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: 30%

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 (>10kg/batch)
- 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 (formerly NexTech)
  - 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 (>10kg/batch)
  + 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	Months ARO																				% Effort
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
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**	**On track**
M2.1	**Down-select thermal process parameters**	**08/2016**	**On track**
M3.1	**Down-select etching process parameter**	**08/2016**	**On track**
M4.1	Demonstrate an optimized process for μpSi powder fabrication	11/2016	
M5.1	Complete preliminary cost model	12/2016	
M5.2	Go/No-Go decision based on technical and economic feasibility	12/2016	

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

Cost $24/kg$_{porous\ Si}$

Proposed

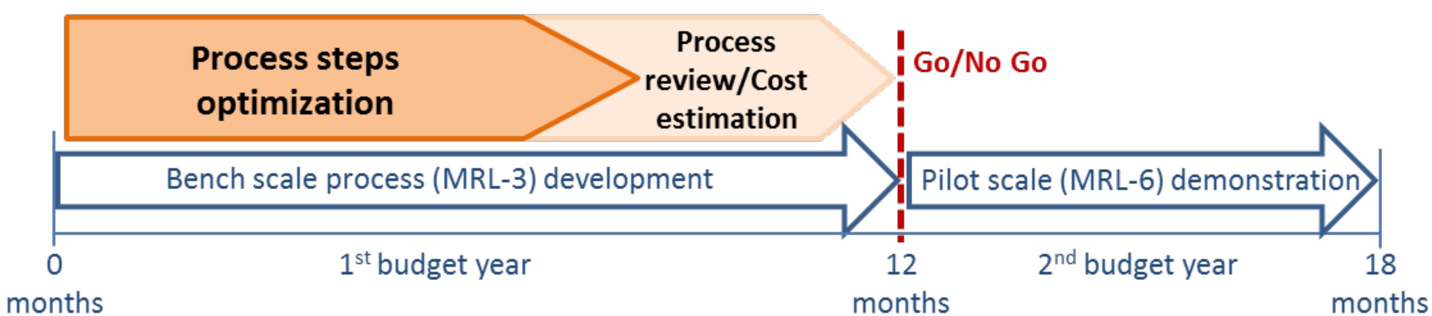
1. Initial raw material
2. 1st Reduction step: Solid State Milling
3. 2nd Reduction step: Thermal Treatment
4. Green Etching Chemistry
5. Filtration/Separation process

Cost: <$10/kg$_{porous\ Si}$

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

Properties	Target Values
Secondary particle size (μm)	1 - 10
Average pore size (μm)	50 - 200
BET surface area (m2/g)	20 - 50
Tap density (g/mL)	0.8 – 1.2
Si content (wt%)	> 90
μpSi capacity (mAh/g)	> 2500
μpSi/Carbon composite capacity (mAh/g)	> 800

Desirable anode active material capacity



Technical Progress: First year

	Objectives	Barriers being Addressed	Status	
1	**Down-select powder milling parameters**	• Optimize process parameters with guidelines for scalability (identify noise and control factors)	• Baseline parameters have been chosen • Parameter design initiated	60%
2	**Down-select thermal process parameters**	• Optimize process parameters with guidelines for scalability (identify noise and control factors)	• Baseline parameters have been chosen • Parameter design initiated	50%
3	**Down-select etching process parameter**	• Optimize process parameters with guidelines for scalability (identify noise and control factors) • Greener manufacturing etching approach	• Baseline parameters have been chosen • Parameter design initiated	40%
4	Demonstrate an optimized process for µpSi powder fabrication	• Current high cost materials and non-scalable processes are barrier to adoption • Optimize process parameters to control impurities and µpSi structure	• Preliminary experiments (half coin cells)	On track
5	Complete preliminary cost model	• Usage of low cost raw materials and manage the waste etching solution and the wash effluent • Reduce operating process cost (i.e. processing time, temperature, etc.)	• Gathering of initial data will start in 07/2016	On track

