Development of High Capacity Anode for Li-ion Batteries

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Project ID#: ES065

Overview

Timeline

- Start date: Oct. 2009
- End date: Sept.2010
- Percent complete:70%

Barriers addressed

- Low capacity of graphite
- Poor cycle life
- Large irreversible loss

Budget

- Total project funding
- FY10: 300K (100% DOE)

Partners

- The Pennsylvania State University
- Princeton University
- Vorbeck Inc.
- North Dakota State University

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Objectives

- Develop novel hybrid anodes with high capacity and good rate capability to replace graphite in Li-ion batteries.
- Develop low cost production methods for high capacity and stable Si-based anode.
- Develop new carbon additive and binder to improve the cycling stability of Si-based anode.

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Milestones

- Synthesize and characterize TiO_2/Graphene and SnO_2/Graphene nano-composite as anode for Li-ion batteries. – *on going*
- Synthesize and characterize Si nanowires as an alternative anode. – *completed*
- Utilize micron-sized porous Si with good electrochemical performance and high packing density. – *on going*
- Develop new carbon additive and binder to further improve the electrochemical performance of Si-based anode. – *on going*

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Approach

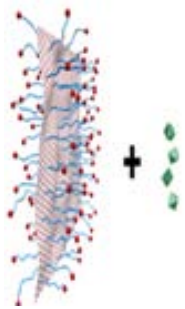
- Use self-assembly method to prepare transition metal oxide to improve their practical capacity and rate.
  - TiO_2/Graphene nano-composite through self-assembly.
  - SnO_2 /Graphene nano-composite through self-assembly.

- Manipulate nano-structure and conductivity of Si to improve its mechanical and electrical stability.
  - Synthesize silicon nanowires from bulk Si particles.
  - Use micron-sized Si with porous structure to improve its mechanical stability and packing density.
  - Incorporate nano-Si into graphene paper to further alleviate the effect of volume variation of porous Si.

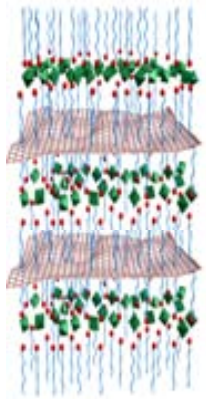
- Explore new carbon additive and binder to further stabilize the long-term cycling of Si-based anode.

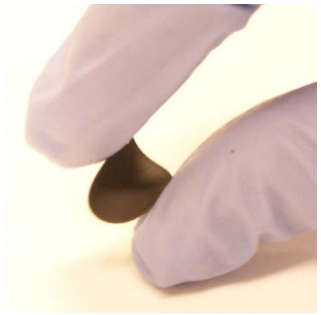
Technical Accomplishments: Self Assembly of Nano-transition Metal Oxide/Graphene Composite

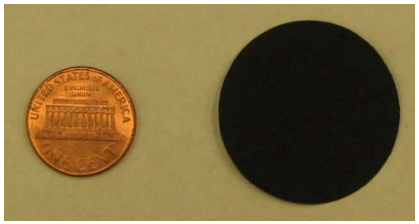
Nanosynthesis: TiO_2, SnO_2, and other cathode materials



