Nano-structured Silicon Anodes for Li-ion Batteries: Cycle Life and First Cycle Capacity Loss Improvement

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Outline

- Why Si? Why nano-structured Si? What are cell level benefits?
- ATC nano-structured anode fabrication and test
- Results
  - Specific capacity
  - Cycle life
  - Rate capability
  - First cycle capacity loss
- Summary

Why Si?

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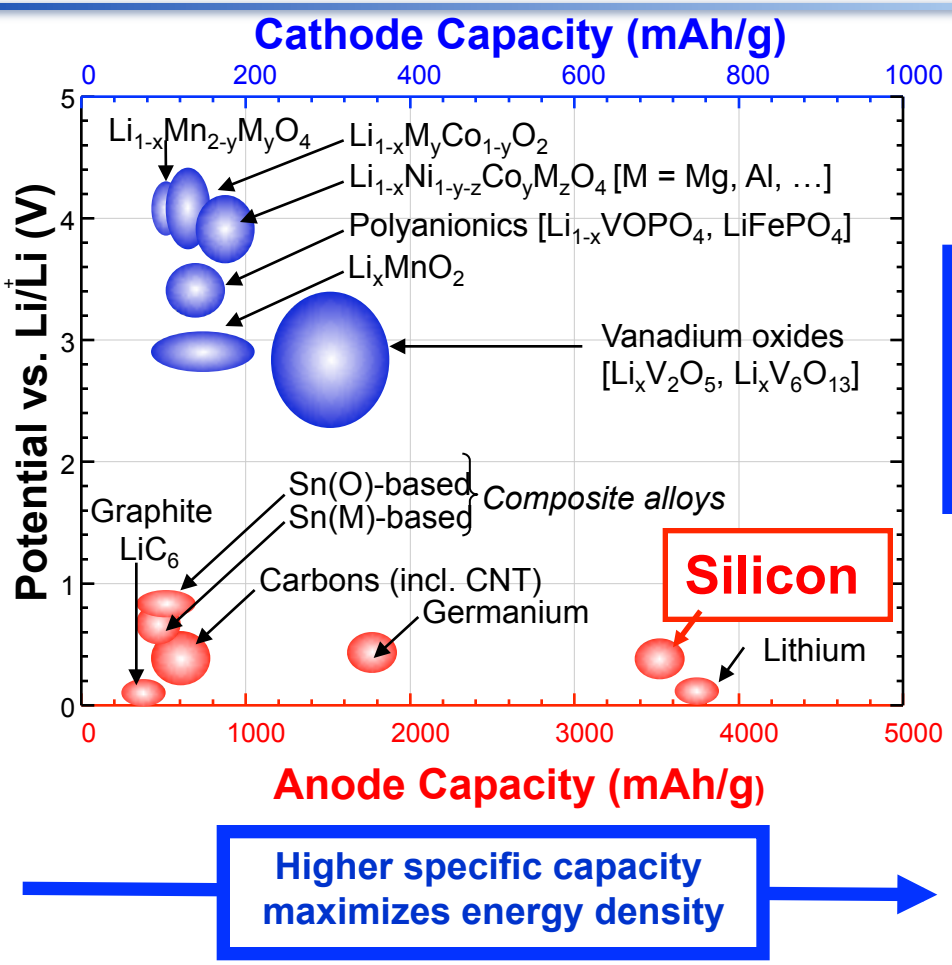

Lower (more negative) anode voltage maximizes energy density

Higher specific capacity maximizes energy density

Note: Except for Li, the specific capacity of anode materials is based on delithiated state (discharged material) whereas Li is based on that of the metal (charged material)

Si has highest Li "storage capacity" of any known material

Why Nano-Si?

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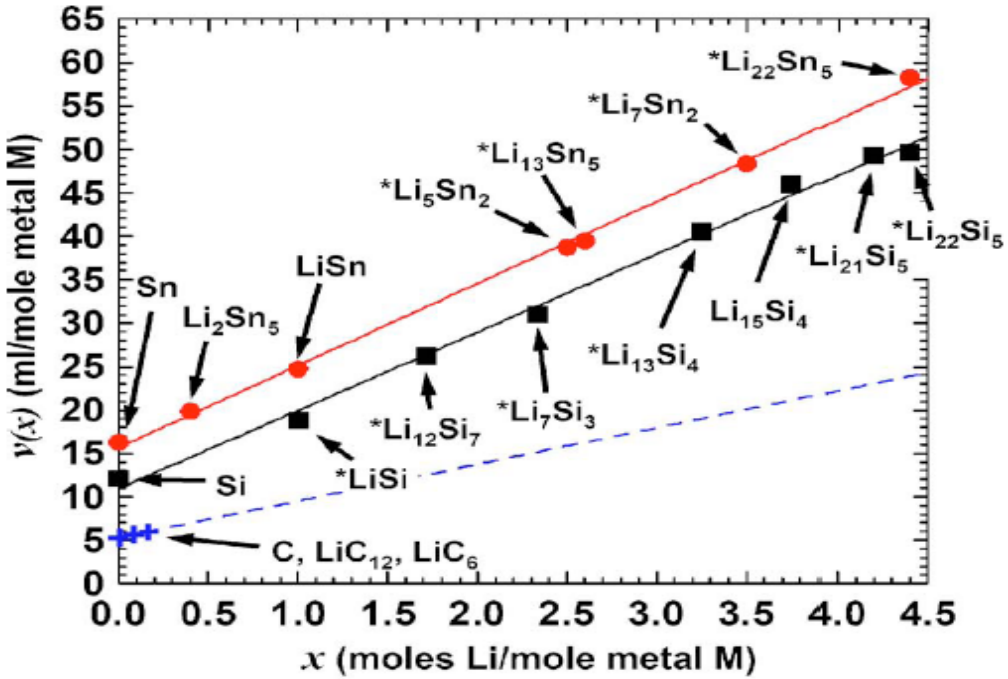

