Development of Nanosized/ Nanostructured Silicon as Advanced Anodes for Lithium-Ion Cells

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Outline

- Introduction/Background
- Advanced Si Anode Development
  - Nanosized Si
  - Nanostructured Si
- Larger format Cell Development
  - Cycling performance
  - Post analysis
- Summary
- Remaining Challenges

Introduction/Background

- **NASA is developing high energy and high capacity Li-ion cell and battery designs for future exploration missions under the NASA Advanced Space Power System (ASPS) Program. The specific energy goal is 265 Wh/kg at 10°C**

- **Part of effort for NASA advanced Li-ion cells**
  - **Anode:** **Silicon (Si) as an advanced anode**
  - **Electrolyte:** **advanced electrolyte with flame-retardant additives for enhanced performance and safety (NASA JPL)**

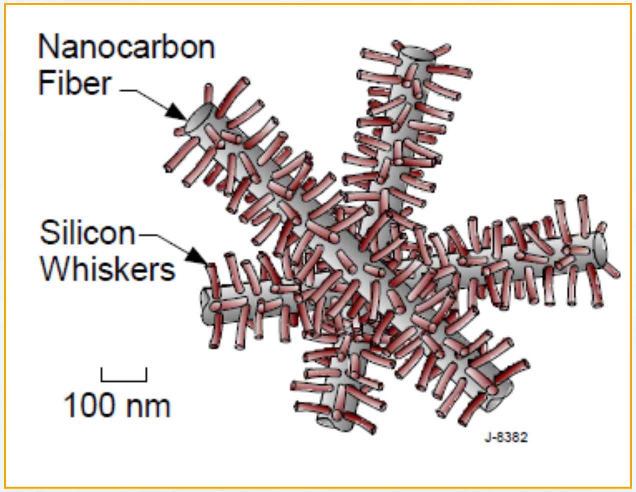
Si: an Attractive Li-Ion Anode Material

- **Features:**
  - High theoretical capacity: 4200 mAh/g
  - Abundant element on Earth

- **Challenges:**
  - Poor electrical conductivity
  - Low diffusion coefficient of Li^+ in Si
  - High volume changes (up to ~400%) in Si particles upon Li lithiation (alloying) and de-lithiation (de-alloying)

Approaches for the Challenges

- Carbon to improve electronic conductivity
- Nano-Si to reduce diffusion path length to help Li^+ diffusion coefficient and mitigate volume changes
  - Nanosized Si powder (GeorgiaTech)
    - Cost-effective
    - Easy scale up for mass production
  - Nanostructured Si: Si Whisker/NCF (PSI, Inc.)

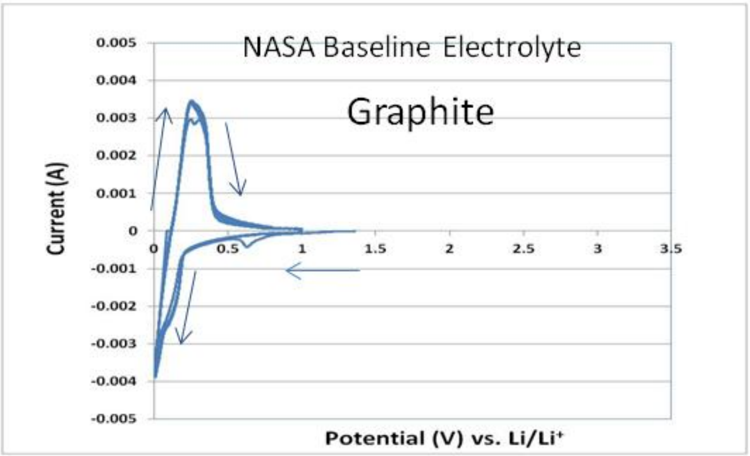


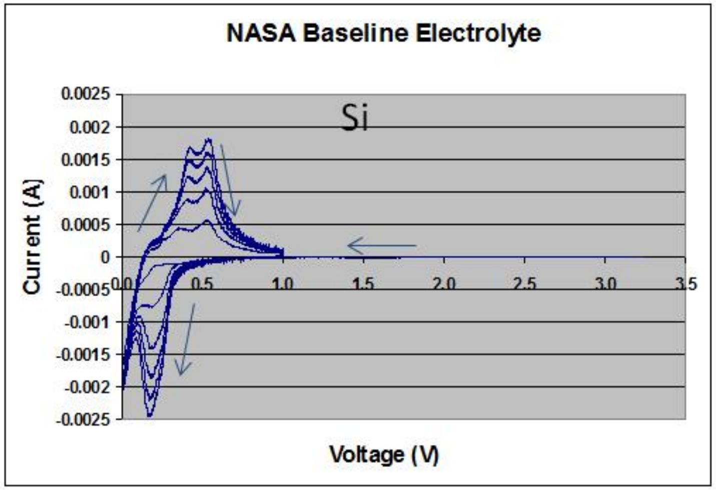
- 100 nm diameter carbon fibers w/silicon whiskers
- Supporting matrix forms an electronically conductive frame work
- High in free volume

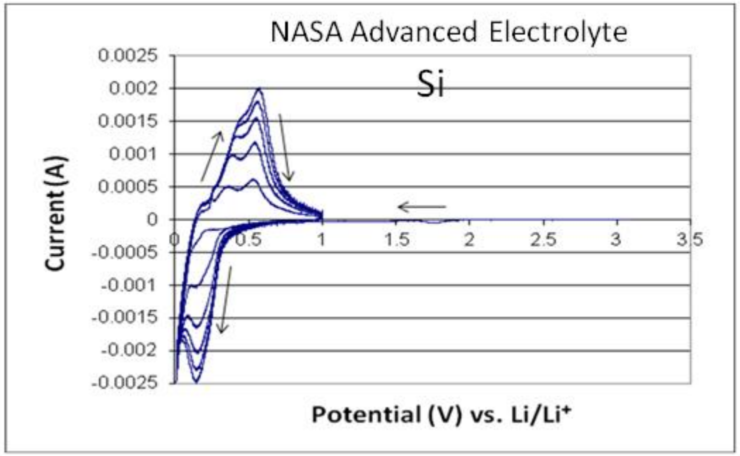
Improve/Stabilize SEI on Si Anode

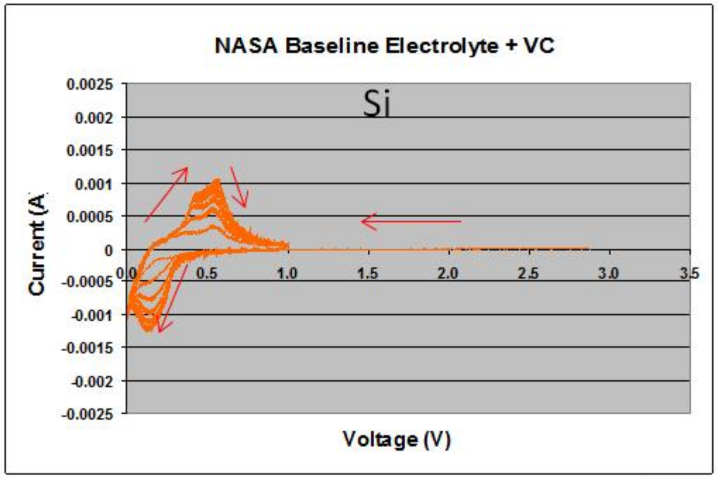
- **Important for rate capability and cycle stability**
- **Desired SEI properties:**
  - **Stabilized thin layer**
  - **highly permeable to Li^+ diffusion**
  - **highly ion-conductive**
- **Electrolyte: important for SEI formation**
  - **NASA baseline electrolyte (1M $LiPF_6$ in EC:DEC:DMC (1:1:1)**
  - **NASA baseline electrolyte + vinylene carbonate (VC)**
  - **NASA advanced electrolyte: 1M $LiPF_6$ in FEC:EMC:TPP (20:65:15)**
- **SEI studies:**
  - **Electrochemical techniques: CV, EIS, galvanstic charge/discharge**
  - **Well-studied graphite anode for comparison**