Self-assembly with graphene

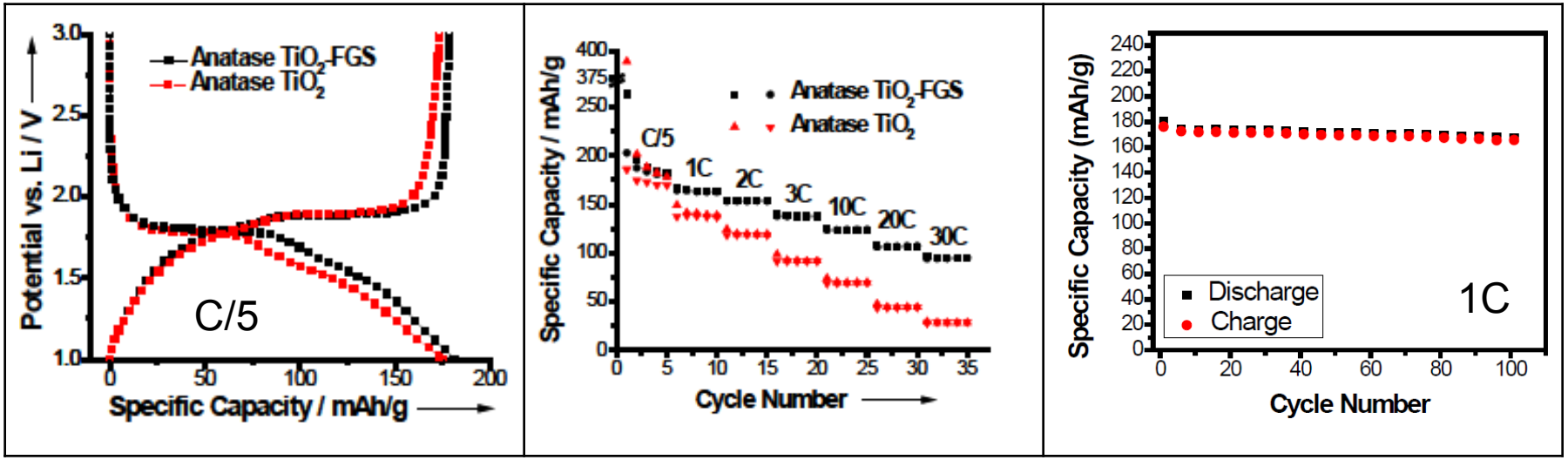






- Highly stable anode (TiO_2, SnO_2) has been prepared by PNNL's unique self assembly method (Metal oxide/graphene super-lattice or composite).
- Direct manufacturing of electrodes and batteries without binders and other additives.

Technical Accomplishments
High Performance Nano-TiO_2/Graphene Composite



- Best rate capability reported on anatase TiO_2 with only 2.5wt% graphene.
- Excellent cycling stability: ~ 170 mAh/g at 1C (PHEV constant output).

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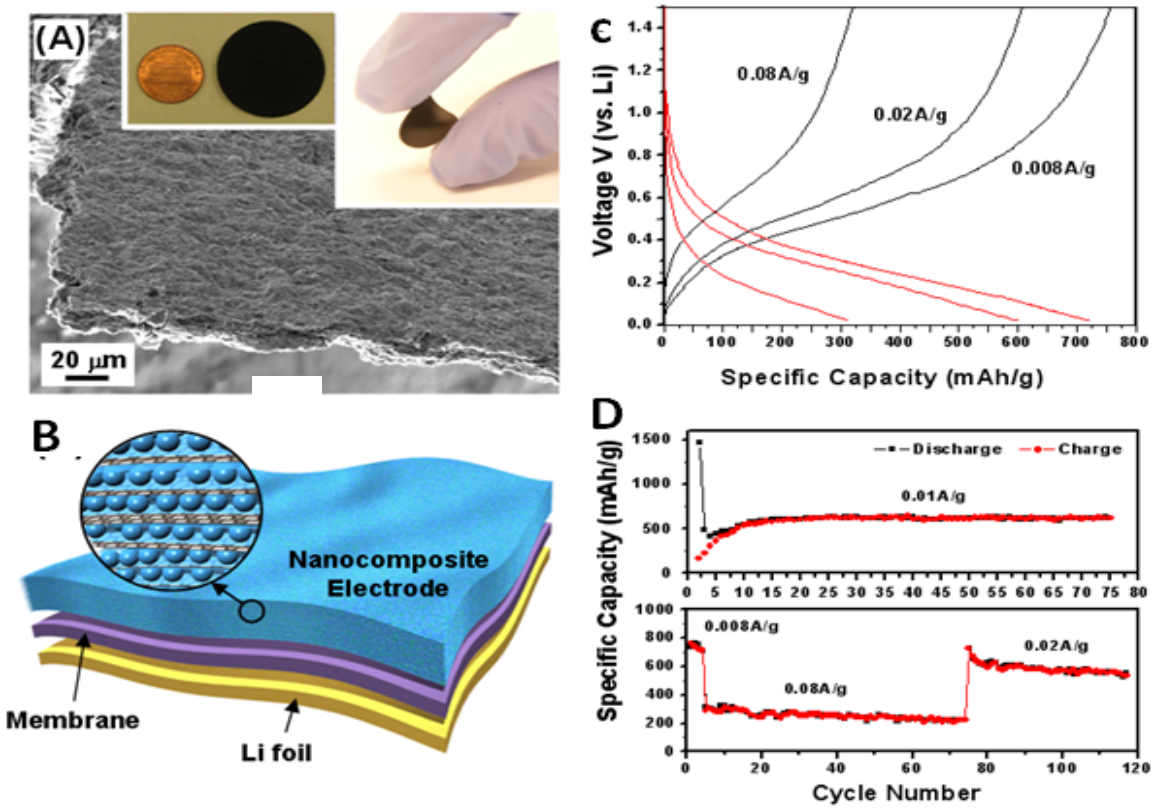
Technical Accomplishments:
High Performance SnO_2/Graphene Composite



