Advanced Solutions Group
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Low-cost, High-capacity Lithium Ion Batteries through Modified Surface and Microstructure

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June 9, 2015

Project ID: ES238

Overview

Timeline

- Project start date: July 28, 2014
- Project end date: July 27, 2016
- Percent complete: 50%

Barriers

- High energy Li-ion battery (300 Wh/kg) by 2015
- Low cost, long cycle life Si anodes are required

Budget

- Total project funding: $1,000,000
  - DOE share: $1,000,000
- Funding received in FY14: $562,830
- Funding for FY15: $437,170

Partners

- Funded Partner: Navitas ASG

Relevance and Project Objectives

- **Project Goal:**
  - Produce a practical and economical high capacity silicon-based anode material for lithium ion batteries
- **Phase I Objectives:**
  - Develop macroporous Si anode with capacity >600 mAh/g and ICL <15%
  - Verify scalable process to support pilot scale validation
  - Demonstrate cycle life >300 at 100% DOD and >600 at 80% DOD
- **Phase II Objectives:**
  - Optimize the process to produce macroporous Si composite anode with >800 mAh/g and <12% ICL
  - Develop the anode material with surface area <20 m^2/g, tap density >0.9g/cm^3 to support >4 mAh/cm^2 coating
  - Scale up to 500g/batch
  - Fabricate >2 Ah lithium ion cell with anode coating >4 mAh/cm^2
  - Achieve Si-composite anode cycle life >1000 at 80% DOD in full lithium ion cell