Difficult SEI Formation for Si Anode



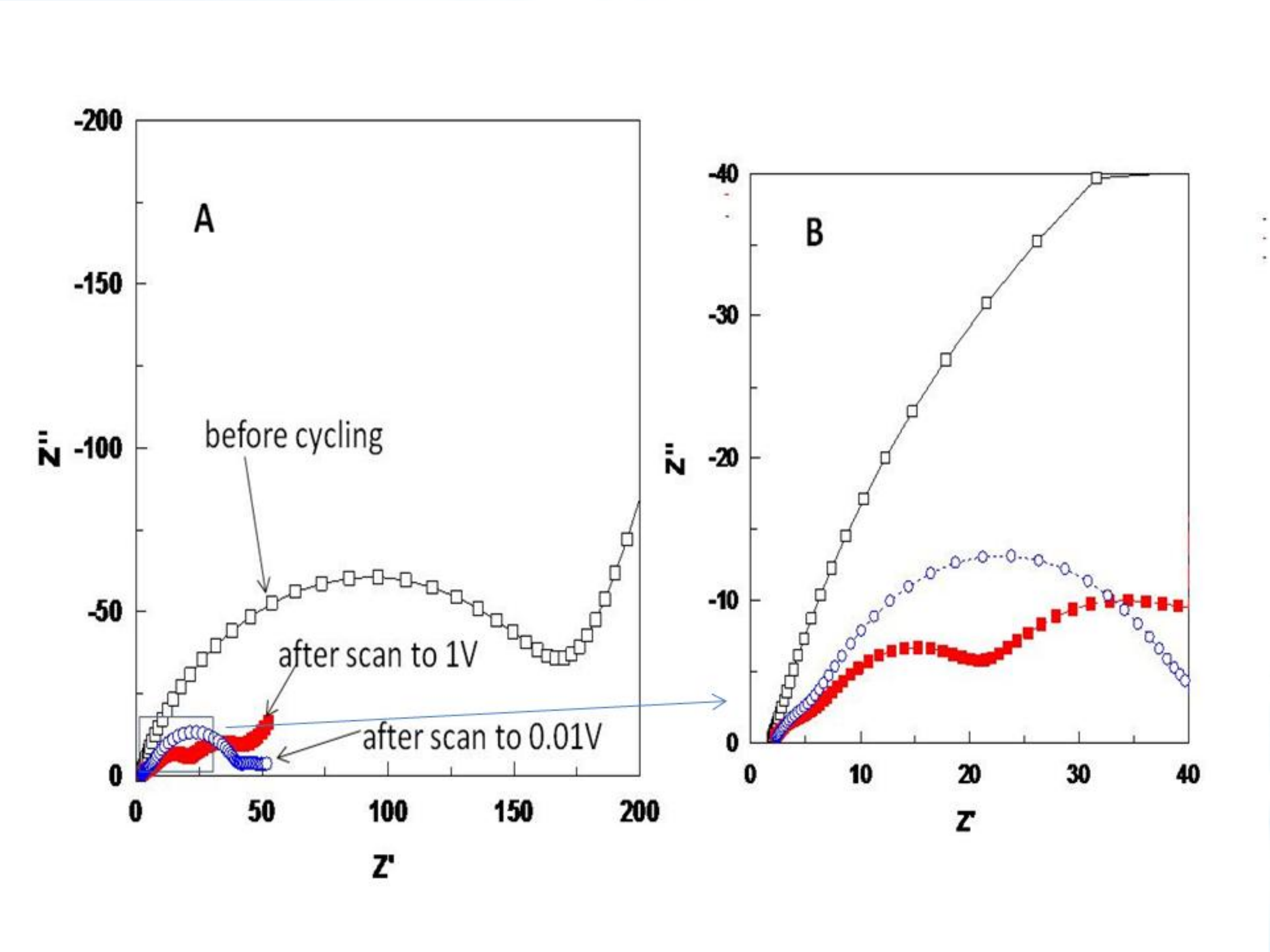




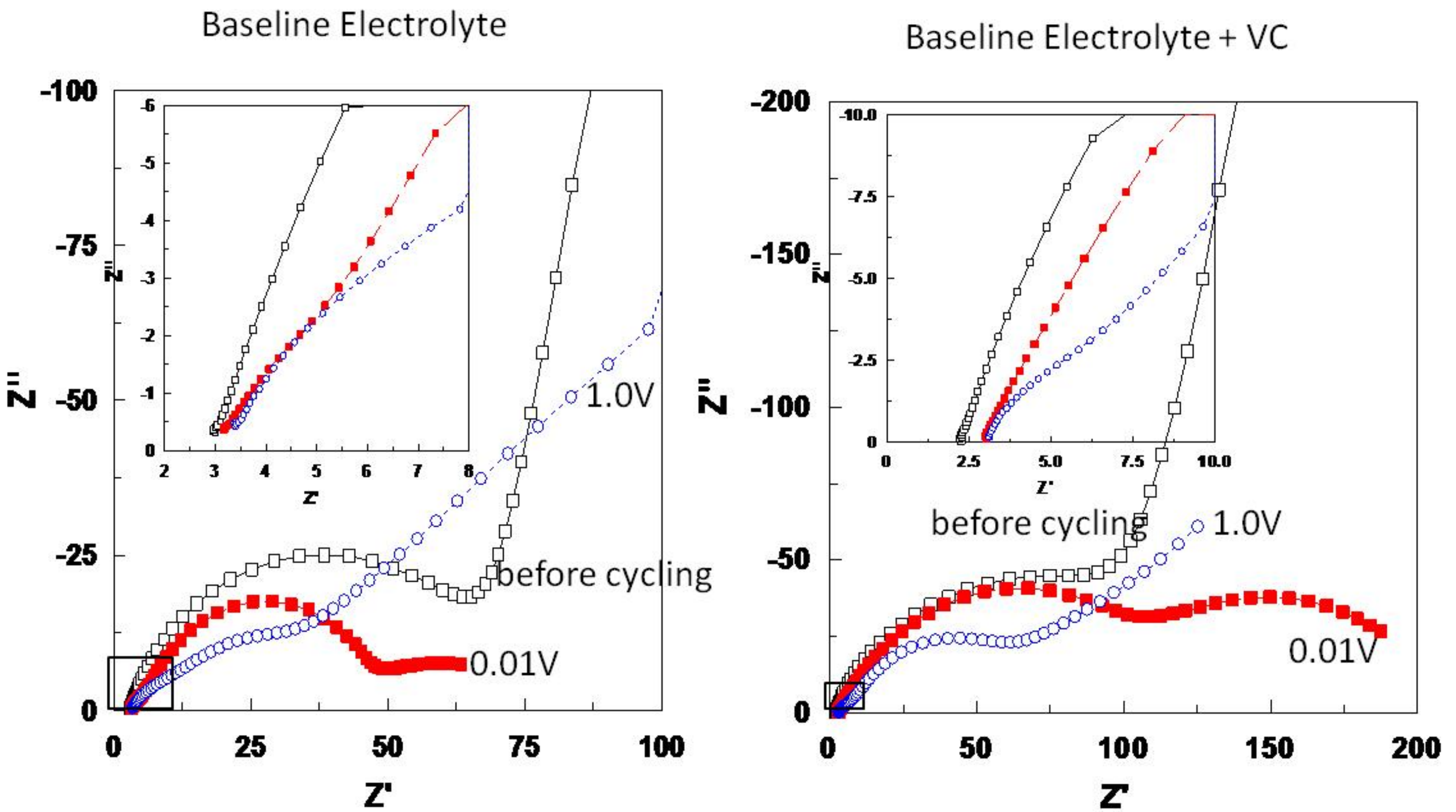


- SEI layer is slow to form on Si anode in comparison with C anode
- VC additive in electrolyte help to stabilize SEI formation