- The self-assembled structure composed of ordered "superlattice" nanocomposite with alternating layers of graphene nanosheets and metal oxides.
- Stable cycling and excellent rate capability are demonstrated.

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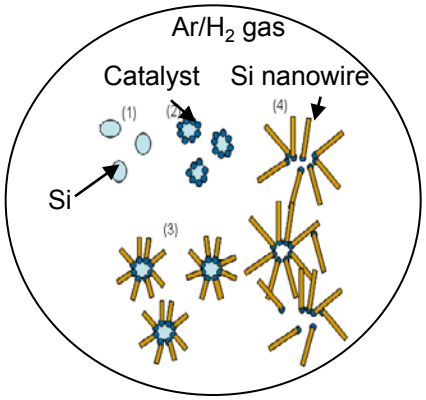
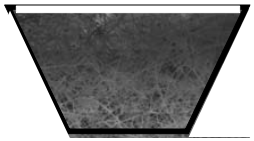
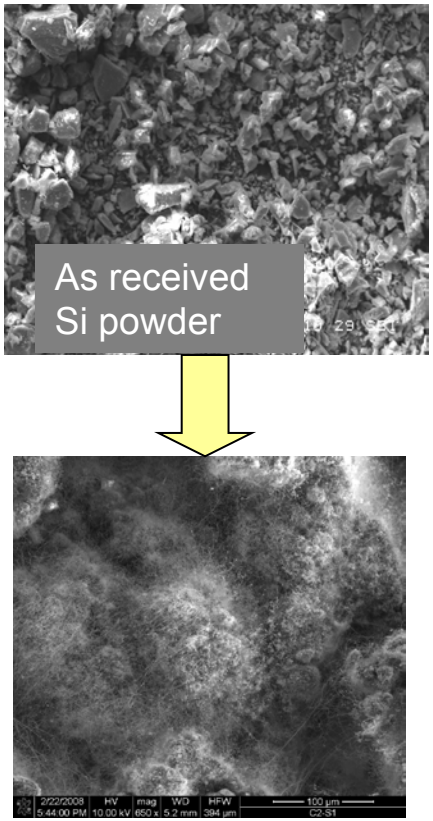
Technical Accomplishments: Large-Scale Synthesize of Silicon Nanowires for Li-Ion Batteries