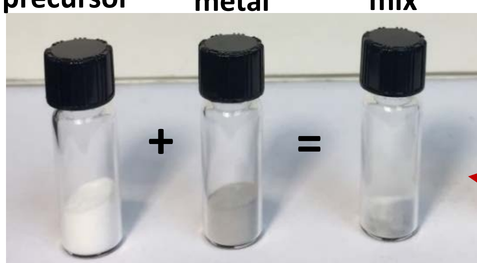
Task 1. Powder Milling Optimization

Mechanical milling as reduction pretreatment

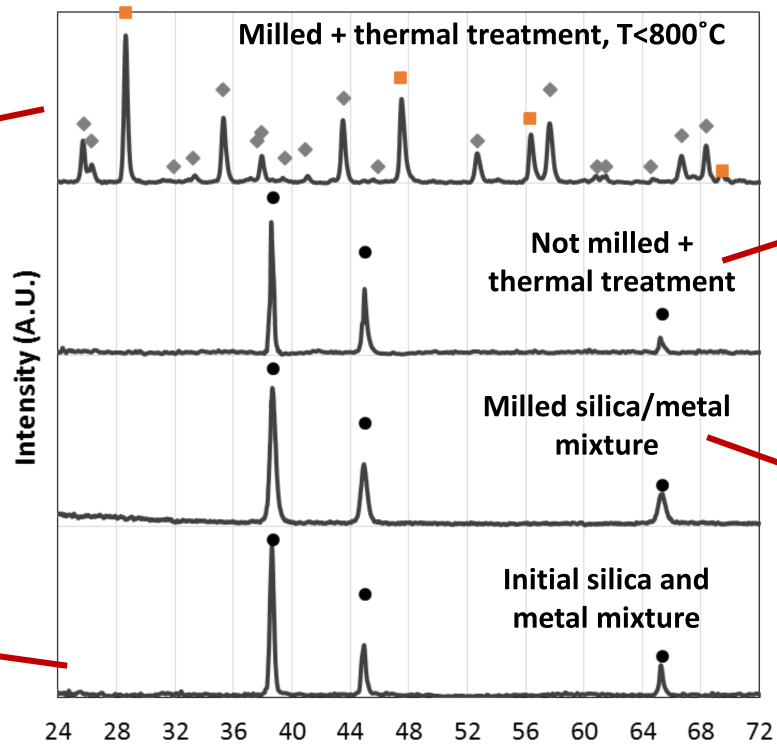
- Effective pretreatment for the reduction Si oxide precursor at low temperatures
- Full reduction of silica at T < 800˚C, which otherwise requires T > 1000˚C

Milled Si-Metal oxide after thermal treatment

Si precursor | Reducing metal | SiO_x/Metal mix



Reactants at stoichiometric mas ratio



Not milled SiO_2-Metal after thermal treatment, no reaction

Silica / Metal after milling

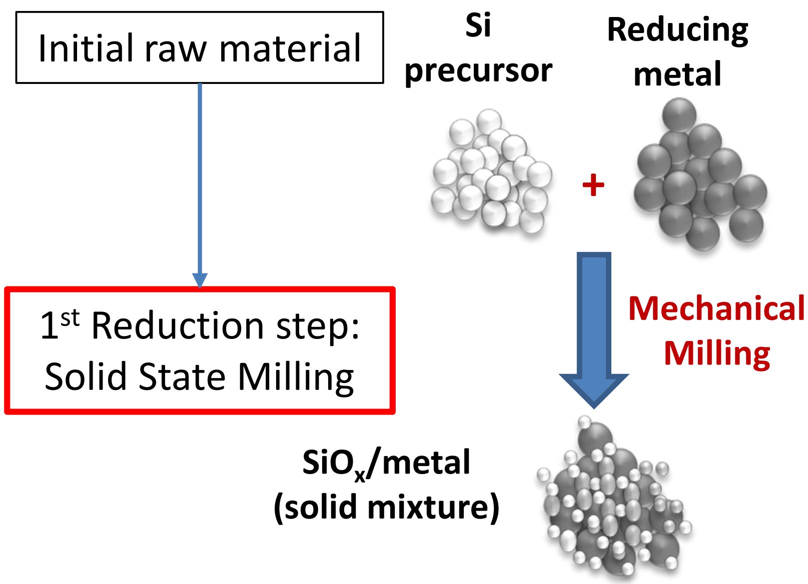
Thermal treatments @ same conditions, XRD patterns (●) reducing metal, (■) silicon, (♦) metal oxide

