Development of Silicon-based High Capacity Anodes

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Pacific Northwest National Laboratory

2016 DOE Vehicle Technologies Program Review
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Project ID #: ES144

Overview

Timeline

- Project start date: Oct. 2014
- Project end date: Sep. 2016
- Percent complete: 75%

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY15: $430k
- Funding for FY16: $540k

Barriers addressed

- Low energy density
- High cost
- Limited cycle life

Partners

- University of Pittsburgh (subcontract)
- Florida State University
- Oregon State University
- General Motors
- Stanford University

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Relevance/Objectives

- Develop high-capacity and low-cost Si/graphite composite anodes with good cycle stability and rate capability to replace graphite in Li-ion batteries.

- Modify the electrode structures to enable high utilization of thick electrodes.

- Use solid state synthesis techniques to generate active-inactive composite of Si based anode with high capacities.

Milestones

FY15

- Identify the stability window of SEI formation on Si based anode (Dec. 2014). **Completed**

- Achieve >80% capacity retention over 200 cycles of thick electrodes (~3 mAh/m^2) through optimization of the Si electrode structure and binder (Jun. 2015). **Completed**

- Synthesize nanostructured Si and lithium oxide nanocomposites by direct reduction of Si sub-oxide to achieve reversible capacities > ~1500 mAh/g, first cycle irreversible loss < 15%(June 2015). **Completed**.

- Synthesize nanostructured Si and lithium oxide nanocomposites by direct reduction of silica to achieve reversible capacities > ~1200 mAh/g, and Coulombic efficiency of the anode > 99.99% during subsequent cycles. (Sept. 2015). **Completed**

FY16

- Identify and synthesize the active-inactive Si based nanocomposite with a specific capacity ~800 mAh/g (Dec. 2016). **Completed**

- Achieve 80% capacity retention over 200 cycles for graphite supported nano Si-carbon shell composite (March 2016). **Completed**

- Optimize the cost effective scalable HEMM and solid state synthesis techniques for generation of active-inactive composite with capacities ~1000-1200 mAh/g, first cycle irreversible loss <20% and columbic efficiency >99.99% for 300 cycles at a current rate of 0.5A/g (July 2016). **Ongoing**

- Further improve the cycling life of nanostructured silicon flakes and nanorods to achieve 500 cycles with a specific capacity >1000 mAh/g and areal capacity > 1.5 mAh/cm^2 (September 2016). **Ongoing**

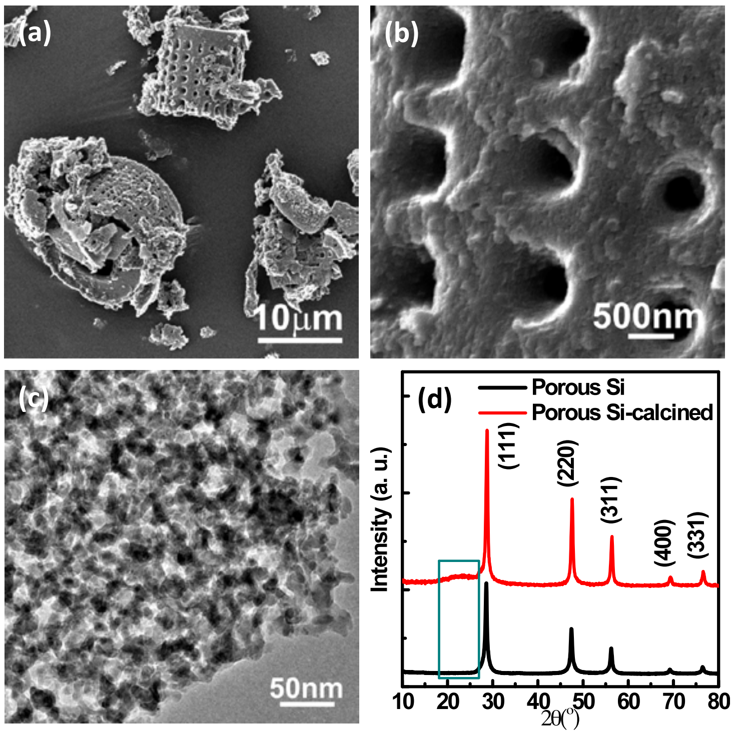
- Achieve >80% capacity retention over 300 cycles for thick electrodes (> 2 mAh/cm^2) through optimization of the Si electrode structure and binder (September 2016). **Ongoing**

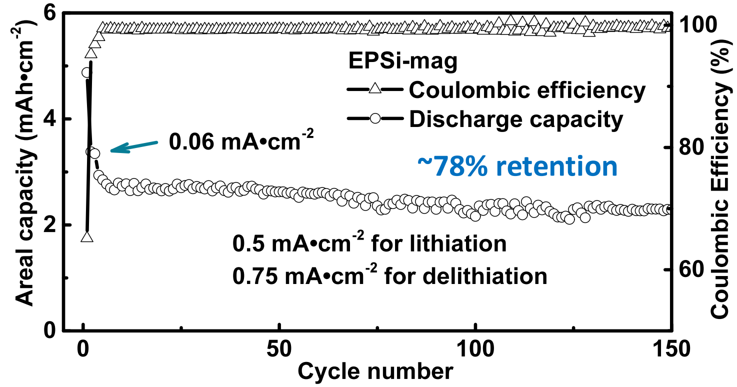
Approach

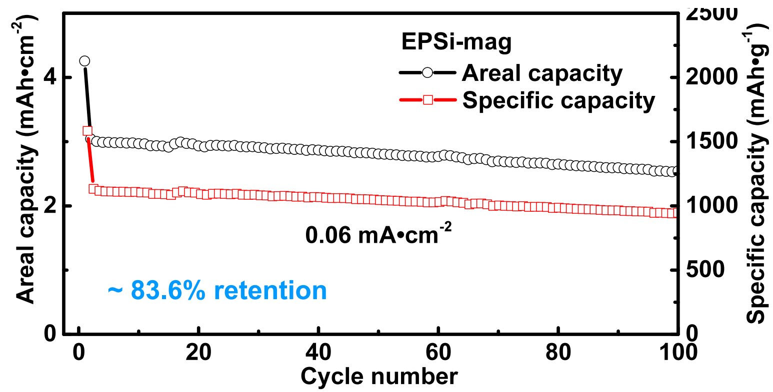
- Modify the thermite reaction method to prepare mesoporous Si from Lowe cost diatom precursors.
- Use a hydrothermal method to synthesize hard-carbon coated nano-Si/graphite composite (HC-nSi/G) using low cost precursors.
- Modify the electrode structures to enable high utilization of thick electrodes
- Low cost synthesis of Si nanostructures:
  - Use High energy mechanical milling (HEMM) to develop template of water soluble abundant and inexpensive precursor material.
  - Use low pressure thermal chemical vapor deposition of silane to develop different silicon nanostructures on this template.
- Reduce SiO using suitable alloy/metallic reducing agents using high energy mechanical reduction (HEMR) process.
- Generate active-inactive Si nanocomposite by HEMR of metal silicides using alloy/metallic/salt reducing agents.

Technical Accomplishments

High-loading anodes of mesoporous Si from thermite reaction







- It is a low cost and scalable method to produce porous Si from diatom.
- It shows ~1100 mAh/g specific capacity based on the whole electrode weight and ~80% retention over 150 cycles at a high areal capacity of ~ 3 mAh/cm^2.

