Low Cost Manufacturing of Advanced Silicon-Based Anode Materials

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Project ID: ES268

Overview

Timeline

- Start Date: January 2016
- End Date: December 2018
- Percent Complete: 60%

Barriers

- Cost: Anode materials that contribute towards the DOE target of $125/kWh
- Performance: Silicon based anodes to improve Li-ion energy density for vehicles
- Life: Maintain current cycle life of graphite anode Li-ion batteries

Budget

- Total Project Funding
  - DOE: $2.81M
  - G14: $1.23M
- Funding received in FY 2016
- Funding for FY 2017

Partners

Relevance

- **Cost**: Current Li-ion battery cost structure will not enable widespread use of battery electric vehicles (BEV) or plug-in hybrid electric vehicles (PHEV)
  - Current technology trajectory will increase performance, but also increase cost
- **Performance**: BEV and PHEV range needs to be extended by increasing Wh/kg and Wh/L and maintaining power capability
- **Cycle Life**: Batteries with short life time i.e. 2-3 years can be tolerated in consumer electronics but not vehicles
- **Group14 targets**:
  - **Reduce cost** of current graphite based anodes
  - **Improve capacity** – increase EV range
  - **Maintain cycle life** of current batteries

Milestones

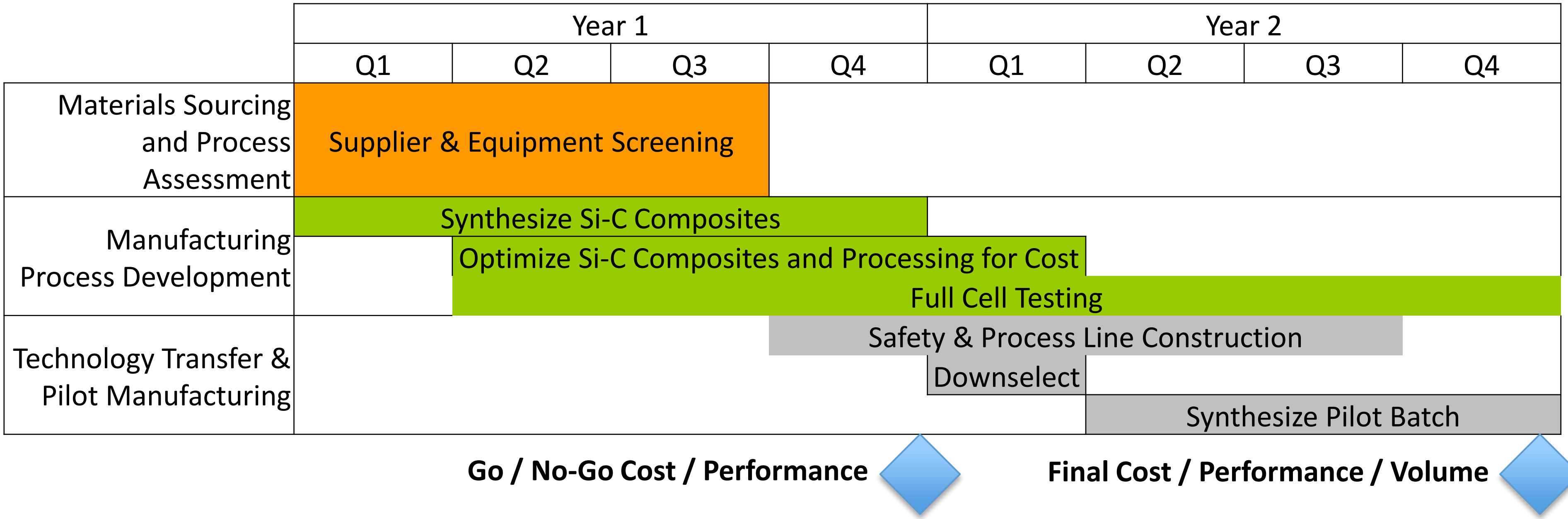
Year 1

Milestone	Type / Timing	Description
Supplier Identification	Technical / Q1	Identify minimum 2 suppliers for each new feedstock material required for Si-C composite. Materials must be available at full scale volume supporting < $125/kWh.
Sample Down-select	Technical / Q2	Down select to 3 lab-scale silicon samples for performance and cost
Synthesize Si-C	Technical / Q3	Synthesize 1x10g Si-C with 1000 mAh/g
Synthesize Si-C	Go/No-Go / Q4	Analysis indicates that the synthesized 1x1g Si-C with 1000 mAh/g is predicted to achieve 500 cycles at a projected cost of <$125/kWh

