Hierarchical Assembly of Inorganic/Organic Hybrid Si Negative Electrodes

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Overview

Timeline

Project started: FY 2013
Project end date: FY 2016
Percent complete: 40%

Budget

Total project funding
-DOE share: $2,000K, 100%
FY13 funding $500K
FY14 funding $500K
FY15 funding request $500K

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 (Vince Battaglia, Venkat Srinivasan, Robert Kostecki, Wanli Yang, Andrew Minor, Lin-Wang Wang)
Pacific Northwest National Laboratry
Argonne National Laboratory
General Motors
Hydro Quebec
FMC Lithium
Daikin America

Relevance – Project Objective

This proposed work aims to enable Si as a high capacity and long cycle-life material for negative electrode to address two of the barriers of lithium-ion chemistry for EV/PHEV application, insufficient energy density and poor cycle life performance.

1. Understand the fundamental issues related to the Si composite electrode failure
2. Develop material strategies, such as functional conductive polymers and electrolyte additives to overcome failure mechanism
3. Develop electrode assembly strategies to overcome the electrode level failures
4. Demonstrate the performance improvement via electrode and cell level testing and analysis

Relevance – Project Objective

This work addresses the adverse effects of Si volume change and minimizes the side reactions to significantly improve capacity and lifetime to develop negative electrode and significantly improve the coulombic efficiency. The research and development activity will provide an in-depth understanding of the challenges associated with assembling large volume change materials into electrodes, and will develop a practical hierarchical assembly approach to enable Si materials as negative electrodes in Li-ion batteries.

Milestones

FY 2013

1. Measure the adhesion of the triethyleneoxide (TEO) containing conductive polymer binder, and characterize the electrode performance (Complete)
2. Design and synthesize the alkyls substituted VC additives (Complete)
3. Investigate the performance of the substituted VC additive electrolyte vs. baseline electrolyte (Complete)

FY 2014

1. Design and synthesis 3 more PEFM functional conductive polymer binders with different EO content to study the adhesion and swelling properties of binder to the Si electrode performance (Complete)
2. Down select Si vs. Si alloy particles and particle sizes based on cycling results (Complete)
3. Prepare one type of Si/conductive polymer composite particles, and test its electrochemical performance (On schedule)
4. Design and synthesize one type of vinylene carbonate derivative that targeted to protect Si surface, and test it with Si based electrode (On Schedule)

Approach – Combine functional organic material synthesis, advanced diagnostic and electrode design to achieve high energy-density Si based electrode

1. Using polymer design and synthesis to developed functional conductive polymer binders for large volume change Si based materials

Understand the three requirements for binders: electrolyte intake and ion conducting, adhesion, and electron conducting; and develop new functional conductive polymer binders for Si.

2. Using in situ TEM to understand the nano and meso scale activities of the Si composite electrode

Visualize charge inequality of the Si composite electrode; understand the the performance of functional conductive polymer in the electrode level; quantified the electrode meso volume change to the bulk electrode volume change.

3. Hierarchical electrode designs to improve energy density

Design and fabricate electrode with elastic properties to accommodate Si volume change and maintain stable interface, and maintain porosity of the electrode during cycling.

4. Understand interface reactivity and develop advanced electrolyte additives to improve SEI and coulombic efficiency

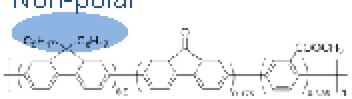
Use spectroscopy techniques to understand the surface chemical properties of the SEI layer; and develop new additives to improve SEI stability.

Accomplishments – Design and synthesize functional conductive polymer binders for large volume change Si based materials

New functional binder design
Combining:
1. Electrically conductivity
2. Binding – adhesive
3. Li-ion transport

