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

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Project ID: ES238

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Timeline

- Project start date: July 28, 2014
- Project end date: July 27, 2016
- Percent complete: 90%

Barriers

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

Budget

- Total project funding: $1,000,000
  - DOE share: $1,000,000
- Funding 2014 - 2015: $562,830
- Funding 2015 - 2016: $437,170

Partners

- Funded Partner: Navitas ASG
  - Electrode coating and cell assembly
- Argonne National Laboratory
  - Material characterization & cost modeling
- A123 Systems, LLC
  - Cell evaluation

Relevance and Project Objectives

- **Project Goal:**
  - Produce a practical and economical high capacity silicon-based anode material for lithium ion batteries
- **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
  - Achieve Si-composite anode cycle life >1000 at 80% DOD

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 <12%	100%
2	High loading Si anode	- Tap density of 0.9 g/cm^3 - Surface area <20 m^2/g - Anode loading 4 mAh/cm^2	08/2015	- Tap density 0.9 g/cm^3 - Surface area <20 m^2/g - loading at 4 mAh/cm^2	100%
3	Process scale up	>500g batch	02/2016	>500g batch	100%
4	Prototype Li ion cell deliverable	10 prismatic cells >2Ah	05/2016	complete	100%
5	Cycle life demonstration	>1000 cycle at 80% DOD	08/2016	500 cycles at 100% DOD in small cells; 2Ah cell test is on going	75%

Approach and Strategy

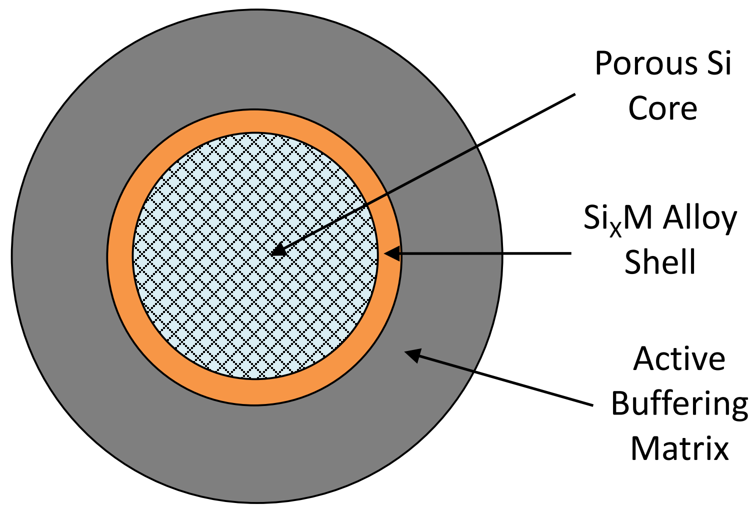
High capacity low cost Si composite (800 mAh/g, $35/kg)

Micro Si precursor < $2/kg

Non-HF Etching

Scalable; Environ. friendly

Industrially Scalable Ball Milling



Surface Mod.

Scalable Process; Low cost raw materials

Final Product

Technical Progress

	Objectives	2015 Results	2016 Results	Status
1	Produce macroporous Si composite anode with >800 mAh/g and <12% ICL	- Capacity >800 mAh/g - ICL 15%	- Capacity >800 mAh/g **- ICL 12%**	Complete
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 0.8 g/cm^3 - Surface area 15 – 20m^2/g - Support >4 mAh/cm^2	**- Tap density 0.9 g/cm^3** - Surface area 15 – 20m^2/g - Support >4 mAh/cm^2	Complete
3	Process scale up (500g batch)	- 200g batch (from 20g) - Qualified the process steps in large scale equipments	**>500g batch**	Complete
4	Prototype Li ion cell deliverable (2Ah prismatic)	Coin half cells and single-layer-pouch (SLP) Li ion cells	**Slot-die coat >20m electrodes and fabricate 2Ah format cells**	Complete
5	Cycle life demonstration - 500 at 100% DOD - 1000 at 80% DOD	200 – 300 cycles	500 cycles at 100% DOD (expecting)	On track

Step 1: Porous Si (Objectives 1 & 5)

