Nanostructured Composites for High Capacity Anodes

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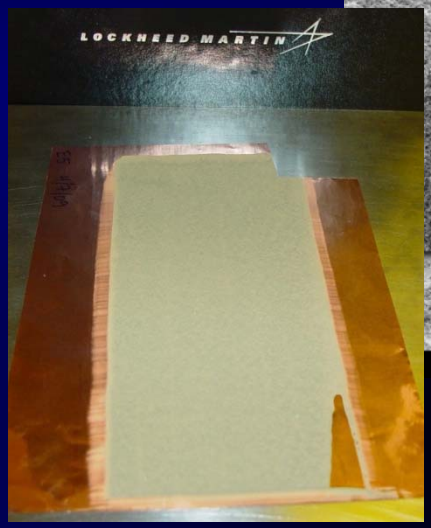
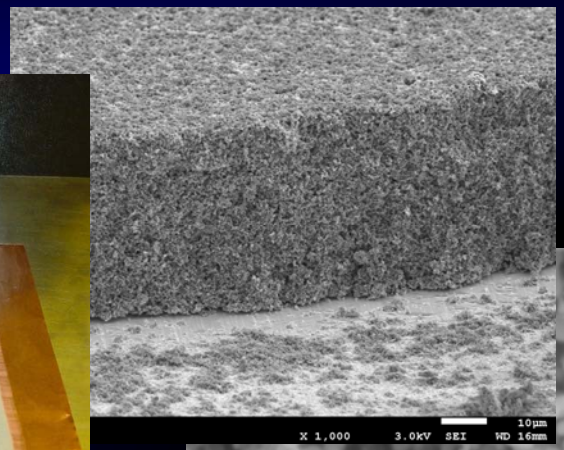
ANSCA – Advanced Nanostructured Silicon Composite Anode

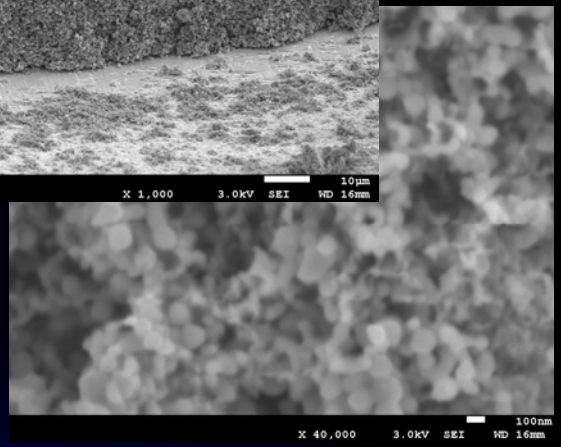
NASA GRC Exploration Technology Development Program – Energy Storage Project

Lockheed Martin Space Systems Company cross-functional team

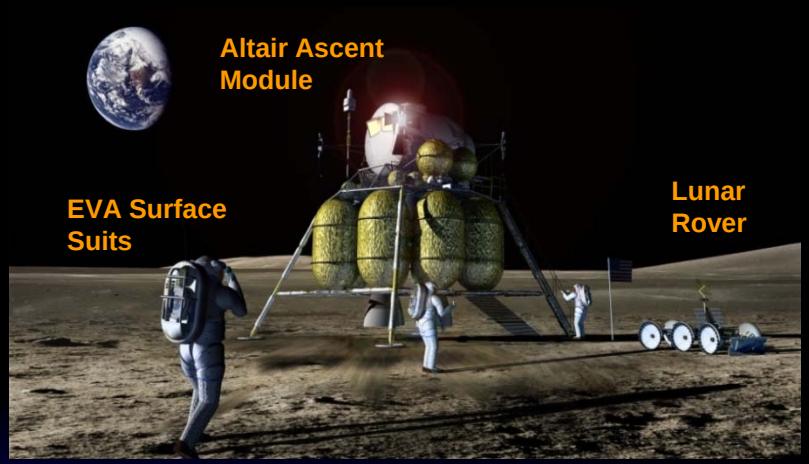
Human Space Flight and Advanced Technology Center







Nanostructured silicon active materials designed to deliver high specific energy and mitigate traditional cycle life limitations



ANSCA Performance Objectives

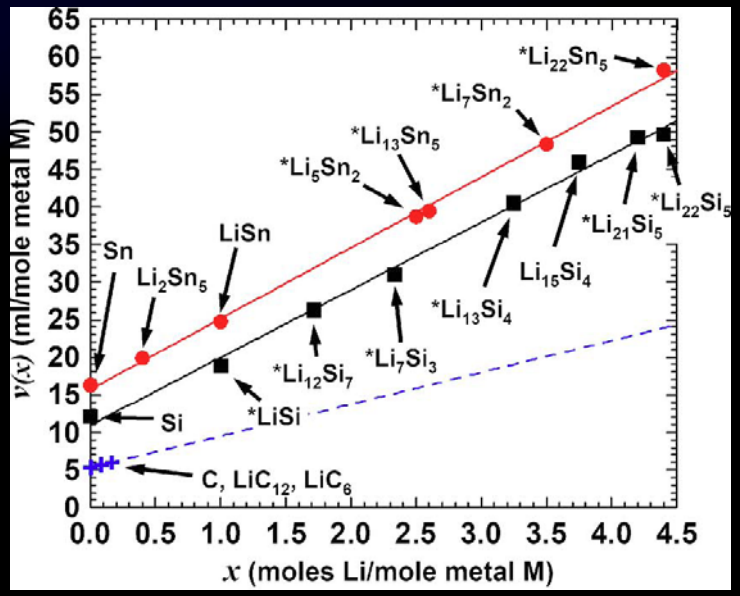
Specific capacity: 1000 mAh/g at 0°C and C/10
Cycle life: 200 cycles at 100% depth of discharge
Capacity retention: 80% through 200 cycles
Methods and materials developed to TRL 4