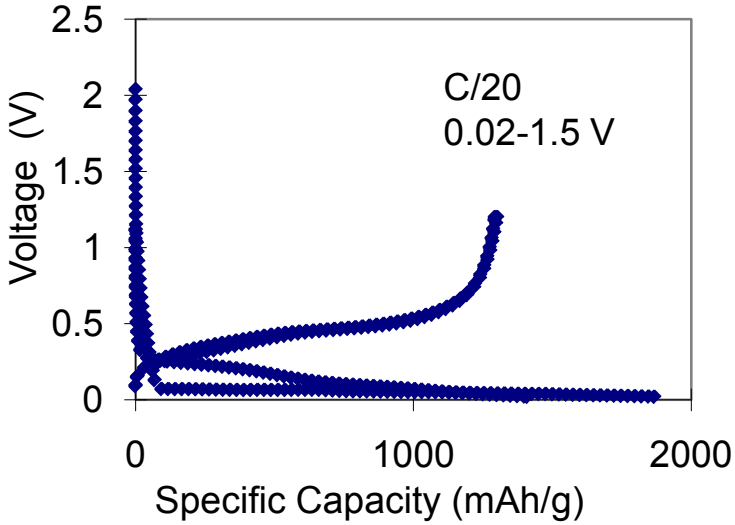
PNNL 's
3D method





3-D volumetric growth





- Synthesis route suitable for high-volume manufacturing
- Low cost relative to thin film deposition methods; No toxic precursors.
- SiNWs demonstrate a discharge capacity of ~1,500 mAh/g.

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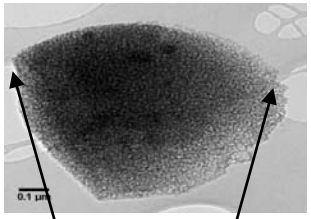
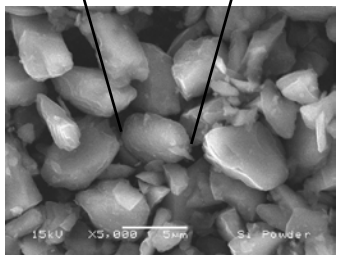
Technical Accomplishments:
Use CVD-Coated-Carbon to Improve Electronic Conductivity of Porous Si

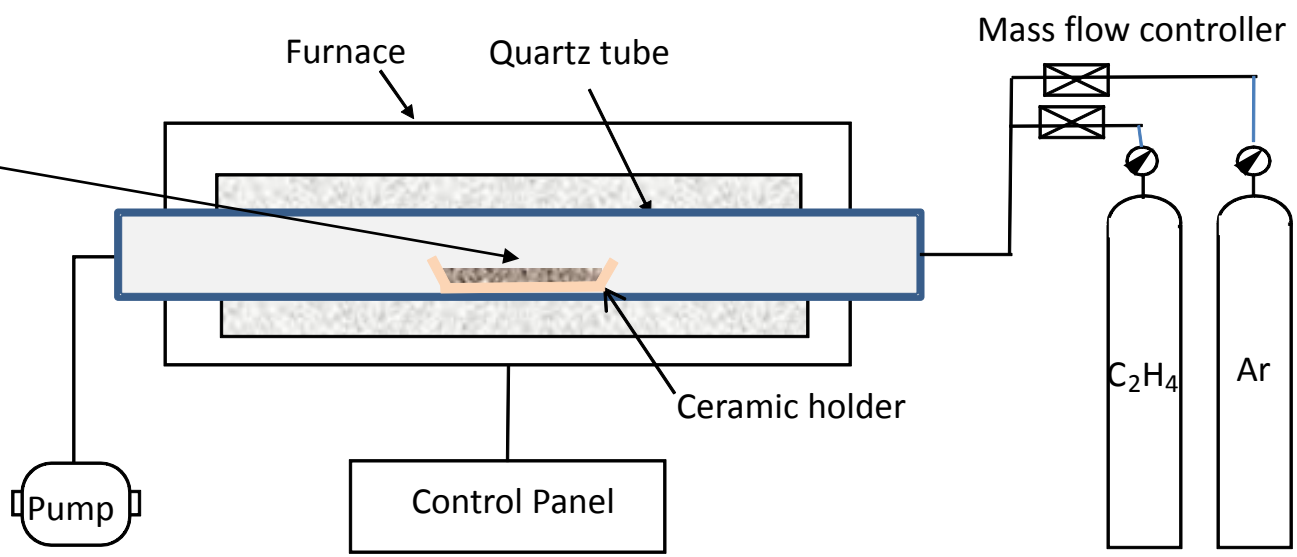
- **Approach:** Highly porous silicon (PS) was used as the active material. The porous structure will accommodate the volume change during charge/ discharge process.
- Carbon was coated on PS by CVD to improve its electronic conductivity.

