ADVANCED BINDER FOR ELECTRODE MATERIALS

Gao Liu

Lawrence Berkeley National Laboratory
Berkeley, CA 94720
May 12th, 2011

Project ID: ES090

Overview

Timeline

Project started: FY 2010
Project end date: FY 2012
Percent complete: 40%

Budget

Total project funding
-DOE share: $1,350K, 100%
FY10 funding $450K
FY11 funding $450K
FY12 funding requested $450K

Barriers Addressed

Performance: Low energy density and poor cycle life
Life: Poor calendar life
Cost: High manufacture cost
(Research in high energy system)

Partners

LBNL (PI. Vince Battaglia, Venkat Srinivasan, Robert Kostecki, Jordi Carbana-Jimenez, Wanli Yang, Zhi Liu, Andrew Minor, Lin-Wang Wang)
Hydro Quebec
Applied Materials
FMC Lithium
Bosch Inc.
Silatronix Inc.
A lead battery manufacturer

Relevance – Project Objective

Develop new conductive polymer binder materials and improve binder/Si interface to enable Si alloy in lithium-ion negative electrode.

Si has the highest lithium-ion storage capacity at 4200 mAh/g. However, three major issues prevent Si material from being used as a negative electrode material in lithium-ion cells.
•Limited cycle life of Si material (Performance barrier)
•Limited energy density (Performance barrier)
•Low coulombic efficiency (Performance and Life barrier)

The goal of this research project is to develop negative electrode binder materials, which improve the following performance criteria of the Si-based electrode.
•Cycle and life stability
•Electrode active material loading to increase energy density
•Compatibility with current lithium-ion manufacturing process
•Cost and commercial availability

Milestones

We have developed one class of conductive polymers in FY09.

This class of conductive polymers is very effective both as a binder and conductive matrix. We studied this class of conductive polymers for Si negative electrode applications in FY 2010. Four milestones were accomplished.

1. Mapped out the doping process for the Si/conductive polymer in the composite electrode. (**FY2010**)
2. Characterized the conductivity of the conductive polymer binders. (**FY2010**)
3. Compensated for the first cycle irreversible capacity of the Si electrode. (**FY2010**)
4. Fabricated and tested lithium-ion cells based on the Si electrode. (**FY2010**)

Milestones

Three milestones are defined for FY 2011

1. Area specific capacity- Study conductive binder properties to Si electrode performance in various electrode compositions and configurations, aim to achieve 3.5 mAh/cm^2 loading electrode. (March 2011) (On Schedule)

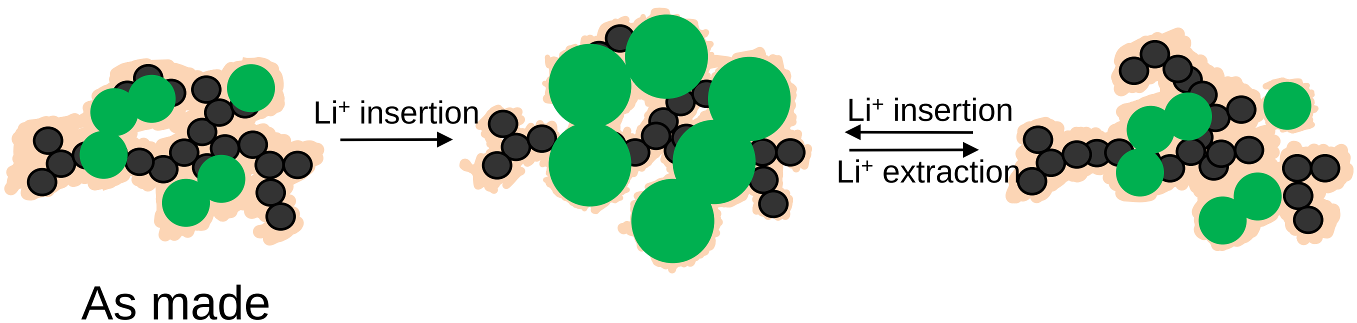
1. Si/binder interface properties- Introduce binder functionalities to stabilized Si surface, minimize side reactions, and increase coulomb efficiency, aim to increase cycling efficiency from current 99% to 99.5%. (Sept. 2011) (On schedule)

2. Cross-cutting- Investigate the effectiveness of the conductive binders in other high capacity material systems. (Sept. 2011) (On schedule)

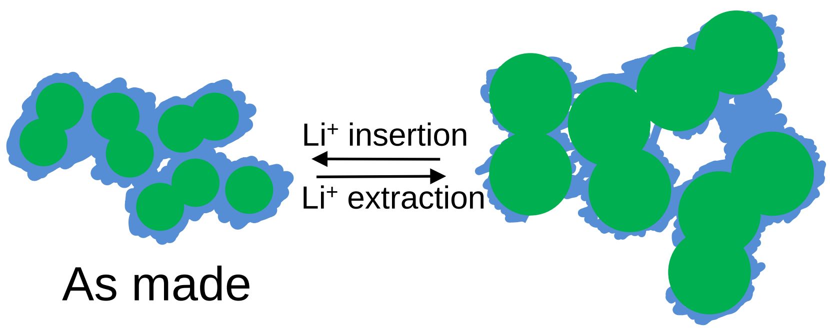
Approach - Conductive Polymer Binder for Large Volume Change Si Materials

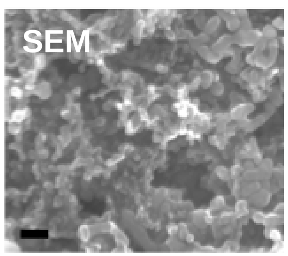
Schematic of electrode nanoscale structure