Stabilized SEI: Graphite Anode in Baseline Electrolyte for Comparison

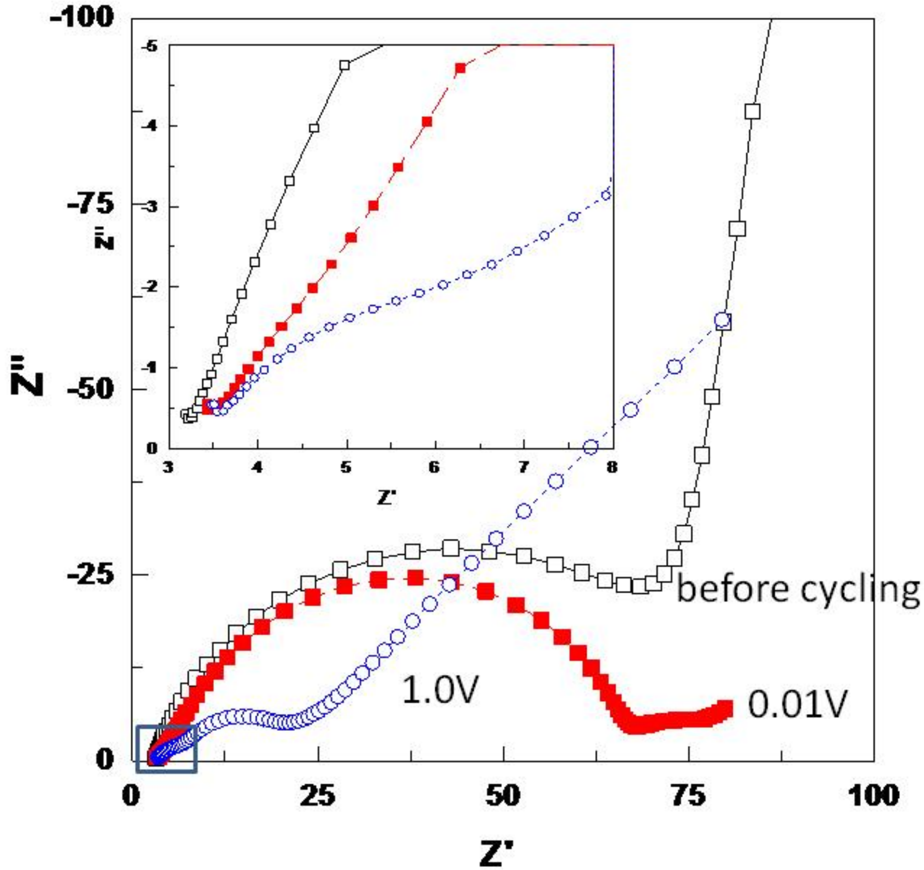


VC Additive Helps to Stabilize SEI for Si Anode



SEI layer is stabilized with VC in electrolyte as evidenced that Si anode resistance remains constant at lithiation state (0.01V) vs. delithiation state (1.0V)

Stabilized SEI in NASA Advanced Electrolyte

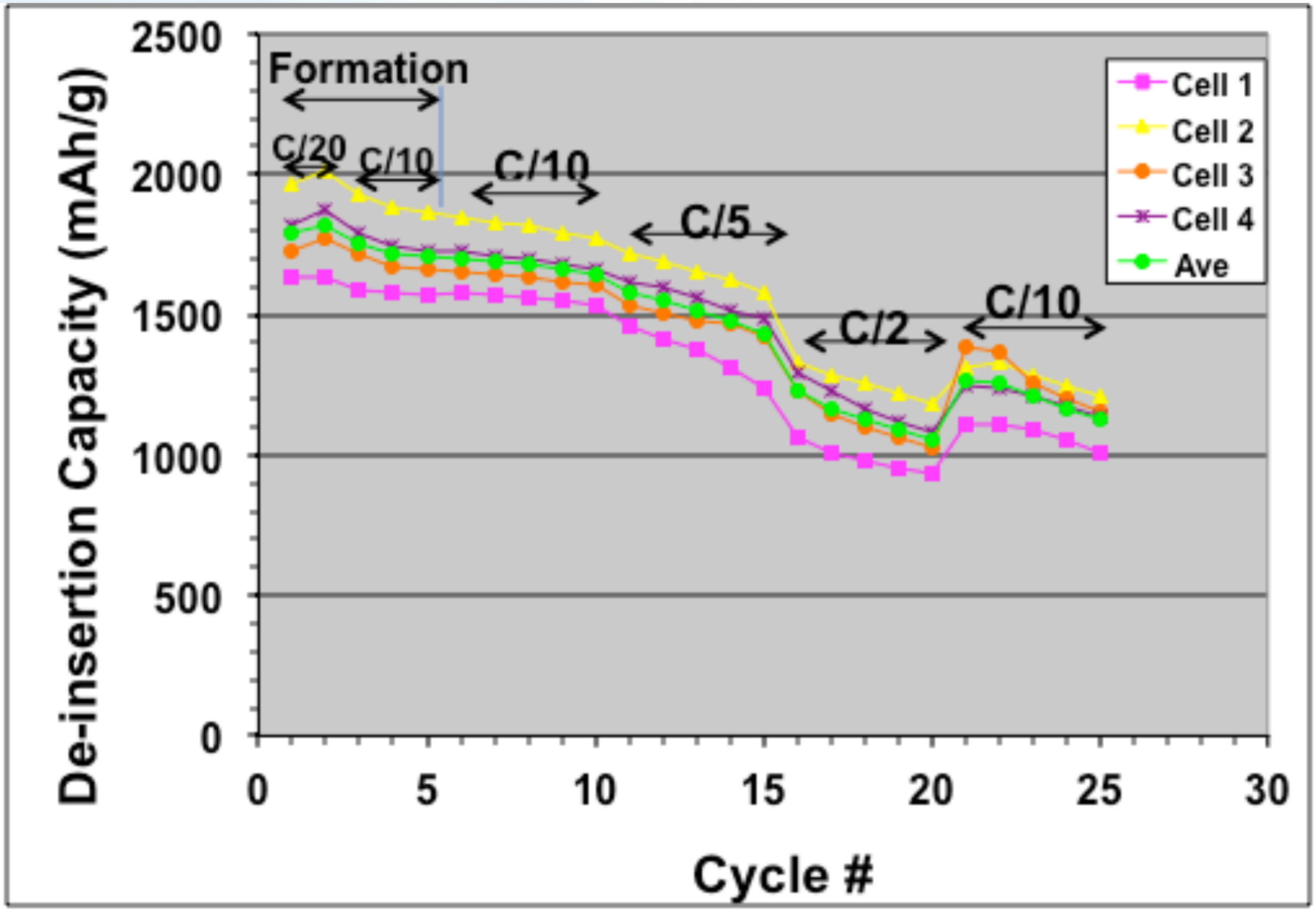


SEI layer is stabilized in NASA advanced electrolyte as seen with VC in electrolyte

