

Detecting Subtle Soft Shorts in Li-ion Cells



By

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Bottom Line Up Front (BLUF)

Motivation

- Improving our methods for detecting subtle charge retention defects in cells is key for providing screened cells to customers of our COTS cell strategic reserve

Methods

- Measure as received (30% SoC) OCV >1 year after born-on-date (BOD) is NASA standard for manned applications
- Measure Δ OCV over 6 months while at as received SOC
- Measure Δ OCV over 3 months while at 0% SOC
- Rapidly (24hr) grade self-discharge rates through cell comparisons at as received SOC
- Tested with 1000 cells each from the 4 cell designs in our reserve

Main Finding to Date

- Wait > 1-yr method found to be not as discriminatory as the 6-month Δ OCV or the rapid self-discharge comparison methods
- These better methods potentially raises the equivalent resistance shorts detected in cells from 2 to 3 Mohms and significantly and drastically reduces measurement time.

Future Work

- Analyze the grades on 30k cells (two designs) to mature this rapid measurement method
- Update NASA cell screening work instructions to de-emphasize the 1-year wait method
- Mature the rapid detection instrument for 21700 cells

Cell Strategic Reserve Motivation

- Problem

- Buying, screening, and certifying numerous COTS cell lots with only enough cells for each individual project is not efficiently utilizing our resources
- We are unable to buy the best cells with small orders
- Some of our primes and subcontractors are making costly mistakes/omissions in screening and certifying for manned space applications

- Solution

- Entice cell manufacturers to sell directly to us for just a few large quantity cell lot orders and get the best quality designs for maximum benefit to our programs
- Control how they are bought, screened, certified, and stored to prevent future cell level issues, anomalies, failure investigations, and risky battery designs



Our High Energy Cell Designs

LG INR18650 M36

- Previous heritage
 - 250 μm can wall
 - Safety fully characterized by JSC
 - Multiple variations beam tested in FTRC
 - 3 batches of ISCD trigger cells delivered to JSC
- At C/10 and room temperature
 - 270 Wh/kg, 710 Wh/L
 - ACR is 23.9 mohms
 - DCR is 29.8 mohms
- 70k lot (Nov 2020) delivered in Apr to JSC



Molicel INR18650-M35A

- Little previous heritage
 - Same manufacturer of ICR18650J, primary power for > 25 EVAs
 - Superior extreme cold performance
 - 214 Wh/kg at C/20 and -20°C
 - Multiple batches of ISCD trigger cells delivered to JSC
- At C/10 and room temperature
 - 277 Wh/kg, 725 Wh/L
 - ACR is 24.4 mohms
 - DCR is 32.5 mohms
- 120k lot (Feb 2021) delivered in Apr to JSC



Our High Power Cell Designs

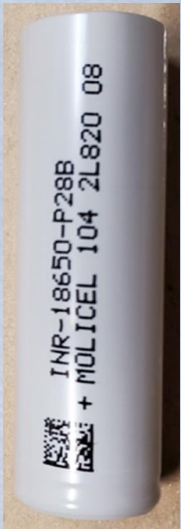
Samsung INR18650-30Q

- Previous heritage
 - X-57 Electric Airplane
 - Safe high power battery demo
- At 3C and room temperature
 - 2483 W/kg, 206.9 Wh/kg
 - 6340 W/L, 528.1 Wh/L
 - 12.4 mohm ACR
 - 26.2 mohm DCR
 - 8.3% average waste heat
- 60k lot (Mar 2021) delivered in June to JSC