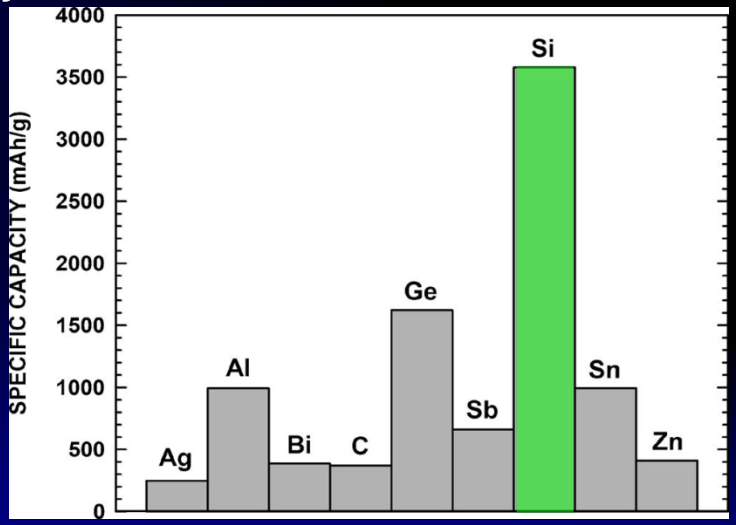
Anode materials engineered for high capacity to reduce mass and volume for advanced batteries to support Constellation and Exploration projects

Image courtesy of NASA

Silicon Materials Are Attractive Candidates for Ultra High Capacity

- Amorphous silicon has nearly 3600 mAh/g specific capacity
- Four lithium ions per silicon leads to very large specific capacity improvements
  - Theoretical graphitic anode: 372 mAh/g
- Silicon has strong potential as a high capacity anode material, but typically exhibits poor cycle life





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)**

Approach Designed to Address Degradation Mechanisms While Considering Scalability

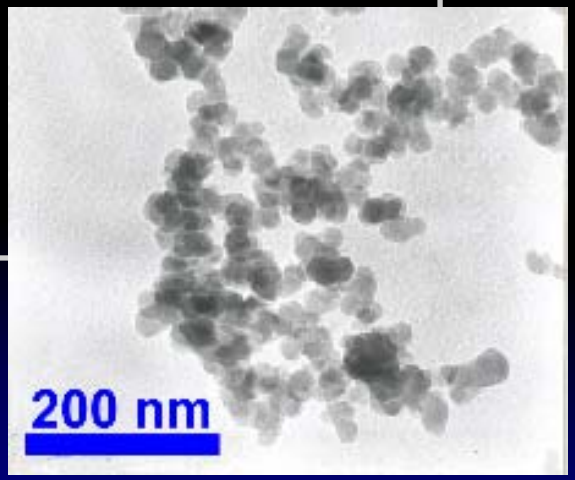
Lockheed Martin ANSCA approach reduces battery mass and volume	
Nanostructured Active Material Active composite materials will be made from Si nanoparticles with diameters of 100 nm or less. **Result:** Size reduction to nano-scale mitigates volume changes from active material lithiation.	**Surface Functionalization/Modification** Binder network is bonded to the nanoparticle surface using reactive functional groups. **Result:** Structure created that is more mechanically robust to volume expansion/contraction.
Elastomer Binder Polymer binder network has controllable modulus of elasticity through composition and cross-linking. **Result:** Binder elasticity can be engineered to be capable of responding to volume changes during lithium intercalation.	**Tailorable Viscosity** Pre-polymers will preferentially accumulate in the interstices between particles because of surface tension. **Result:** Pre-polymers will form a strong bond at key points during curing process, leaving active surface area accessible to Li during charge/discharge cycles.
Electrode Mixing Process The uncured pre-polymers are added directly to the coating slurry and then cured in the drying and/or calendaring processes.	

Strategy is to improve cycle life using materials and processes easily transferrable to existing battery manufacturing infrastructure.

Silicon Nanoparticles May Enable Ultra High Capacity

Benefits of Working at the Nanoscale

- **Improved cycle life**
  - Lower mechanical stress during cycling
- Faster charge and discharge rates
  - Extremely high surface area
    - Higher 1st cycle capacity loss
  - Shorter Li^+ diffusion path length
  - Shorter electronic conduction path

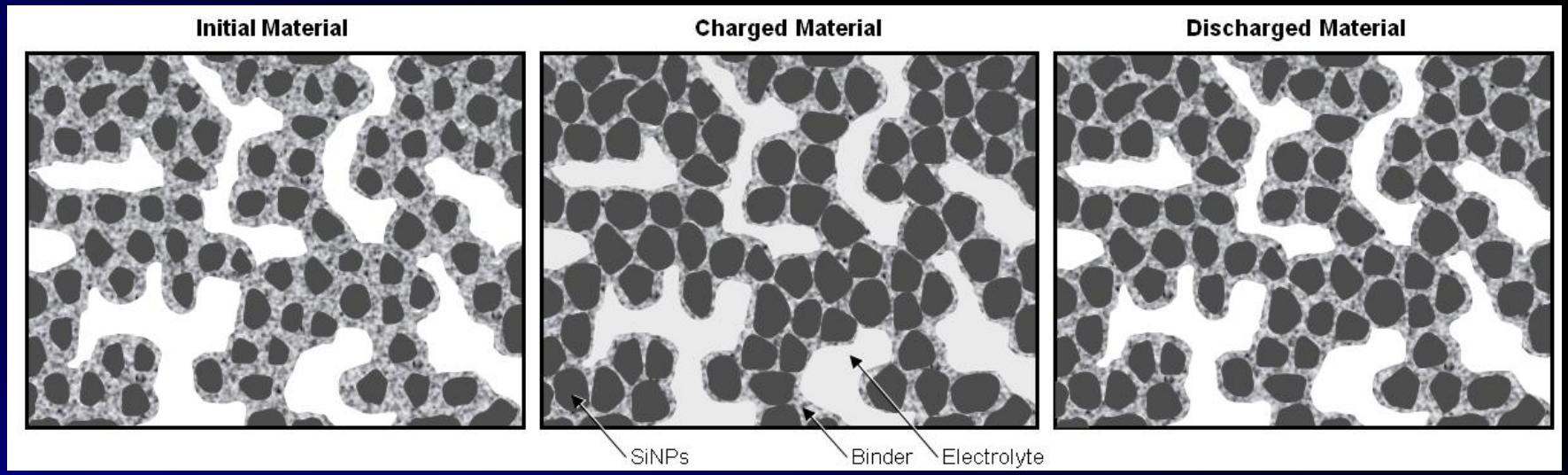


High Capacity and Long Cycle Life Enabled by Electrode Design

Porous electrode provides continuous electrolyte pathways and electronic conductivity