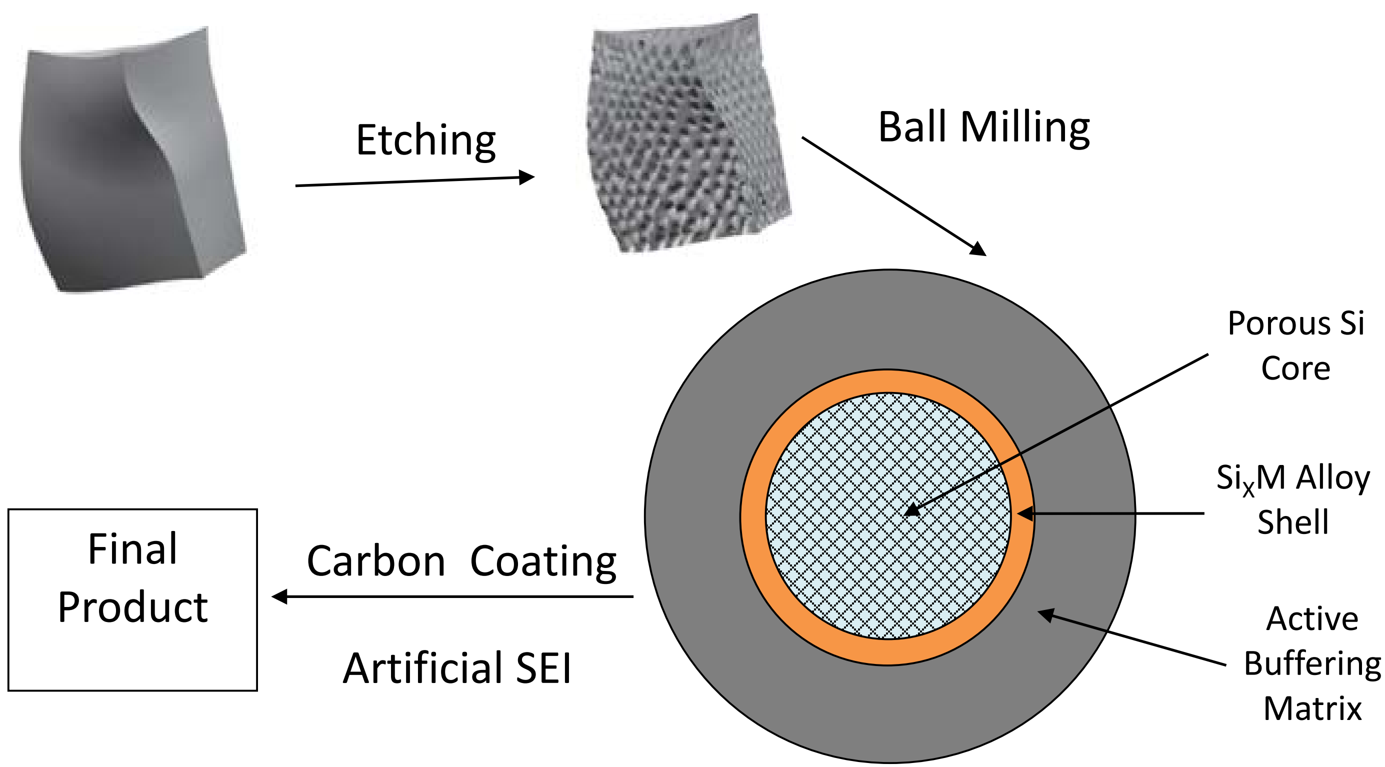
Milestones

TASK	Months ARO																								% Effort
	Year 1												Year 2												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	
1. Porous Si preparation																									10%
2. Si composite synthesis																									15%
3. Conformal carbon coating																									5%
4. Artificial SEI coating																									13%
5. Anode process scale-up																									15%
6. Electrode Coating																									17%
7. Cell assembly and test																									20%
8. Process modeling																									5%
Milestones									***1***			***2***						***3***			***4***			***5***	**100%**

Milestone		Metric	Date	Status	
1	Anode capacity and ICL	- Capacity >800 mAh/g - ICL <12%	05/2015	**- Capacity >800 mAh/g** - ICL <15%	On track
2	High loading Si anode	- Tap density >0.9 g/cm^3 - Surface area <20 m^2/g - Anode loading 4 mAh/cm^2	08/2015	- Tap density 0.83 g/cm^3 **- Surface area <20 m^2/g** **- loading at 4 mAh/cm^2**	On track
3	Process scale up	>500g batch	02/2016	Identification of the scale-up equipments	On track
4	Prototype Li ion cell deliverable	10 prismatic cells >2Ah	05/2016	Active material qualification	On track
5	Cycle life demonstration	>1000 cycle at 80% DOD	08/2016	Active material qualification	On track