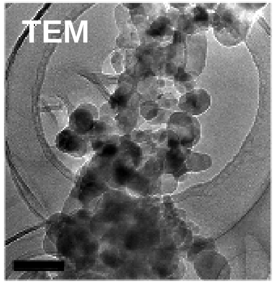
Non-conductive binder



Conductive binder







Scale bars 100 nm

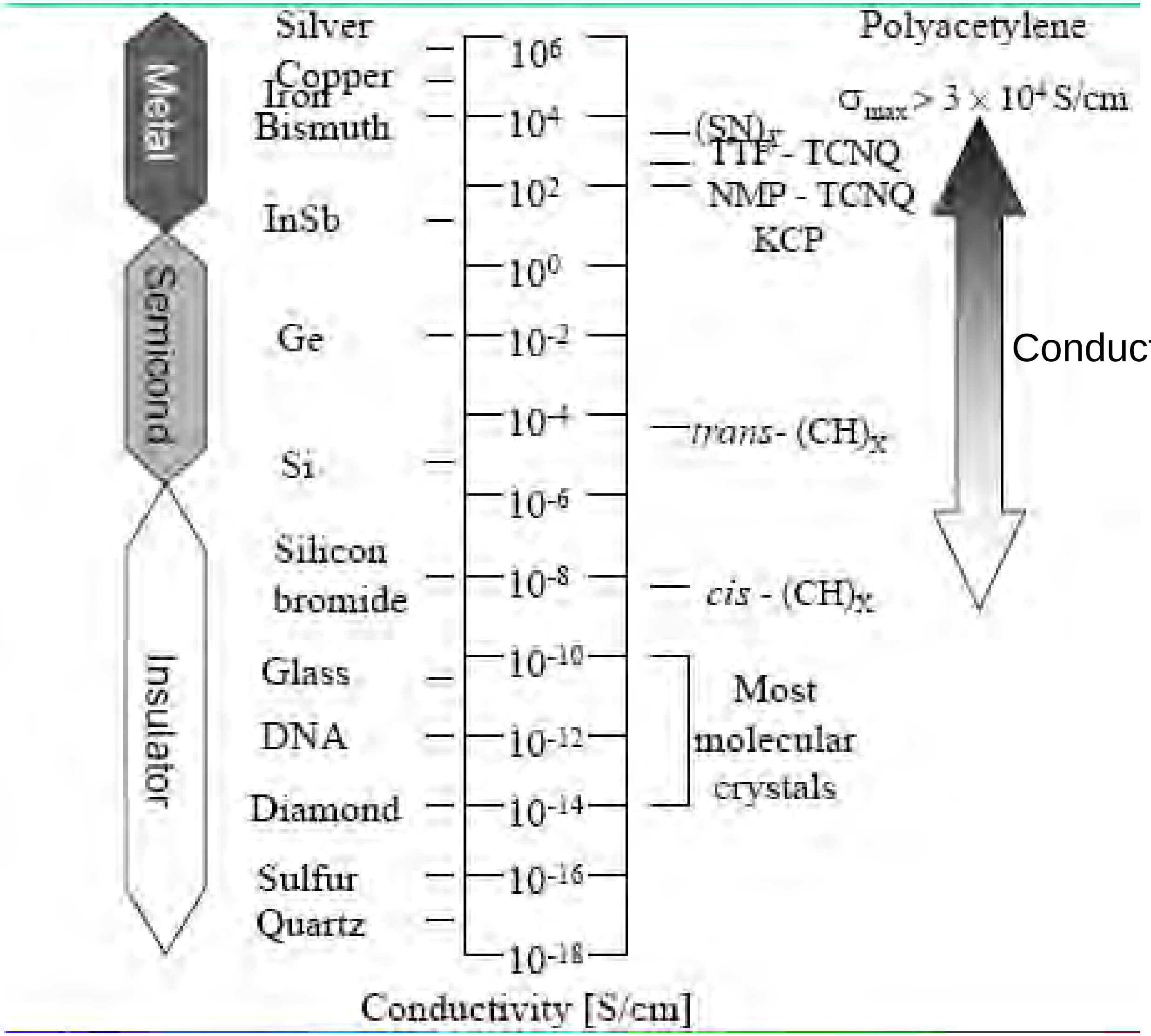
- Non-conductive binder
- Conductive binder
- Alloy particles
- Acetylene conductive (AB) additive

Advantages

•Commercial Si nanoparticles is available.

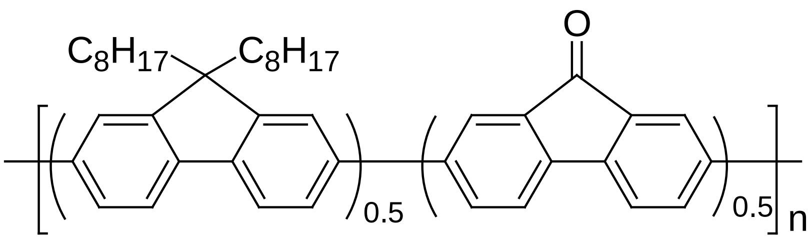
•Fully compatible with conventional lithium-ion technologies.

