

ADVANCED BINDER FOR ELECTRODE MATERIALS



Gao Liu

Lawrence Berkeley National Laboratory
Berkeley, CA 94720
June 8th, 2010

Project ID: ES090

Overview

Timeline

Project started: FY 2009.

Project end date: FY 2012.

Percent complete: 35%.

Budget

FY09 funding \$300K.

FY10 funding \$450K.

Up-to-date spending \$520K

FY11 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 Kostecky,

Wangli Yang, Lin-Wang Wang)

Hydro Quebec (PI. Karim Zaghreb)

Applied Materials

Bosch Inc.



Relevance – Project Objective

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

Si has the highest lithium ion stage 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.

- Cycling and life stability.
- Loading in the electrode to increase energy density.
- Compatibility with current lithium-ion manufacturing process.



Milestones

We have developed one type of conductive polymer in FY09.

This conductive polymer is very effective as both binder and conductive matrix. The milestones in FY10 are to optimize this conductive polymer for Si negative electrode applications. Four milestones were defined for this year.

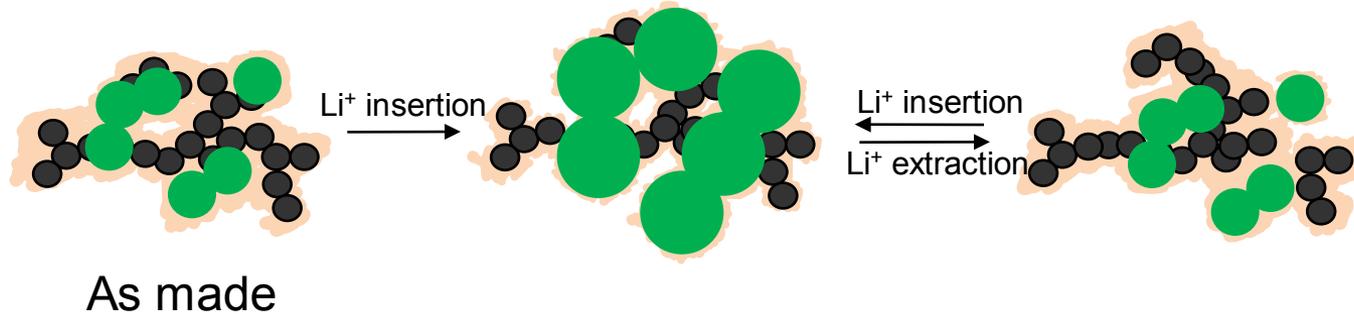
1. Map out the doping process for the Si/conductive polymer in the composite electrode. **(04/2010)** *(80% accomplished)*
2. Characterize the conductivity of the conductive polymer binders. **(04/2010)** *(90% accomplished)*
3. Compensate for the first cycle irreversible capacity of the Si electrode. **(09/2010)** *(20% accomplished)*
4. Fabricate and test lithium-ion cells based on the Si electrode. **(09/2010)** *(80% accomplished)*



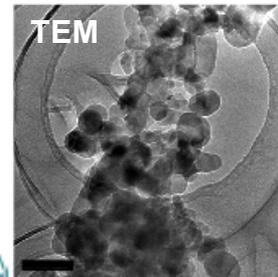
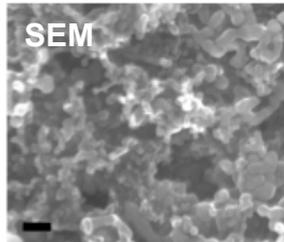
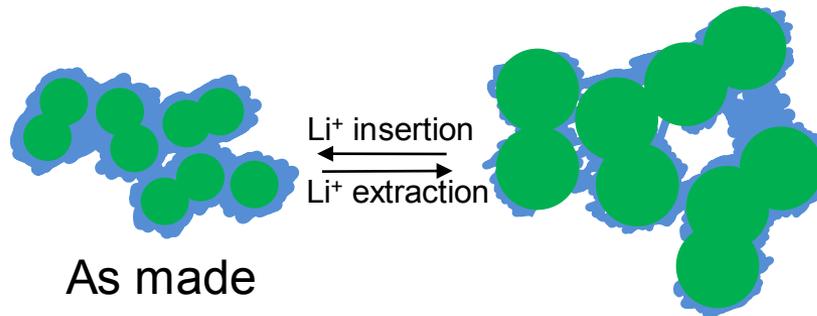
Approach - Conductive Binder for Large Volume Change Si Materials

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

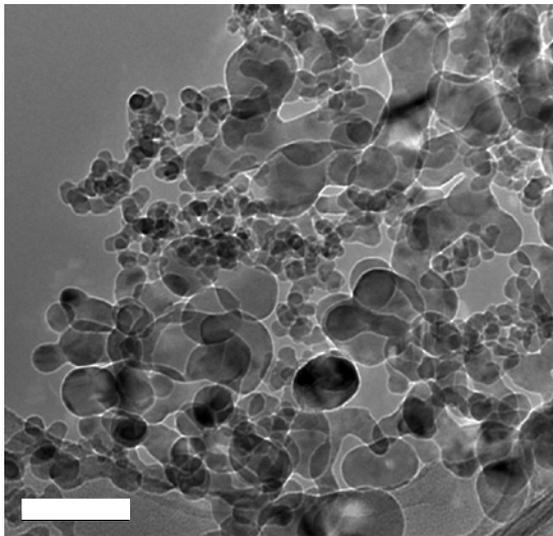
Advantages

- Large scale synthesis of commercial Si nanoparticles is available.
- Fully compatible with conventional lithium-ion technologies.

