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Commercially Scalable Process to Fabricate Porous Silicon

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Project ID: ES267

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Overview

Timeline

- Project start date: January 1, 2016
- Project end date: June 30, 2017
- Percent complete: 85%

Budget

- Total project funding: $1,406,787
  - DOE share: $1,125,430
  - Navitas cost share: $281,357
- Funding for FY16: $883,344
- Funding for FY17: $523,443

Barriers

- Scalable process, from lab to pilot scale
- Control impurity level and nature of the product throughout the manufacturing process
- Achieve low cost
- Low environmental footprint

Partners

- Argonne National Laboratory
  - Subcontract, material characterization and cost modeling
- Nexceris, LLC.
  - Subcontract, scale up demonstration

Relevance and Project Objectives

- **Project Goal:**
  - Develop a novel, commercially scalable approach to produce microporous silicon (μpSi)
- **Project Objectives:**
  - Bench scale optimization of the 3 processes to fabricate μpSi powder
  - Qualify low-cost precursor materials and transfer technology to establish pilot scale production (>2kg of μpSi powder)
  - Validate materials performance in an open-source baseline prototype cell design
  - Establish the economic feasibility of μpSi manufacturing process
- **Relevance:**
  - Eliminate the use of hazardous materials such as silane and hydrofluoric acid
  - Reduce process cost through higher intensity and throughput and retain desired electrode powder morphology
  - Provide/deliver μpSi in adequate quantities to support pilot scale electrode coating by EV battery OEM's

Milestones

Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	% Effort
	Months ARO																		
Performance Period 1																			
Task 1. Lab Scale Process Optimization- Powder Milling																			15%
Task 2. Lab scale process optimization-thermal process																			15%
Task 3. Lab scale process optimization-etching																			15%
Task 4. Lithium ion battery material grade demonstration																			15%
Task 5. Process Review and Cost Estimation												Go/No Go							5%
Performance Period 2																			
Task 6. Pilot scale demonstration																			30%
Task 7. Process modeling/cost estimate																			5%
Final Report																			**100%**

	First Year Milestones	Date	Status
M1.1	Down-select powder milling parameters	08/2016	Complete
M2.1	Down-select thermal process parameters	08/2016	Complete
M3.1	Down-select etching process parameter	08/2016	Complete
M4.1	Demonstrate an optimized process for μpSi powder fabrication	11/2016	Complete
M5.1	Complete preliminary cost model	12/2016	Complete
M5.2	Go/No-Go decision based on technical and economic feasibility	12/2016	**GO**
	Second Year Milestones	**Date**	**Status**
M6.1	Pilot manufacturing line	04/2016	Complete
M6.2	Complete validation testing	04/2016	Complete
M6.3	Successful pilot scale demonstration	06/2017	On track
M7.1	Update and validate cost model	06/2017	On track

Approach and Strategy

- **Microporous Si fabrication:**

Conventional

1. Initial raw material (Si)
2. Metal Catalyst Deposition
3. Hydrofluoric Acid Etching
4. Neutralization/Rinse
5. Filtration/Separation process

Proposed

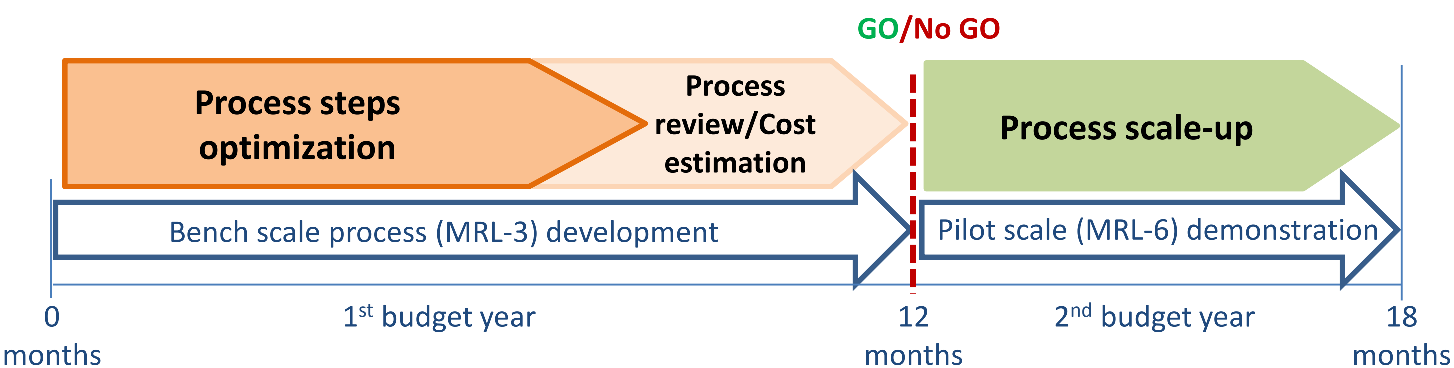
1. Initial raw material
2. 1st Reduction step: Solid State Milling
3. 2nd Reduction step: Thermal Treatment
4. Etching process
5. Filtration/Separation process