Approach - Conductivities of Materials

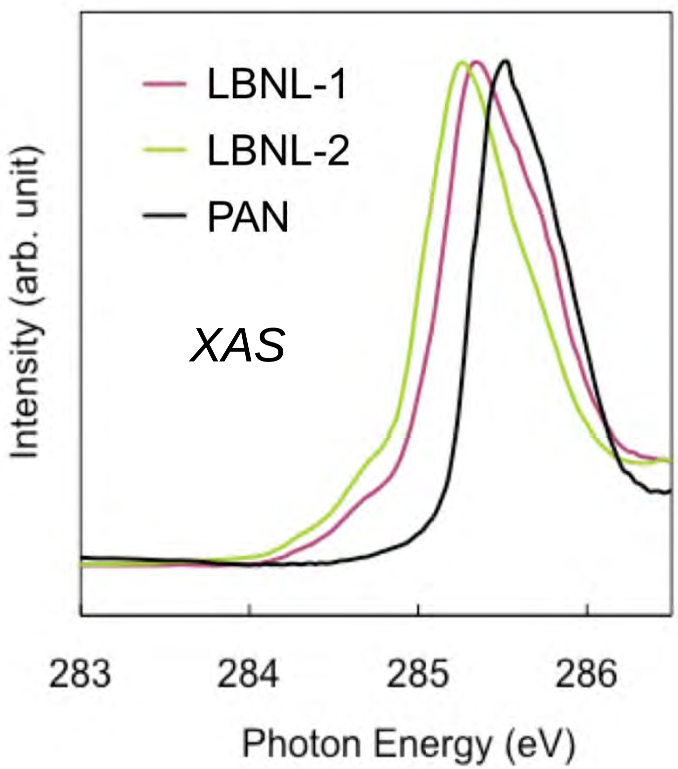


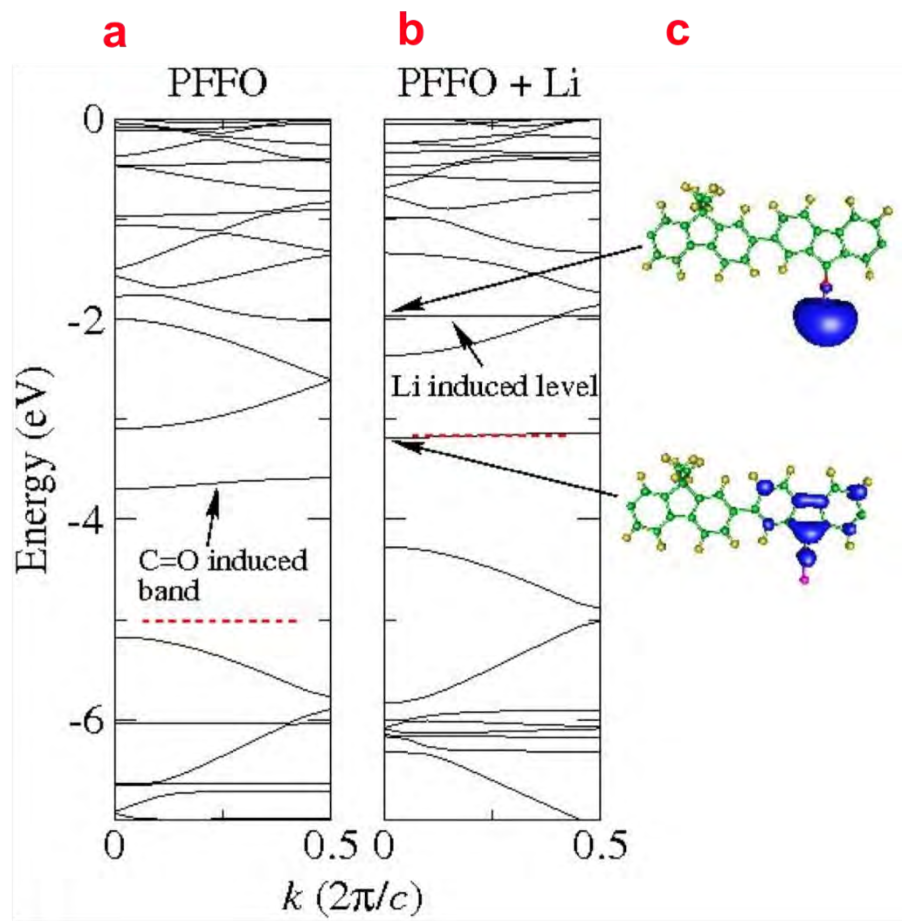
Conductive polymers

Accomplishments - Conductive Polymer Design Based on XAS and Calculation

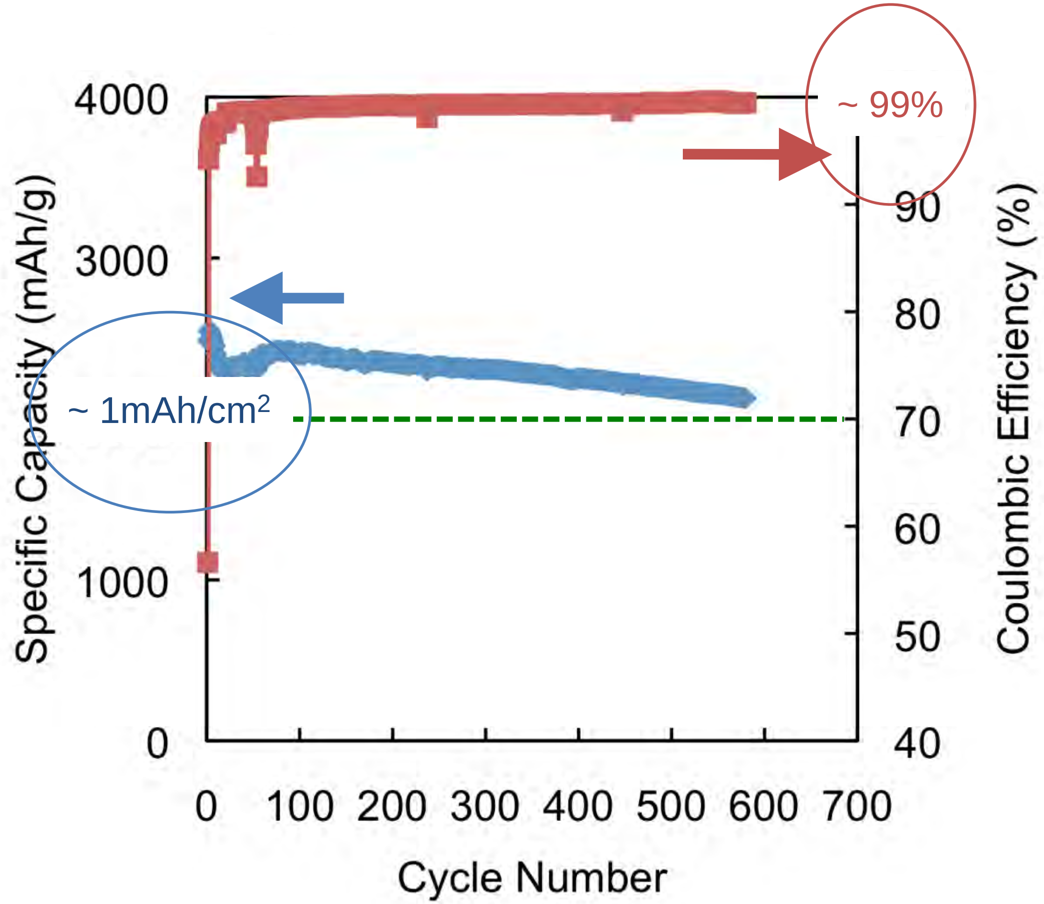


PFFO (LBNL-1)





Accomplishments - Cycling performance comparison among different approaches

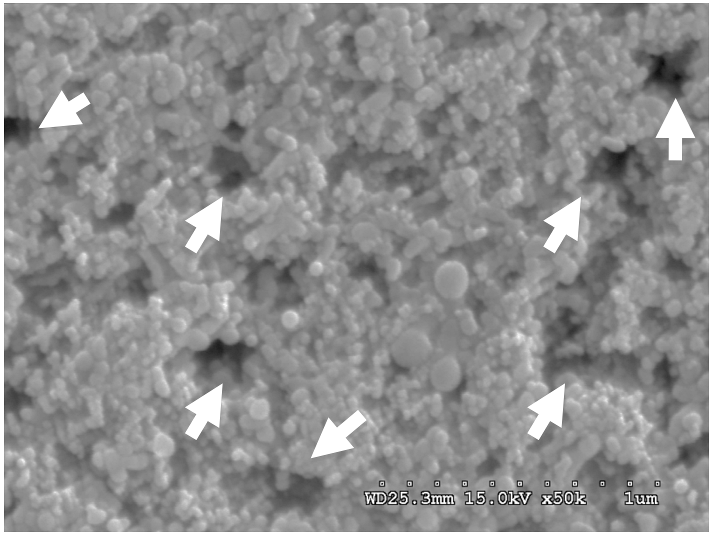


Electrode composition by weight
Si 67%, LBNL-2 binder 33%
No conductive additives
Deep cycling 1V-0.01V

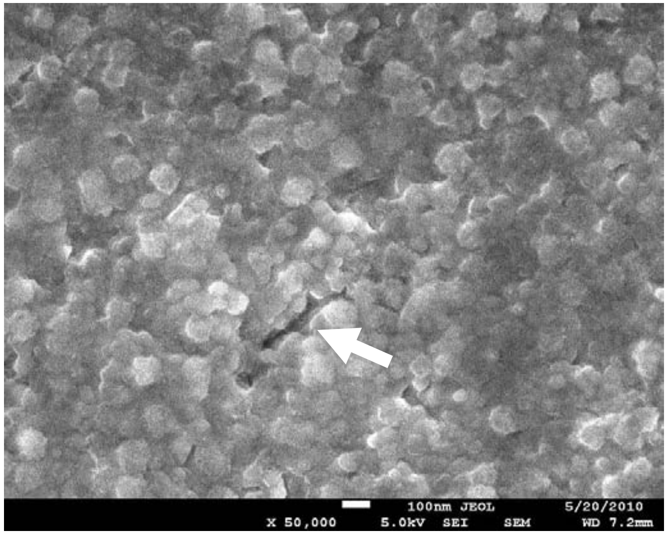
Accomplishments - Understand the limitations

SEM of the Electrode Surfaces

Fresh Before Cycling



After the 1st Cycle



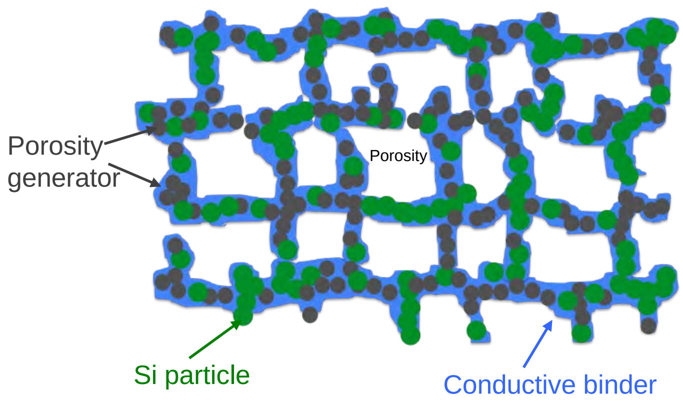
Scale bar ▬ 300 nm

The electrode porosity has visibly decreased due to the formation of side reaction products. The shrinking porosity limits Li ion transport to the Si particle. This effect is worsen at higher electrode loading.

Accomplishments - Improve electrode porosity to improve electrode loading

Porosity generator particles provide additional porosity while maintaining electronic conductivity with conductive binder.

