Development of Large-Format Lithium-Ion Cells with Silicon Anode and Low Flammable Electrolyte

James J. Wu[1], D. M. Hernaddez-Lugo[1], M. C. Smart[2],
B. V. Ratnakumar[2], T. B. Miller[1], V. F. Lvovich[1] and J. K. Lytle[1]

[1]NASA Glenn Research Center, Mail Stop 309-1, Cleveland, Ohio 44135
[2]Jet Propulsion Laboratory, Caltech, Pasadena, California 91109

10th Annual Lithium Power Battery Power 2014
Washington DC, November 11-12, 2014

Outline

- Introduction/Background
- Goals/Key Deliverables
- Performance Results
- Possible Causes for Capacity Fade
- Summary

Introduction/Background

- NASA is developing high energy and high capacity lithium (Li)-ion cell designs and batteries for future exploration missions (target specific energy density 265 Wh/kg at 10ºC) under NASA Space Power System program

- Part of effort for NASA advanced Li-ion cells
  - Anode: Development of silicon (Si) as advanced anode (NASA SBIR – Physical Science Inc. (PSI))
  - Electrolyte: advanced electrolyte with fire-retardant for enhanced performance and safety (NASA JPL)

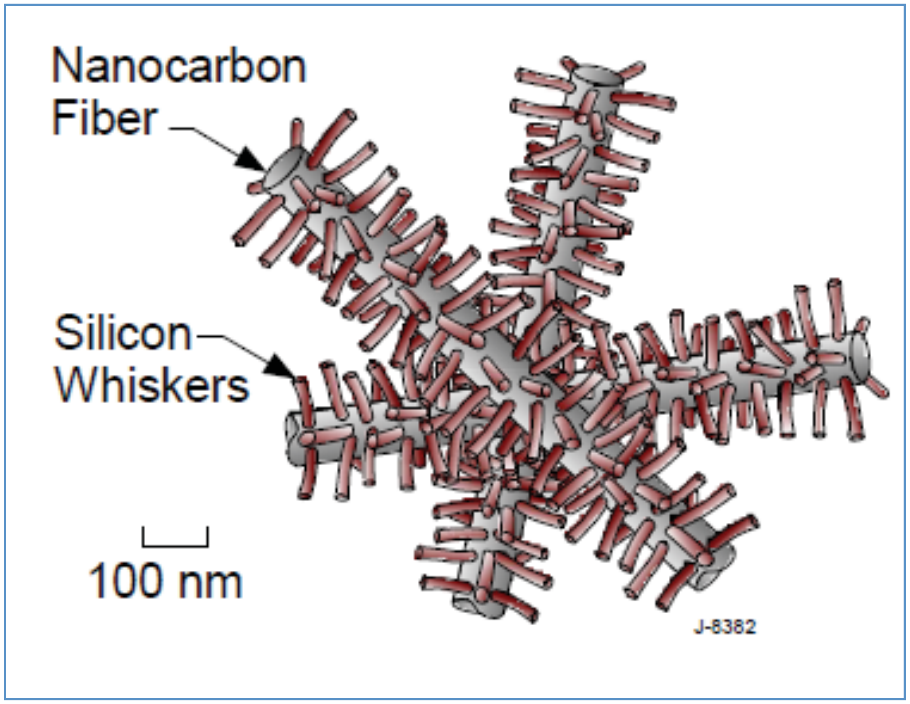
Silicon: an Attractive Li-Ion Anode Material

- **Features:**
  - **High theoretical capacity: 4200 mAh/g (~10 times of graphite anode)**
  - **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 and de-lithiation**

- **Ways to Overcome:**
  - **Improve electrode material: nanostructured-Si, Si/C..**
  - **Improve electrode/electrolyte interface: stable SEI..**

PSI: Silicon Whiskers/Nanocarbon Fiber



Characteristics

- 100 nm diameter carbon fibers with silicon whiskers
- Rated capacity: >1000 mAh/g
- Rate capability: 0.1C to 1C
- Electrode loading: 2-4 mAh/cm^2

Advantages

- Supporting matrix forms an electronically conductive framework
- High in free volume
- Free of polycrystalline domains
- Tailorable silicon loadings
- Scalable production process

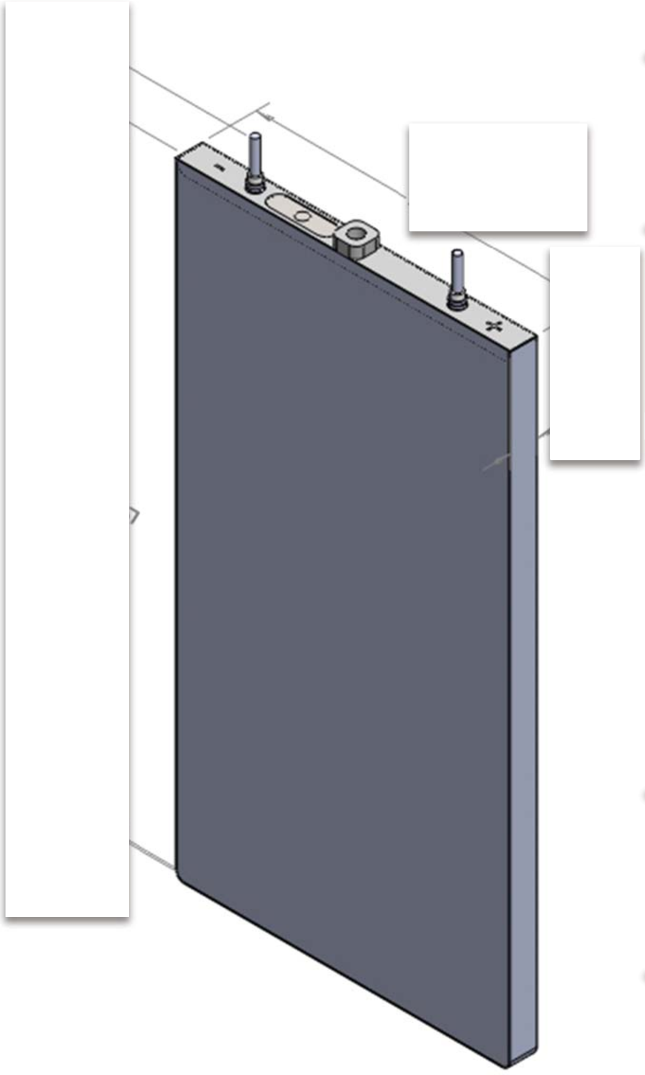
(provided from PSI)

Large-Format Flight-Type Prismatic Li-ion Cells with Si Anode

- To advance technology readiness level (TRL) of Si anode, large-format flight-type (hermetically sealed) prismatic Li-ion cells (experimental cells) were built by NASA SBIR phase III program
  - Si whiskers/nanocarbon fibers, scale-up and produced by PSI, as anode
  - Low flammable electrolyte with fire-retarded additive, developed by NASA JPL
  - Commercial available NCA, produced by Yardney, as cathode
  - Full cells were fabricated by Yardney
  - Cells with graphite anode and NCA cathode (baseline cells) were also built for comparison