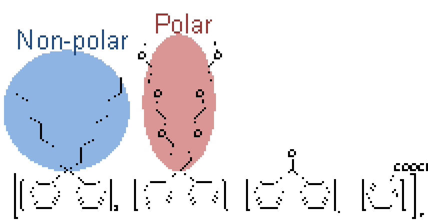
Frist generation: PFM

Non-polar



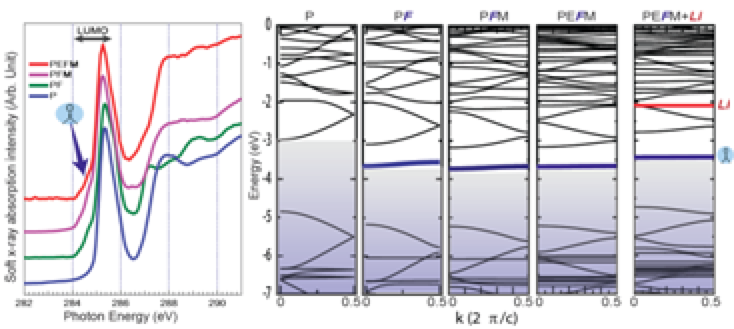
Electric conduction

Second generation: PEFM

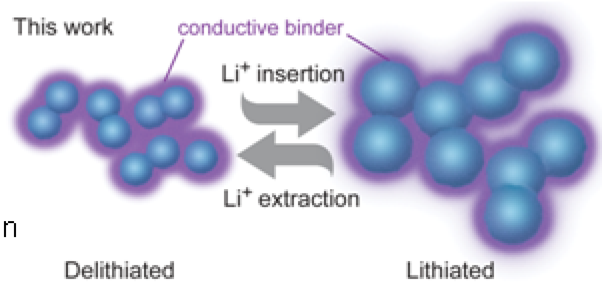


Electric conduction

Similar LUMO energy levels

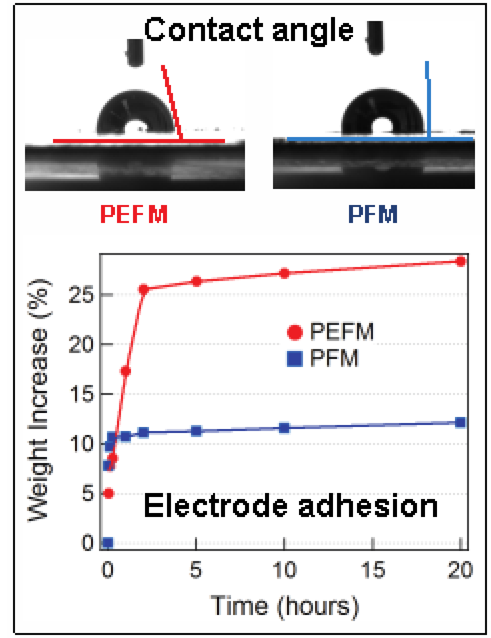


Functional conductive polymer binder/Si electrode

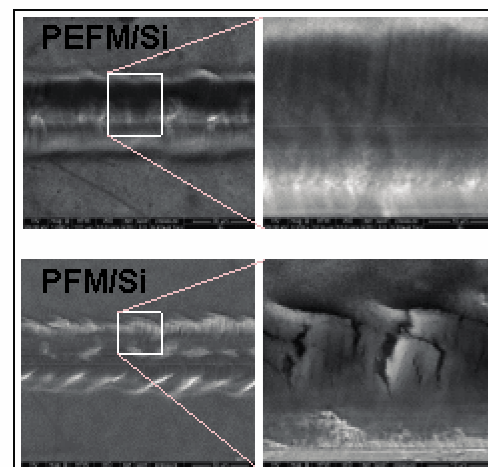


Advantages
- Use Si particles
- Fully compatible with conventional lithium-ion technologies

R&D100 award winning invention of 2013

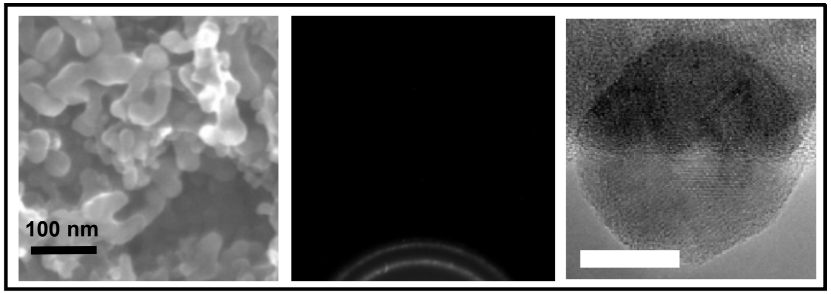


Scratch test of electrodes

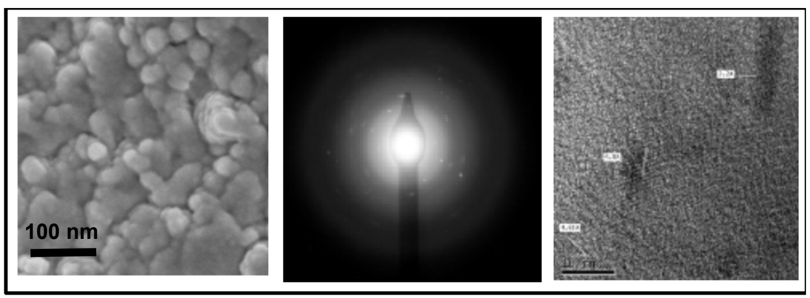


Accomplishments – Design and synthesize functional conductive polymer binders for large volume change Si based materials