Year 2

Milestone	Type	Description
Synthesize Si-C 1000 cycles	Technical / Q2	Synthesize 1x10g Si-C with 1000 mAh/g; predicted 1000 cycles; < $125/kWh projected cost
Performance Validation	Technical / Q3	Validate performance of at least one pilot-scale-synthesized material in the lab
Commission Equipment	Technical / Q3	Complete installation and commissioning of all new process equipment
Synthesis with Demo	Technical / Q4	The synthesis of 10 kg completes a demonstration 1000 mAh/g and predicted 1000 cycles at < $125/kWh at full scale volume

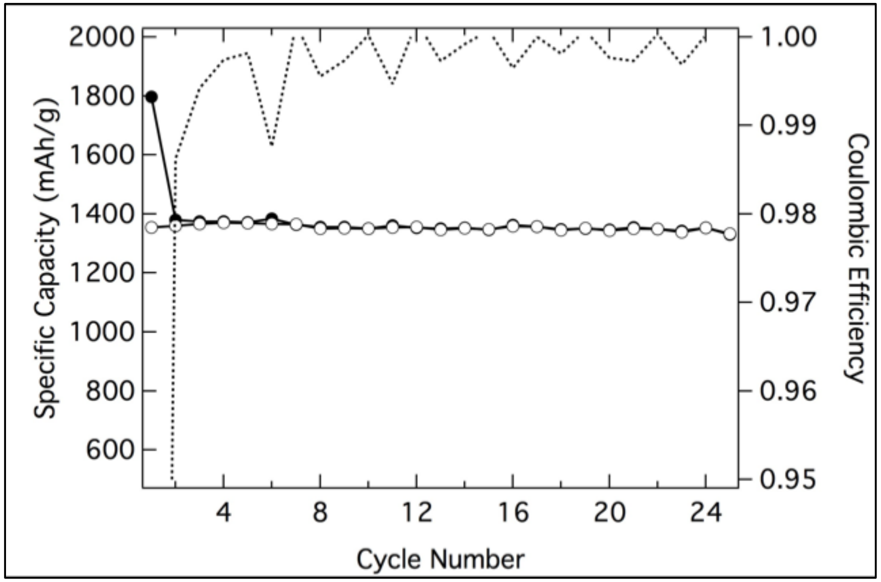
Approach / Strategy

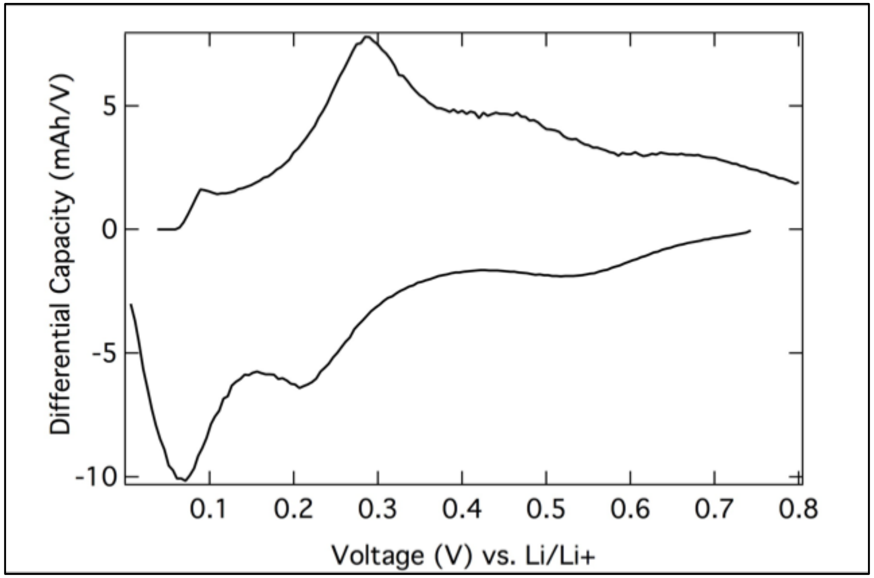


- Leverage EnerG2 expertise in carbon materials manufacturing to create an ideal silicon support matrix material
- Develop and implement low cost silicon synthesis process compatible with the carbon platform
- Demonstrate success of the approach in full cell LIBs
- Manufacture pilot scale material in volumes suitable for qualification with LIB customers using low cost process