→ 60% cost reduction

- **Material properties targets for Go/No Go**

Properties	Target Values
Secondary particle size (μm)	1 - 10
Average pore size (nm)	50 - 200
BET surface area (m^2/g)	20 - 50
Tap density (g/mL)	0.6 – 1.0
Si content (wt%)	> 90
μpSi capacity (mAh/g_{Si})	> 2500
μpSi/Carbon composite capacity (mAh/g)	> 800

Desirable anode active material capacity

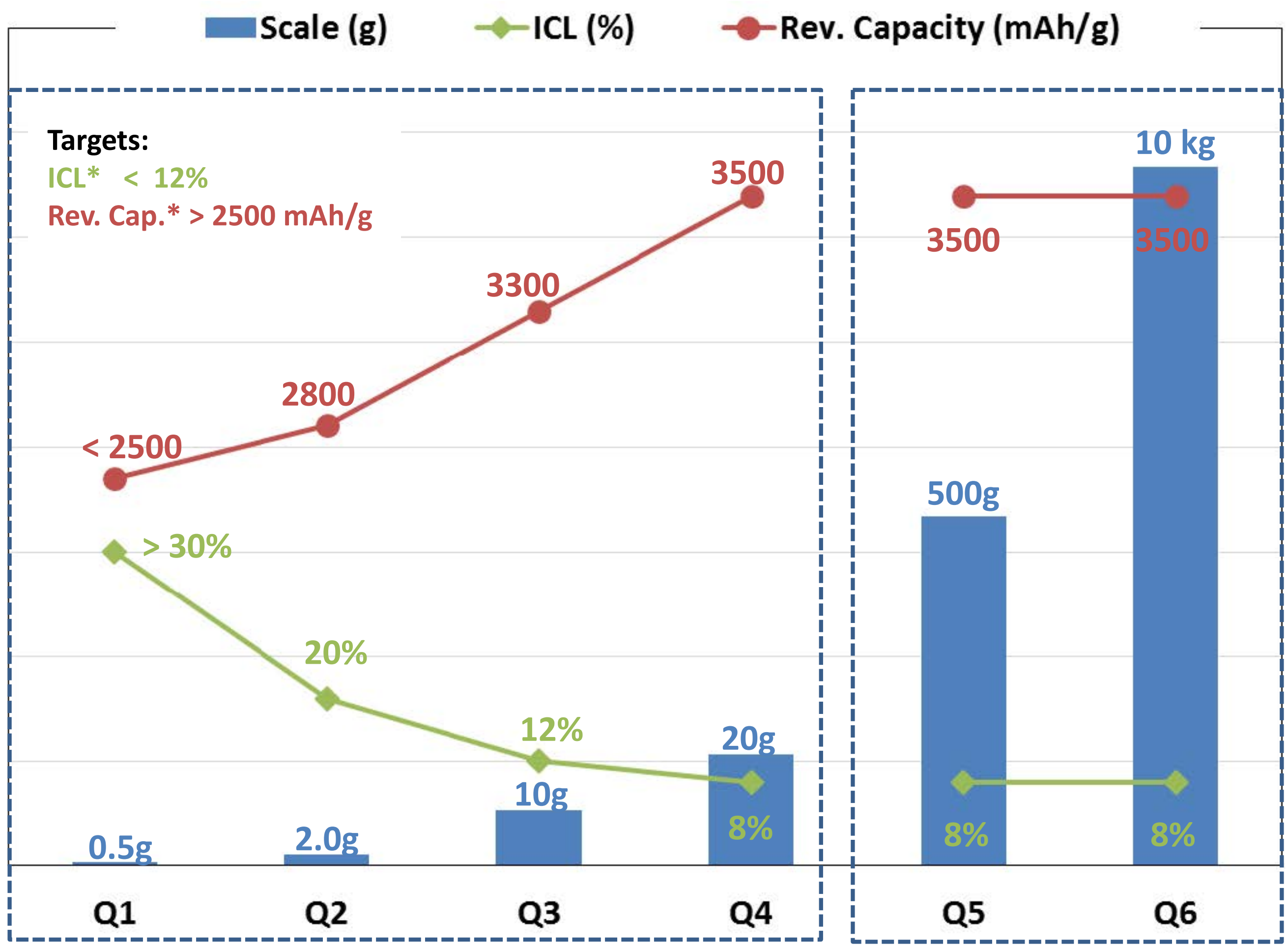


Technical Progress

Milestones		Results by AMR 2016	Results by AMR 2017	Status
1	Down-select powder milling parameters	• Baseline parameters selected and parameter design initiated	• Optimized Milling parameters • Scaled up experiments started	Complete
2	Down-select thermal process parameters	• Baseline parameters selected and parameter design initiated	• Thermal process optimized • Selected ramp, soak temperature and time	Complete
3	Down-select etching process parameter	• Baseline parameters selected and parameter design initiated, batch size 2g	• Acid type and etching condition selected • 20g batch size	Complete
4	Demonstrate an optimized process for µpSi powder fabrication	• Preliminary experiments (half coin cells)	• µpSi powder produced at lab scale was qualified by ANL • Physical properties within target • µpSi tested alone and as a composite in half and full Li-ion cells	Complete
5	Complete preliminary cost model	• No started	• Navitas initiated milling process scale up • Navitas and Nexceris have developed a preliminary cost model	Complete