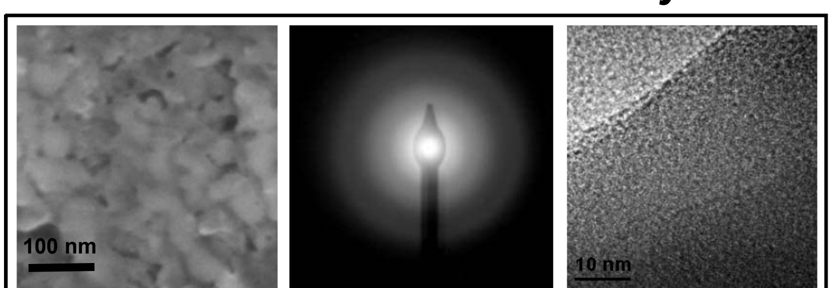
Un-cycled Si electrode



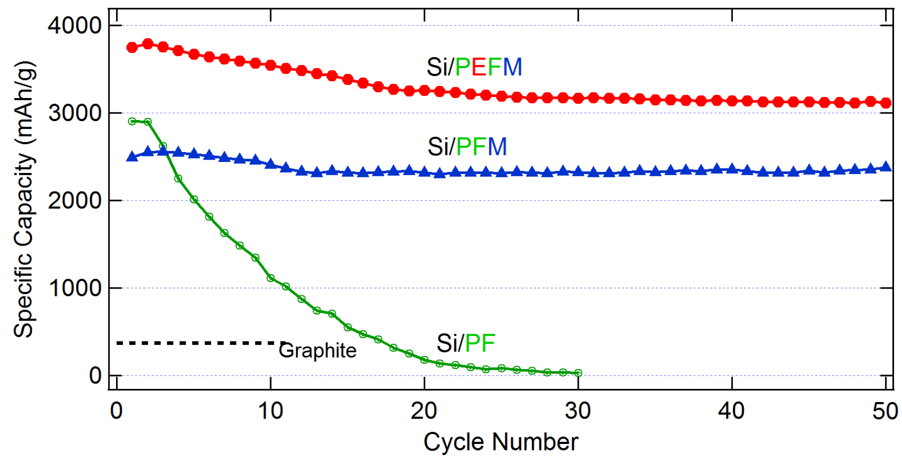
Si/PFM electrode after 1st cycle

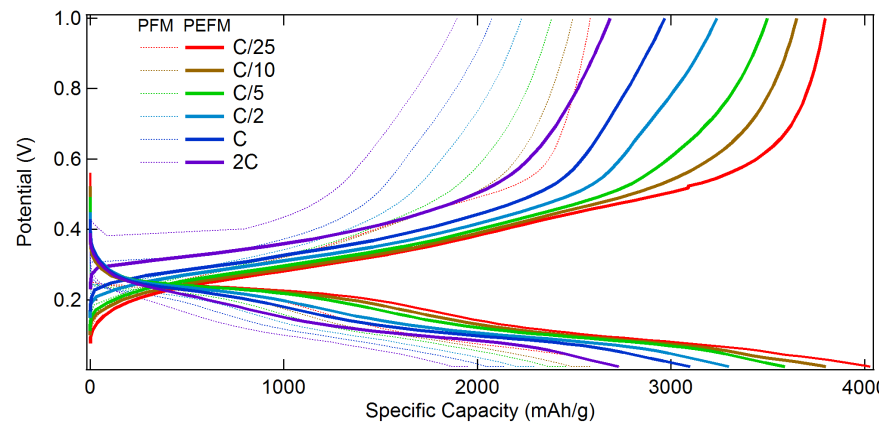


Si/PEFM electrode after 1st cycle



Si electrode cycling performance

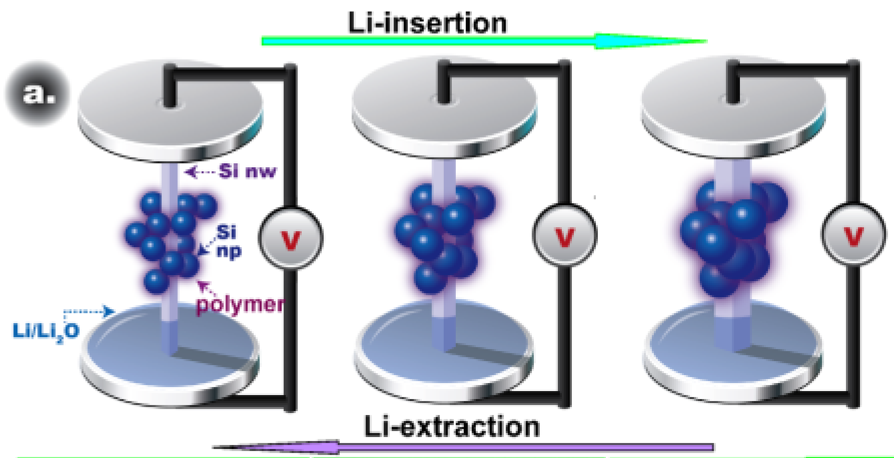




Si/PEFM delivers higher capacity and better rate performance.

Accomplishments - Use in situ TEM to understand the nano and meso scale activities of the Si composite electrode, in collaboration with Dr. Chongmin Wang of electron microscopy center at PNNL

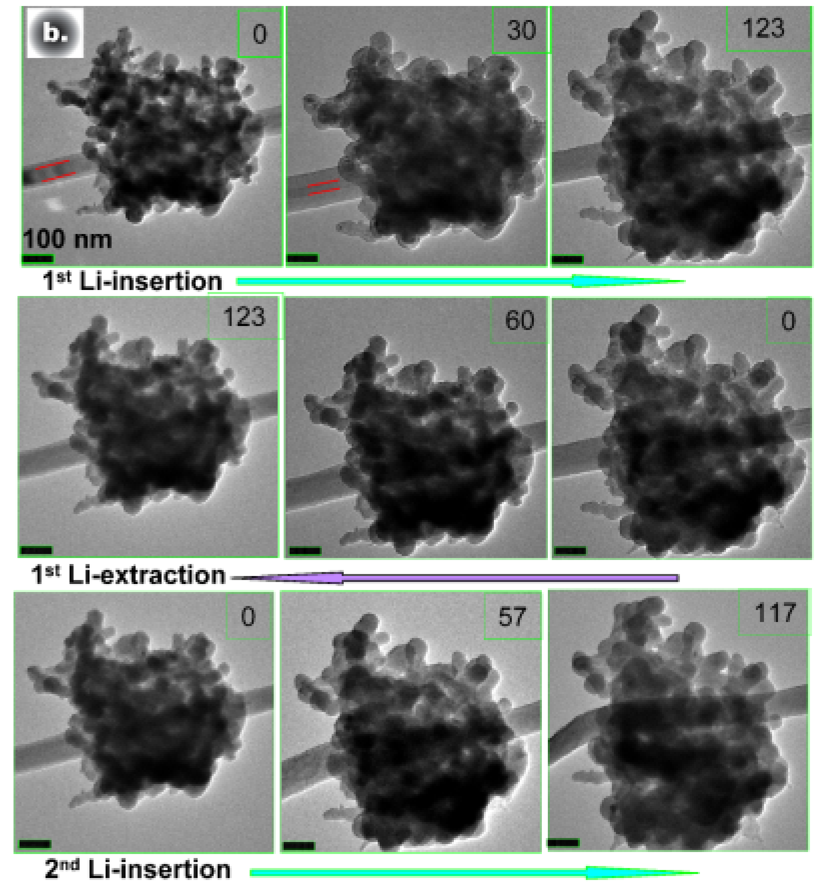
Schematic drawing of the Si anode on Si NW during lithium insertion and extraction



The functional conductive polymer approach exhibits superior electrochemical cycling stability and higher energy density due to the resilient bonding between the conductive polymer and Si NPs. All Si NPs can be lithiated and cycled stably without electrical contact disruption in this approach.