Porous Si (VESTA Ceramics)
Pore size ~5nm





Particle size~4μm



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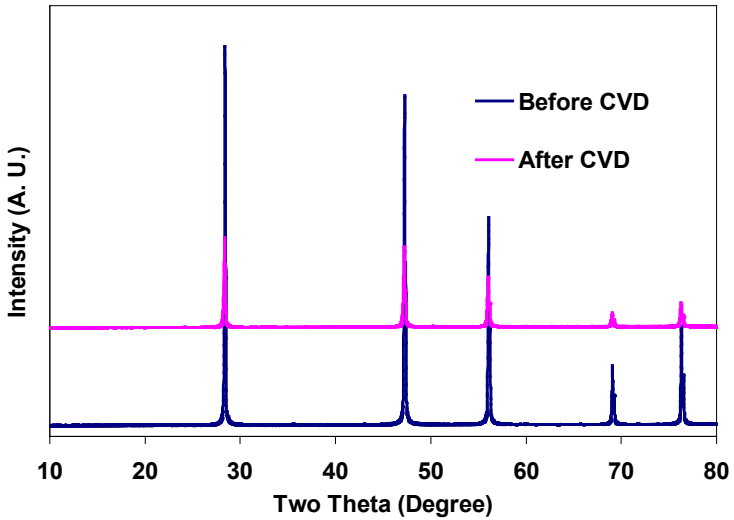
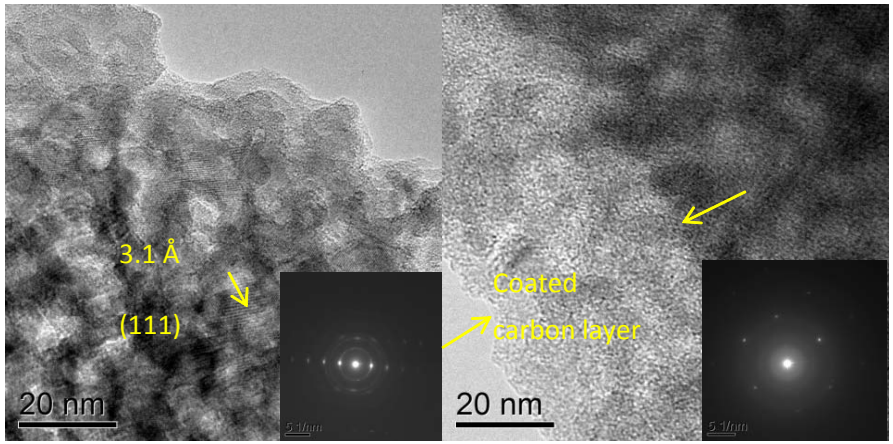
Technical Accomplishments:
Characterization of Porous Si Coated with Carbon





Porous Si

Porous Si after CVD carbon coating

- Highly porous Si with pore size of ~ 5 nm and particle size > 4 μm.
- CVD treatment: Amorphous carbon (XRD) is coated on the surface and within the pores (TEM).
- Total weight of coated amorphous carbon in Si/C composite is ~ 6%.
- Applicable to other electrode materials to increase the electronic conductivity.