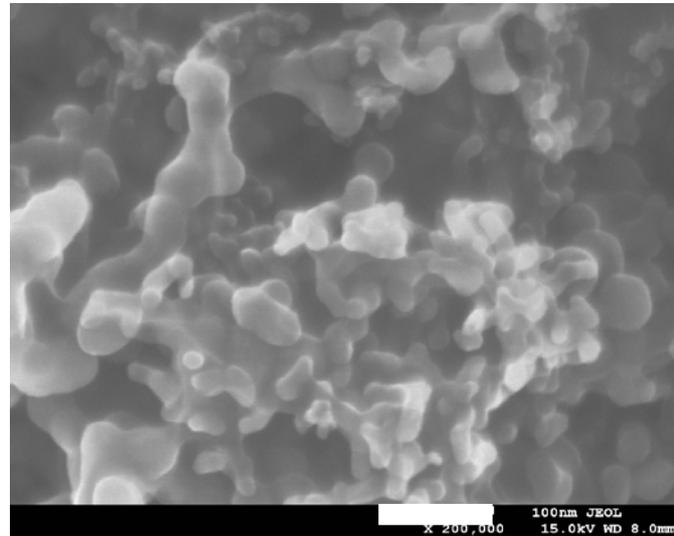
Accomplishments - Commercial Si Nanoparticle and Si/Conductive Binder Composites

Powder & Electrode Images

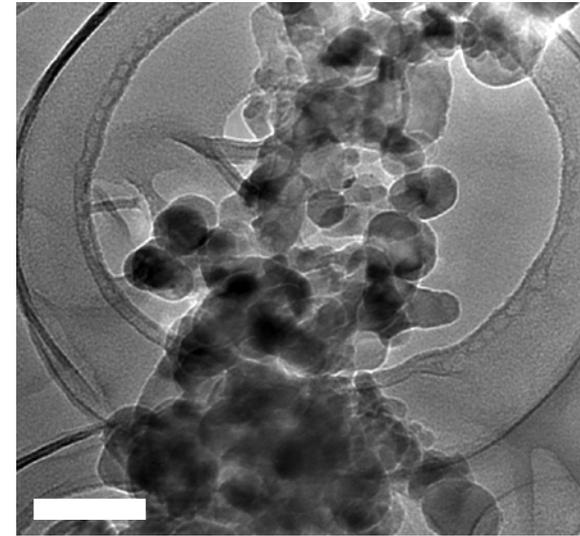
Si Particles-TEM



Electrode-SEM



Electrode-TEM



Commercial source material.

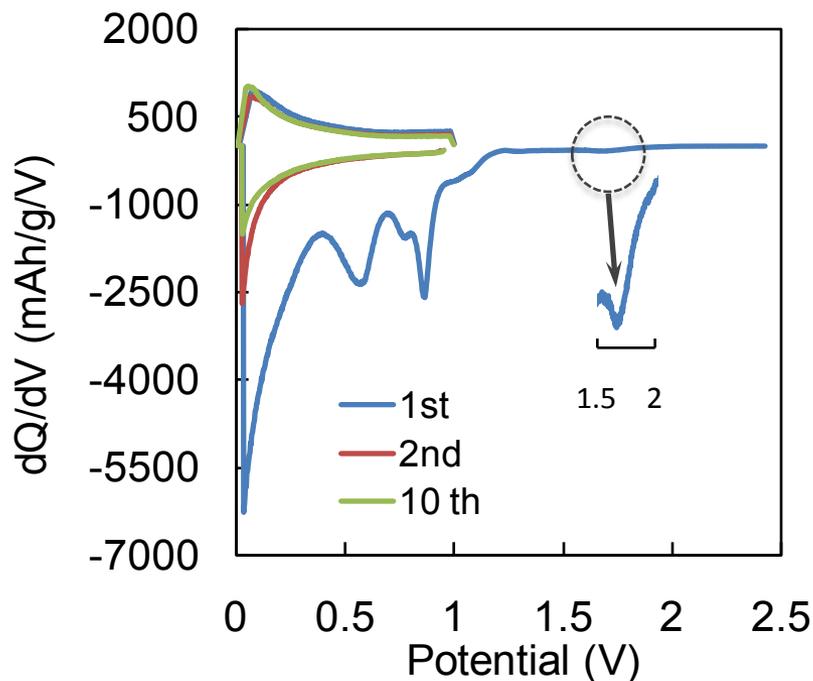
Scale bars 100 nm

The conductive binder connects all the nanoparticles together.