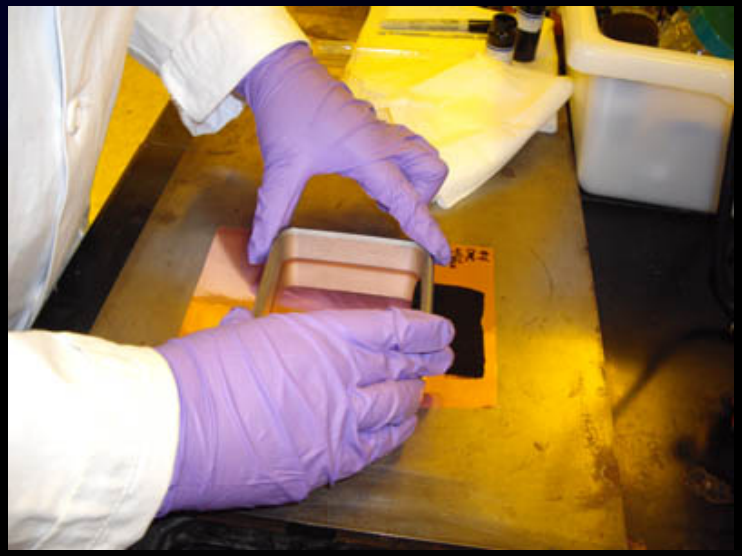
Silicon swells to 2.5 times the original size upon lithium insertion

Binder is designed to accommodate volume expansion and maintain electronic structure



Binder is optimized to accommodate expansion effects during cycling

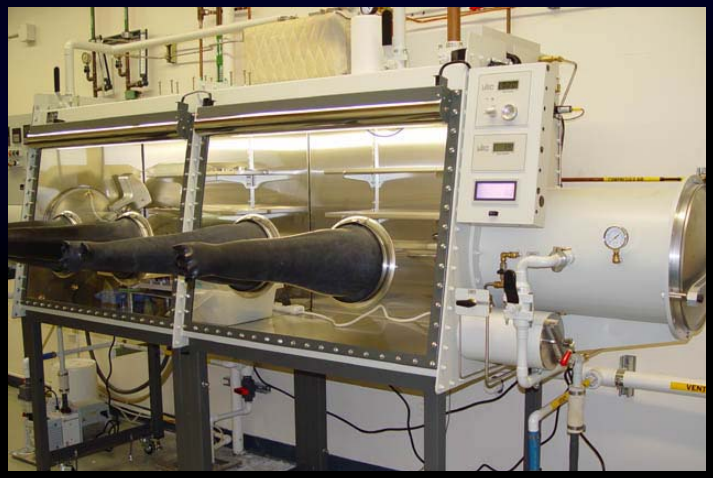
Electrodes Coated onto Copper Foil and Prepared for Pouch Cells



- Slurry made from silicon nanoparticles, conductive carbon, and binder
  - Mixing performed using homogenizer
  - Viscosity adjusted to similar consistency
- Electrodes coated using drawdown
  - Manual coating process
  - 200 um (8 mil) coating onto film
- Electrodes dried in vacuum oven, then calendered
- Electrodes cut from foil using template
  - Template ensures size uniformity between electrodes

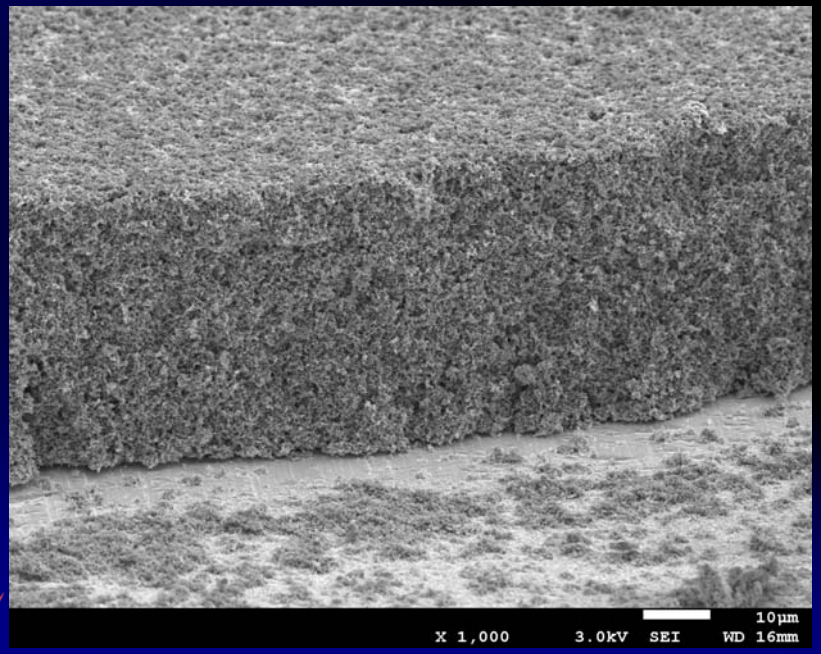
Pouch Cells Assembled in Glove Box and Tested in Parallel

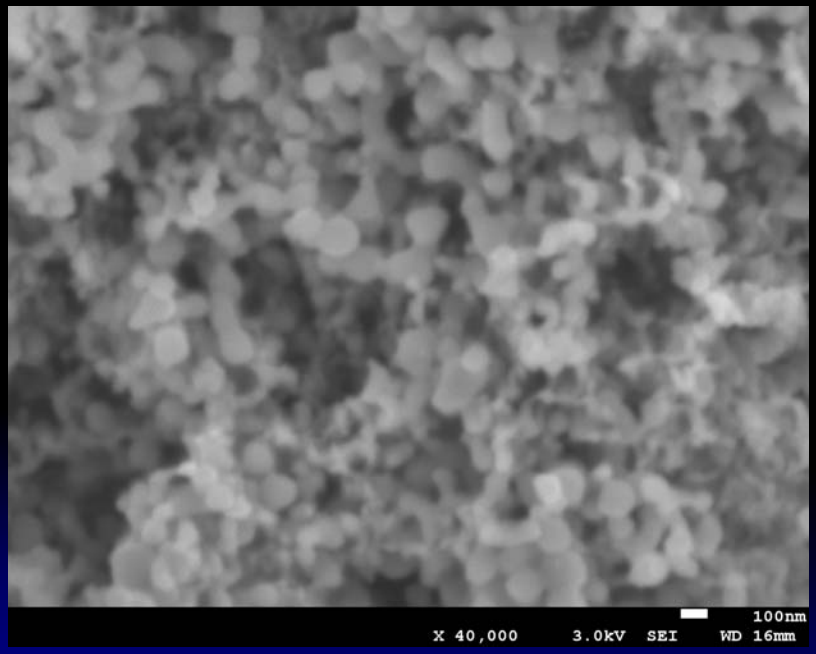
- Electrode materials kept dry
- Pouches assembled in glove box
- Electrolyte $LiPF_6$ in EC/DEC/DMC
- Multiple cells built and tested