Step 1: Porous Si Preparation (via metal reduction of silica)

Previous

- Initial raw material (Si)
- Metal Catalyst Deposition
- Hydrofluoric Acid Etching
- Neutralization/Rinse
- Filtration/Separation process

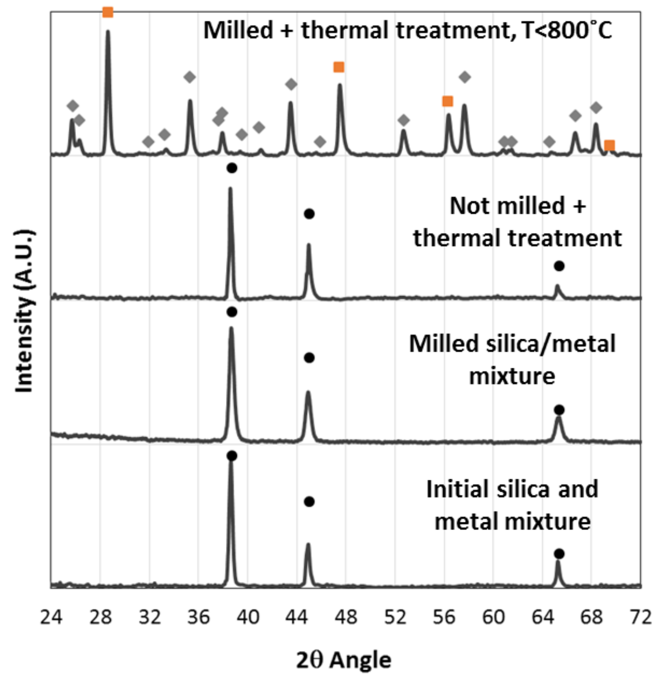
Cost $24/kg$_{porous\ Si}$

New

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

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

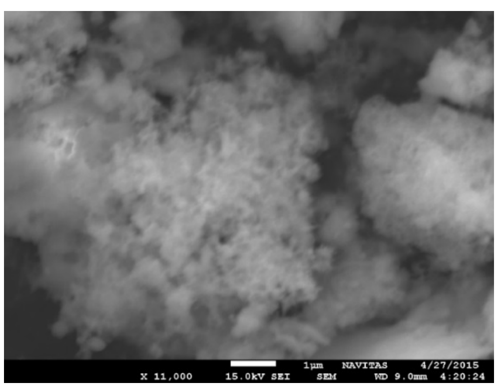
- Mechanical milling is an effective pretreatment to fully reduce Si oxide at low temperatures
- Fully reduction of silica at T < 800˚C, which otherwise requires T > 1000˚C



XRD of various samples

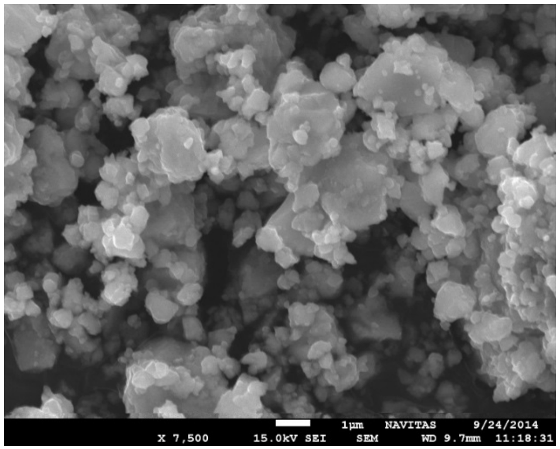
Thermal treatment was performed at the same conditions <800 ˚C