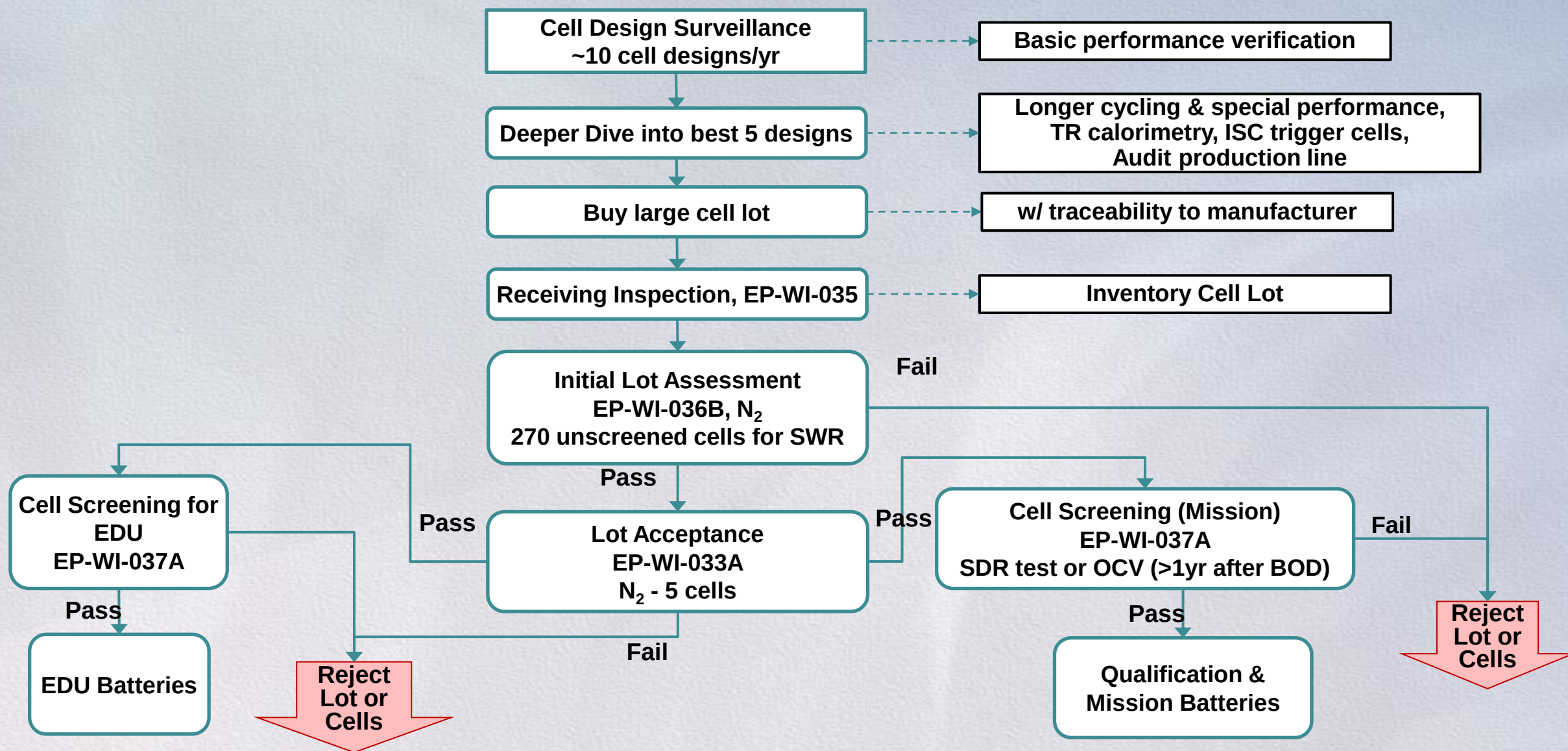


Molicel INR18650-P28B

- No previous heritage
- Not mass produced due to 2nd cathode tab
- At 3C and room temperature
 - 2528 W/kg, 202.3 Wh/kg
 - 6376 W/L, 510.3 Wh/L
 - 9.2 mohm ACR
 - 22.3 mohm DCR
 - 5.5% waste heat
- 60k lot (Aug 2021) delivered in Oct to JSC



Cell Process Flow Chart

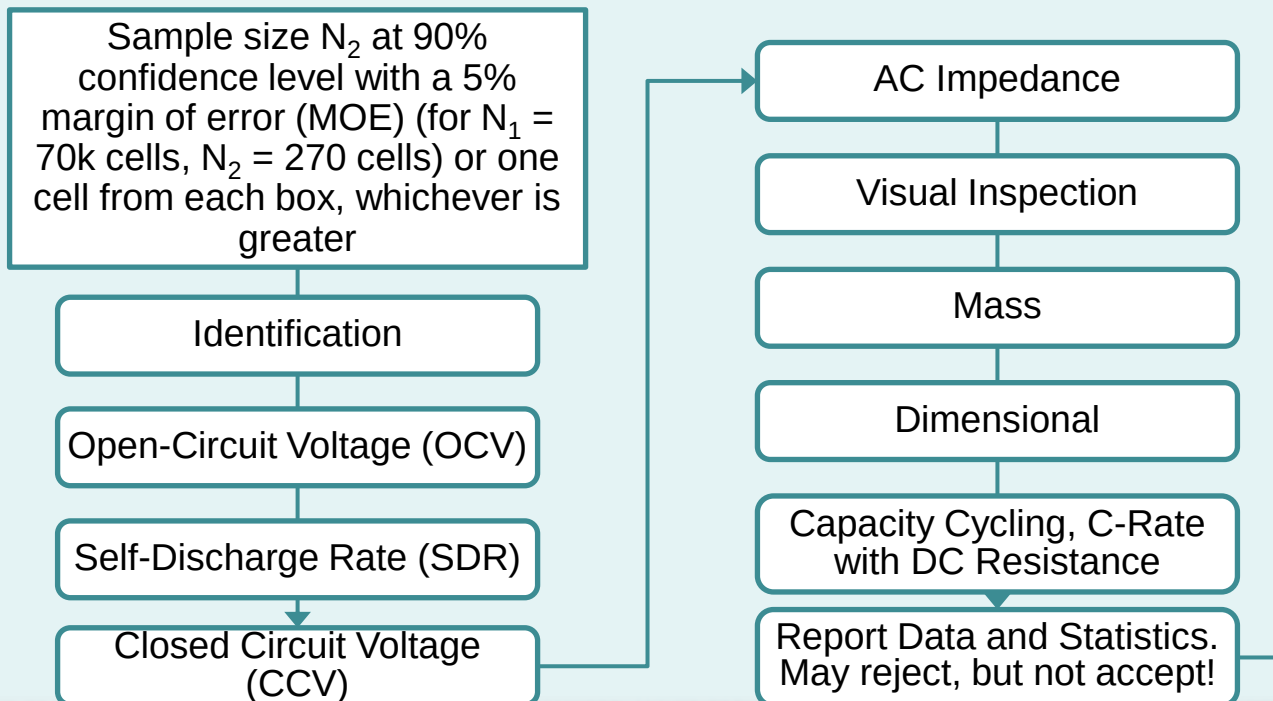


Initial Lot Assessment (ILA)

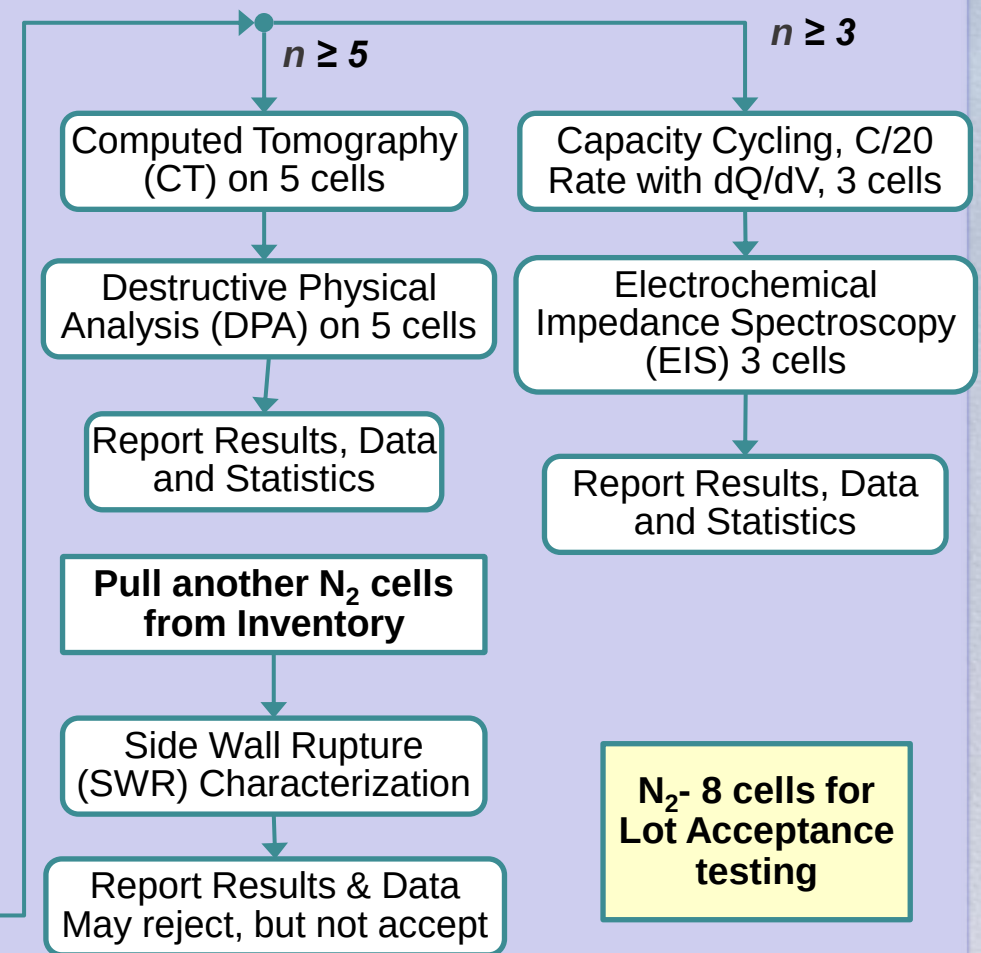
EP-WI-036 Specification for Initial Lot Assessment of Commercial Lithium-ion Cells Lots