Porous Electrodes Structure is Confirmed by SEM Analysis

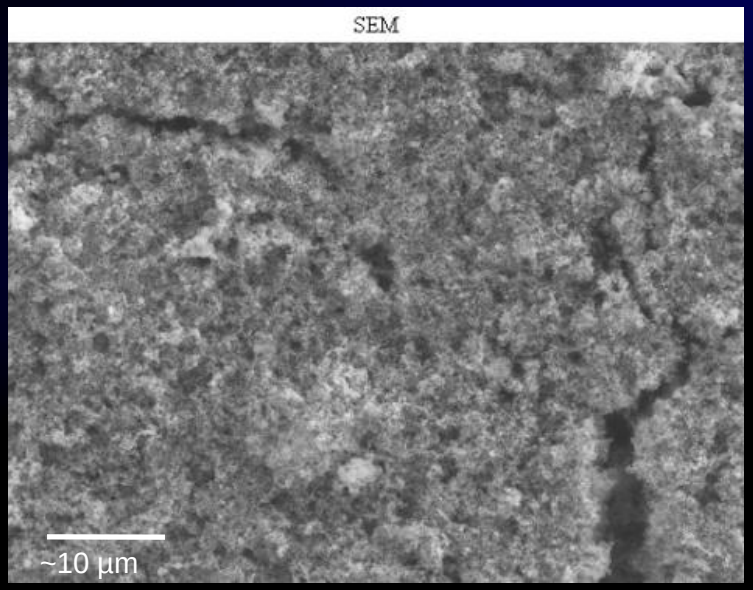
- 50 µm electrode thickness targeted
- Calendered electrode retains good porosity
  - Allows electrolyte penetration and lithium transport
  - Accommodates volume expansion during lithiation

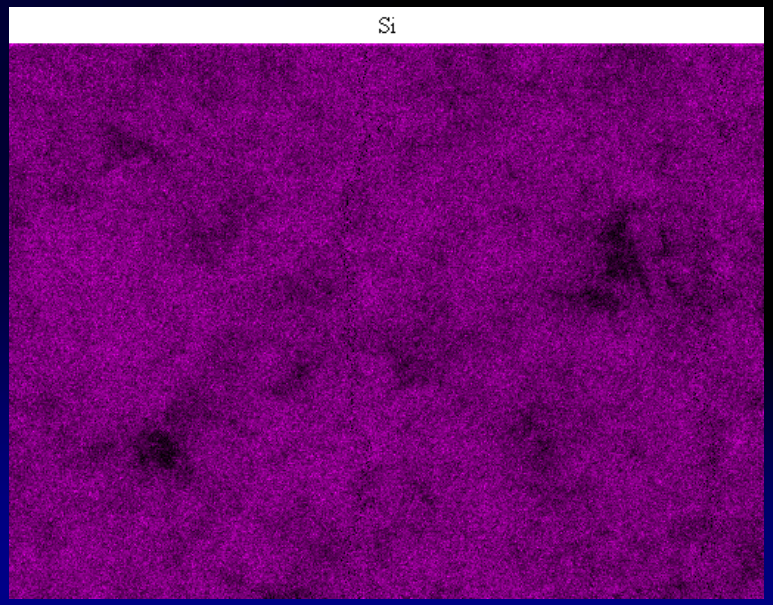


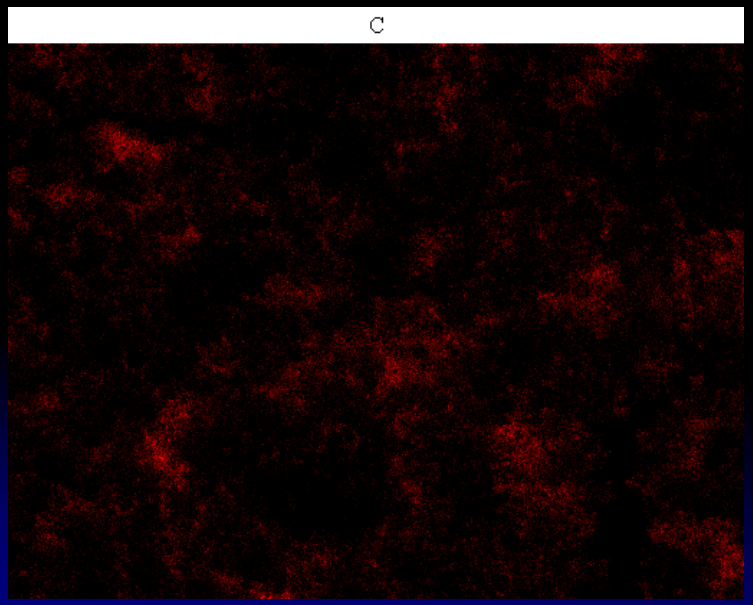


Silicon Distribution Even Throughout Electrode

- EDS analysis confirms uniform distribution of silicon throughout electrode
  - Dark areas in Si EDS map correspond to carbon-rich areas