Technical Accomplishments: G14's Si-C Composite

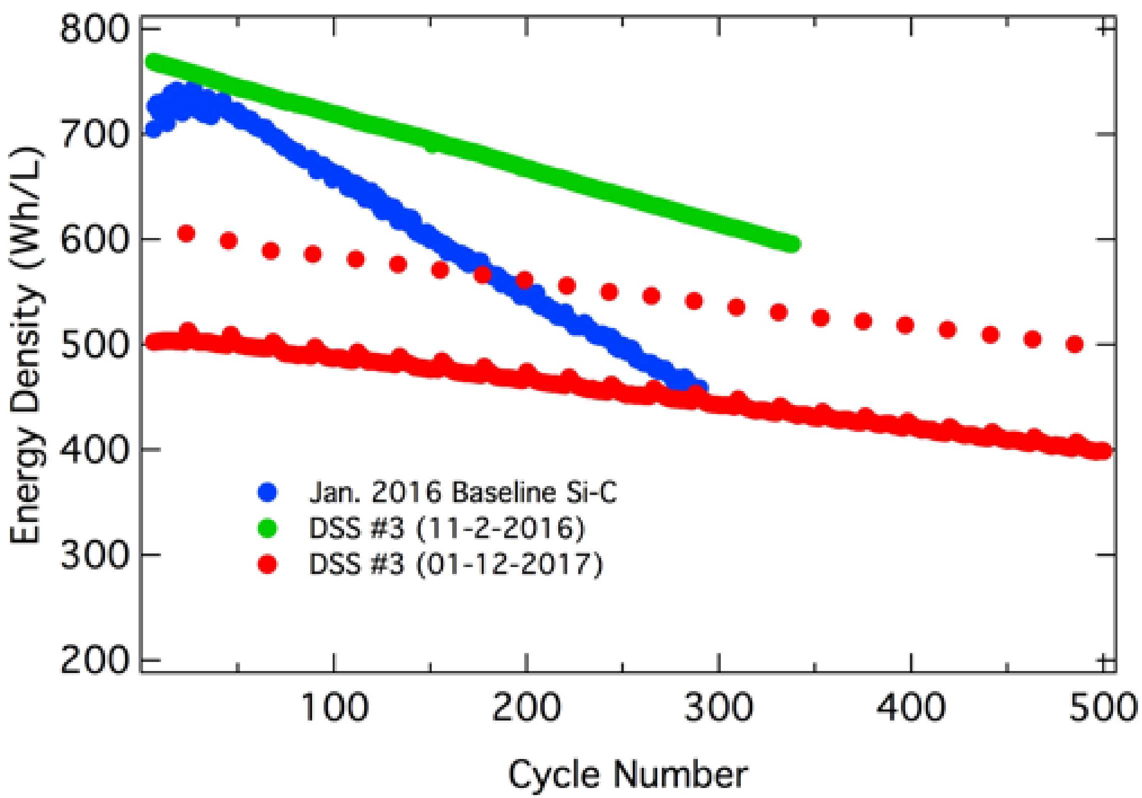
- Group14 has developed its own Si-C composite material
  - Both carbon and silicon are produced from low-cost precursors
- Representative half-cell data:





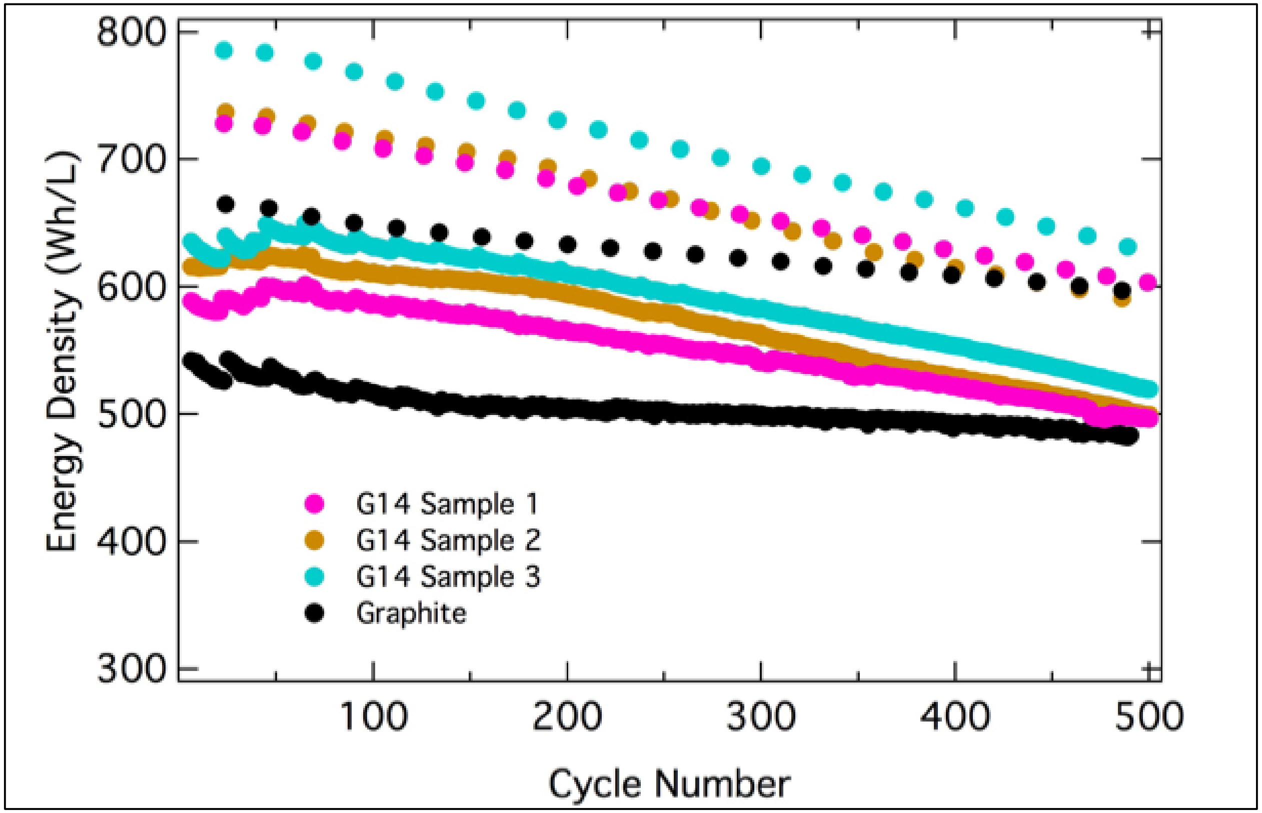
Half cell cycled at C/10 (5 cycles), then C/5, 0.005 – 0.8 V, with I/2 hold, 1 M $LiPF_6$ in EC:DEC w/10% FEC, Li cathode, anode = 20% super C45, 20% CMC-SBR, 60% Si-C

Technical Accomplishments: Example of Progress in Full Cell Performance



Volumetric energy (Wh/L) for DSS-3, Sample "Jan. 2016" and "11-2-2016" cycled at C/2 rate, 2.0 – 4.2 V, with I/2 hold and "1-12-2016" cycled at 1C, 2.5 – 4.2V, with C/10 every 20 cycles, and I/2 hold, 1 M $LiPF_6$ in EC:DEC w/10% FEC, LiNiCoAlO cathode, 16-20% excess anode (anode=10% CMC-SBR, 10% Super-P, 28% Si-C, 52% graphite).