Initial Formation Results w/Nanosized Si

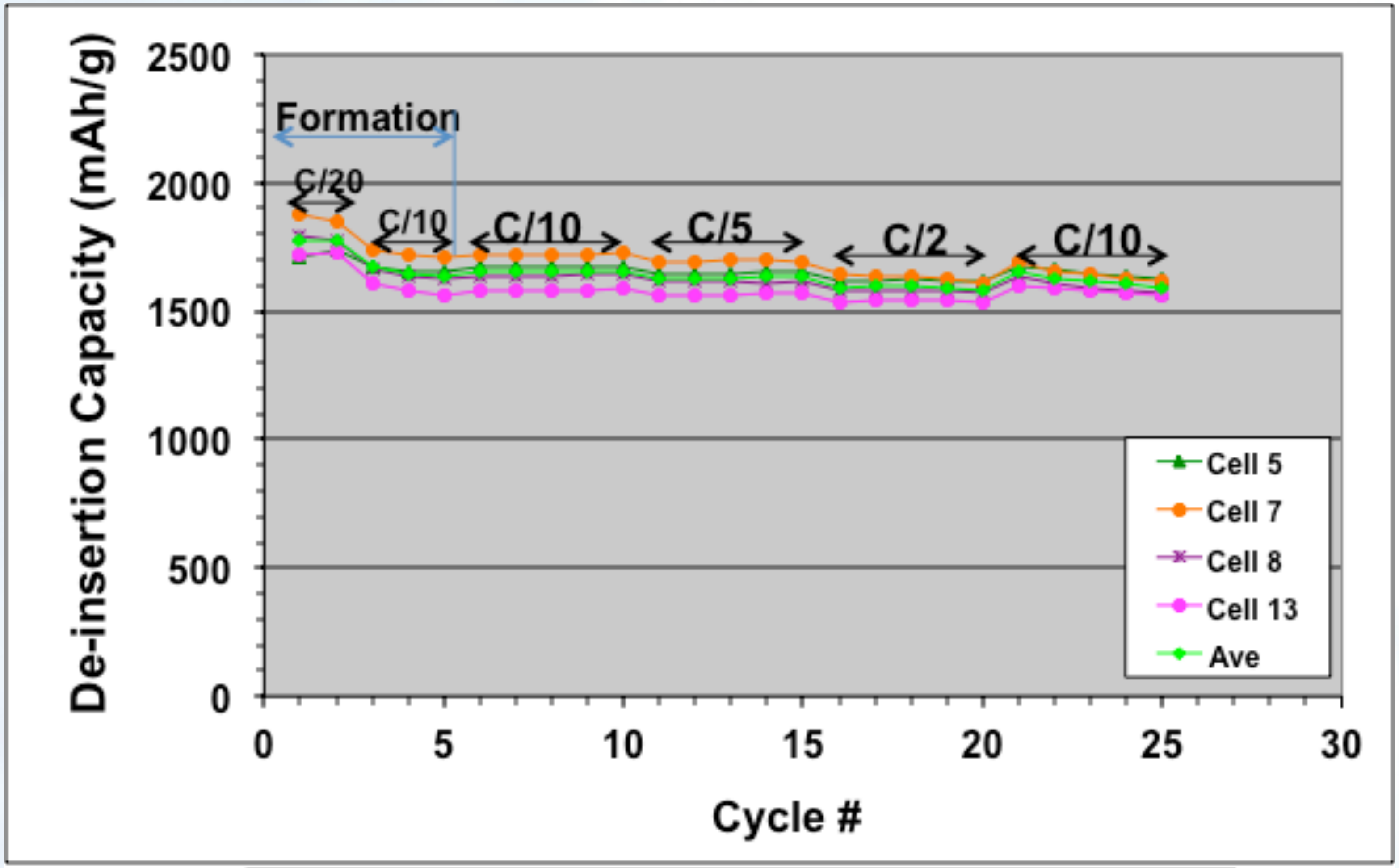
		Formation Cycles at C/20				Subsequent Cycles at C/10					
		1st cycle		2nd cycle		3rd cycle		4th cycle		5th cycle	
Anode	Electrolyte	Capacity (mAh/g)	CE (%)	Capacity (mAh/g)	CE (%)	Capacity (mAh/g)	CE (%)	Capacity (mAh/g)	CE (%)	Capacity (mAh/g)	CE (%)
Si	Baseline	1787	93.5	1758	96.9	1756	94.3	1721	95.6	1705	96.2
	Baseline + VC	1776	90.8	1773	95.5	1670	94.5	1646	98.0	1637	98.2
	Advanced electrolyte	1779	89.0	1802	97.0	1703	93.4	1679	96.6	1671	97.4
Graphite	Baseline	341	94.0	342	99.3						

Rate Characterization of Si Anode in NASA Baseline Electrolyte



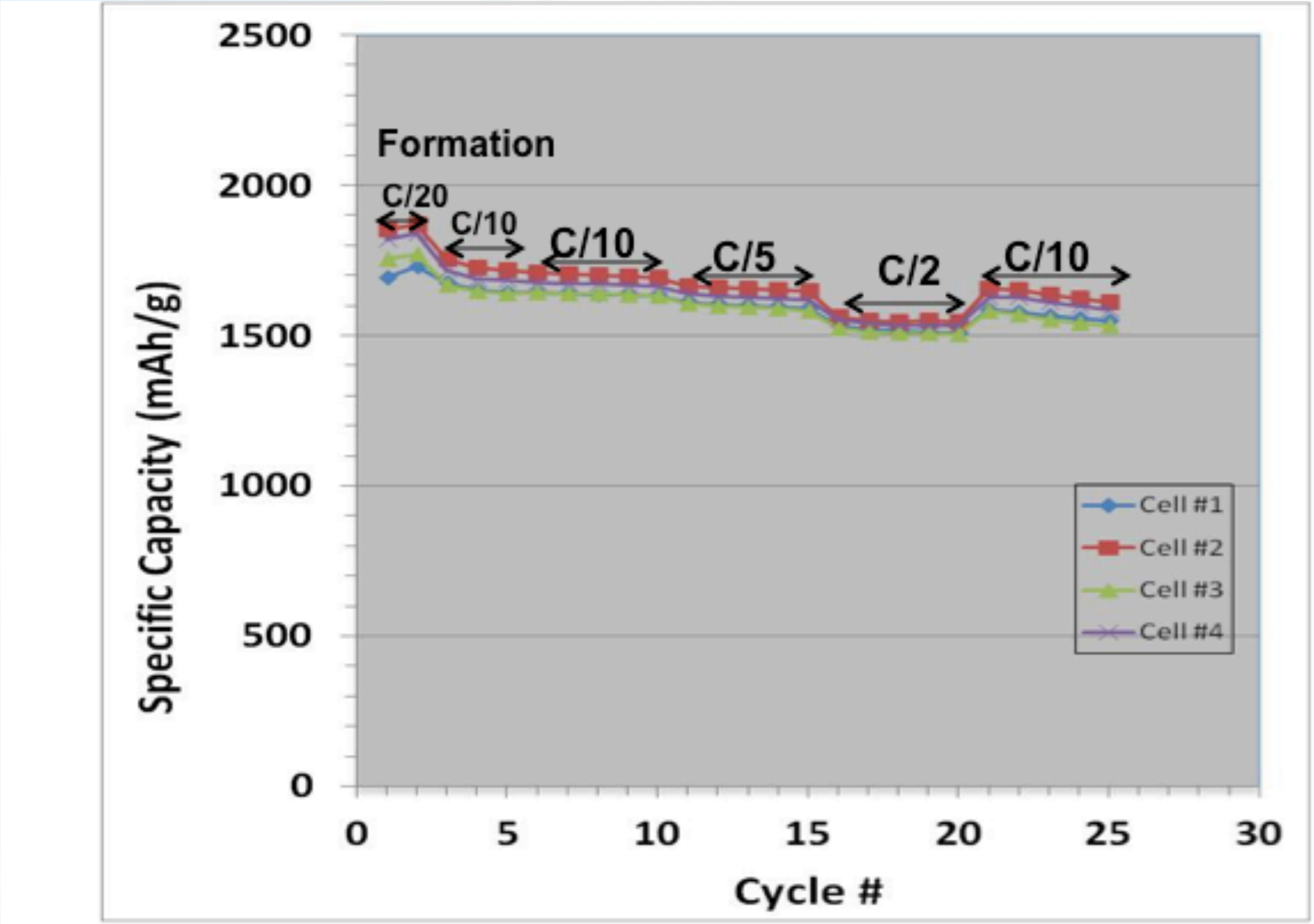
Capacity fade at each rate, further fade at increased rate (C/10 to C/2), and capacity at subsequent C/10 only partially recovered (~75%) vs. the initial C/10, all indicate the SEI is not stable and the electrode degrades