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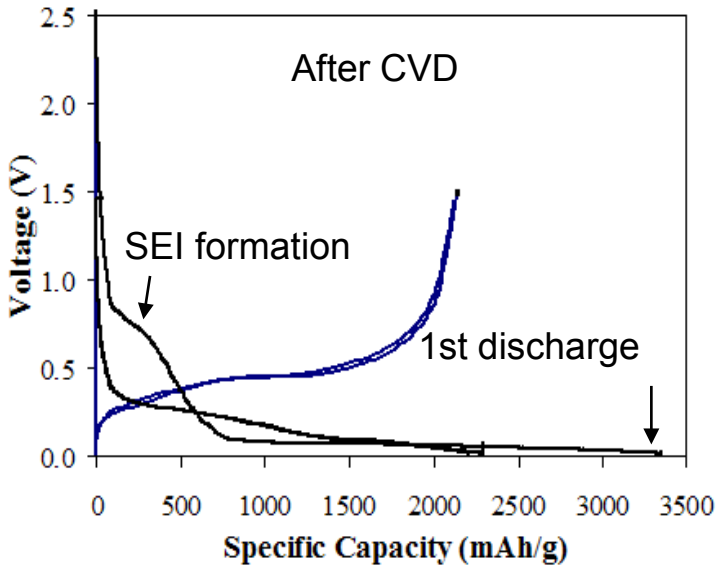
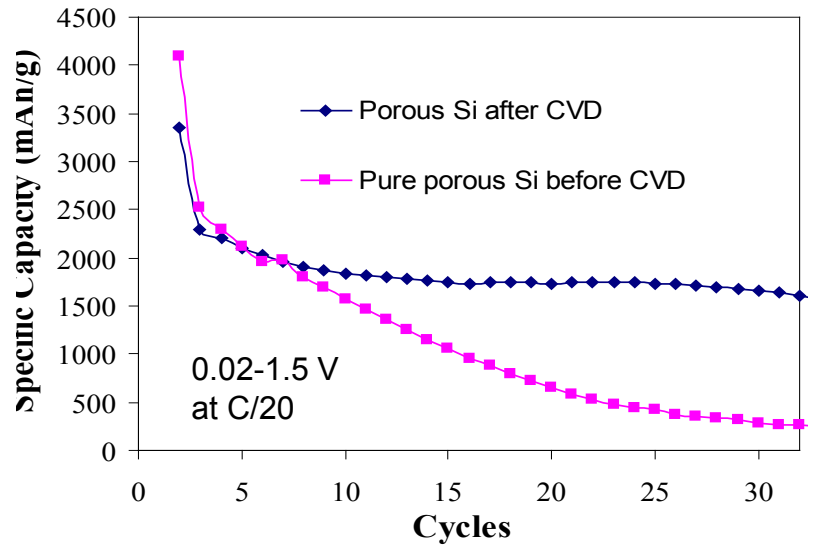
Technical Accomplishments: CVD-Coated-Carbon Improves Cyclability of Porous Si





- The nano-pores on the Si surface accommodate the volume variation and facilitate the Li^+ diffusion within the interconnected walls.
- After CVD treatment: Stable cycling is extended with a high reversible capacity.
- Irreversible capacity in the first cycle is due to the SEI formation and surface SiO_x.

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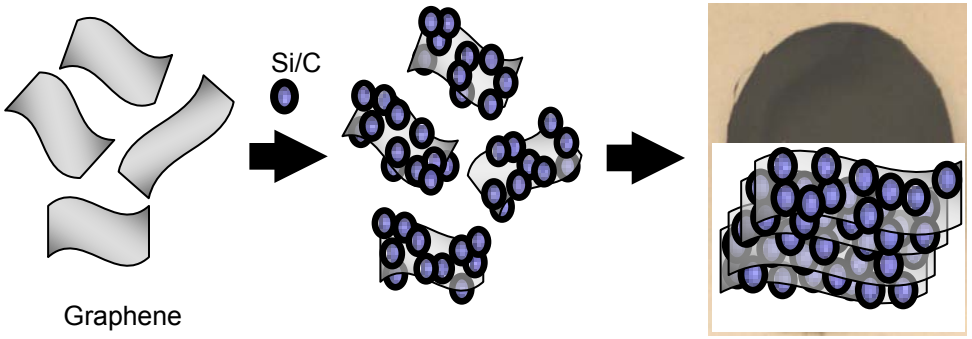
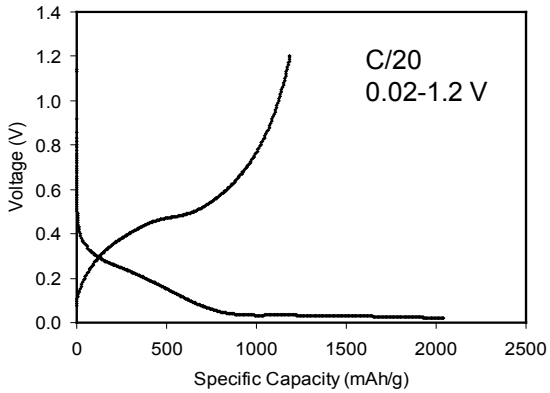
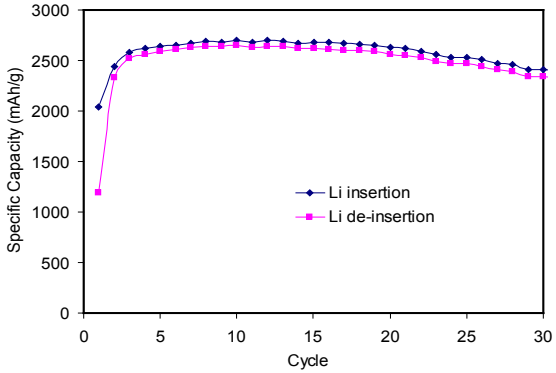
Technical Accomplishments:
Porous Si/Graphene Composite Demonstrated Improved Cyclability