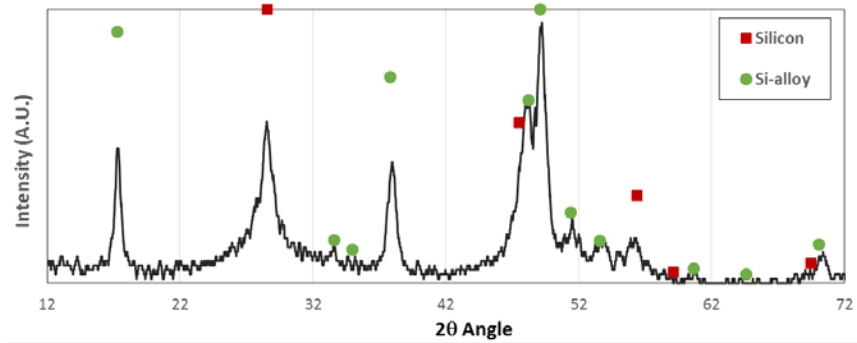
XRD patterns (●) reducing metal, (■) Si, (♦) metal oxide

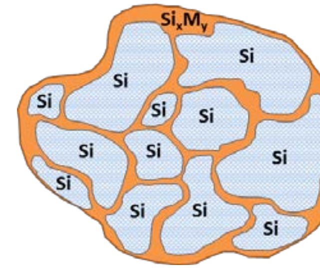


Step 2: Si / Alloy / Carbon Composite (Objectives 1, 2, & 5)