Accomplishments -

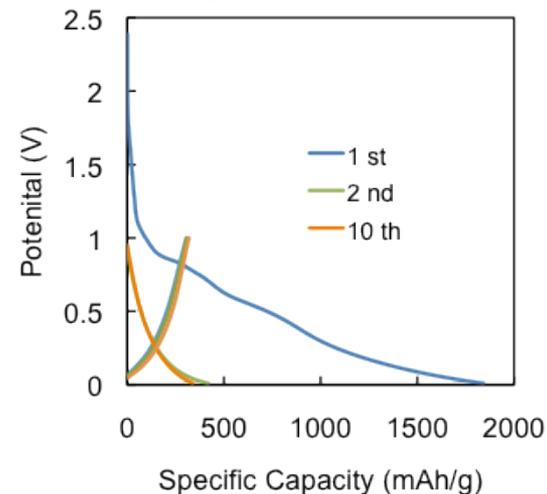
Reversible and Irreversible Conductive Polymer Doping

dQ/dV of the Conductive Polymer

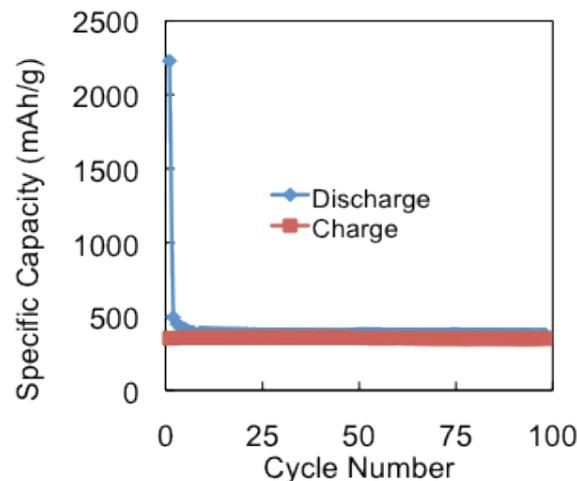


The conductive binder is very stable during Li-ion reversible doping.

Voltage vs. Capacity

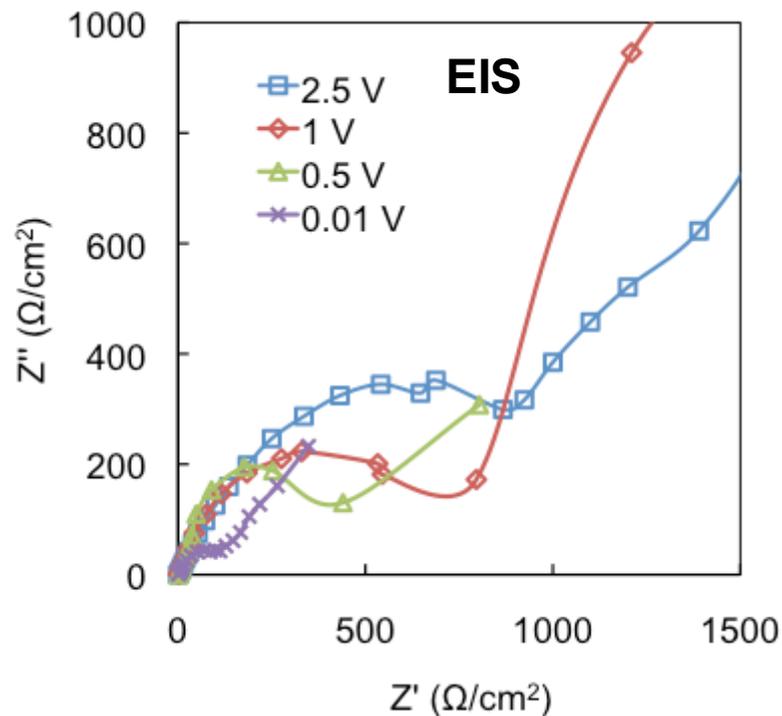
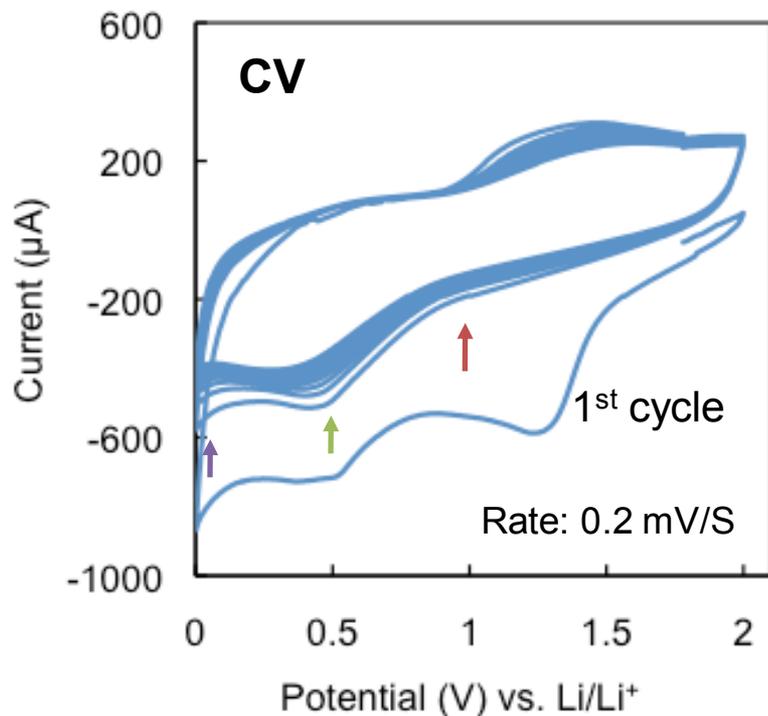