Video clips will be showing at the ARM review presentation

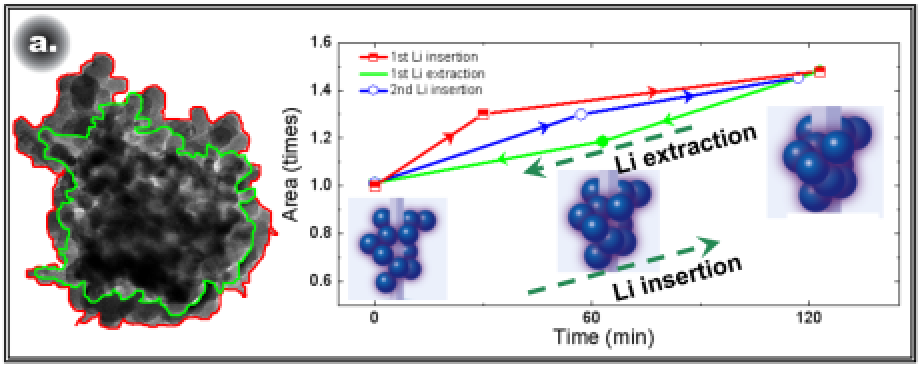
Frames of the in-situ TEM observation lithium insertion and extraction processes of the Si/functional conductive polymer anode at different time



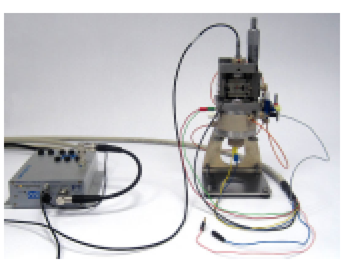
First row : 1st lithium insertion; second row: 1st lithium extraction; third row: 2nd lithium insertion

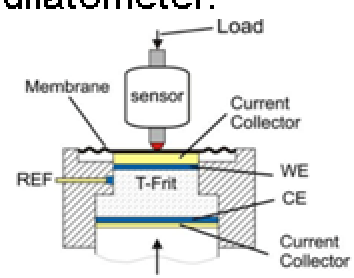
Accomplishments - Using in situ TEM to understand the nano and meso scale activities of the Si composite electrode

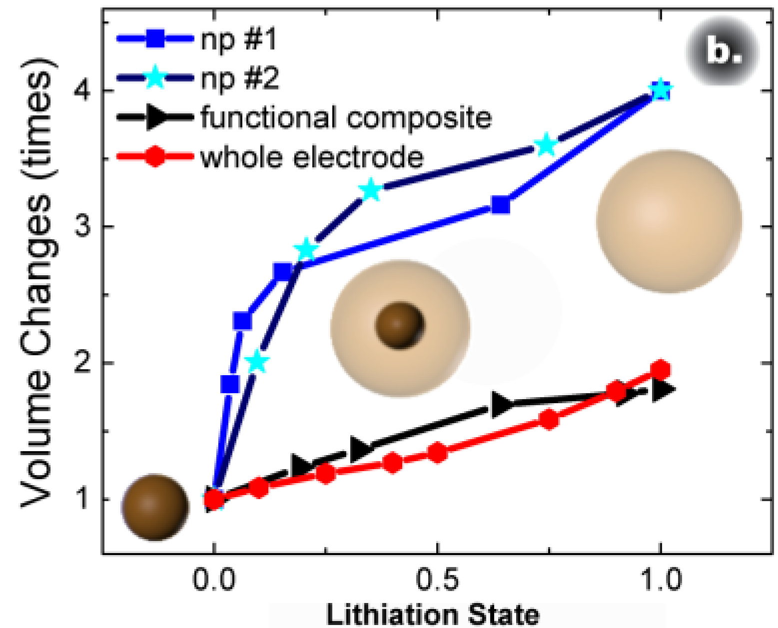
The in situ TEM investigates a small piece of composite electrode. The expansion and contraction of the composite can be calculated based on the TEM imaging.



The bulk electrode volume change during cycling is mainly in the form of electrode thickness change, which can be observed directly by electrochemical dilatometer.





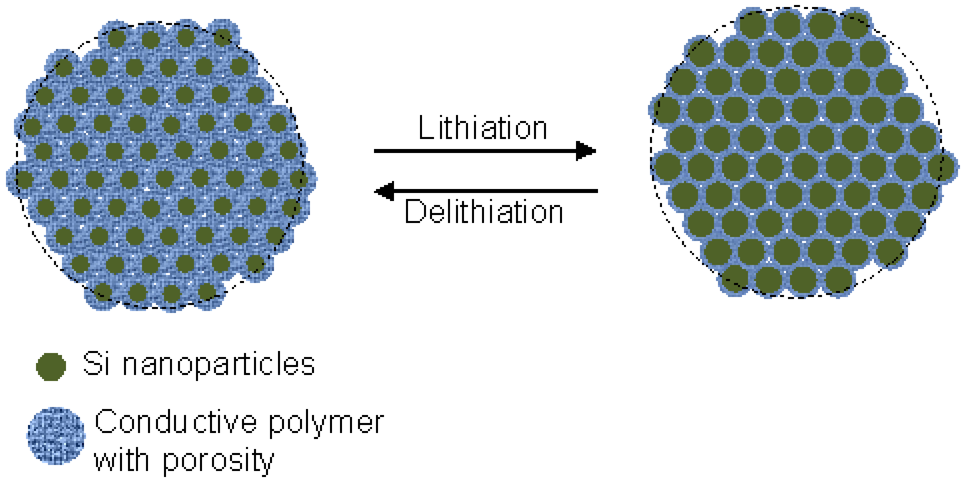


Although the material level volume change is as high as 300% for Si nanoparticles, the composite level volume change is around 100%.