Initial Experiments Suggest Materials Utilization is Poor

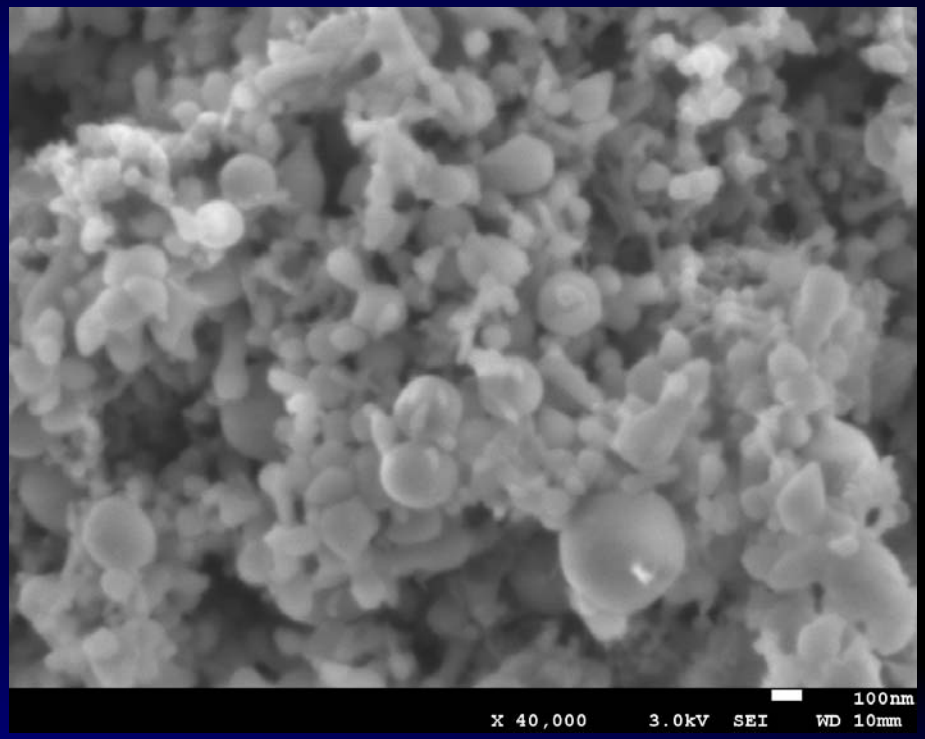
- 80% Silicon; 10% Carbon Black; 10% Binder
- Active materials charge/discharge capacity through three cycles
- ~14% of theoretical materials utilization
- Coulombic efficiency from 40% for cycle 1 to 70% for cycle 3
- Cycling gets better over time

SC12		
Cycle	Charge Cap (mAh/g)	DsChg Cap (mAh/g)
1	908	386
2	724	448
3	639	447

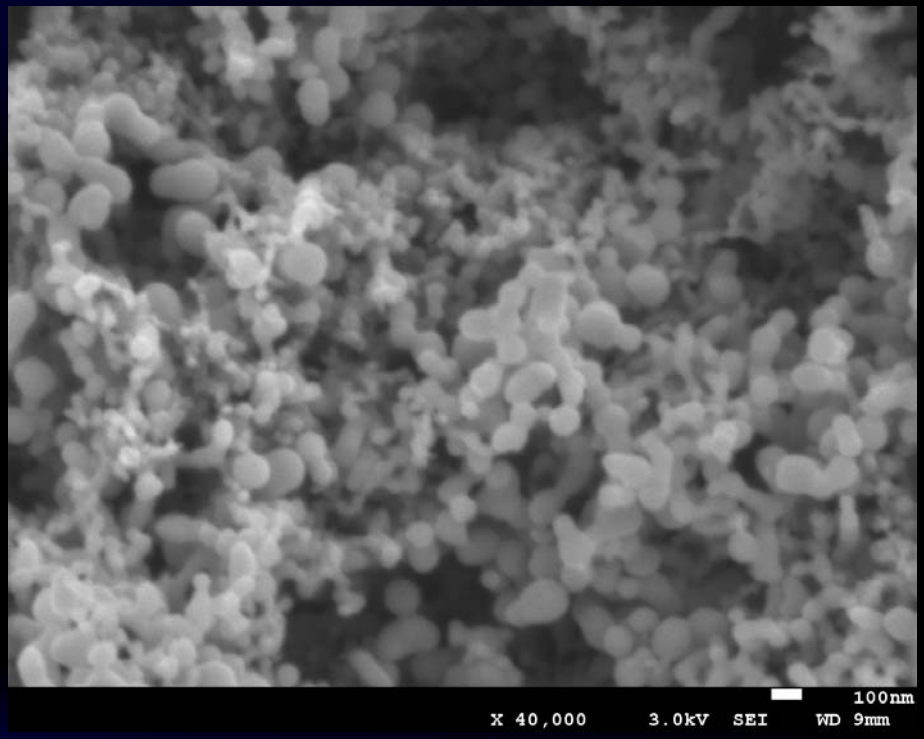
SC13		
Cycle	Charge Cap (mAh/g)	DsChg Cap (mAh/g)
1	807	357
2	775	451
3	697	496