Cycling Performance



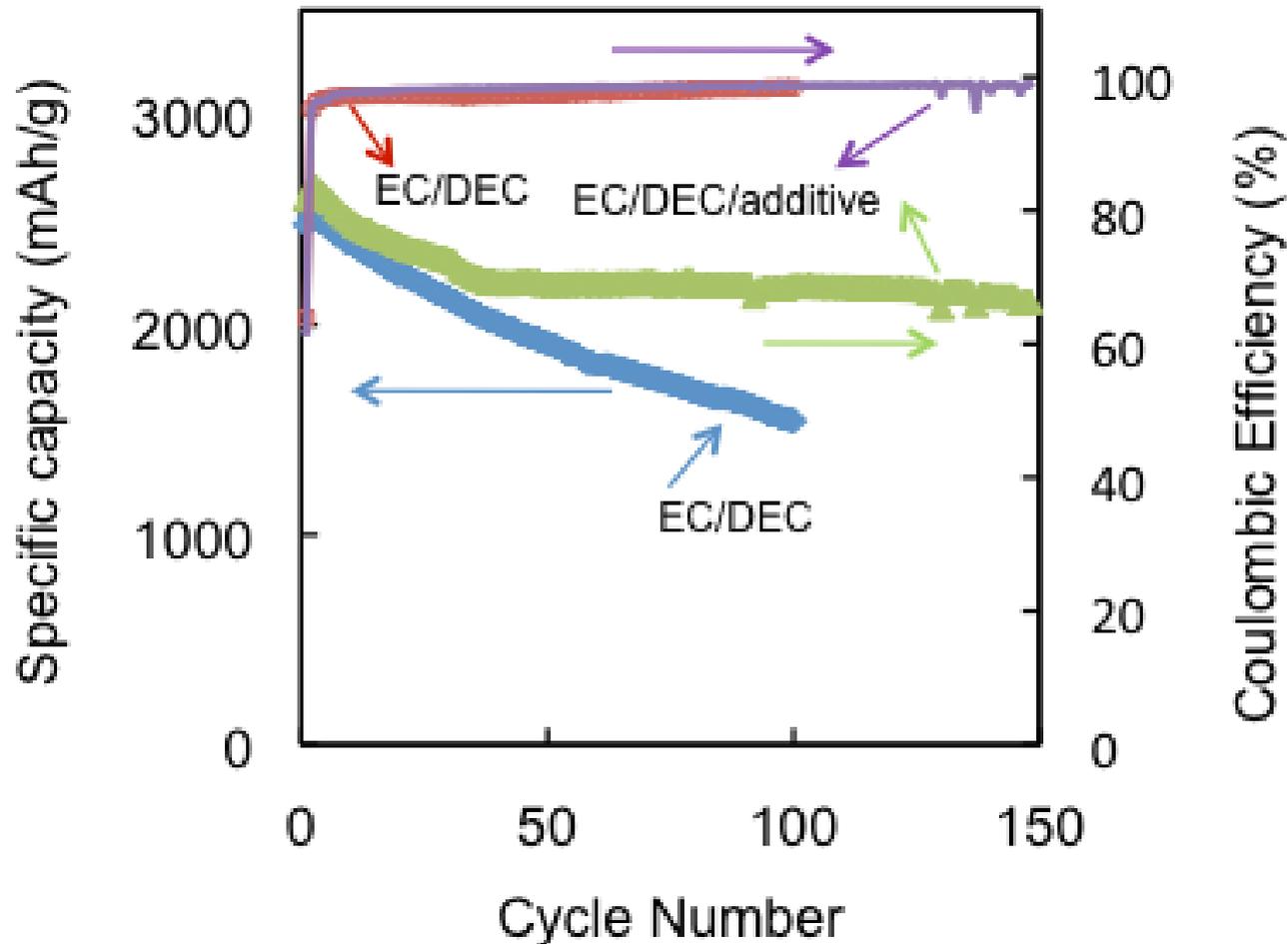
Accomplishments - Conductive Polymer Conductivity

