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: 60%

Budget
Total project funding
-DOE share: $2,000K, 100%
FY14 funding $500K
FY15 funding $500K
FY16 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, Cheng Wang, Andrew Minor)
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 2014

1. Design and synthesis three 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. (Complete)
4. Design and synthesize one type of vinylene carbonate derivative that targeted to protect Si surface, and test it with Si based electrode. (Complete)

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 (on schedule)
4. Apply hierarchical electrode design to achieve a 3 mAh/cm^2 loading. (go/no-go, 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 on a radical polymerizations process.

2. Using time of flight secondary ion mass spectrometry (TOF SIMS) to understand the binder and Si particles adhesion

Adhesion functional groups on the binder is critical to provide electrode mechanical properties; TOF SIMS method reveals the covalent nature of the bonding between the binder and Si particles.

3. Hierarchical electrode designs to improve energy density

Porous carbon coating on SiO, and the covalent bonding between the binder and Si particles provide the stability of the Si based electrode at very low binder content.

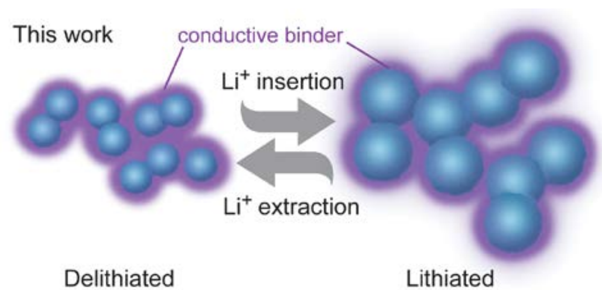
4. Prelithiation to further improve energy density

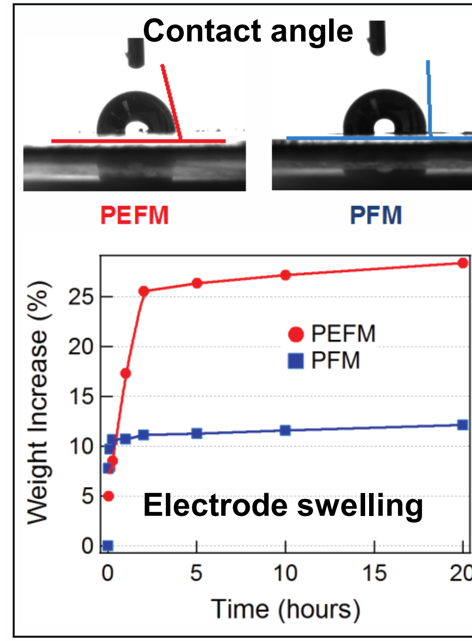
Use Stabilized Lithium Metal Powder (SLMP) to prelithiate Si electrode to decrease first cycle lithium loss.

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

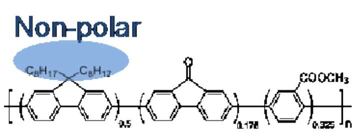
Functional conductive binder design
Combining:
1. Electrically conductivity
2. Binding – adhesive
3. Li-ion transport

Functional conductive polymer binder/Si electrode



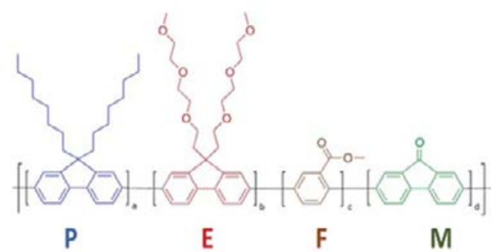


Frist generation: PFM



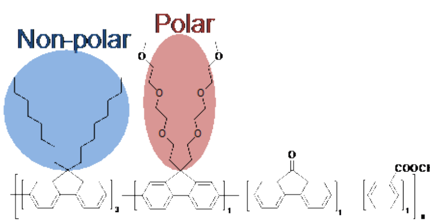
Electric conduction

Second generation derivatives

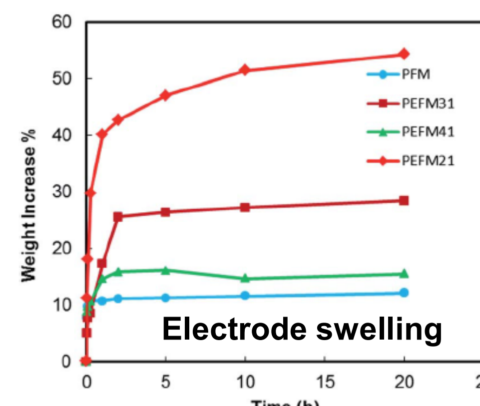


a:b:c:d = 2:0:1:1 PFM
a:b:c:d = 4:1:1.5:1.5 PEFM41
a:b:c:d = 3:1:1:1 PEFM31
a:b:c:d = 2:1:0.5:0.5 PEFM21

Second generation: PEFM



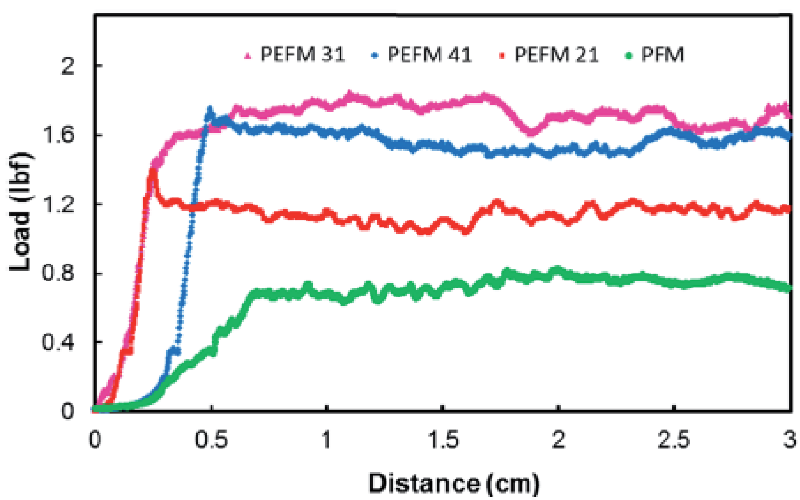
Electric conduction



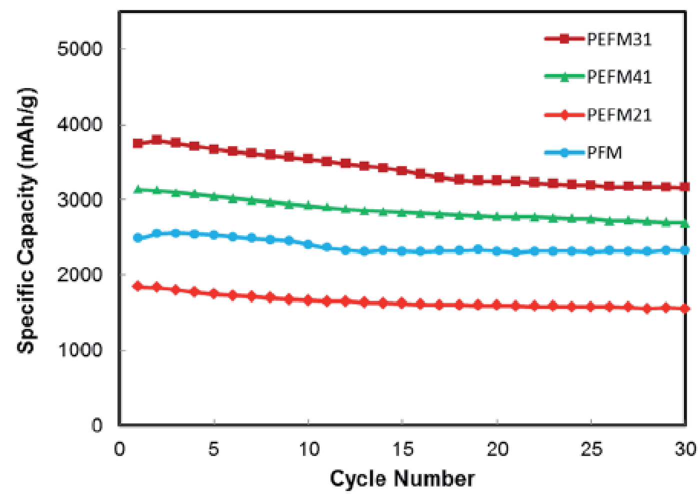
Wu, M.; Liu, G. et al JACS **2013,** *132*, 12048–12056.
Wu, M.; Liu, G. et al J. Mater. Chem. A **2015**, 3, 3651-3658

Accomplishments – The performance of second generation of functional conductive polymer binders