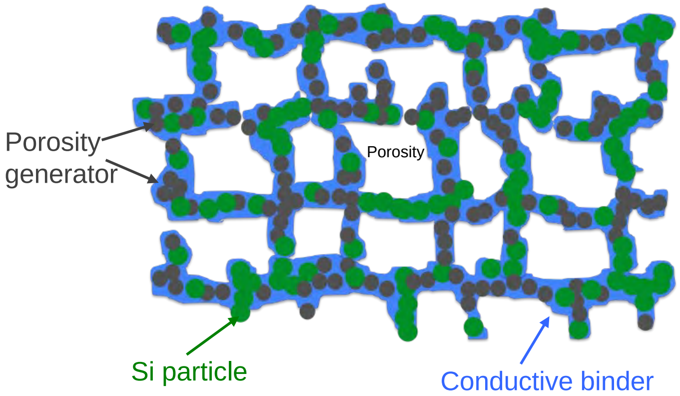
Schematic of the high porosity electrode

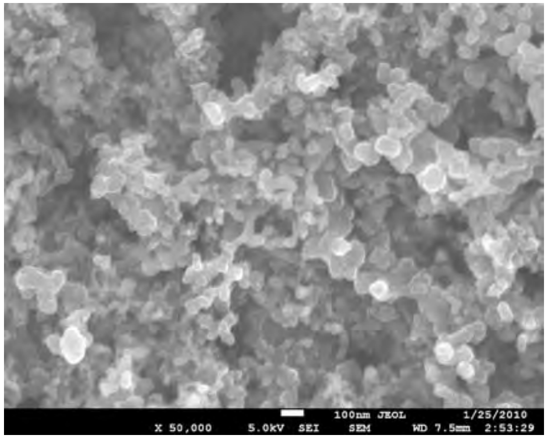


Accomplishments - Improve electrode porosity to improve electrode loading

Porosity generator particles provide additional porosity while maintaining electronic conductivity with conductive binder.

Schematic of the high porosity electrode



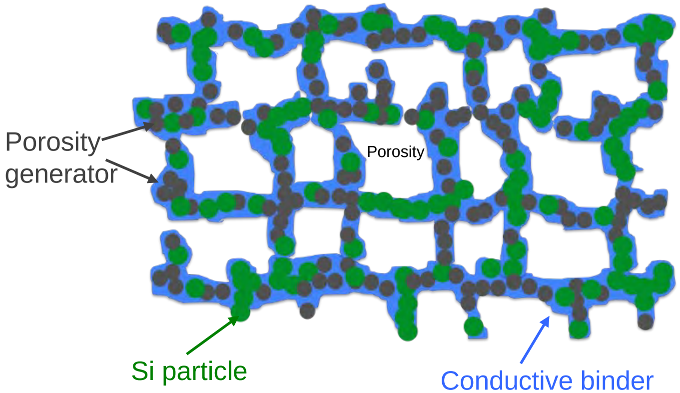


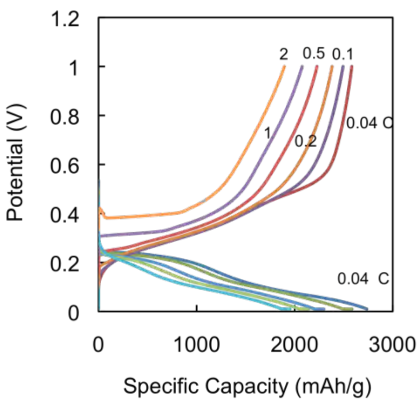
70% Porosity Si electrode

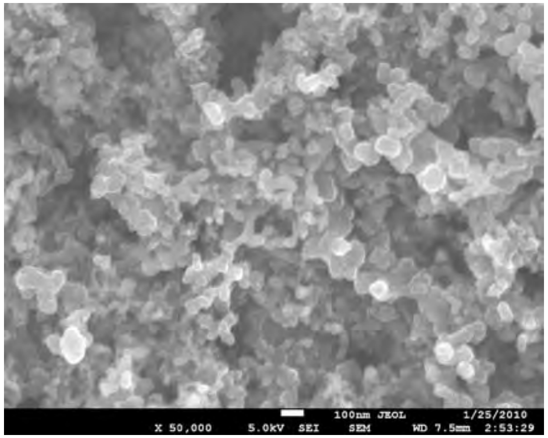
Accomplishments - Improve electrode porosity to improve electrode loading

Porosity generator particles provide additional porosity while maintaining electronic conductivity with conductive binder.

Schematic of the high porosity electrode







Scale bar

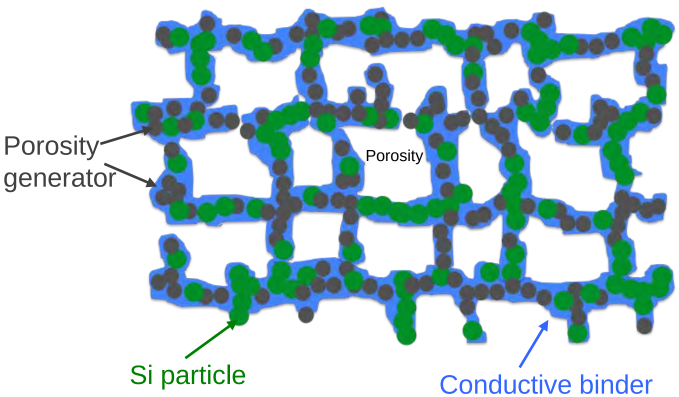
200 nm

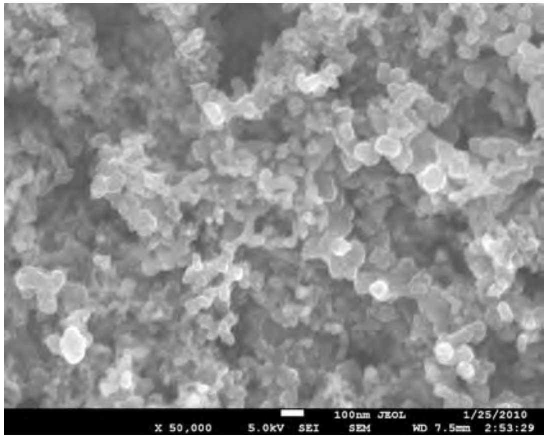
70% Porosity Si electrode

Accomplishments - Improve electrode porosity to improve electrode loading

Porosity generator particles provide additional porosity while maintaining electronic conductivity with conductive binder.

Schematic of the high porosity electrode



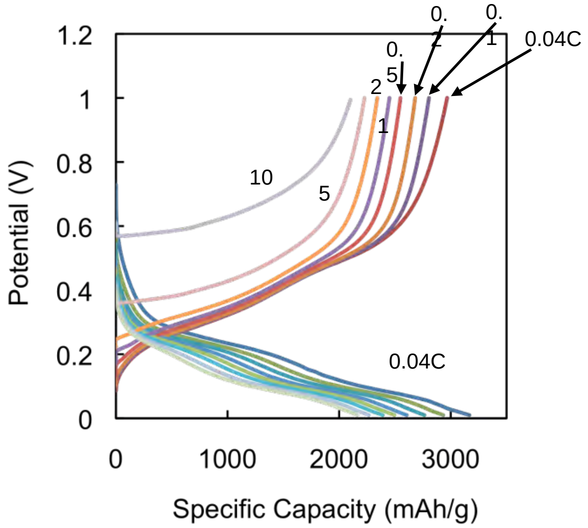


Scale bar

200 nm

70% Porosity Si electrode

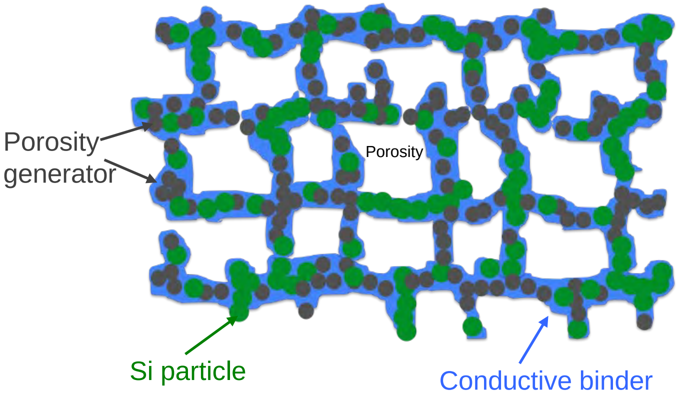
Rate performance improves with porosity

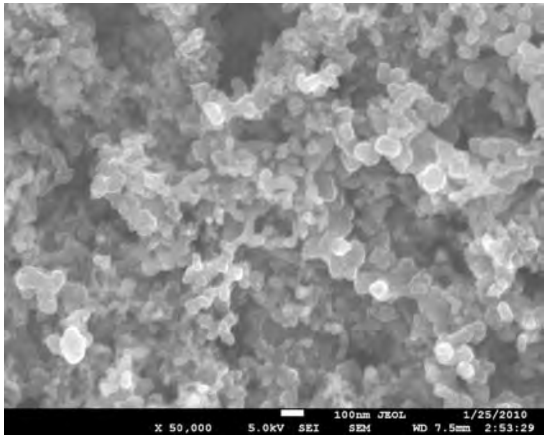


Accomplishments - Improve electrode porosity to improve electrode loading

Porosity generator particles provide additional porosity while maintaining electronic conductivity with conductive binder.