Technical Accomplishments: Achieved ~600 Cycle Stability



Volumetric energy (Wh/L) for three representative Si-C samples, cycled at C/2 rate, 2.5 – 4.2 V, with I/2 hold, cycled at C/10 every 20 cycles, 1 M $LiPF_6$ in EC:DEC w/10% FEC, LiNiCoAlO cathode, 5-15% excess anode (anode=5% CMC-SBR, 5% Super-C45, ~30% Si-C, ~60% graphite).

Technical Accomplishments: Summary of *In Situ* TEM Analysis of Si-C

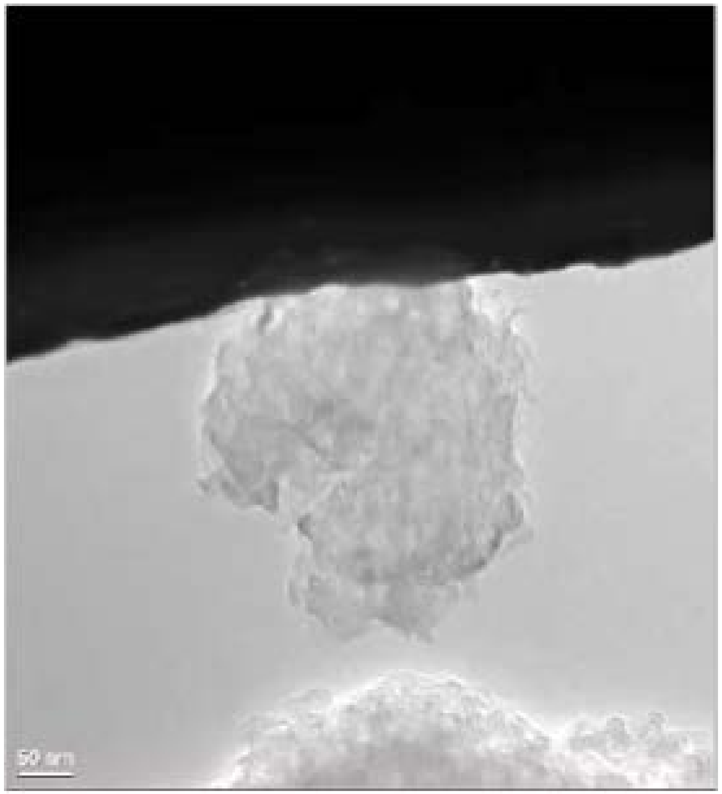
Sample #	Si wt%	Primary/Secondary Paricle Size	Measured 2D Expansion	Phase of Silicon/Carbon	General Structure	Homo-geneity
1	40	5μm	20%~47%	a-Si&L-Gr-C	Dense porous structure	Good
2	46	5nm/ 2-5μm	20%~36%	Poly-Si&a-C	Fine Si NPs in a-C matrix	Good
3	48	10-20nm/ 2-5μm	55%~76%	a-Si&L-Gr-C	Uniform dense particle of LGC with a-Si	Great
4	42	50-100nm/ 2-5μm	20%~42%	Poly-Si&a-C	c-Si NPs on porous C scaffold	Good
5	34	50-100nm/ 2μm	19%~45%	Poly-Si&Gr-C	c-Si NPs on porous C scaffold with C coating	Good
6	41	30-40nm/ 2μm	37%	Poly-Si&a-C	c-Si NPs aggregates on a-C	Great
7	39	20-30nm/ 2-8μm	19%~59%	Poly-Si&Gr-C	c-Si NPs aggregates covered with Gr-C	Great

Gr-C: Graphitic Carbon; **L-Gr-C**: Less Graphitic Carbon; **Poly-Si**: very fine poly Si NPs which shows on SAED pattern; **a-C**: amorphous carbon; **c-Si**: larger Si NPs which show scattered spots on SAED pattern; Homogeneity rate is based on the portion of the major phase

