Development of Silicon-based High Capacity Anodes

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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
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/m²) 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/cm² (September 2016). **Ongoing**

- Achieve >80% capacity retention over 300 cycles for thick electrodes (> 2 mAh/cm²) through optimization of the Si electrode structure and binder (September 2016). **Ongoing**
Approach

- Modify the thermite reaction method to prepare mesoporous Si from low-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/cm².

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.

X.L. Li et al, Nano Energy, 2016, 20, 68-75
Porous Si/graphite composite electrode

Technical Accomplishments

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

X.L. Li et al, manuscript under preparation
Technical Accomplishments
The effect of charge cut-off voltage

Si anode (2.4 mg/cm²); 5 mV to 1V
Capacity: ~2.25 mAh/cm² (~950 mAh/g) at low current density and ~1.85 mAh/cm² (~780 mAh/g) at higher current density.
Capacity retention: ~65% over 100 cycles.

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Capacity retention: ~65% 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)

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

- 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.

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
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
Technical Accomplishments

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

**Si Nanoflakes**
- Particle size < 20µ
- HEMM 2 hr
- LPCVD Si
- Water wash
- Template 1

**Si Nanorods**
- Particle size <5µ
- HEMM 20 hr
- LPCVD Si
- Water wash
- Template 2

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/cm² - 1.3 mg/cm²
- **Electrolyte:** 1M LiPF₆ 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:

- **Nanorods:** specific capacity ~1050mAh/g, fade rate ~0.05% loss per cycle
- **Nanoflakes:** 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.

P. N. Kumta, University of Pittsburgh
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%

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.

P. N. Kumta, University of Pittsburgh
Technical Accomplishments

*nc*-nano Si: HEMR SiO-Mg$_2$Si system

\[
2\text{SiO} + \text{Mg}_2\text{Si} \rightarrow 3\text{Si} + 2\text{MgO}\quad \text{HCl wash}
\]

\[
\text{Si} + \text{SiO}/\text{SiO}_2 \quad \text{HF wash} \quad \text{Nanocrystalline Si nanoparticles}
\]

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

P. N. Kumta, University of Pittsburgh
Technical Accomplishments
HEMR SiO-LiAl system

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.

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

\[
4\text{SiO} + 2\text{LiAl} \rightarrow 4\text{Si} + \text{Li}_2\text{O} + \text{Al}_2\text{O}_3
\]
Technical Accomplishments
Si-Inactive matrix system

\[ \text{Si-B} + M \xrightarrow{\text{HEMR}} \text{Si} + M-B \]

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 \( \sim 800 \text{mAh/g} \)
- Theoretical limit =1300mAh/g

P. N. Kumta, University of Pittsburgh
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.
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/cm²) 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).
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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  Upitt: Prashant N. Kumta, Moni K. Datta, Bharat Gattu, Prashanth H. Jampani
Technical Backup Slides
Technical Accomplishments

Characterization: Nanoflakes (NF)/Nanorods (NR)

- 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.

P. N. Kumta, University of Pittsburgh
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 \(~3.5\ \text{mAh/cm}^2\) (~1150 mAh/g) at low current density and a capacity of \(~2.9\ \text{mAh/cm}^2\) (~930 mAh/g) at high rate.

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