Polymer Conductivity Change with Doping Level



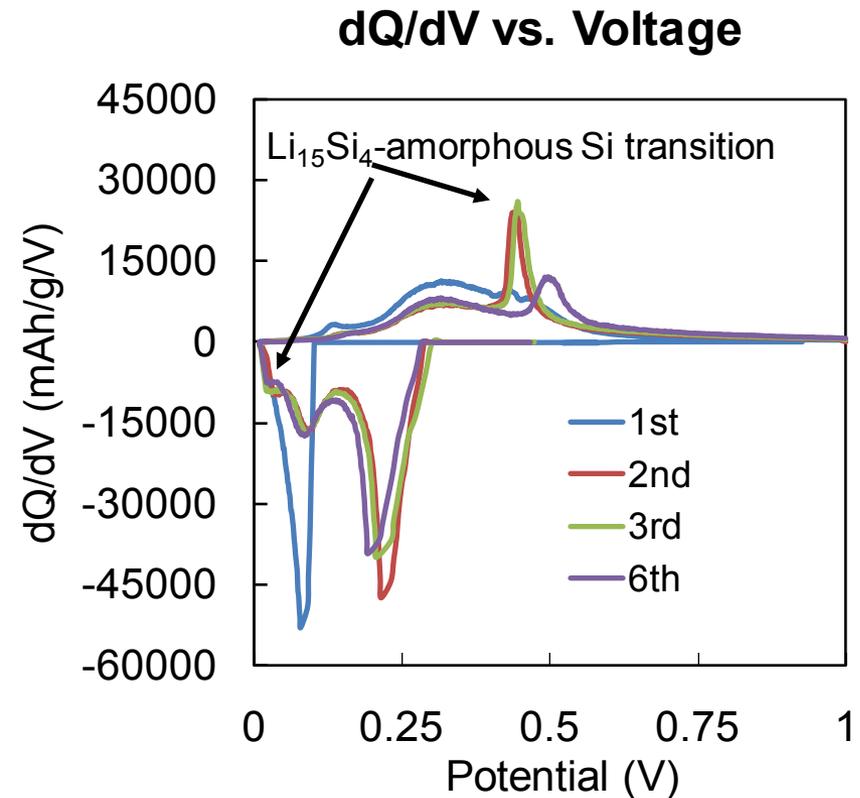
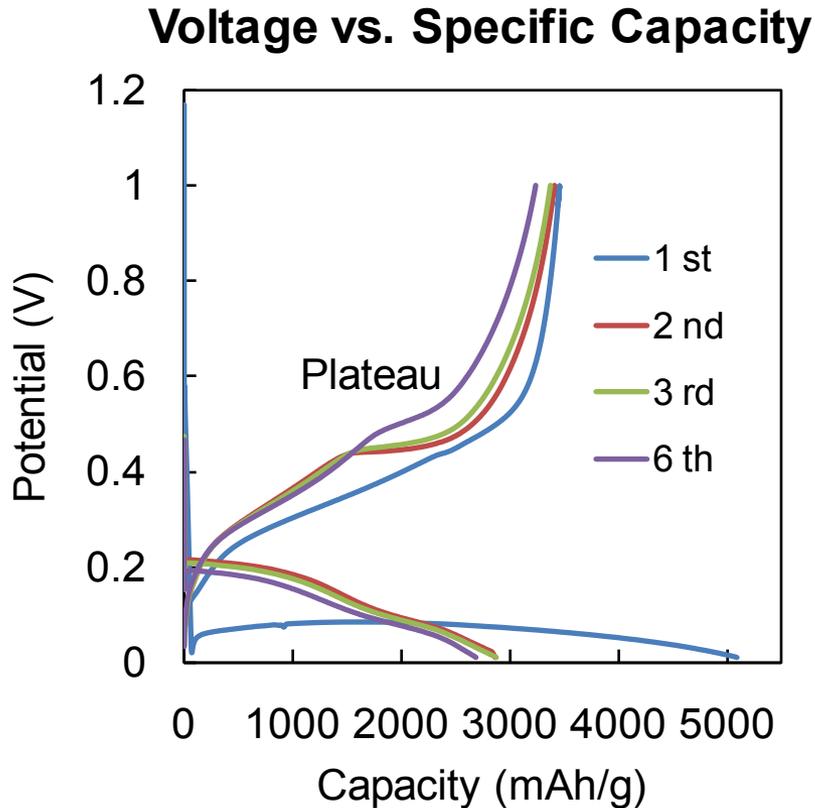
The electronic conductivity of the binder increases during Li-ion doping .

Accomplishments - Extended Cycling Performances of Si/Conductive Binder Electrodes



This performance is repeatable. All the cells show stable cycling above 2000 mAh/g-Si. Cycling behavior beyond 150 cycles is being tested.

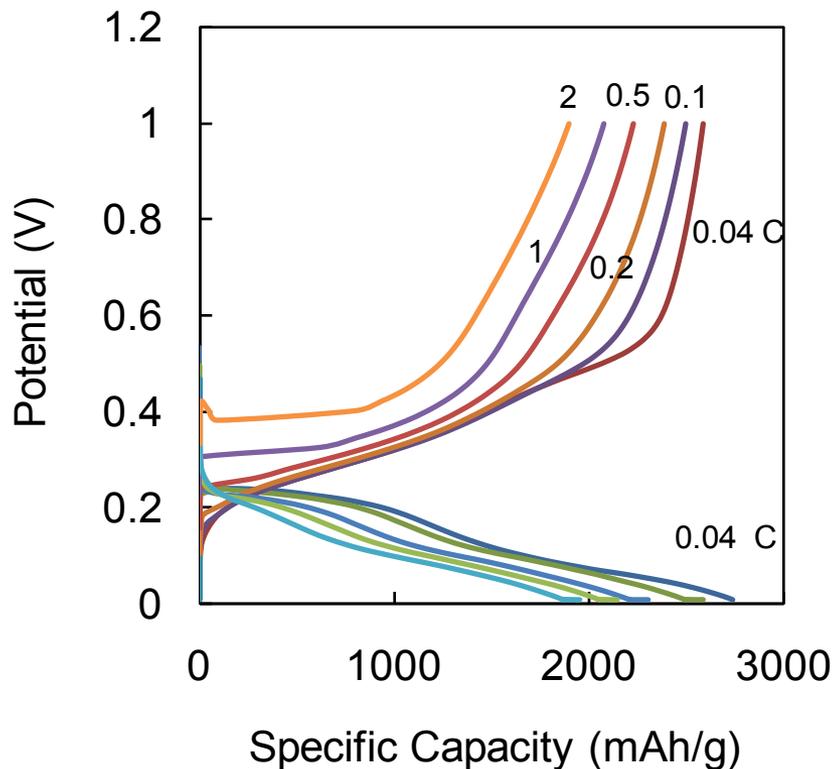
Accomplishments - Si Material Phase Change



