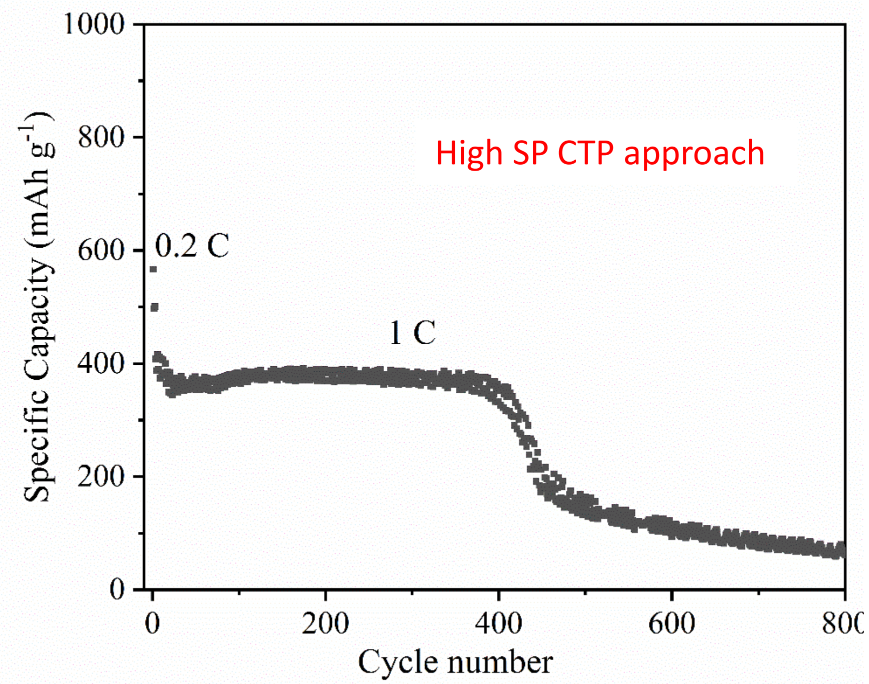
Glove Box

Coin-cell Tester

Si/C Anode Battery Testing

Battery Testing Results



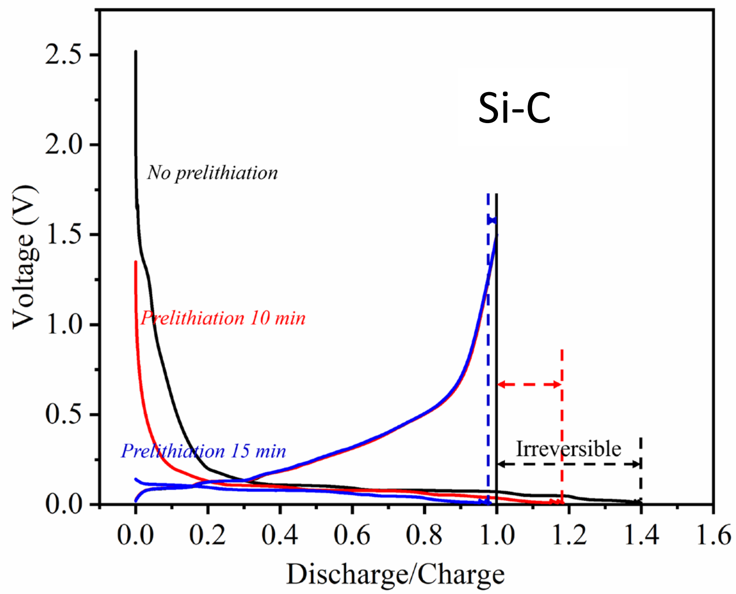


xC stands for charging the cell to 100% capacity by x hours

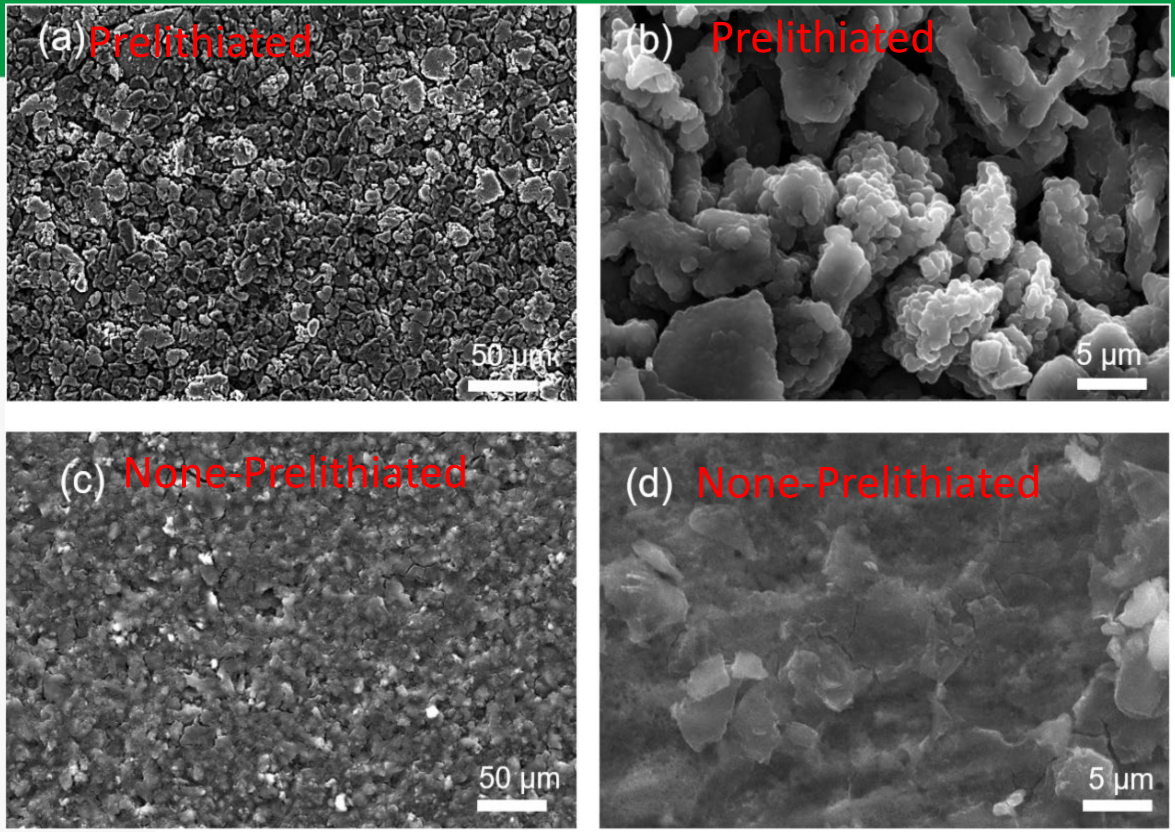
Si/C Anode– Prelithiation

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:**
  - 71.9% (No prelithiation)
  - 89.6% (10 mins)
  - 103.1% (15 mins)



Si/C Anode– Prelithiation