Schematic of the high porosity electrode



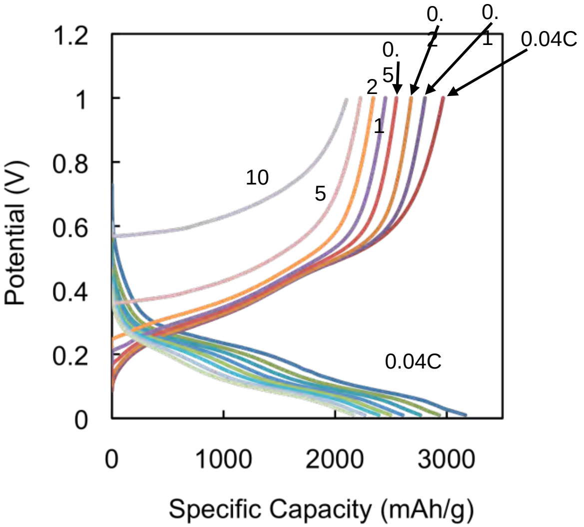


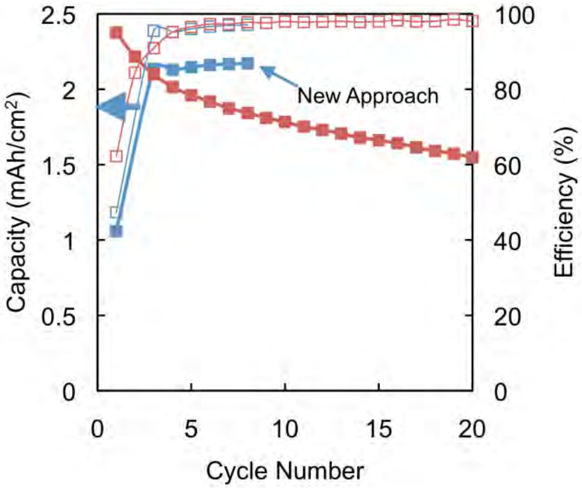
Scale bar

200 nm

70% Porosity Si electrode

Rate performance improves with porosity





Improved cycling stability at higher loading

Critical Assumptions and Issues (From the last review)

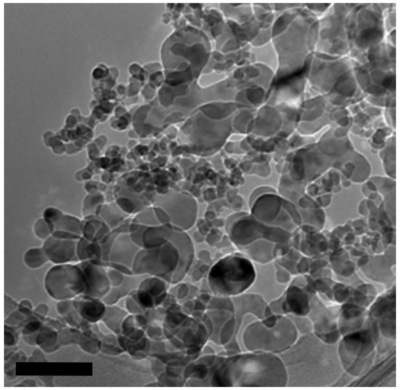
Commercial Sources of Si Nanoparticles

It is the advantage of this project to use commercial sources of unmodified Si nanoparticles to fabricate electrode. However, we are experiencing the lack of quality control over the commercial particles. The particle size distribution varies from one batch to another.

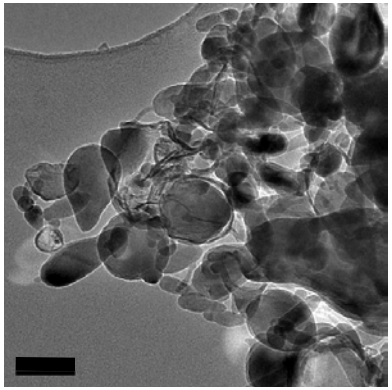
It is possible that we will report different performances with different sources of the Si nanoparticles in the further. However, we will try to point out the different between each batch of Si from the commercial sources.