Source: Alloy Design for Lithium-Ion Battery Anodes; M. N. Obrovac, L. Christensen, D. Ba Le, J. R. Dahn; J. Electrochem. Soc., 154 9 A849-A855 **(2007)**

- ***Volume expansion during Si insertion causes mechanical stress***
- ***Mechanical stress leads to particle fracture porous electrode failure and poor cycle life***

Nano-structuring of Si anodes is strategy for mitigating negative effects of volume expansion and thereby improving cycle life

Li-ion Cell Mass Breakdown & Benefits of Si Anodes

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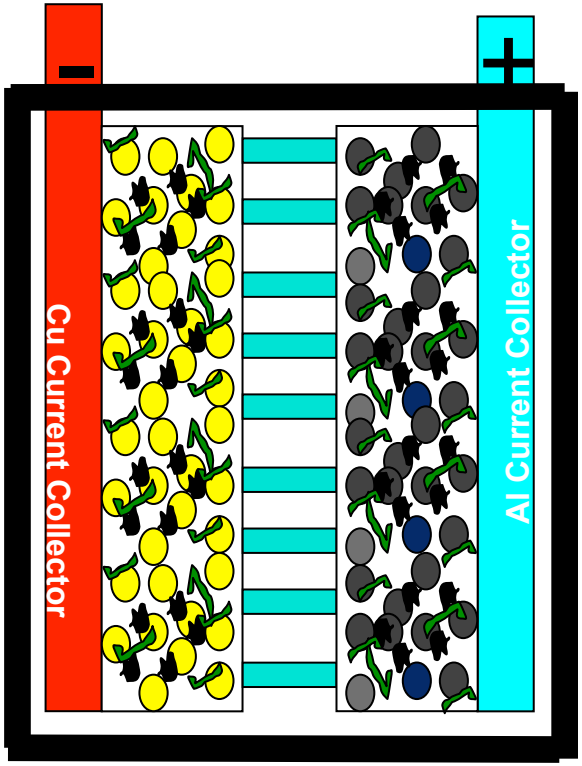

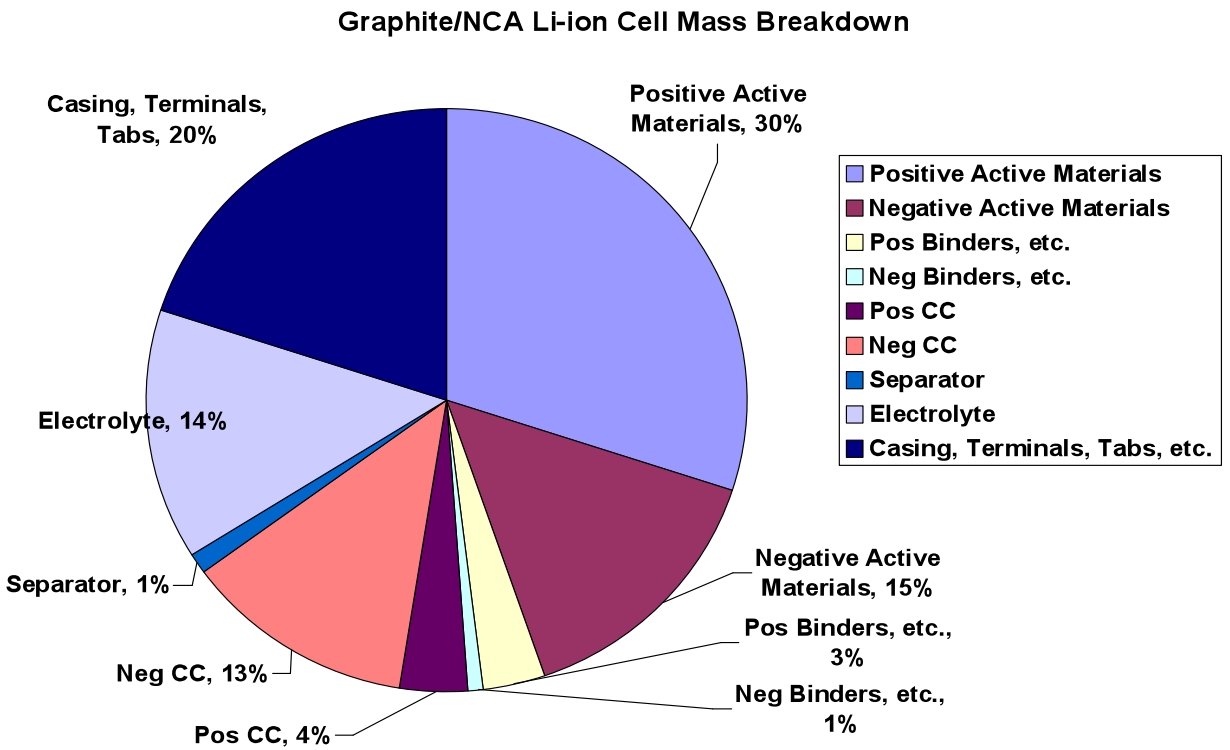

- Negative active material comprises ~ 15% of Li-ion cell mass
- Factor of 10 decrease in battery mass not possible with anode improvements alone* (despite what it may say on the internet)