Approach and Strategy

Si composite process

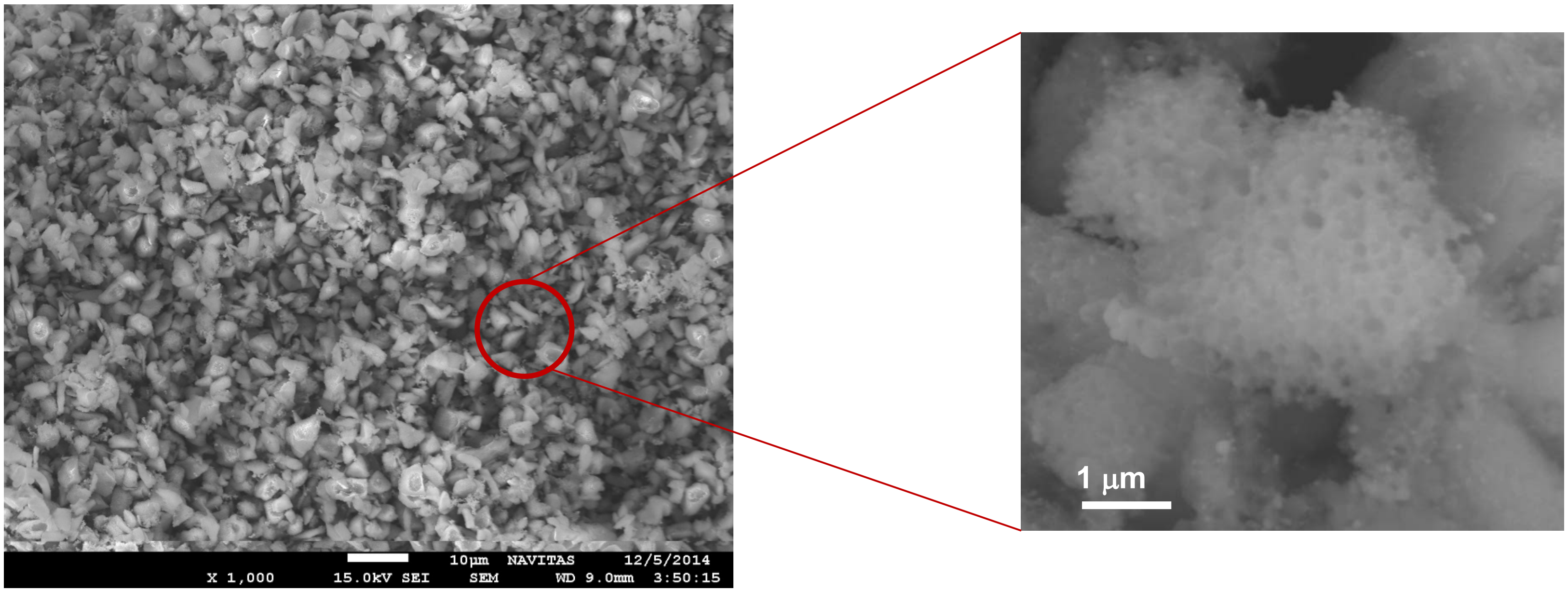


Technical Progress

	Objectives	Results	Status		Details
1	Produce macroporous Si composite anode with >800 mAh/g and <12% ICL	- Capacity >800 mAh/g - ICL <15%	Optimizing the process to reduce ICL	On track	**Slides 7 - 11**
2	Develop the anode material with surface area <20 m^2/g, tap density >0.9g/cm^3 to support >4 mAh/cm^2 coating	- Tap density 0.83 g/cm^3 - Surface area 15 - 20 m^2/g - Anode loading 4 mAh/cm^2	Optimizing the composition to increase the tap density	On track	
3	Process scale up	Qualified the **Ball Milling** and **Carbon Coating** processes in large scale equipments	Developing **Etching** and **Artificial SEI** coating processes in pilot scale	On track	**Slide 12**
4	Prototype Li ion cell deliverable	Tested coin half cells and single-layer-pouch (SLP) Li ion cells	Will fabricate large format cells in next period	On track	**next review**
5	Cycle life demonstration	Evaluated GEN1 material in half cells and SLP cells as a baseline	Improving the material towards GEN2 and demonstrate cycle life in next period	On track	**Slides 7 - 11, 13**

Step1: Porous Si Synthesis (Objectives 1 & 5)

Step 1: Porous Si



- Conventional HF etching process

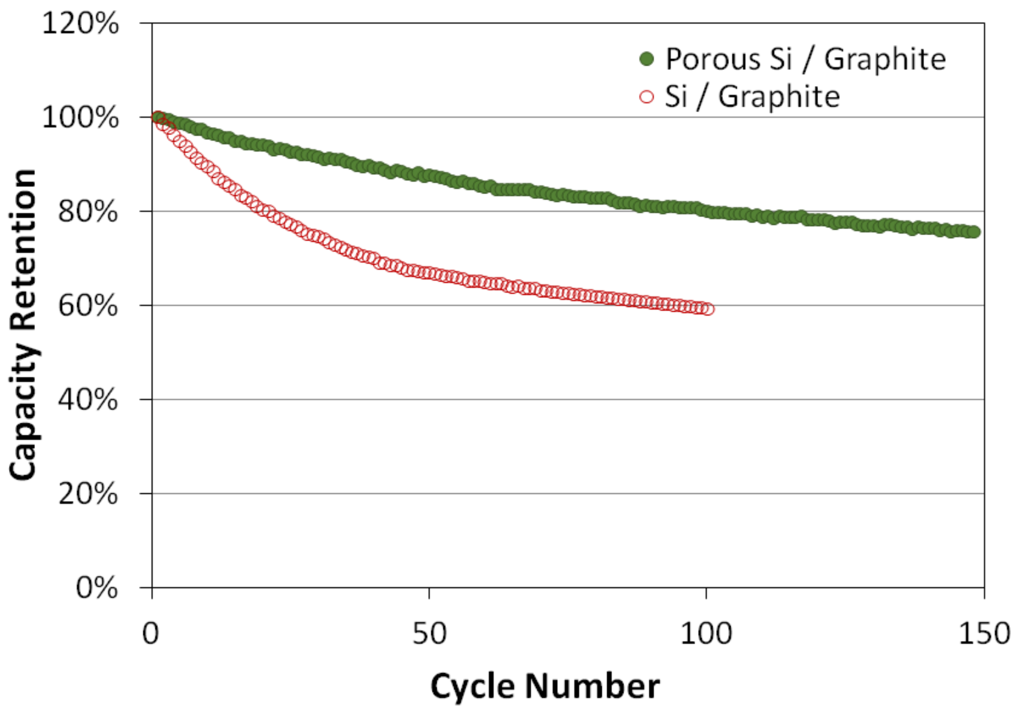
Cathode reaction	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O, E^0 = 1.78V$
Anode reaction	$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e, E^0 \cong 0.91V$
	$SiO_2 + 6HF \rightarrow [SiF_6]^{2-} + 2H_2O + 2H^+$
Total reaction	$Si^0 + 2H_2O_2 + 6F^- + 4H^+ \rightarrow \{SiF_6\}^{2-} + 4H_2O$