Impact of VC on Rate Characterization



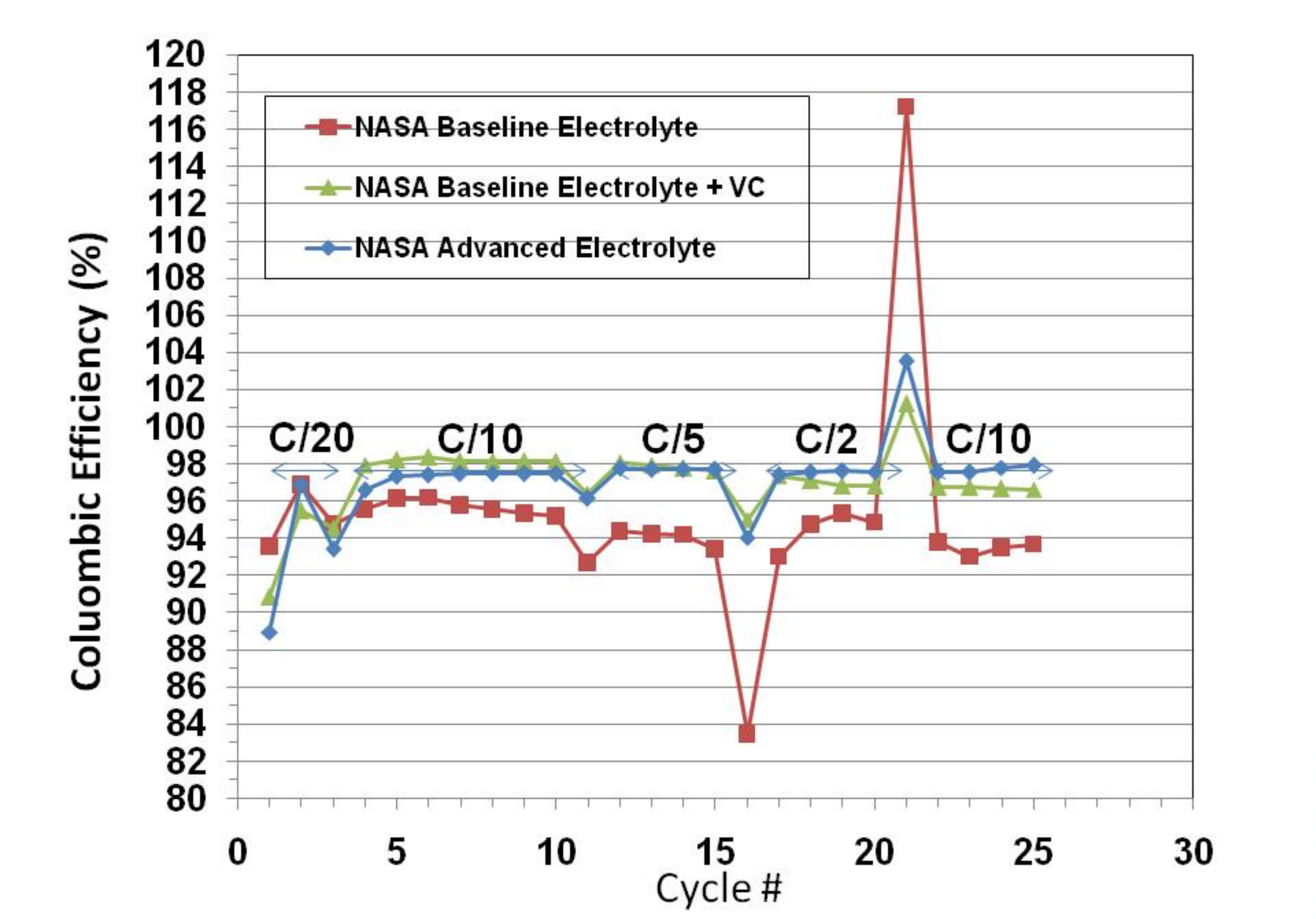
VC in electrolyte minimizes data variation and significantly improves rate cycling capability

Rate Capability Cycling of Si Anode in NASA Advanced Electrolyte



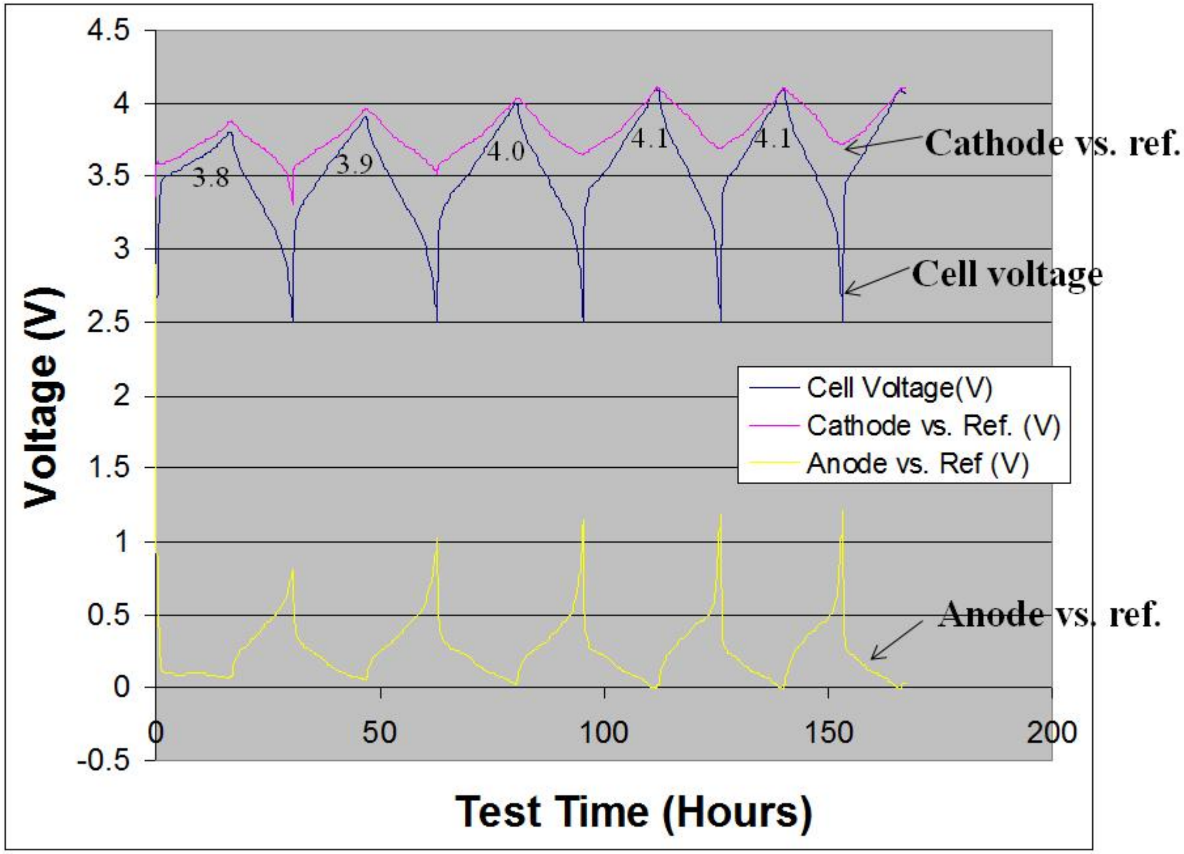
NASA advanced electrolyte is similar to VC in electrolyte in minimizing data variation and significantly improves rate cycling capability