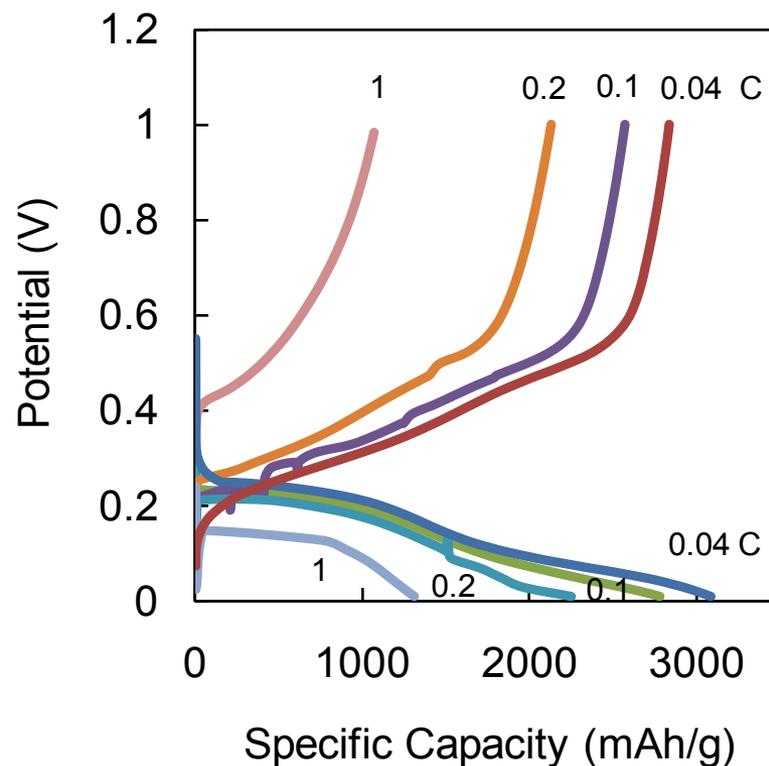
Si Nanoparticles experience same phase transition as micron size particles.

Accomplishments - Rate Performances

**C/25-Rate Charge
Variable C-Rate Discharge**



Variable C-Rate Charge & Discharge



C/2 performance is adequate for EV/PHEV-40 applications

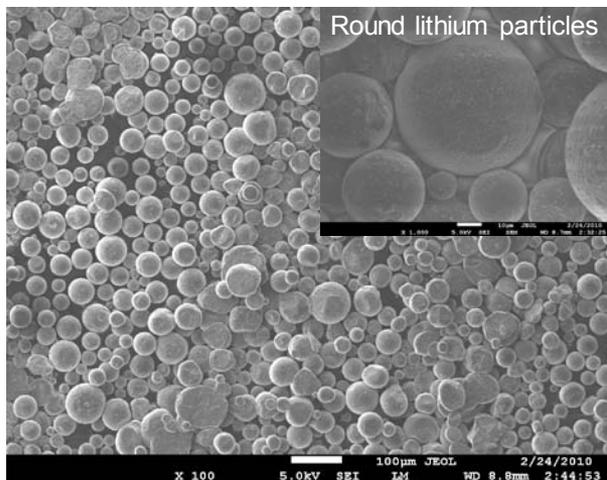
Accomplishments -

Compensation of First Cycle Irreversible Capacity

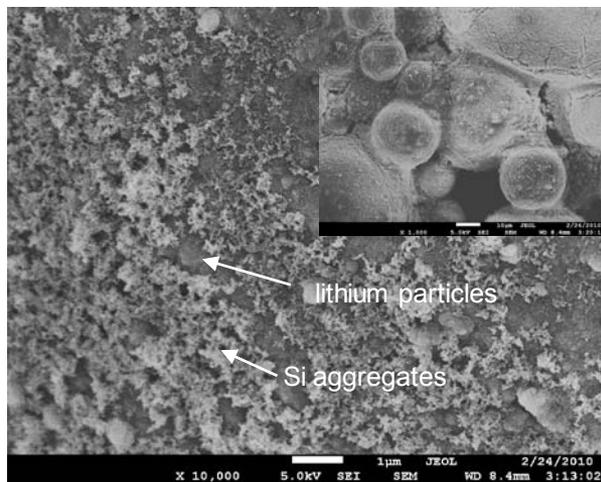
Si-based electrodes tend to have high first cycle irreversible capacity. The Si/polymer binder electrode has around 40% irreversible capacity. We proposed 3 methods to compensate for this irreversible capacity loss.

- Use electrochemical cycling until the capacity stabilized.
- Use FMC stabilized lithium powder doping of the negative electrode.
- Modify binder to stabilize the Si surface.