- An alternative non-HF process is being developed

Porous Si Advantage (Objective 1 & 5)

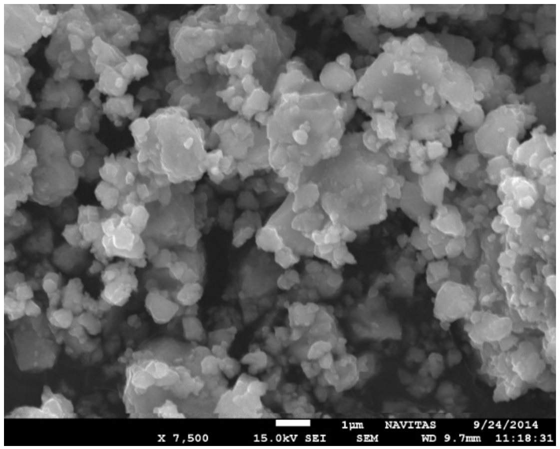
Cycle life of porous Si vs. non-porous Si

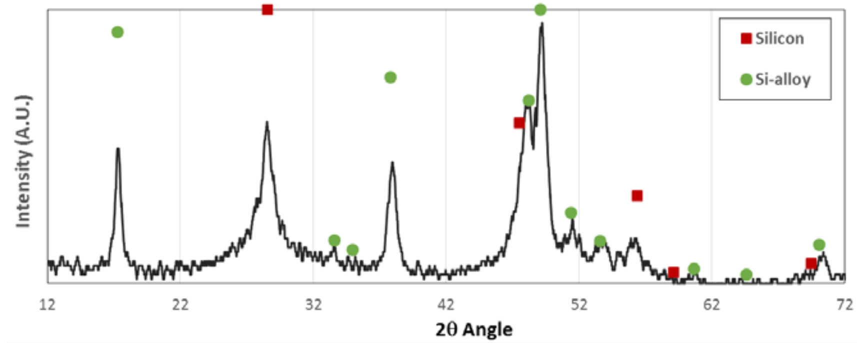
- Both materials are Si-graphite composites
- tested in half cells: 1.0V – 0.01V at C/2
- **Porous Si composite shows >100% improved cycle life vs. non-porous Si composite**

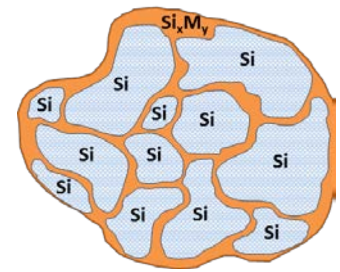


Step 2: Si / Alloy / Carbon Composite (Objectives 1, 2, & 5)