- Key Goals of These Experimental Cells
  - Energy density: >=200 Wh/Kg at C/10
  - 80% capacity retention for 100 cycles (100% DOD)
  - 80% capacity retention for 200 cycles (50% or greater DOD)
  - 10% or greater increase in energy density as compared to cells with graphite anodes

Cell Components and Design



(Hermetically sealed cells)

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

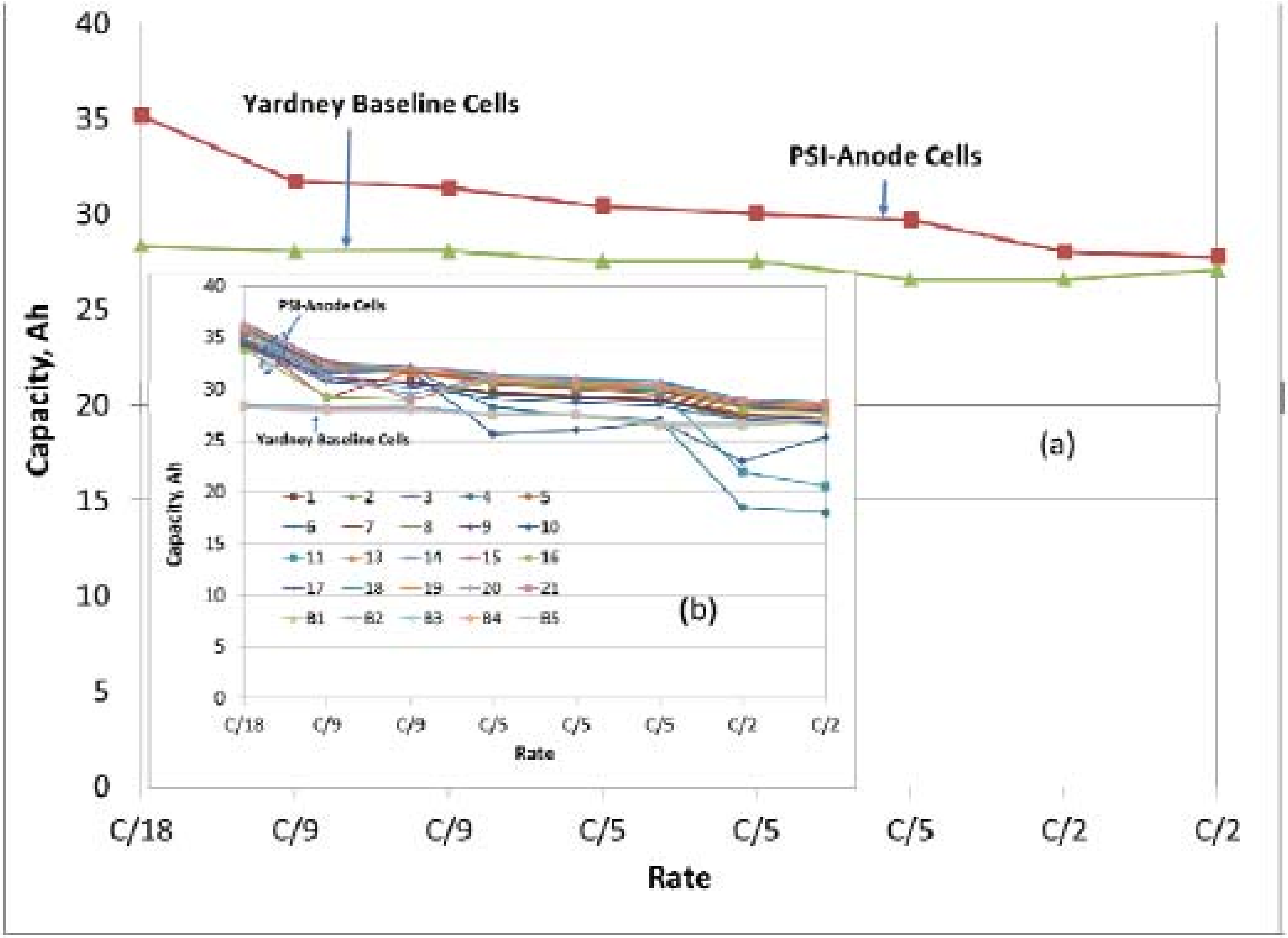
(20 Experimental Cells)

(5 Baseline Cells)

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

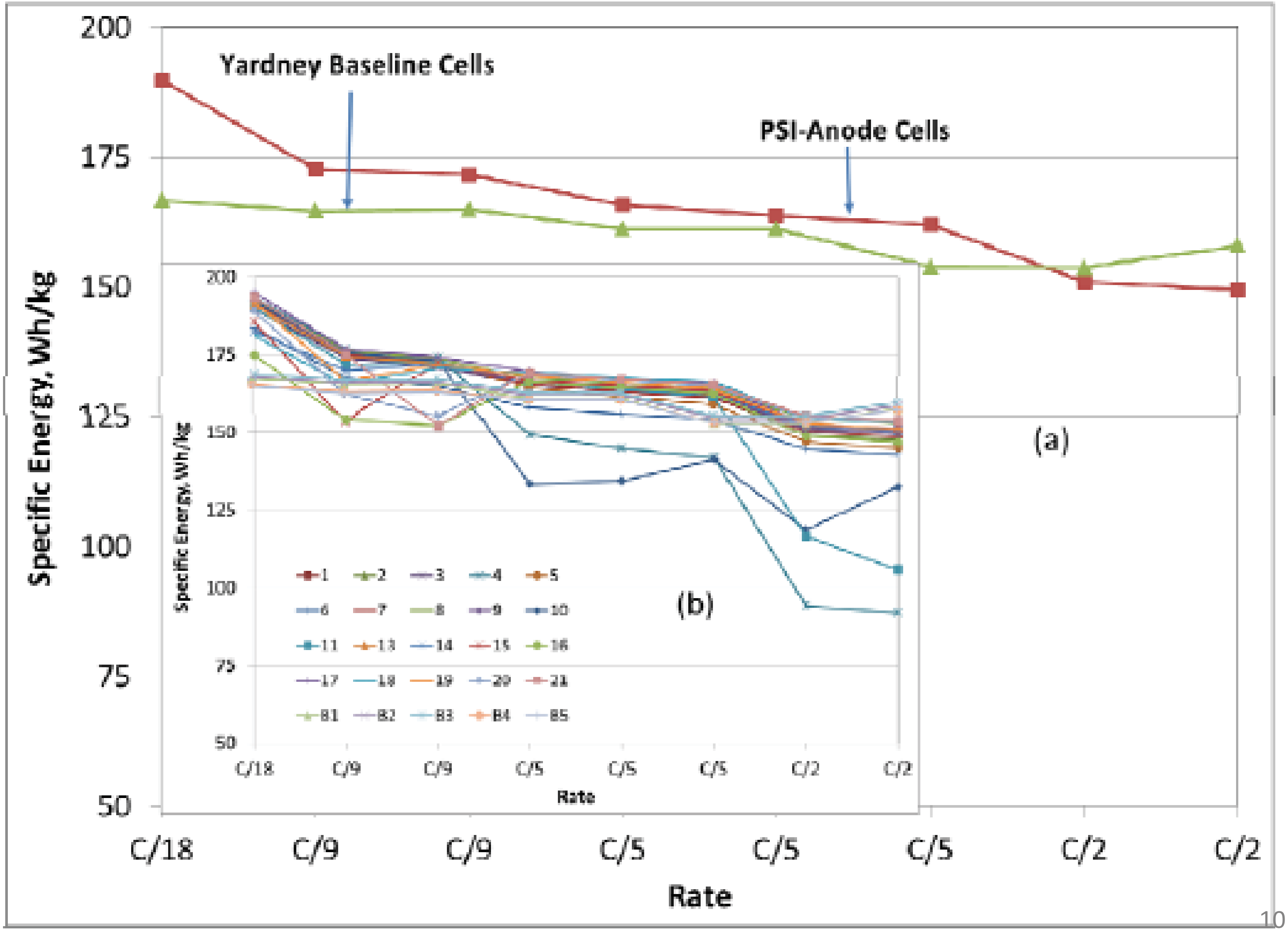
Initial Cell Capacities at Various Current Rates