Step 2A: Si / Si_xM_y Alloy Composite

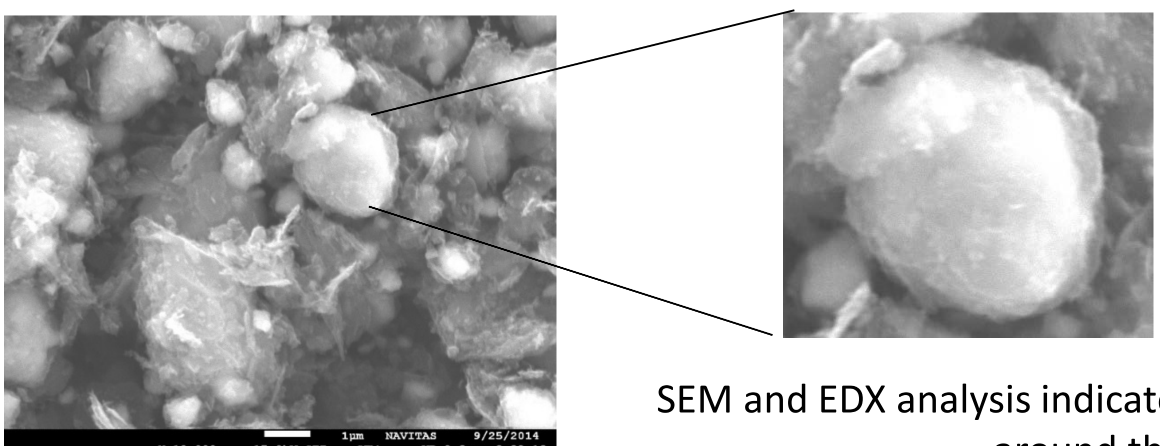


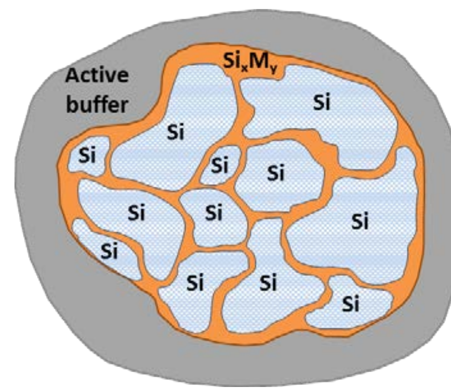




XRD pattern shows mixture of Si and Si-metal alloy

Step 2B: Si / Alloy /Carbon Composite

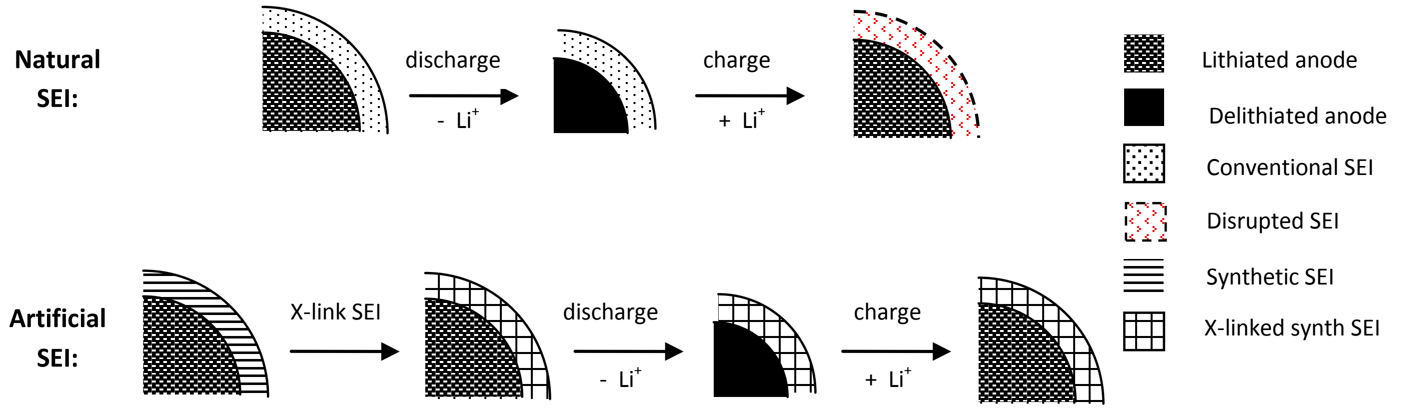


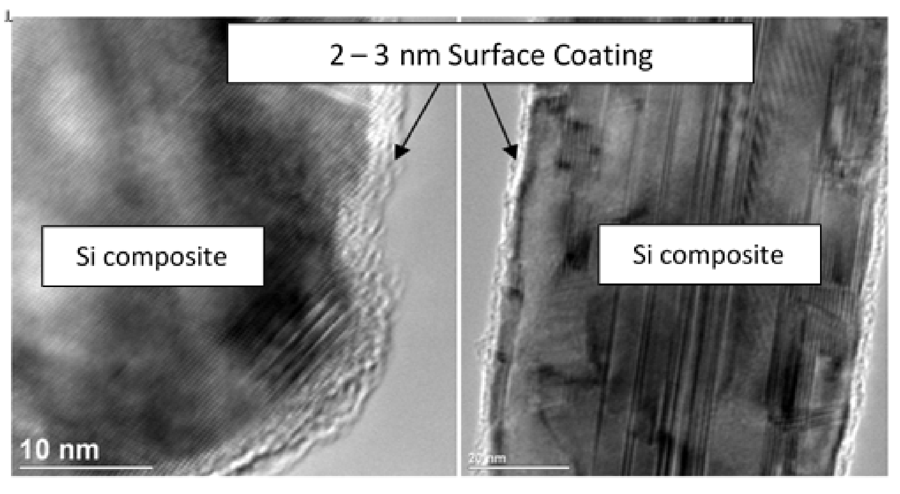


SEM and EDX analysis indicates active buffering coating around the Si /alloy matrix

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

- Step 3: surface modification – being developed for large scale material





Surface Treatment:

- Manage ICL
- Improve cycle life
- Improve anode slurry processability

Process Scale-up (Objectives 3)

Process	Phase I		Phase II	
	Equipment / Method	Batch Size	Equipment / Method	Batch Size
Porous Si Forming	HF etching	<20g	Mechano-thermal reduction	>500g
High energy ball milling	SPEX 8000 mill		Industrial ball mill	
Surface coating	Lab scale furnace		6” tube furnace and reactor	