* NASA's Advanced Li-ion Cell for Exploration Missions Program includes cathode, electrolyte and cell tasks

Significant Recent Improvement in Cycle Life

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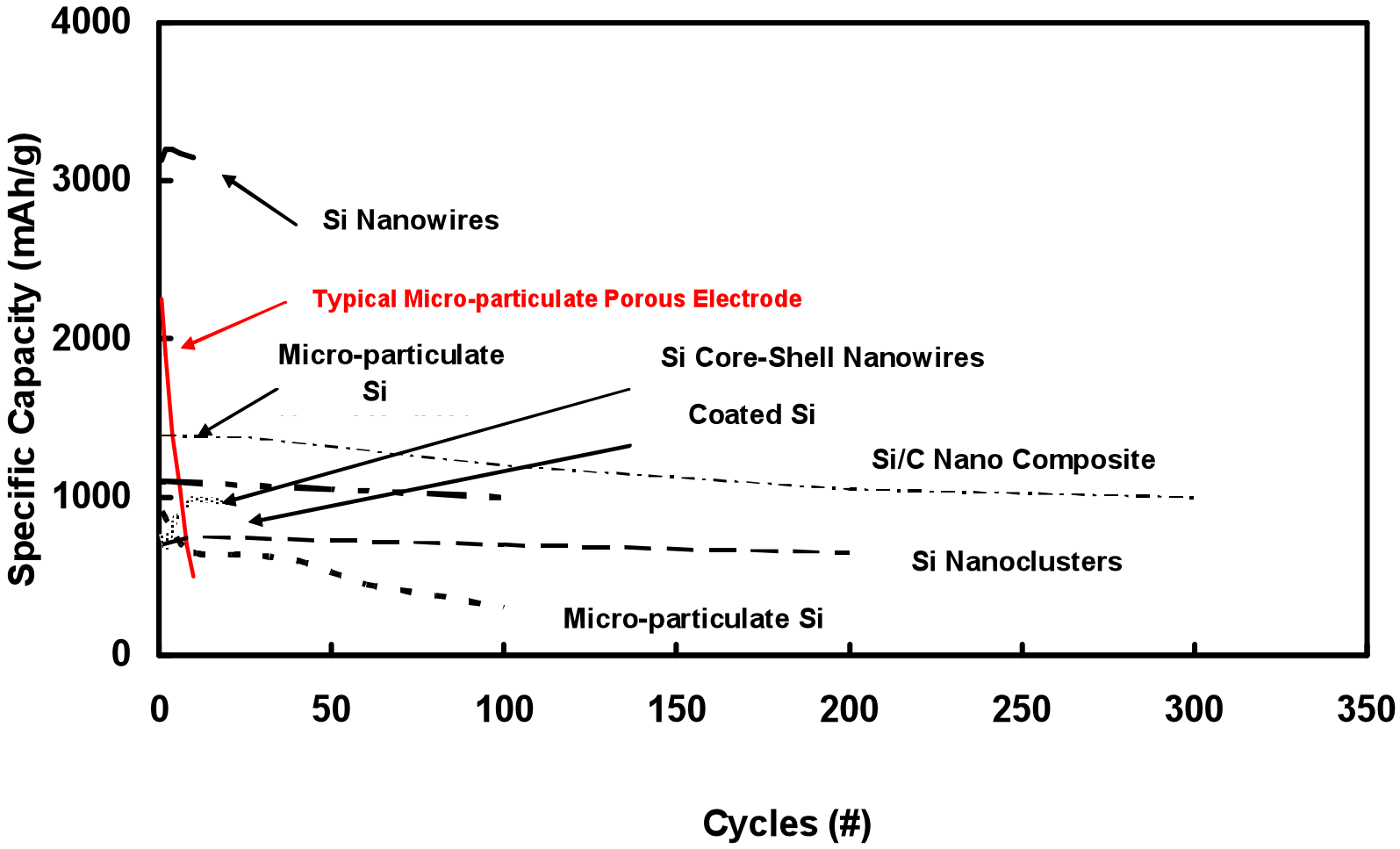

State-of-art is 1000-1500 mAh/g and 200-300 Cycles

Electrode and Cell Fabrication

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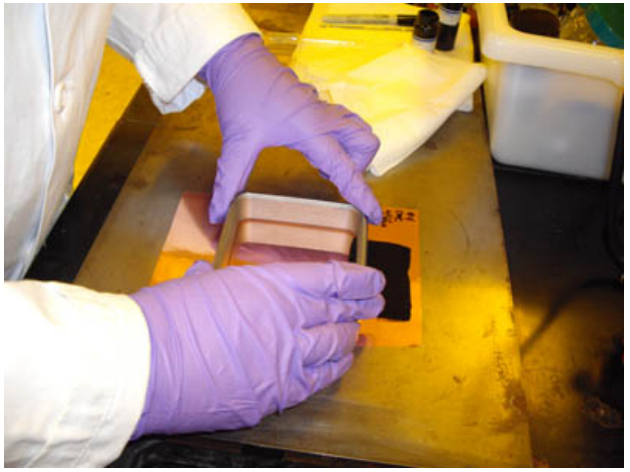
- Electrode formulation
  - Silicon nano-materials
  - Conductive diluents
  - Polymer binders
- Electrode fabrication process
  - Slurry mixing/homogenizing
  - Coating
  - Drying
  - Calendering
- Test cell design & material
  - ~12 cm^2 electrode
  - Cu current collector
  - Celgard 2320 or similar separator
  - Li counter electrode (unless noted)
  - Metallized foil pouch