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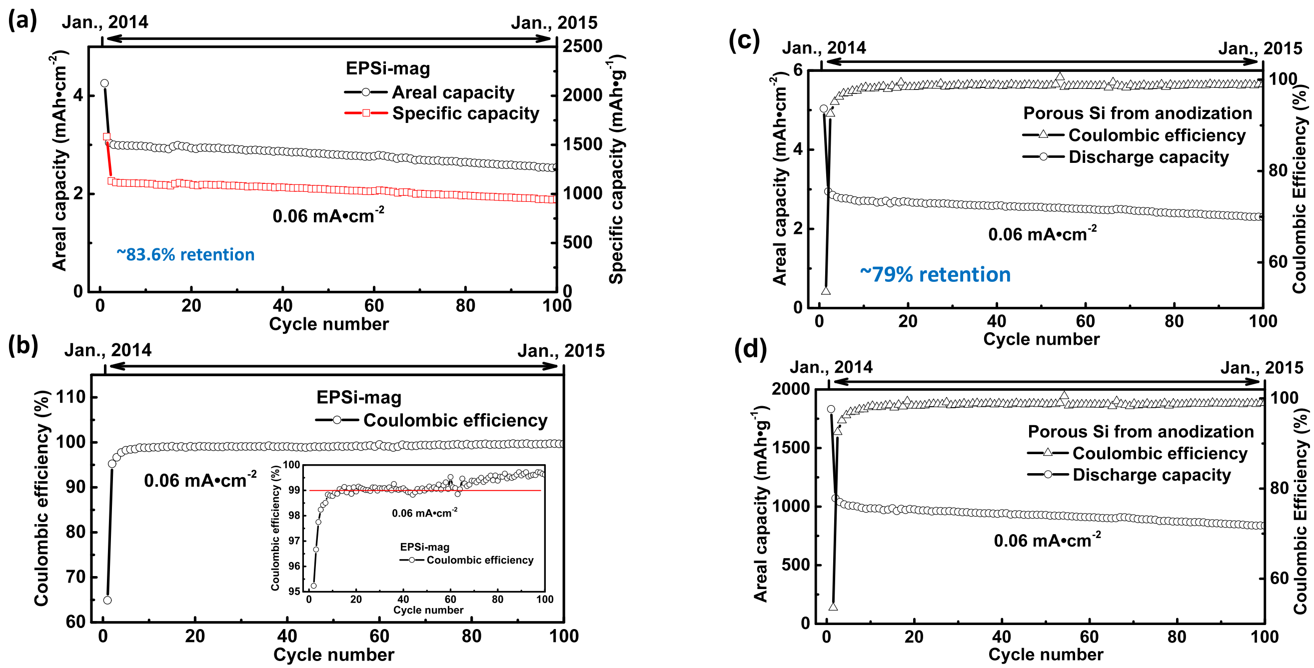
X.L. Li et al, Nano Energy, 2016, 20, 68-75

Technical Accomplishments

High-loading anodes of mesoporous Si from thermite reaction



- The Coulombic efficiency is >99% even at a low charge/discharge current density.
- Porous Si from the magnesiothermic reaction can be engineered to have better performance than electrochemical etched porous Si.

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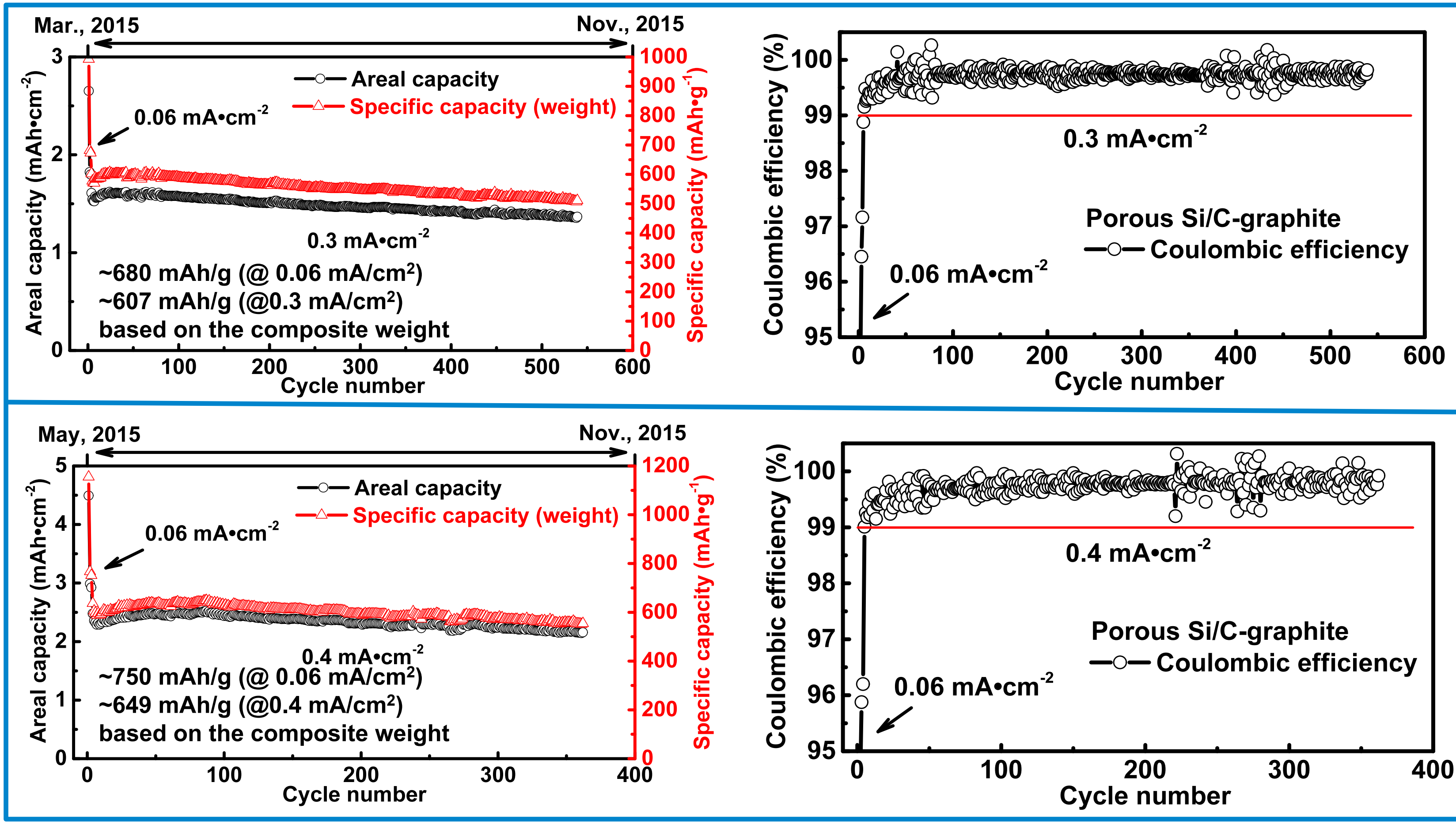
X.L. Li et al, Nano Energy, 2016, 20, 68-75

Technical Accomplishments
Porous Si/graphite composite electrode



- Porous Si/C-graphite composite electrodes can have doubled specific capacity to graphite electrodes and good cycling stability over long term test.

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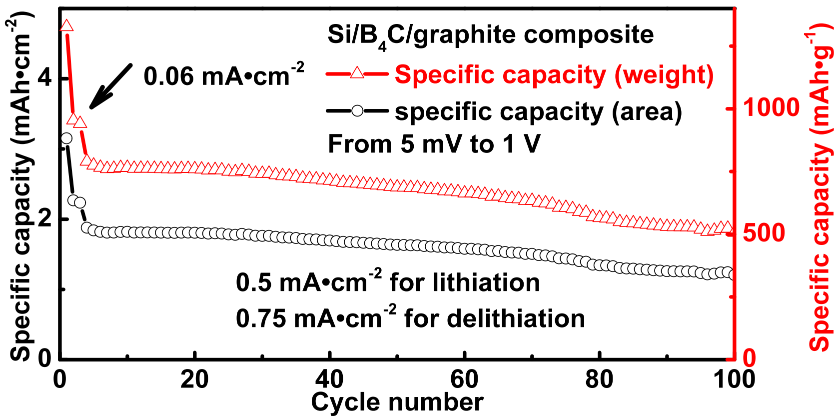
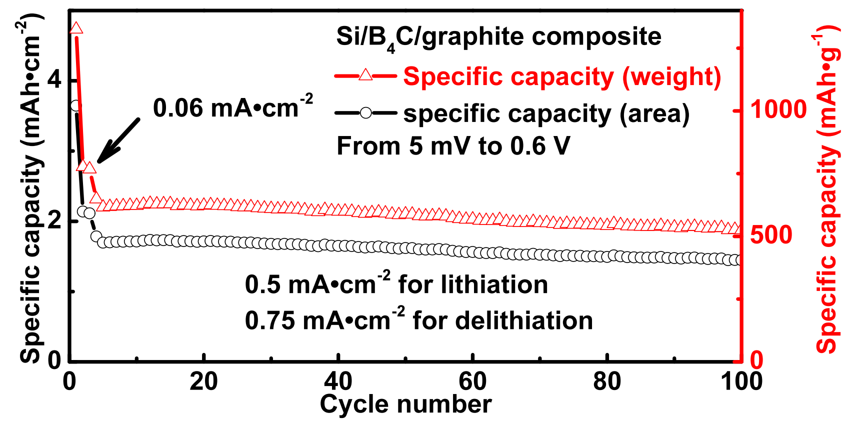
X.L. Li et al, manuscript under preparation

Technical Accomplishments
The effect of charge cut-off voltage





Si anode (2.4 mg/cm^2); 5 mV to 1V
Capacity: ~2.25 mAh/cm^2 (~950 mAh/g) at low current density and ~1.85 mAh/cm^2 (~780 mAh/g) at higher current density.
Capacity retention: ~65% over 100 cycles.