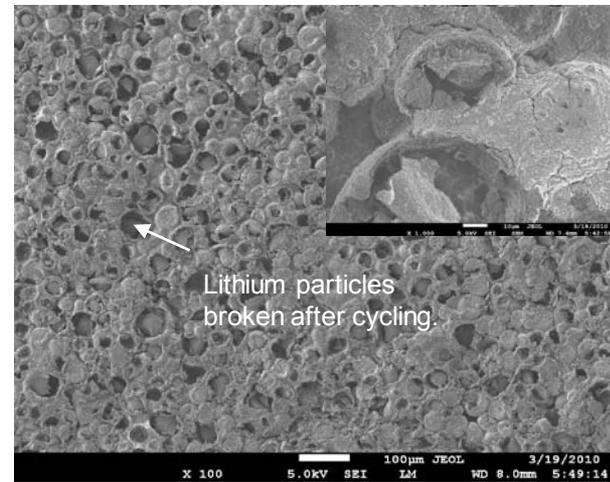
FMC Stabilized Lithium Powder



Si/Conductive polymer with FMC Lithium



Cycled Electrode

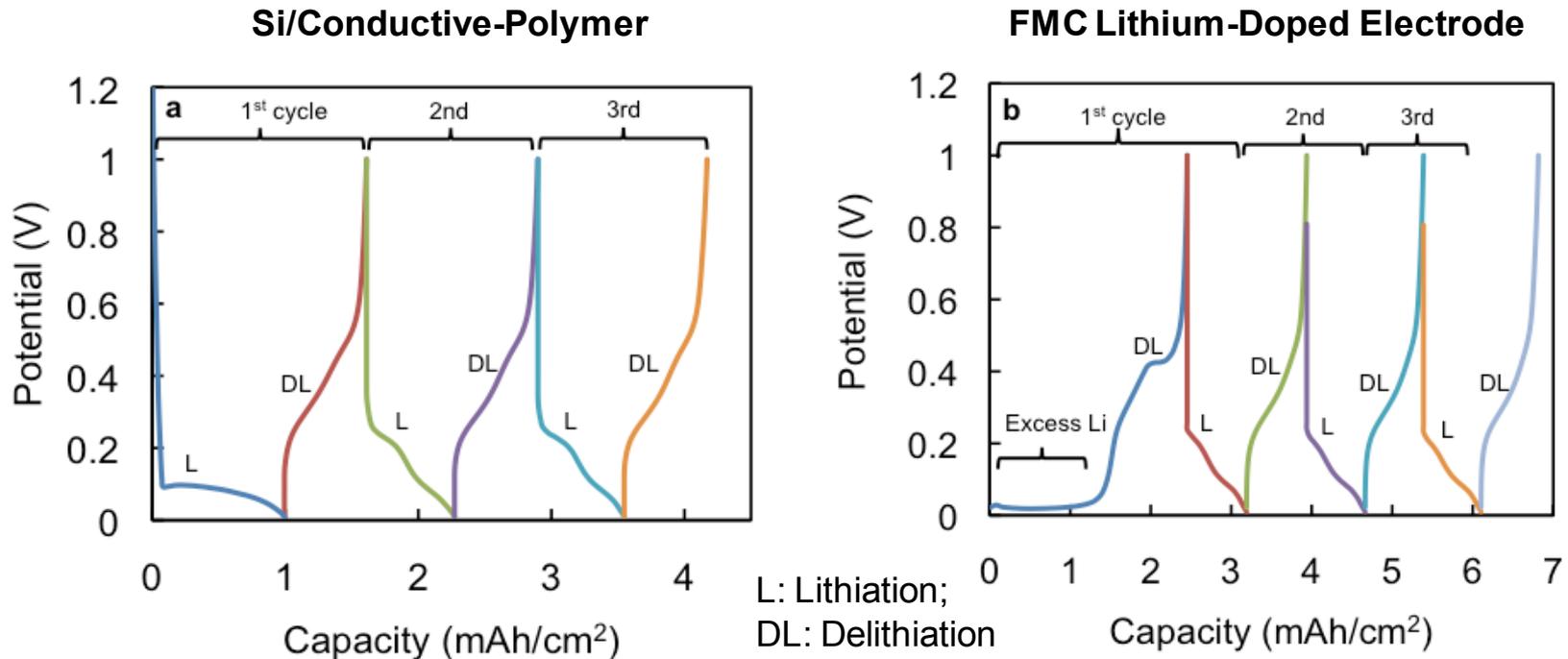


The FMC Stabilized Lithium particles are significantly larger than Si. The distribution is not uniform. It left large amount of residue after cycling.

Accomplishments -

Compensation of First Cycle Irreversible Capacity

Initial cycling performance of FMC stabilized-lithium-power doped Si/conductive polymer electrode. Electrode cycling against lithium counter electrode.



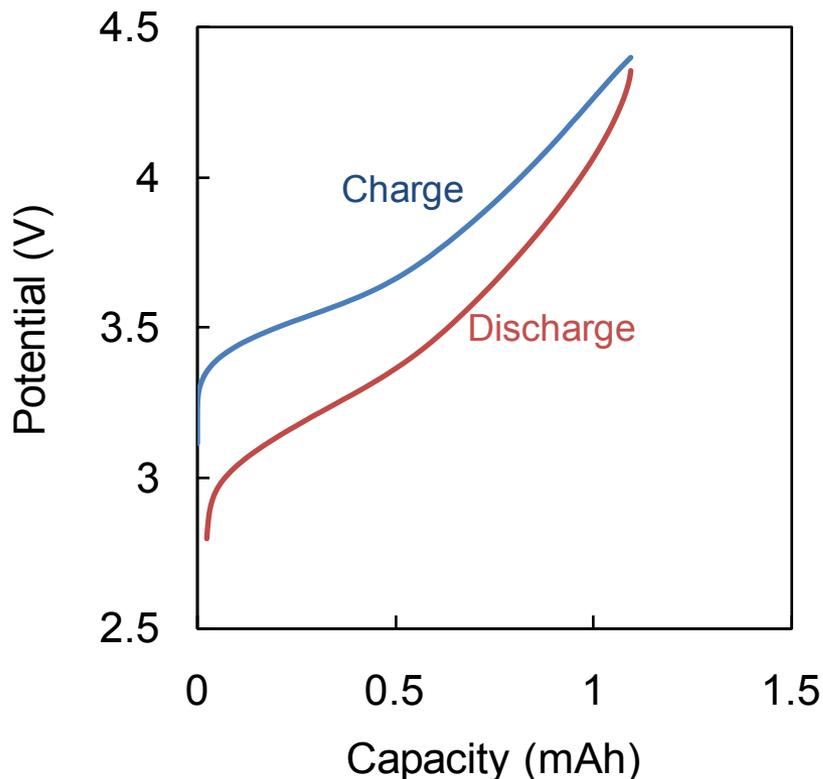
Excessive amount of FMC Lithium was used in our initial testing process. Upon assembling the cell, the Si electrode is fully lithiated. The FMC lithium-doped electrode begins from delithiation rather than lithiation in a normal Si electrode.