Task 1. Powder Milling Optimization

Process optimization: parameters design

- Robust engineering will be used to optimize mechanical milling process parameters
  - + Control milling parameters have been selected
  - + Next identification of control and noise factors

Step-1: Mechanical milling pretreatment



Parameters
- Milling speed
- Media to material mass ratio
- Media material
- Reactants mass ratio
- Charge volume
- Milling time

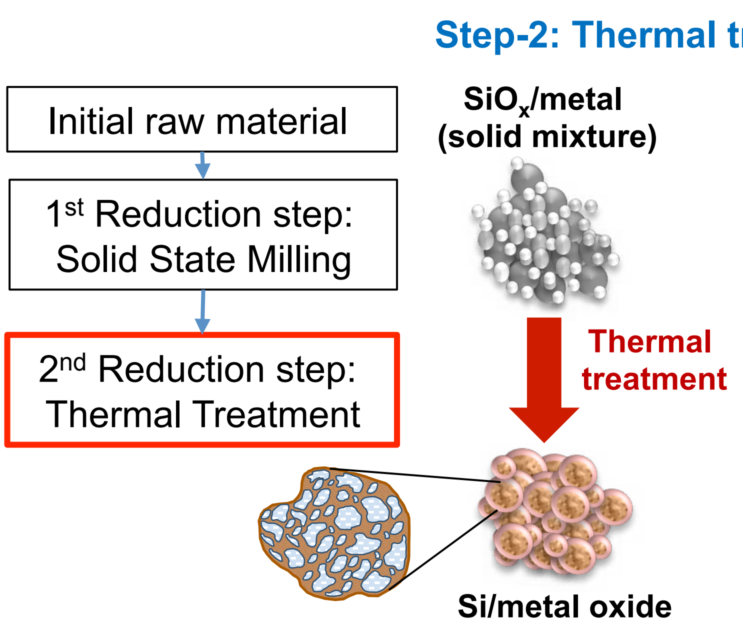
Task 2. Thermal Treatment Optimization

Down-select thermal treatment parameters

- Parameters influence composite (Si/metal oxide) morphology and oxide phase
- Composite particle morphology crucial to obtain high porosity

Process optimization

- Robust engineering to optimize process parameters targeting adequate powder morphology and composition
- Baseline chosen, control and noise factors will be identify towards desirable pre-etch particle properties and aiming cost reduction



Parameters

- Heating/cooling ramp
- Dwell temperature
- Dwell time
- Atmosphere
- Loading conditions

Task 3. Metal Oxide Removal

Oxide etching process

- Mechanical milling and thermal treatment conditions affect composition of pre-etched material
- Etching agent and process conditions depend on oxide phases and concentration