Si anode (2.8 mg/cm^2) between 5mV to 0.6V
Capacity: ~2.1 mAh/cm^2 (~770 mAh/g) at low current density and ~1.71 mAh/cm^2 (~620 mAh/g) at higher rate.
Capacity retention: ~85% over 100 cycles.

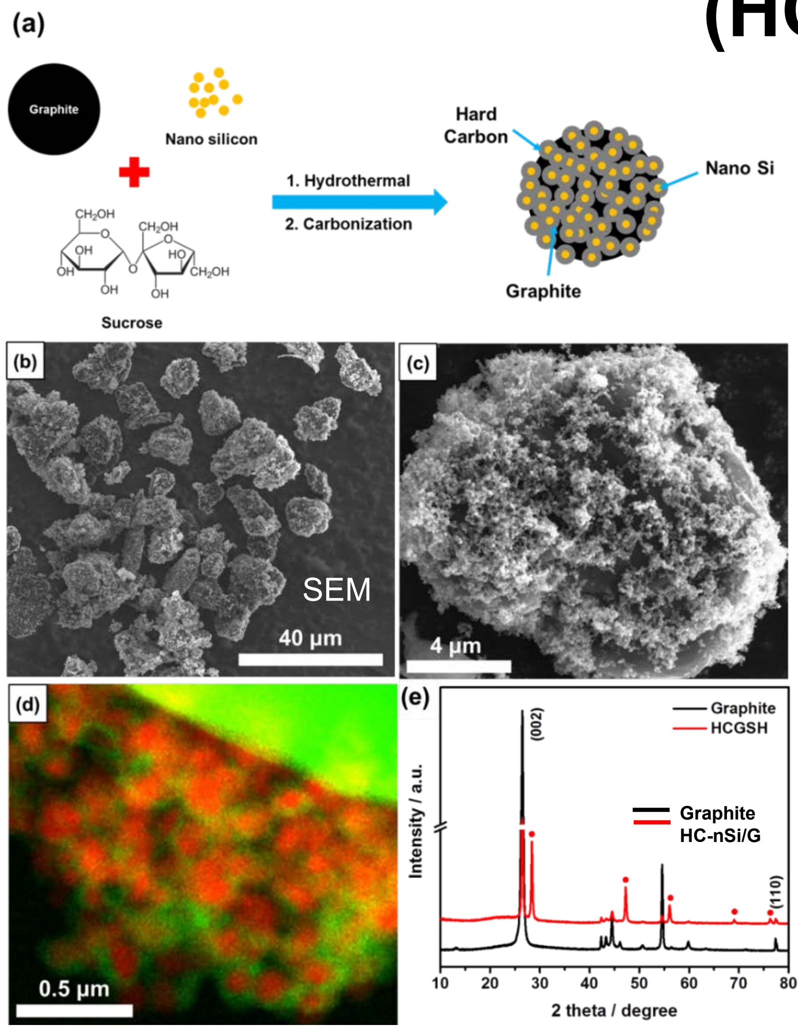
- The capacity retention of Si anodes of similar loading can be improved by 20% by lowering the charge cut-off voltage from 1V to 0.6V.

- The capacity drops by ~20%.

X.L. Li et al, manuscript under preparation

Technical Accomplishments

Hard-carbon coated nano-Si/graphite composite (HC-nSi/G)



EDX elemental mapping (green: carbon and red: silicon)

XRD patterns

The state of the art:

- Mechanical mixing of graphite and nano-Si
- Amorphous hard carbon coated nano-Si anodes.

➢ New Approach: Use hard carbon to bind the graphite and nano-Si and form a composite.

➢ A hydrothermal method was developed to synthesize graphite/nano-Si/hard carbon composite using low cost precursors.

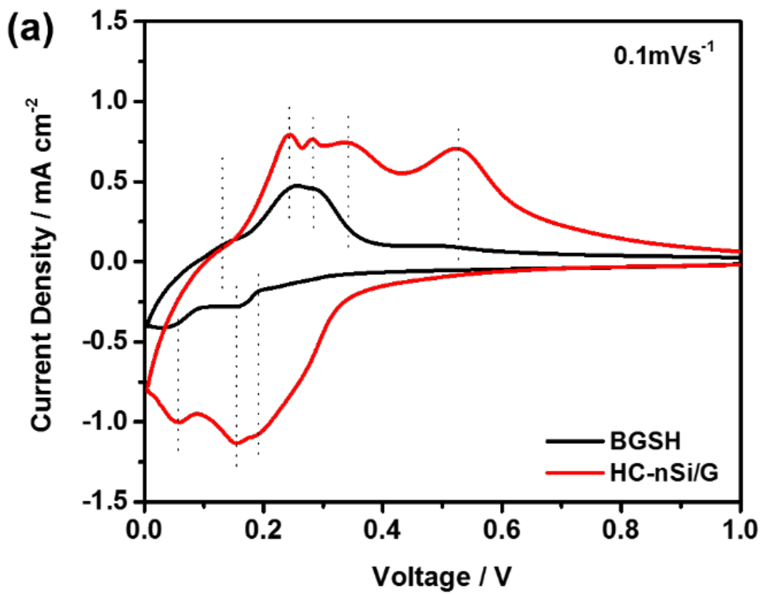
➢ Graphite provides stable core structure and also contributes to capacity.

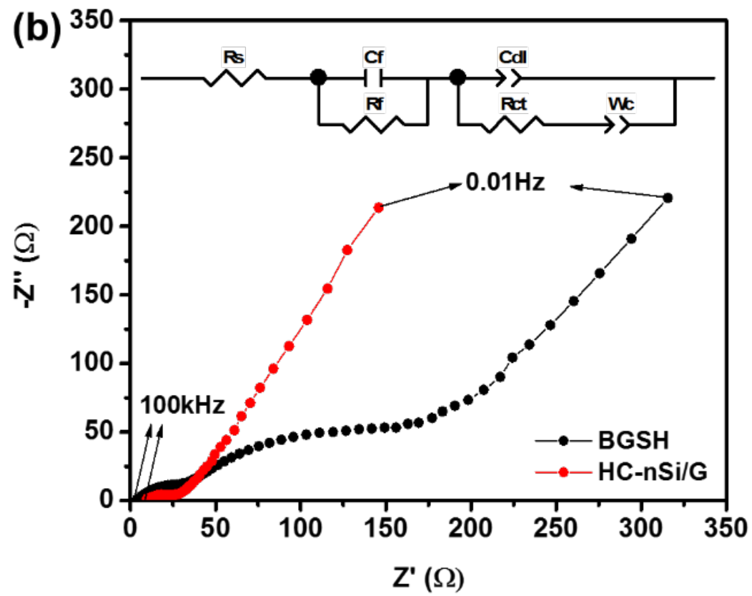
S.K. Jeong et al, submitted for publication

Technical Accomplishments
Hard-carbon coated nano-Si/graphite composite

Comparision of Cyclic voltammograms vs. Li/Li^{+}

Comparision of Impedance spectra





- Hard-carbon coated nano-Si/graphite (HC-nSi/G) composite exhibits much lower impedance and better Li intercalation capabilities as compared to mechanically blended graphite/nano-Si/hard carbon (BGSH) mixture.