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



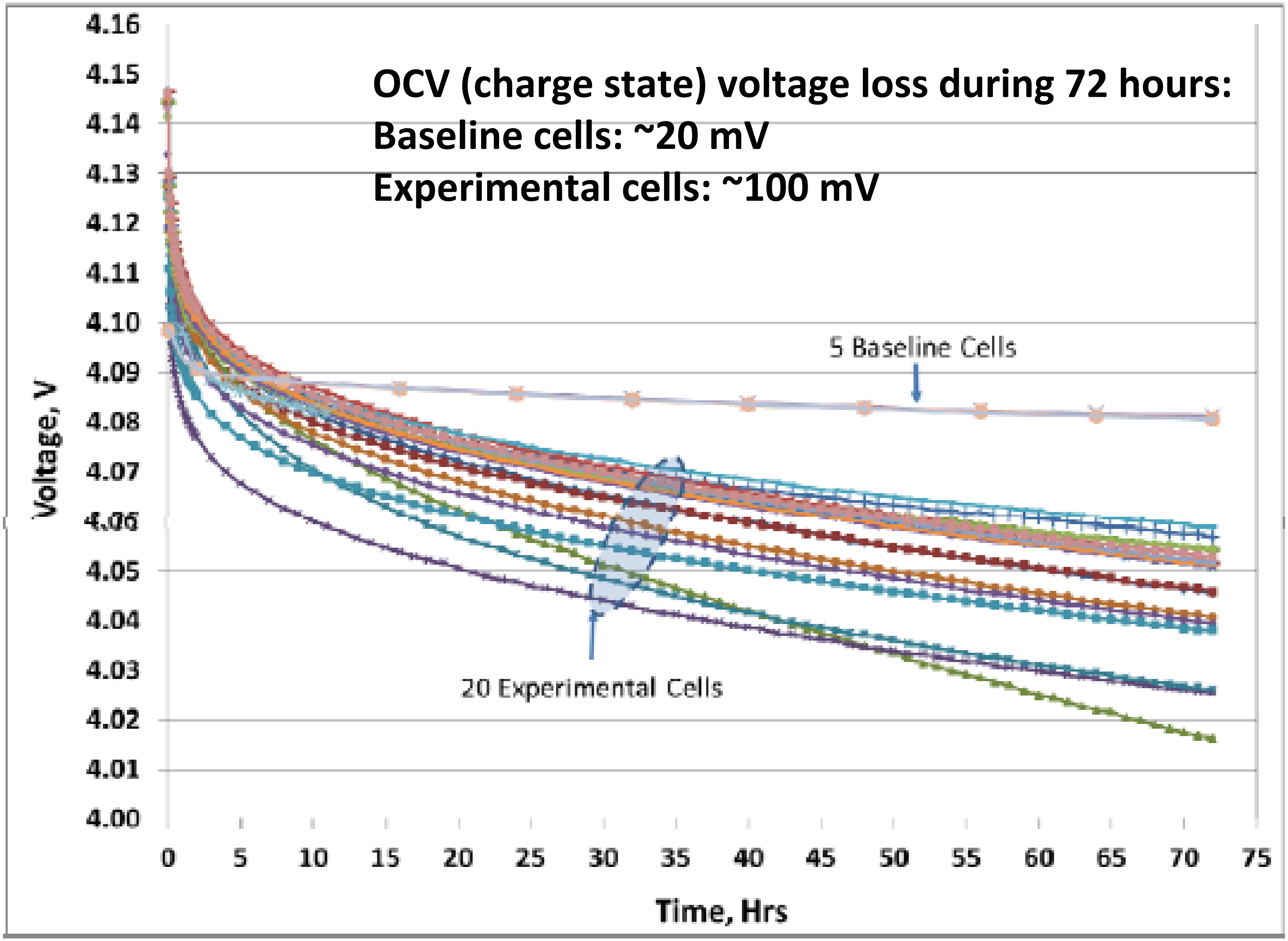
Initial Specific Energies at Various Current Rates

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



Self-Discharge Test (72 Hour Stand Test)

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



OCV (charge state) voltage loss during 72 hours:

Baseline cells: ~20 mV

Experimental cells: ~100 mV

Cell Capacity and Specific Energy after Cells Shipped to NASA GRC

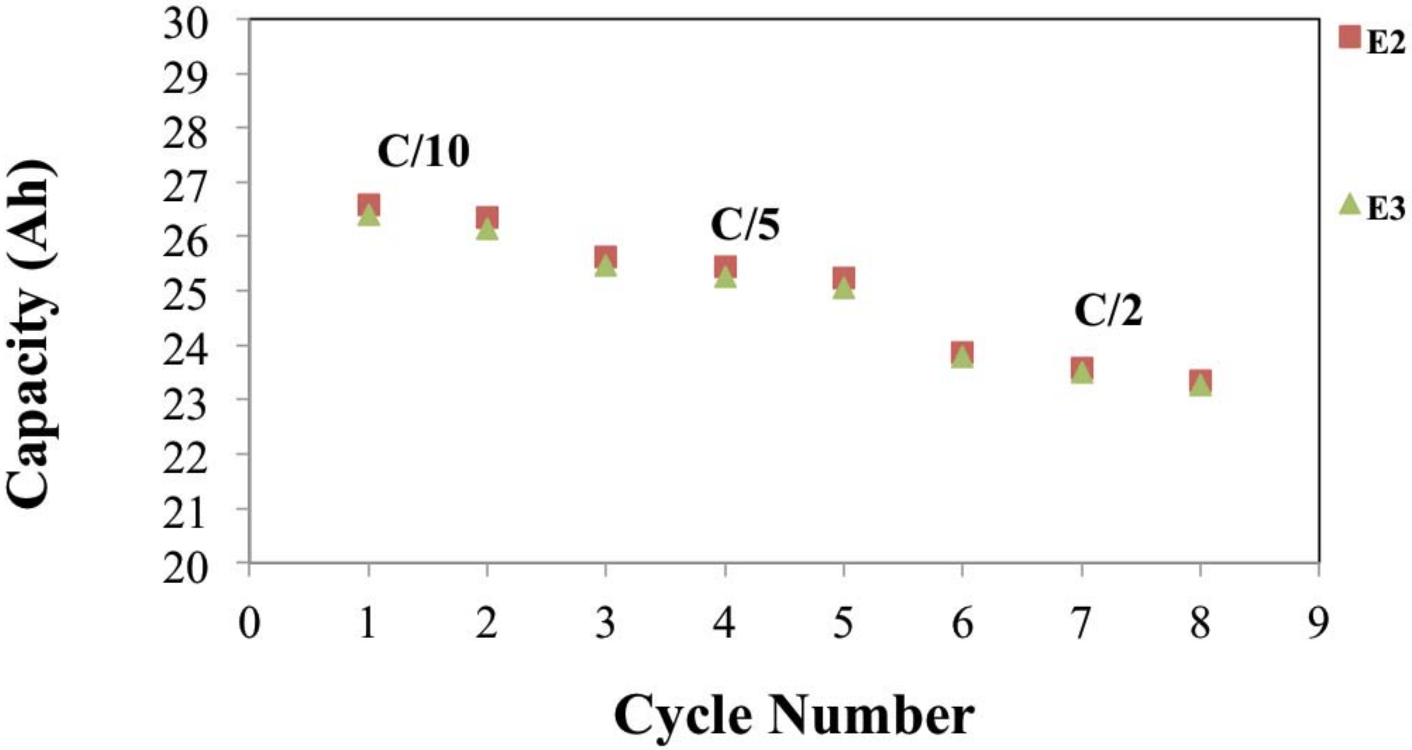
	Experimental Cells	Baseline Cells
	20^{o}C	**20^{o}C**
Ah	26.4	27.3
Wh/kg	164.0	159.7
Wh/L	387.5	415.2

- 10 cells at each temperature (20^{o}C and 10^{o}C) for experimental cells.
  5 cells for baseline cells at 20^{o}C

* Results at C/10

Cell capacity and specific energy can not be recovered to initial values for experimental cells

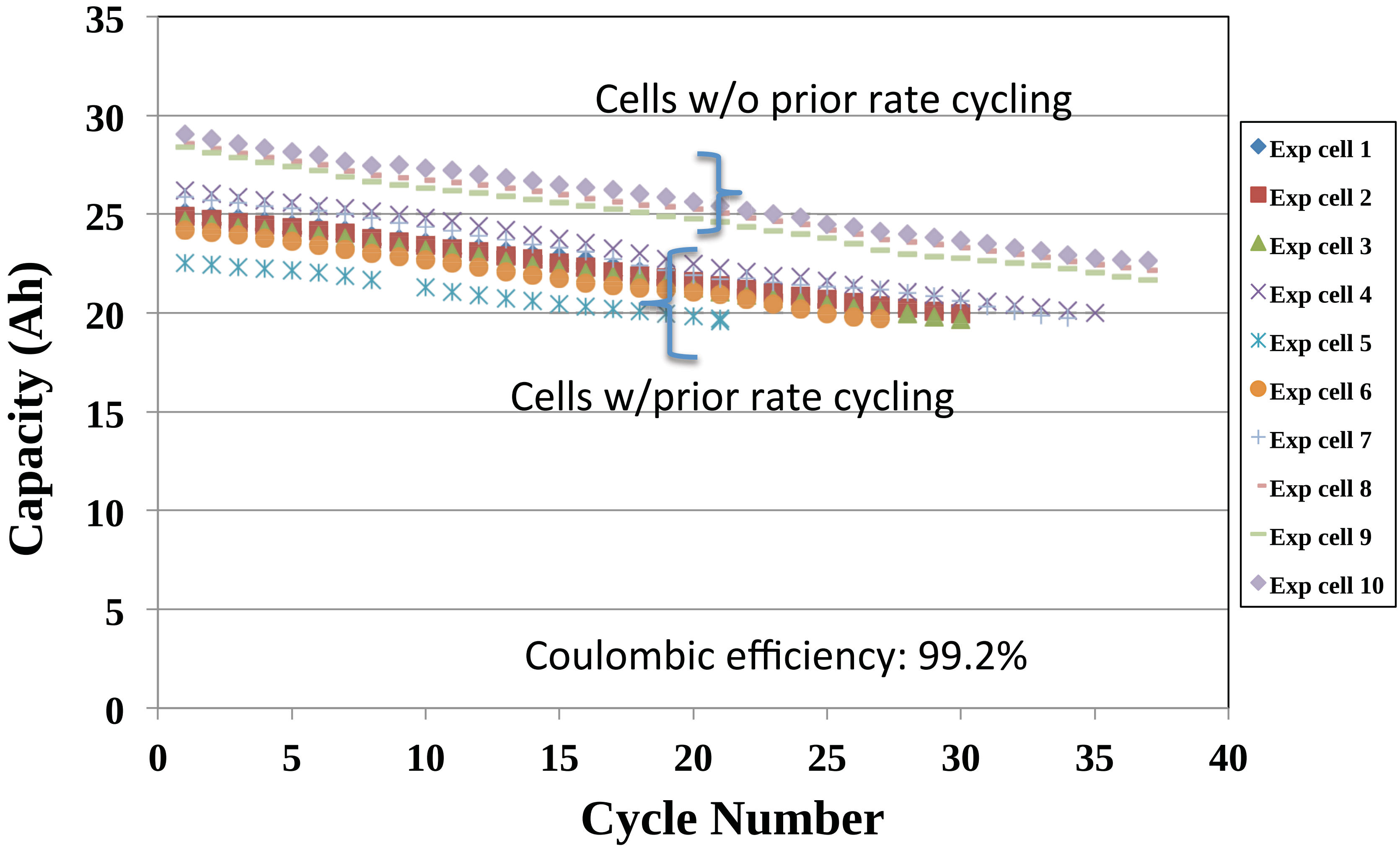
Experimental Cells: Rate Cycling at 20°C