- Determine if cell lot (N_1 lot size) is worthy before proceeding with an expensive lot acceptance testing - Quick & less expensive (8 weeks, ~\$150k)
 - Expected performance in accordance with cell surveillance results
 - Acceptable lot uniformity of performance, particularly charge retention
 - Acceptable quality of manufacture
 - Propensity to sidewall rupture during TR (90% confidence level, 5% MOE)

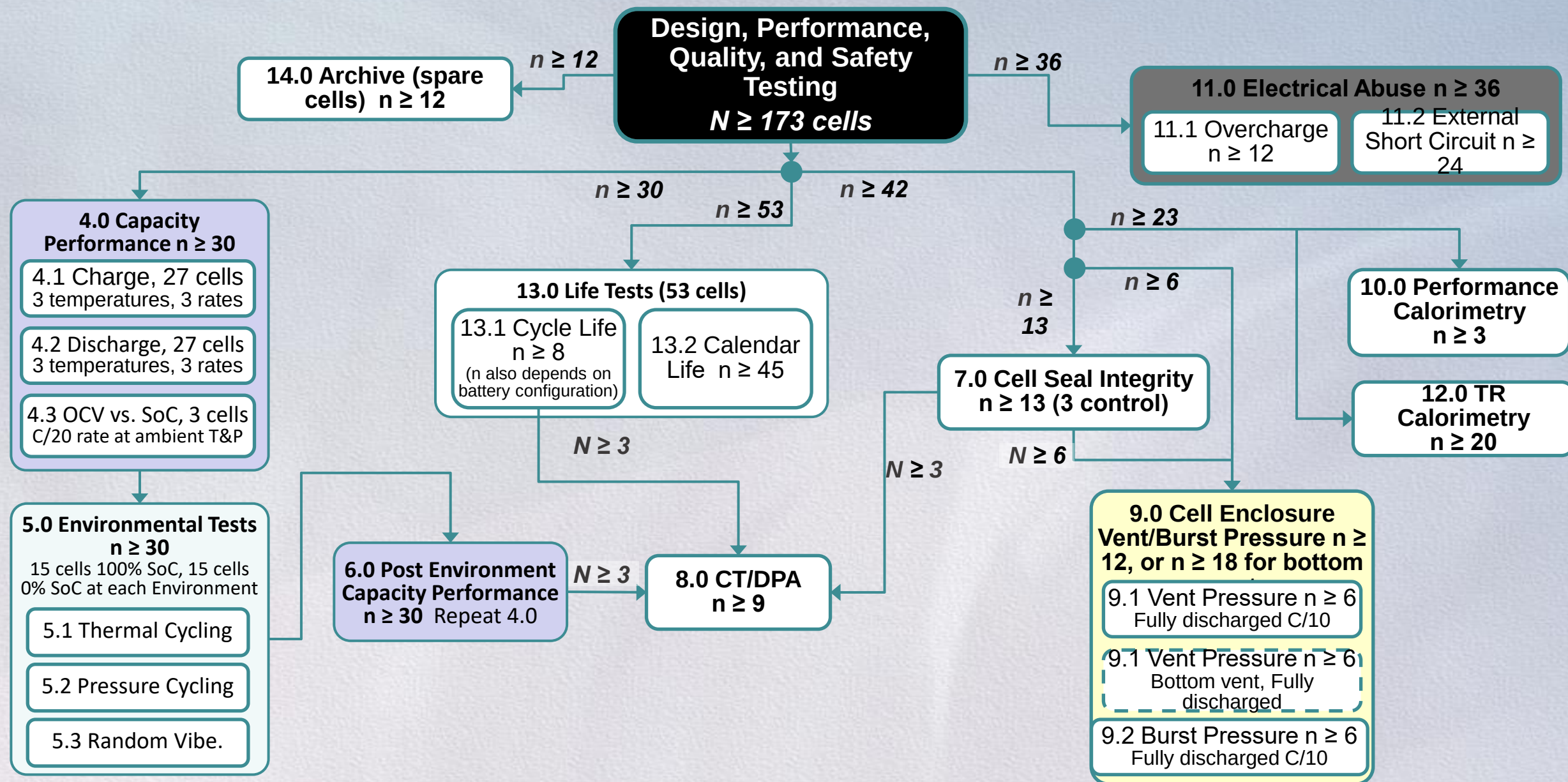
Assess manufacture performance and quality



Verify cell design has not changed

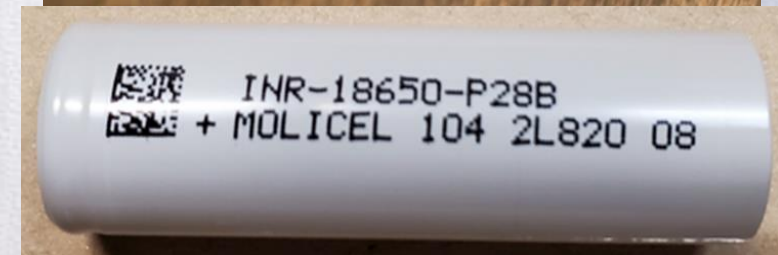


Lot Acceptance Testing



Screened Cells From Certified Lots

- Available and in storage
 - Room temperature and humidity controlled and 30% SoC
 - Freezer (-18°C) storage available
- Screened cells available for \$36/cell and cost includes
 - ILA debriefing
 - LAT debriefing
 - Screening results
 - Calendar life annual updates