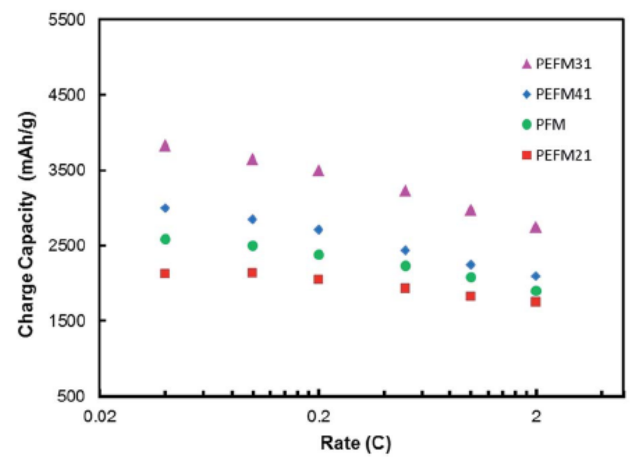
Electrode peel strength



Electrode cycling performance



Electrode rate performance

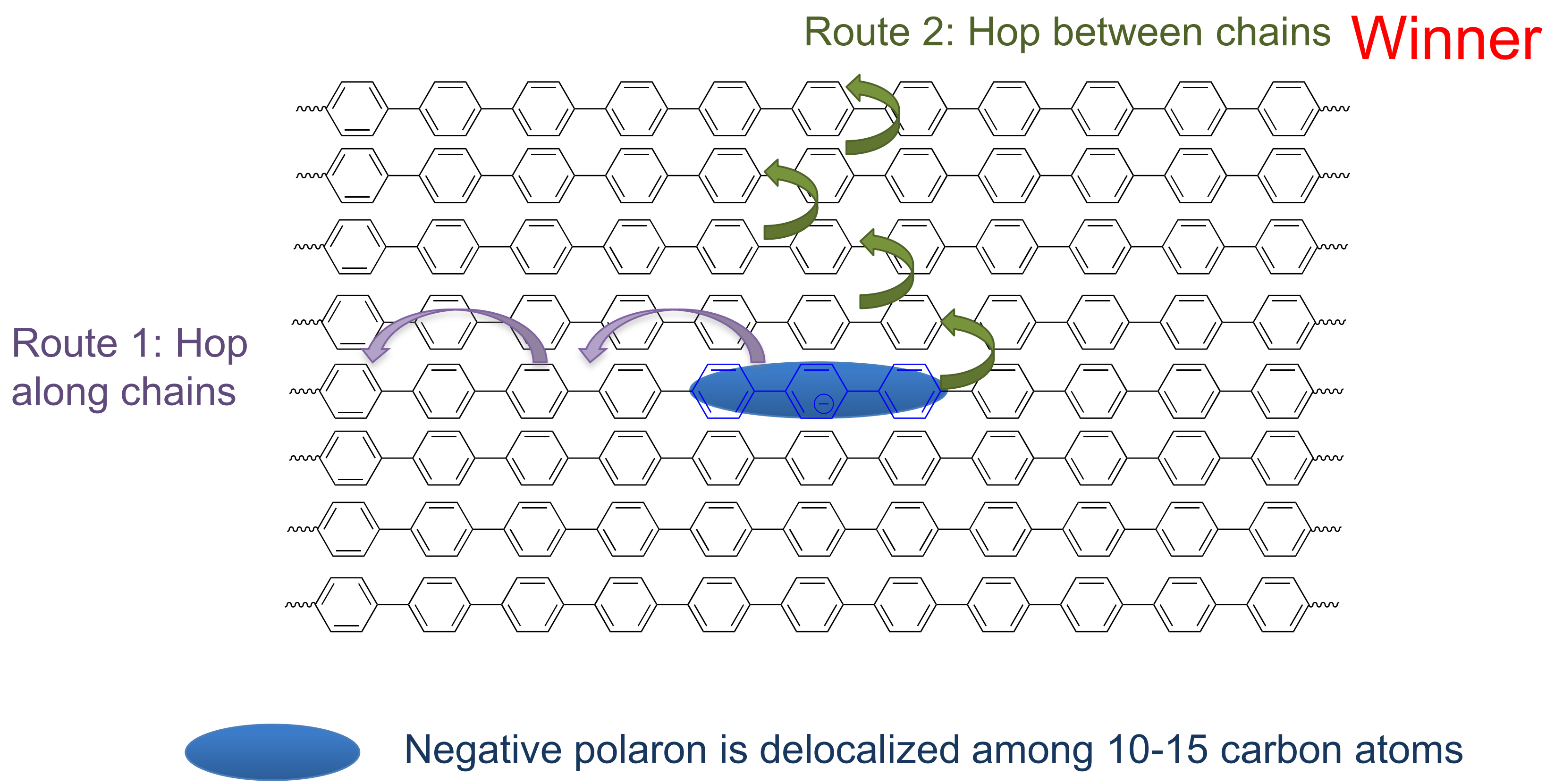


There is an optimum polarity for the binders

Wu, M.; Liu, G. et al *J. Mater. Chem. A* **2015**, 3, 3651-3658

Accomplishments – Third generation of functional conductive polymer binder provides flexibility in synthesis and introduction of functionalities

The charge mobility in a conductive polymer

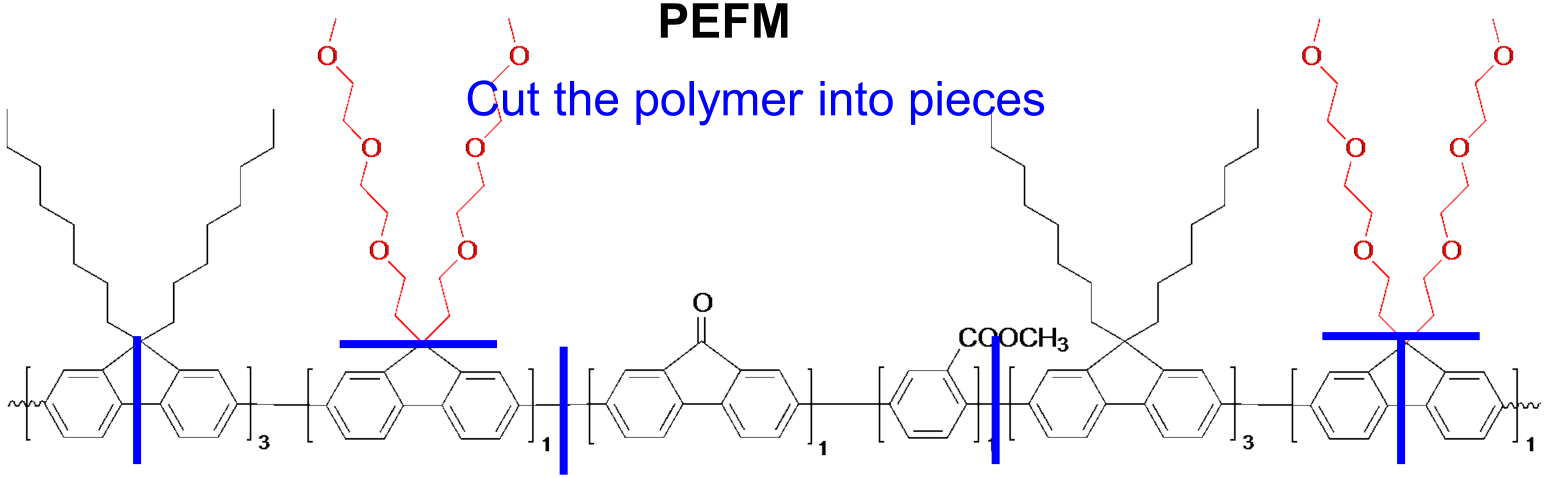


Negative polaron is delocalized among 10-15 carbon atoms

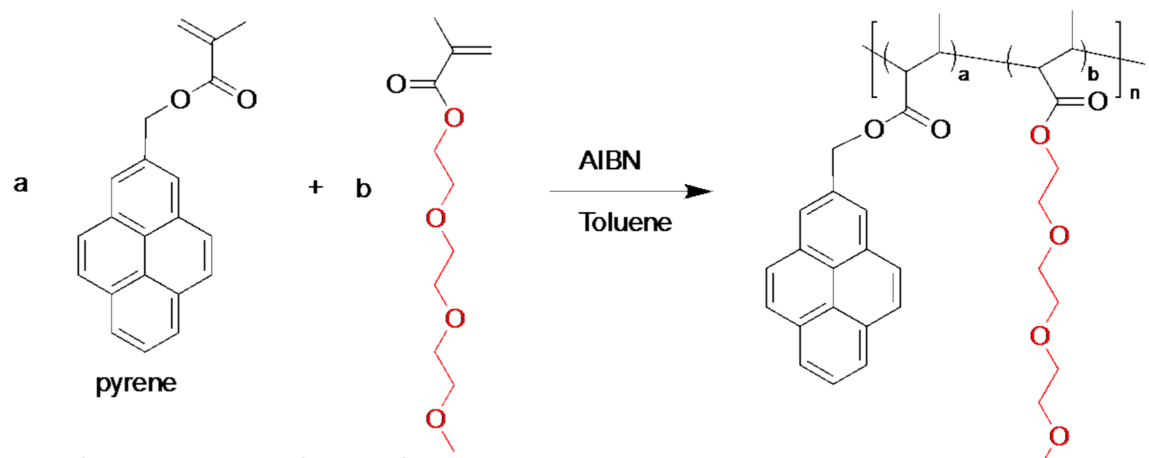
Park, S; Zhao, H.; Ai, G.; Wang, C.; Song, X.; Yuca, N.; Battaglia, V.S.; Yang, W.; and Liu, G. Side-chain conducting and phase-separated polymeric binders for high performance silicon anodes in lithium-ion batteries *J. Am. Chem. Soc.*, **2015**, 137, 2565-2571.

Accomplishments – Third generation of functional conductive polymer binder provides flexibility in synthesis and introduction of functionalities