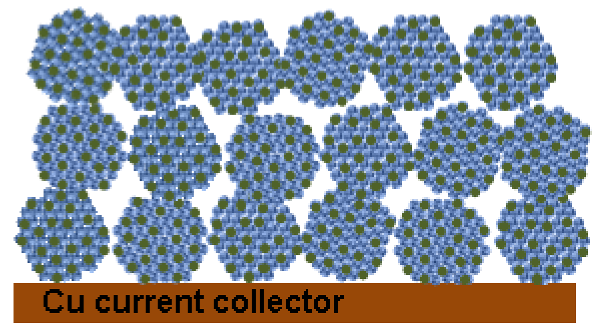
The information is important for electrode level architecture design.

Accomplishments – Hierarchical electrode designs to improve energy density

Secondary composite particle

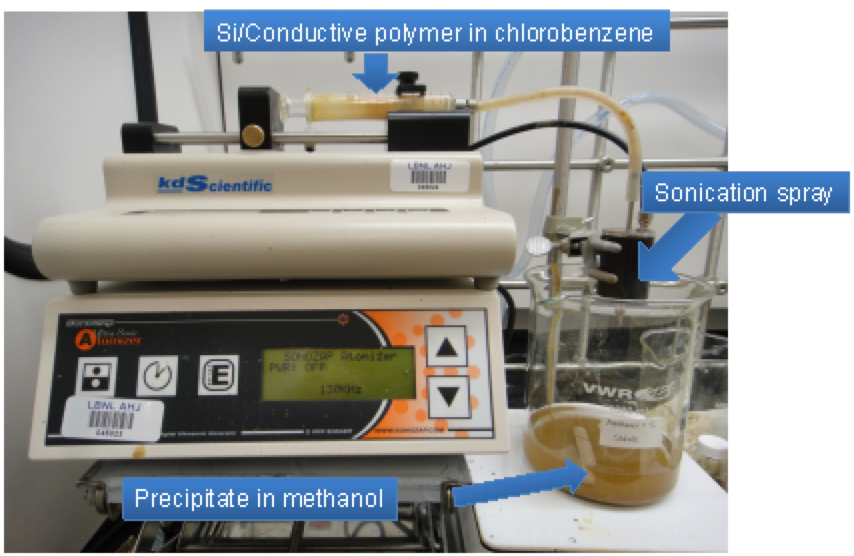


Secondary composite particles electrode

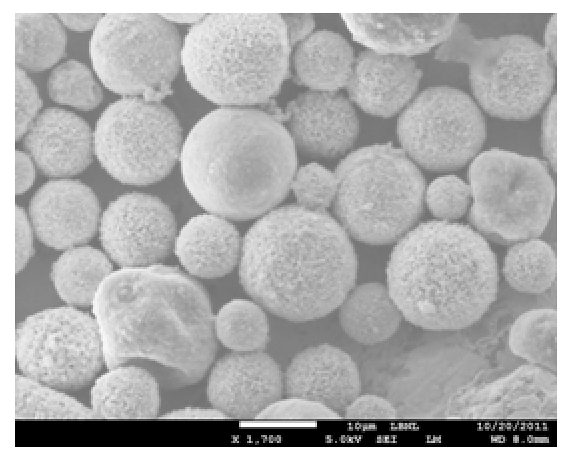