Initial raw material

↓

1st Reduction step: Solid State Milling

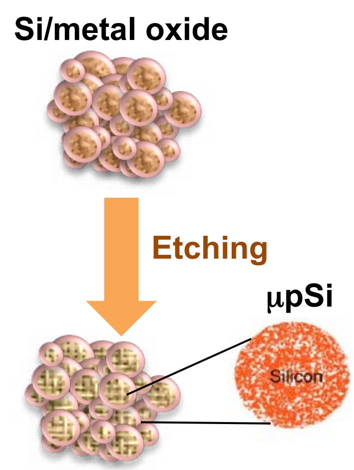
↓

2nd Reduction step: Thermal Treatment

↓

Green Etching Chemistry

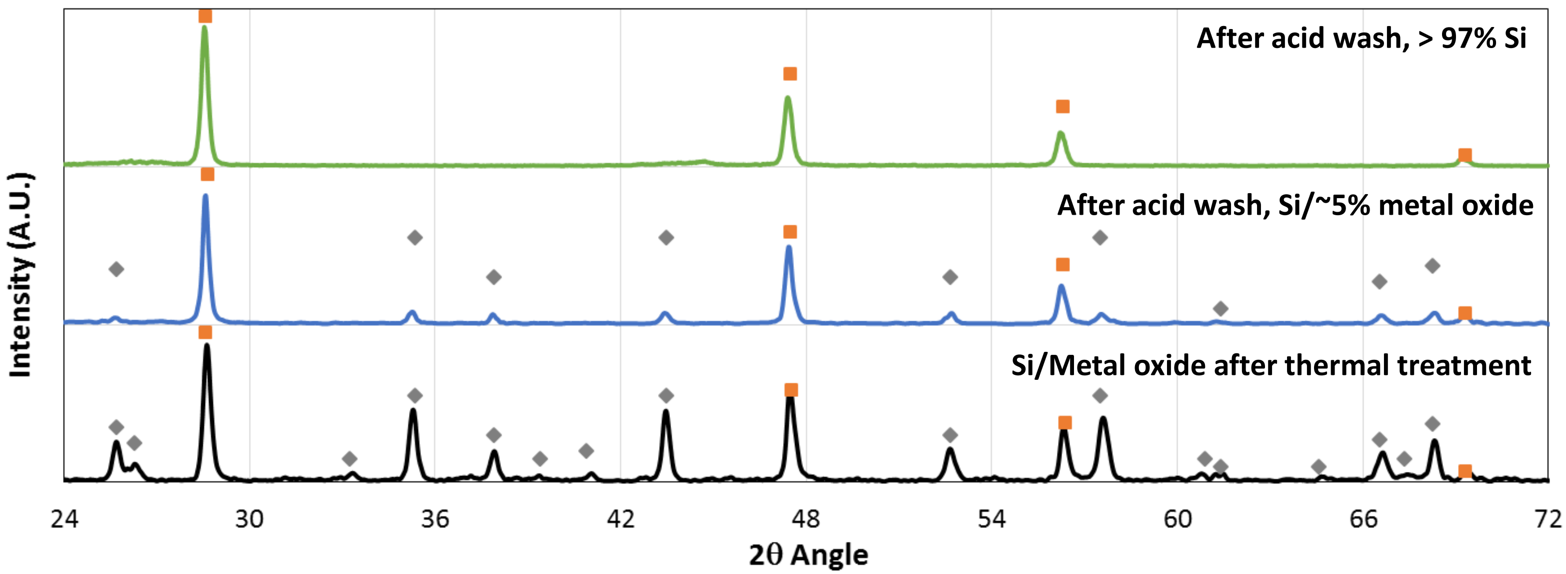
Step-3: Metal oxide removal



Parameters

- Etchant solution
- Etchant concentration
- Reaction time
- Reaction temperature
- Powder and etchant mass ratios