Acknowledgements: Chongmin Wang & Langli Luo, PNNL

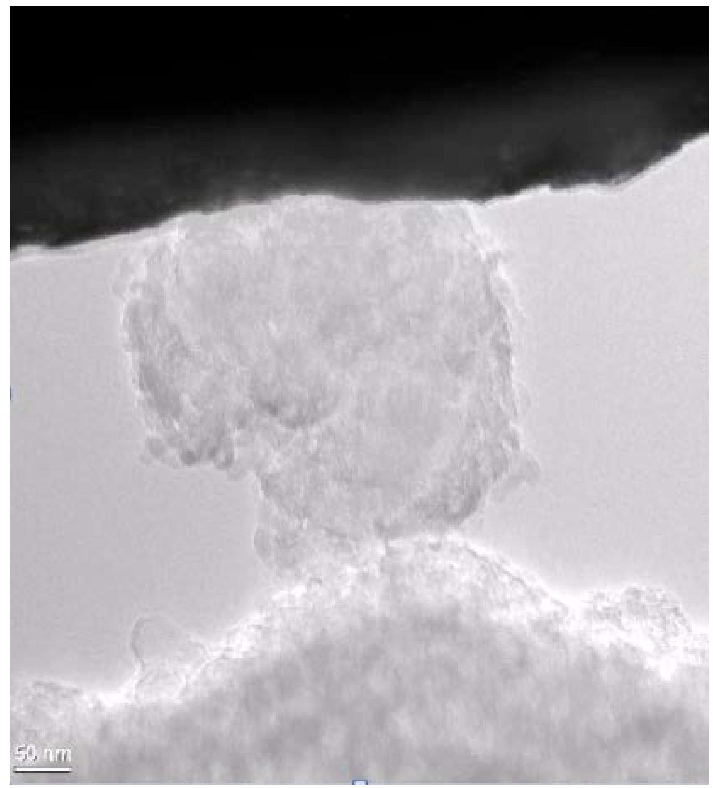
Technical Accomplishments: Low Particle Expansion by *In Situ* TEM

Sample 5, Before Lithiation



Sample 5, After Lithiation

2D Expansion ~29.2%



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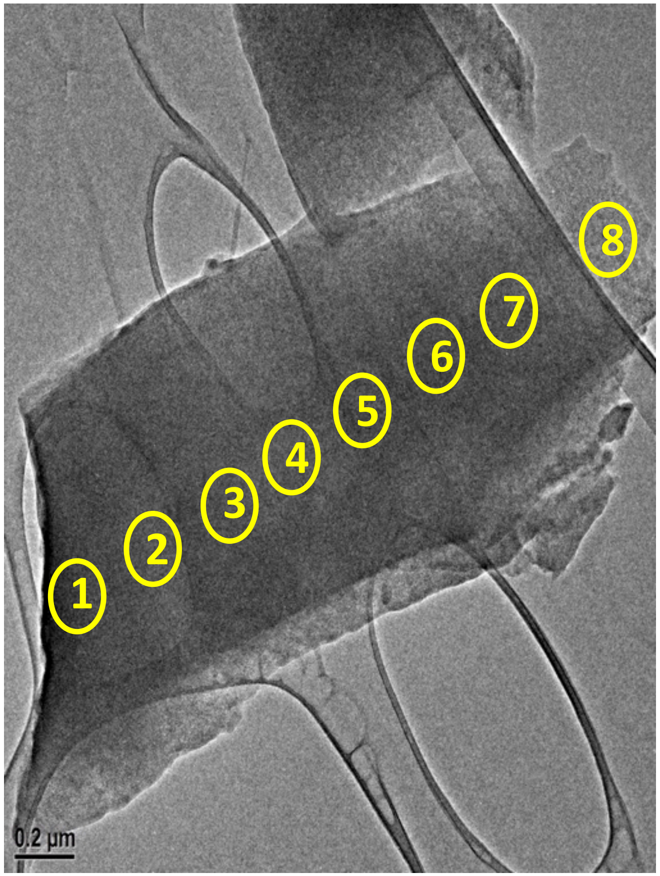
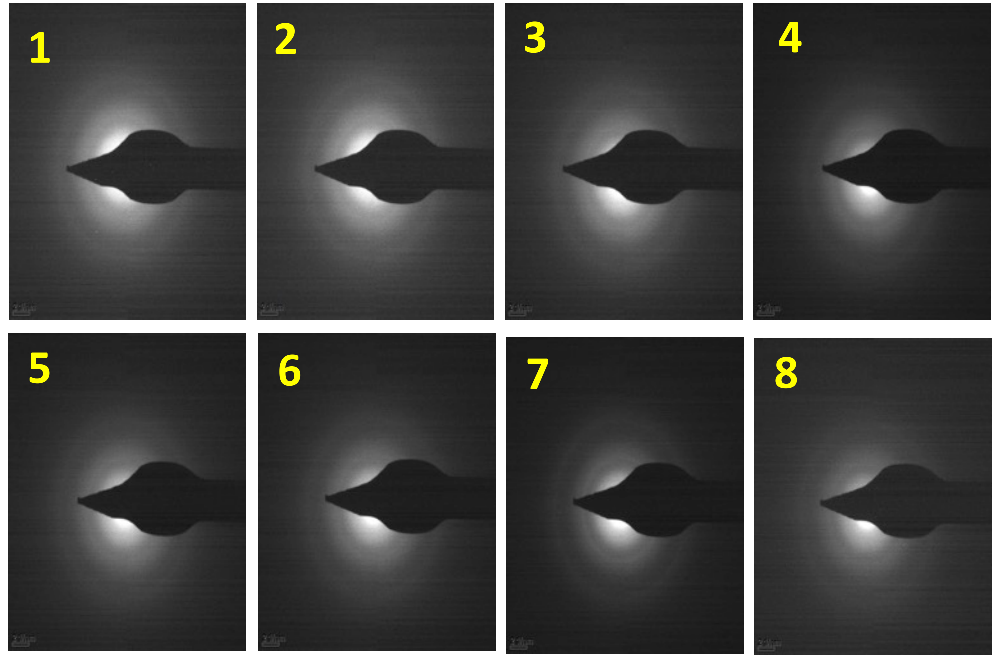
Technical Accomplishments: Example of Homogeneity of Si in Composite