Cell	C/10 Ah	C/5 Ah	C/2 Ah
2	26.5	25.4	23.6
3	26.3	25.3	23.5

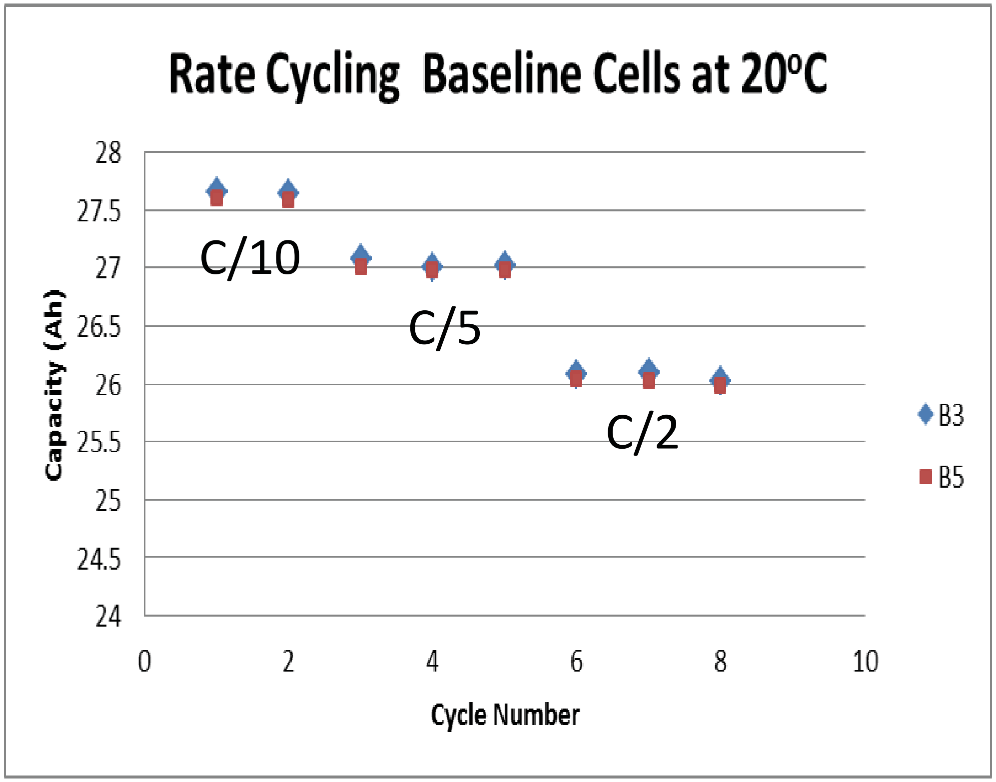
	C/10 Ah	C/5 as % of C/10	C/2 as % of C/10
Average	26.4	96.1%	89.3%

Experimental Cells: C/10 Cycling at 20ºC

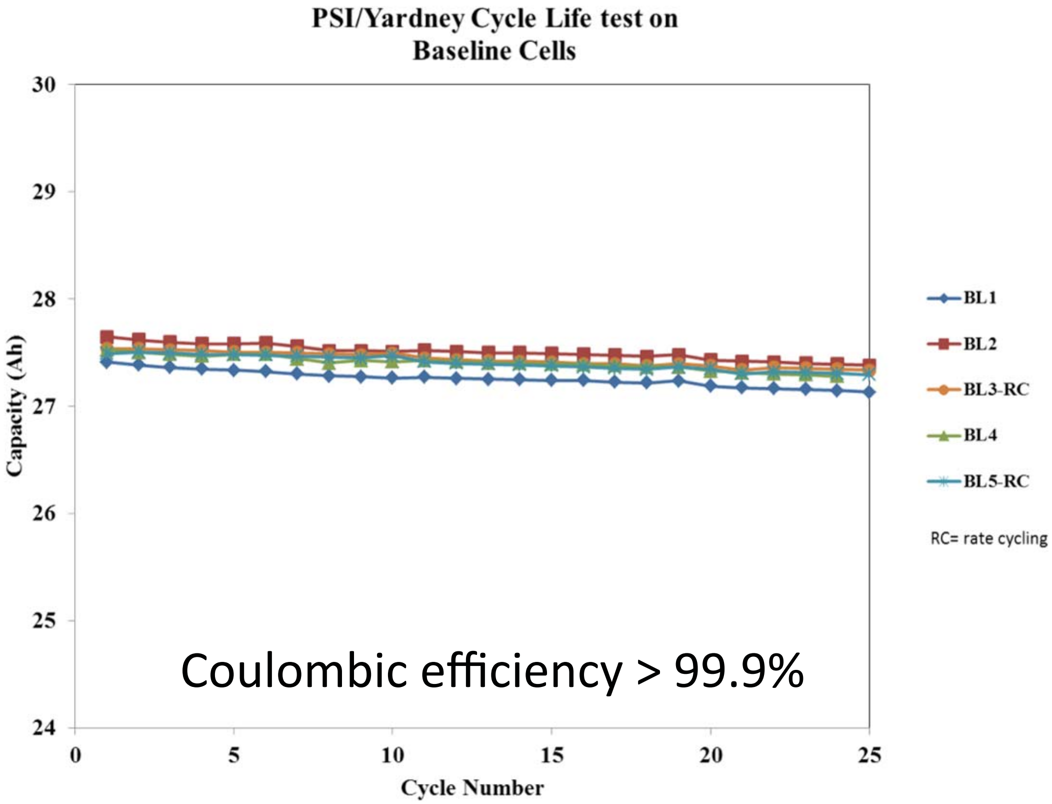


Higher capacity for the cells w/o prior rate cycling,
but the same fade trend with the cells w/prior rate cycling