Accomplishments - Commercial Si nanoparticals

Supplier 1- 100 nm Si particles

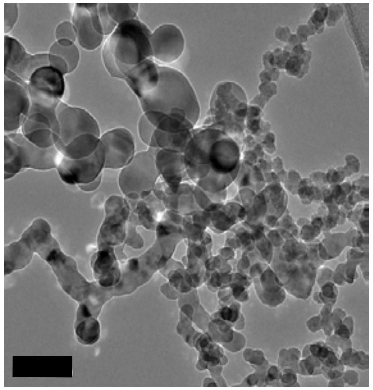


Batch 1

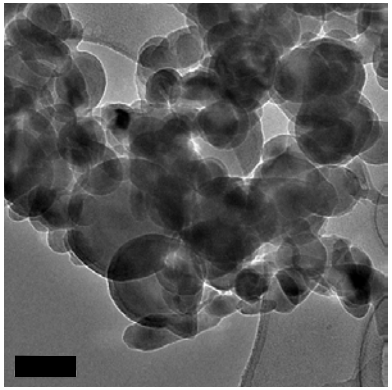


Batch 2

Supplier 2



20-30 nm diameter sample



50 nm diameter sample

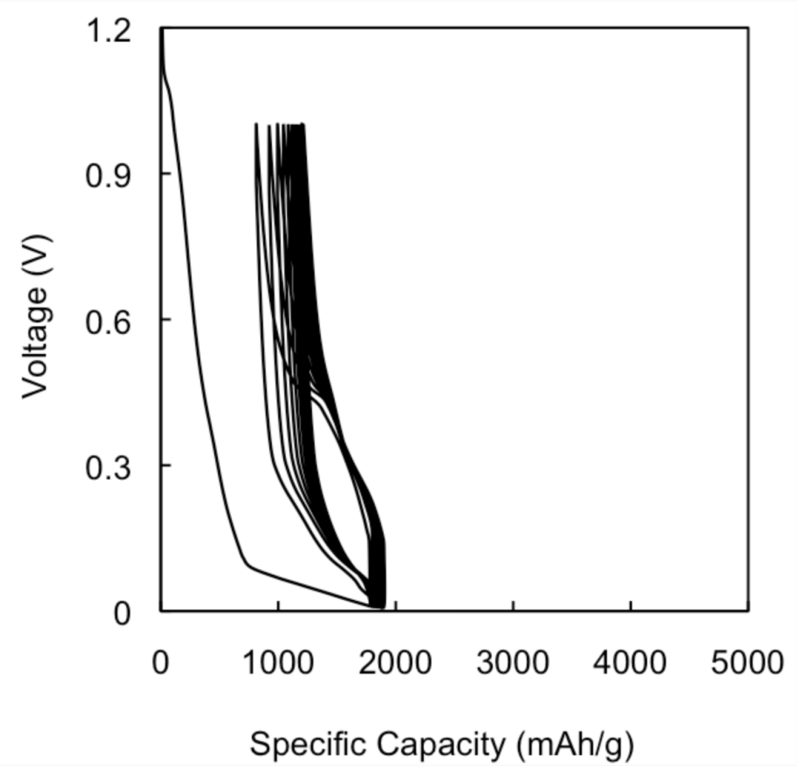
Available product types

20-30 nm diameter
30-50 nm
50 nm
50-70 nm
100 nm

Scale bar
100 nm

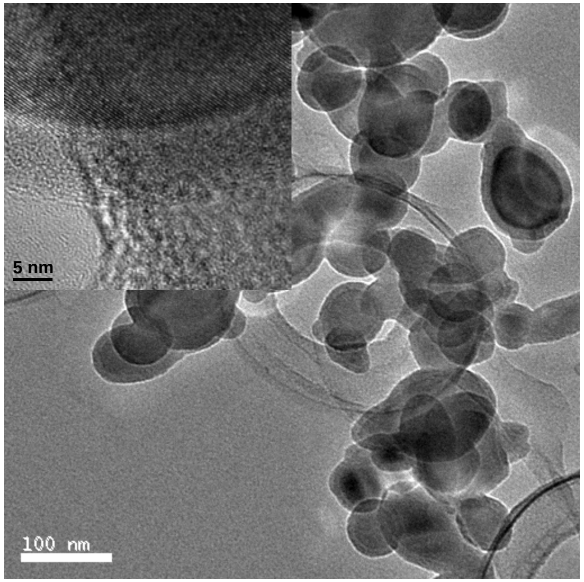
Accomplishments - 50 nm diameter Si sample initial cycling performance

Initial Cycling Performance



Limited cycling capacity

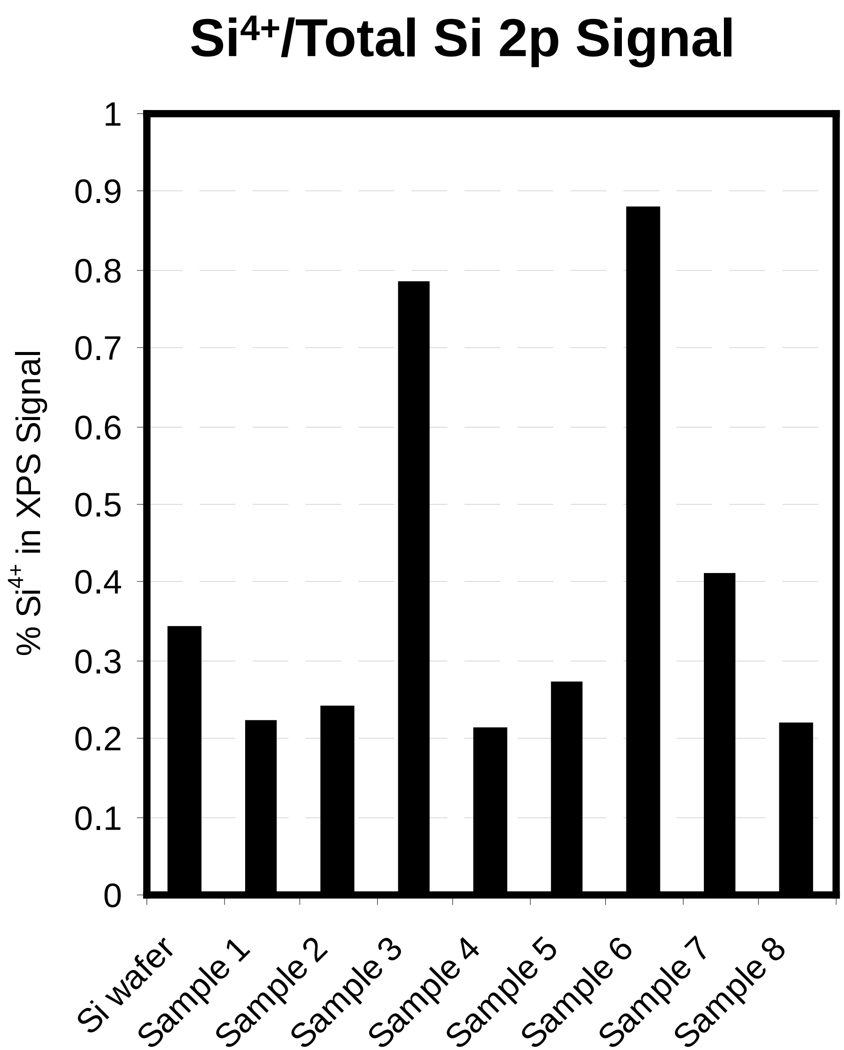
TEM Image of the Particles

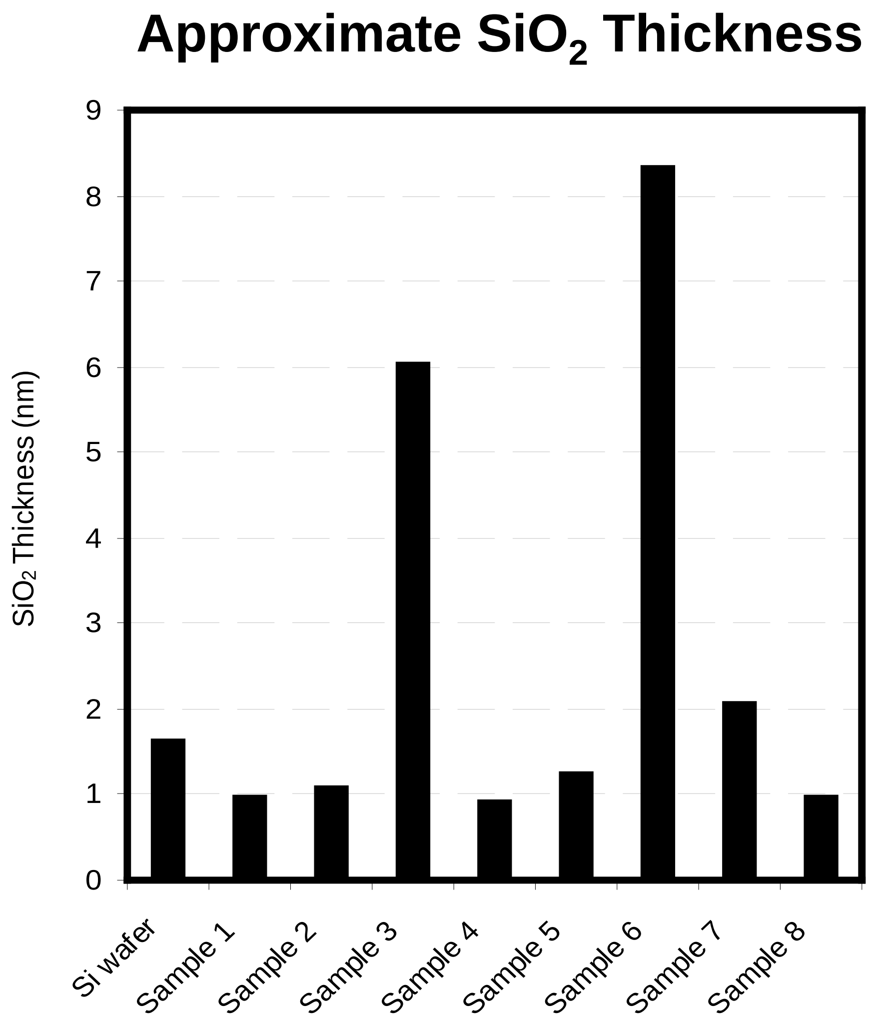


Commercial nano Si sample. Supplier claims 99% purity. Observed core-shell structure from TEM analysis.

Note: Electrodes were made of Si/AB/PVDF at 1:2:1 weigh ratio.