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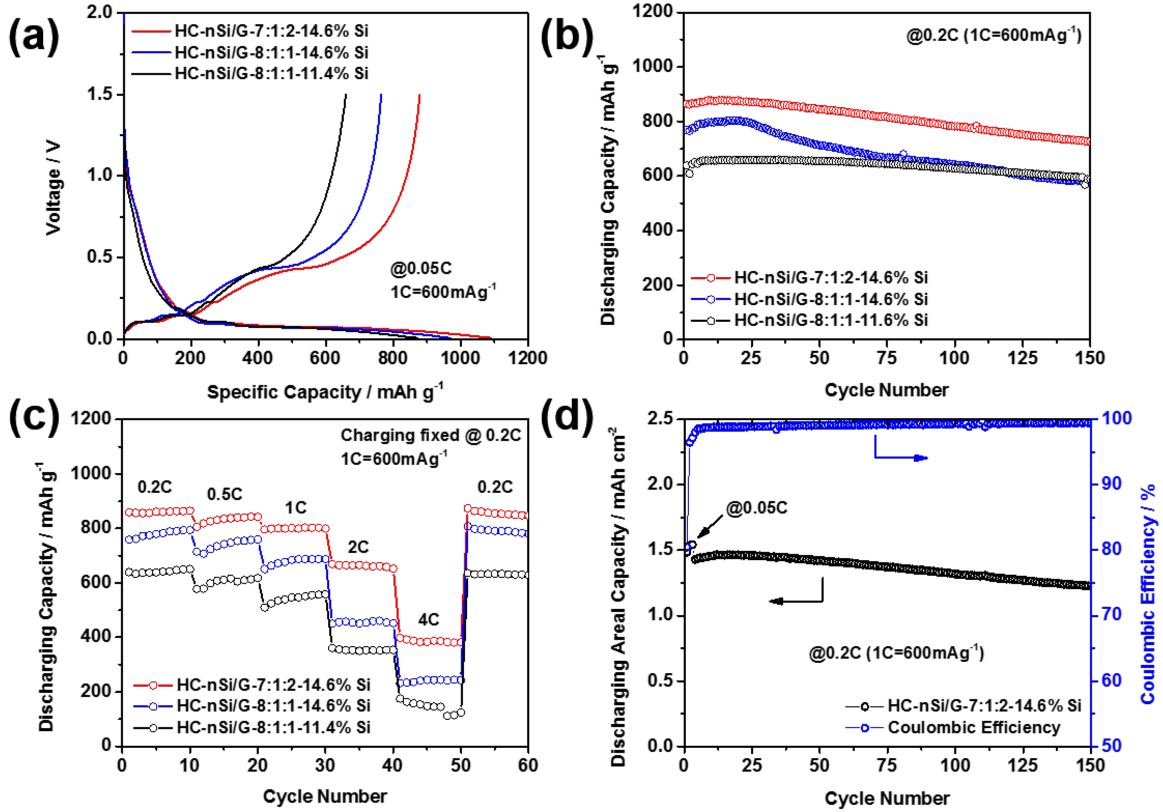
S.K. Jeong et al, submitted for publication

Technical Accomplishments
Cycling Stability of HC-nSi/G Composite



- Specific capacity: ~800 mAh/g based on the weight of Si/C composite
- Cycling stability: ~80% retention over 150 cycles

S.K. Jeong et al, submitted for publication

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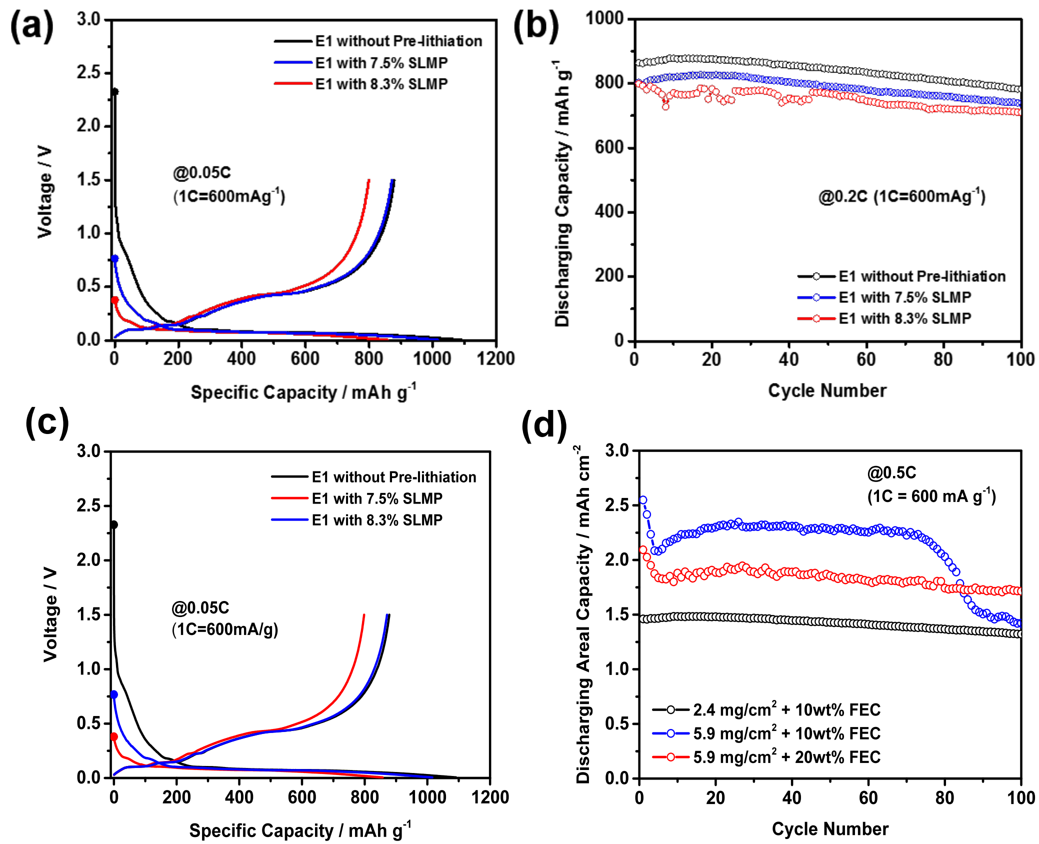
Technical Accomplishments
Prelithiation of the HC-nSi/G Composite



- Prelithiation with SLMP greatly improves the first cycle Coulombic efficiency
- HC-nSi/G composite shows long term cycling and rate performance even at high areal capacities.

S.K. Jeong et al, submitted for publication

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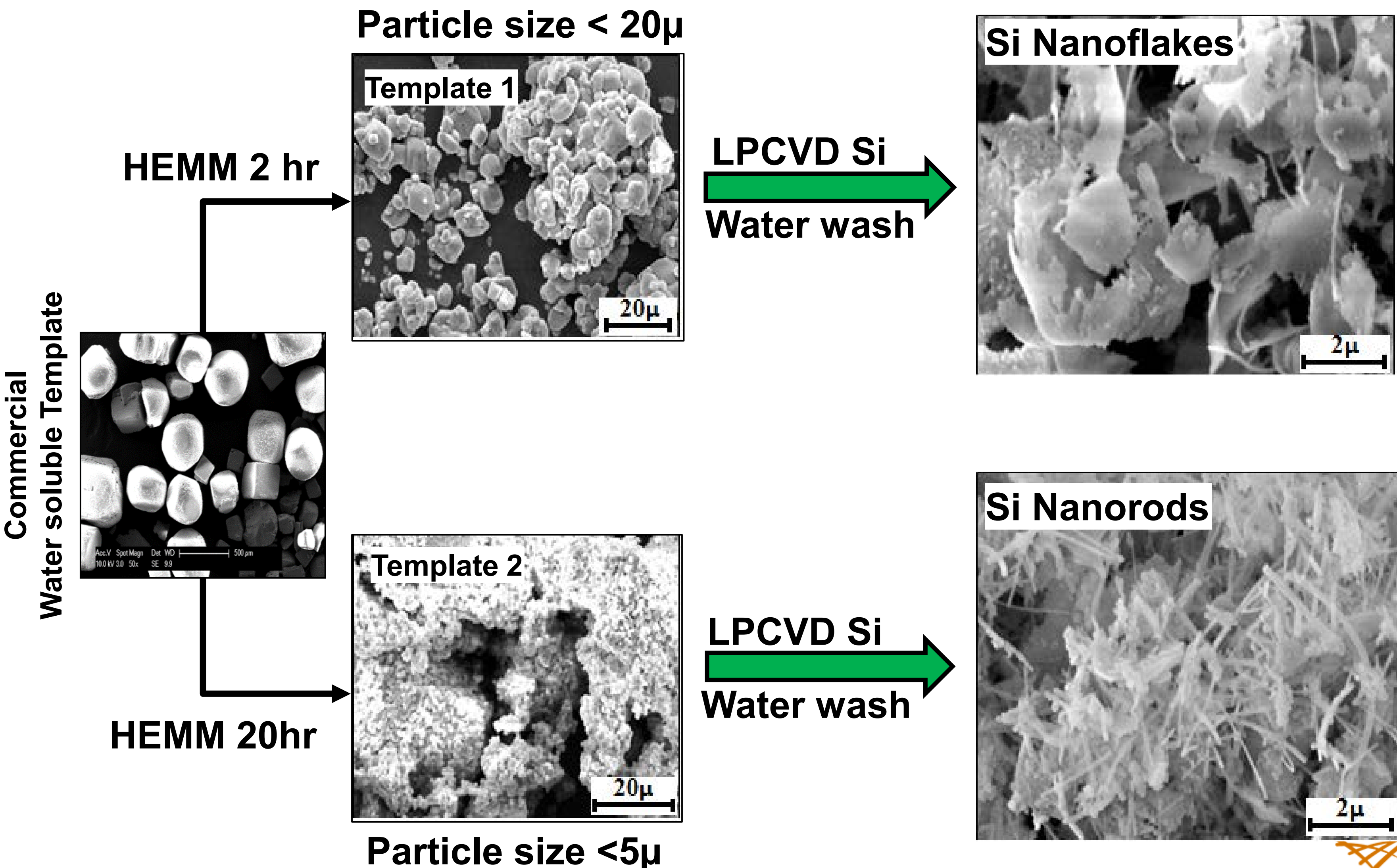
Technical Accomplishments