PEFM

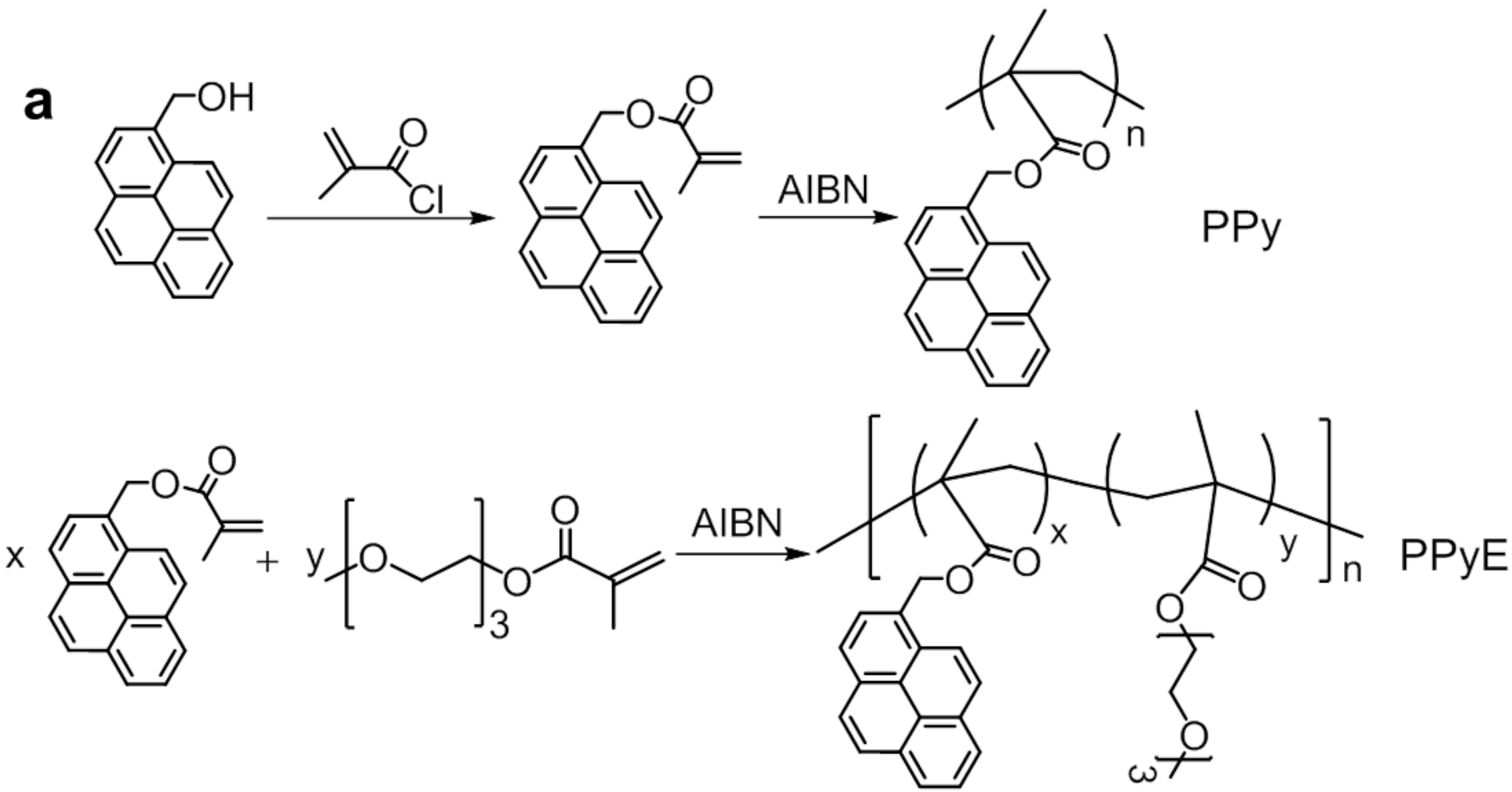


Reassemble them into polymerizable units



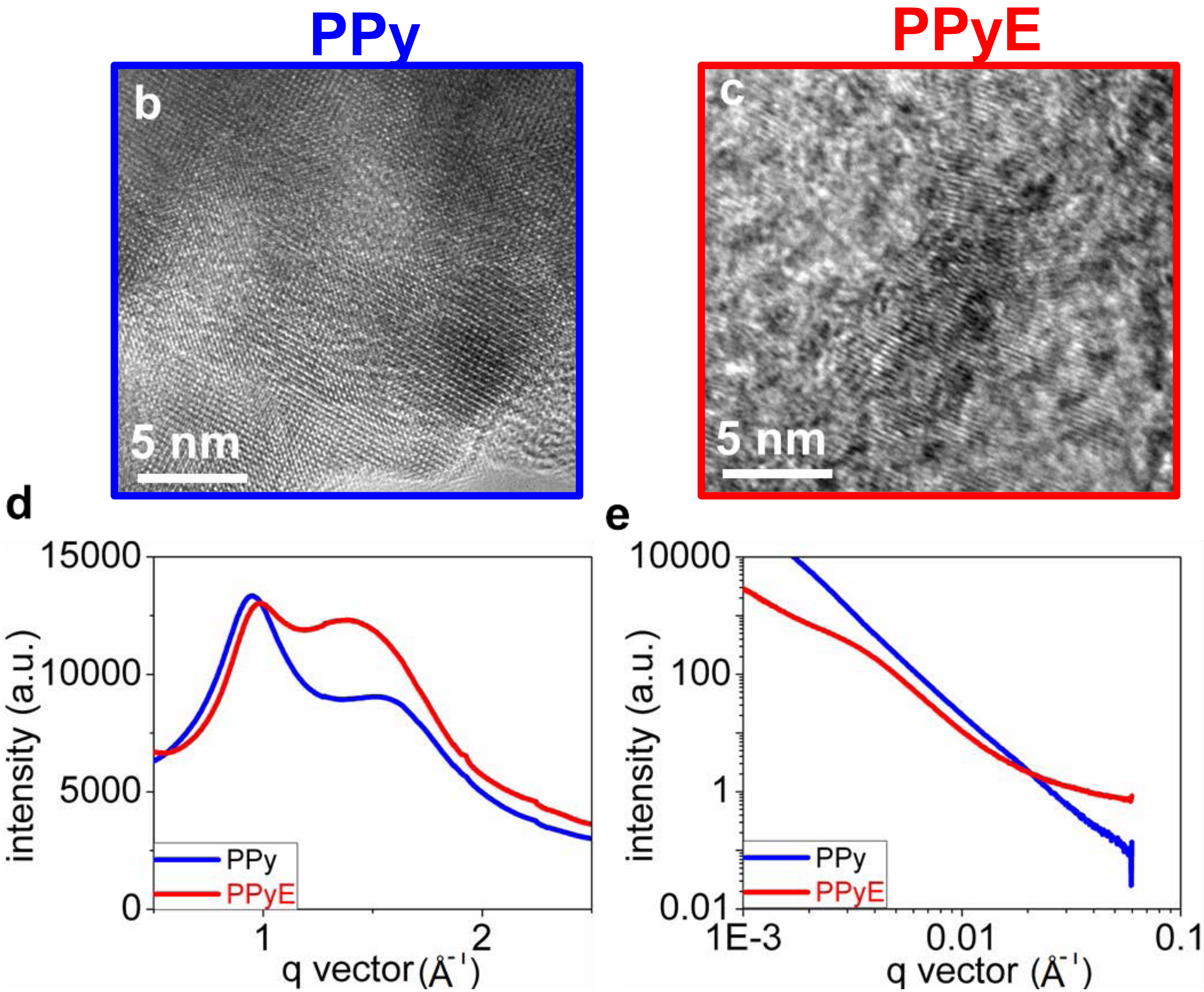
Park, S.; Zhao, H.; Liu, G. et al. J. Am. Chem. Soc., **2015**, 137, 2565-2571.

Accomplishments – Synthesis of third generation side-chain conducting polypyrene conductive polymer binders



Park, S.; Zhao: H. Liu, G. et al. *JACS*, **2015**, *137*, 3181-3184.

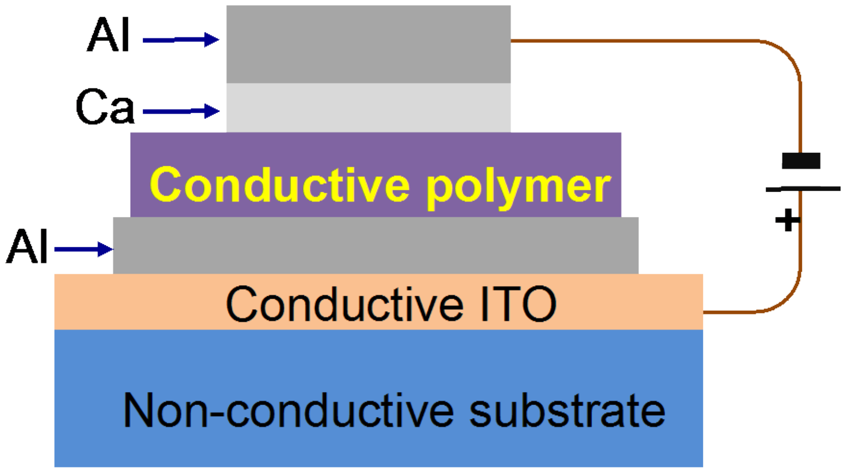
Accomplishments – Morphology of polypyrene conductive polymer binders



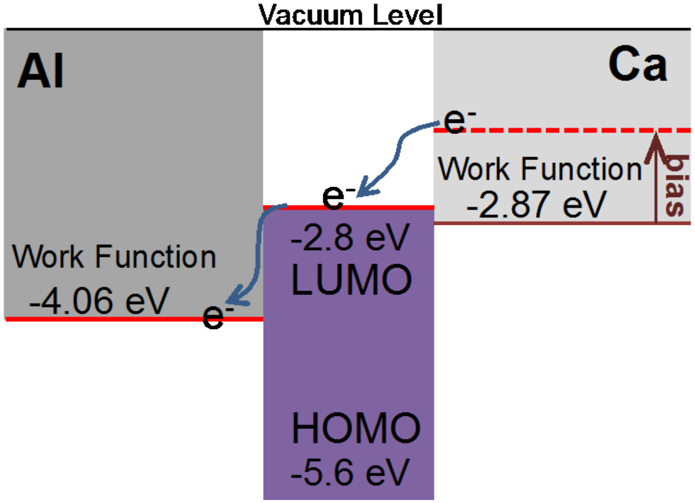
Park, S.; Zhao: H. Liu, G. et al. *JACS*, **2015**, *137*, 3181-3184.