Anode Leverages existing Li-ion Manufacturing Infrastructure

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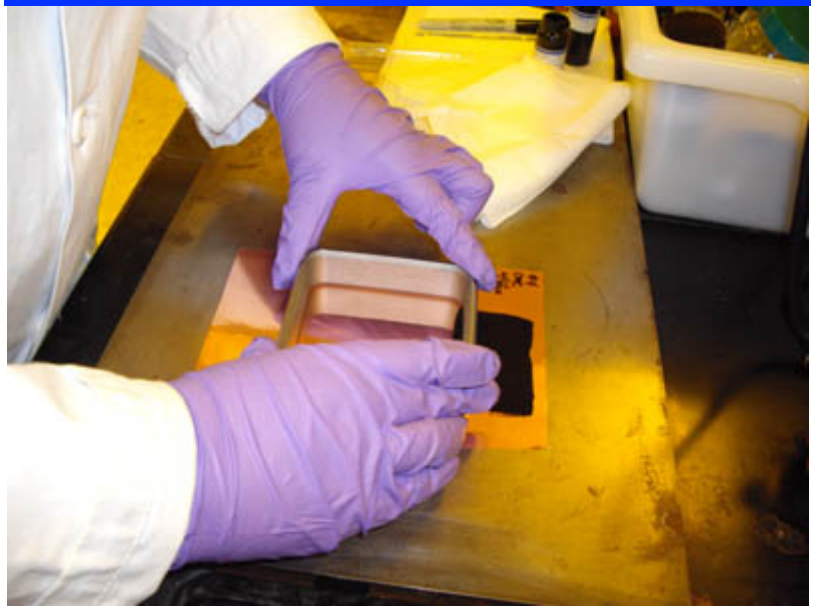
Lab Coating Process



Industrial Coater

- Nano-sized scale active materials substitutes for existing anode material
- Can use existing mixing, coating, drying, compression and packaging equipment