6	Build pilot manufacturing line	• No started	• Designed and fabricated: thermal treatment substrate plates, etching reactor, and filtering system	Complete
7	Complete validation testing at intermedium scale	• No Started	• Process validated at > 500 g/batch • µpSi powder validated	Complete
8	Demonstrate > 2kg production	• No Started	• Progress and demand have increased final deliverable to 10kg of µpSi powder	On track
9	Update and validate cost model	• No Started	• Identified hurdles to cost-effective process scale-up • Pilot line data has been gathered to validate cost model	On track

Project Progress Summary

* μpSi Reversible capacities and ICL values using half cells



Lab Scale Optimization (2016 BP1, Task 1-5)

Scale-up (2017 BP2, Task 6-7)

- **Physical, chemical and electrochemical properties of μpSi have been preserved during scale-up process**

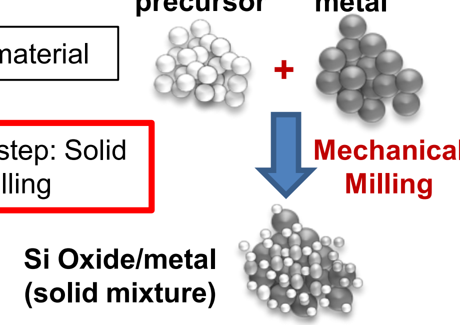
Tasks 1-3. Lab-scale Process Optimization

- **Task 1 : Powder milling:**
  - Process optimization: reduced milling time and speed
  - Mechanical milling was proved to be an effective powder pre-treat to reduce thermal reaction temperature

Step-1

Initial raw material

1st Reduction step: Solid State Milling

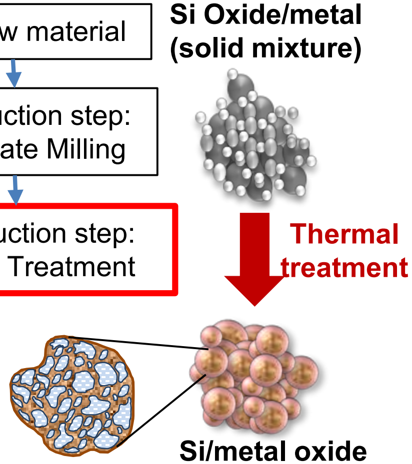


Step-2

Initial raw material

1st Reduction step: Solid State Milling

2nd Reduction step: Thermal Treatment



- **Task 2 : Thermal treatment:**
  - Optimized parameters: soak temperature < 800˚C, heating ramp < 10 ˚ C/min
  - Si/metal oxide pomegranate-like structure to form porous silicon structures (after metal oxide removal)