Motivation for Better Detection of Subtle Soft Shorts

- Despite extensive QC/QA, standardized industry safety testing, and over 31 years of manufacturing learning, major recalls have taken place and incidents still occur.
- Many safety incidents that take place in the field originate due to an internal short (that was not detectable or predictable at the point of manufacture) - **Latency**
- These internal short incidents are estimated at 1 to 5 million probability (well beyond 6σ) in consumer applications using cells from experienced and reputable manufacturers¹
- CSPC recalls are typically triggered when failure rates are more likely than 1 ppm²
 - Sony Laptop in 2006 failure rate 1:100,000
 - Samsung Galaxy Note 7 failure rate 1:40,000
- **Some latent defects could be showing very subtle OCV decays**
- **We need to improve our sensitivity and speed of our detection screens**



1. B. Barnett, TIAX, NASA Aerospace Battery Workshop, Nov 2008

2. C. Mikolajczak, et.al., "Li-ion Battery Hazards and Use Assessment" Fire Protection Research Foundation, July 2011

EP-WI-037A

- Identification
- OCV after 1 yr
- Self-Discharge (CST)
- Stripping
- Visual Inspection
- Mass
- Dimensional
- Temporary resleeving
- ACR
- Capacity & DCR

Specification for Screening Cells from Accepted Lots of Commercial Lithium-Ion Cells

Engineering Directorate

Propulsion & Power Division

EXPORT ADMINISTRATION REGULATIONS – 15 CFR 730-774

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Mar 2022



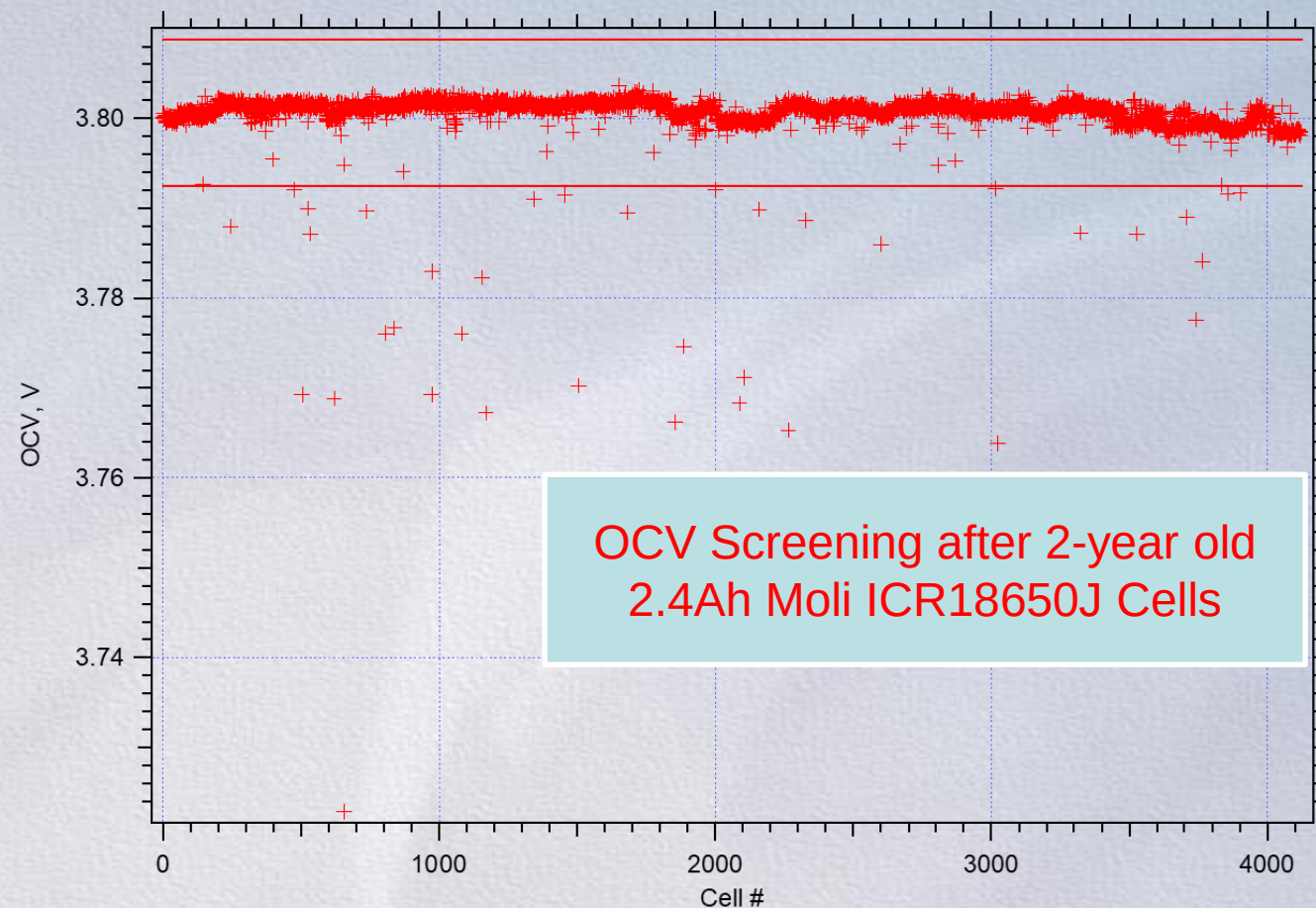
National Aeronautics and
Space Administration

Lyndon B. Johnson Space Center
Houston, Texas

See cover for full disclosure. Verify correct version before use.