500g batch milestone has been met

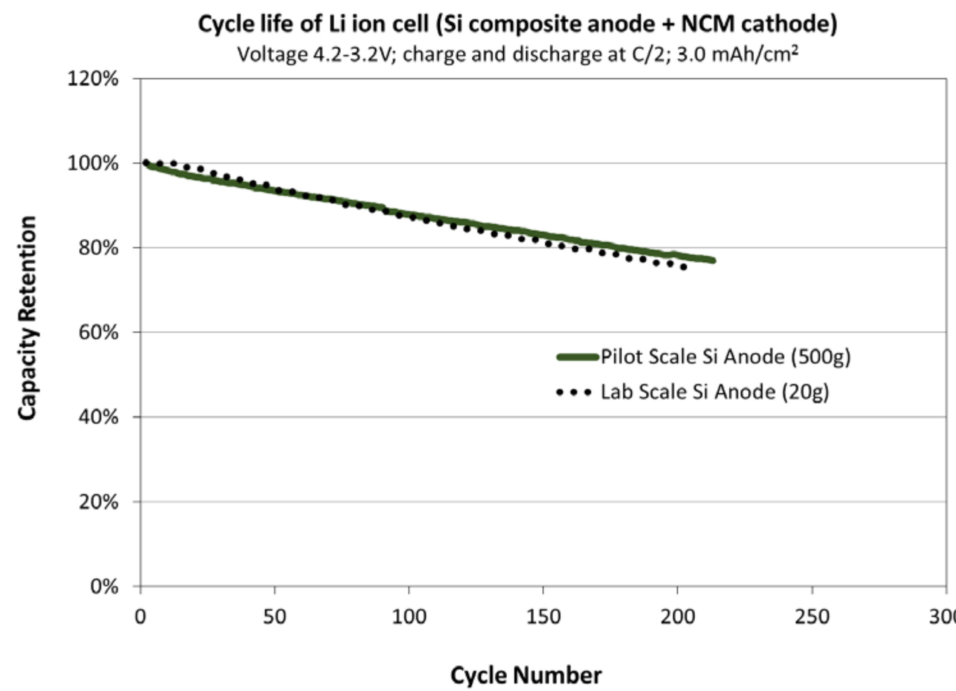
Industrial Mill

- Qualified the low cost process to form porous Si precursors
- Qualified the large scale equipments for ball milling and surface coating processes
- 500g batch sample has been produced and qualified with comparable performance as the 20g batch sample

6” Tube Furnace

Process Scale-up (Objectives 3)

- Electrode fabrication
  - Si Anode: 92% Si composite / 1.5% carbon black / 6.5% Li-PAA; porosity 35%
  - NCM Cathode: 93% NCM 523 / 3% carbon black / 4% PVDF; porosity 30%
  - Loading 3.0 mAh/cm^2 (reversible) and A/C = 1.1
- Cell assembly:
  - Single-layer-pouch cell (active area: 47 cm^2)
  - 20um PE separator and proprietary electrolyte
- Cycle life test :
  - 4.2 – 3.2V, +0.5C / -0.5C, room temperature



Anode	Capacity (mAh/g)	ICL of Composite	Tap Density of Composite (g/cm^3)
500 g batch	900 - 1000	11%	0.9
20 g batch	900 - 1000	11%	0.9

Pilot scale sample is comparable to the lab sample

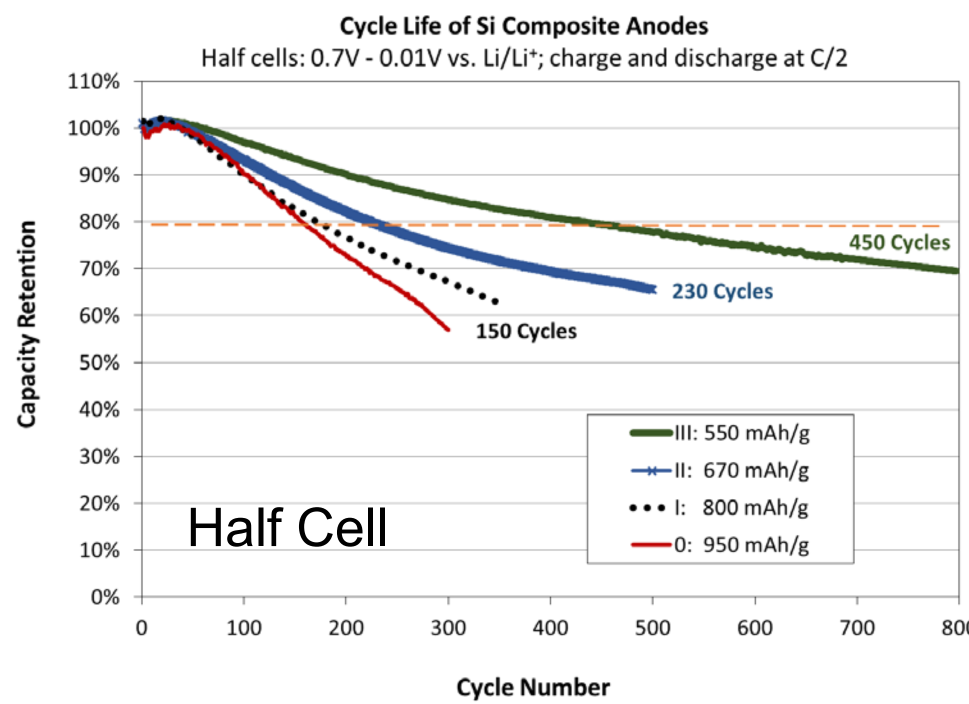
Towards High Energy Long Cycle Life (Objectives 5)