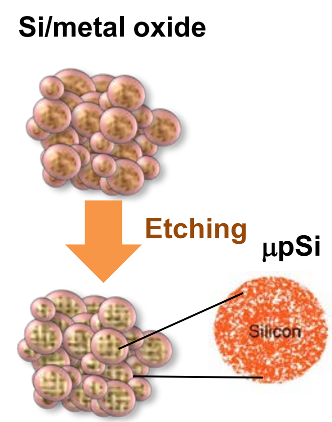
Step-3

Initial raw material

1st Reduction step: Solid State Milling

2nd Reduction step: Thermal Treatment

Etching Process

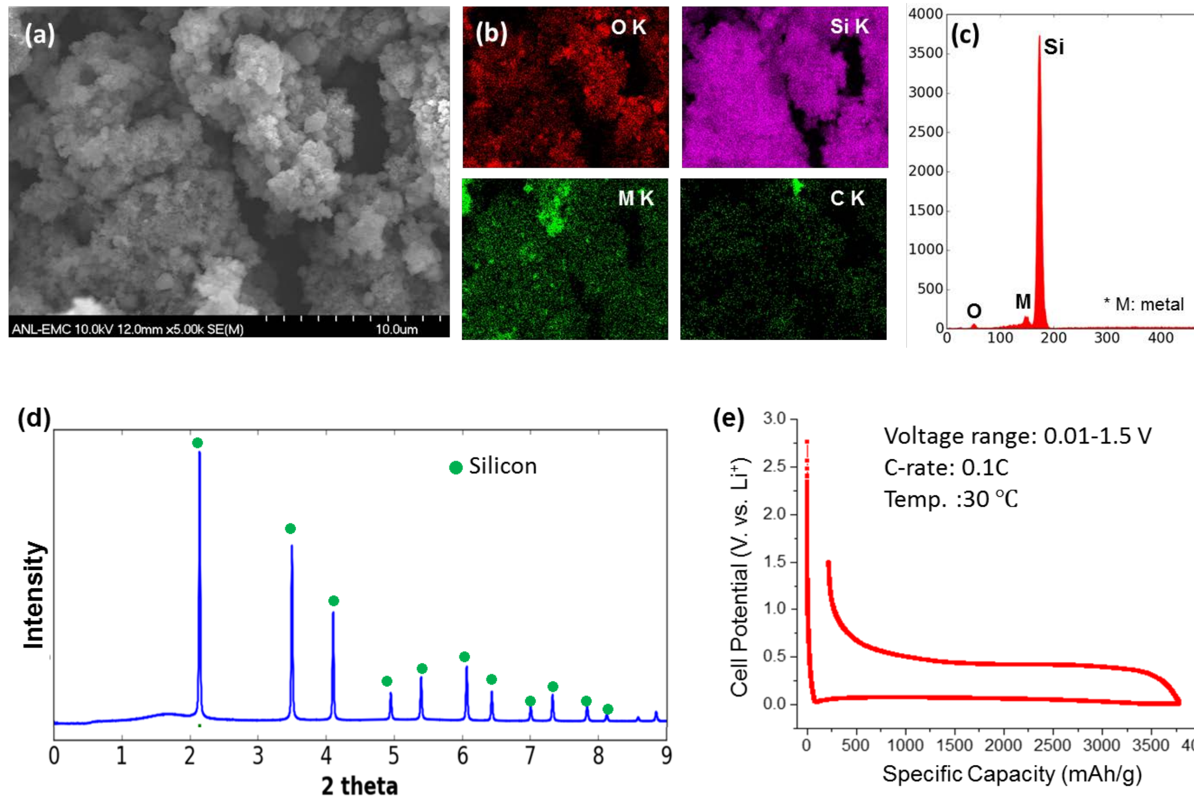


- **Task 3: Metal oxide etching:**
  - Selected etching parameters based on Si/metal oxide mixture composition and oxide content
  - Selected parameters increased process lab-scale from 0.5 g (Q1) to 20 g (Q4)

Task 4. LiB Material Demonstration: µpSi Properties

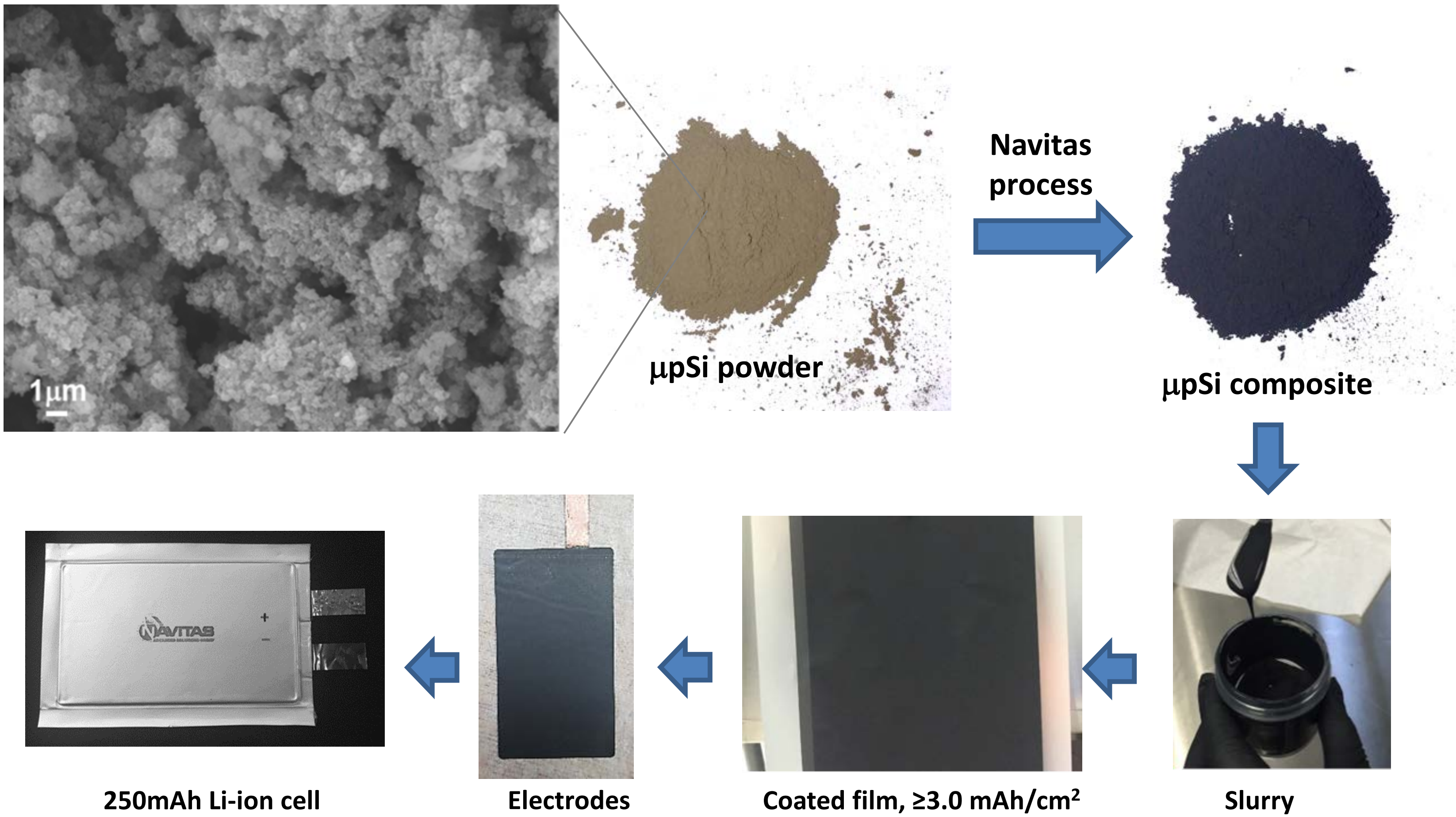
Material characterization performed at ANL