Paper-like sample of
Si-graphene
Wt% of Si: 33%







- Capacity based on Si and whole Si/graphene hybrid electrode are ~2400 and 800 mAh/g, respectively.
- Initial increase of capacity can be attributed to the incomplete wetting of the dense electrode by the electrolyte.
- Graphene sheets buffer the volume variation of Si during cycling leading to a high reversible capacity and cycling stability.

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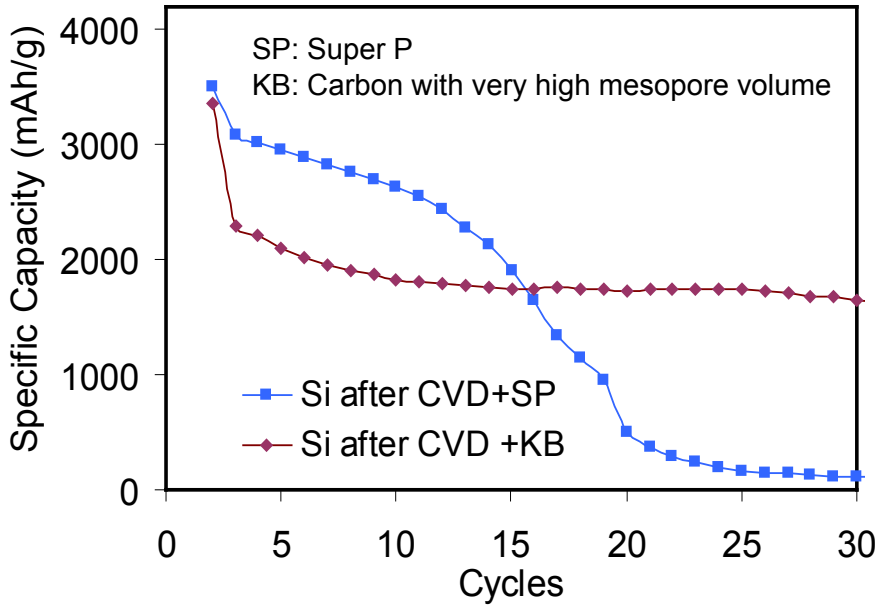
Technical Accomplishments:
Carbon Additive Has Significant Effect on The Cycling Stability of Micron-Sized Porous Si



- Si:carbon:binder = 6:3:1 in both electrodes.
- Cycling stability of micron-sized Si is significantly improved by using KB as carbon additive.
- The volume of KB carbon expands in the electrolyte absorbing part of Si particles into the pores of the KB — constant contact between Si particles is provided.
- Low-cost and effective approach to improve Si cycling simply by substituting Super P with KB carbon in the electrode preparation process.