Step 2A: Si / Si_xM_y Alloy Composite

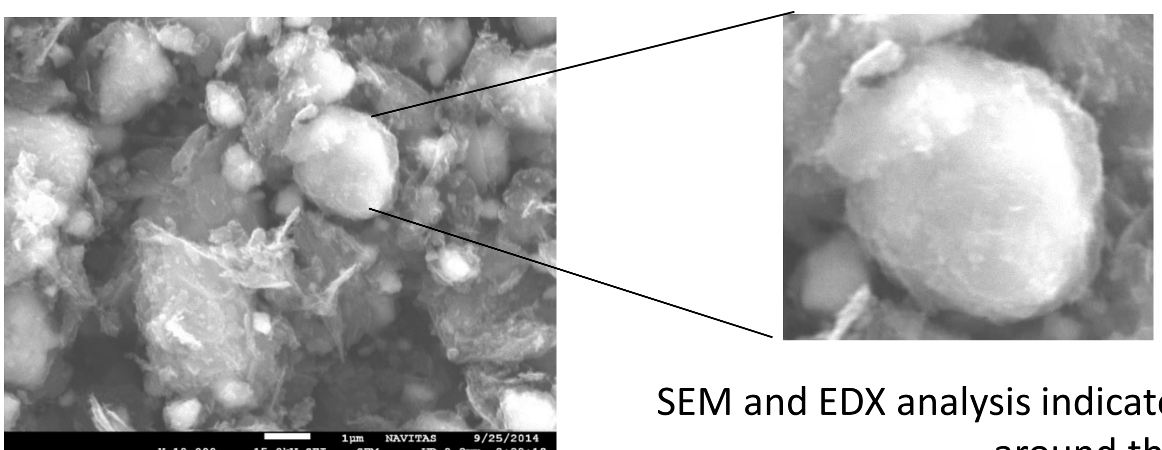


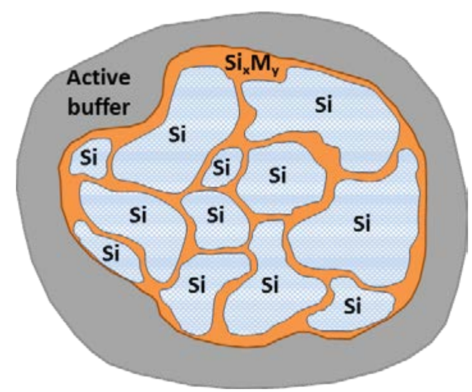




XRD pattern shows mixture of Si and Si-metal alloy

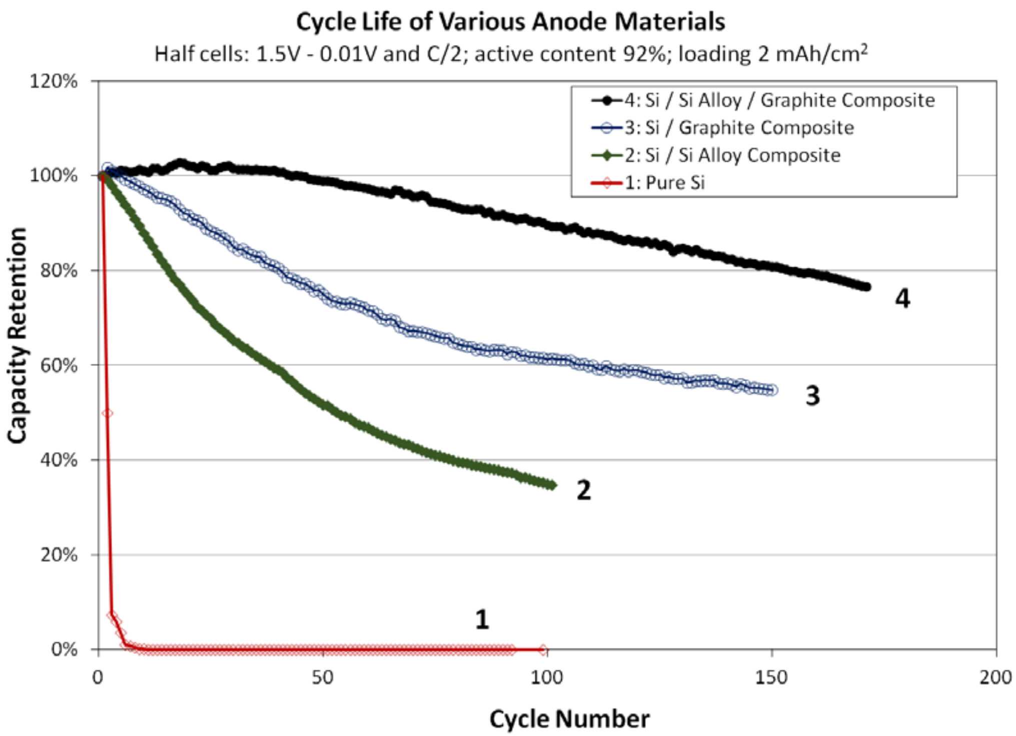
Step 2B: Si / Alloy /Carbon Composite





SEM and EDX analysis indicates active buffering coating around the Si /alloy matrix

Si Composite Advantage (Objectives 1, 2, & 5)