SEM images for the 500-cycle P-anode (a, b) and 500-cycle NP-anode (c, d) at magnifications of 500x (a, c) and 5,000x (b, d).

Zhang, X.; Hou, X.; Hou, Y.; Zhang, R.; Xu, S.; Mann, M., Insights into Chemical Prelithiation of SiOx/Graphite Composite Anodes through Scanning Electron Microscope Imaging. *ACS Applied Energy Materials* **2023,** *6* (15), 7996-8005.

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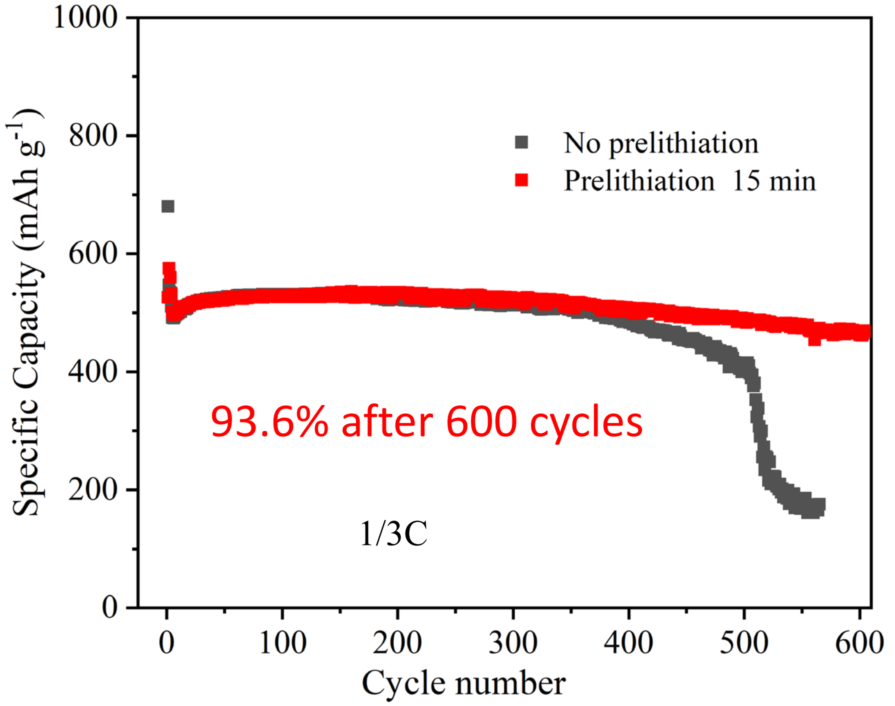
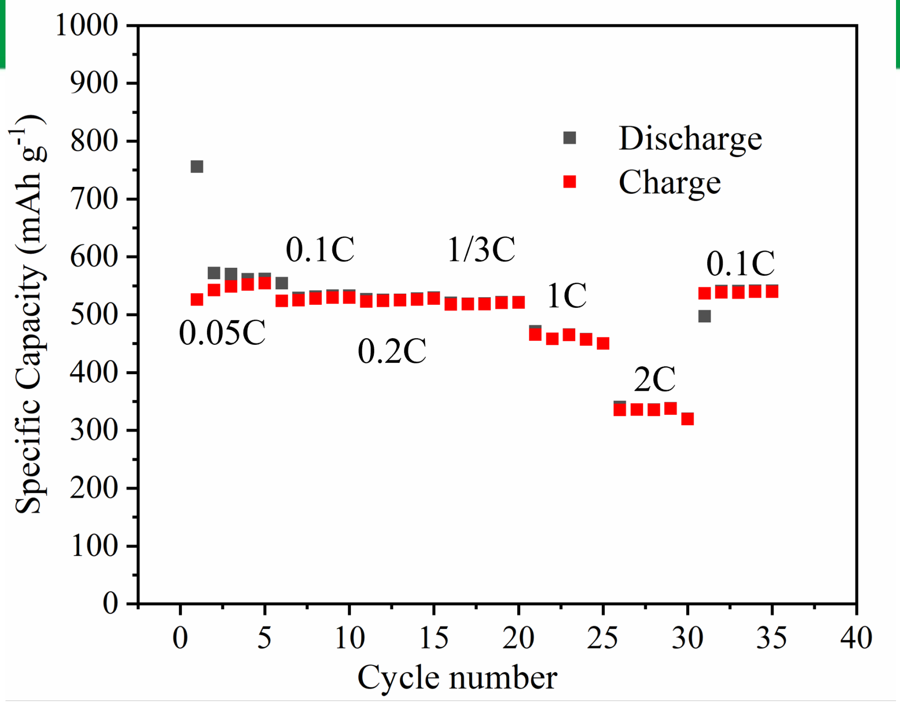
Si/C Anode Cycling and Rate Performance