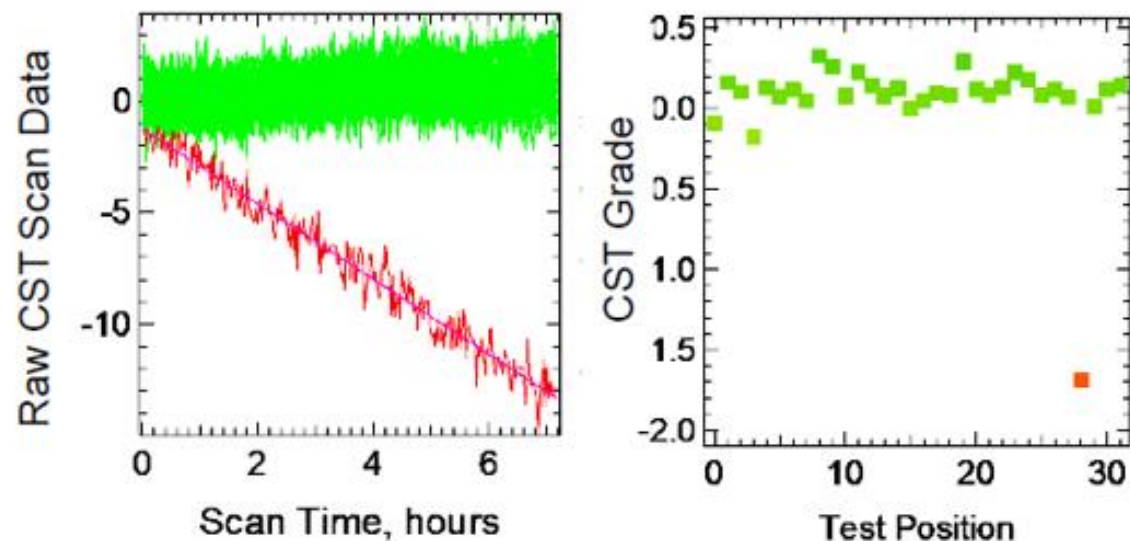
Our Previous OCV Screening Methods

- 1-yr wait at 30% SOC
 - Simple, just need patience
 - Depends on consistency of the SOC set by cell manufacturer
 - After all outliers removed, uniformity as graded by $6\sigma\% < 1\%$ indicates high quality manufacturing
- ΔOCV over 6 months at 30% SOC
 - Quicker, but requires two OCV measurements
 - Ideal if you get the initial OCV from cell manufacturer
- ΔOCV over 3 months at 0%
 - Quickest, but requires discharging all cells, measuring OCV after x days and after 3 months
- OCV Bounce Back Test
 - Deep discharge at CV to minimum operating voltage to low taper current
 - Cells with declining OCVs after 14-28 days are outliers
 - Quick but only found to catch ~30% of rejects found with 1-yr wait method in previous studies



New Rapid Self Discharge Detection Method

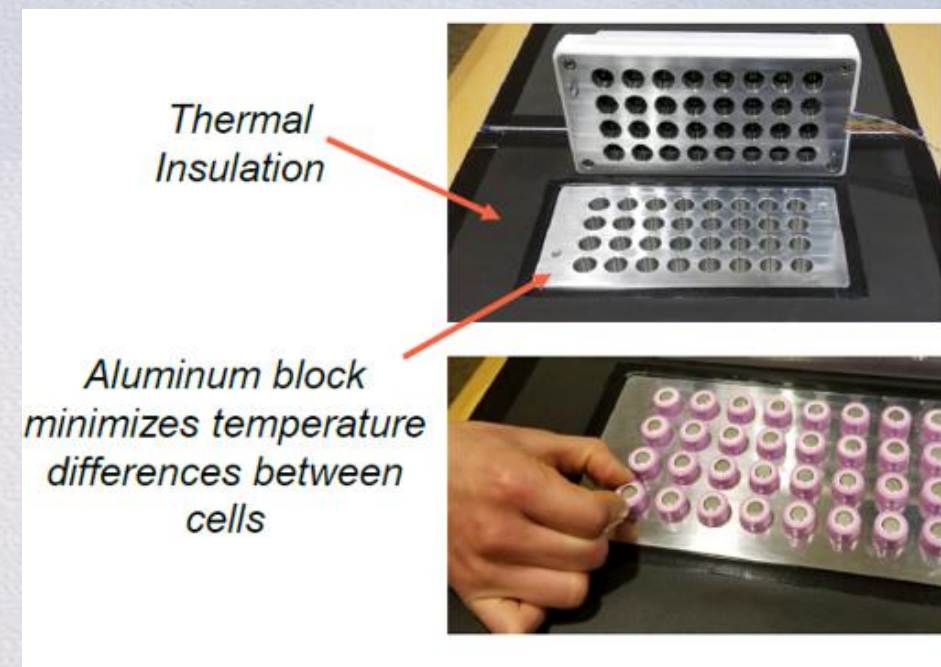
Scan Results: Commercial Cell Found to have Anomalous Self-Discharge at the $\approx 1\text{M}\Omega$ Level.



Cell manufacturers observe cells over two weeks prior to shipping

- Allows them to detect gross defects ($\sim 100\text{ k}\Omega$ short)
- Our standard OCV test after cells are > 1 yr old is much better ($\sim 2\text{M}\Omega$ short) using 16 or 18-bit resolution meters

CAMX Cell Screening Technology (CST) compares OCV retention of 32 cells to a known good reference cell after > 3 days equilibration preparation and while at a uniform temperature over a 24-hr scan cycle and grades them



Rate of OCV decay compared with 24-bit resolution

Test Plan at Symmetry Resources, Inc (SRI)

- Compare 4 methods at SRI with 4000 cells, all as received
 - Measure all OCVs after receipt and 3.5-6 months later
 - Measure CST grade with two 32-cell instruments from CAMX
 - On half of the cells from each design
 - wait > 1 year after BOD of cells
 - measure OCVs
 - On the other half
 - discharge the cells at C/3 to 0% at CC to minimum operating voltage
 - measure Δ OCVs between months 2 & 3 to remove bounce back bias
 - OCV typically takes ~1 month to stabilize after discharge
 - CST grades measured on 128 of these cells

