Anodes-Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

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Project ID #: ES061

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Overview

Timeline

- Start: Jan 2011
- Finish: December 2015 •
- 100% complete

Budget

- Total project funding
 - \$1, 082.7K
- Funding received in FY11
 - \$310.3K
- Funding for FY12
 - \$330.8K

• Barriers

- Low specific energy and energy density
- Poor cycle life and coulombic efficiency
- Poor rate capability

Targets for PHEV (2015)

- Available Energy: 3.5-11.6 kWh
- Cycle life: 3,000-5,000 deep discharge
- > Recharge rate : 1.4-2.8 kW

Partners/Collaborators/Students

- Industries
 - Ford Motor Company
- National Laboratory
 - Dr. Robert Kostecki, LBNL
 - Dr. Vincent Battaglia, LBNL

Other Universities

 Dr. Spandan Maiti, University of Pittsburgh

Research Faculty/Students

- Dr. Moni Kanchan Datta, University of Pittsburgh
- Rigved Epur, University of Pittsburgh

Objectives of this Study May 2011-May 2012

- Identify new alternative nanostructured anode materials to replace synthetic graphite that will provide higher gravimetric and volumetric energy density
- Similar or lower irreversible loss (≤15%) in comparison to synthetic graphite
- Similar or better coulombic efficiency (≥99.9%) in comparison to synthetic graphite
- Similar or better cyclability and calendar life in comparison to synthetic graphite
- Investigate microcrystalline (μm-Si), nano-crystalline (nc-Si), nanoparticle (np-Si) and amorphous Si (a-Si) based nanocomposite anodes
- Improve the specific capacity, available energy density, rate capability and cycle life of nano-structured and amorphous Si based anode materials
- Identify elastomeric thermoplastic binders capable of binding the active materials preventing de-lamination

Milestones

Month/Year	Milestones or Go/No-Go Decision
July 2011	Milestone: Reduce Irreversible loss to less then ~15% of Si/C and Si/carbon nanotubes (CNT) nanocomposite anodes using cost effective processing methods
September 2011	Milestone: Improve the coulombic efficiency of Si/C and Si/CNT nanocomposite above 99.5%
December 2011	Milestone: Achieve Si/C and CNT/Si composite exhibiting low irreversible loss, high couloumbic efficiency, stable reversible capacity higher than ~1200mAh/g
March 2011	Milestone: Characterize the hetero-structures for structure and composition using electron microscopy techniques such as, SEM, TEM and HREM
May 2011	Milestone: Identify suitable elastomeric thermoplastic binders for anode materials

Si: Silicon, C: Graphite or Carbon, CNT: Carbon nanotube

Approach

- Explore *Si and carbon/CNT* based nanocomposite anode
 - Explore <u>novel low cost approaches</u> to generate Si/C and Si/CNT composite comprising microcrystalline (µm-Si), nanocrystalline (nc-Si), nanoparticle (np-Si) or amorphous Si (a-Si) and a variety of carbon precursors:
 - High energy mechanical milling (HEMM)
 - Chemical reduction followed by HEMM
 - Chemical vapor deposition (CVD)
 - Pulsed laser deposition (PLD)
 - *RF magnetron sputtering (RFMS)*
 - Fluidized bed reactor (FBR)
- Explore suitable surface control additives (SCA), interface control additives (ICA), and surface electron conducting additives (SECA) in Si/C and Si/CNT nanocomposite which will reduce 1st cycle irreversible loss (IR) and improve the coulombic efficiency (CE) in subsequent cycles
 - Use of selective microstructure of graphite (e.g. KS6, MCMB, SFG) as matrix exhibiting low (< 20%) first cycle irreversible loss.
 - **Coating of Si/C composite** with suitable element or compound surface control additives (SCA) **to improve CE and cycling stability**.
 - Use of highly conductive additives to improve CE.
- Explore high strength, high ductility *elastomeric thermoplastic binders* to bind the active materials
- Full cell and long cycling tests:
 - Coin cell and pouch cell configuration with suitable cathode

Technical Accomplishments (FY-11) **Problems with Si/Graphite Nanocomposite**

1st cycle Irreversible loss and Coulombic efficiency

In FY-10, Si/C nanocomposite synthesized by HEMM using PAN as interface reaction barrier

Si microstructures used in FY-10:

- ■microcrystalline (≤44µm)
- amorphous (a-Si)
- ■nanocrystalline (*nc*-Si) (~10-20nm)
- ■nanoparticles (*np*-Si) (~50-100nm)

Carbon source used in FY-10: □Graphite flake (1-2µm, Aldrich) □PAN based carbon





Cycled at 160mA/g (C/6), 0.02V-1.2V, Loss per cycle: 0.2%, CE: **99.2%**, **IR: 30%**

Si/C composite with a-Si and graphite flake



Cycled at 160mA/g (C/6), 0.02V-1.2V Loss per cycle: **0.09%**, CE: **99.2**%, <u>IR: 37%</u>

Si/C nanocomposite synthesized by HEMM, studied in FY-10, within a wide range of composition shows: **Advantage:**

High reversible capacity: 700-1200mAh/g

Excellent cyclability: 0.01-0.2% loss per cycle

Disadvantage:

□Large irreversible loss: ≥30% □Low coulombic efficiency: ≤99.5%

Technical Accomplishments (FY-11) Probable cause of 1st cycle irreversible loss of Si/C Nanocomposite



- Large first cycle irreversible loss (>30%) arising due to carbon matrix (graphite flake and PAN-C)
- Low coulombic efficiency (<99.5%)
- Major challenge/Target
 - Irreversible loss reduction (≤15%)
 - Improve the coulombic efficiency (≥99.9%)
- Concepts
 - **<u>Reduce the SEI layer formation</u>** which may arise due to the presence of graphite flake and PAN-C
 - Increase <u>electronic conductivity</u> to improve the coulombic efficiency <u>using (SECA)</u>
 - Improve the IR, CE and stability of Si/C composite <u>using SCA</u>

Technical Accomplishments (FY-11) Reduction of 1st cycle irreversible loss of Si/C composite

Use of *low first cycle irreversible loss based synthetic graphite as matrix*



Major challenge: improve the coulombic efficiency of KS6/Si above 99.9%

Technical Accomplishments (FY-11) Improve the coulombic efficiency of Si/C nanocomposite using surface electron conducting additives (SECA)



<u>**µm-Si/KS6/SECA</u>** nanocomposite with **microcrystalline Si**:</u>

Cycled at 160mA/g, 0.02V-1.2V

Irreversible loss: 14%

Coulombic efficiency: 99.8%

➤Loss per cycle: 0.3%

>KS6/Si/SCA improve the coulombic efficiency while maintaining low 1st cycle irreversible loss

Target: improve the cyclability while maintaining low first cycle irreversible loss and high

<u>coulombic efficiency</u> using a-Si or np-Si



a-Si/KS6/SECA based composite
Cycled at 160 mA/g, C/6.5, 0.02V-1.2V
Reversible capacity: ~1050mAh/g
Fade in capacity: 0.04% per cycle
First cycle Irrversible loss:~ 17%
Coulombic efficiency: 99.8%

Identify and engineer a Si/C nanocomposite structure which shows high specific capacity with low IR, high CE and excellent cyclability

<u>Target for FY-12</u>: Long cycle life ≥300 cy. and tested in full cell configuration

Technical Accomplishments (FY-11) Improve the CE, IR and stability of Si/C nanocomposite using surface control additives (SCA)

Target:

Improve the stability of µm-Si/KS6 composite using surface control additives (SCA)



<u>μm-Si/KS6</u> nanocomposite without SCA Cycled at 160mA/g, 0.02V-1.2V 1st discharge: ~1317mAh/g, 1st charge: ~1131mAh/g ≻Irreversible loss: **14%** ≻Coulombic efficiency: **99.1%** ≻Loss per cycle: 1%

<u>µm-Si/KS6</u> nanocomposite with SCA Cycled at 160mA/g, C/5, 0.02V-1.2V 1st discharge: ~923mAh/g, 1st charge: ~798mAh/g ➢Irreversible loss: **13.5%** ➢Coulombic efficiency: **99.8%** ➢Loss per cycle: 0.1%

Surface control additive improve the stability while maintaining the IR and CE

<u>Target for FY-12</u>: Proper design and precise surface control to achieve high specific capacity with low IR and CE

Technical Accomplishments (FY-11) Formation of amorphous or nanocrystalline Si (*a*-Si/nc-Si) by chemical reduction of silicon precursors



Raman spectra obtained at 2 different regions of the obtained Silicon product confirming a-Si and nc-Si.