*1C = 500 mA/g



554.2 mAh/g @ 0.05C (100%)
529.5 mAh/g @ 0.1C (95.5%)
337.3 mAh/g @ 2C (60.8%)

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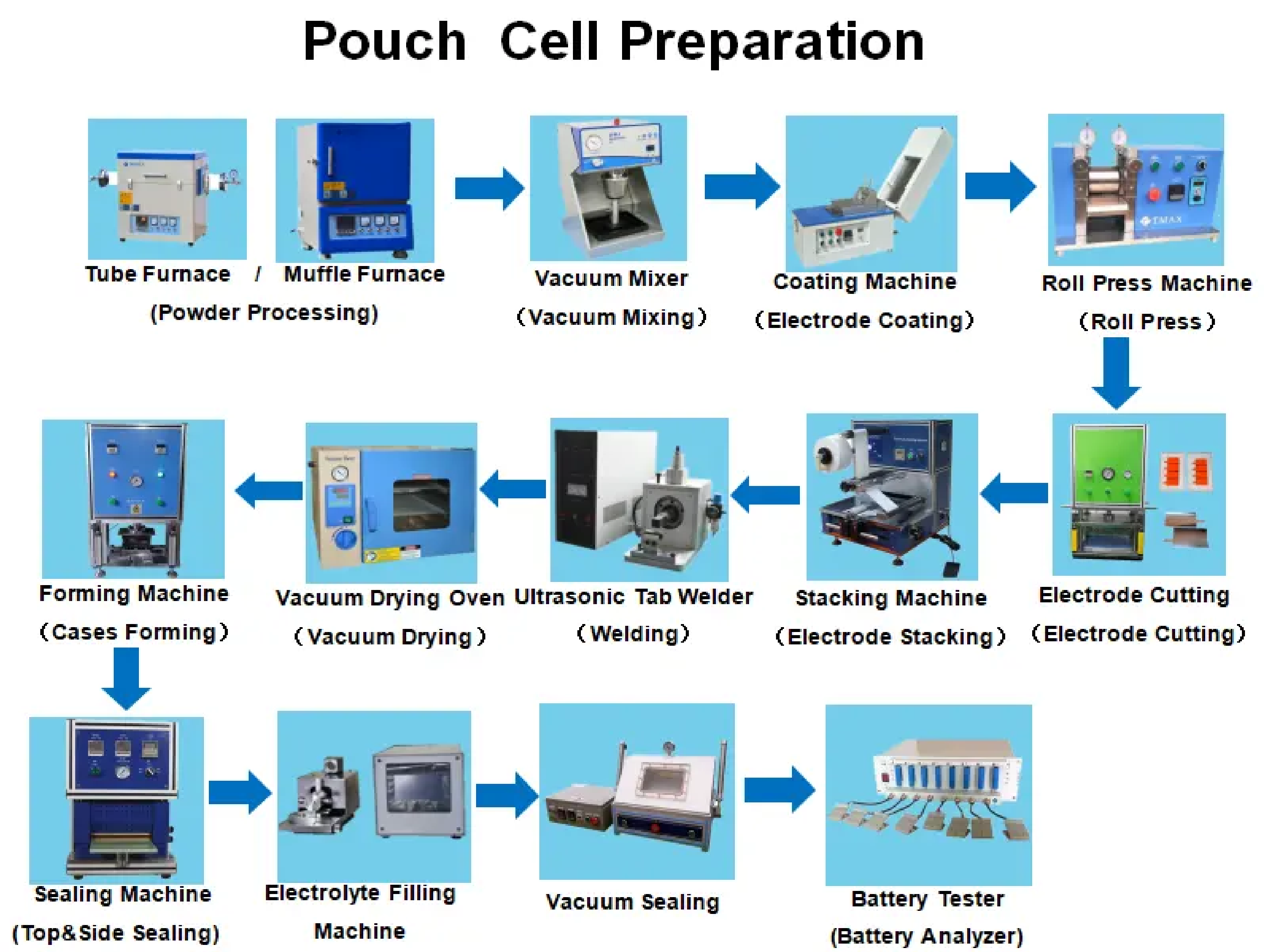
Bench-Scale Testing

- Repairing of a broken equipment delayed the project for 3 months
- An amount of ~ 2.0 kg coal tar pitch has been coked to green coke with a high yield
- Si/C composite anode (multiple batches >1 lb)

Si/C Anode

Pouch Cell & 18650 Fabrication

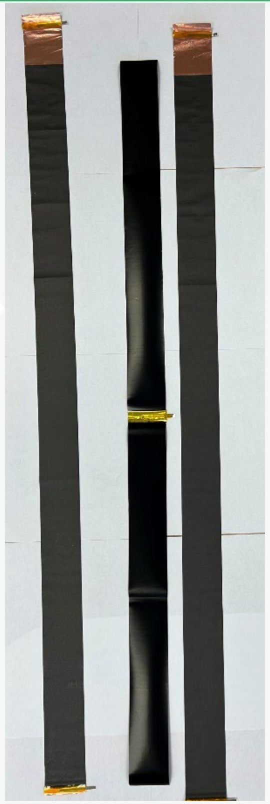


Challenges

- 8 major steps
- >20 Steps
- >12 Machines
- High Precision

Pouch Cell & 18650 Fabrication

18650 Electrode :
58 mm*820 mm



Pouch Cell Electrode :
62 mm*82 mm

Coating Precision and consistency are crucial:

Press Density: **1.60-1.75** g/cm^3

Double-side thickness: **100-120** µm

Thickness variation: **+/- 3** µm

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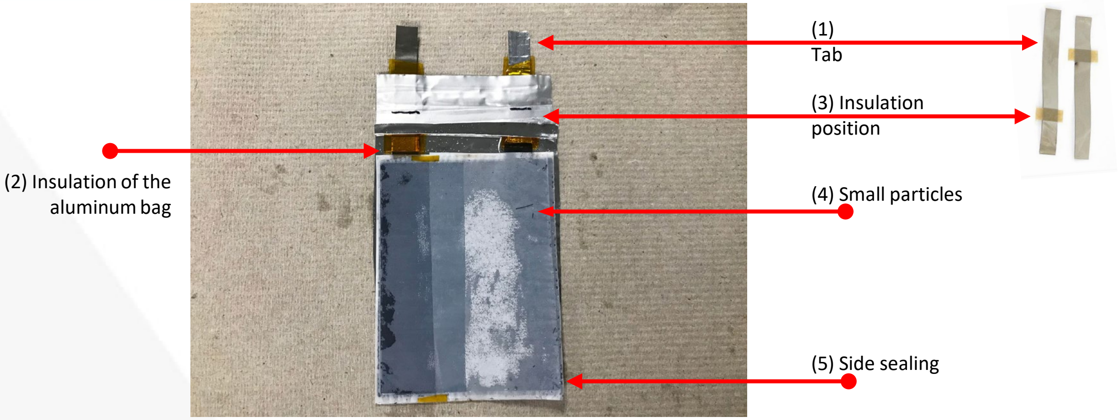
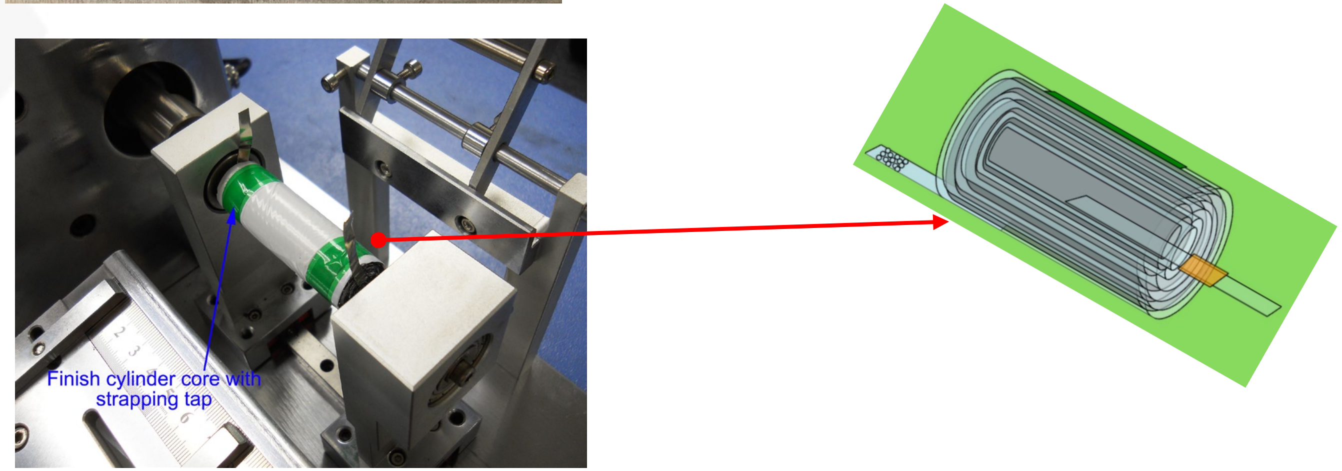
Pouch Cell & 18650 Fabrication

Challenges with Short Circuit:

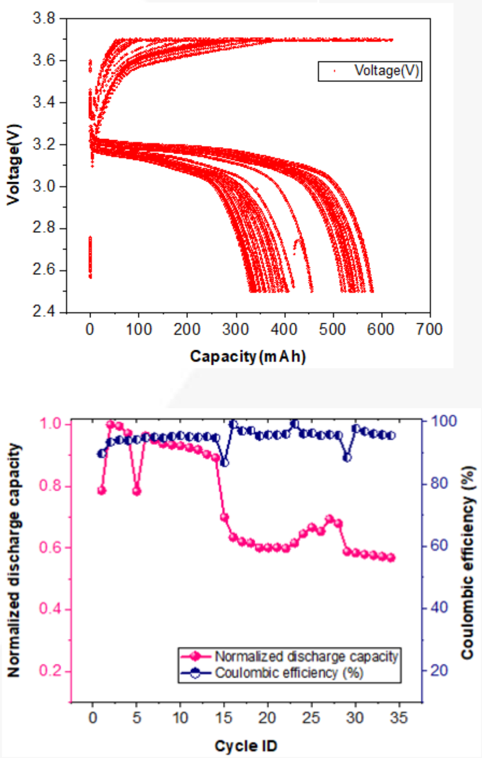
1. Keeping tabs are isolated from the pouch cell bag.
2. Isolation of the pouch cell bag from the electrode and tab joint.
3. Insulation width of the tab is narrow compared to the sealing head. A 1/2-mm of displacement short the cell.
4. Small particles from the electrodes hurts the separator and creates short circuit.
5. Small displacement of the side sealing position breaks the separator.