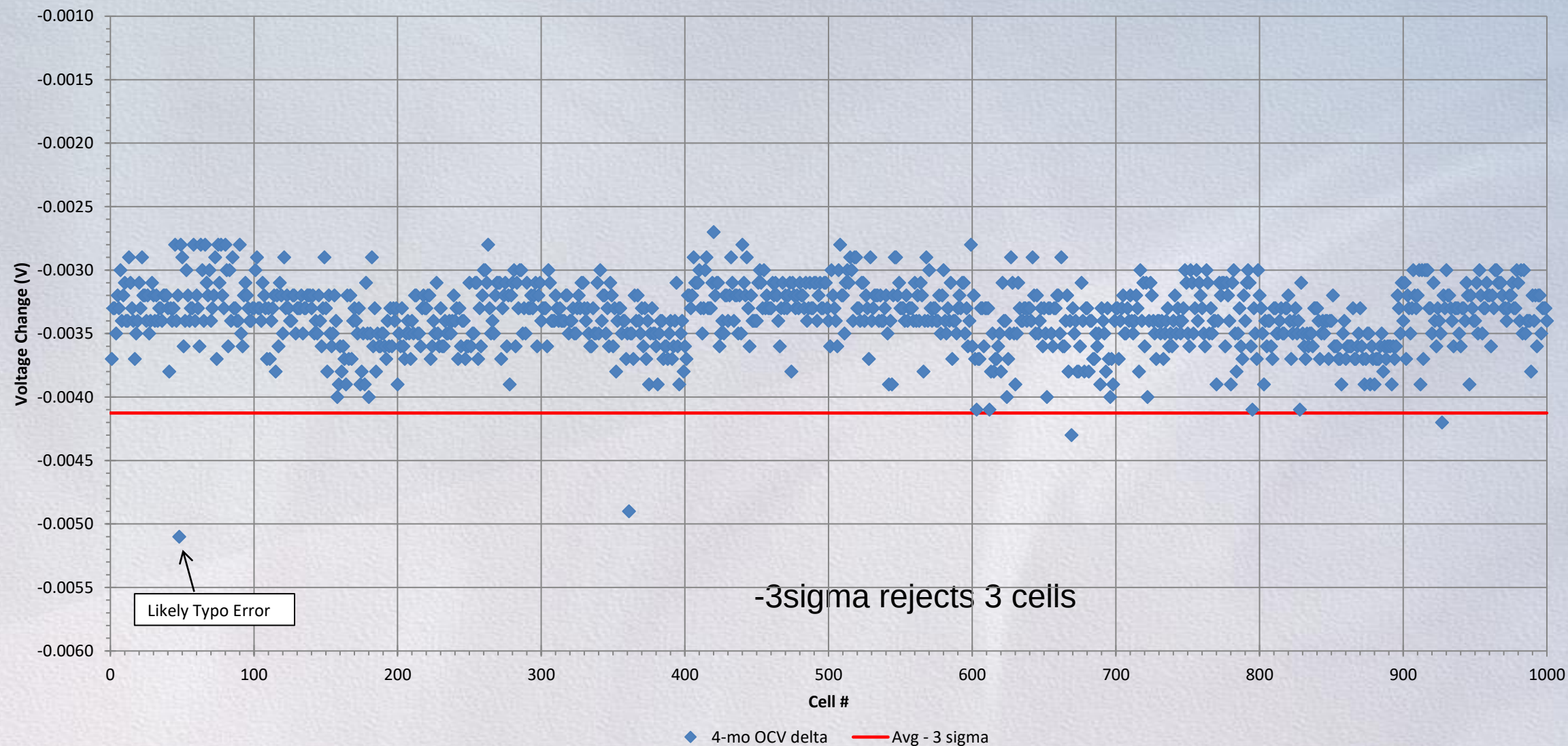
1000 M36 OCVs 1-yr after BOD of cells

LG M36 Cells; OCV ~1 Year Old, Room Temp Storage



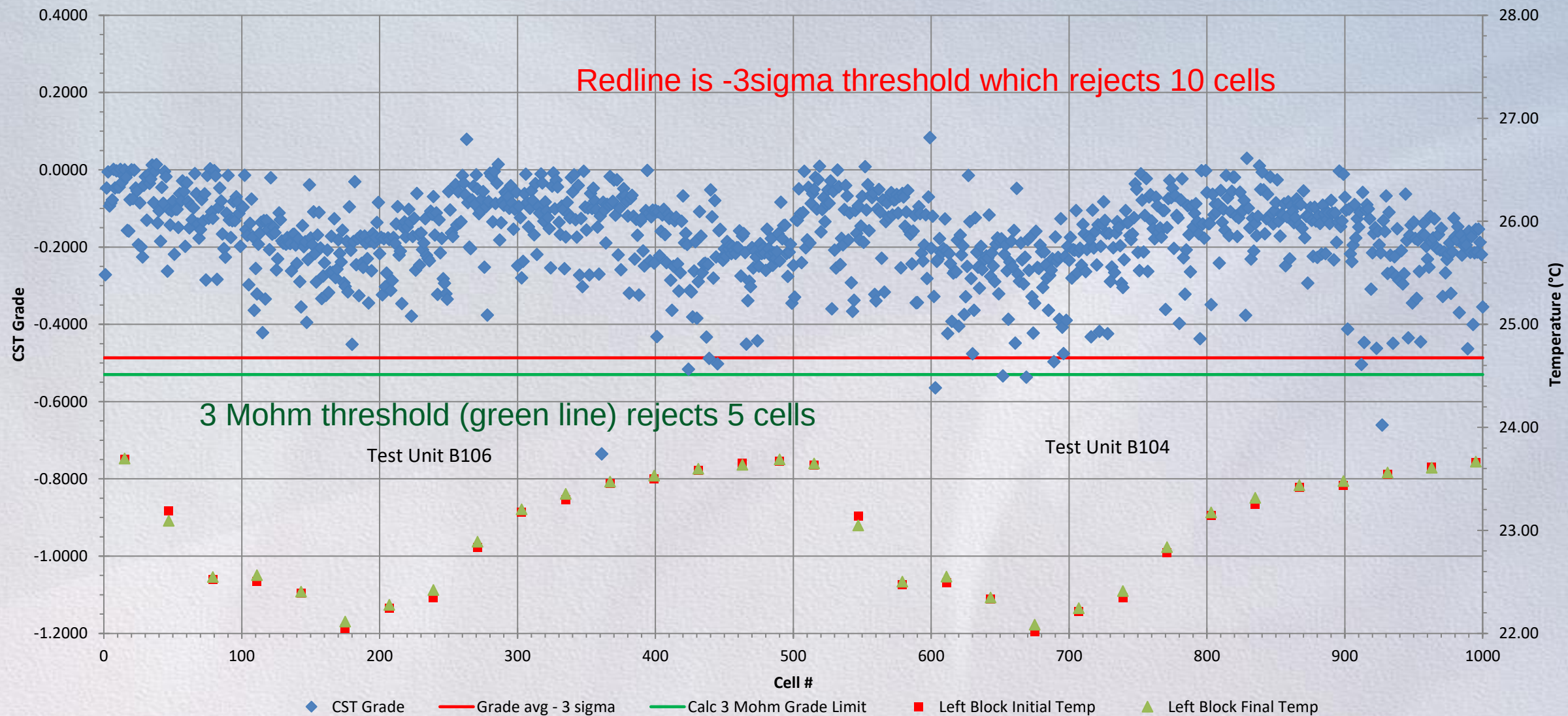
M36 Δ OCV over 4 months at 30% SOC