Nanoparticle Size Effects Investigated

Active Material A



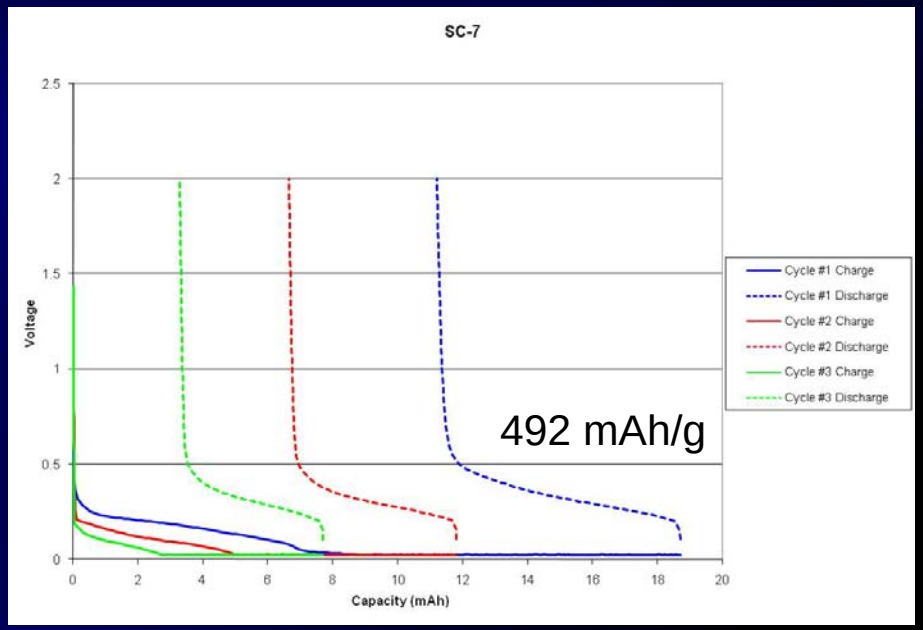
Active Material B



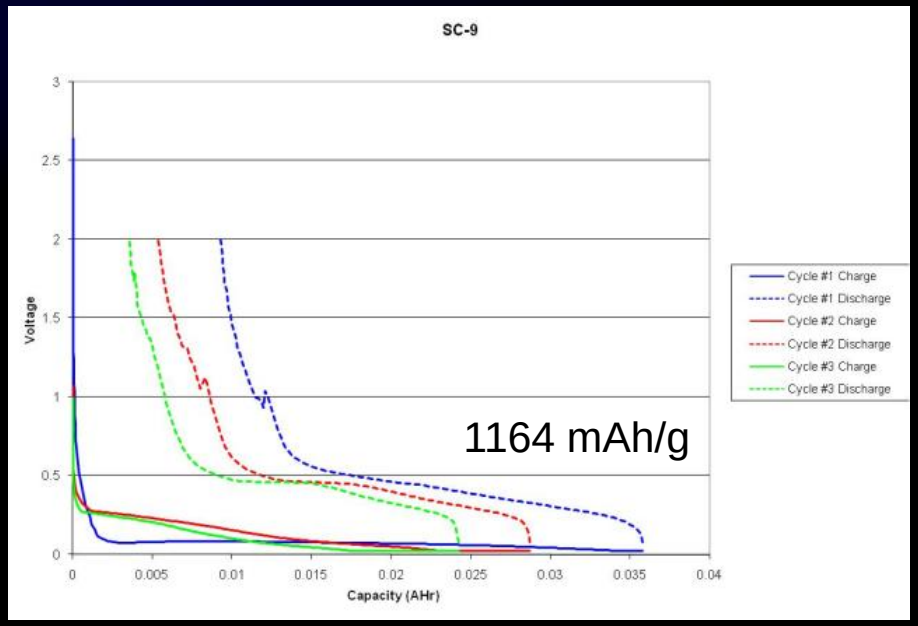
Active Material A has a size distribution described as <100 nm
Active Material B has a size distribution centered roughly at 60 nm

Nanoparticle Size Affects Specific Capacity

Active Material A



Active Material B



Early test data demonstrated the importance of active material selection. Active material A does not exhibit as high of a capacity as the Active material B. Similar processing conditions were used for both electrodes.

Improvements to Materials and Assembly Led to Increased Capacity

- 70% Silicon; 10% Carbon Black; 20% Binder
- Active materials charge/discharge capacity through multiple cycles
- Initial tests use 1 mA chg // cascade dschg cycles – CI/CV//CI cycle
  - Re-test used 2mA chg // cascade dschg
- Capacity is improved, and now fades

SC19		
Cycle	Charge Cap (mAh/g)	DsChg Cap (mAh/g)
1	2802	2509
2	2045	2055
3	1640	1772

SC20		
Cycle	Charge Cap (mAh/g)	DsChg Cap (mAh/g)
1	2734	2447
2	2481	2394
3	2475	2385
Break – then re-test		
4	3198	2952
5	3079	2835
6	2869	2254

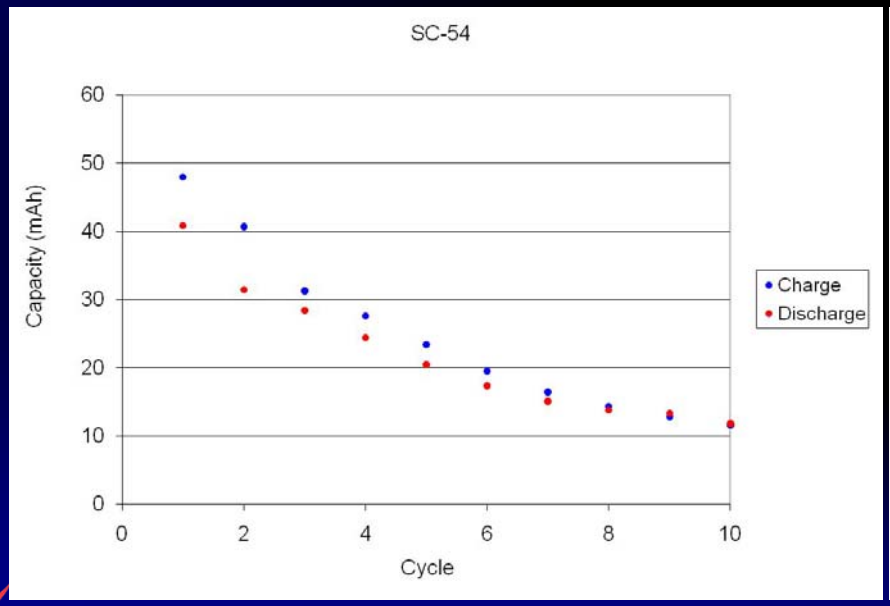
Increase in 1st cycle capacity of 600%

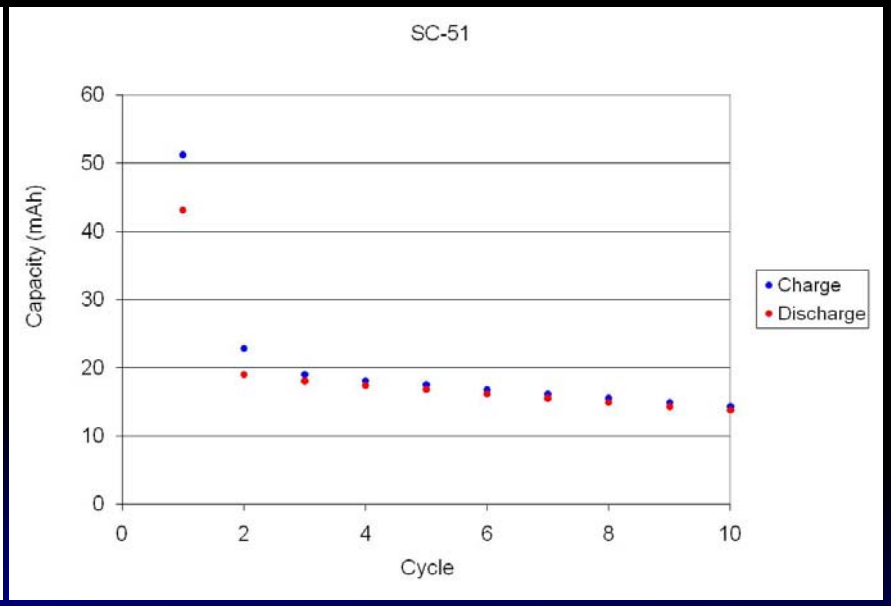
Combinatorial Investigation of Materials Implemented