- µpSi synthesized at lab scale (0.2-20g)
- Highly porous micron size Si particles (secondary)
- Crystalline µpSi powder
- µpSi delithiation capacity: 3500 mAh/g and 8% ICL (half cell, 70% µpSi electrode)



Physical Property	Target	Actual
Particle size (µm)	5 - 50	**10 - 30**
BET surface area (m^2/g)	< 200	**25-35**
Tap density (g/cm^3)	> 0.6	**0.65**
True density (g/cm^3)	2.0 – 2.4	**2.2**

Task 4. LiB Material Demonstration: Electrochemical Evaluation



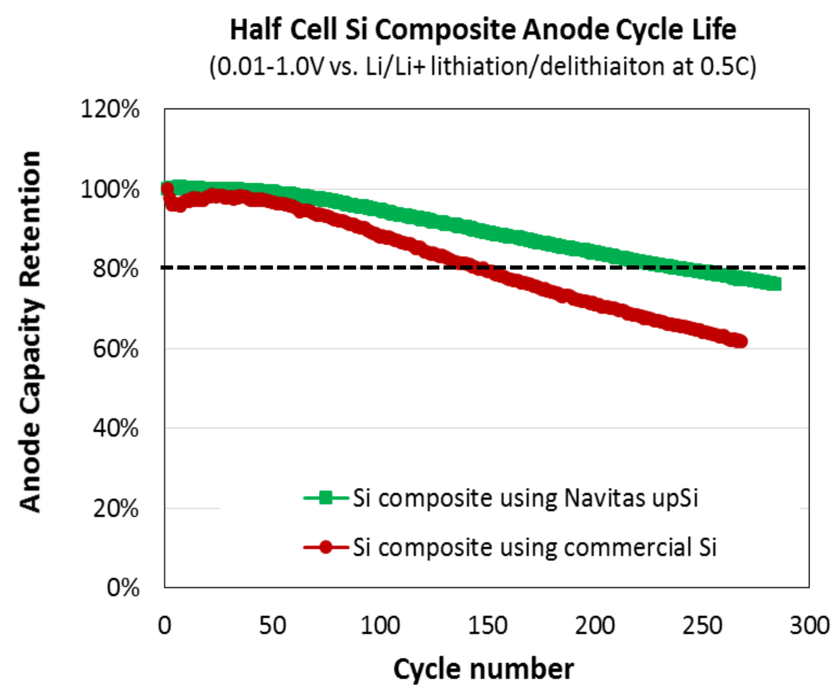
- μpSi powder was used as a precursor to fabricate Si composite anode material
- Electrodes fabricated using slurries made with the μpSi composite
- Half coin and Li-ion pouch cells were made with these electrodes

Task 4. LiB Material Demonstration: Half Cell Evaluation

- μpSi and commercial Si (used as reference) powder were used to fabricate Si composite anodes
- Electrodes were made with 92% active material and aqueous binder

Anode	Formation Capacity at C/20 (mAh/g)	
	Lithiation	Delithiation
Si composite*	1115	955
μpSi composite	**1170**	**946**

