Hierarchical Assembly of Inorganic/Organic Hybrid Si Negative Electrodes

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Project ID: ES223

Overview

Timeline
Project started: FY 2013
Project end date: FY 2016
Percent complete: 85%

Budget
Total project funding
-DOE share: $2,000K, 100%
FY15 funding $500K
FY16 funding $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, Cheng Wang, Andrew Minor)
UC Berkeley
Argonne National Laboratory
Pacific Northwest National Laboratory
General Motors
Hydro Quebec
Zeptor Corporation
FMC Lithium
Daikin America

Relevance – Project Objective

This proposed work aims to enable Si Based material 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 activities 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 2015

1. Design and synthesis a new class of functional conductive polymers for Si based electrode. (Complete)
2. Develop methodologies to improve the Si electrode first cycle efficiency to 90%. (Complete)
3. Design and synthesize new surface stabilizing additive, and test it with Si based electrode. (Complete)
4. Apply hierarchical electrode design to achieve a 3 mAh/cm^2 loading. (go/no-go, Complete and achieved the milestone. The decision is go.)

FY 2016

1. Investigate the impact of different side chain conducting moieties to the electric conductivity of the functional conductive binders. (Complete)
2. Quantify the adhesion groups impact to the electrode materials and current collector. (Complete)
3. Fabricate higher loading electrode (>3 mAh/cm^2) based on the Si electrode materials and select binder, and test cycling stability. (On schedule)
4. Fabricate NMC/Si full cell and quantify the performance. (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: adhesion, and electron conducting and electrolyte intake and ion conducting; and develop new functional conductive polymer binders for Si based materials via a radical polymerizations process.

2. Use Atomic Force Microscope (AFM) to measure the binder and Si particles adhesion strength

Adhesion functional groups on the binder is critical to provide electrode mechanical properties; AFM force measurement reveals the adhesion bonding strength between a single binder molecule and SiO_2 substrate, which is the surface of Si particles.

3. Hierarchical electrode designs to improve energy density

The functional conductive polymer binder has high adhesive strength to bond Si particles together during Si high volume change process, improving cycling performance. Addition of designed porosity to the electrode improves both loading and rate performance.

4. Prelithiation to further improve energy density

Use Stabilized Lithium Metal Powder (SLMP®) to prelithiate Si electrode to decrease first cycle lithium loss.

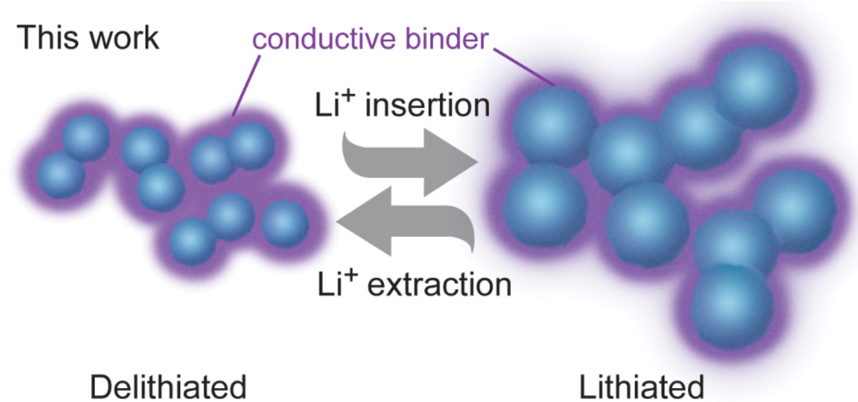
Accomplishments – First, second and third generation of functional conductive polymer binders for large volume change Si based materials

Functional conductive binder design

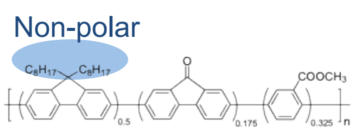
Combining:

1. **Electrically conductivity**
2. **Binding – adhesive**
3. **Li-ion transport**

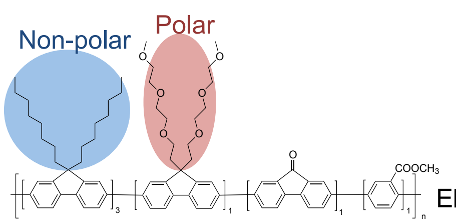
polymer binder/Si electrode



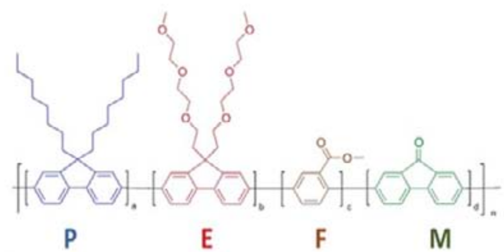
Frist generation: PFM



Second generation: PEFM

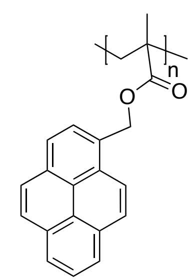


Second generation derivatives



a:b:c:d = 2:0:1:1 PFM
a:b:c:d = 4:1:1.5:1.5 PEFM41
a:b:c:d = 3:1:1:1 PEFM31
a:b:c:d = 2:1:0.5:0.5 PEFM21