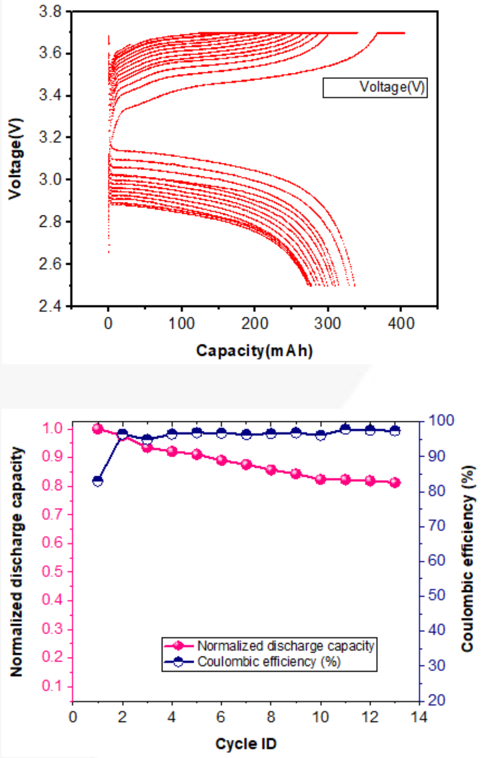


Pouch Cell & 18650 Fabrication- Pouch Cell

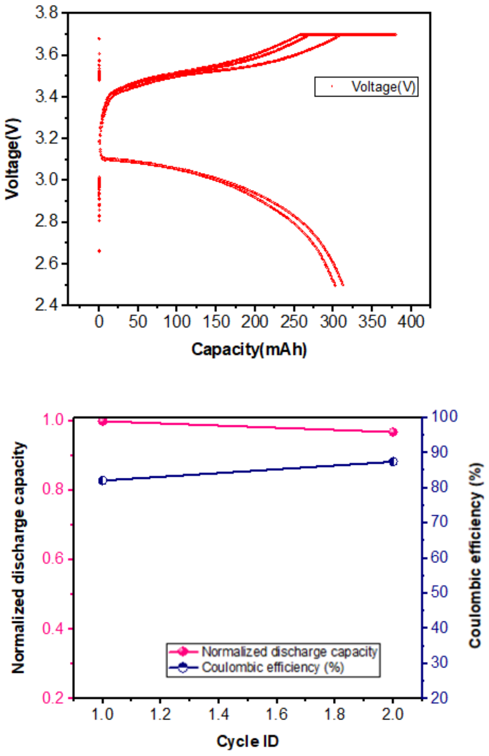
Batch 1



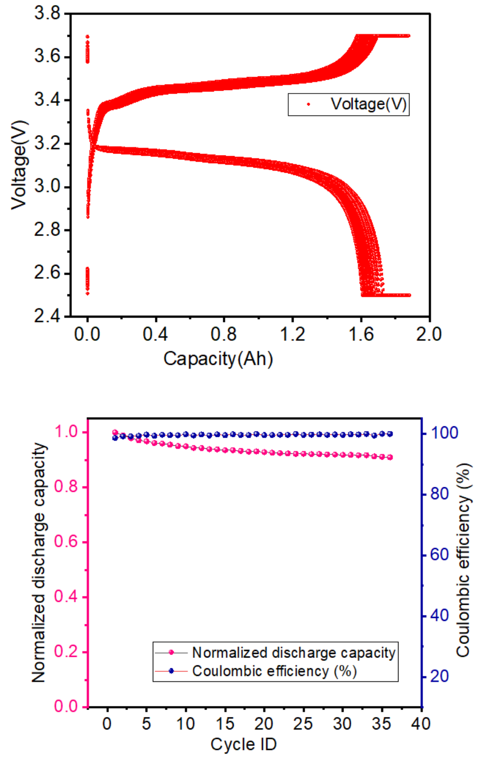
Batch 2



Batch 3



Batch 4



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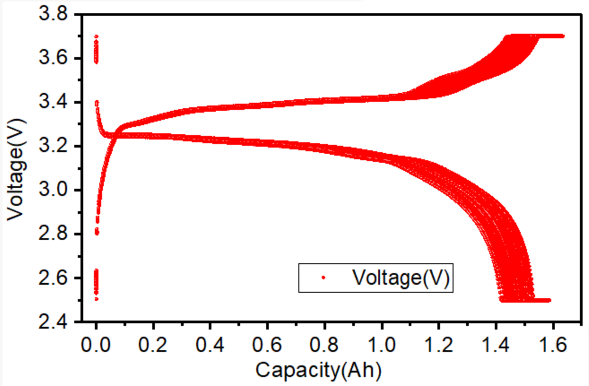
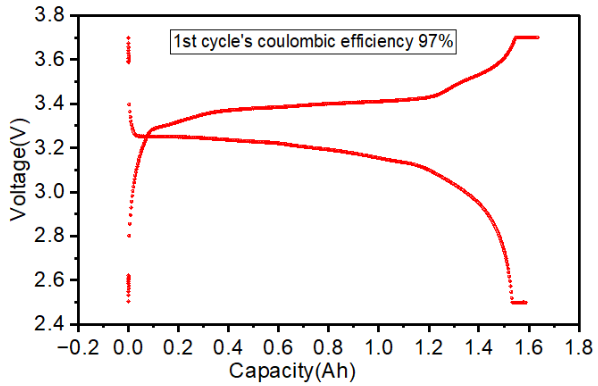
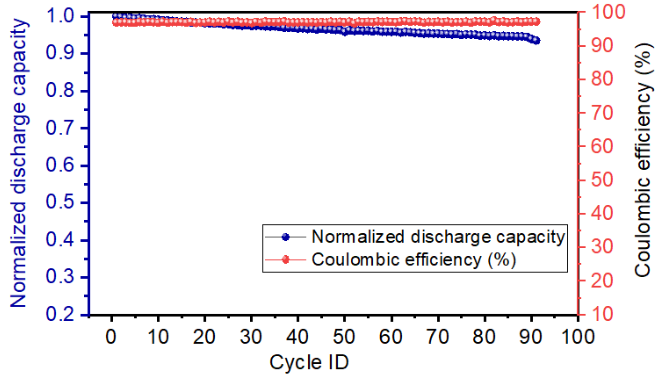
Pouch Cell & 18650 Fabrication- Commercial Reference materials