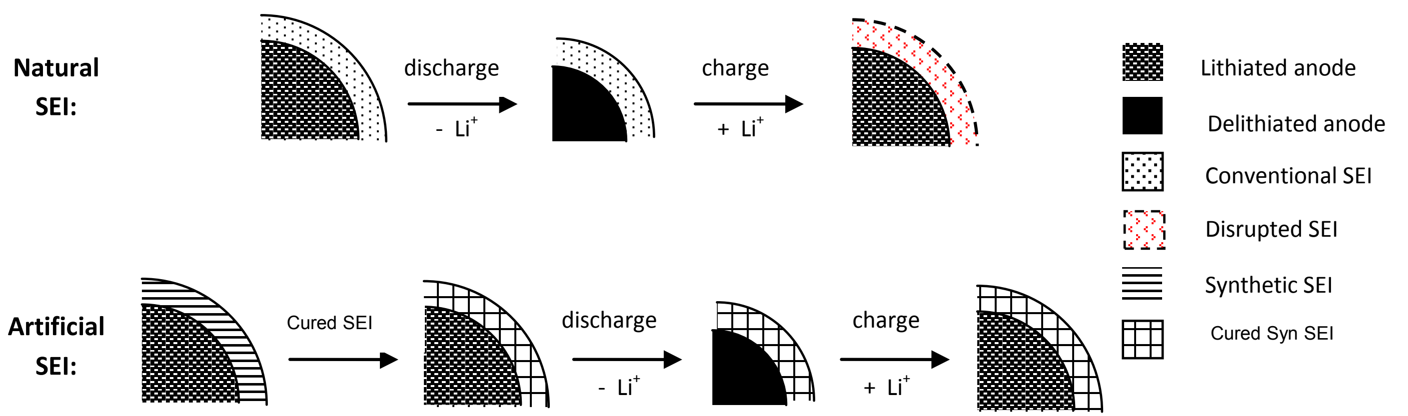
- Cycle life improvement from **Si-metal alloy protection**
  - Plot 2 vs. Plot 1
  - Plot 4 vs. Plot 3
- Cycle life improvement from **graphite matrix buffering**
  - Plot 3 vs. Plot 1
  - Plot 4 vs. Plot 2

Step 3: Surface Modification (Objectives 1, 2, & 5)

- Step 3A: carbon coating

Carbon Coating (Y/N)	Tap Density (g/cc)	BET Surface Area (m^2/g)	Reversible Capacity (mAh/g)	ICL
No	0.64	160	1062	24%
Yes	0.83	18	864	**15%**

- Step 3B: Artificial SEI – will be developed for GEN2 material



Process Scale-up (Objectives 3)

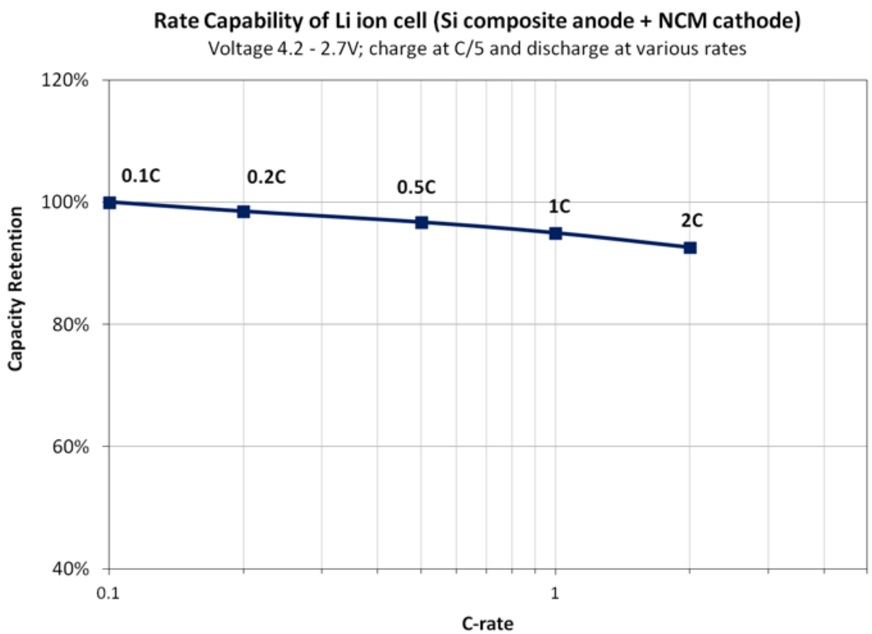
Process	Phase I		Phase II	
	Equipment	Batch size (g)	Equipment	Batch size (g)
Chemical etching	Hot plate and flasks	<20	Pilot scale reactor	>500
High energy ball milling	SPEX 8000 mill		Industrial ball mill	
Carbon coating	2” tube furnace		6” tube furnace	
Artificial SEI forming	Hot plate and flasks		Pilot scale reactor	