Synthesis of Si nanoflakes (NF) and nanorods (NR)



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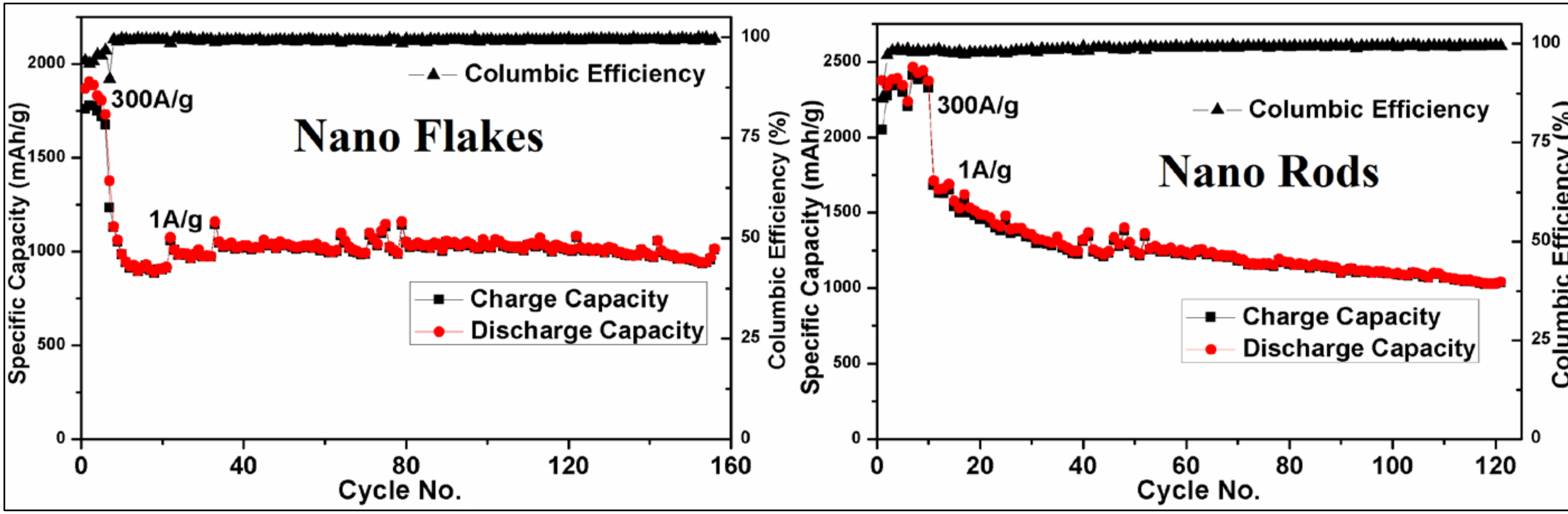
P. N. Kumta, University of Pittsburgh

Technical Accomplishments

Long Term Cycling: Nanoflakes (NF)/Nanorods (NR)



Testing Conditions:

Voltage range: 0.01V – 1.2V Loading: 1.1mg/cm^2 - 1.3 mg/cm^2

Electrolyte: 1M $LiPF_6$ in EC:DEC:FEC = 45:45:10 (%vol.)

Current rates: 300mA/g for 5 cycles, other cycles at 1A/g

End of 100 cycles and current rate of 1A/g:

<u>Nanorods:</u> specific capacity ~1050mAh/g, fade rate ~0.05% loss per cycle

<u>Nanoflakes:</u> specific capacity ~1125mAh/g, fade rate ~0.01% loss per cycle

Columbic efficiency of ~99.85 – 99.95 %.

- The capacity fade of nanorods is higher than that of nanoflakes due to the crystalline nature of Si in nanorods.

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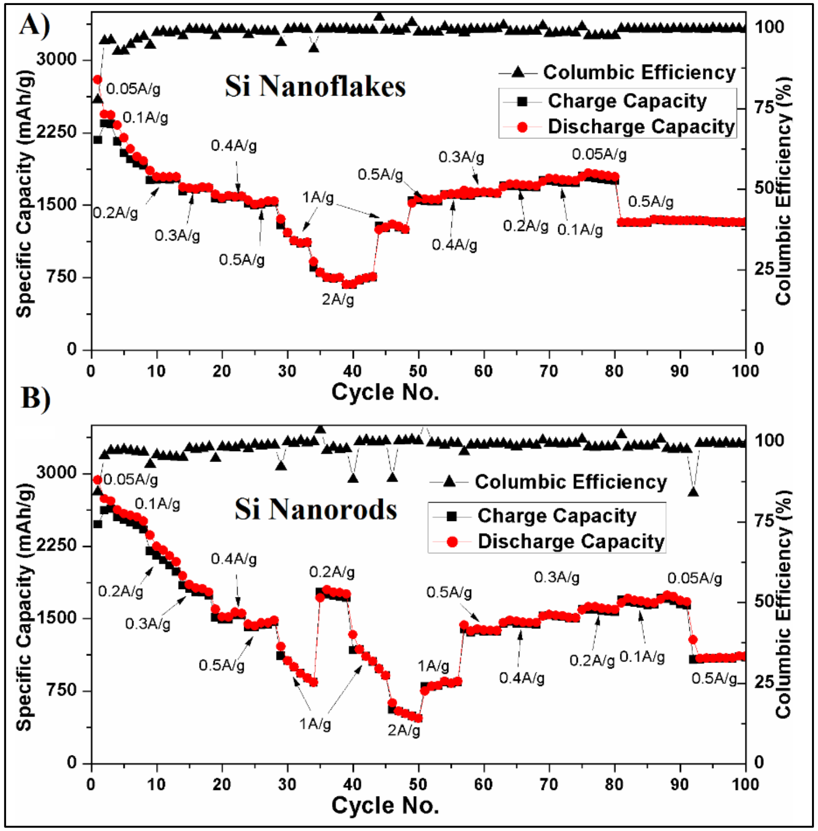
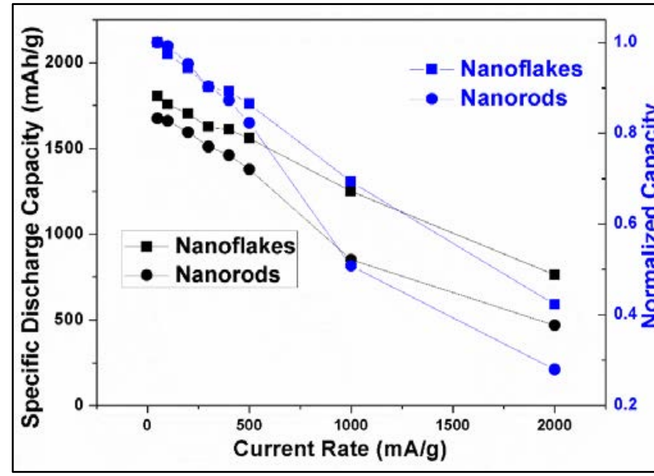
Technical Accomplishments

Rate Capability/FIR Loss: Nanoflakes (NF)/Nanorods (NR)





Nanorods show drastic decrease in capacity at higher current rates of 1A/g (800 mAh/g) and 2A/g (500 mAh/g).