Accomplishments - SiO_2 content of the commercial samples based on XPS analysis





Accomplishments - Process to reduce surface SiO_2

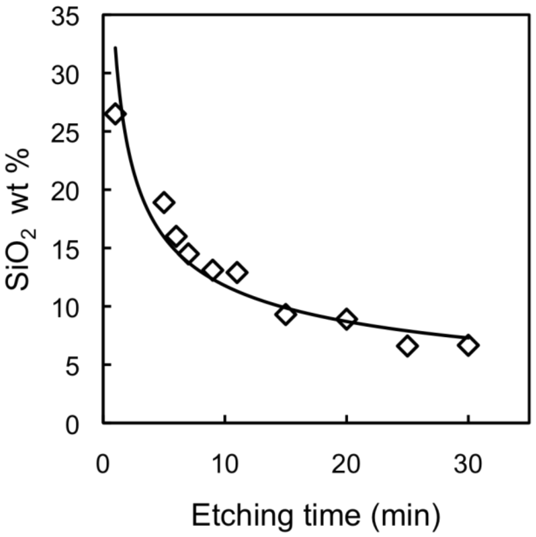
25 parts (volume) 1 part HF (49%) to make 2% HF solution.

Two spatulas of Si nanopowder were put in a 50 ml centrifuge tube, 15 mL of 2% HF was added, and then sonicated for a period of time.

After sonication, 25 mL of ethanol was added to dilute HF solution and then centrifuge, decant the supernatant. Repeat this process for 5 times.

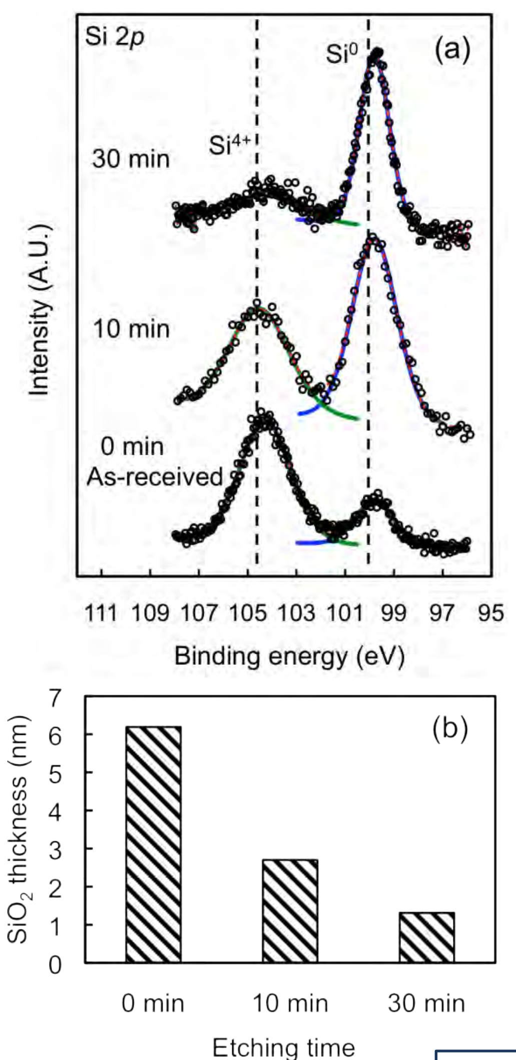
Dry etched Si powder under vacuum at room temperature overnight and dry at 130 C for 16 hrs.