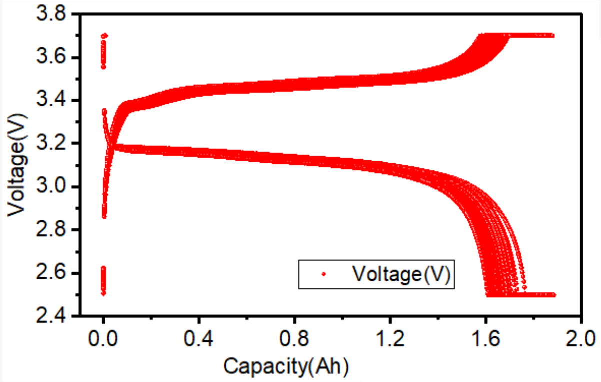
18650 cell performance (LFP as active material)

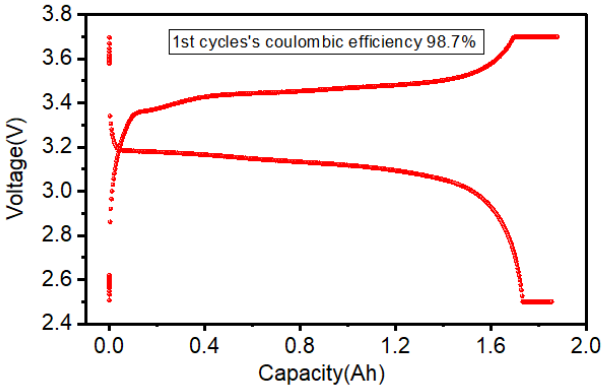


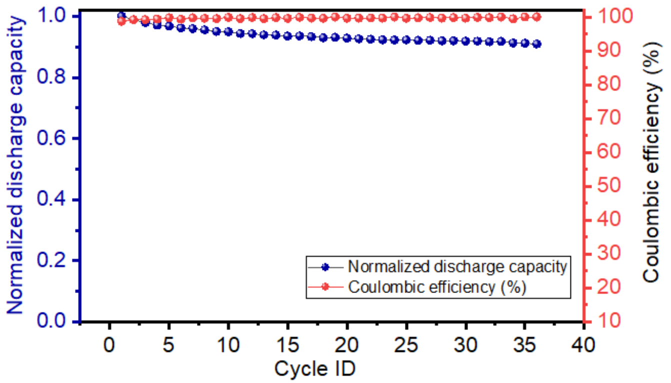




Pouch cell performance (LFP as active material)







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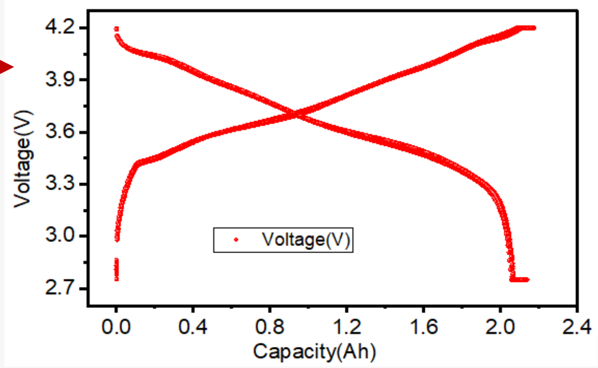
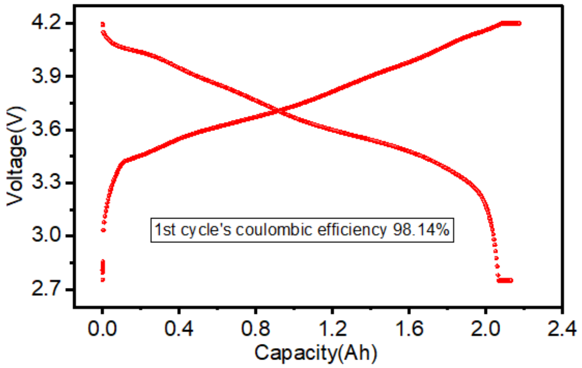
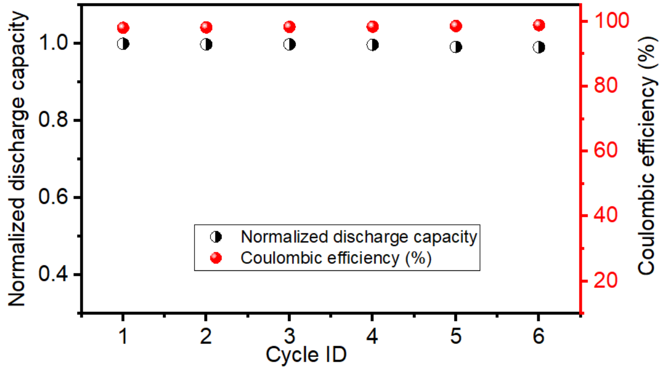
Pouch Cell & 18650 Fabrication- Our Si/C Anode Materials

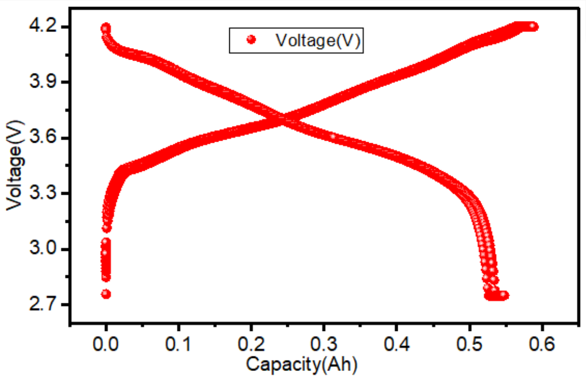
18650 cell performance (NMC as active material)