Nanoflakes show better rate capability and higher capacity (1300 mAh/g @1A/g and 850 mAh/g @2A/g) as compared to nanorods.

Si Nanoflakes (NF):

First cycle capacity: @50mA/g
Discharge: 2790 mAh/g Charge: 2230 mAh/g
Second cycle capacity: @50mA/g
Discharge: 2445 mAh/g Charge: 2350 mAh/g
FIR Loss ~ 15-20%

Si Nanorods (NR):

First cycle capacity: @50mA/g
Discharge: 2930 mAh/g Charge: 2475 mAh/g
Second cycle capacity: @50mA/g
Discharge: 2740 mAh/g Charge: 2620 mAh/g
FIR Loss~ 12-15%

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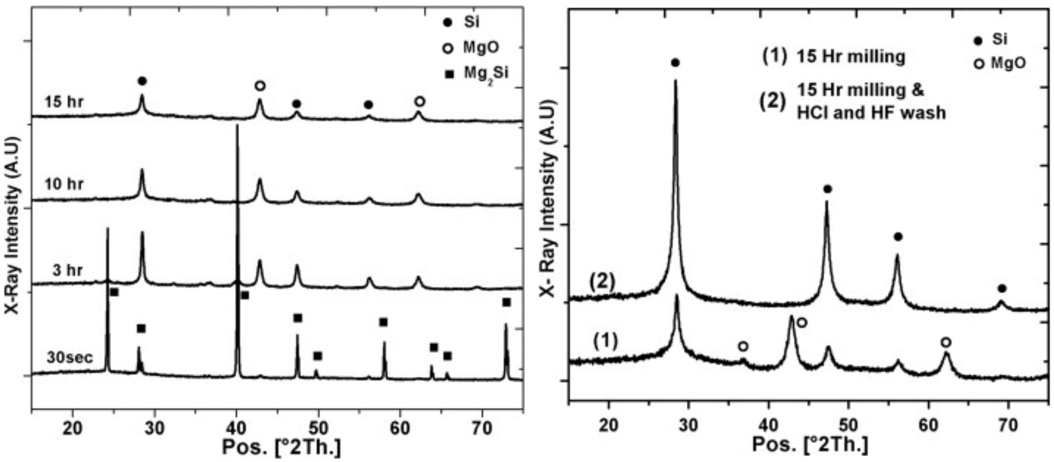
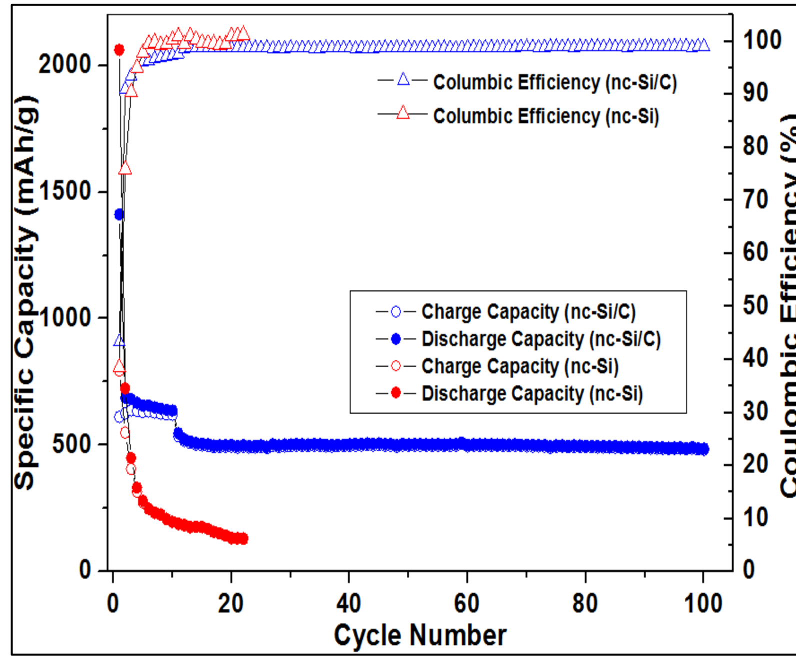
Technical Accomplishments
nc-nano Si: HEMR SiO-Mg_2Si system

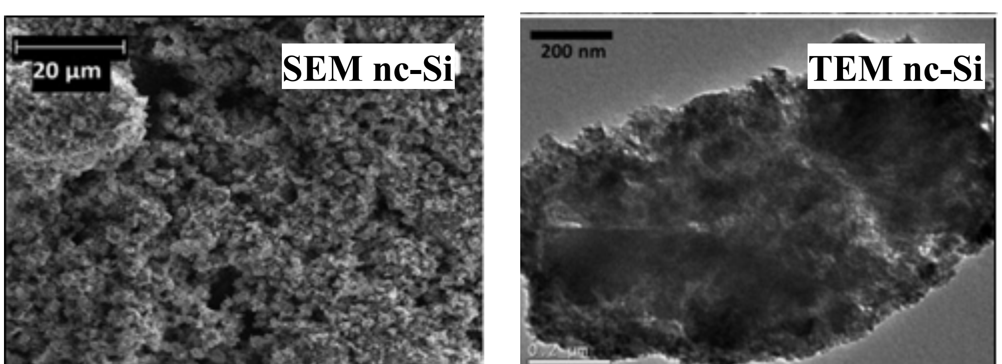
$2SiO + Mg_2Si \rightarrow 3Si + 2MgO \xrightarrow{\text{HCl wash}} Si + SiO/SiO_2 \xrightarrow{\text{HF wash}}$ Nanocrystalline Si nanoparticles

XRD pattern of material at different stages





SEM and TEM images of nano-Si



Active Material: nc-Si/C
Capacity ~ 750 mAh/g @300 mA/g

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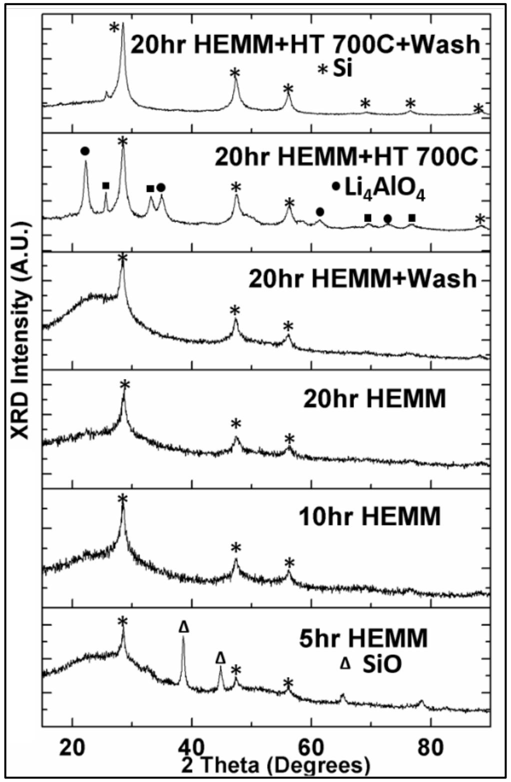
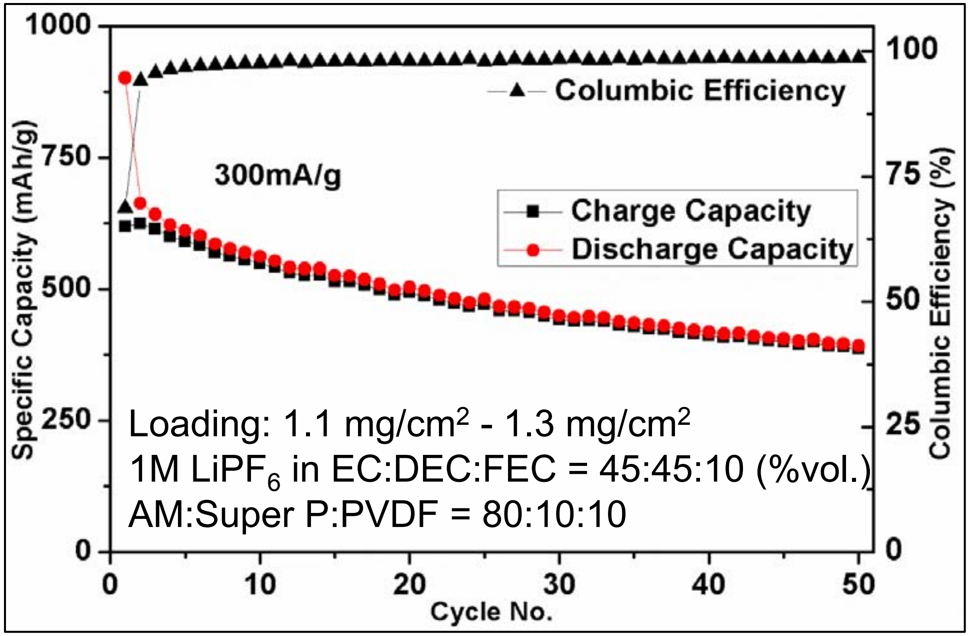
Technical Accomplishments
HEMR SiO-LiAl system