Third generation: Polypyrene

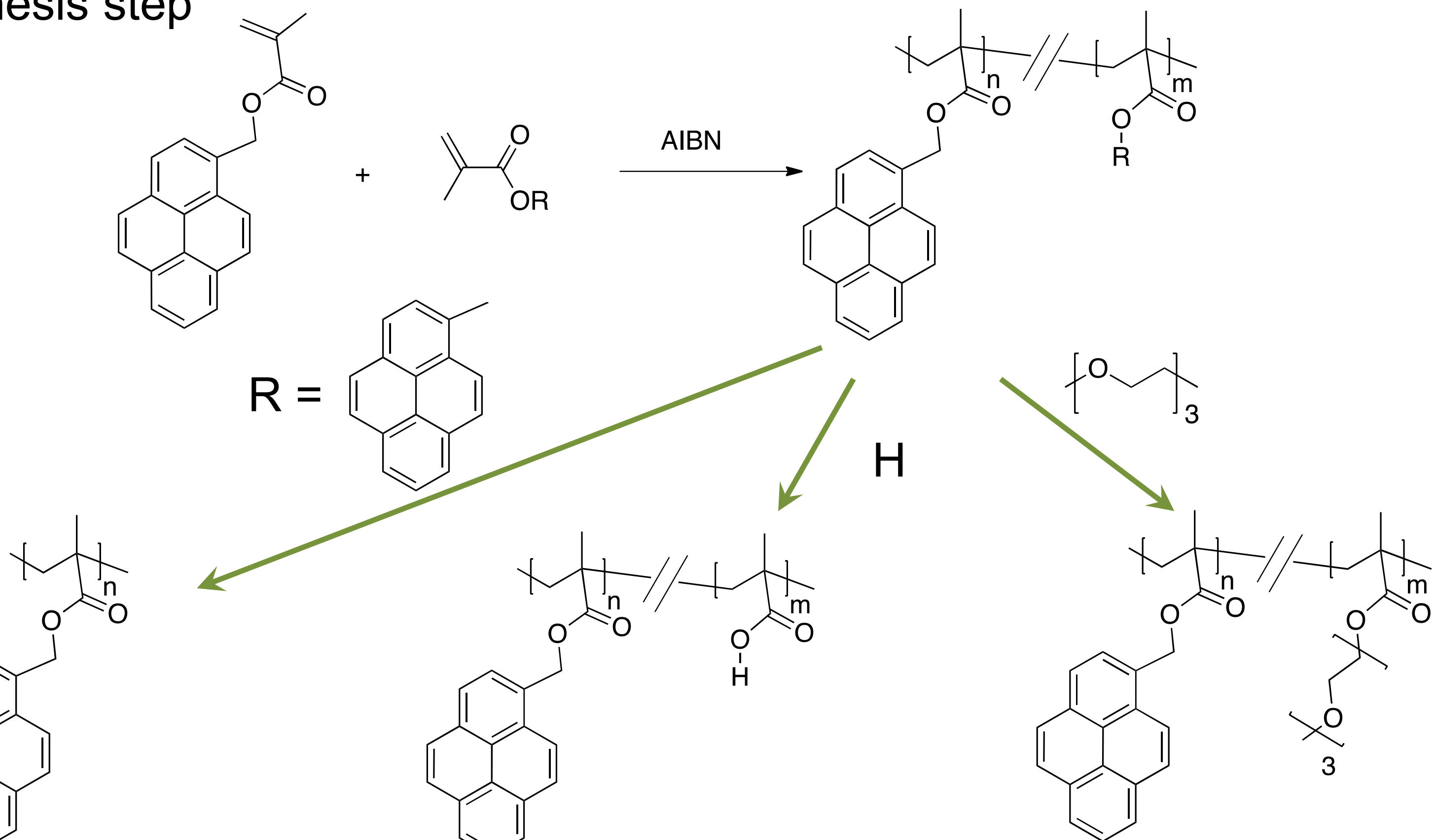


Pyrene unit is connected through a ester bond with a methylmethacrylate unit.

Wu, M.; Liu, G. et *J. Am. Chem. Soc.* **2013,** *132*, 12048–12056.
Wu, M.; Liu, G. et al *J. Mater. Chem. A* **2015**, 3, 3651-3658
Park, S.; Zhao, H.; Liu, G. et al. *J. Am. Chem. Soc.*, **2015**, 137, 2565-2571.

Accomplishments – The versatility of third generation of functional polymer binders to incorporate functionalities via a simple and robust radical polymerization process

Generic synthesis step



PPy
Homopolymer

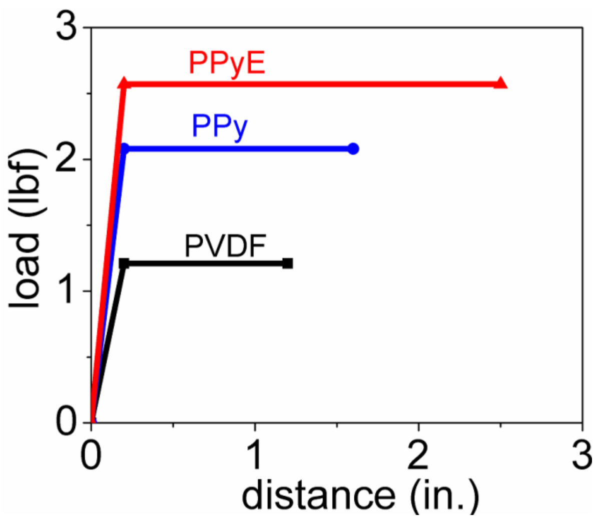
PPyMAA
High adhesive strength

PPyE
Improve ion-transport
Improve adhesion

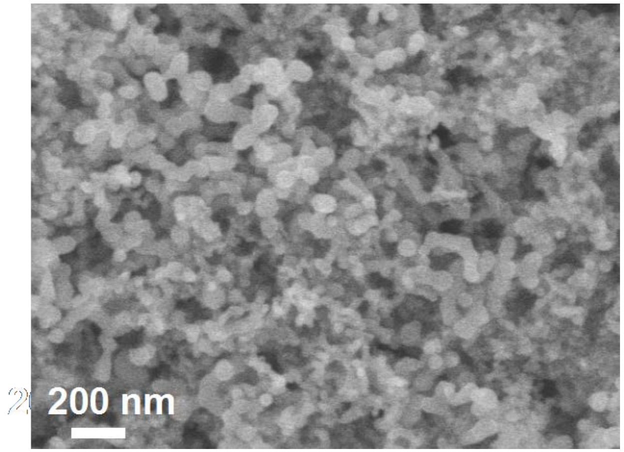
Park, S.; Liu, G. et al. *JACS*, **2015**, *137*, 3181-3184.
Zhao H., Liu, G. et al. *Nano Lett.* **2015**, 15, 7927−7932