Accomplishments -

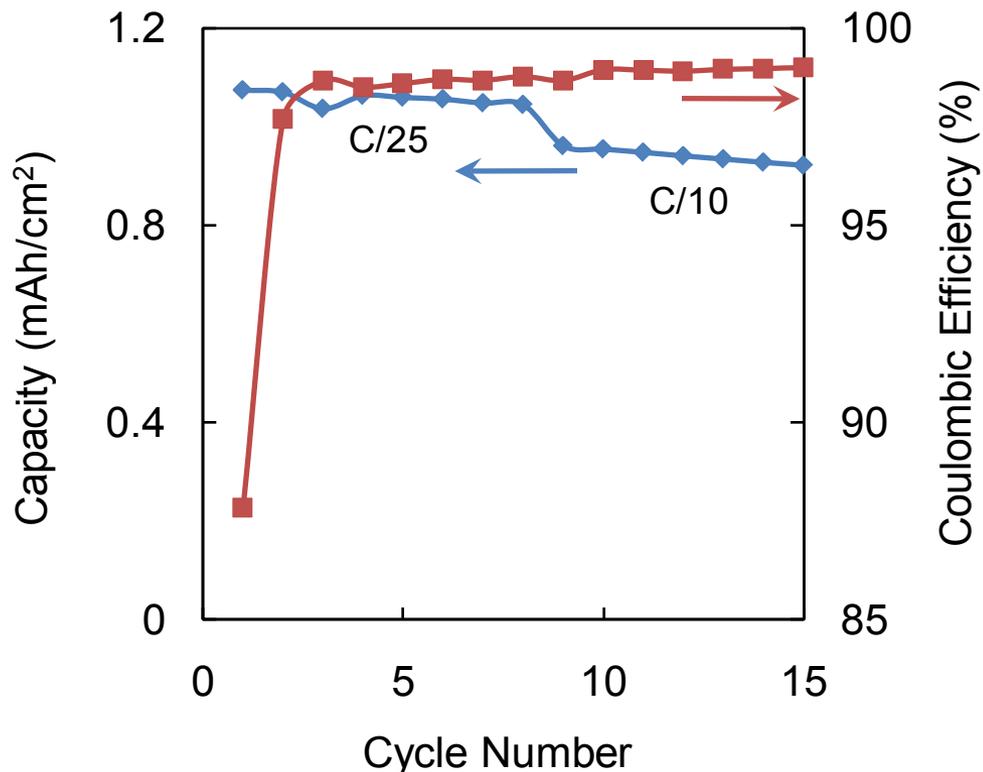
Lithium-ion Full Cell Cycling Performance

Full Cell Chemistry: Si/Conductive polymer (-)//LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (+)

Round Trip Energy Efficiency Over 85%



Initial Full Cell Cycling Performance



The 1st cycle irreversible capacity of Si/conductive polymer electrode has been compensated before assembling the full cell. The Si electrode was cycled in a lithium metal counter electrode until its capacity is stabilized at 2000 mAh/g.



Collaborations

PI	Institution	Details	Directions
Vince Battaglia (VT)	LBNL	SEM and TEM analysis of materials and electrodes. Cell level performance analysis.	Knowledge accumulation
Venkat Srinivasan(VT)	LBNL	Modeling of Si/conductive polymer electrode.	Knowledge accumulation
Robert KostECKI (VT)	LBNL	Raman analysis of the electrode.	Knowledge accumulation
Wangli Yang	LBNL/ALS	X-ray analysis of the polymer band gaps.	Knowledge accumulation
Lin-Wang Wang	LBNL	Calculation of conductive polymer energy levels.	Knowledge accumulation
Karim ZaghIB (VT)	Hydro Quebec	Material transfer agreement in process.	Application into different systems
Connie Wang	Applied Materials	Develop AMAT's new electrode process.	Commercialization
Jake Christensen	Bosch Inc.	New high energy lithium-ion system.	Commercialization

Proposed Future Work

1. We are on schedule to accomplish the milestones that defined in the remaining FY2010 year.
2. For the FY 2011, we propose to investigate in the following areas.
 - a. Develop electrode that has high Si material loading and high capacity per unit area (up to 5 mAh/cm²) to meet the EV/PHEV energy density goals.
 - b. Explore binder functionalities along with electrolyte additives to stabilize Si surface, minimize side reactions, and increase coulombic efficiency.
 - c. Explore the conductive binders in other high energy systems such as Sn negative material.



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 acceptable rate performance (C discharge at 1900 mAh/g-Si) of this electrode.
3. Li-ion doping into the conductive polymer has improved the electronic conductivity of the polymer binders.
4. Electrolyte additive was effective in stabilizing cycling capacity and improving efficiency.
5. Further improvement of electrode matrix conductivity is necessary to improve both Si material loading and rate performance.
6. Further improvement of the Si surface stability is necessary to stabilize Si electrode cycling.