Performance of Baseline Cells



C/10 Cycling

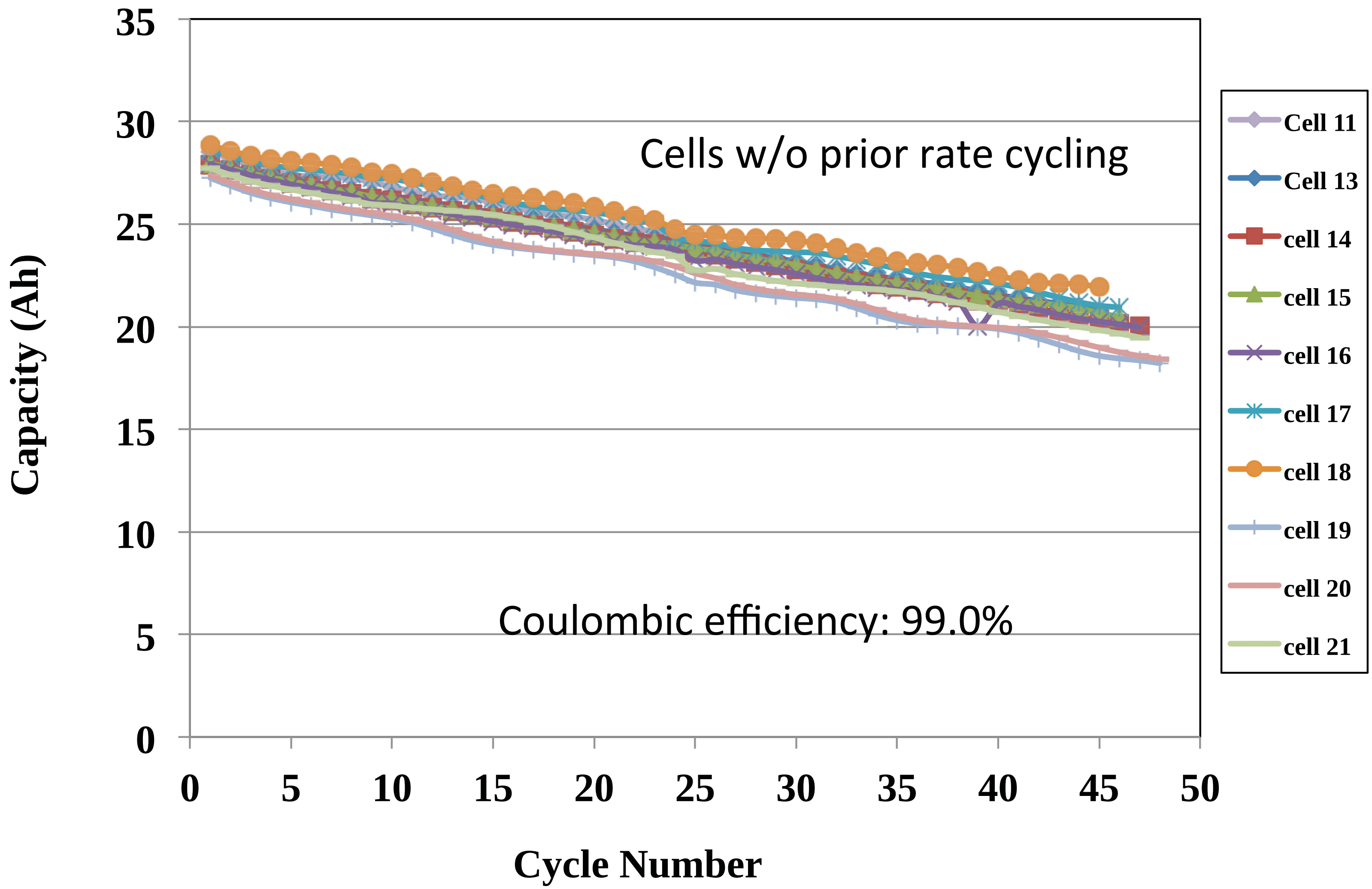


Coulombic efficiency > 99.9%

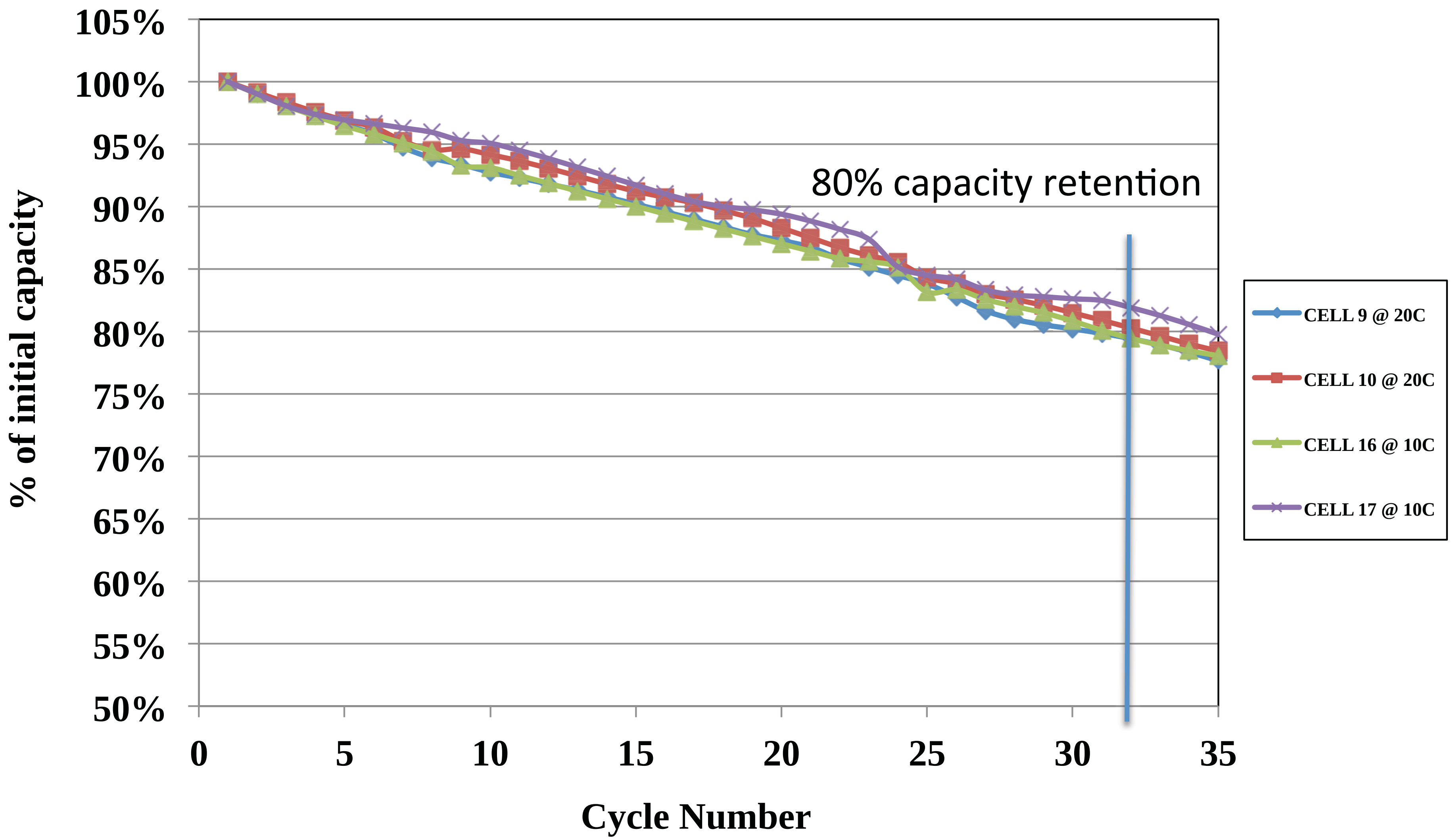
Cell	C/10 Ah	C/5Ah	C/2 Ah
3	27.6	27.0	26.1
5	27.6	27.0	26.0
Avg	**27.6**	**27.0**	**26.0**

Cell	C/10 (Ah)	Wh/kg	Wh/L
BL1	27.1	159.3	412.0
BL2	27.4	161.4	418.4
BL4	27.3	158.6	415.2
Average	**27.3**	**159.7**	**415.2**

Experimental Cells: C/10 Cycling at 10ºC



Experimental cells: C/10 Cycling 20ºC vs. 10ºC



At 80% capacity retention, the cycle # is ~ 30-35 cycles

Why Capacity Fade So Fast for Cell w/Si Anode ?