Accomplishments – The ethyleneoxide unites in PPyE improve adhesion of the Si composite electrode

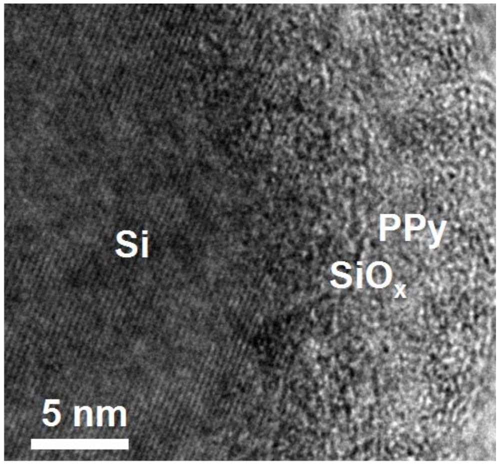
Peel test results of Si based composite electrodes



SEM image of the pristine PPy/Si



TEM images of the pristine PPy/Si electrode

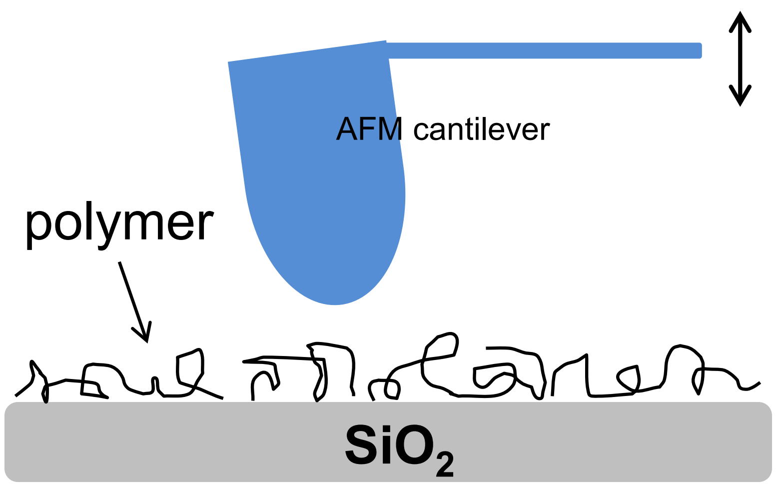


The PPy binder based Si electrode has better adhesion compared to PVDF based electrode. When additional polar functional groups of ethyleneoxide are included in the binder, as PPyE, the electrode adhesion is significantly improved.

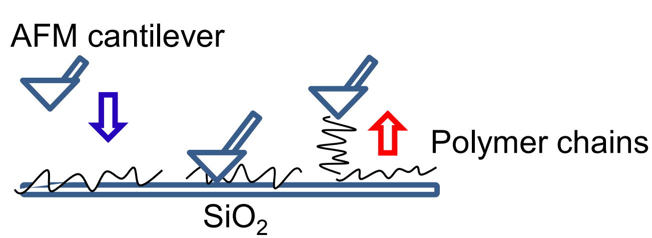
Park, S.; Zhao, H.; Liu, G. et al. *J. Am. Chem. Soc.*, **2015**, 137, 2565-2571.

Accomplishments – PPyMAA has significantly improved adhesion based on AFM measurements

AFM measures the adhesion strength of a single molecule



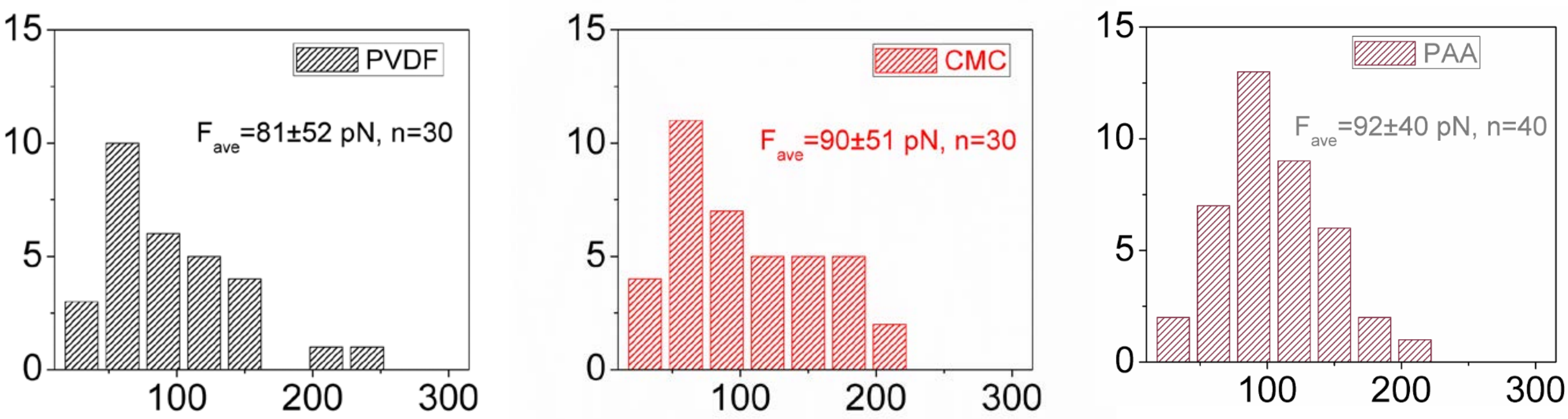
Measurement process



Unbinding force of pulling a single binder on a glass substrate.