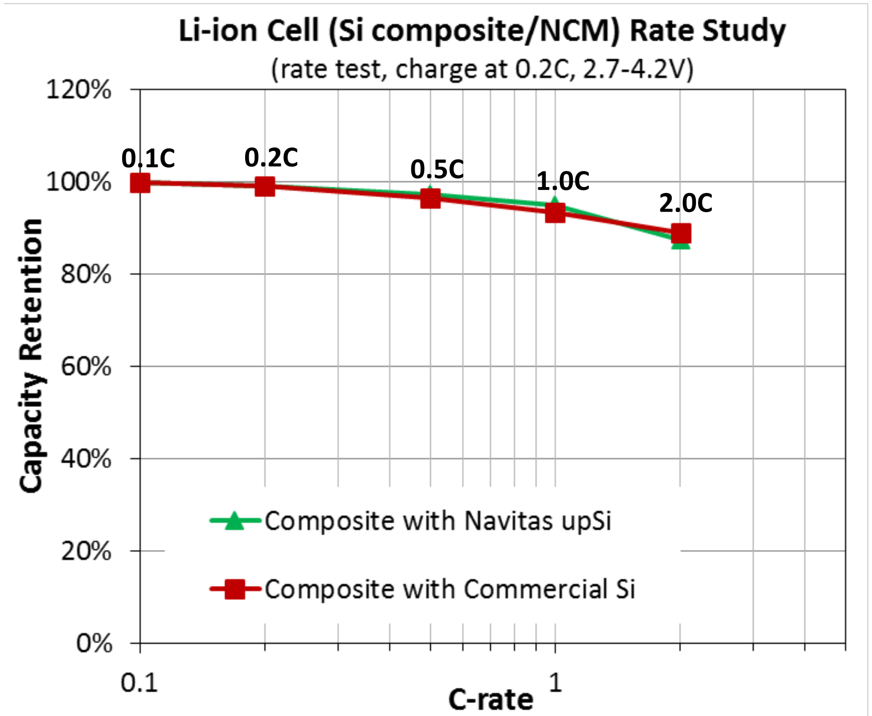
* Made using commercial Si (1-5μm)

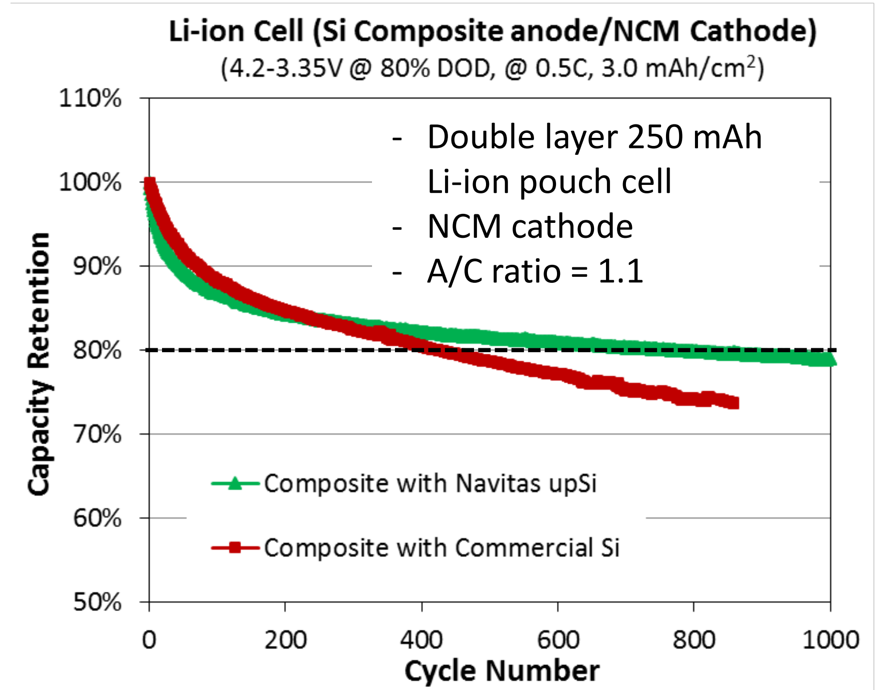


- Cycle life test at 0.5C lithiation/delithiation rate 0.01-1.5V (800 mAh/g initial capacity)

➢ **The μpSi composite electrode shows > 50% enhancement in cycle life vs. composite made with baseline Si precursor**

Task 4. LiB Material Demonstration: Full Li-ion Cell Evaluation





- Electrode fabrication
  - Si anode: 92% μpSi composite with aqueous binder
  - Si composite capacity 650 mAh/g
  - NCM cathode: 93% NCM 523 with PVDF binder
  - Loading 3.0 mAh/cm^2 and A/C = 1.1
- Cell assembly:
  - 250 mAh Double-layer-pouch cell (active area: 47 cm2)
  - 270 Wh/kg if in EV format (cell level)

- **Good rate capability, 90% capacity retention at 2C**
- **900 cycles at 80% DOD and 80% capacity retention (or 250 cycles at 100% DOD)**
- **LiB cells with μpSi composite anode showed 2X life performance improvement over reference**