Task 3. Metal Oxide Removal



XRD patterns, after oxide etching step: (■) silicon and (◆) metal oxide

- Navitas has reduced residual metal oxides to < 3%

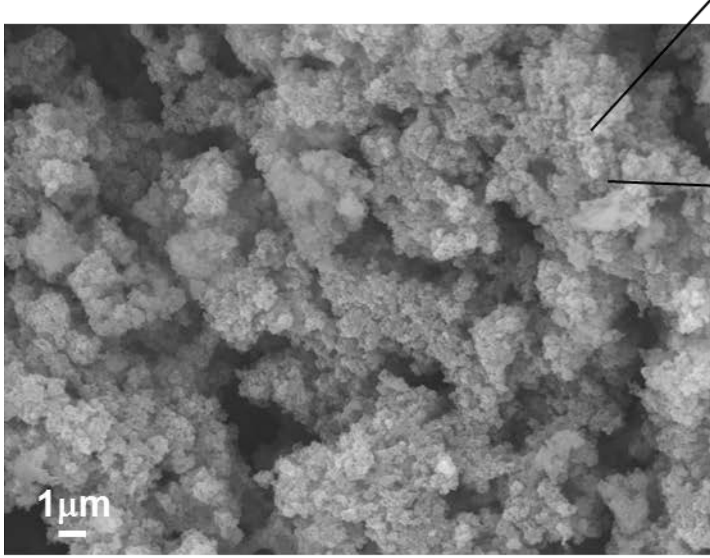
Property	Commercial Si	μPSi with (>97% Si)
Total Pore Area (m^2/g)	8.6	11.5
Average Pore Diameter (nm)	310	150
Bulk Density (g/mL)	0.81	0.84
Skeletal density (g/mL)	1.78	1.34
BET surface area (m^2/g)	4.3	36.2

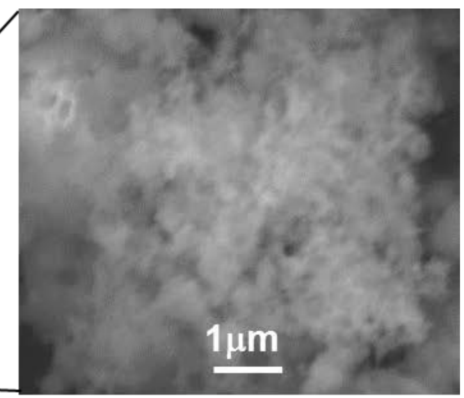
Task 3. Metal Oxide Removal

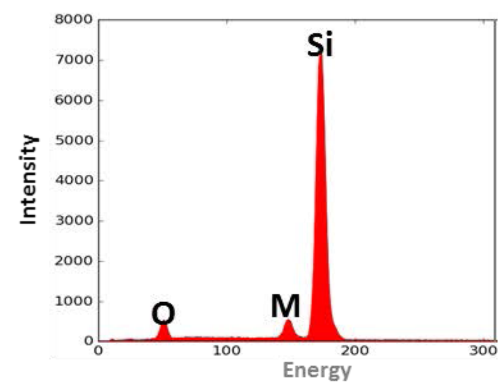
Etching process optimization

- Robust engineering to tune etching parameters to fully or partially remove amounts of metal oxide
- Baseline control and noise factors will be identified towards scale up and usage of environmentally friendly solvents and targeting low cost