Accomplishments – PPyMAA has significantly improved adhesion based on AFM measurements

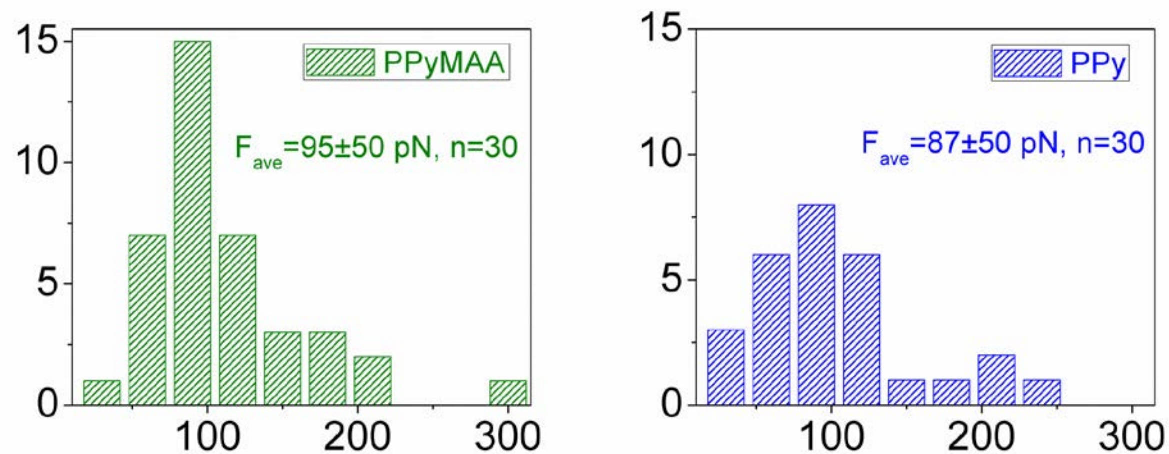
Commercial binders



Experimental binders

Vertical axis counts

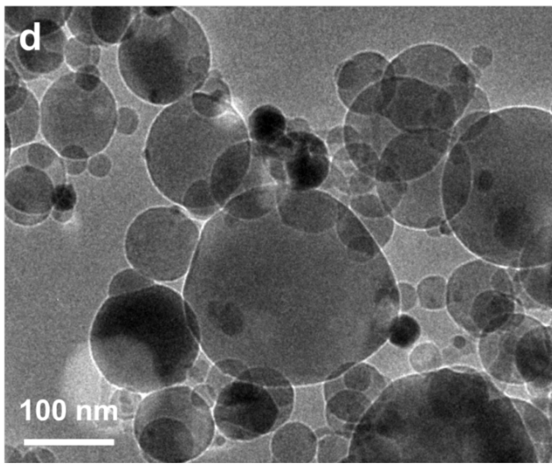
Horizontal axis force in pN

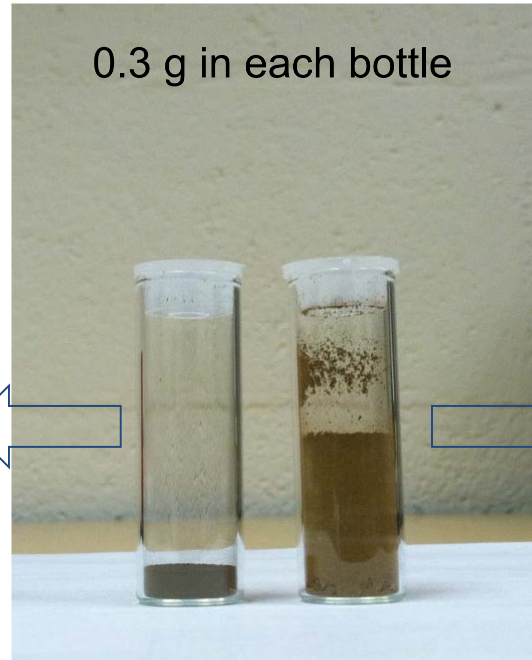


Zhao H., Liu, G. et al. Nano Lett. 2015, 15, 7927−7932

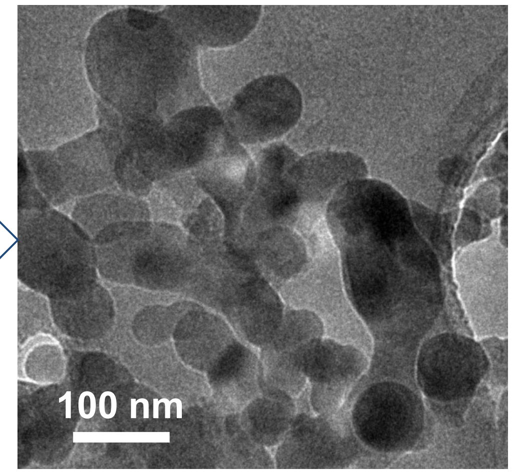
Accomplishments – Pure Si nanomaterials come in different morphology. High tap-density nano-Si has much smaller gravimetric specific surface area.