Balance of Energy and Life

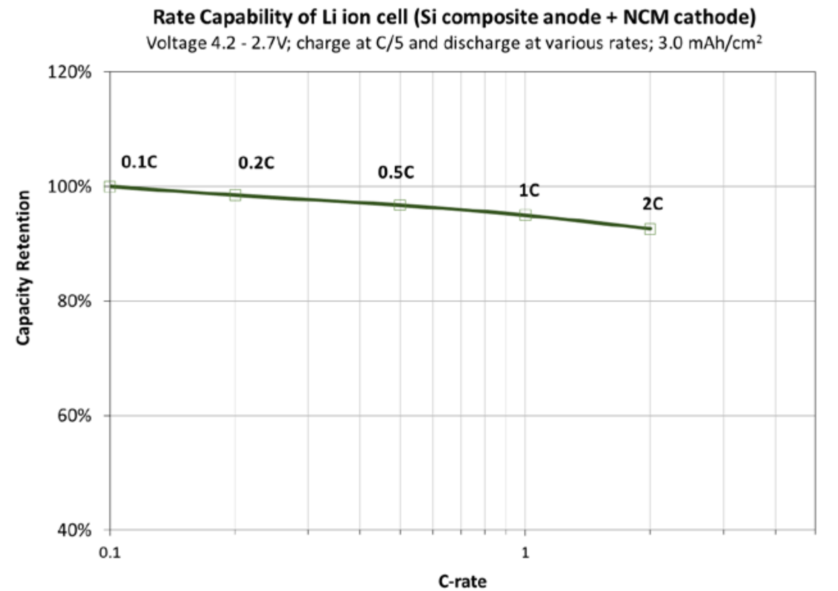
- Program goal:
  - 1000 cycle at 80% DOD (or 500 cycles at 100% DOD)
  - also a USABC goal for EV batteries
- Systematic optimization for performance improvement:
  - Material level: micro-structure, alloy protection, carbon buffering, surface treatment
  - Electrode level: active components, carbon, binder, slurry mixing, coating condition, electrode thick/porosity
  - Cell level: separator selection, cathode development, electrolyte development / optimization, cell design
  - System level: formation protocol, mechanical and thermal management