Technical Accomplishments (FY-11) *a*-Si/nc-Si by chemical reduction of silicon precursors







(a) SEM (b) EDAX & (c) TEM image of the *nc/a*-Si obtained after vacuum drying.EDAX shows presence of Si and O.

Technical Accomplishments (FY-11) (a-Si/nc-Si/G-PAN-C) compsoite synthesized by chemical reduction of silicon precursors followed by HEMM



Cycled at : 100 mA/g, Voltage: 0.02 - 1.2 V vs. Li⁺/Li

- First discharge capacity ~ 1180 mAh/g
- First cycle irreversible loss: ~ 38%
- Possible reasons for IR loss :
 - > Surface oxide (SiO_x)
 - SEI layer formation



- 0.3V: P(III)→P(II)
- 0.45V: $P(II) \rightarrow P(I)$ for all cycles

Composition:

PI: Li-50at.% Si (LiSi), PII: Li-30at.% Si (Li₇Si₃), PIII: Li-24at.% Si (Li_{3.16}Si)

Target at FY-12: Reduce the $IR \le 15\%$ and $CE \ge 99.9\%$

Wang et al., 2011, Elec. Comm , 13, 429 Datta et al., 2009 , J. Power Sources, 194, 1043 Technical accomplishments (FY-11) Novel Synthesis of *nc*-Si/CNT composite anodes using Interface Control Additives (ICA)



Technical accomplishments (FY-11) Structural analysis of *nc*-Si/CNT Heterostructures by CVD





Silicon coated as uniform film on CNTs

Silicon coated as film droplets at uniform spacing on CNTs

- > Film Higher partial pressure of SiH_4 (SiH₄:Ar=1:10)
- > **Droplet** Lower partial pressure of SiH₄ (SiH₄:Ar=1:30)
- **Size of silicon droplets** : 40-60 μm

Wang et al., 2011, Elec. Comm , 13, 429 Wang et al., 2010, ACS Nano, 4, 2233

Technical accomplishments (FY-11) Electrochemical behavior of different morphologies of Si on MWCNTs (grown on Inconel 600 alloy)



- Cycled at 100mA/g, 0.02V-1.2V
- 1st discharge specific capacity ~2078mAh/g
- >1st charge capacity ~1958mAh/g
- >Irreversible loss : ~6% and excellent coulombic
 efficiency (~99.5%)
- Lithiation (1st cycle):
 - 0.20V : Lithiation of *a*-Si to form Li_xSi alloys
 - 0.08V: $P(II) \rightarrow P(III)$
- Lithiation (2nd, 5th and 20th cycles):
 - 0.28V: P(I)→P(II)
 - 0.08V: P(II)→P(III)
- Delithiation
 - 0.3V: P(III)→P(II)
 - 0.45V: P(II)→P(I) for all cycles

>No need of conductive polymer additive in the preparation process : "Binder-Free" approach

Composition:

PI: Li-50at.% Si (LiSi), PII: Li-30at.% Si (Li₇Si₃), PIII: Li-24at.% Si (Li_{3.16}Si)

Datta et al., 2009, J. Power sources, 194 , 1043 Wang et al., 2011, Elec. Comm , 13, 429 Wang et al., 2010, ACS Nano, 4, 2233 Technical accomplishments (FY-11) CNT/Si/ICA – Interface Control

ICA – Interface control additives



Technical accomplishments (FY-11) CNT/Si/ICA heterostructures



Technical Accomplishments (FY-11) Synthesis of CNT/Si by Pulsed laser deposition

SAMPLE PLUME TARGET LASER Holder

• E = 10 to 150 eV

• KrF excimer laser operating at 248 nm with pulse duration of 25ns, 600 mJ/pulse , and maximum 50 Hz repetition rate

Non steady-state atom concentrations



CNT

Si coating

Silicon thickness: 15-20 nm

Technical Accomplishments (FY-11) CNT/Si by Pulsed laser deposition



- Raman spectra shows the presence of CNTs (D' band) with I_g/I_d ~ 1
- Presence of both amorphous and crystalline phases of Silicon



Cycled at :100 mA/g , Voltage: 0.02-1.2 V vs. Li+/Li

- Reversible capacity: ~1500mAh/g with 99.8% CE
- Capacities calculated based on silicon weight of the composite