High tap density





Low tap density

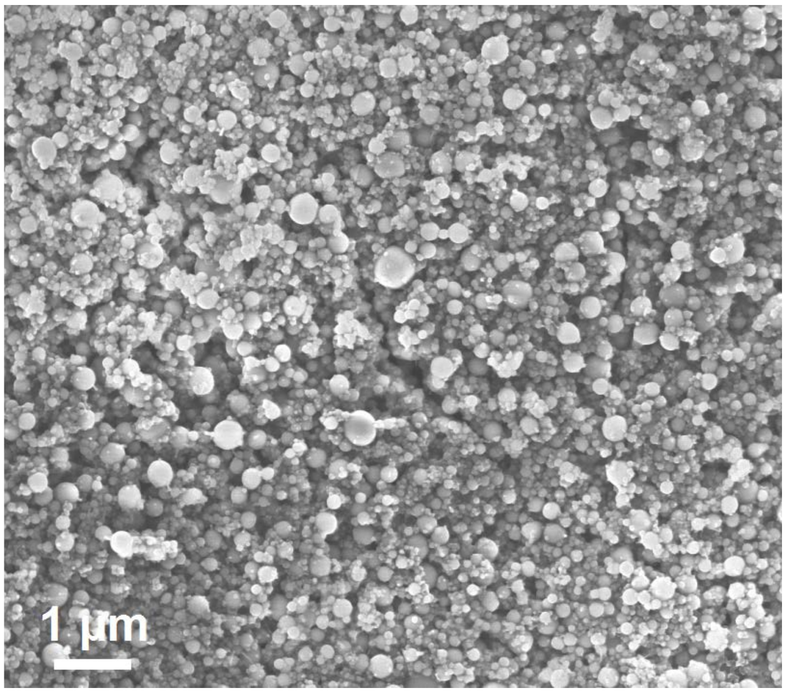


	High tap-density nanoSi	Regular nanoSi
Particle morphology	Well-defined round shaped particles, easily condensed after electrode laminate	particles fused together even after electrode laminate
Particle size	~200 nm	50 nm
Tap density	0.51 g/cm^3	0.10 g/cm^3
BET Surface area	12 m^2/g	55 m^2/g
Electrode porosity (10% PPyMAA)	79%	86%
First cycle efficiency (at C/10 rate)	82.08%	74.39%

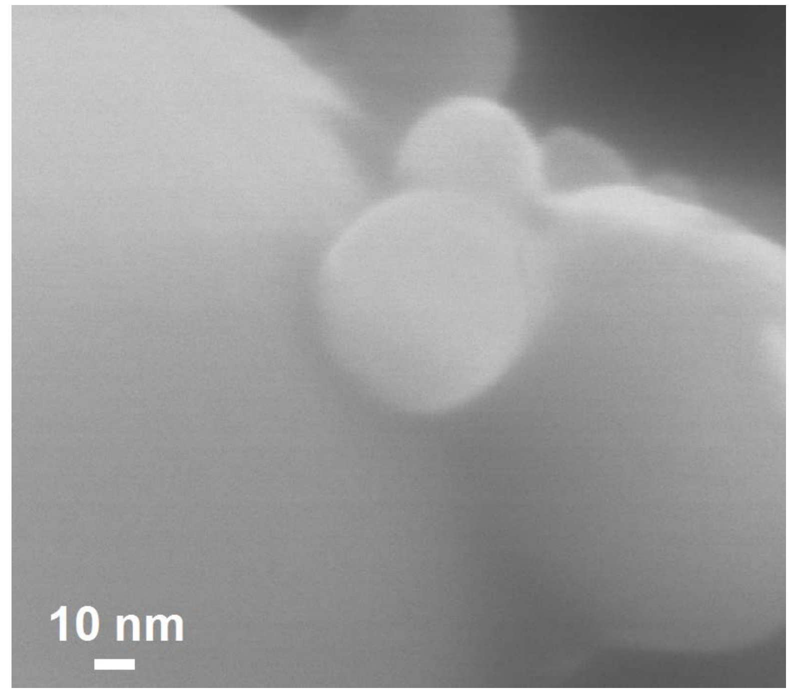
Zhao H., Liu, G. et al. *Nano Lett.* **2015**, 15, 7927−7932

Accomplishments – High tap-density Si nanoparticles form dense electrode by the highly adhesive PPyMAA binder.