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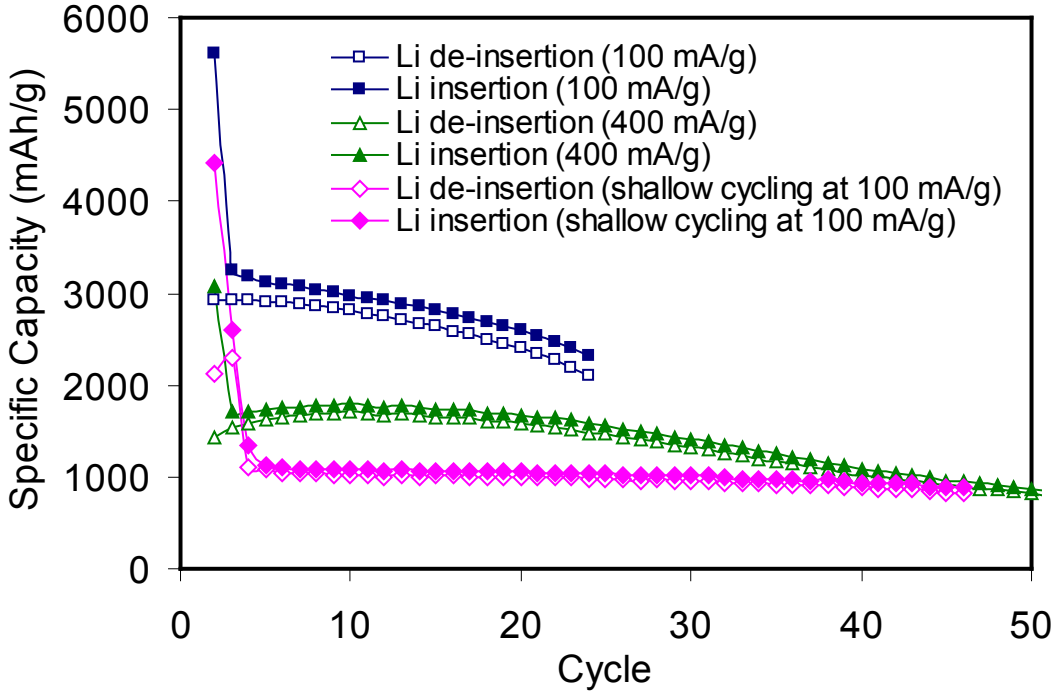
Technical Accomplishments:
Binder P Developed in PNNL Stabilizes Si



- Si:carbon:binder = 6:3:1 in all tests.
- High current rate (400 mA/g): Capacity fading rate decreases and reversible capacity stays ~ 1000 mAh/g.
- Shallow cycling (0.17-0.9 V): Only 0.7% capacity loss per cycle after first two formation cycles.
- Binder P can be applied on cathode material as well and its interaction with Si surface is under investigation.

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Collaboration and Coordination with Other Institutions

Partners:

- The Pennsylvania State University: Collaboration on the synthesis of metal oxide/graphene composite.
- Princeton University: Preparation and characterization of graphene.
- Vorbeck Inc.: Provider of graphene sheet.
- North Dakota State University: Collaboration on characterization of silicon nanowires prepared by electrospinning method.

Future Work

- Continue to improve the performance of silicon based anodes for Li-ion batteries.
  - Optimize the composition of Si/graphene to balance the high capacity and cycling ability.
  - Optimize the size and morphology of Si and graphene in the Si/graphene composite to increase the utilization rate of Si.
  - Further improve cycling stability of silicon based anode by optimizing binder P and new additives developed in PNNL recently.

- Further Improve the performance of SnO_2/graphene by optimizing the size and surface properties of the graphene.

- Investigate stabilized lithium metal anode (preventing the dendrite growth) for their application in lithium batteries.

Summary

- ✓ **Highly stable SnO_2/graphene and TiO_2/graphene composites were successfully prepared through a unique self-assembly approach.**
  - Preparation of free standing electrodes without binder.
  - Stable cycling and excellent rate capability were achieved in both composites.
- ✓ **Si has been evaluated as an anode candidate for Li-ion batteries.**
  - Synthesized Si nanowires from silicon powder.
  - Micron-sized porous Si showed high reversible capacity and extended cycling after uniform carbon coating.
  - Porous Si sandwiched by graphene sheets exhibited improved cycling stability and high capacity (>2,300 mAh/g in 35 cycles).
- ✓ **New carbon additive and binder are identified at PNNL and utilized to further improve the long-term cycling stability of Si-based anode.**

Acknowledgements

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- ✓ Team Members:
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