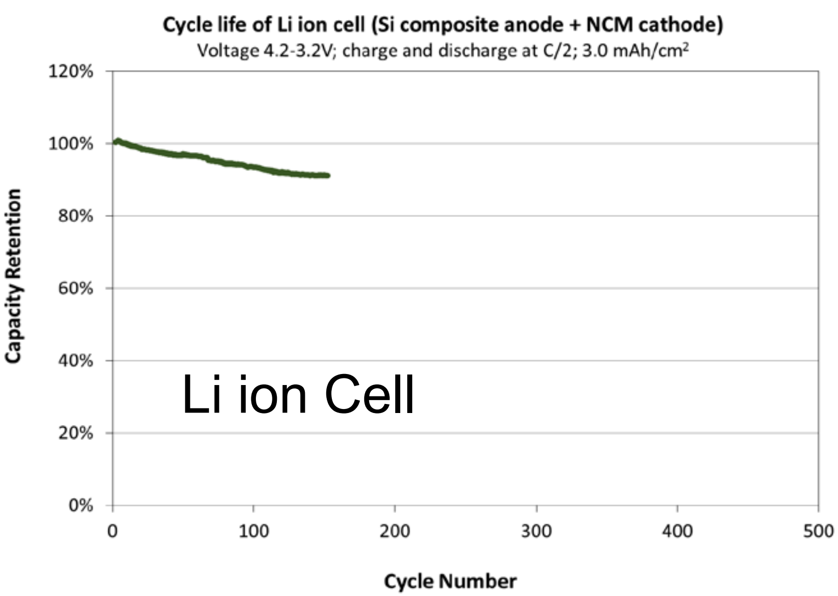
Conditions

- Si composite capacity (Grade)
  - "0" 950 mAh/g
  - "I" 800 mAh/g
  - "II" 675 mAh/g
  - "III" 550 mAh/g
- Si Anode
  - 92% active/ 1.5% carbon / 6.5% Li-PAA
  - Porosity 35%
- Cycle life test :
  - Li half cell
  - Voltage 0.7 – 0.01V vs Li/Li^+
  - Rate +0.5C / -0.5C



Towards High Energy Long Cycle Life (Objectives 5)



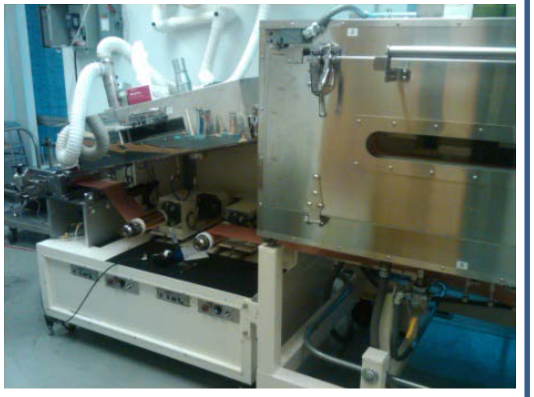


- Electrode fabrication
  - Si Anode: 92% Si composite / 1.5% carbon black / 6.5% Li-PAA; porosity 35%
  - Si composite capacity 800 mAh/g
  - NCM Cathode: 93% NCM 523 / 3% carbon black / 4% PVDF; porosity 30%
  - Loading 3.0 mAh/cm^2 and A/C = 1.1
- Cell assembly:
  - Single-layer-pouch cell (active area: 47 cm^2)
  - 20um PE separator and proprietary electrolyte
  - 300 Wh/kg if in EV format (cell level)
- Cycle life test :
  - 4.2 – 3.2V (85% DOD)
  - +0.5C / -0.5C

Cycle life of >500 is expected in a Li ion cell

Pilot Scale Coating and Prismatic Cell Fabrication (Objective 4)

Large-scale Powder Production



Slot-die Electrode Coating

Li-ion Cell Assembly

- Powder properties are similar to graphite
- Standard slurry mixing and electrode coating conditions
- Prismatic Li ion cells (>2Ah) assembly in May 2016
- Performance demonstration in August 2016

Responses to Reviewers' Comments

<table>
<tr><th>2015 AMR comments</th><th>Responses</th></tr>
<tr><td>Cost:
“HF may not be the best method use”
“the title contains low cost, but no information was found”</td><td>• We have developed a non-HF method to synthesize porous Si which is economically efficient and environmentally friendly (Slide 7)
• Low cost comes from both raw materials and processes (Slides 5, 8 – 11)
  ○ Micron-sized Si precursor <$2/kg
  ○ All the processes are industrially scalable
  ○ No expensive steps such as vapor deposition, nano fiber growth
• The cost model shows <$35/kg for the Si composite material</td></tr>
<tr><td>Cycle life
“using coin cells as proof is good, but need full cell data”
“the main focus of the future work has to be improving cycle life”
“4 mAh/cm^2 is a large coating, may need lower for EV”</td><td>• The coin cells are used as fast screening tools in the program. The materials are evaluated in full cells following the initial screening (Slides 11 – 13)
• Electrodes are coated with a roll-to-roll slot-die coater and large format full cells (2Ah) are assembled as the final delivery (Slide 14). Cycle life will be demonstrated in the large cells
• The electrode loading has been designed to 2.5 – 3.0 mAh/cm^2 for EV relevant cells</td></tr>
<tr><td>Collaboration
“project team also needs high-energy cathode collaboration”
“collaborating with other partners, particularly when it comes to the artificial SEI work”
“It is unclear how and if they (the partners) will support this project, or if they would be appropriate at this stage of development”</td><td>• For our internal high energy cell development, we have collaborated with several companies for high-energy cathode materials including Toda America, BASF and TIAX
• We are working with ANL to characterize the anode (SEI) structures and will improve the structure by consulting the partner
• When qualified large scale process, we plan to send the needed powder (typically >2kg) to A123 Systems to coat anode in its pilot coating line and assemble/test prototype Li ion cells in its development facility
(Slide 16)</td></tr>
</table>