Surface SEM of the high tap-density Si nanoparticles electrode



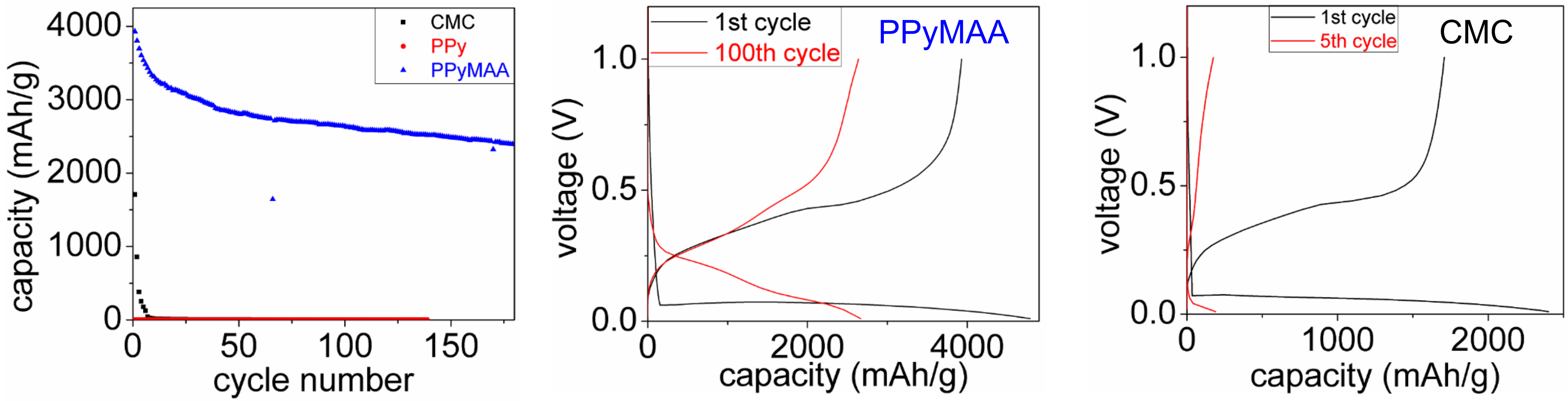
Si nanoparticles bond by PPyMAA



Surface SEM of the high tap-density Si nanoparticles electrode shows small porosity and tight bonding of particles.

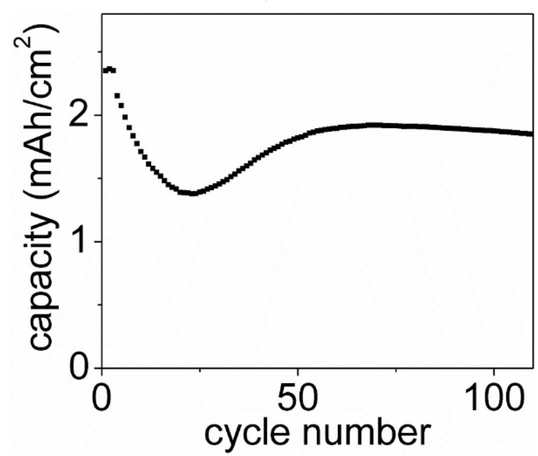
Accomplishments – Highly adhesive functional conductive polymer binder enables high tap-density pure Si electrode

The cycling performance of pure high tap-density nano-Si electrodes based on different binders



		nanoSi/PPyMAA	nanoSi/CMC	nanoSi/graphite/PPyMAA
1st cycle	Q_c^a(mAh/g)	3928.8	1708.5	579.3
	η^b (%)	82.08	71.18	87.05
5th cycle	Q_c^a (mAh/g)	3536.7	175.5	511.5
	η^b (%)	97.27	92.49	98.49
100th cycle	Q_c^a (mAh/g)	2638.1	2.4	461.9
	η^b (%)	98.94	X	99.52

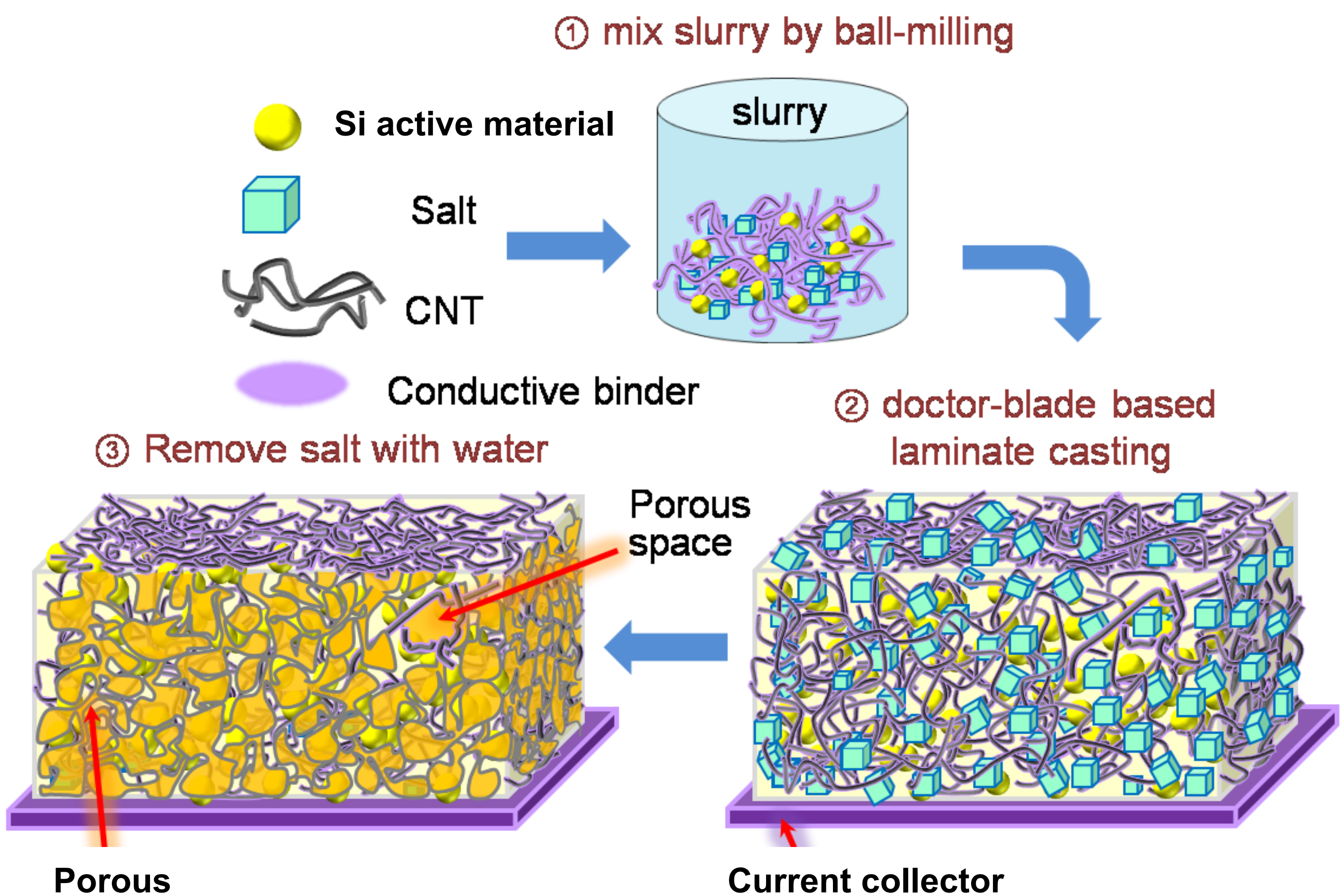
Cycling of high tap-density Si/Graphite/PPyMAA electrode