Accomplishments – Measure the electron mobility of the conductive polymer

Experimental set up

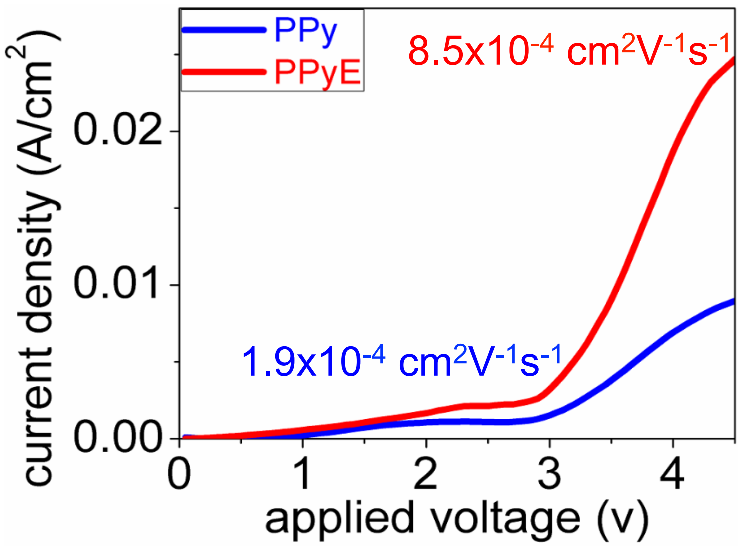


Energy diagram



Park, S.; Zhao: H. Liu, G. et al. *JACS*, **2015**, *137*, 3181-3184.

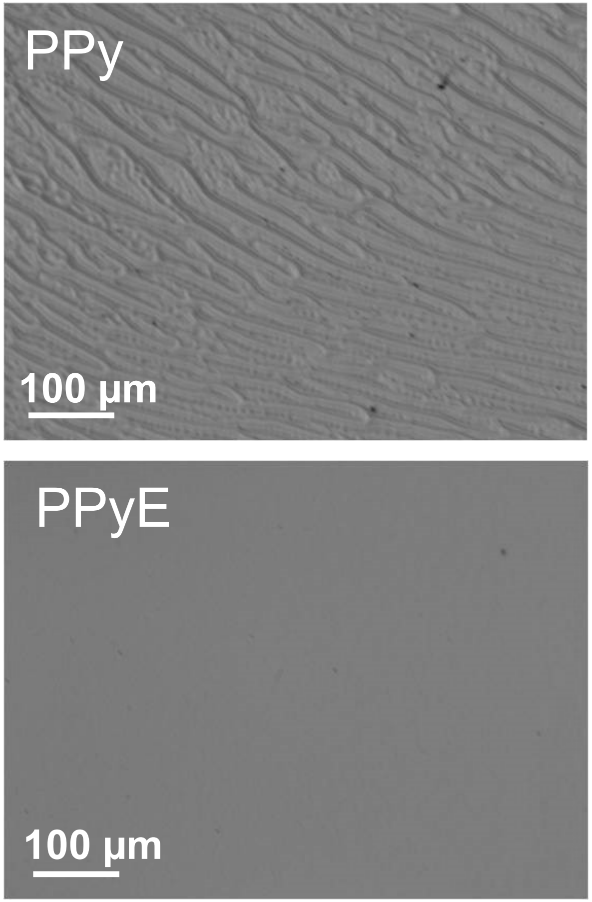
Accomplishments – Measure the electron mobility of the conductive polymer



The current prefers injection limited model instead of transport-limited model, and the *J*–*V* characteristics are dominated by space-charge limited current, given by the Mott–Gurney law

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu_n \frac{(V - V_{bi})^3}{L^3}$$

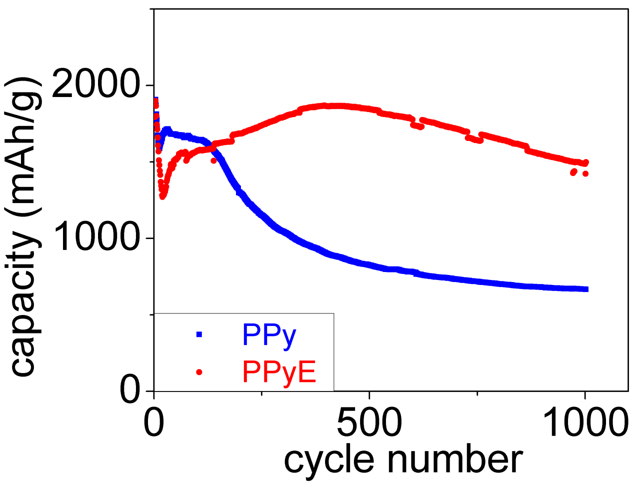
Optical images

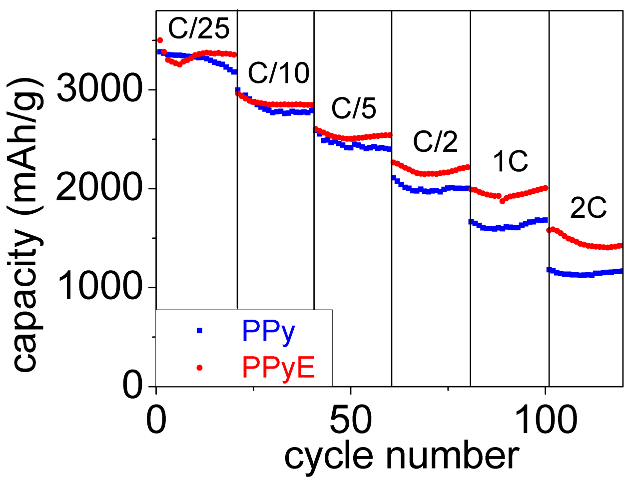


Park, S.; Zhao: H. Liu, G. et al. *JACS*, **2015**, *137*, 3181-3184.

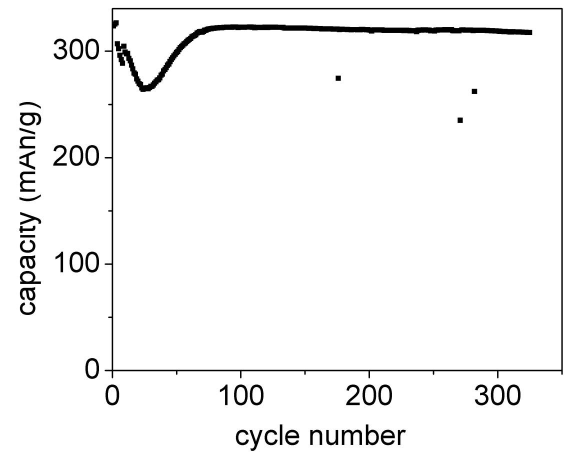
Accomplishments – Polypyrene (PPy) type of binders works with a broad range of anode materials

Si material with Ppy of binders



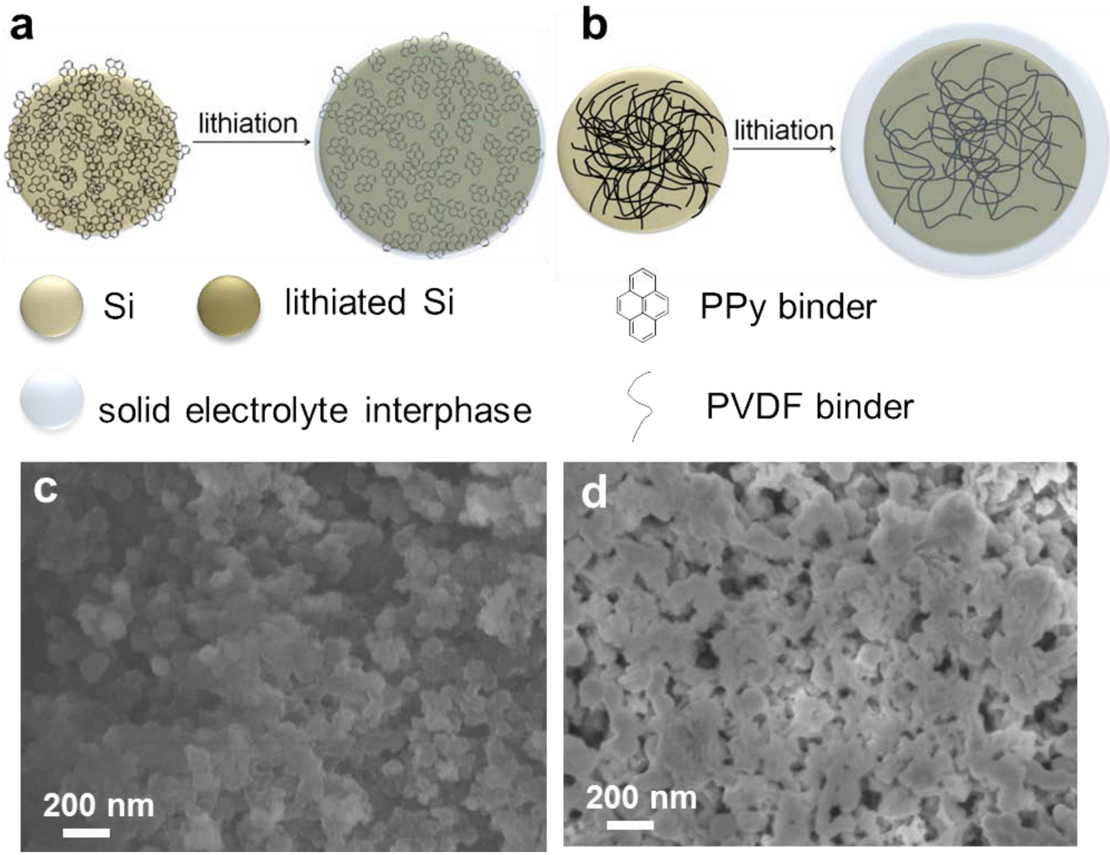


Graphite/Ppy



The versatile synthesis to include different functional groups makes the functional polymer binders suitable for a broad spectra of applications.