Advantages: Large micron size porosity, and stable dimension

Spray precipitation method to generate secondary particles

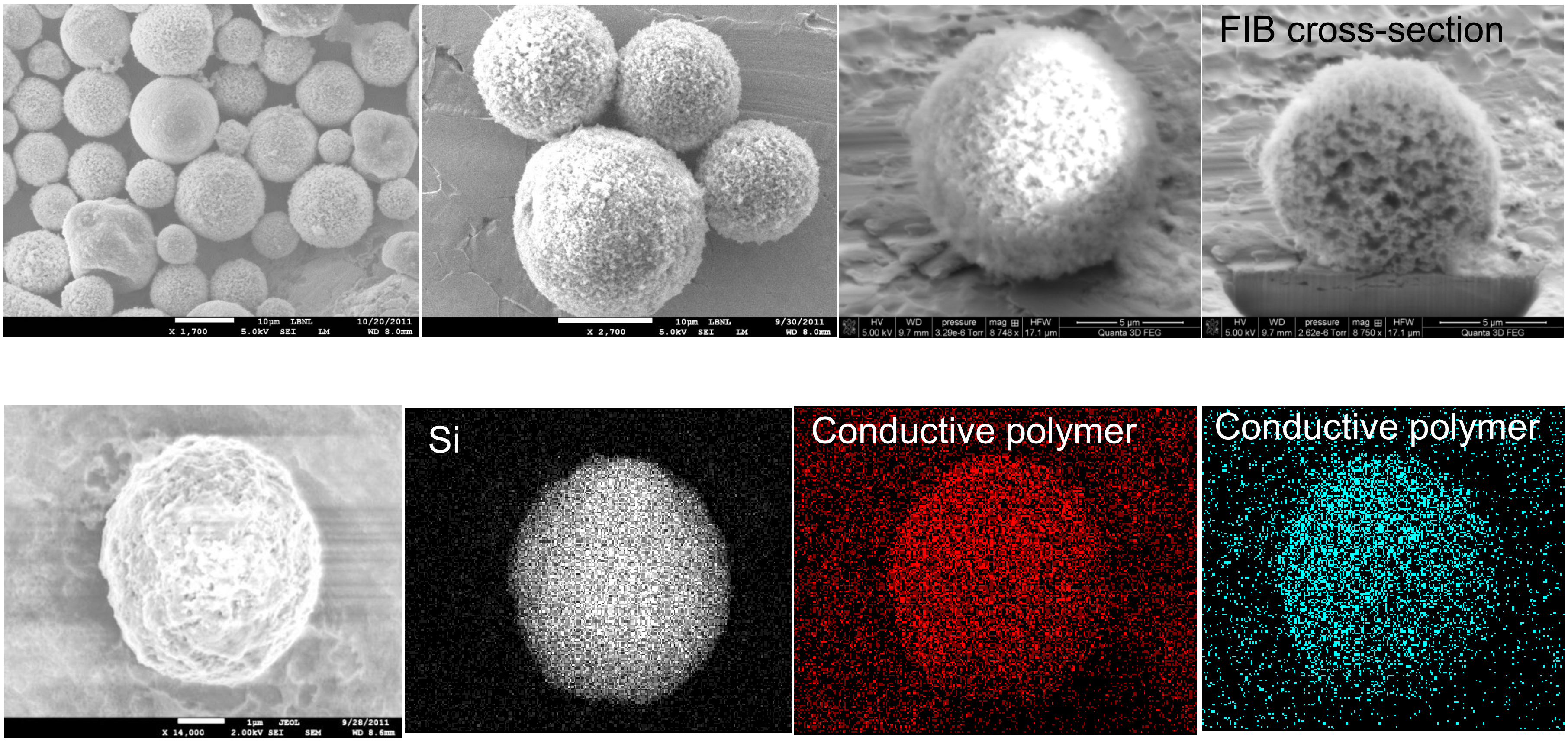


SEM image of Si/PFM Secondary particles



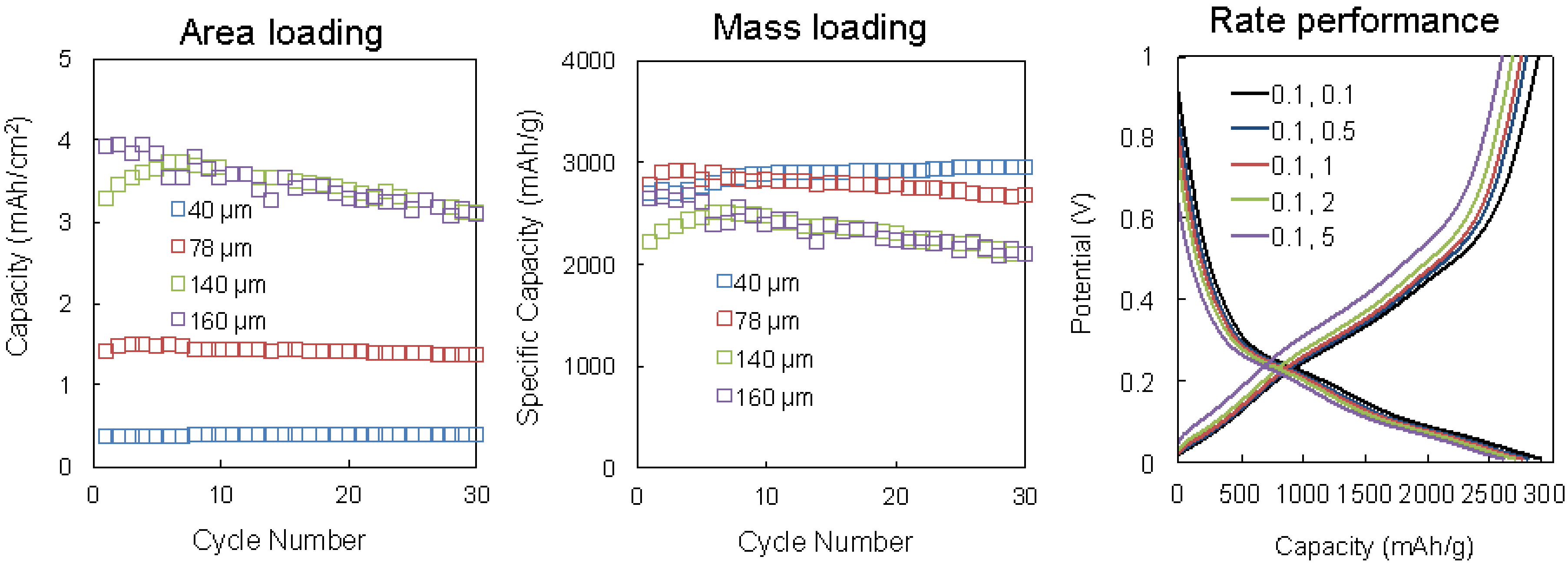
Accomplishments – Hierarchical electrode designs to improve energy density