Optimization decreases Resistance and increases Efficiency

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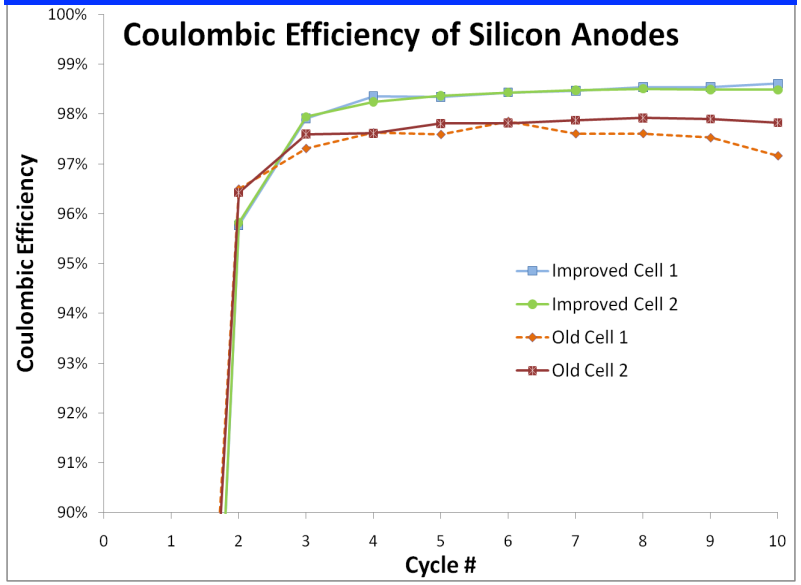
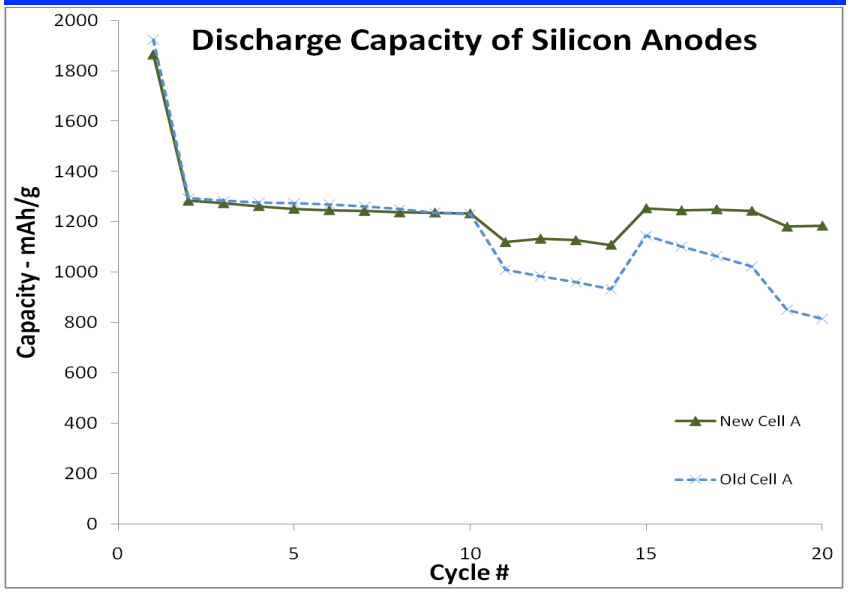
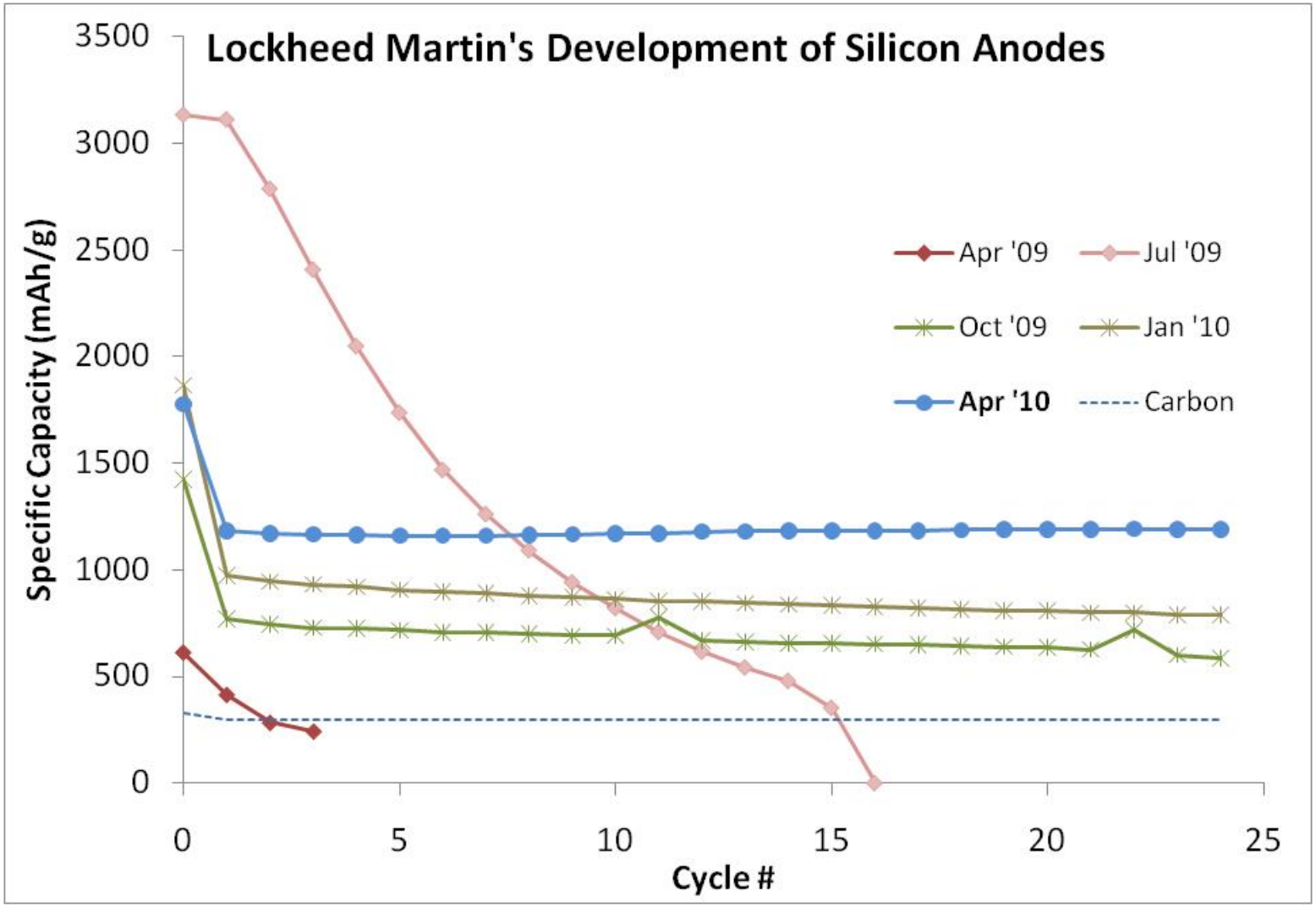
Increased Coulombic Efficiency



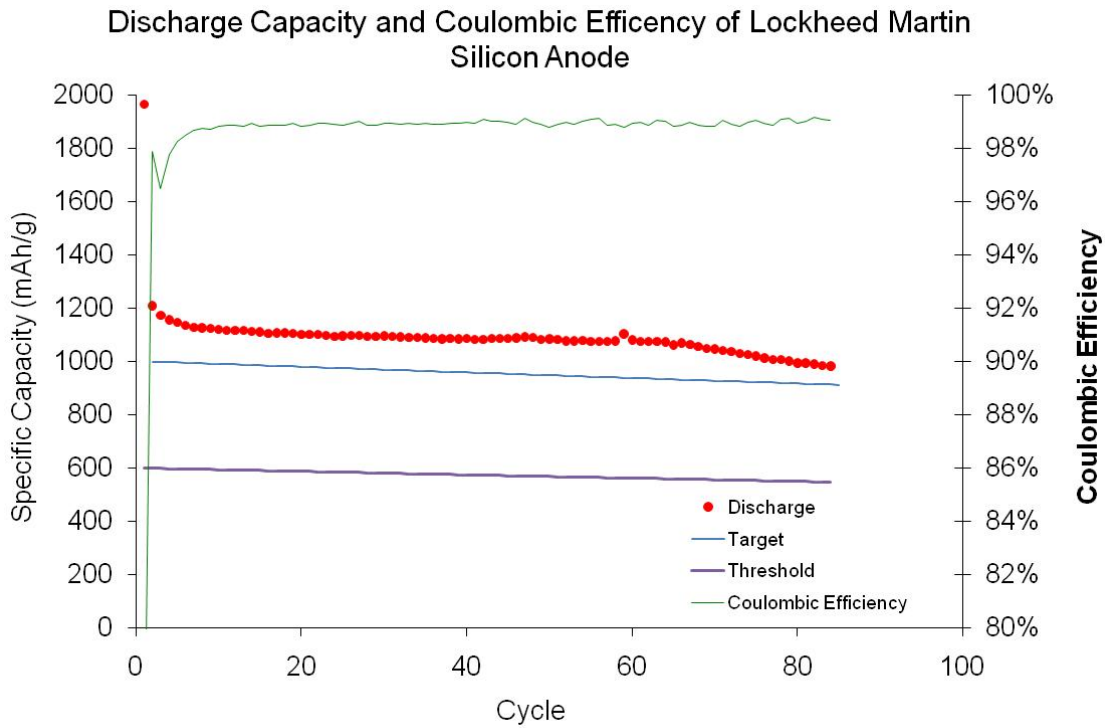
Lower Internal Resistance and Better Rate Capability