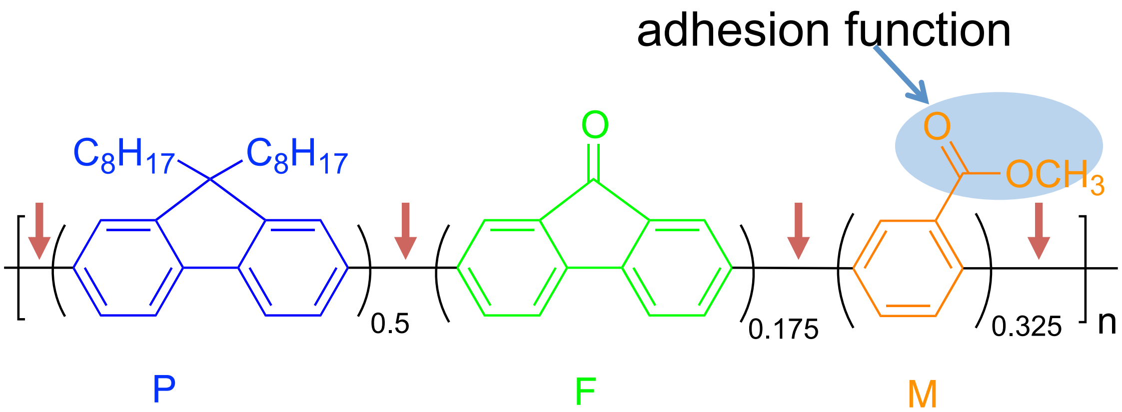
Accomplishments – Polypyrene binder maybe able to stabilized Si surface by forming an elastic coating



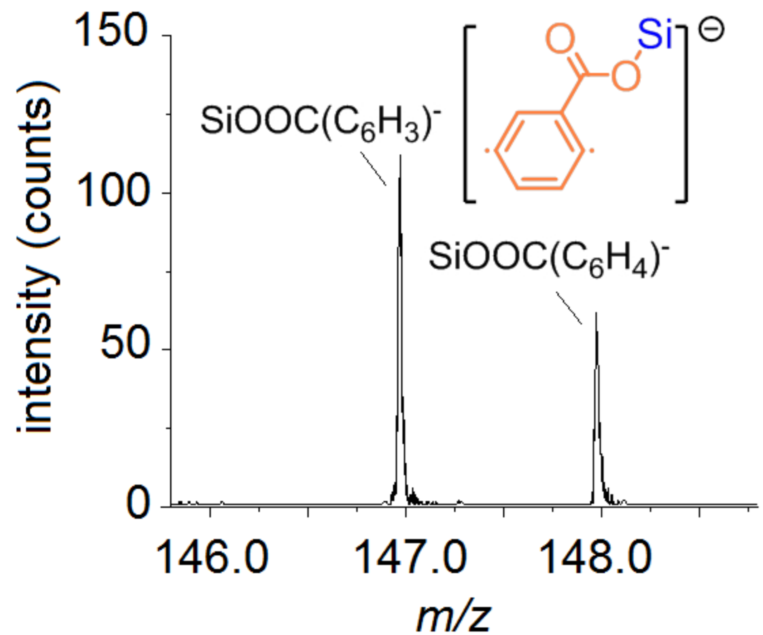
After 500 cycles **After only 40 cycles**

Park, S.; Zhao: H. Liu, G. et al. *JACS*, **2015**, *137*, 3181-3184.

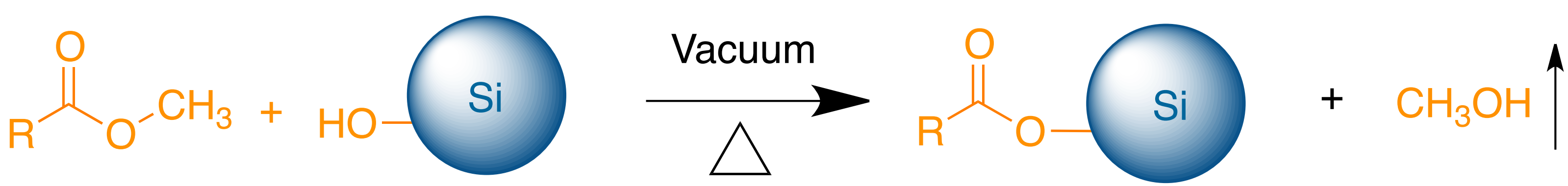
Accomplishments – Using time of flight secondary ion mass spectrometry (TOF SIMS) to understand the covalent binding between binder and Si particles



TOF-SIMS measurement



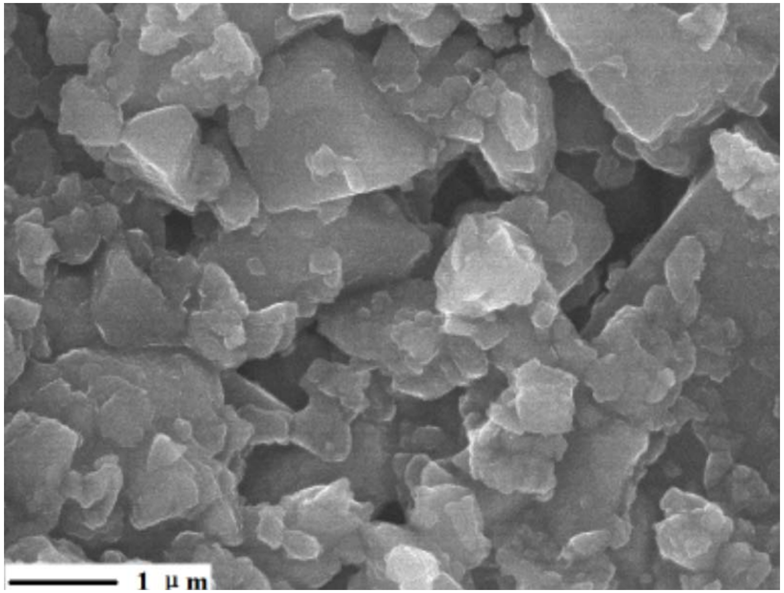
Electrode drying process



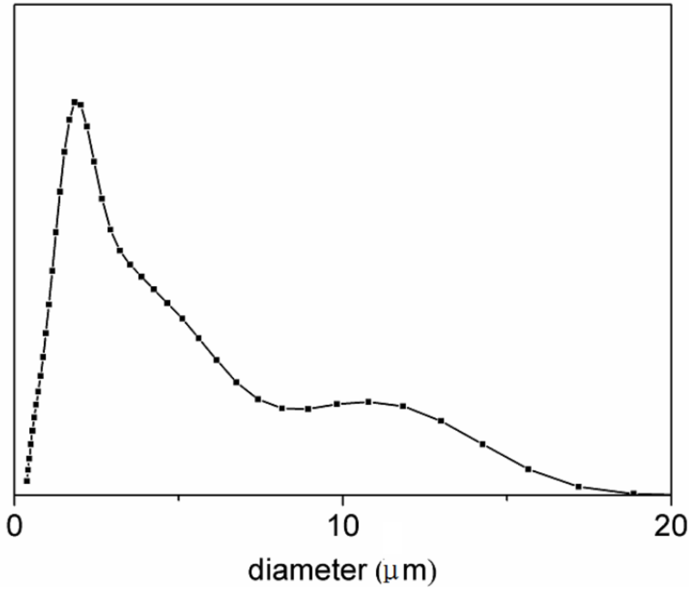
H. Zhao, G. Liu et al *Nano Lett*. **2014**, 14, 6704-6710

Accomplishments - Hierarchical electrode designs to improve Si based electrode energy density: Materials choice

SEM image



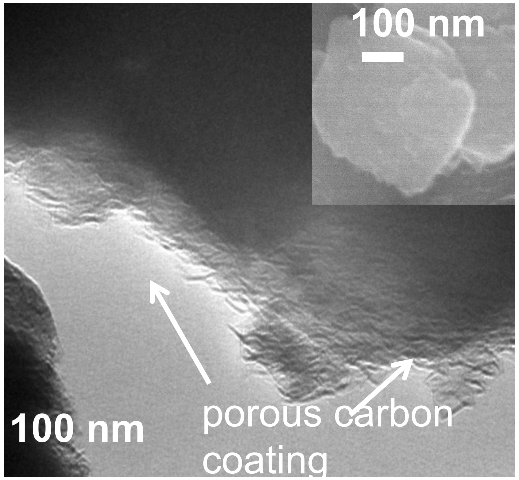
PSA Analysis



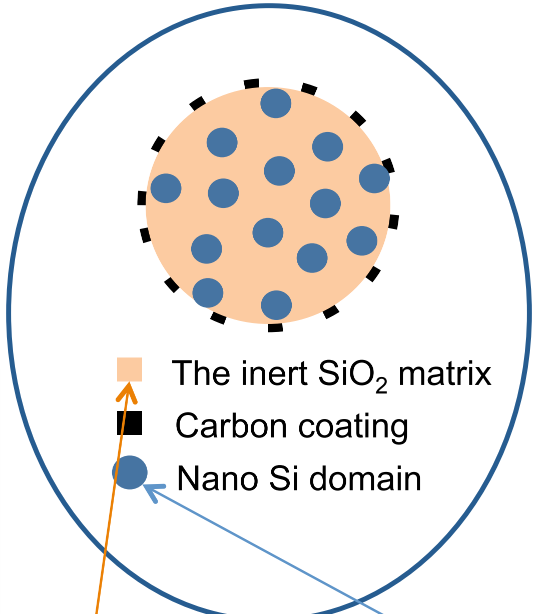
Carbon coated SiO micron size particles

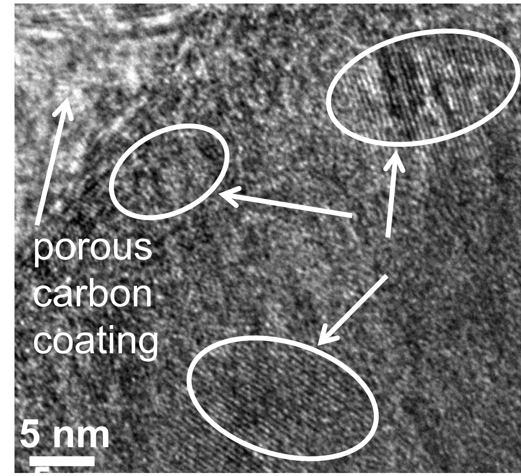
H. Zhao, G. Liu et al *Nano Lett*. **2014**, 14, 6704-6710