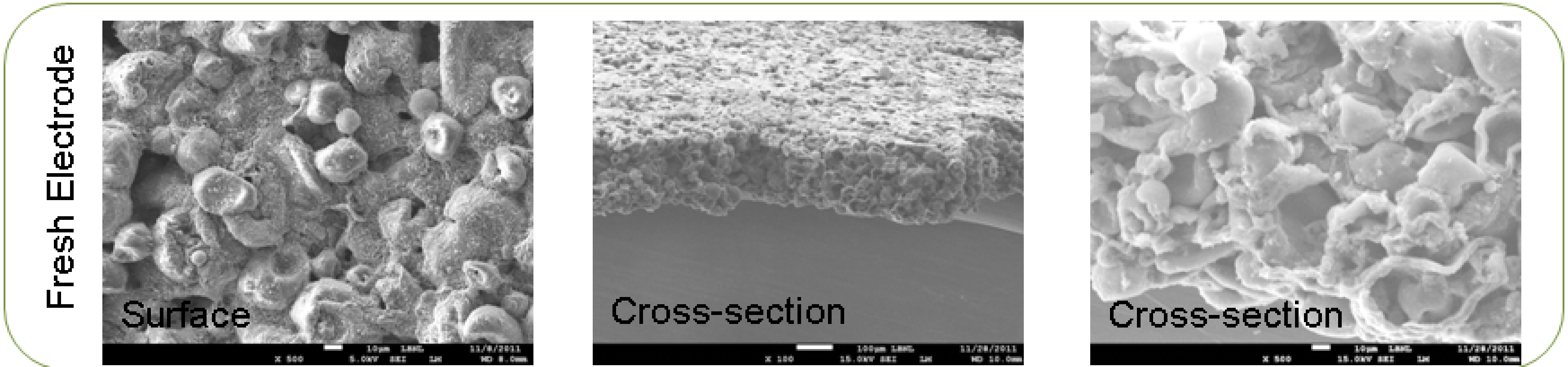
Si composite secondary particles



Accomplishments – Hierarchical electrode designs to improve energy density

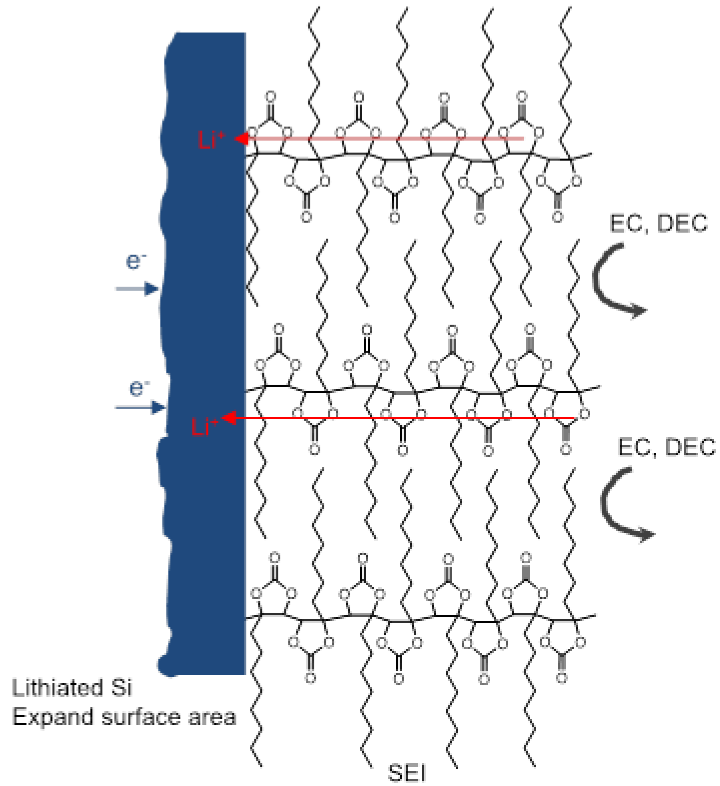
Electrochemical performance of the Si secondary particle composite electrode



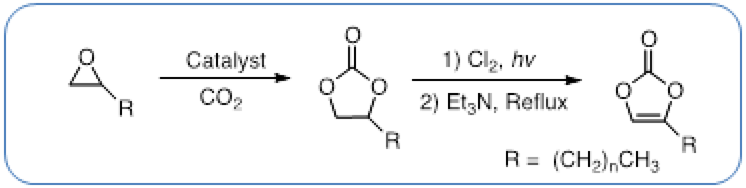


Accomplishments - Understand interface reactivity and develop advanced electrolyte additives to improve SEI and coulombic efficiency

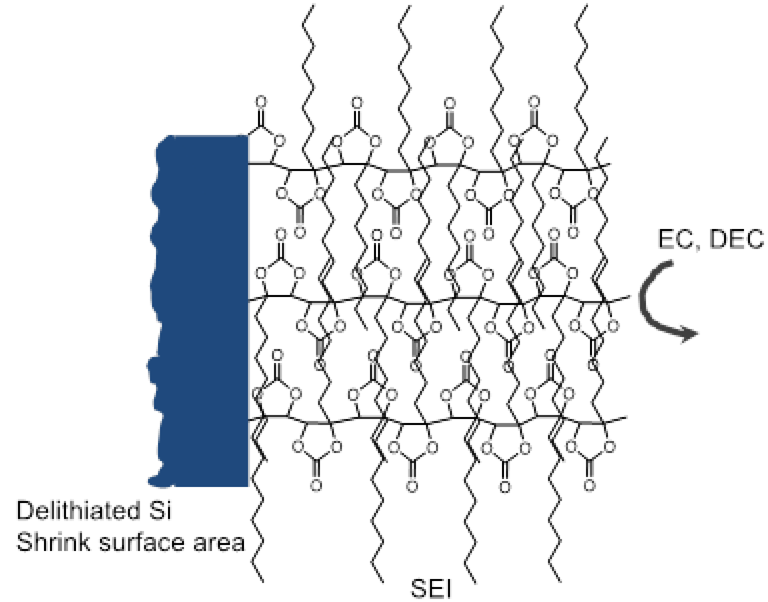
Compliant SEI layer formation with octyl-VC on the surface of Si when Si is lithiated.



Alkyl vinylenecarbonate additives



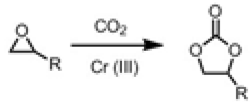
The compliant SEI layer compressed when Si is delithiated rather than breaks and falls off.

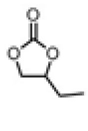


Alkyl vinylenecarbonate additives may form elastic SEI on the surface of Si, preventing SEI cracking and reforming during cycling.