- Active Material Composition
  - 60% to 90% of total weight of electrode
- Conductive Carbon Additives
  - Several types of conductive carbon investigated
  - Both graphitic carbon and carbon black used
  - Different manufacturers tested
    - Particle size and shape variation
  - Relative amounts of carbon type varied
- Binder
  - Multiple binders tested along with variations of each binder type
  - Mixing processes and curing protocol investigated

Cycle Life Increased By Improved Testing Protocol

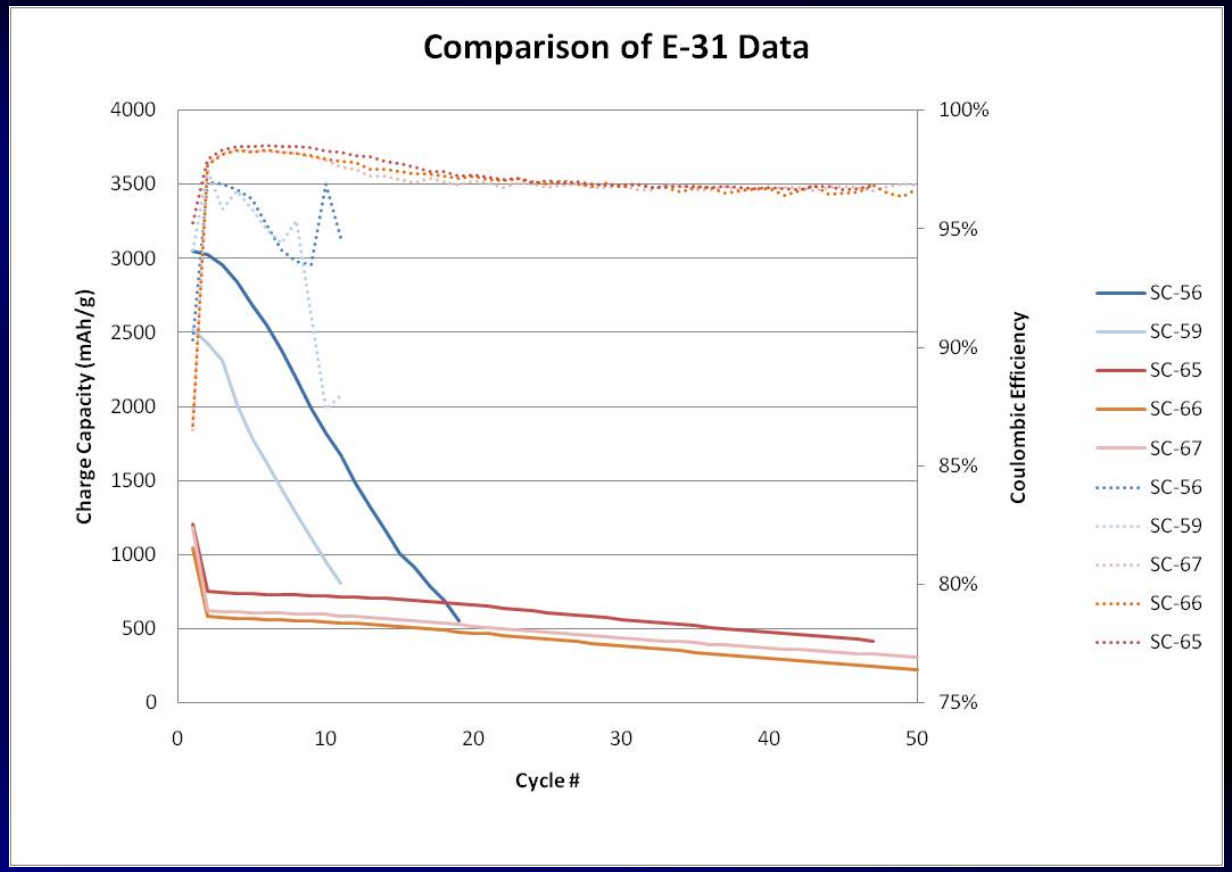
- Initial cycle – formation cycle – cycled under same conditions
  - Subsequent cycles were set to approximately C/10
  - SC-54 constant current/constant voltage to 25 mV
  - SC-51 constant current/constant voltage to 170 mV
    - Voltage limit reduces lithium intercalation into silicon





Test protocol inspired by Obrovac, et al. Journal Electrochem. Soc. 154 A103 (2007)

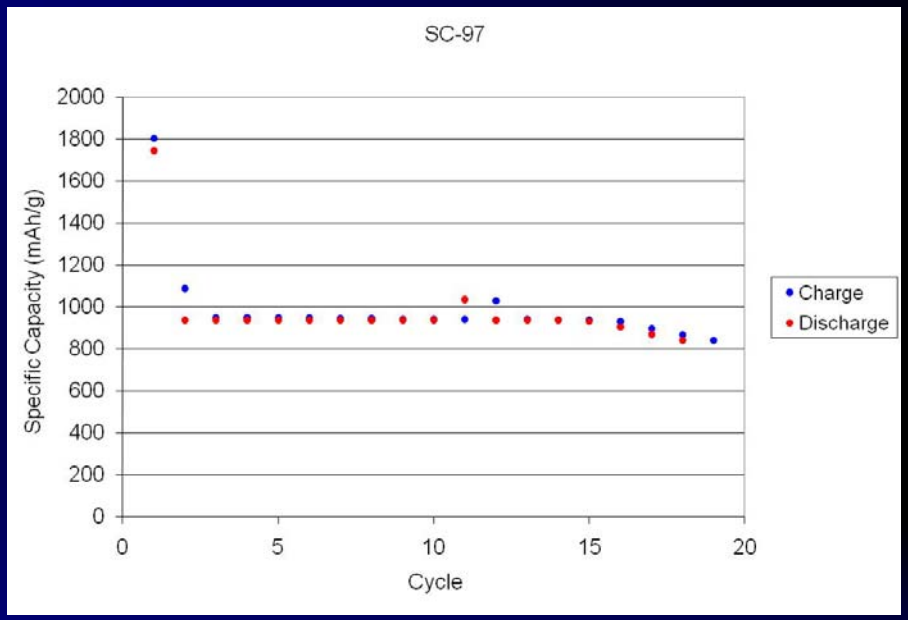
Improved Test Regimens Improve Cycle Life in 60 % Silicon Electrodes