XRD pattern showing evolution of nc-Si/metal oxide matrix and finally nc-Si on heat treatment and acid wash.

$$4SiO + 2LiAl \longrightarrow 4Si + Li_2O + Al_2O_3$$



Active Material: SiO/LiAl-20 hr + Graphite composite

- Capacity = 740 mAh/g @50mA/g, 640 mAh/g@300 mA/g
- Increase in milling time and heat treatment induces complete reduction of SiO to enhance the capacity.

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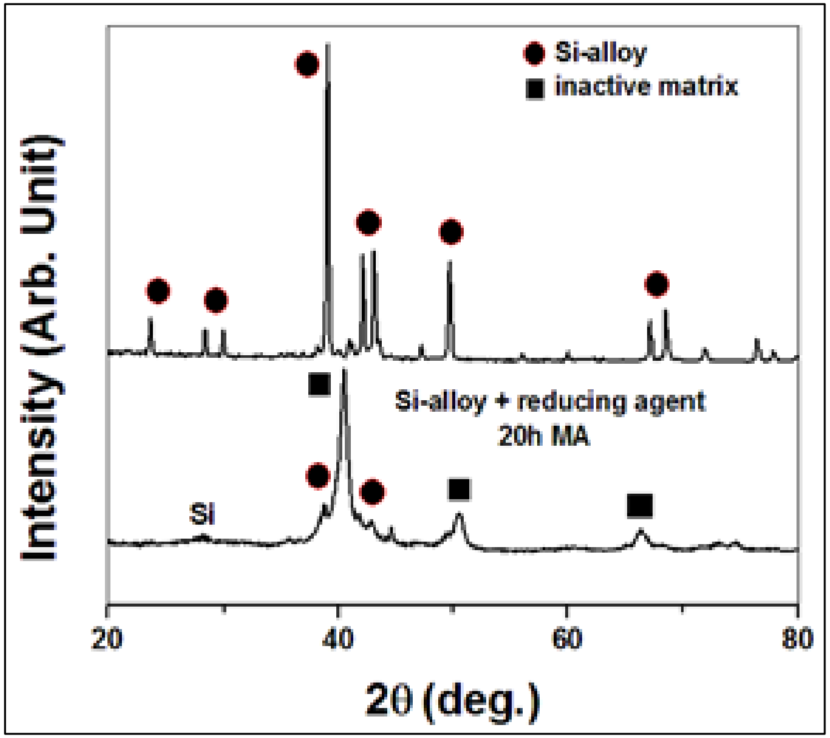
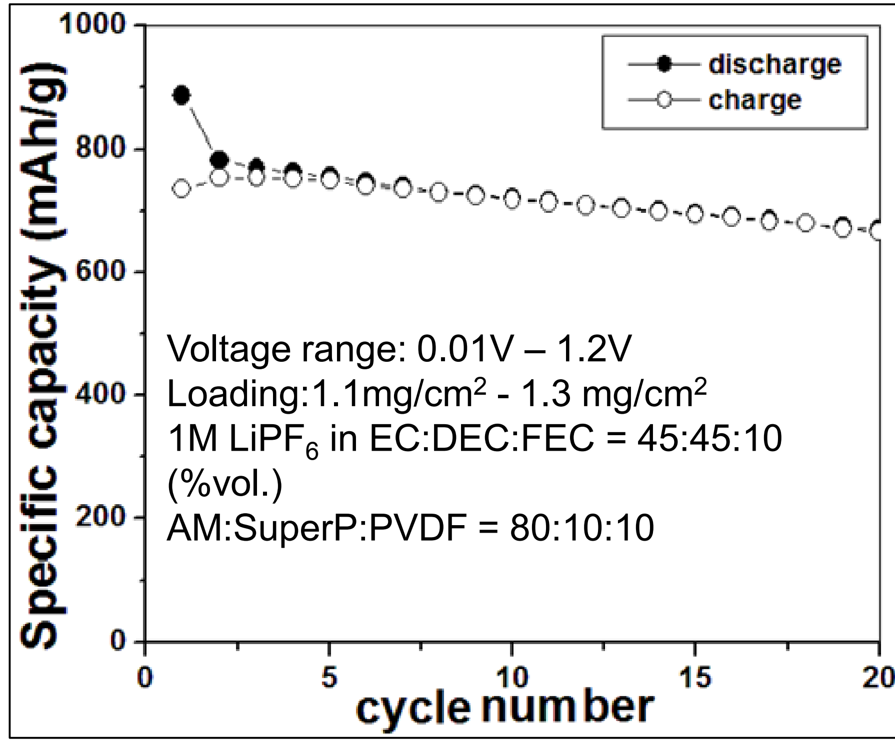
Technical Accomplishments
Si-Inactive matrix system

$$\text{Si-B} + \text{M} \xrightarrow{\text{HEMR}} \text{Si} + \text{M-B}$$



XRD pattern showing evolution of nc-Si/inactive matrix on mechanical alloying

- ➢ The capacity can be further enhanced by inducing complete reduction of silicide.



Active Material: nc-Si/MB---33 at% Si in AM

- ➢ Specific capacity ~800mAh/g
- ➢ Theoretical limit =1300mAh/g

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Collaboration and Coordination with Other Institutions

Partners:

- University of Pittsburgh (subcontract): Synthesis of *nc*-nano Si.
- Oregon State University: Collaboration on the porous Si from magnesiothermic reactions.
- Florida State University: pre-lithiation of silicon anode.
- General Motors: Collaboration on the in-situ measurement of electrode thickness change upon lithiation/delithiation.
- Stanford University: Study the failure mechanism of Si.

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Future Work

- Identify and synthesize the active-inactive Si based nanocomposite with a specific capacity ~1000 mAh/g for full electrode and good cyclability.
- Develop interface control agents and surface electron conducting additives to reduce the first cycle irreversible loss and improve the Coulombic efficiency of Si based anode.
- Achieve > 80% capacity retention over 500 cycles for thick electrodes (> 2 mAh/cm^2) through optimization of the Si electrode structure and binder.
- Enhance the specific capacity of nc-Si/metal oxide/Graphite composite system derived from HEMR of SiO with alloys/metal reducing agents by inducing complete reduction.
- Develop new solution coating techniques to synthesize Si/C based nanostructured composites to improve the performance of the synthesized materials (NF and NR).

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Summary

- Si based anode prepared by a low cost magnesiothermic method demonstrated good capacity and cyclability.
- A low cost and scalable approach was developed to prepare hard-carbon coated nano-Si/graphite composites with a capacity of 800 mAh/g (based on the weight of composites) and ~80% retention over 150 cycles.
- Porous Si-graphite composite electrode demonstrated a stable cycling for more than 500 cycles.
- High performance silicon nanostructures (NF/NR) were developed from a completely recyclable water soluble template with specific discharge capacity of ~1100 mAh/g at a current rate of 1 A/g.
- Synthesis of nc-Si and composite systems based on nc-Si using high energy mechanical reduction of SiO/SiO_x/metal silicide by suitable metals/alloys exhibiting specific capacities of ~ 800 mAh/g.