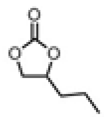
Accomplishments - Understand interface reactivity and develop advanced electrolyte additives to improve SEI and coulombic efficiency

Cyclic carbonate derivatives: synthesis and properties

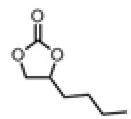




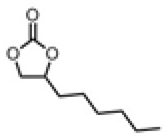
Butylene Carbonate (BuC)



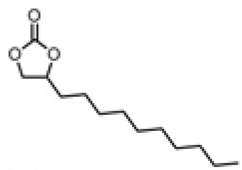
Pentylene Carbonate (PeC)



Hexylene Carbonate (HeC)

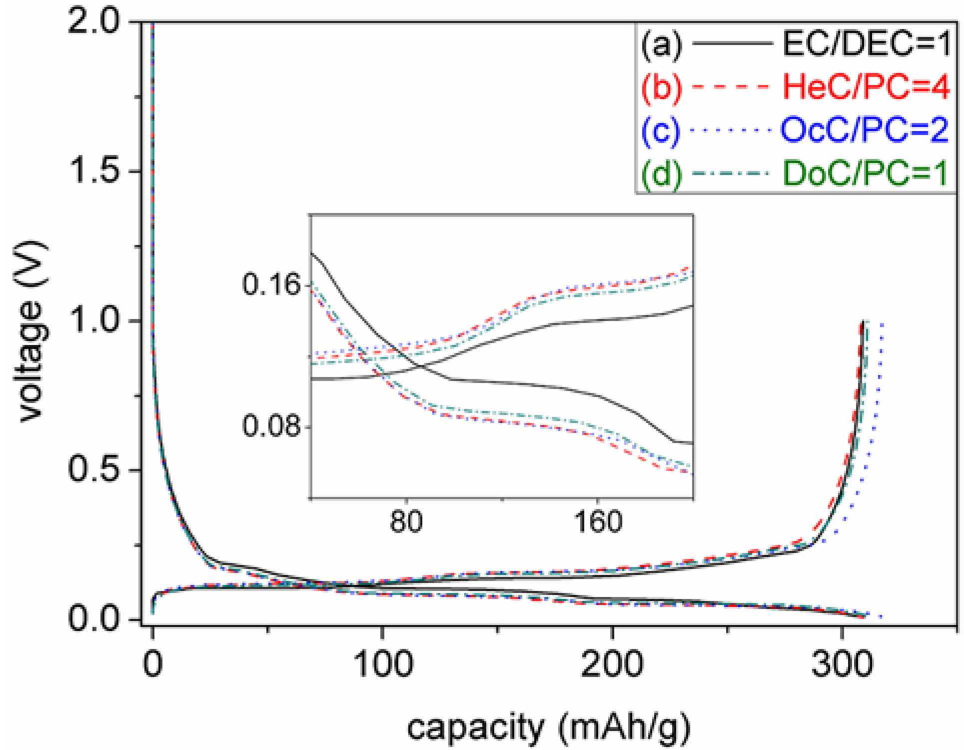


Octylene Carbonate (OcC)



Dodecylene Carbonate (DoC)

Cyclic carbonates	Conductivity of 1 M $LiPF_6$ in different cyclic carbonate solvents at 30 °C (mS/cm)
PC	5.1
BuC	3.1
PeC	2.3
HeC	0.5
HeC/PC=4 [a]	2.3
OcC	0.4
OcC/PC=2 [a]	1.9
DoC [b]	X
DoC/PC=1 [a]	1.2



With increasing of alkyl chain length, the dielectric constant of the additives decrease. However, the additives can successfully prevent PC intercalation for the graphite electrode. The effectiveness of this additive for Si is being investigated.

Collaborations - Team functions

1. **Lawrence Berkeley National Laboratory**

In collaboration with BATT PIs, conducted functional conductive polymer design and synthesis for Si based anode materials, performed electrode design fabrication and testing.

In Collaboration with DOE user facility scientists, conducted soft X-ray diagnostic of the materials and electrode, performed advanced TEM analysis of materials, and performed modeling study of materials and electrodes

2. **Pacific Northwest National Laboratory**

Performed In situ TEM analysis of the nano and meso scale phenomenon in the functional conductive polymer binder/Si composite electrode

3. **General Motors**

Measured in situ bulk physical dimension change of electrode using dilatometer and mechanical response characterization using nano-indentation. Performed electrode and surface chemical analysis using TOF-SIM techniques.

Collaborations - Team functions

4. Argonne National Laboratory
Provided information for material screening and evaluation of the conductive polymer binder and Si materials.

5. Umicore
Provided pilot scale NanoGrain experimental Si materials.

6. Hydro Quebec
Provided new Si based materials

7. Daikin American
Provided electrolytes for Si based materials and electrode

8. FMC Lithium
Provided lithium based materials

Proposed Future Work

1. The team are on schedule to accomplish the milestones defined in the remaining FY2014.

2. For the FY 2015, we propose to investigate in the following areas. The detailed milestones will be developed based on the on-going investigation, AMR review comments and discussions between the collaborators.

    a. Design and synthesis at least two functional conductive polymers for Si based electrode.
    b. Develop methodologies to improve the Si electrode first cycle efficiency to 90%.
    c. Design and synthesize new surface stabilizing additive, and test it with Si based electrode
    d. Apply hierarchical electrode design to achieve a 3 mAh/cm^2 loading.

Summary

1. Functional conductive polymer binders play a critical function in deliver stable and high capacity cycling for the large volume change Si materials in a composite electrode.
2. The design of functional binders need to consider three aspects: electron conductivity, adhesion and mechanical properties, and electrolyte swelling for ion-conduction.
3. Characterization based on in situ TEM of the composite electrode has demonstrated the superb performance of the functional conductive polymer binder over the conversional non-conductive polymer binder and conductive additive system.
4. Hierarchical design of particles and electrode architecture maintain electrode 3D structure to ensure a higher area capacity and stable cycling performance.
5. Electrolyte additives form stable SEI, improving coulombic efficiency.