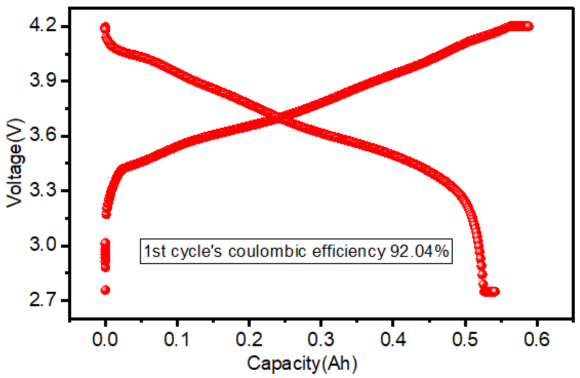


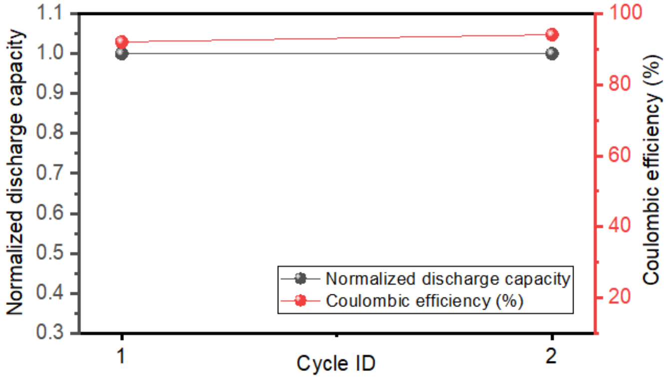




Pouch cell performance (NMC as active material)







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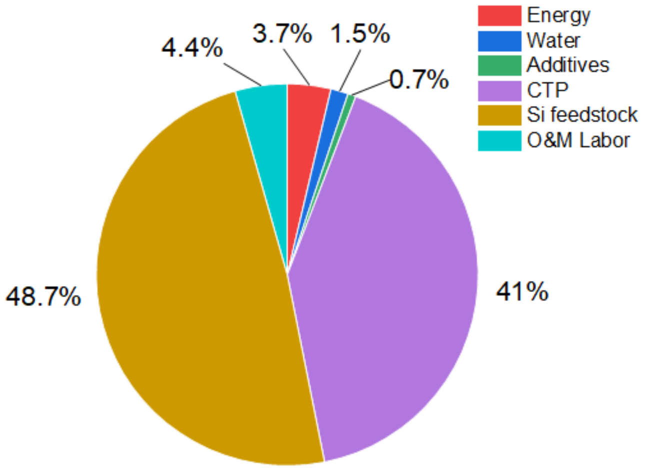
Technoeconomic Analysis (TEA)

- Target at American Association of Cost Engineers (AACE) **Class 5** (-50% to +100% accuracy), may land at **Class 4** (-30% to + 50%), or at least in-between

- Our TEA were factored from the three Class 4 projects: REE pre-FEED, CLC and CO_2 Capture. Equipment is factored, and mass and energy balance calculation using Aspen's process simulation tool

- Annual Production capacity 67,000 tons/year, **$3,440/ton, $3,964/ton** @ 30% of utilization. Projected price at $9,800/ton, **60%** profit margin

- The feedstock cost is the dominant factor, and with high fluctuation. Energy cost is significantly lower than Asian Market



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TEA Sensitivity Analysis

At the materials level

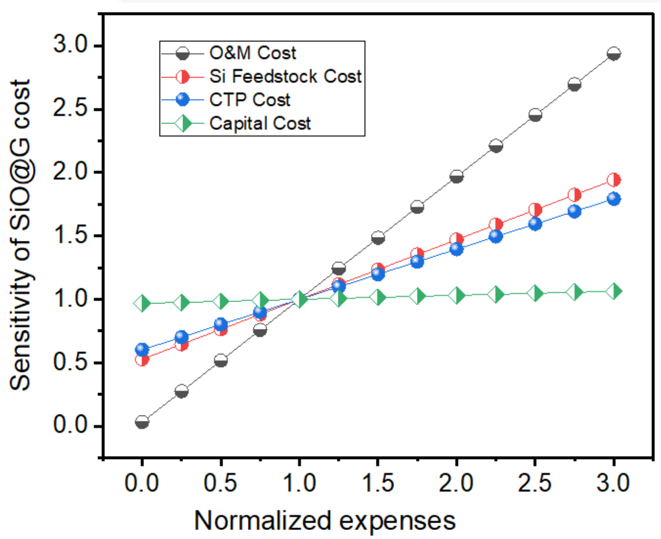

Fig. Production cost sensitivity

- O&M cost includes labor cost, raw materials, and energy cost.
- Capital cost assumed as the initial investment.

At the cell level:

The cost of cells is not sensitive to the cost of the anode!

Cathode (40-50%)
Anode (5-7%)
Separator (5%)
Electrolyte (5%)

Price in 3/2024 ($/MT):
Si: $17,000-$123,000
SG: $2,200-8,800
NG: $3,300-7,215

For NMC/SG cells:

1. SG cost increases by 100%, cells cost increase only by 5%
   ....by 300%, cells ....by 15%

The pursuit of high performance is much more important than the pursuit of low cost!