SAED diffraction patterns of Sample 3



No observable phase variation/amorphous C and Si throughout.

Acknowledgements: Chongmin Wang & Langli Luo, PNNL

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Technical Accomplishments: Progress on Scale-up to Achieve Cost and Performance Requirements

- COGS model established for $/kg or $/Ah basis
  - Feasibility of <$0.034/Ah confirmed at lab scale
  - Future scale up and larger full cell device test data will allow for translation into $/kWh basis
- Multiple concepts explored for ~kg scale and beyond
  - Lead concept identified and tested at lab-pilot scale (~10g)
- Exploring multiple vendors/manufacturing sites, expect to finalize plans for ~kg scale production in near future

Responses to Previous Year Reviewers' Comments

Comment: "…cell level goals are missing, and without those investing in process scale-up is not reasonable."

> **Response**: Our cell level goal is to achieve 1000 cycles at < $125/kWh at full scale volume. In order to assess progress towards this goal, we have moved from lab scale to a lab pilot scale, and will ultimately move into pilot scale, all with the intent to engage a major US battery construction and testing lab, also in accordance with another reviewer's comment (see below).

Comment: "…consider adding a partner with extensive electrode/cell making/testing experience."

> **Response**: We are currently producing material at lab-pilot scale and future pilot scale with the intent to collaborate with a major US battery construction and testing lab for evaluation.

Comment: "…the approach does not show any novelty and how to address the critical issues related with Si, such as mechanical fracture and low cycle efficiency."

> **Response**: Based on 3rd party analysis, our Si-C composites comprise as low as 5 nm amorphous silicon homogeneously dispersed throughout a carbon matrix. Also from 3rd party analysis, our Si-C composites provide for very low particle expansion, without observation of particle fracturing. At this time, our materials exhibit cycle efficiency suitable to achieve over 500 cycles to 80% degradation in full cells, and we are committed to improving this performance to 1000 cycles per our stated project goal.