Optimization reduces Capacity Fade and Increases Cycle Life



Good specific capacity and cycle life in half cells



- 1000-1500 mAh/g Si
- 80+ cycles with < 20% capacity loss
- 99+% coulombic efficiency

ATC Anode cycle life is near state-of-art

Good discharge rate capability

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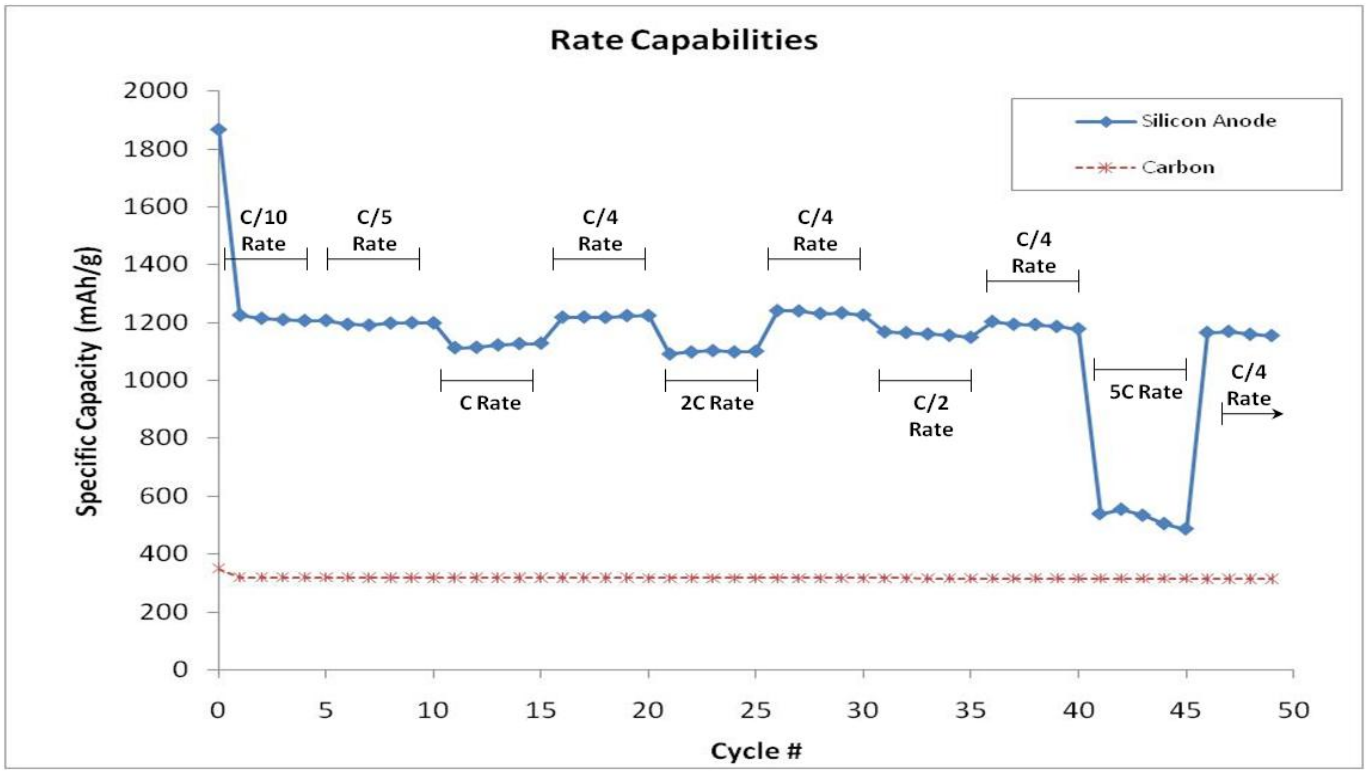

Note: Test is at Room Temperature

Discharge rates to 1C with little capacity loss

Why do we care about coulombic efficiency?