Coulombic Efficiency at Rate Characterization



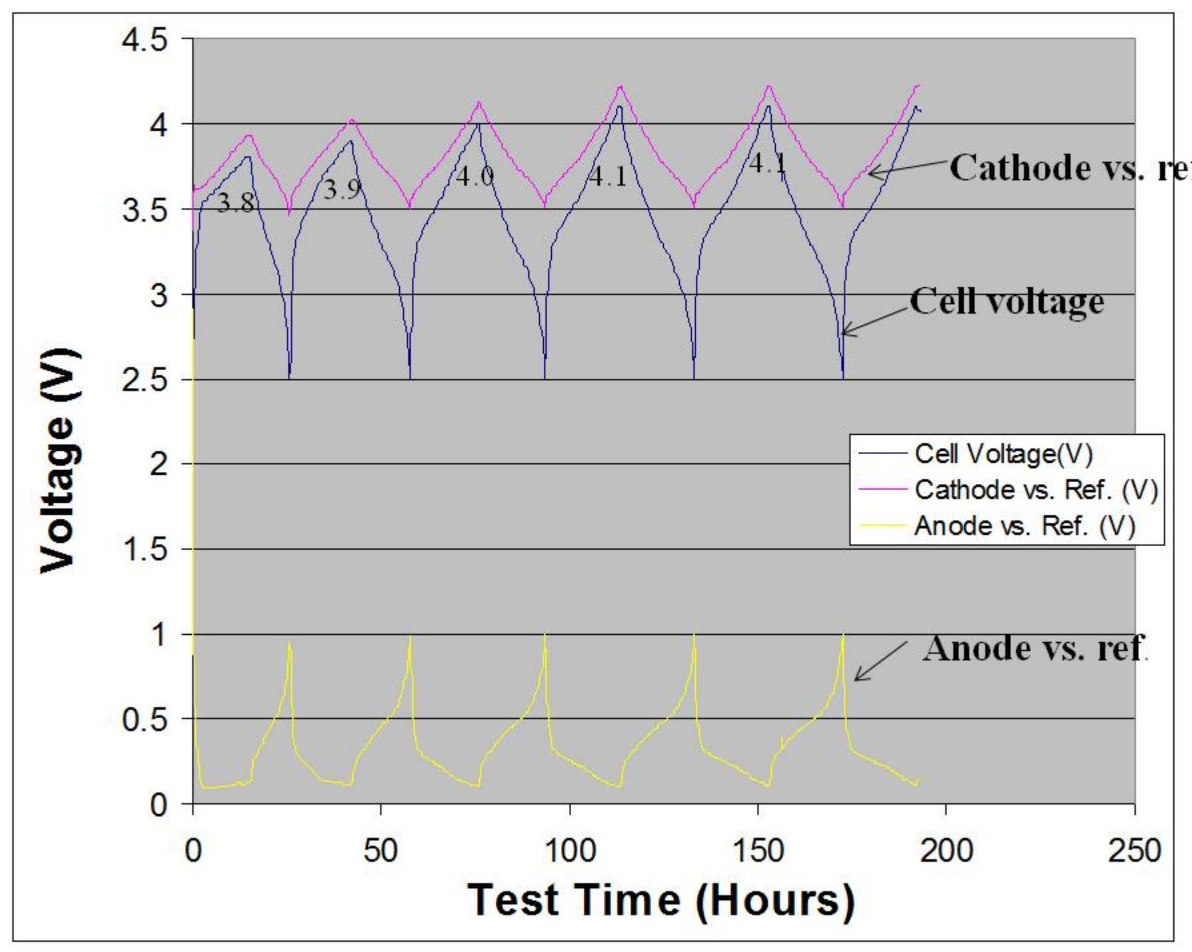
NASA advanced electrolte and VC in electrolyte improves coulombic efficiency, but still < 99%

Si/NCA Full Cell Pouch Cell: Si Anode Loading (1.8 mg/cm^2) is Too Low



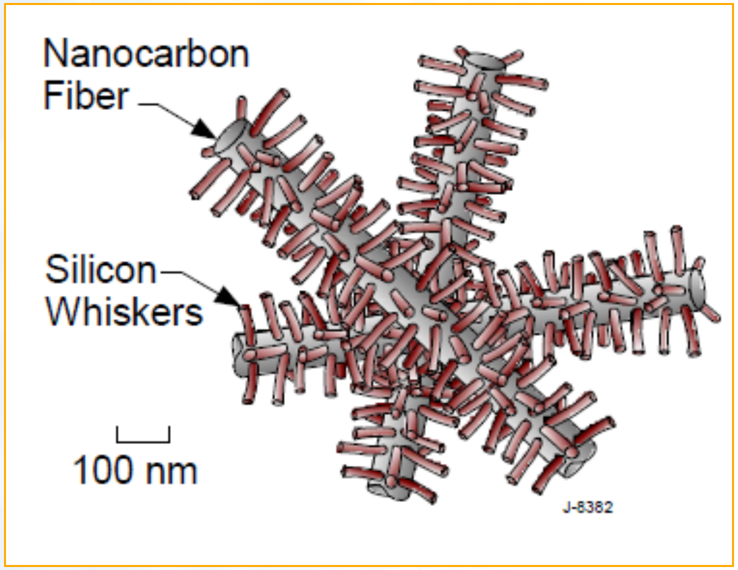
At this anode loading, the Si anode is overcharged and the anode voltage reaches 0V (if end cell charged voltage to 4.1V), and the end discharge voltage of anode increases, it is not safe for this anode loading to charge the cell to 4.1V

Si/NCA Full Cell Pouch Cell: Si Anode Loading (3.9 mg/cm^2) is Fine



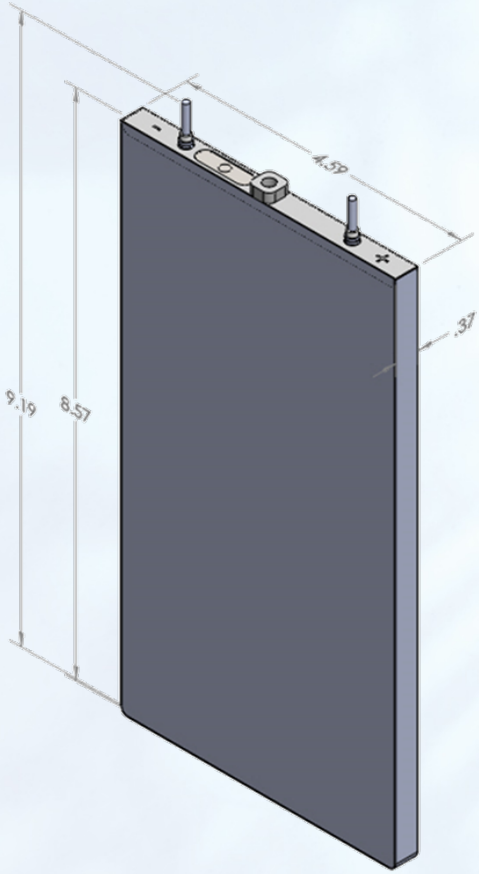
At this anode loading, the anode voltage profile is stabilized between ~110 mV (ECV) to 1V (EDCV), it is ok for the cell charged to 4.1V

Nanostructured Si: Si Whiskers/Nanocarbon Fiber



- Rate capacity > 1000 mAh/g
- Rate capability: 0.1C to 1C
- Electrode loading: 2-4 mAh/cm^2
- Scalable production process

Cell Components and Design



Components	Experimental Cells	Baseline Cells
Anode	Si whisker/ carbon nanofiber	Graphite
Cathode	NCA	NCA
Electrolyte	Low flammable electrolyte (JPL)	Yardney electrolyte
Projected (Wh/Kg)	193	160
Projected (Wh/L)	500	409

Initial Cycling Results

(20 Experimental Cells)

(5 Baseline Cells)

Measured *Initial* Value	Experimental Cells	Baseline Cells
Ah	35	28
Wh/Kg	191	163
Wh/L	505	410