μpSi after etching, ~5% oxide

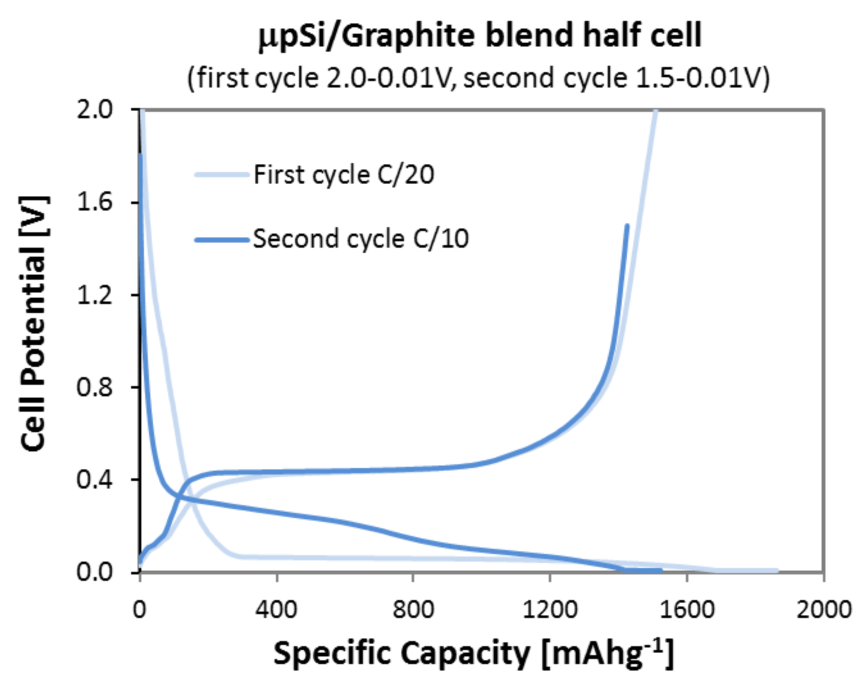




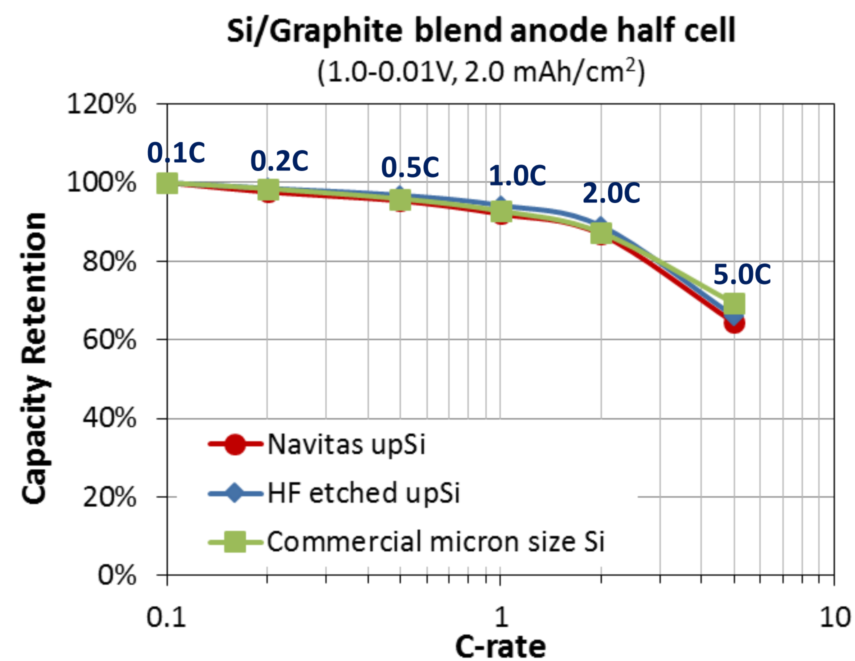


Task 4. Preliminary Anode Evaluation: Half Cell

- **Formation cycle**



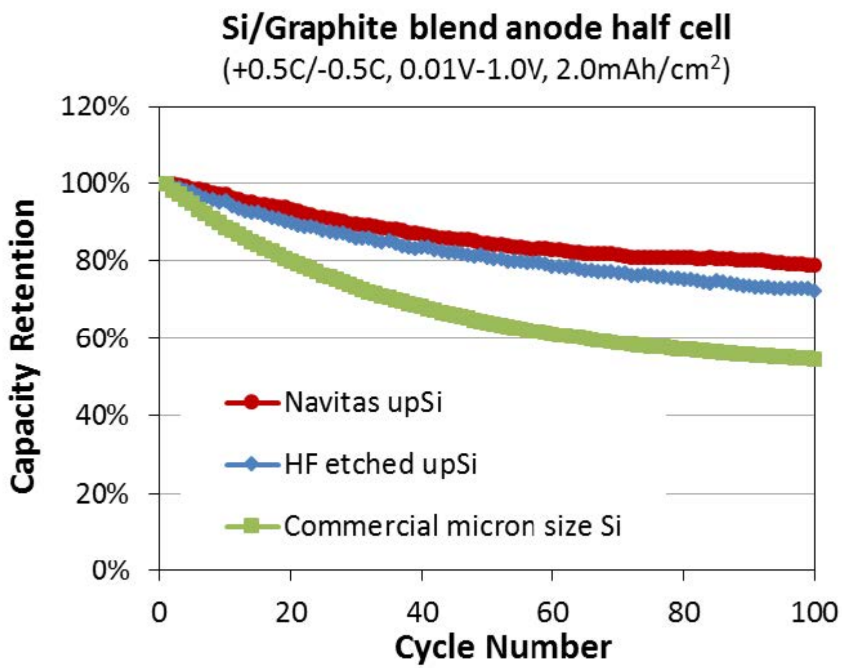
- **Rate Capability**



- Si powders were blended with graphite to form (Si:Graphite 1:1 mass ratio, 92% active material, 6.5% binder) with 2.0 mAh/cm^2 loading
- Fist cycle reversible capacity and ICL were ~1500mAh/g and 18% in all cells
- Commercial non-porous Si was used as baseline, and it was the precursor to make hydrofluoric acid etched μpSi

Task 4. Preliminary Anode Evaluation: Half Cell

- **Cycle life @ 0.5C charge/discharge**



- *Porous Si materials show improved cycle life over the non-porous Si, confirming the advantage of porous structure of Si*
- Electrodes used in this experiment were not optimized
- Attaining longer cycle life will require additional approaches: artificial SEI, electrolyte additive, higher binder content, etc.

Responses to Reviewers' Comments

New Project – No Comments

Collaborations

- ✓ Nexceris, LLC., scale-up partner
  - Input for process scale up (>1.0kg/batch)
  - Transfer process parameters to pilot scale
  - Demonstration of 10-100kg 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 will collaborate with Li ion battery OEMs (A123) and battery material manufacturers (XG-Sciences) for anode evaluation
- ✓ Collaboration with Prof. Raj Rajamani (University of Utah) to scale up powder milling process

Remaining Challenges and Barriers

This Project has only completed the first 5 months

- Further reduce precursor material cost
  - Reduced amounts of excess reducing metal (closer to stoichiometric)
  - Qualify low-cost precursor materials
- Process optimization
  - Process parameters need to be optimized targeting lower cost without affecting final product properties