Task 5. Process Review And Cost Estimation

- Navitas transferred the thermal and acid treatment processes to Nexceris for review and evaluation
- Nexceris identified opportunities for cost reduction and strategies to manage potential hazards associated with scaling-up
- Cost model projected high volume (1MT/month) manufacturing cost of μpSi to be 60% lower than that of the conventional HF etching process
- A Si composite anode made with μpSi precursor will meet the EV Everywhere goal of $125/Wh for EV battery pack (when combined with High Ni cathode)

➢ **The μpSi process will significantly reduce the cost on $/mAh basis versus existing anode materials**

Task 6.1. Pilot Scale Demonstration: Pilot Manufacturing Line

Process	BP1 (Lab-scale)		BP2 (pilot scale)	
	Approach/Equipment	Batch size	Approach/Equipment	Batch size
Mechanical Milling	SPEX/Retsch planetary mill	**20g**	Industrial pilot scale mill	**1kg (deliverable 10kg)**
Thermal Treatment	6" tube furnace		5kg capacity furnace	
Oxide Etching	1-2L glass reactor		20L reactor	

Nexceris, LLC. (Scale-up partner)

- Replicated Navitas' process conditions
- Performed analysis of processing cost and cost drivers
- Selected alternative etchants and etching conditions
- Identified cost effective process steps

- **Pilot scale demonstration (> 10kg μpSi), end June 2017**
- **Cost model update and validation with pilot scale data, end June 2017**

Task 6.2. Pilot Scale Demonstration: Validation Testing

Nexceris, LLC. :

- Validated manufacturing at intermediate scale, 500g per batch
- 10kg pilot scale demonstration in progress

Step-1

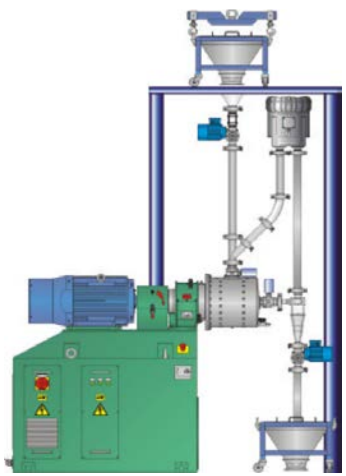
Milled powder

Step-2

Thermally treated powder

Step-3

Scale up process validation μpSi (> 500g)

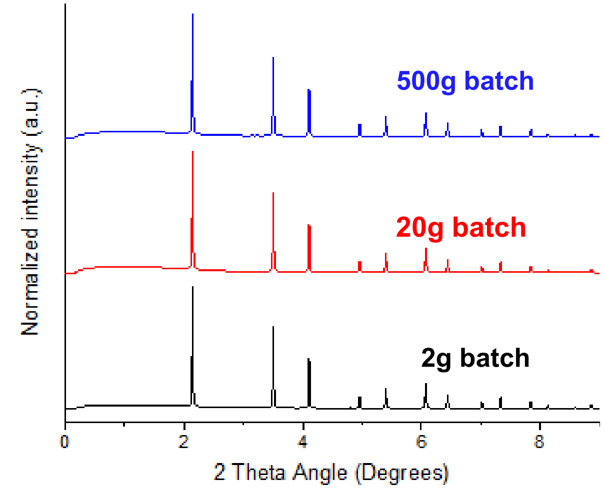


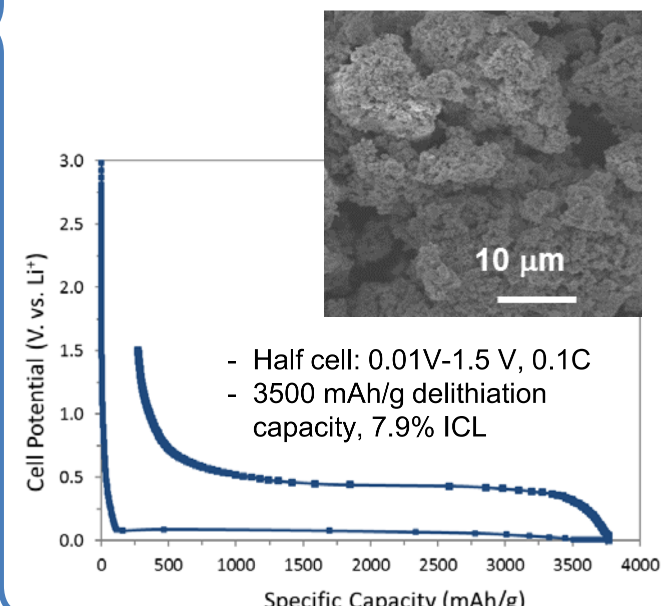
Industrial mill

5kg controlled furnace

20L etching reactor

ANL Material characterization:





Responses to Reviewers' Comments

<table>
<tr><th>2016 AMR comments</th><th>Responses</th></tr>
<tr><td>Cost:
“more information to support the cost claims”
“Additional information on cost benefits should be broken down to the various process steps, and that a second way to express cost reduction, such as dollars-per-kWh savings, may be helpful ”</td><td>✓ Low cost comes from both raw materials and processes:
○ Micron-size Si dioxide precursor <$0.5/kg
○ All the processes are industrially scalable
○ No expensive steps such as vapor deposition, nano fiber growth, HF etching
✓ Projected (1MT/month) manufacturing cost of μpSi is 60% lower than conventional process.
✓ A Si composite anode made with μpSi precursor will meet the EV Everywhere goal of $125/Wh for EV battery pack at anode cost < $25/kg (when combined with high Ni cathode).</td></tr>
<tr><td>Performance / Cycle life
“It has not been demonstrated that porous Si would meet the requirement of the anode materials on cycle life, volumetric energy density, and cost”
“Potential issues associated with porous Si have not yet been solved, including low cycle efficiency and tap density”</td><td>✓ The goal of this project is to develop a low-cost porous silicon as a precursor to make Si anode composite. The porous Si itself is not the final active material. Optimized anode is outside of program scope.
✓ Navitas has used μpSi to prepare Si composite anodes showing improved performance than that of its counterpart made with regular Si. Similarly, end users can employ different strategies to form Si composites with this μpSi precursor (carbonaceous layers/wraps, artificial SEI, intermetallic structure, etc.).
✓ μpSi has a tap density 0.65g/cm^3, and a anode composite made with μpSi has tap density > 0.85 g/cm^3.
✓ Navitas proprietary μpSi composite anode (650 mAh/g) has reached 1000 cycles at 80% DOD in a Li-ion cell.</td></tr>
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Collaborations

- ✓ Nexceris, LLC., scale-up partner
  - Transfer process parameters to pilot scale
  - Demonstration of 10 kg pilot scale
- ✓ Argonne National Lab, Material characterization and cost modeling
  - Material characterization: physical, chemical and electrochemical properties, together with morphological study
  - Cost modeling using ANL BatPac
- ✓ Navitas is collaborating with an industrial milling company to scale up powder milling process
- ✓ Navitas is also working with several companies for technology transfer and/or joint development, including a Si anode material company (SiiLion and XG Sciences), a global material manufacturer, and a Li ion battery OEM

Remaining Challenges and Barriers

- Pilot scale demonstration: process to reach MRL-6 (June 2017)
  - Identify throughput-limiting process steps and hurdles to cost-effective process scale-up
  - Demonstrate pilot scale manufacturing of porous silicon with adequate properties for Li-ion battery application, at a scale to support pilot scale coating
- Further reduce precursor material cost
  - Reduced amounts of excess reducing metal (closer to stoichiometric)
  - Qualify alternative low-cost precursor materials
- Identify advantages and potential limitations of μpSi material
  - Dimensional and thermal stability
  - Abuse tolerance
  - Other applications by balancing energy and cycle life
    - Consumer electronics
    - Specialty military devices

Proposed Future Work

Remaining Work (Project ends June 2017)

- Pilot scale demonstration 10kg of μpSi powder
- Cost model update and validation using pilot scale data
- Validate electrochemical properties of pilot scale μpSi powder in Li-ion cells

Beyond DOE Funding

- Review μpSi synthesis process to identify opportunities for cost reduction:
  - Advances on mechanical milling and thermal treatment
  - Qualifying lower cost raw materials
- Provide μpSi powder to potential partners for external evaluation
- Continue to work with the key industrial partners to commercialize the material - licensing / JD
- Evaluate the anode applications in other areas than EV
  - Consumer electronics
  - Specialty military devices

➢ Any proposed future work is subject to change based on funding levels

Summary

Relevance

Develop a novel, commercially scalable approach to produce microporous silicon

- Usage of low cost precursor materials
- Eliminate the use of hazardous materials
- Reduce process cost through higher intensity and throughput and retain desired electrode powder morphology
- Provide µpSi in adequate quantities to EV battery OEM's

Approach

Navitas' proposed synthesis process:

- Mechanical milling: pre treatment/reduction step
- Thermal treatment: fully reduce silicon precursor to obtain Si/oxide mixture
- Etching: removes oxide to attain µpSi
- Final µpSi powder cost estimated 60% cheaper than conventional process

Technical Accomplishments

- Lab scale process optimization
- ANL confirmed µpSi properties suitable for Li-ion battery application
- Cycle life tests confirmed ~2X advantage of anodes made with µpSi over those made with non-porous Si
- µpSi process was transferred to Nexceris for review and scale-up
- High volume manufacturing cost of µpSi projected to be 60% lower than that of the conventional process
- µpSi fabricated at large scale has similar properties to lab scale powder

Future Work

- Pilot scale demonstration 10kg of µpSi powder
- Update and validated cost model
- Submit final report
- Identify potential market areas and commercialization partners