Collaboration and Coordination with Other Institutions

- University of Washington Subcontract
- Pauzauskie Lab: Funded graduate student
  - Material modeling
  - Advanced characterization

- PNNL Subcontract
- Chongmin Wang Group: Funded post-doc
  - *In situ* TEM of Silicon Expansion
  - SAED
  - Advanced spectroscopy

Remaining Challenges and Barriers

- Improve Si-C full cell stability from 500 to 1000 cycles
- Down-select and optimize material manufacturing process
- Procure and install process equipment
- Commission and validate process strategy
- Produce pilot material and demonstrate performance in industrially relevant full cells
- Validate Si-C performance and cost according to DOE targets

Proposed Future Work

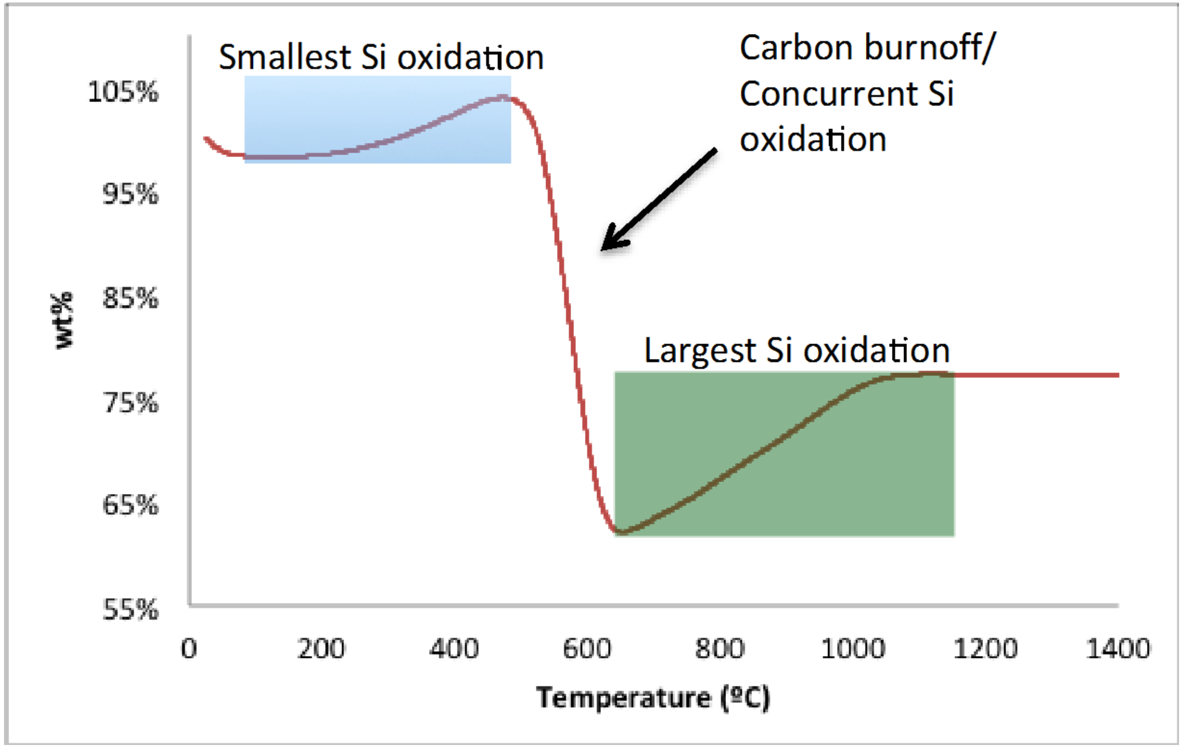
- Pilot scale equipment purchase, installation and commissioning
- Materials and process optimization at lab-pilot scale (~10g), followed by pilot scale (~kg)
- Pilot-scale validation of performance in full cells while maintaining projected cost target
  - Employ 3rd party for device construction
- Customer validation of Si-C performance

Summary

- Down selected raw materials and lab (~g) processes suitable to achieve >500 cycle stability in Li ion full cells
- Group14 Si-C composites exhibit low particle expansion and uniform dispersion of nano-sized silicon within carbon matrix
- Currently at lab-pilot scale (~10 g)
- Progressing towards final project milestones
  - Procurement, commissioning, and operation of pilot scale equipment towards validating Si-C composite cost and performance in industrially relevant full cells

Technical Backup Slide

Back Up Technical Slide:
Use of TGA for Insight into Silicon Structure



Sample	% "Small" Si	% "Large" Si
Lab example	66-95	5-34
Lab-pilot example	66-99	1-34

- Weight loss via TGA @ 10 C/min from RT to 1400 C in air
- Differentiation into surface and bulk diffusion regimes