- Green etching process
  - Currently low concentration inorganic acids have been used
  - Need for more environmentally friendly methods
- Process to reach MRL-6 (2nd year)
  - Demonstrate pilot scale manufacturing of porous silicon with adequate properties for lithium ion application, at a scale to support pilot scale coating

Proposed Future Work

- Finalize lab scale process optimization (mechanical milling, thermal treatment, and oxide removal)
- Investigate alternative etching chemistries to reduce cost with reduced environmental footprint
- Validate electrochemical properties of μpSi powder in lithium ion battery cells
- Review μpSi synthesis process to identify opportunities for cost reduction using initial economic assessment and to manage potential hazards associated with scaling-up the processes
- **Go/No Go:** verify if μpSi material and manufacturing process have technical and economic advantages over current battery material manufacturing processes (12/2016)

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 mix
- Etching: removes oxide to attain µpSi
- Final µpSi powder cost estimated < $10/kg

Technical Accomplishments

- Lab scale process optimization initiated
- Mechanical milling allows thermal reduction to happen at T < 800˚C
- Milling parameters affect properties of Si/metal oxide powder properties
- Thermal reduction conditions to achieve desirable particle structure and composition
- Etching parameters can be altered to fully remove metal oxide
- Half cell cycle life testing confirmed advantage of porous structure over non-porous Si

Future Work

- Finalize lab scale process optimization
- Electrochemical validation of µpSi powder in lithium ion cells
- Conduct cost analysis
- Review synthesis process to identify opportunities for cost reduction and potential scale-up risks