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Acknowledgments

✓ Support from the DOE/OVT/BMR program is greatly appreciated

✓ Team Members:

PNNL: Xiaolin Li, Sookyung Jeong, Chongmin Wang, Pengfei Yan

Upitt: Prashant N. Kumta, Moni K. Datta, Bharat Gattu, Prashanth H. Jampani

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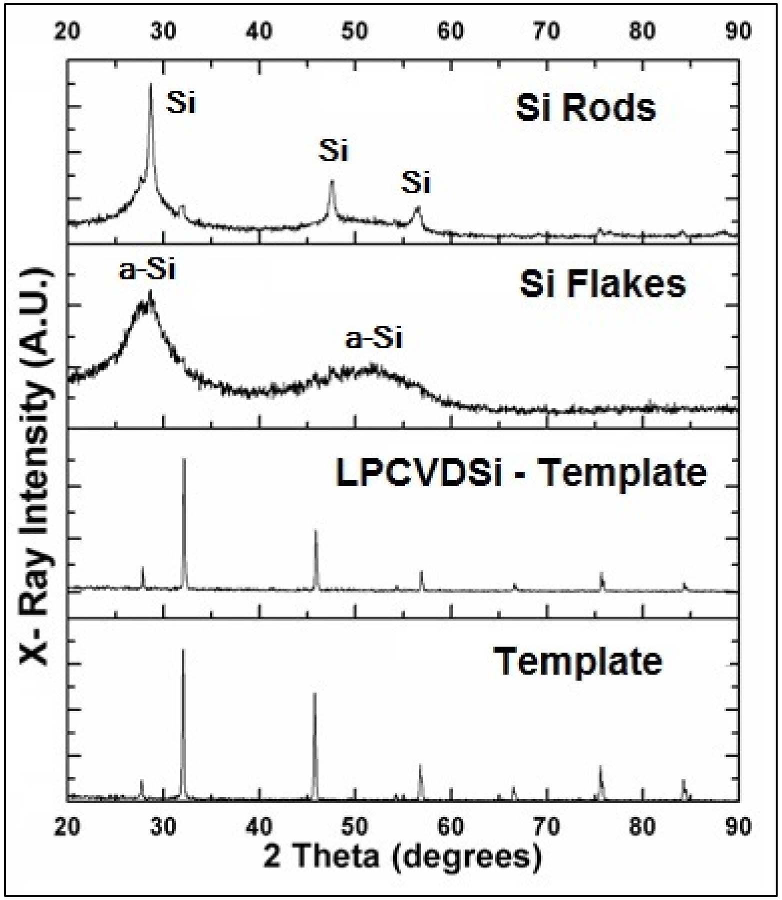
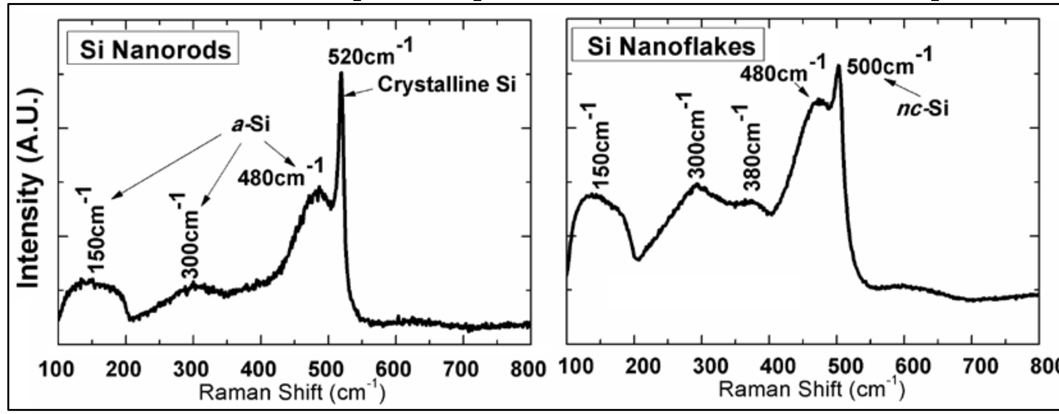
Technical Accomplishments

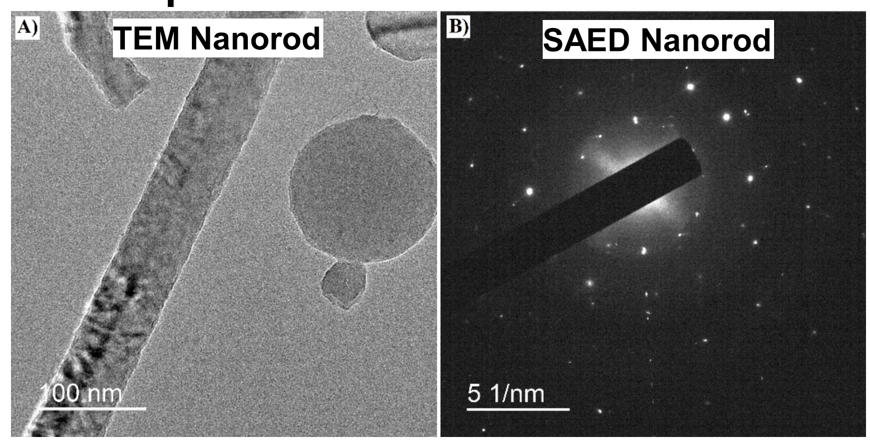
Characterization: Nanoflakes (NF)/Nanorods (NR)



XRD pattern of material at various stages



Raman spectra of Si nanoflakes and nanorods



TEM and SAED pattern of Nanorods showing strong nature of crystalline Si

- Nanorods show presence of major crystalline peak ($520 cm^{-1}$) and a minor amorphous hump($480 cm^{-1}$) of Si.
- Nanoflakes show presence of amorphous($480 cm^{-1}$) and nano crystalline ($520 cm^{-1}$) Si peaks.

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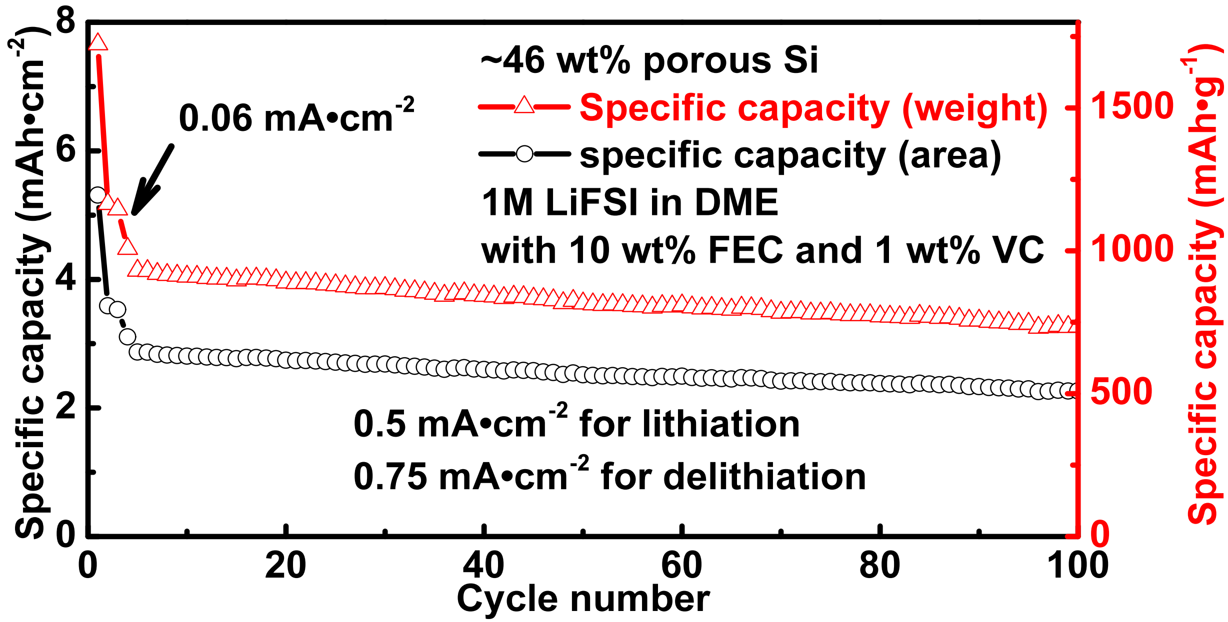
Technical Accomplishments

The electrolyte effect



- Porous Si electrode in 1M LiFSI in DME with 10 wt% FEC and 1 wt% VC shows a capacity of ~3.5 mAh/cm^2 (~1150 mAh/g) at low current density and a capacity of ~2.9 mAh/cm^2 (~930 mAh/g) at high rate.

- The capacity retention is ~79% over 100 cycles.

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