LG M36 Cells; OCV Change after ~4 Months Room Temp Storage



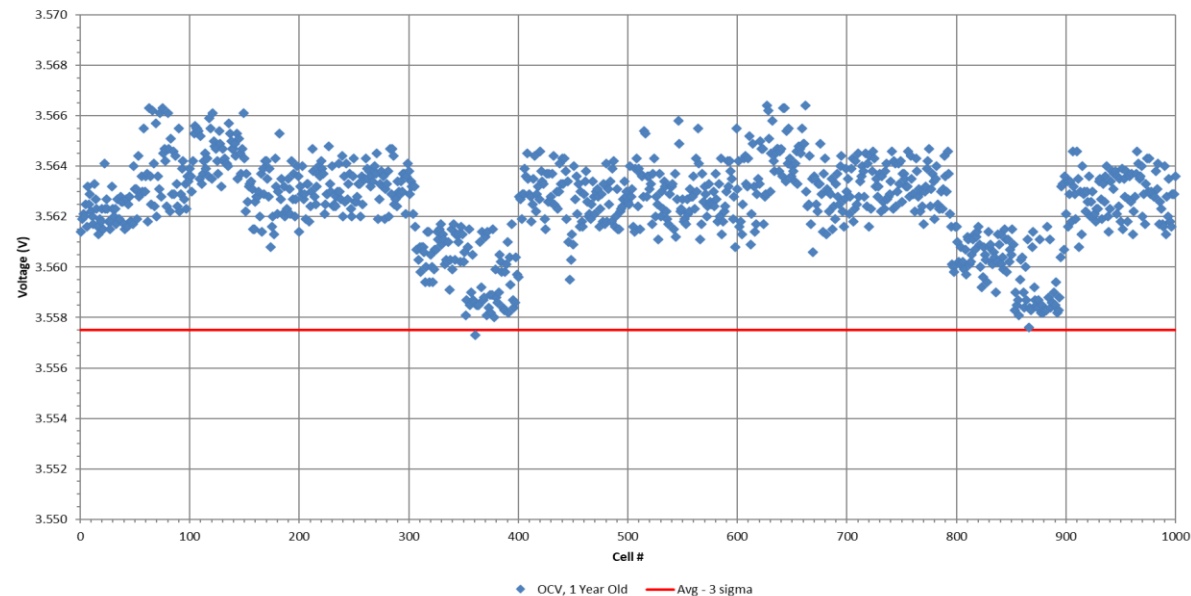
M36 CST Grading

LG M36 Cells; Raw CST Grades

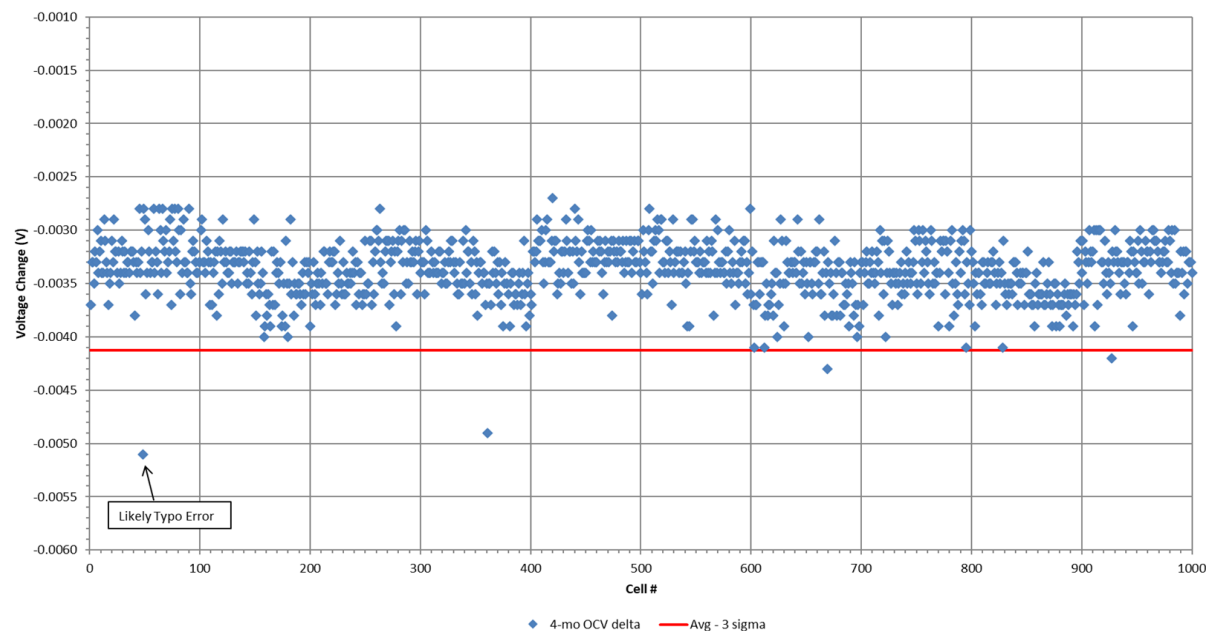


Comparison of 3 Methods with M36 Cells