Collaborations

- Navitas 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
  - a funded subcontractor
- We are working with Argonne Nation Laboratory (ANL) to characterize the anode structures and cost modeling
  - partner (special test and modeling)
- For our internal high energy cell development, we have collaborated with several companies for high-energy cathode materials including Toda America, BASF and TIAX; anode powder also is scheduled to ship to TIAX (in April 2016) to match its high energy cathode.
  - funded by Navitas
- When qualified large scale process in May, we plan to send the needed powder (typically >2kg) to A123 Systems to coat anode in its pilot coating line and assemble/test prototype Li ion cells in its development facility.
  - in-kind

Remaining Challenges and Barriers

- Scale up the process beyond 500g batch
  - 500g batch process has been developed and qualified
  - Next level production capability is needed (e.g., metric tons)
    - Establishing cost modeling based on raw materials and processes
    - Seeking industrial partners for collaborations (licensing, JD)
- Achieve a cycle life of 1000
  - Need to demonstrate the cycle life in the newly assembled large format prismatic cells in addition to the lab scale cells
- Identify advantages and potential limitations of the new Si material and the high energy batteries based on such
  - Dimensional and thermal stability
  - Abuse tolerance
  - Other applications by balancing energy and cycle life
    - Consumer electronics
    - Specialty military devices

Proposed Future Work

Under the program

- Demonstrate cycle life in a large format (>2 Ah) prismatic cells as a final delivery
- Conduct critical performance evaluations on the cells:
  - Dimensional stability (swelling, gassing) during cycling
  - High temperature storage
  - Abuse tolerance (e.g., over-charge, over-discharge, short-circuit, and nail-penetration)
- Establish cost model for the Si material
  - DOE BatCap cost model
- Complete the program and submit final report

Internal investment

- Provide anode powder and/or coated anode to potential partners for external evaluation
- Identify 2 – 3 key industrial partners to commercialize the material - licensing / JD
- Evaluate the anode applications in other areas than EV
  - Consumer electronics
  - Military specialty devices
- Continue to improve the performance / lower the price
  - Evaluating / selecting advanced electrolytes (cycle life, high temperature, safety) and advanced cathode
  - Qualifying lower cost raw materials and processes

Summary

Relevance

Produce a practical and economical high capacity silicon-based anode material for lithium ion batteries

- >800 mAh/g and <$35/kg
- Scale up to at least 500g/batch
- Fabricate >2 Ah lithium ion cell
- Achieve Si-composite anode cycle life >1000 at 80% DOD

Approach

Develop a low lost micron-sized Si material by combination of microstructure design and surface modification

- Porous Si core: accommodates the volume change during Si cycling
- Protection shell: limits surface Si volume change and keeps the large volume change within the Si core
- Surface coating: reduces ICL and improves the cycle life

Technical Accomplishments

- Developed a high energy and low cost Si composite anode of >800 mAh/g and <$35/kg
- Scaled up the powder production to >500g /batch; all the processes are industrially scalable
- Fabricated electrode coating in pilot scale coater and assembled large format Li ion cells at 2Ah
- Demonstrated long cycle life in Li ion cells and large cell demonstration in on going

Future Work

- Demonstrate cycle life in 2Ah cells
- Conduct cost analysis
- Submit final report
- Identify potential market areas and commercialization partners