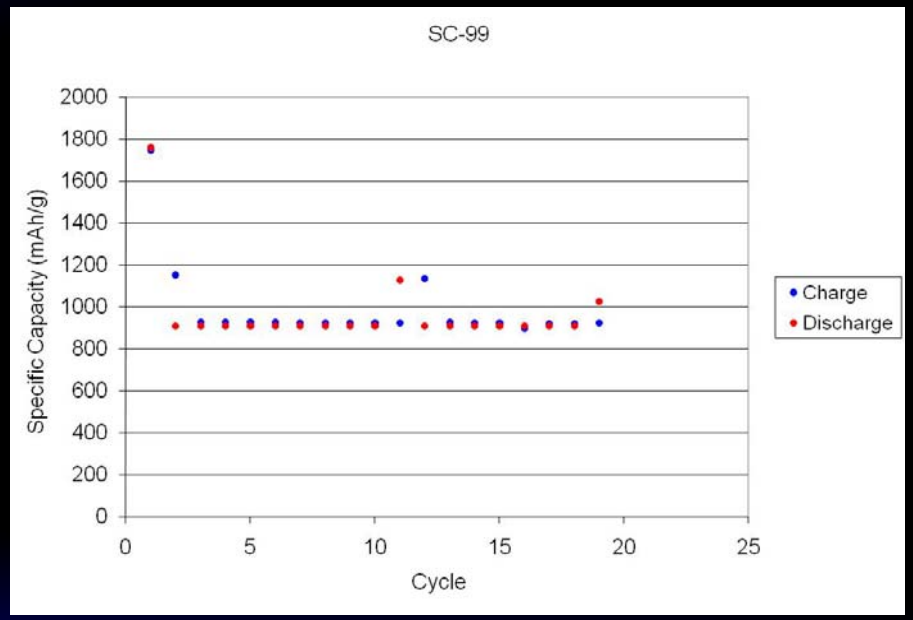


- Dotted lines represent coulombic efficiency
- Blue/grey lines are charged to 25 mV
- Red/orange lines charge limited on first cycle, and subsequent cycles to 170 mV

Extremely Promising Results Shown with Specific Cells

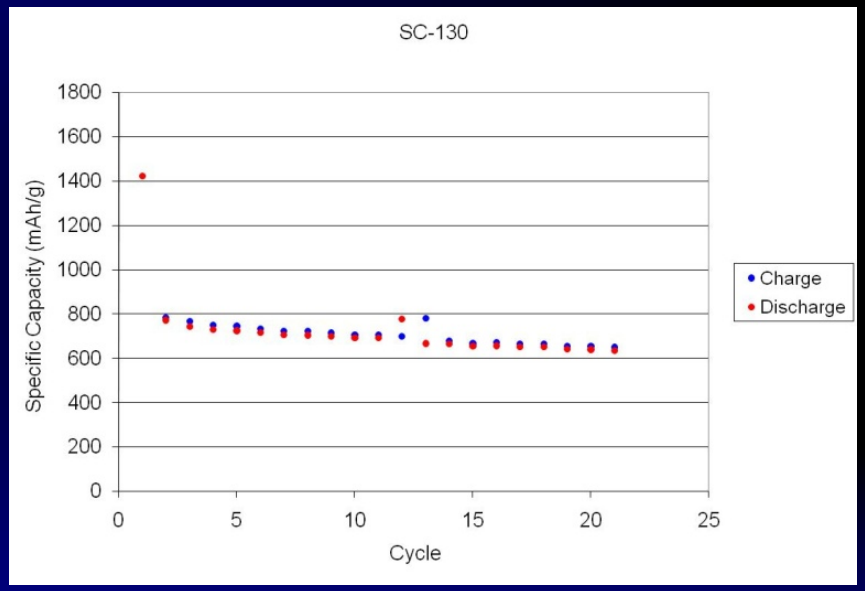
- SC-97 and SC-99 are two different formulations with exciting data
- Other cells in run did not display such promising results

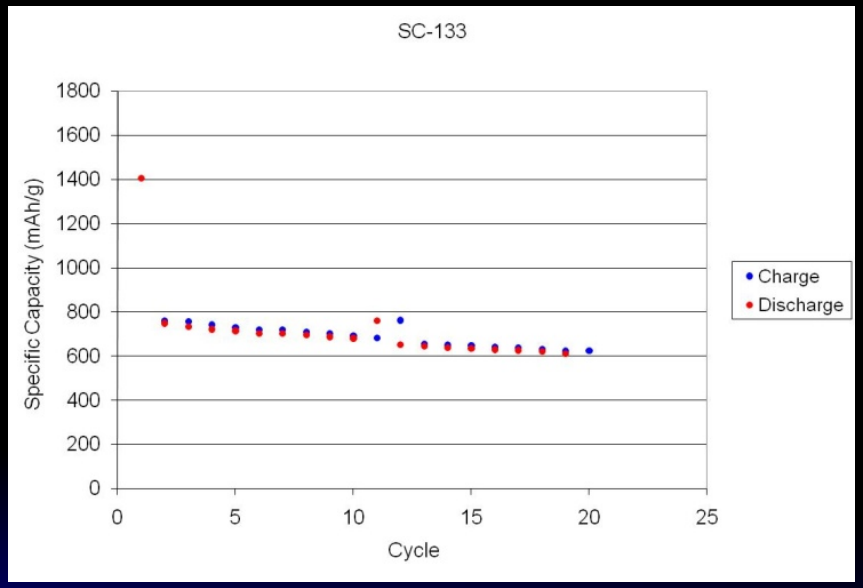




High Coulombic Efficiency Obtained with Selected Formulations

- Capacity fade reduced significantly with increased coulombic efficiency
  - Coulombic efficiency of nearly 98% obtained with recent formulations





Improvements to Anode are Ongoing

- Optimize electrode
  - Processing
  - Binders
  - Conductive Materials
- Improve cell design
- Investigate charging regimens

THANKS!

Special acknowledgements to NASA as this work has been supported by the NASA Energy Storage Project under contract number NNC08CB02C