<u>**Target for FY-12</u>**: Optimize the process control to reduce the $IR \le 15\%$ and $CE \ge 99.9\%$ </u>

Technical Accomplishments (FY-11) Synthesis of a-Si/C by RF magnetron sputtering



Low irreversible loss (~20%)

(0.09% loss per cycle)

to 30 cycles

>a-Si shows excellent cyclability (0.11% loss

>Improve the stability of a-Si/C thin film in

Datta et. al., Elec. Acta., 2011, 56, 4717

comparison to a-Si film beyond 30 cycle

Excellent rate capability up to 3.5C

per cycle) and columbic efficiency (~99.8%) up



Technical Accomplishments (FY-11) Development of higher fracture strength thermoplastic binder



Technical Accomplishments (FY-11) Development of higher fracture strength thermoplastic binder



Use of

functionalized

polymers for

better binding

Use of

conductive

polymers

Cycled at 300mA/g, 0.02V-1.2V

- Better adhesion of Silicon with polymer
- High capacity retention (>1000mAh/g by 30 cycles)
- Better cyclability
- Loading of active materials: 2-3mg/cm²
- Preliminary results indicate promise of novel binder

Collaborations

Industry

• Ford Motor company (A. Drews, T. Miller)

National Laboratory:

 LBNL (Vince Bhattaglia); ANL (Chris Johnson), NREL (Dillon); PNNL (J. Liu, C. Wang)

University*:

- University of Pittsburgh (S. Maiti)
- Pennsylvania State University (D. Wang)

*Collaborators within the VT Program

Activities for next fiscal year

- Synthesize nanostructured and amorphous Si based anode by cost effective methods and identify new binders to achieve stable *reversible capacity* (~1200mAh/g) with low irreversible loss (≤ 15%) and high coulombic efficiency (≥99.9%) in full cell configurations.
- Identify interface control additives (ICA) to minimize first cycle irreversible loss and improve coulombic efficiency in hierarchical nano-scale structures.
- Identify novel SECA and SCA to achieve IR of ~15% and CE ~99.9% in HEMM derived systems.
- Novel thermoplastic binders with better coupling to active material resulting in improved cyclability.
- Coin cell and pouch cell configuration with suitable cathode.

Summary

- Approaches to generate scaled up quantities of high performance amorphous Si (a-Si) and nanocrystalline Si (nc-Si) indicate promising electrochemical response.
 - Results on HEMM and CVD derived composites indicate capacities in the 1000 mAh/g – 2000 mAh/g range.
 - low irreversible loss (~5-18%) have been achieved.
 - Excellent coulombic efficiency (~99.5-99.8%) has been attained.
 - Binderless concept of VASCNT exhibit capacities ~1400-2000 mAh/g.
- Use of ICA, SECA and SCA are useful for lowering first cycle irreversible loss, improving the coulombic efficiency and cyclability as well as rate capability.
- Project initiated on generation of novel thermoplastic binders.
 - Initial results indicate improvements compared to PVDF.

List of Publications and Presentations

Publications

- M. K. Datta, J. Maranchi, S. J. Chung, R. Epur, K. Kadakia, P. Jampani, and P. N. Kumta, "Amorphous silicon-carbon based nano-scale thin film anode materials for Li-ion batteries", Electrochimica Acta 56 (2011) 4717-4723.
- Wei Wang, R. Epur, and P.N. Kumta, "Vertically Aligned Silicon/Carbon Nanotube (VASCNT) Arrays: Hierarchical Anodes for Lithium-ion Battery", Electrochemistry Communications 13 (2011) 429-432.
- Wei Wang and P. N. Kumta, "Nanostructured Hybrid Silicon/Carbon nanotube heterostructure: Reversible high capacity lithium ion anodes" ACS NANO 4 (2010) 2233-2241.
- M. K. Datta and P. N. Kumta, "In situ electrochemical synthesis of lithiated Silicon-Carbon based composite anode Materials for Lithium Ion Batteries", J.
 Power Sources 194 (2009) 1043.
- R. Teki, M. K. Datta, R. Krishnan, T. C. Parker, T. M. Lu, P. N. Kumta and N. Koratkar, "Nanostructured Si anodes for Lithium ion rechargable batteries", Small 5(2009) 2236.
- J. Nanda, M. K. Datta, J. T. Remillard, A. O'Neil and P. N. Kumta, "In-situ Raman microscopy during discharge of high capacity silicon-carbon composite Li-ion battery negative electrode" Electrochemistry Communication, 11 (2009) 235-237.
- M. K. Datta and P. N. Kumta, "Alloying/dealloying behavior of Li-ion with Si during electrochemical reaction", in preparation.
- R. Epur, M. Ramanathan, F.R. Beck, A. Manivannan, P. N. Kumta, "Electrodeposition of Amorphous Silicon Anode for Lithium Ion Batteries", Mat Sci & Engg: B (2012) In Press
- M. K. Datta, P. N. Kumta, "Si/C composite anode with surface control agent", J. Power Sources, Under preparation,
- M. K. Datta, P. N. Kumta, "Si/C composite anode with addition of electronic conducting agents", Electrochimica Acta, Under preparation.