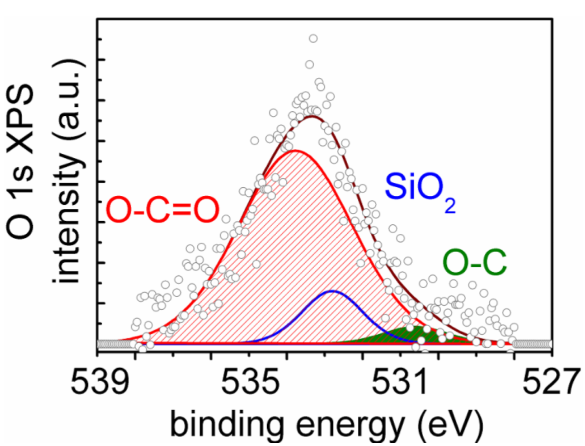
Accomplishments - Hierarchical electrode designs to improve SiO based electrode energy density: Interface engineering

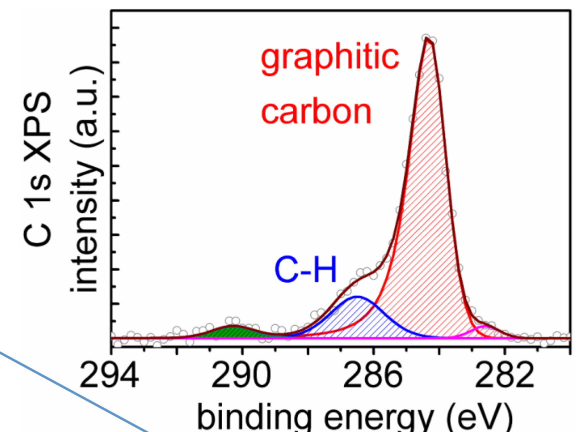


Carbon coated SiO





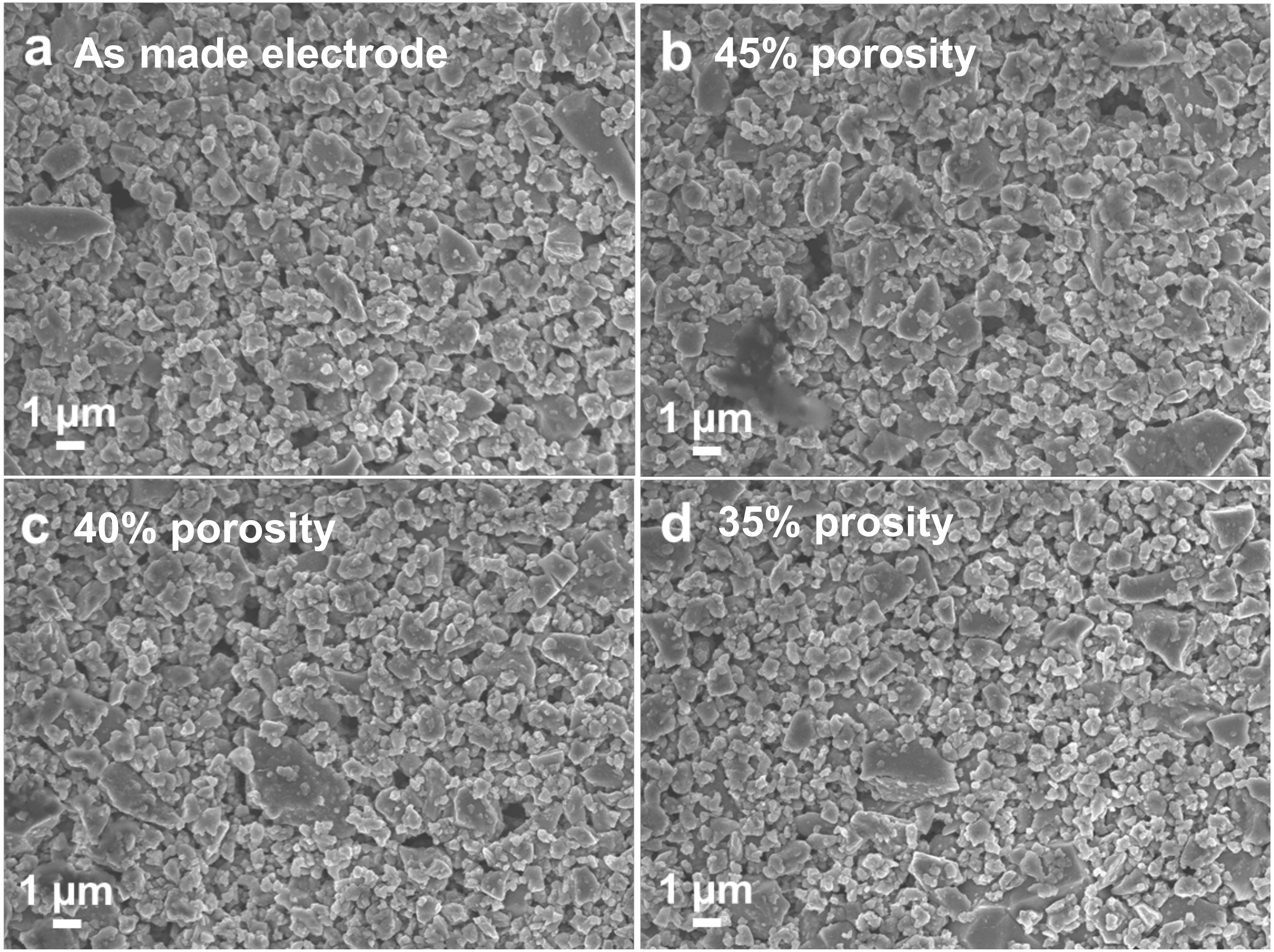




Design a binder that binds with SiO_2 matrix, leaving Si for lithiation/delithiation

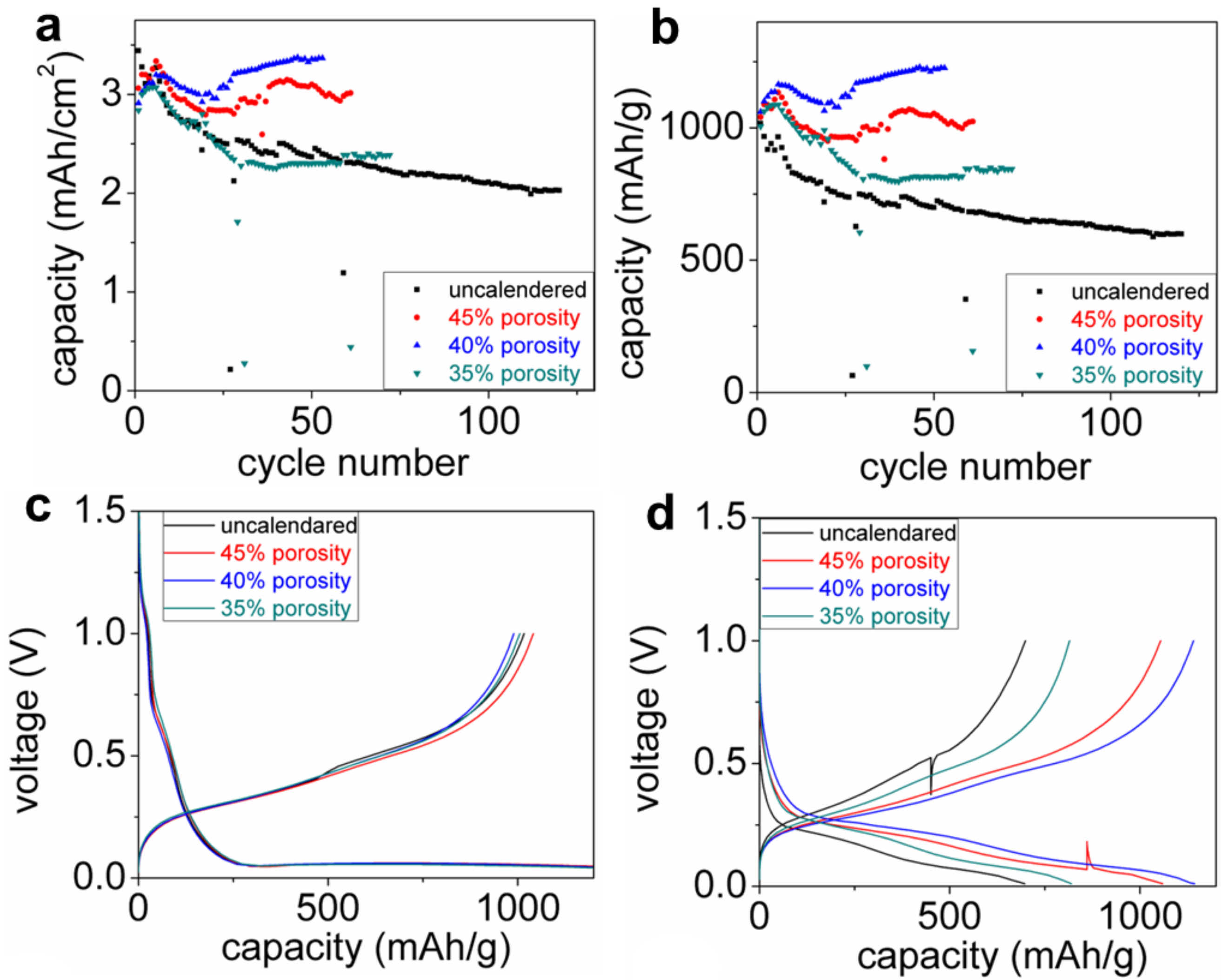
H. Zhao, G. Liu et al *Nano Lett*. **2014**, 14, 6704-6710