Electrodes compositions

- Pure nano-Si electrode; Si 90%, PPyMAA 10%.
- Si/Graphite composite electrode: Si 10%, graphite 80%, PPyMAA 10%.

Accomplishments – Introducing control porosity into Si electrode through template



Schematics of forming the template Si based electrode via NaCl dissolution.

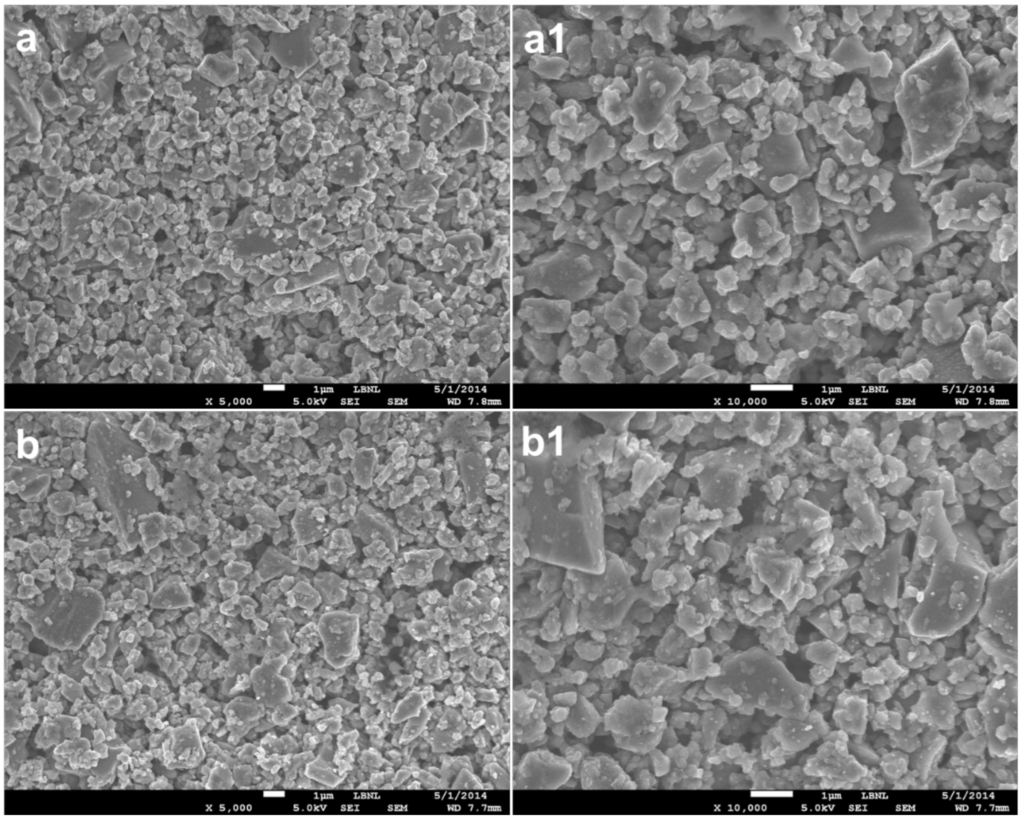
Accomplishments – SEM surface images and X-ray tomography of the SiO_x electrode with and without template