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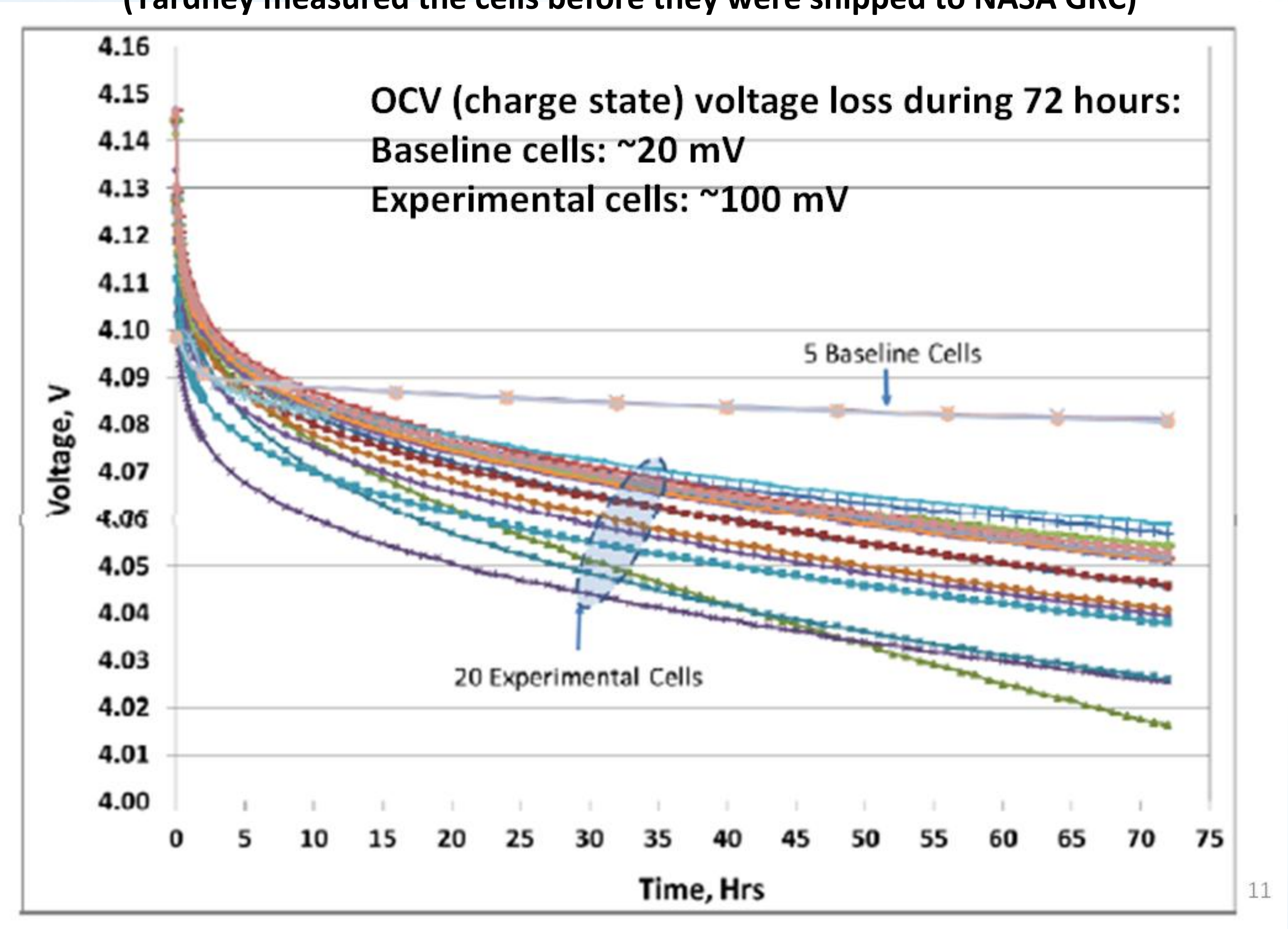
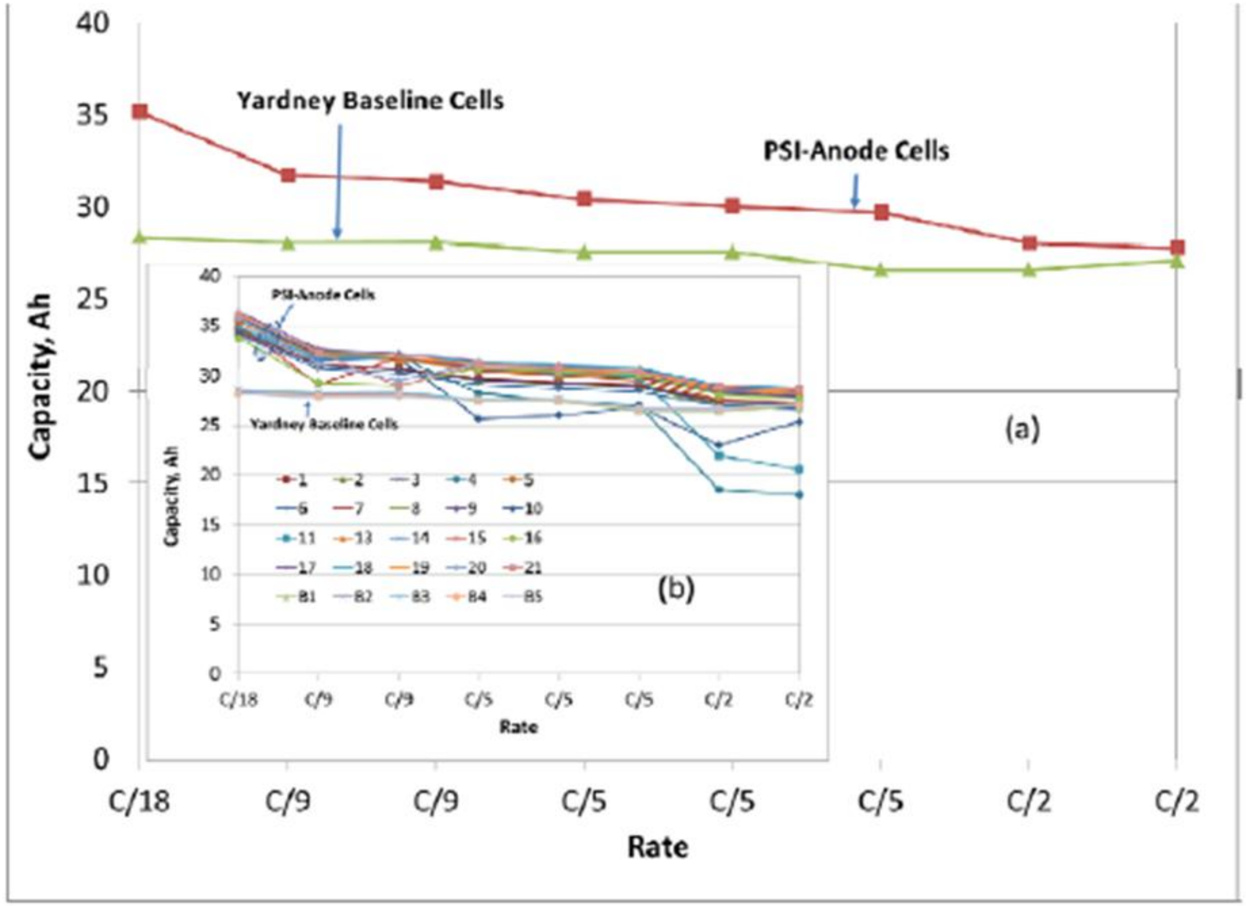
Self-Discharge Test (72 Hour Stand Test)

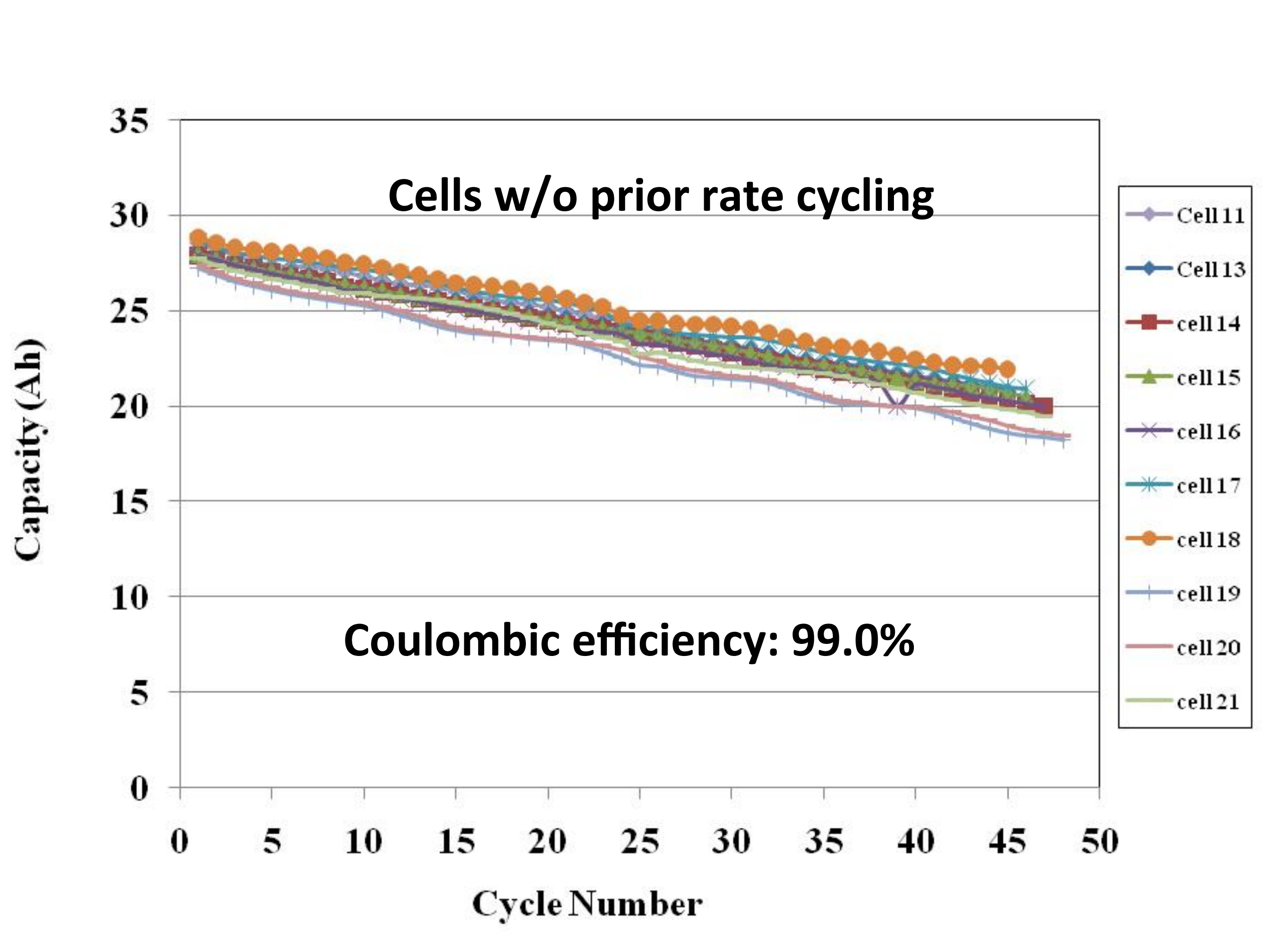
(Yardney measured the cells before they were shipped to NASA GRC)