Accomplishments – Hierarchical electrode designs to improve energy density: higher electrode density through calendaring



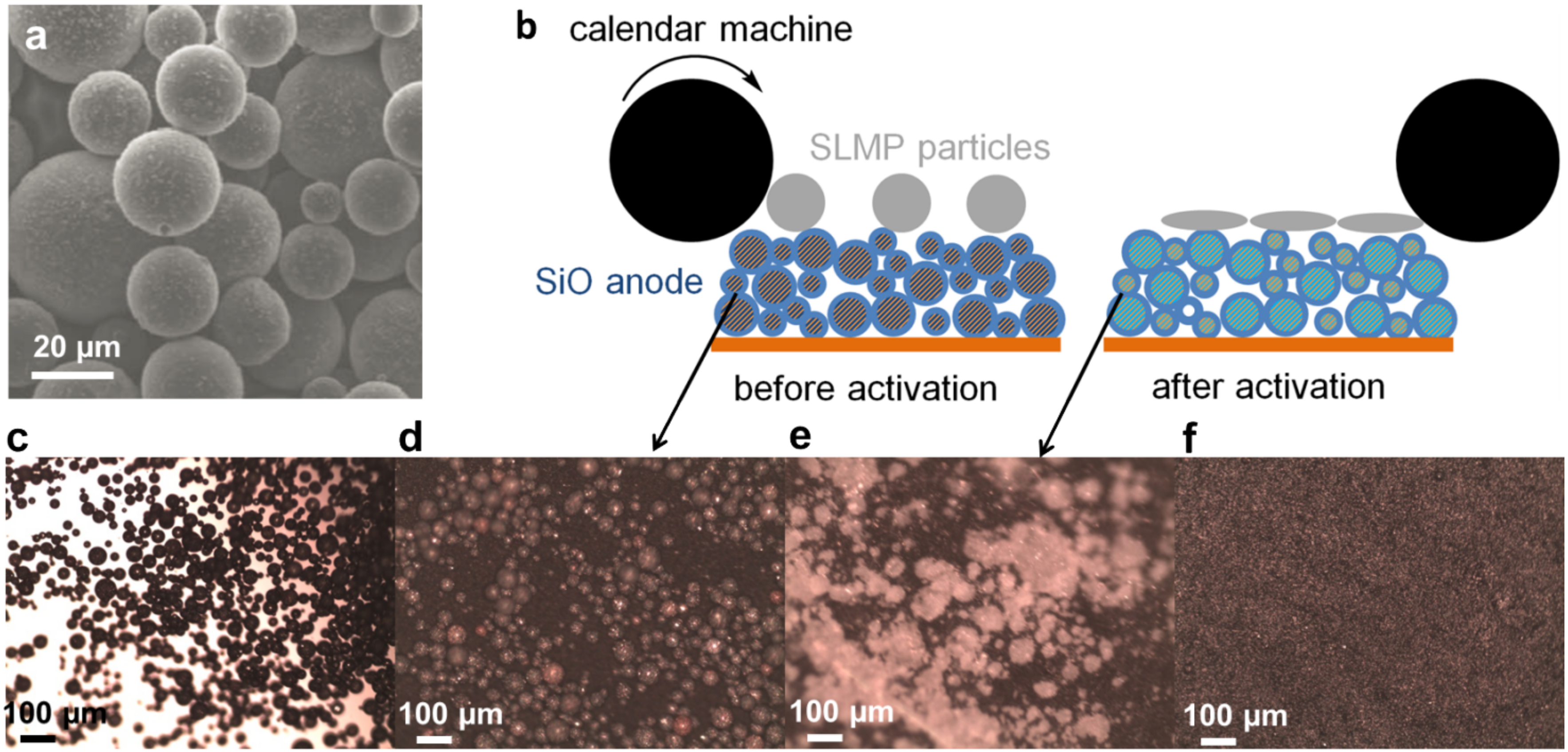
H. Zhao, G. Liu et al *ACS Appl. Mater. Interfaces* **2015**, 7(1) 862-866

Accomplishments – Hierarchical electrode designs to improve energy density: high loading electrode cycling



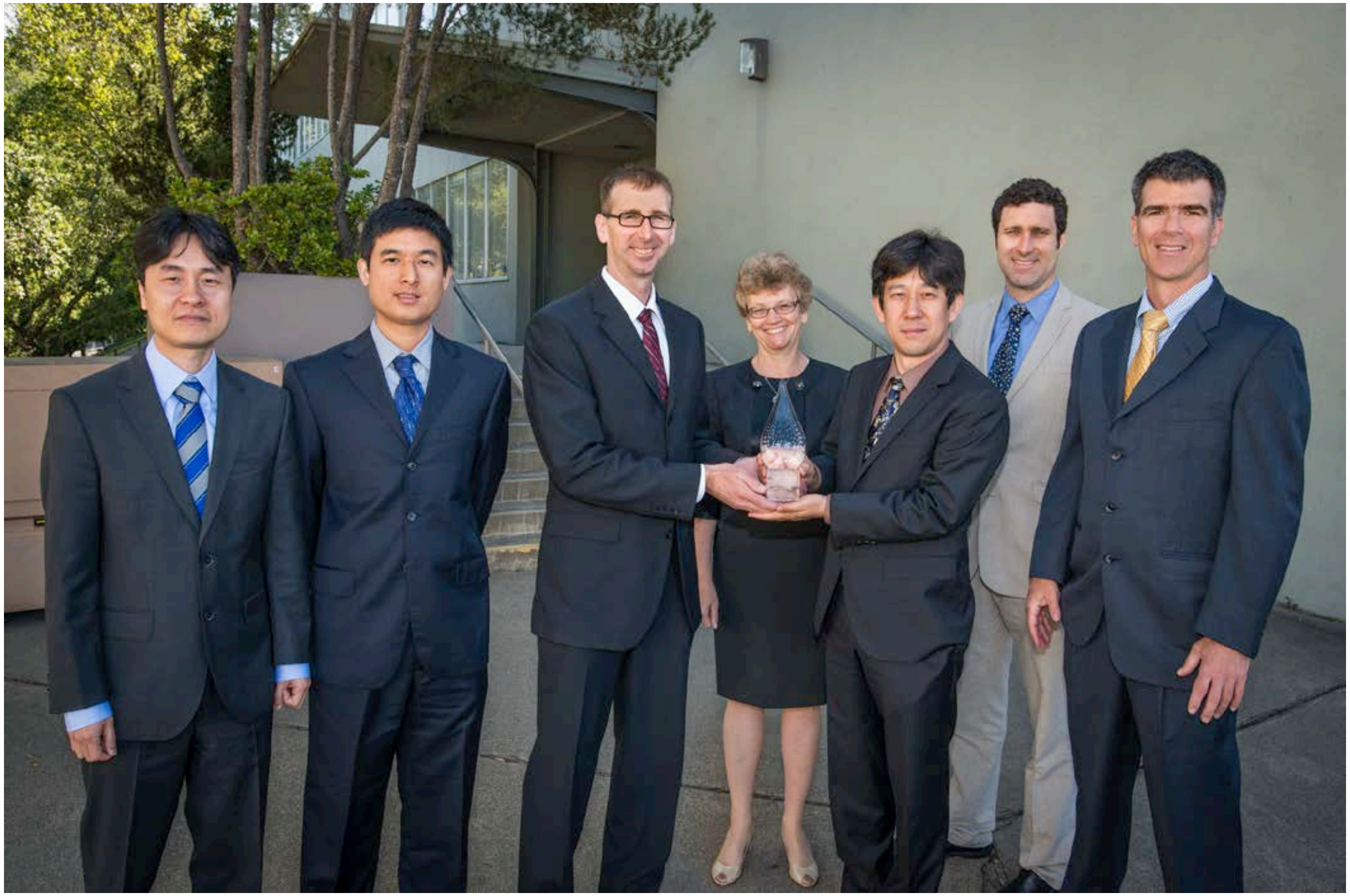
H. Zhao, G. Liu et al *ACS Appl. Mater. Interfaces* **2015**, 7(1) 862-866

Accomplishments - Prelithiation using Stablized Lithium Metal Powder (SLMP®) to further improve energy density