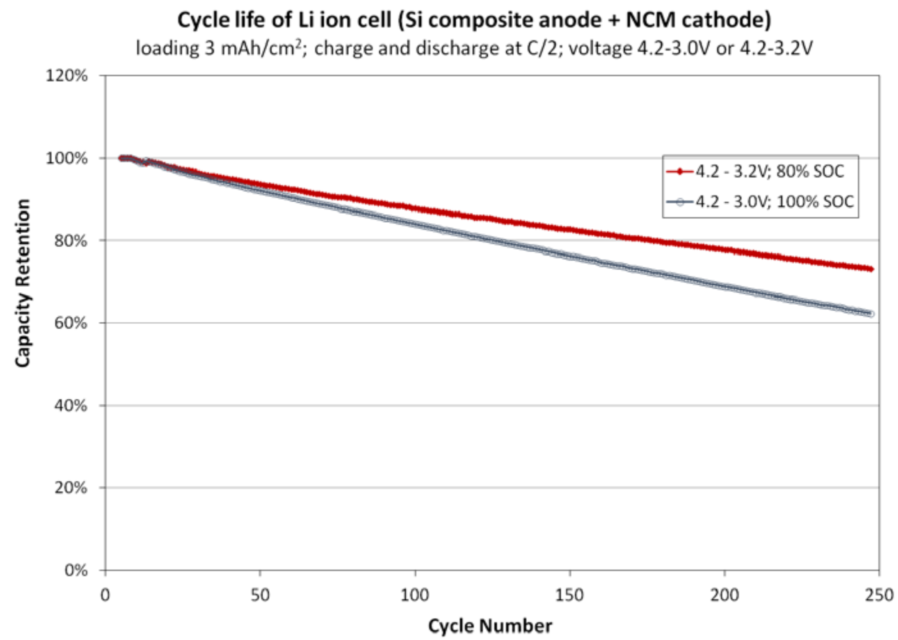
Industrial Mill

- **Qualified the large scale equipments for ball milling and carbon coating processes**
- Will qualify the pilot scale reactors for etching and artificial SEI forming processes

6” Tube Furnace

Li-ion Cell Evaluation on GEN1 Anode (Objectives 5)





- GEN1 material was developed as a baseline to qualify the large scale processes
  - Rate capability :
    - >90% retention at 2C; comparable to graphite
  - Cycle Life:
    - 130 cycles (100% DOD) and 180 cycles (80% DOD) at 80% capacity retention
- GEN2 material is under development (to be completed by Month 18)
  - Optimize material composition, synthesis parameters, and surface treatment processes
  - Meet the cycle life target

Responses to Reviewers' Comments

- **This project is a new start**

Collaborations

- Navitas Advance Solutions Group (ASG) is a sub-contractor to provide electrode fabrication, cell assembly and cell testing labor in support of the program. ASG is a wholly-owned subsidiary of Navitas Systems
- Navitas is evaluating pilot scale partners for Si precursors
- Navitas will collaborate with Li ion battery OEMs (A123 and XALT Energy) for anode evaluation

Remaining Challenges and Barriers

- Reduce the ICL to <12%
  – ICL has been reduced from 25% to 15%
  – Need to further reduce it to <12% that is comparable to graphite anode
- Scale up the process to >500g
  – Phase I process (20 g) has been transferred to pilot scale equipments
  – Need to demonstrate >500g batch for TRL 6
- Achieve a cycle life of 1000 at 80% DOD
  – All of the qualifications are at EV relevant levels
    - Anode active content 92%
    - Anode loadings 2 – 4 mAh/cm^2
  – Need to meet the cycle life target for EV battery

Proposed Future Work

- Optimize synthesis condition and surface modification process to reduce ICL to <12%
- Develop GEN2 anode material by optimizing material composition and synthesis conditions
- Develop artificial SEI coating to improve the performance
- Scale up the process to > 500 g
- Demonstrate performance in EV relevant prototype Li ion cells

Summary

- GEN1 material has been developed with 800 mAh/g capacity and 15% ICL
- The advantages of “porous Si”, “Si alloy protective phase”, and “active buffering matrix” have been confirmed
- Carbon coating is effective to lower the surface area and reduce the ICL
- Qualification of pilot scale equipments are being conducted. The projected readiness is TRL 6 for the material upon completion of the program
- Improvement towards GEN2 material has been started (including material composition, synthesis parameters, and surface treatment development) to meet the program goal