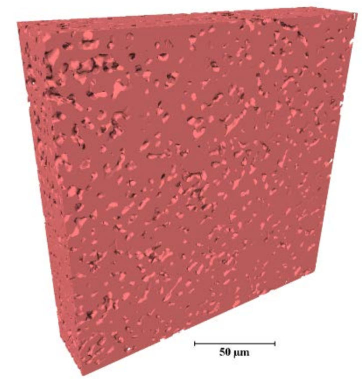
SEM

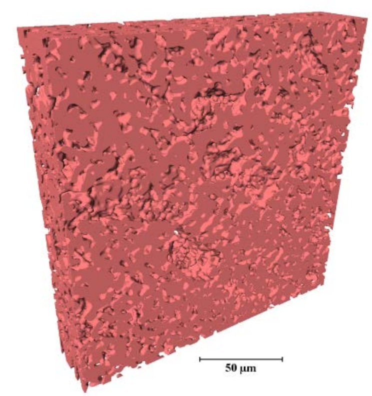
X-ray tomography

No template

Salt template and wash out the NaCl

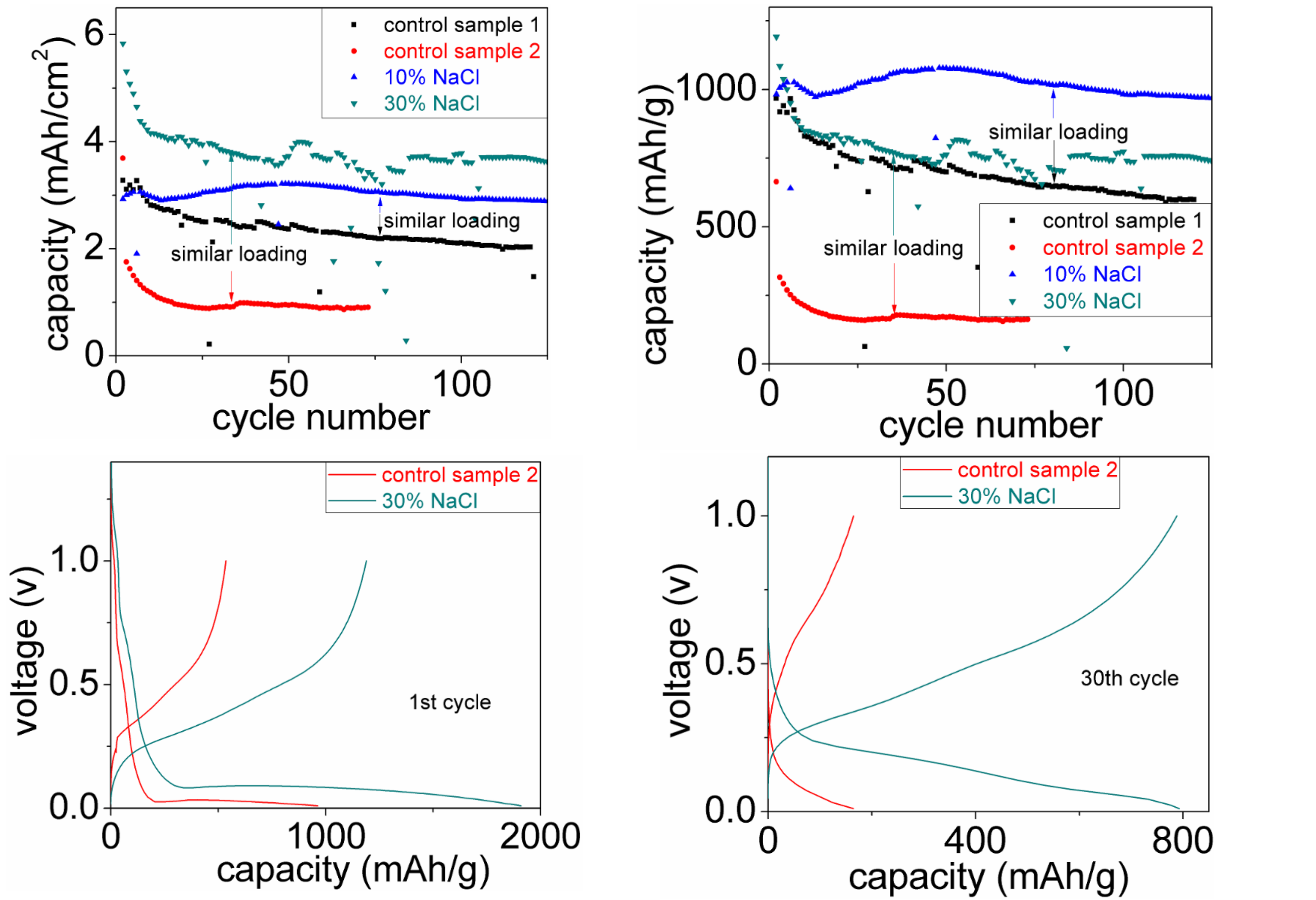






30% by weight of NaCl in the SiO_x in the salt template electrode before washing out the NaCl.

Accomplishments – Controlled porosity improves electrode material utilization and area capacity for high volume change SiO_x materials



SiO_x loading: control sample 1: 3.2 mg/cm^2; control sample 2: 5.0 mg/cm^2

Collaborations - Team functions

1. Lawrence Berkeley National Laboratory

In collaboration with BMR 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 and wide and small angle X-ray diffraction and tomography measurements of the materials and electrode, performed advanced TEM analysis of materials, and performed modeling study of materials and electrodes

2. UC Berkeley

In collaboration with Professor Phillip Messersmith, performs AFM single molecule adhesion tests between different types of binder and SiO_2 glass substrate.

3. Pacific Northwest National Laboratory

Performed In situ TEM analysis of the nano and meso scale phenomenon for the functional conductive polymer binder/Si composite electrodes.

Collaborations - Team functions

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

5. Umicore
Provided pilot scale NanoGrain experimental Si materials.

6. Hydro Quebec
Provided new Si and SiO_x based materials. Perform carbon coating on SiO_x. Hosting Berkeley Lab visiting students.

7. Zeptor Corporation
Provide new carbon coated SiO_x based materials, and carbon nanofiber coated copper current collector.

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

9. FMC Lithium
Provided lithium based materials, especially Stabilized Lithium Metal Powder (SLMP) and provide guidance of how to use SLMP.

Proposed Future Work

1. The team are on schedule to accomplish the milestones defined in the remaining FY2016.

2. This project ends on FY2016.

Summary

1. A class of side-chain conducting functional polymer binder and its derivatives are synthesized via radical polymerization process.
2. A highly adhesive functional conductive binder was synthesized.
3. This highly adhesive binder enables high tap-density nano-Si materials made into highly dense pure Si electrode, and cycled at high capacity.
4. The adhesion force of different binders are quantified by single molecule AFM unbinding measurement.
5. Hierarchical design by salt template Si based electrode was demonstrated. The electrode was cycled over 3.5 mAh/cm^2.