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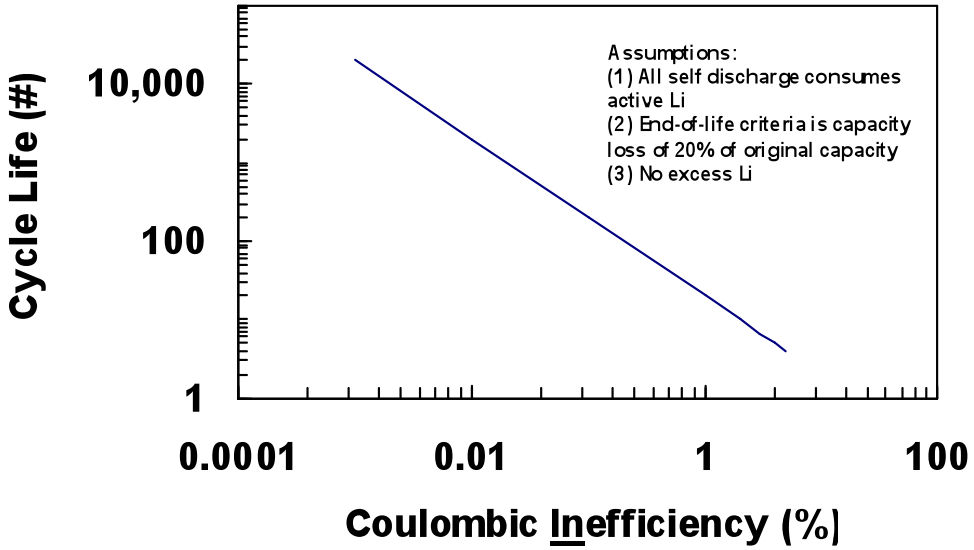
Sources of coulombic inefficiency

- Electronic short
  - e.g. A particle bridging the separator
    - Benign w/regard to cycle life
- Electrochemical self-discharge
  - Reversible (shuttle reaction)
    - Benign w/regard to cycle life
  - ➢ Irreversible
    - Reduces battery life
      - Consumes active Li and solvent
      - Increases SEI resistance



- Cells on life test for 9 yeas at LM have capacity fade much less than predicted by coulombic efficiency
- Actual capacity fade may be much less than that projected from coulombic efficiency
- Coulombic efficiency provides estimate for "worst case" capacity fade

Irreversible self discharge reactions cause capacity fade but some self discharge mechanisms may be benign: Full cell cycle tests required !

Good Cycle Life in Full Cells

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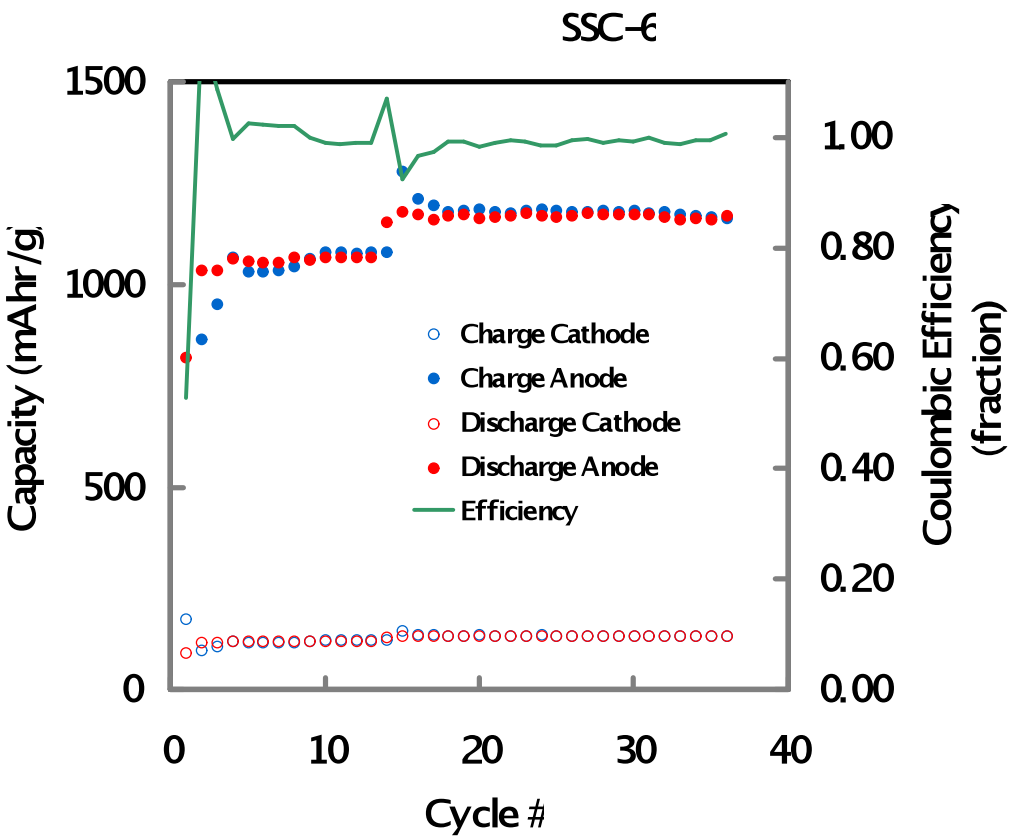
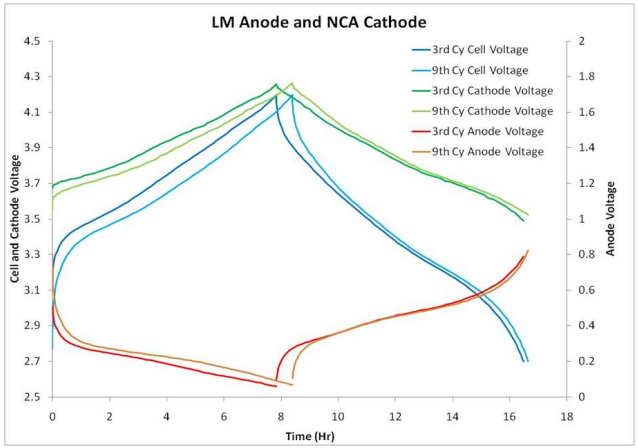