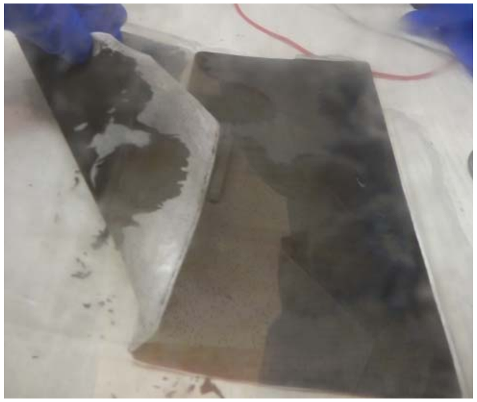
- **Non-destructive analysis**
  - Cycled cell impedance was increased significantly vs. prior cycling

- **Destructive physical analysis (DPA)**
  - No noticeable free electrolyte observed
  - Anode, cathode and separator appeared in relative dry condition
  - Delamination was seen on one side of Si anode while the other side of Si anode is ok
  - No cathode delamination was seen

What We Observed from DPA

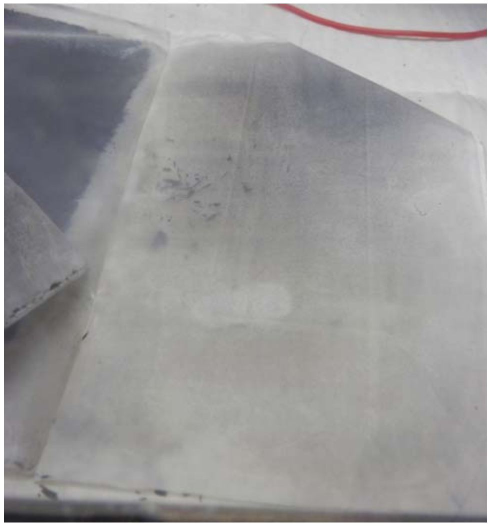
Si Anode

tap



The delaminated Si electrode materials adhered to adjacent separator

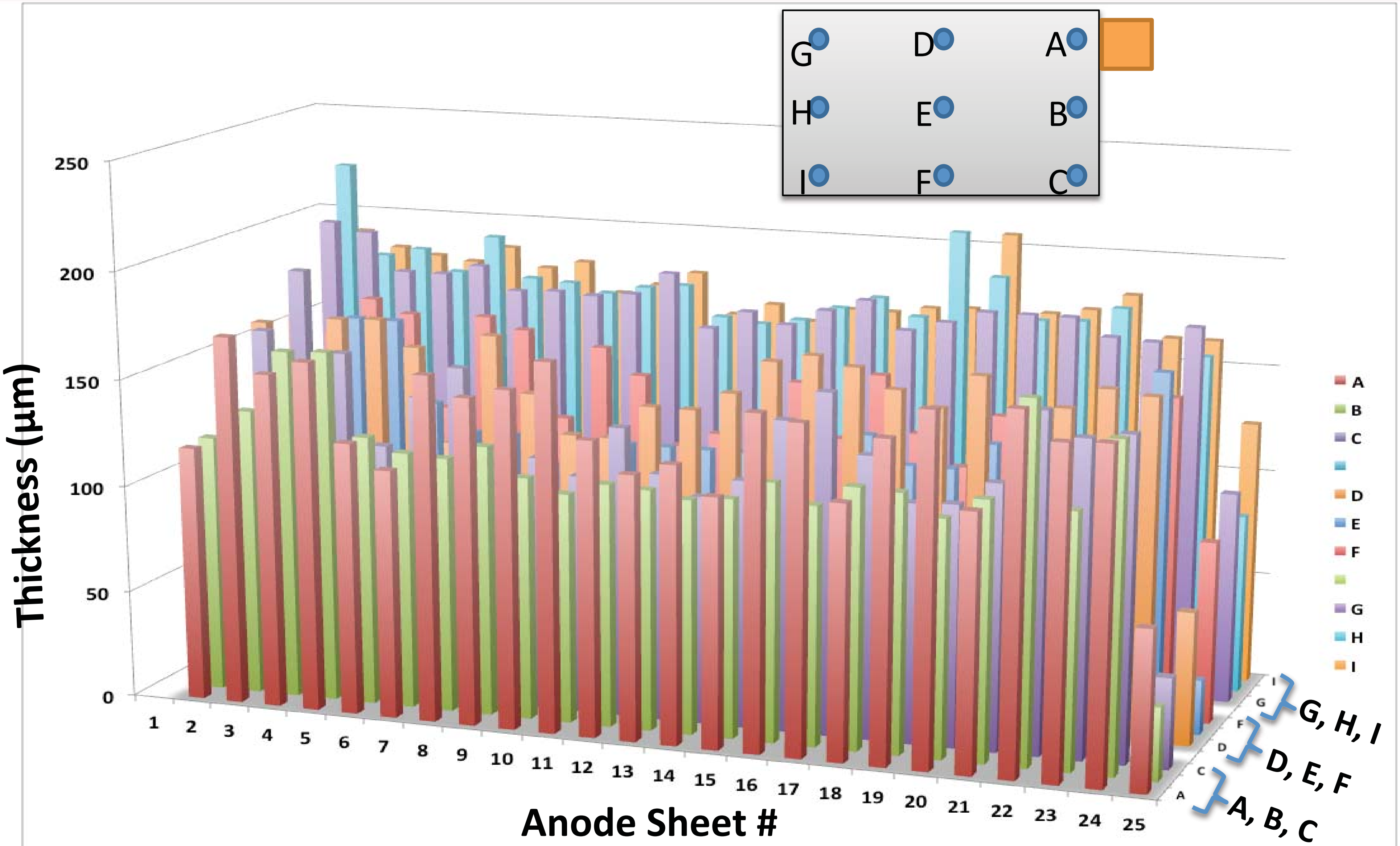
NCA Cathode



No cathode delamination was seen

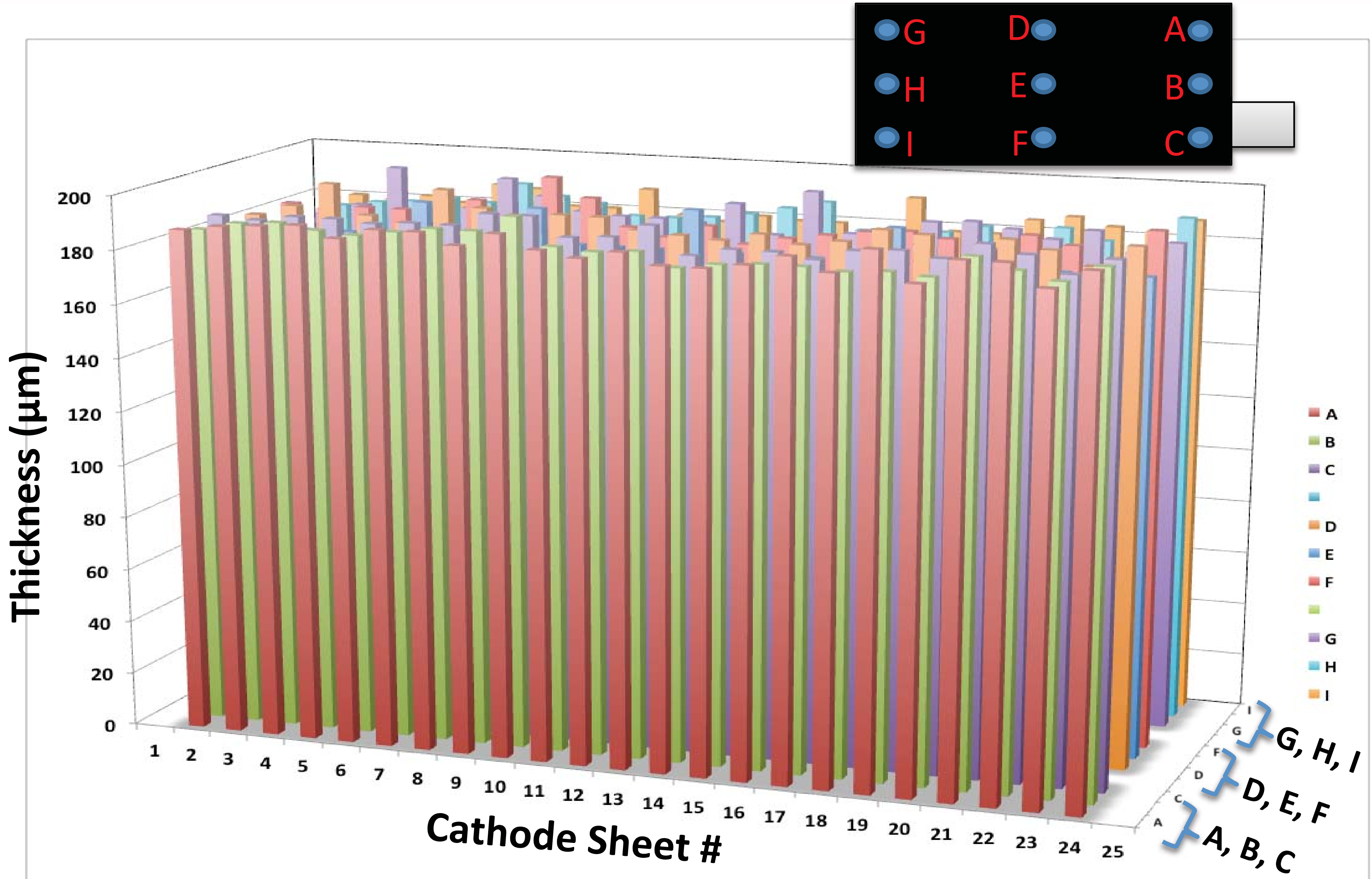
- **Delamination was seen on one side of anode sheet (the other side is ok) (<u>this happens on each anode sheet</u>)**
- **The delaminated Si anode materials adhered to adjacent separator**

Thickness of Cycled Si Anode Sheets



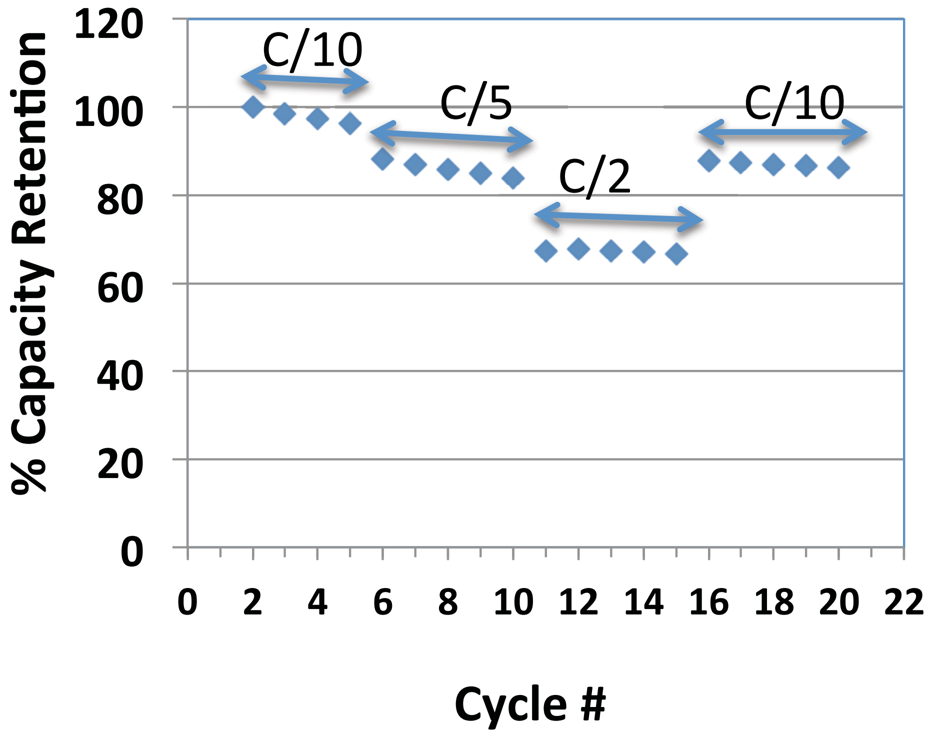
- The thickness was not uniform, possible due to delamination: relative thinner closer to current collector tap portion (A-C, D-F), relative uniform far away (G-I)
- The expansion of cycled Si anode is ~ 10-15%

Thickness of Cycled NCA Cathode



- The cathode thickness was fairly uniform
- The expansion of cycled NCA cathode is ~ 5%

Rate Capability Cycling for Coin Cell Full Cells from Harvested Electrodes:



- **The ratio of anode capacity vs. cathode capacity from harvested electrodes may not be the same as the original due to Si anode delamination**

- **Cells fabricated with all the harvested electrode components but with the addition of fresh electrolyte cycles well, implying electrolyte starving is a possible factor for the original cell capacity fade**

Possible Causes for Fast Capacity Fade

- Si anode delamination, resulting in disintegration of Si anode and non-uniform current distribution in anode; and the delaminated anode blocks the separator pores
- Not adequate electrolyte in the cell
- Higher lever of moisture in Si anode (~1100ppm) , which was hard to be reduced in the large-format cell fabrication

Summary

- 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 fast capacity fade

Acknowledgments

- Dr. Chris Lang (PSI) for discussion and input
- Dr. Joe Gnanaraj (Yardney) for discussion and input
- Matthew Schrandt (summer graduate student from SDSMT) for help in the DPA analysis
- Bill Bennett for discussion and help in open the cell
- NASA SBIR program and Advanced Space Power System (ASPS) project to support this work

Thanks!

Questions?