Outreach and Workforce Development Efforts or Achievement

- **Outreach**
  - Build a strong partnership with NACoal and its partner CTP producer **Americarbon** (10 ton/day)
  - NDIC-Funded Project: Engineering Design for Commercial Graphite Manufacturing Plant from Lignite-Derived Carbon Pitch (15,000-ton/year)

- **Workforce development**
  - One postdoc, three graduates and three under graduates
  - Two REU (Research Experience for Undergraduates) students

- **Achievements**
  - Electrodes For Battery, US Patent Application Serial No. **63/489,953,** provisional application filed 3/13/2023, a follow-up non-provisional application files in March 2024.
  - Zhang, X.; Hou, X.; Hou, Y.; Zhang, R.; Xu, S.; Mann, M., Insights into Chemical Prelithiation of SiOx/Graphite Composite Anodes through Scanning Electron Microscope Imaging. *ACS Applied Energy Materials* **2023,** *6* (15), 7996-8005.
  - Zhang, X.; Wang, H.; Pushparaj, R. I.; Mann, M.; Hou, X., Coal-derived graphene foam and micron-sized silicon composite anodes for lithium-ion batteries. *Electrochimica Acta* **2022,** *434*, 141329.
  - Xu, Shuai; Hou, X. et al, Synthesis of Hierarchical Graphene Coated Porous Si Anode for High-performance Lithium-Ion Batteries. *Journal of Energy Storage,* **under review**
  - Xu, Shuai; Van der Watt, J.; Laudal D., Zhang, R.; Ahmed, R.; Hou, X.; Review on Coal-Derived Carbon Anodes for Lithium-Ion Batteries. *Journal of power Source,* **under review**

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Summary

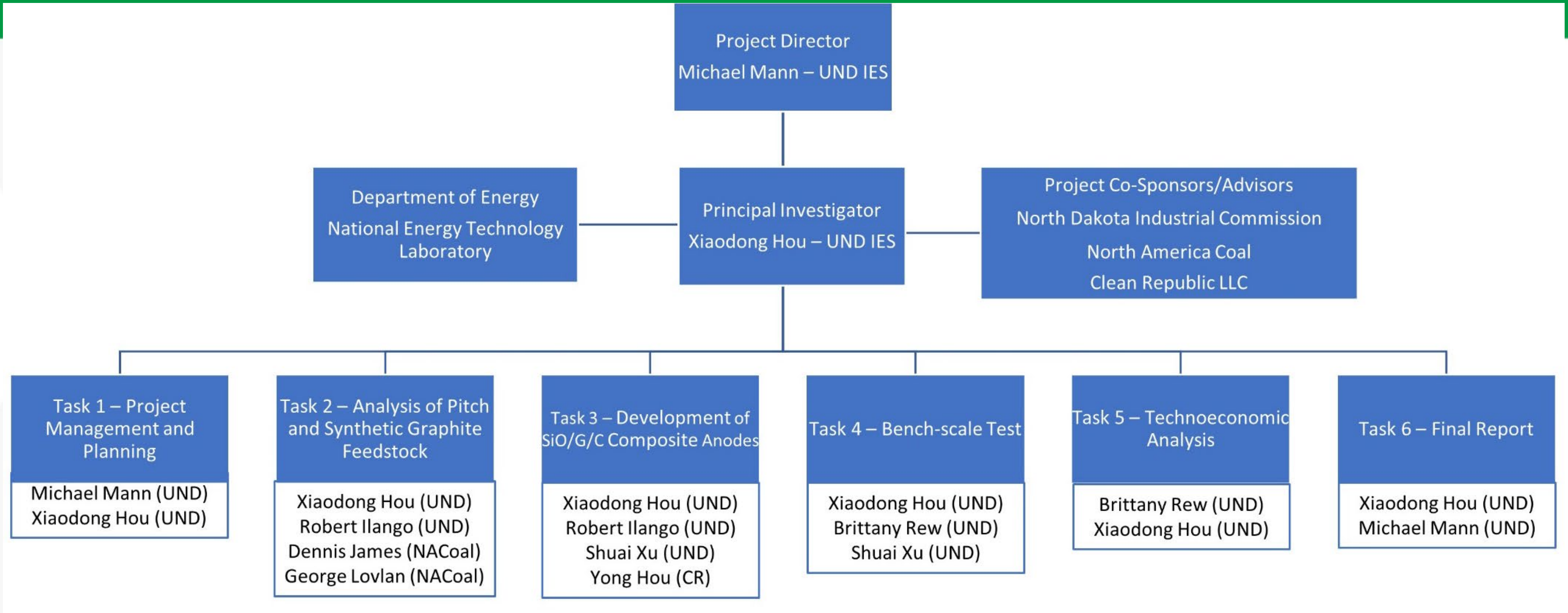
- Si/C anode was successfully developed using ND lignite CTP feedstock, with the synthetic process reliant on the pitch's properties.
- Prelithiation can improve the battery performance, in particular the Initial Columbic Efficiency and cycling performance
- Coin-cells battery performance results are better than commercial refences, and beat our targets
- Undertake the challenging task of building our lab's capability of 18650/Pouch-cell fabrication, with the high-quality of our Si/C anode verified on the large cells
- TEA shows the Si-C costs at $3,400/ ton, based on 67,000 ton/year production capacity

Acknowledgement

- **Sponsors**

- **UND Team**
  - Shuai Xu
  - Rahate Ahmed
  - Xin Zhang
  - Bellal Abdulmalek
  - Molly Rayhorn

Organizational Chart



Gantt Chart

ID	Task Name	Start	Finish
1	**Task 1 - Project Management and Planning**	1/20/21	6/30/24
	Subtask 1.1 - Project Management Plan	1/20/21	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	10/31/21
	Milestone D		
3	**Task 3 - Development of SiO/G/C Composite Anodes**	4/1/21	8/31/22
3.1	*Subtask 3.1 - Preparation of SiO/G/CTP Porous Microspheres*	4/1/21	11/30/21
	Milestone E		
3.2	*Subtask 3.2 - Preparation of SiO/G/C Composite Anodes*	7/1/21	3/31/22
	Milestone F		
3.3	*Subtask 3.3 - Electrochemical Performance Testing*	8/1/21	8/30/22
	Milestone G		
4	**Task 4 - Bench-scale Test**	9/1/22	3/31/24
	Milestone H		
5	**Task 5 - Techno-Economic Analysis**	4/1/23	12/31/23
	Milestone I		
6	**Task 6 - Final technical report**		6/30/24
	Milestone I		9/30/24