Initial Cell Capacities at Various Current Rates



Experimental Cells: C/10 Cycling at <u>10^{o}C</u>

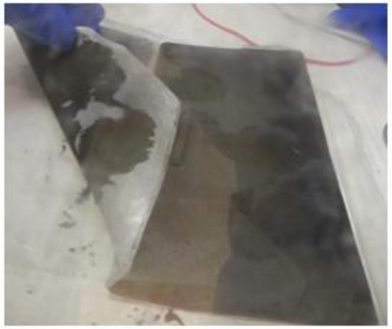


What We Observed after DPA

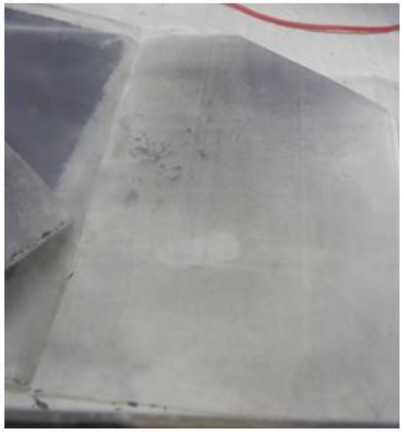
Si Anode

NCA Cathode

tap



The delaminated Si electrode materials adhered to adjacent separator



No cathode delamination was seen

- **Delamination was seen on one side of anode sheet (the other side is ok) (<u>this happens on each anode sheet</u>)**
- **The delaminated Si anode materials adhered to adjacent separator**

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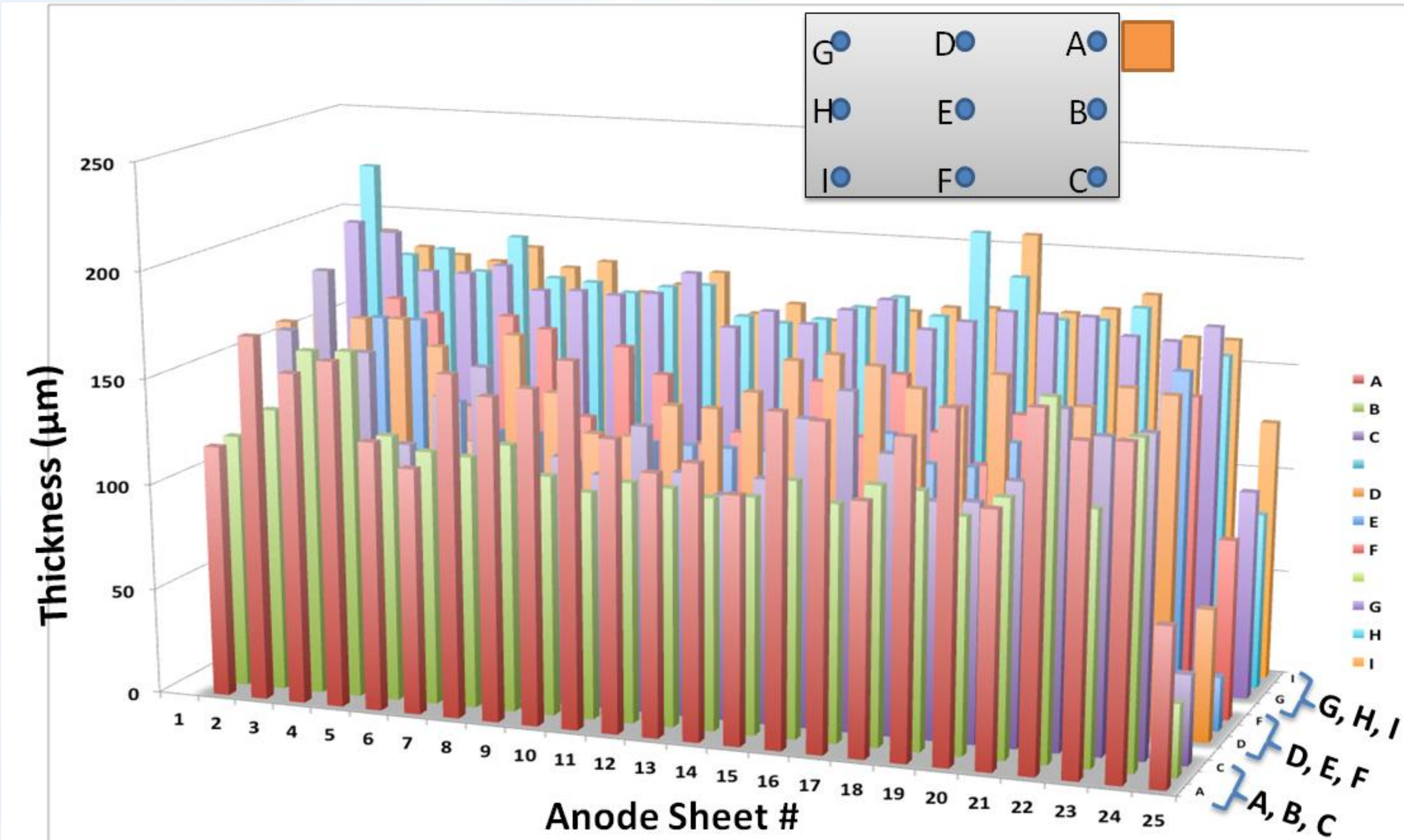
Thickness of Cycled Si Anode Sheets



- The thickness was not uniform, possible due to delamination: relative thinner closer to current collector tap portion (A-C, D-F), relative uniform far away (G-I)
- The expansion of cycled Si anode is ~ 10-15%

- The thickness was not uniform, possible due to delamination: relative thinner closer to current collector tap portion (A-C, D-F), relative uniform far away (G-I)

Summary

- Developed and scaled up both nanosized Si and nanostructed Si anodes, which demonstrated reversible capacity (>1000 mAh/g) at ***practical*** loadings (>3 mg/cm^2)
- Large-format flight-type prismatic cells with NASA supported Si anode and low flammable electrolyte were successfully fabricated
- The Si cells initially delivered the anticipated gain in capacity and performance over the cells constructed with graphite anode
- The cycling performance however fell short of the targeted value, the high moisture in the Si anode, Si anode delamination after cycling, and inadequate electrolyte are the possible causes for the capacity fade

Remaining Challenges

- **Promoting fast SEI formation and further stabilizing the formed SEI layer**
    - **Initial formation coulombic efficiency is <99%**
    - **Irreversible capacity loss for the initial two formation cycles is still high (10% - 20%)**
    - **Capacity fade needs to be further reduced**

- **Compatible and stable electrolytes (required for high voltage cathode materials)**

Acknowledgements

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Thank you!