Capacity Loss Projections from Coulombic Efficiency

- 710 mAh/g anode
- 81 mAh/g cathode
- 20% of anode theoretical
- 48% cathode theoretical



Capacity Loss less than projected from coulombic efficiency

1st Cycle Capacity Loss Reduction

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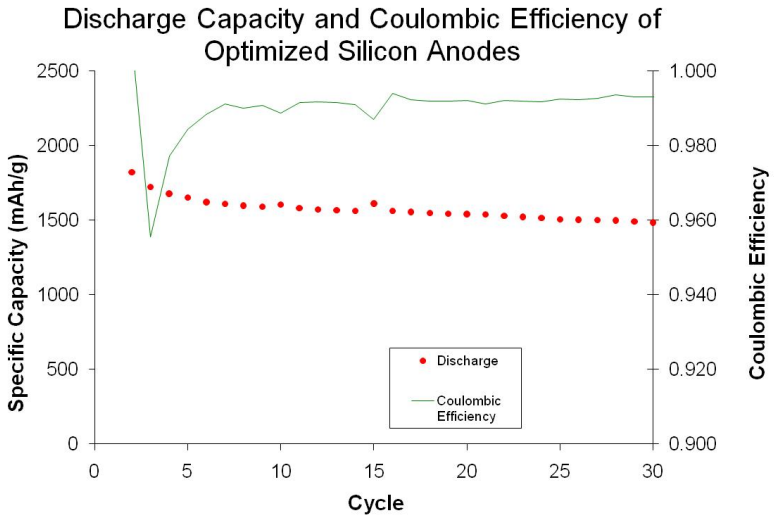
- 1st cycle capacity loss reduced by up to 100% (may not be achievable industrially)
- Significant additional work needed to demonstrate viability



Destructive Physical Analysis

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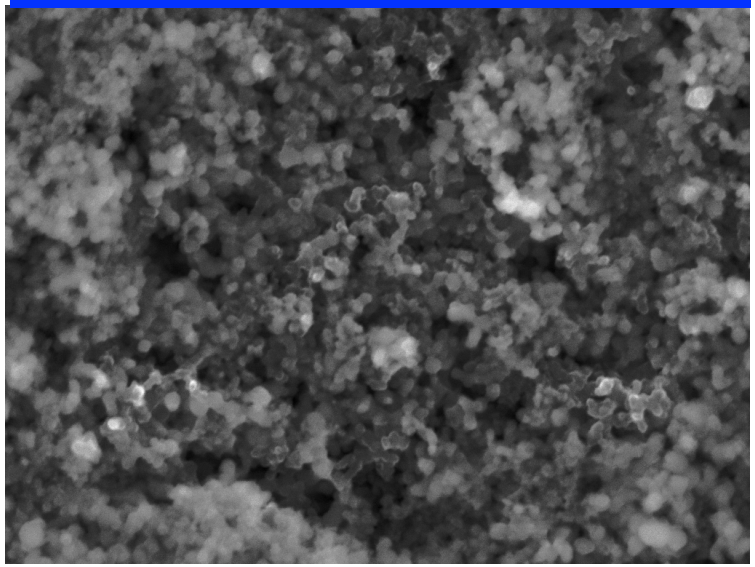
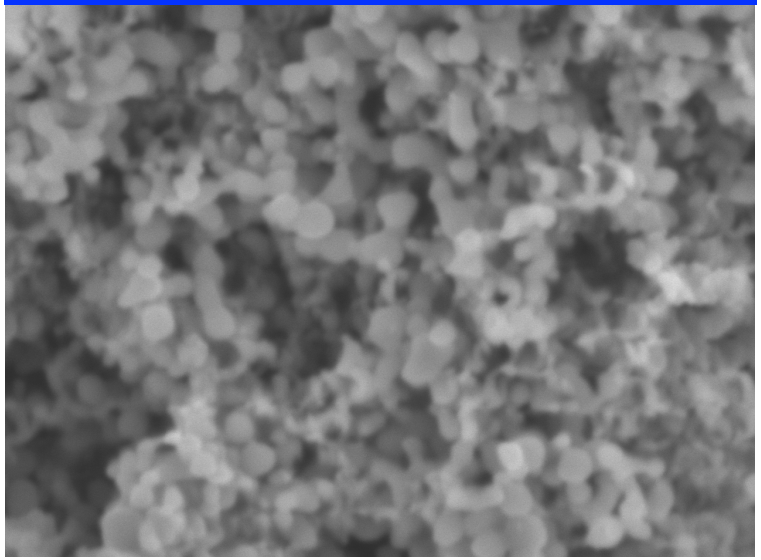
Electrode removed from cell after 37 cycles and analyzed by SEM

Post-test Electrode



Pre-test Electrode



No evidence for material degradation

Summary

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- High capacity silicon-based Li-ion battery anode materials under development at Lockheed Martin

- Significant recent improvements in cycle life, coulombic efficiency and 1st cycle capacity

- Cycle life and specific capacity are near state-of-art values reported in literature

- Material utilizes existing Li-ion equipment and manufacturing processes

THANKS!

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