Presentations

- M. K. Datta nd P. N. Kumta, "Alloy design for long term cyclability of Si based anode materials for lithium ion batteries", Society of Automotive Engineers, 2007 Oral presentation.
- R. Epur, S.J. Chung, M. Datta, A. Manivannan and P.N. Kumta, "Engineering Novel Si-CNT Heterostructures" MRS meeting, Boston (2011) Oral presentation.
- R. Epur, S. J. Chung, R. Kuruba, A. Manivannan and P. N. Kumta, "Nanocrystalline-Amorphous silicon composite anode by chemical reduction of silicon halides", 220th ECS meeting at Boston, MA - Oral presentation
- R. Epur, M. K. Datta, A. Manivannan & P. N. Kumta, "Nanocrystalline Silicon/Graphite/MWCNT based Heterostructured Electrodes High Capacity Anodes for Lithium Ion Batteries", 219th ECS meeting at Montreal, Canada – Oral Presentation
- R. Epur, M. K. Datta, W. Wang, J. Maranchi, P. Jampani and P. N. Kumta, "Silicon/ Carbon based nanocomposite anodes for lithium-ion batteries", 218th ECS meeting at Las Vegas, NV, USA - Oral presentation
- R. Epur, W. Wang, M. K. Datta and P. N. Kumta, "Hybrid nanostructures of silicon and vertically aligned multiwalled carbon nanotubes: Reversible high capacity lithium ion anodes", 218th ECS meeting, Las Vegas, NV, USA Poster
- R. Epur, W. Wang and P. N. Kumta "Carbon nanotube and silicon based novel heterostructures as high capacity anodes for lithium ion batteries", 15th IMLB meeting 2010, Montreal, Canada – Poster
- R. Epur, W. Wang and P. N. Kumta, "Nanostructured hybrid silicon/Carbon nanotube hetereostructures: Novel reversible high-capacity lithium-ion anodes", 217th ECS meeting 2009, Vancouver, Canada – Oral presentation
- P.N. Kumta, "Nano-scale Engineered Electrochemically Active Silicon Based Heterostructures" MRS meeting, Boston (2011) Oral presentation

Patent

– P.N. Kumta, "Nano-Scale Silicon Based Compositions and Methods of Preparation", Patent Filed, September 2010.

TECHNICAL BACK – UP SLIDES

1st cycle irreversible loss of Nanoparticle Si used in the present study

Nanoparticle Si (MTI Corporation): spherical crystalline Particle size: 100nm, surface area: 80m²/g,



Cycled at 160mA/g, 0.02V-1.2V 1st cycle discharge capacity ~1500mAh/g and 1st cycle charge capacity ~1260mAh/g with an irreversible loss of only ~16%

Long cycle life of nc-Si/KS6 composite



Cycled at 160mA/g, 0.02V-1.2V 1st cycle discharge capacity ~1400mAh/g and 1st cycle charge capacity ~1200mAh/g with an irreversible loss of only ~10%. Fade in capacity: 0.19% per cycle upto 100 cycles

Vertically aligned CNTs by CVD



CNT/Si Heterostructures by CVD



Other low cost approaches for generating large area amorphous silicon

SEM/EDAX/Raman of *a*-Si derived by electrochemical reduction



(a) SEM (b) EDAX & (c) Raman results of the electrodeposited a-Si film on copper foil

b

Electrochemical characterization of *a*-Si films derived by electrochemical reduction