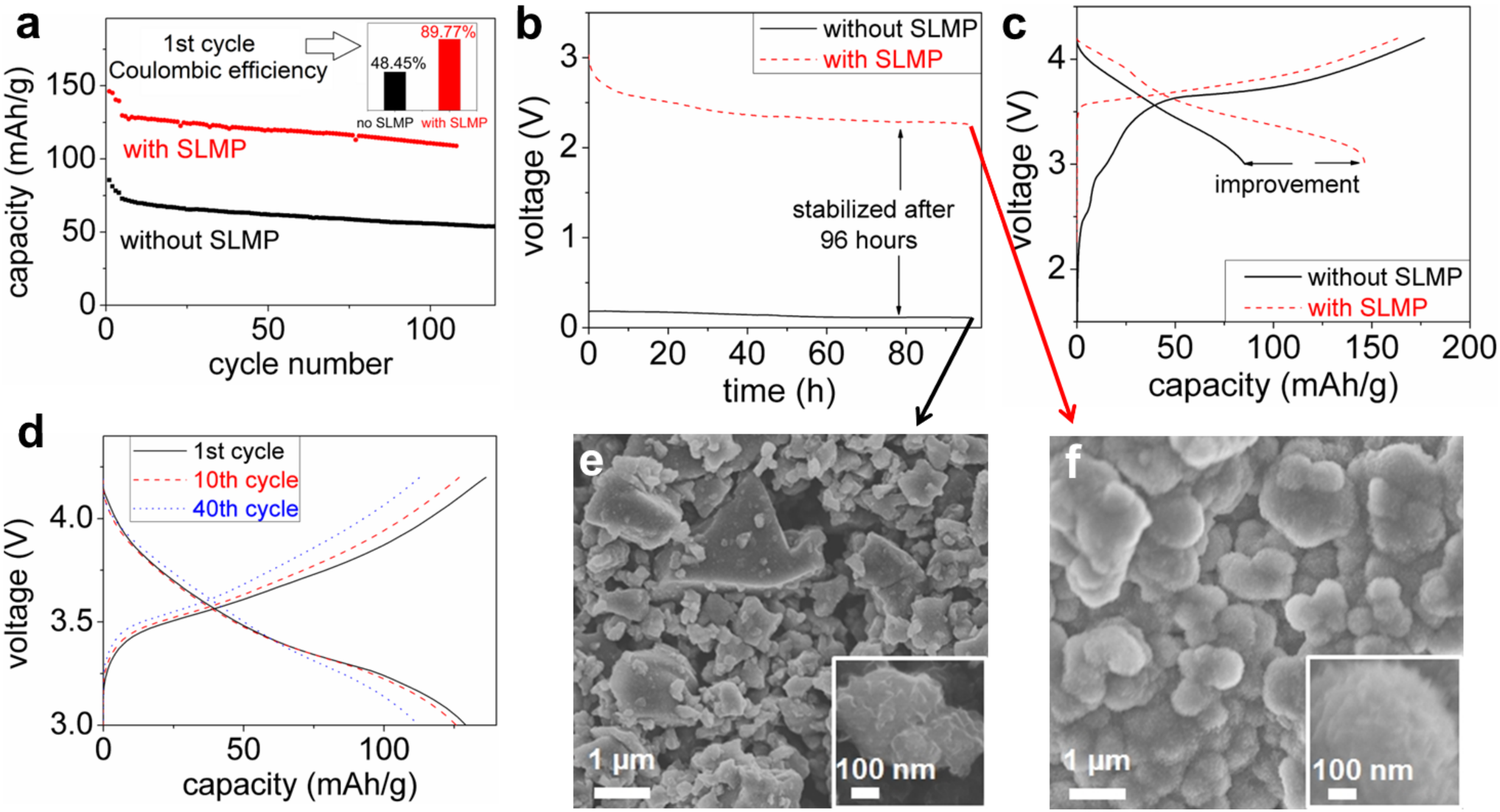
H. Zhao, G. Liu et al *Nano Lett*. **2014**, 14, 6704-6710

Accomplishments - Prelithiation using SLMP to further improve energy density: won the FMC Corporation Scientific Achievement Award in 2014



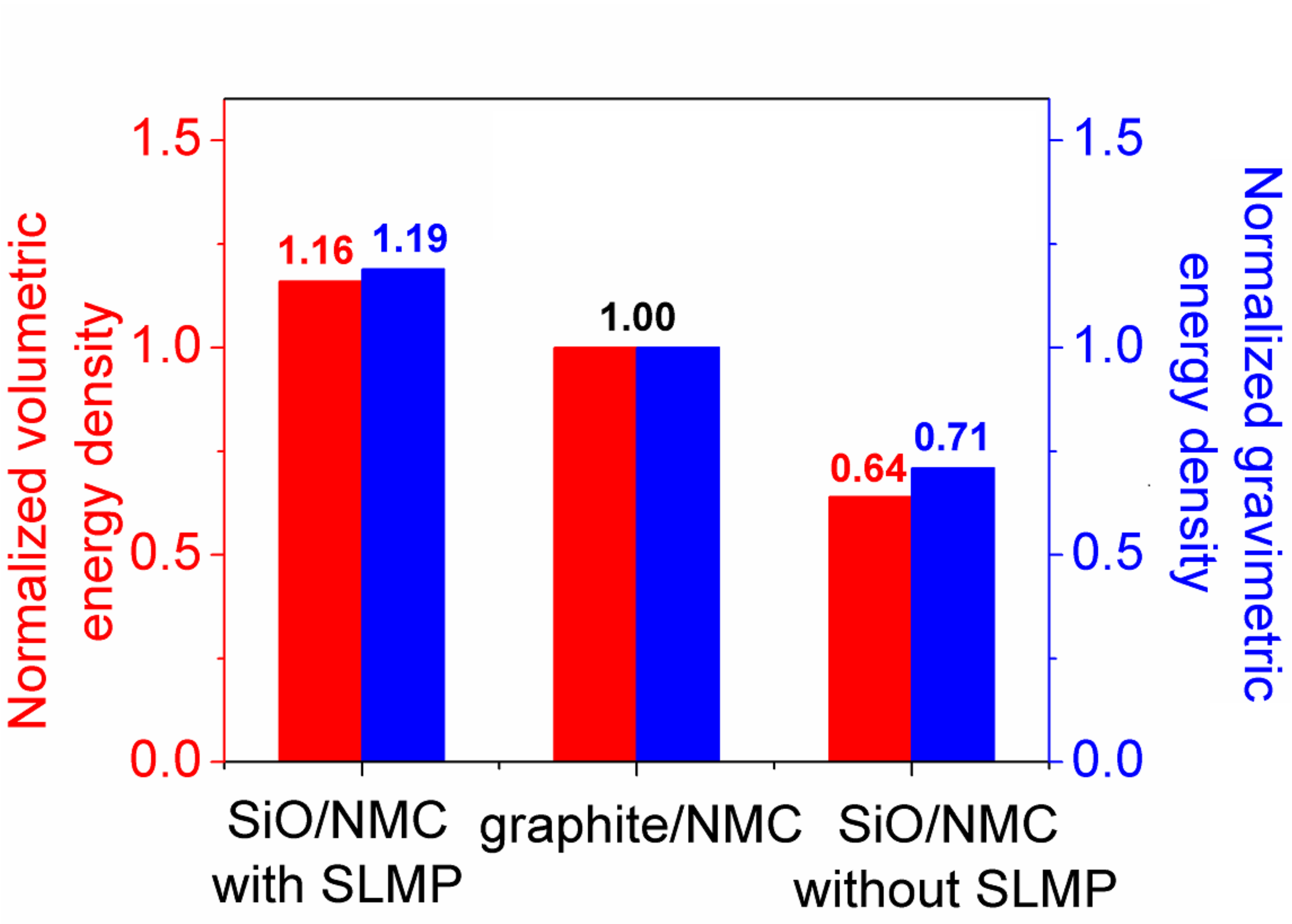
Award ceremony: April 9th, 2014, Berkeley, CA

Accomplishments - Prelithiation to further improve energy density: Full NMC/SiO cells



H. Zhao, G. Liu et al *Nano Lett*. **2014**, 14, 6704-6710

Accomplishments - Prelithiation to further improve energy density: Energy density comparison



H. Zhao, G. Liu et al *Nano Lett*. **2014**, 14, 6704-6710

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 measurements of the materials and electrode, performed advanced TEM analysis of materials, and performed modeling study of materials and electrodes

2. General Motors

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

3. 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

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 and SiO based materials. Perform carbon coating on SiO. Hosting Berkeley Lab visiting students.

7. Zeptor Corporation
Provide new carbon coated SiO 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 FY2015.

2. For the FY 2016, 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. Investigate the impact of different side chain conducting moieties to the electric conductivity of the functional conductive binders.
   b. Quantify the adhesion groups impact to the electrode materials and current collector
   c. Fabricate higher loading electrode (>3 mAh/cm^2) based on the Si electrode materials and select binder, and test cycling stability. (go/no-go)
   d. Fabricate NMC/Si full cell and quantify the performance.

Summary

1. A class of side-chain conducting functional polymer binder is synthesized via radical polymerization process.
2. The versatile synthesis process enables the binders to fine tune the three aspects critical for a binder: electron conductivity, adhesion and mechanical properties, and electrolyte swelling for ion-conduction.
3. The covalent bonding between the functional conductive polymer binder with the active Si material surface has been positive identified via TOF-SIMS method.
4. Hierarchical design of particles and electrode architecture maintain electrode 3D structure to ensure a high density, high area capacity and stable cycling performance.
5. For application of the three generations of functional conductive polymer binders in other Si based system, please refer to ARM presentations, ES208, ES210, and ES212