SiO_2 Content

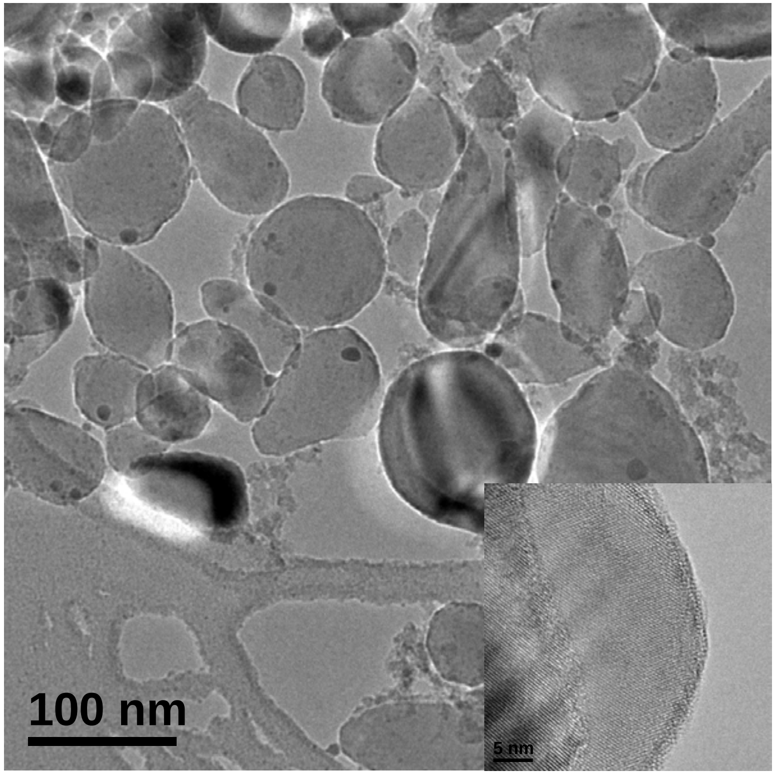


Accomplishments - Effectiveness of SiO_2 removal process

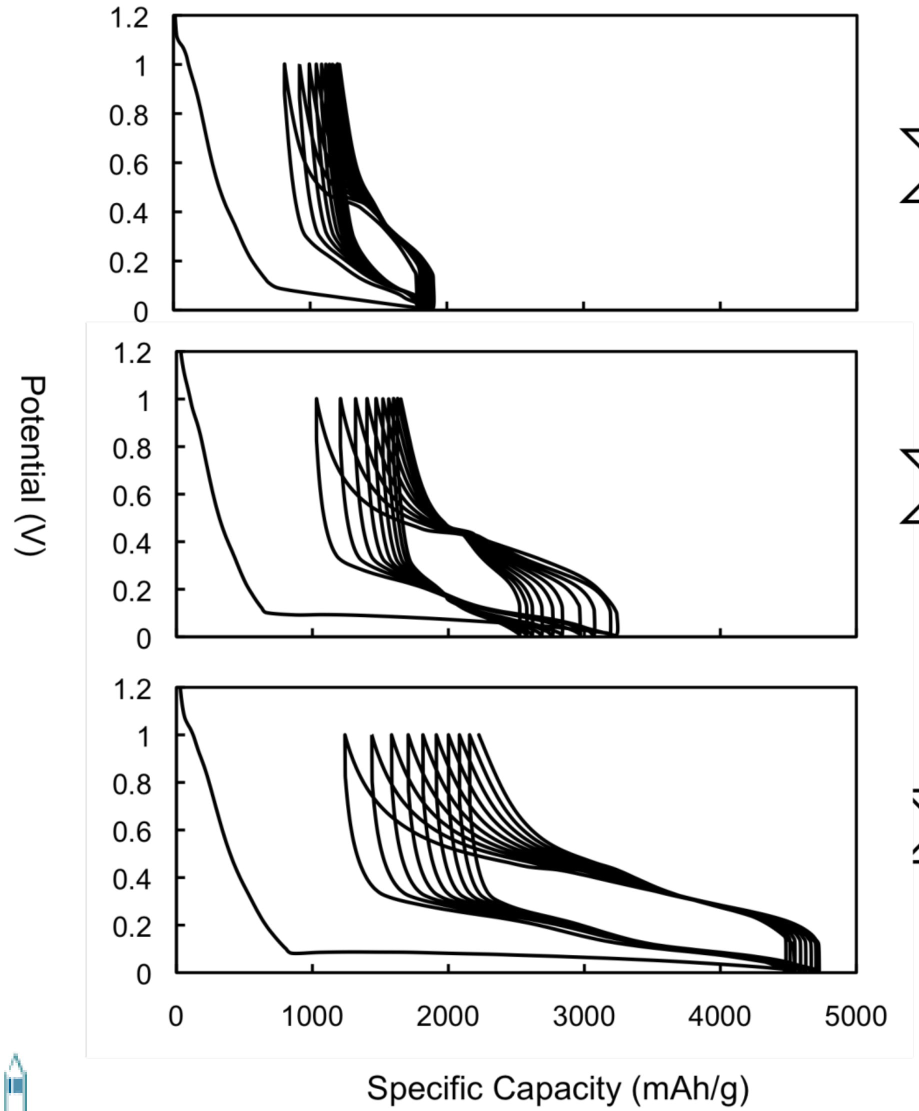
XPS measurements



TEM of Si sample after 30 minutes HF cleaning



Accomplishments - Initial cycling performance before and after SiO_2 removal



Si without etching

1st efficiency: **54.4 %**
1st delithiation: **967 mAh/g**

Si after 10 min etching

1st efficiency: **68.2 %**
1st delithiation: **1509 mAh/g**

Si after 30 min etching

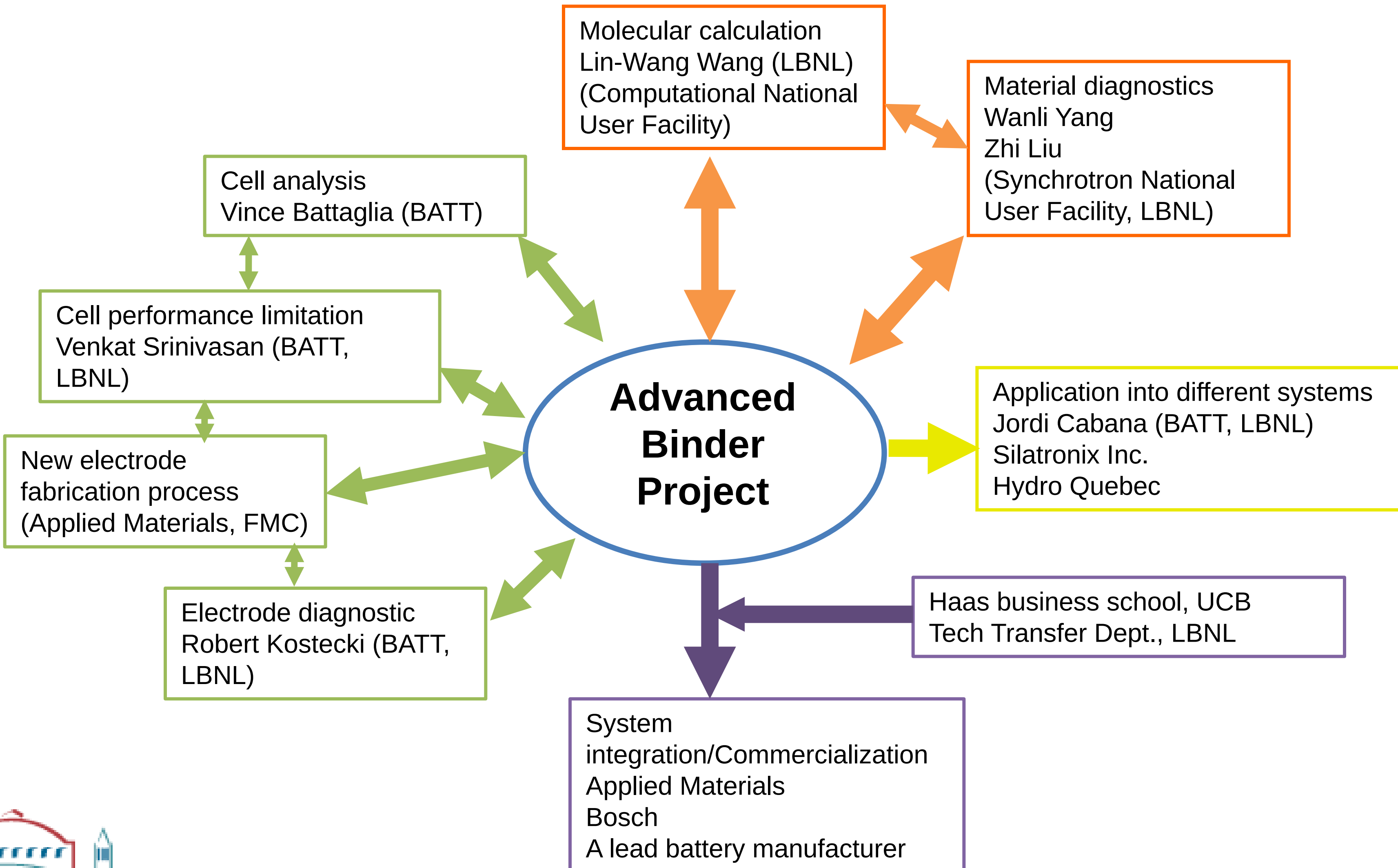
1st efficiency: **72.8 %**
1st delithiation: **3280 mAh/g**

Note: Electrodes were made of Si/AB/PVDF at 1:2:1 weigh ratio.

Collaborations

PI	Institution	Details	Directions
Vince Battaglia (VT)	LBNL/BATT	Materials, electrodes, and cell level performance analysis	Knowledge accumulation
Venkat Srinivasan (VT)	LBNL/BATT	Modeling of Si/conductive polymer electrode	Knowledge accumulation
Robert Kostecki (VT)	LBNL/BATT	Raman analysis of the electrode	Knowledge accumulation
Jordi Cabana (VT)	LBNL	Binder for other alloys	Application into different systems
Wanli Yang	LBNL/ALS	X-ray analysis of the polymer band gaps	Knowledge accumulation
Zhi Liu	LBNL/ALS/XPS	XPS analysis of Si	Knowledge accumulation
Phil Ross	LBNL retiree	Electrochemical diagnostic	Knowledge accumulation
Lin-Wang Wang	LBNL	Calculation of conductive polymer energy levels	Knowledge accumulation
Karim Zaghib (VT)	Hydro Quebec	Test the binder in metal oxide system	Application into different systems
Connie Wang	Applied Materials	New electrode fabrication process	Commercialization
Marina Yakovleva	FMC Lithium	Additives for electrode	Knowledge accumulation
Jake Christensen	Bosch Inc.	New high energy lithium-ion system	Commercialization
Robert Hamers	Silatronix/U. Wisconsin	Electrolyte for Si materials	Knowledge accumulation
Subject to NDA	A lead battery manufacturer	Binder testing	Commercialization
C2M program	Haas Business School, UCB	Si nanoparticle market analysis	Commercialization

Collaborations



Proposed Future Work

1. We are on schedule to accomplish the milestones defined in the remaining FY2011 year.

2. For the FY 2012, we propose to investigate in the following areas.

   a. Develop new binder functionalities to further improve capacity retention during cycling.
   b. Develop electrode structures that has high Si material loading, aim to achieve 5 mAh/cm^2 to meet the EV/PHEV energy density goals.
   c. Investigate binder/Si interface, and develop practical strategies to further improve Si surface stability to increase coulombic efficiency.

Summary

1. Demonstrated high specific capacity cycling (>2000 mAh/g-Si) of Si materials using electronic conductive binders in a coin cell with Li counter electrode. ***The electrode does not contain other conductivity additives.***
2. Demonstrated limited porosity is a major issue for high Si electrode loading and rate performance.
3. Demonstrated initial success to generate higher loading electrode by network electrode design.
4. Demonstrated SiO_2 as a major impurity in commercial particles and developed an effective method for its removal.
5. Demonstrated significantly improved commercial Si performance by surface oxide removal process.