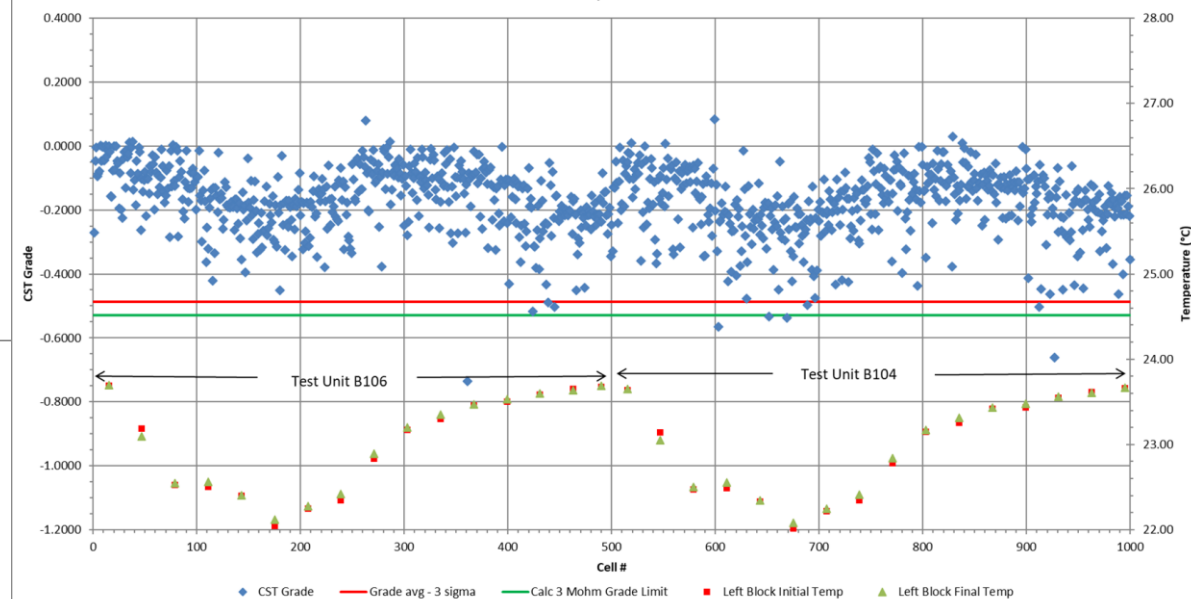
LG M36 Cells; OCV ~1 Year Old, Room Temp Storage



LG M36 Cells; OCV Change after ~4 Months Room Temp Storage

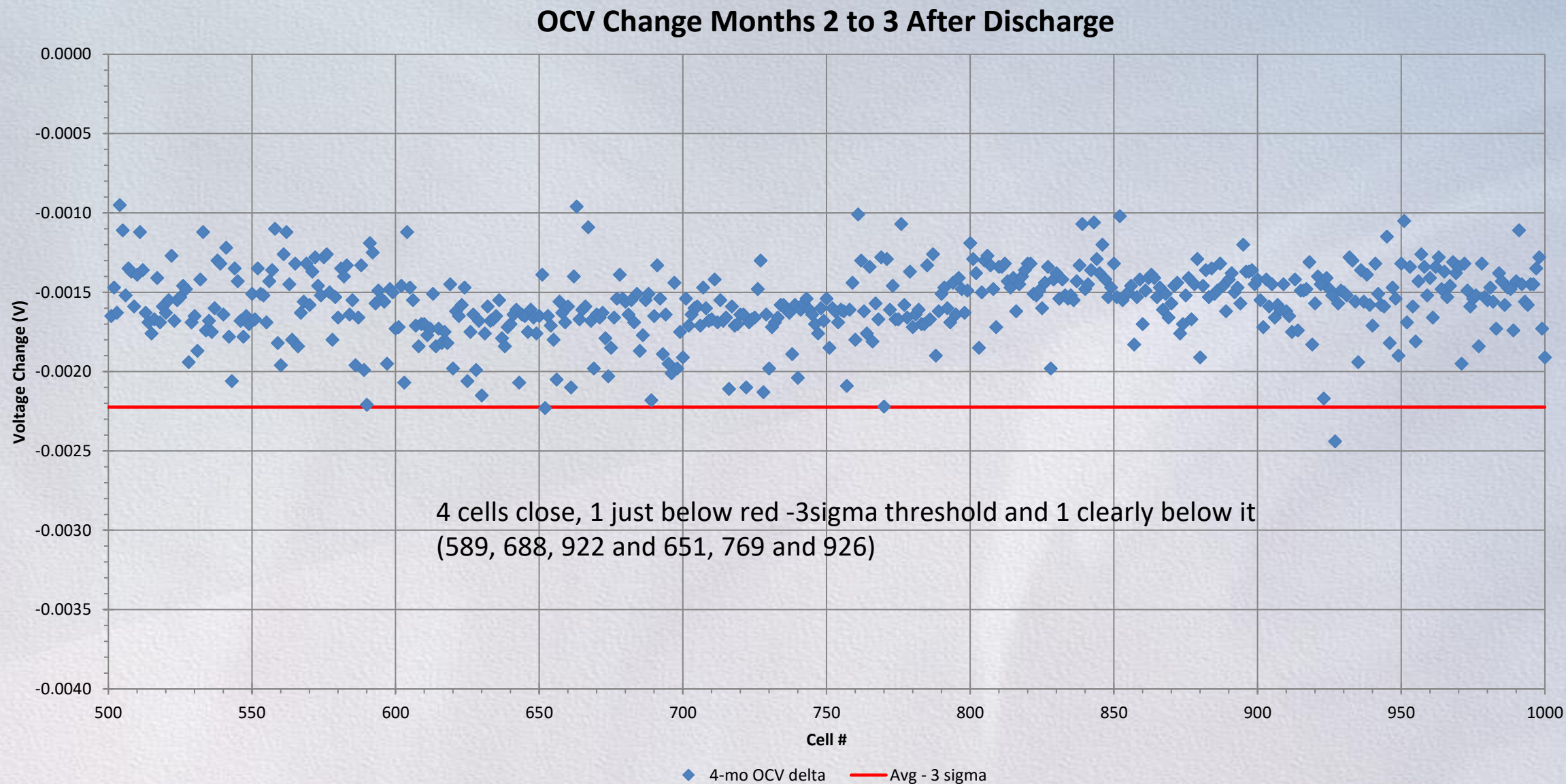


LG M36 Cells; Raw CST Grades



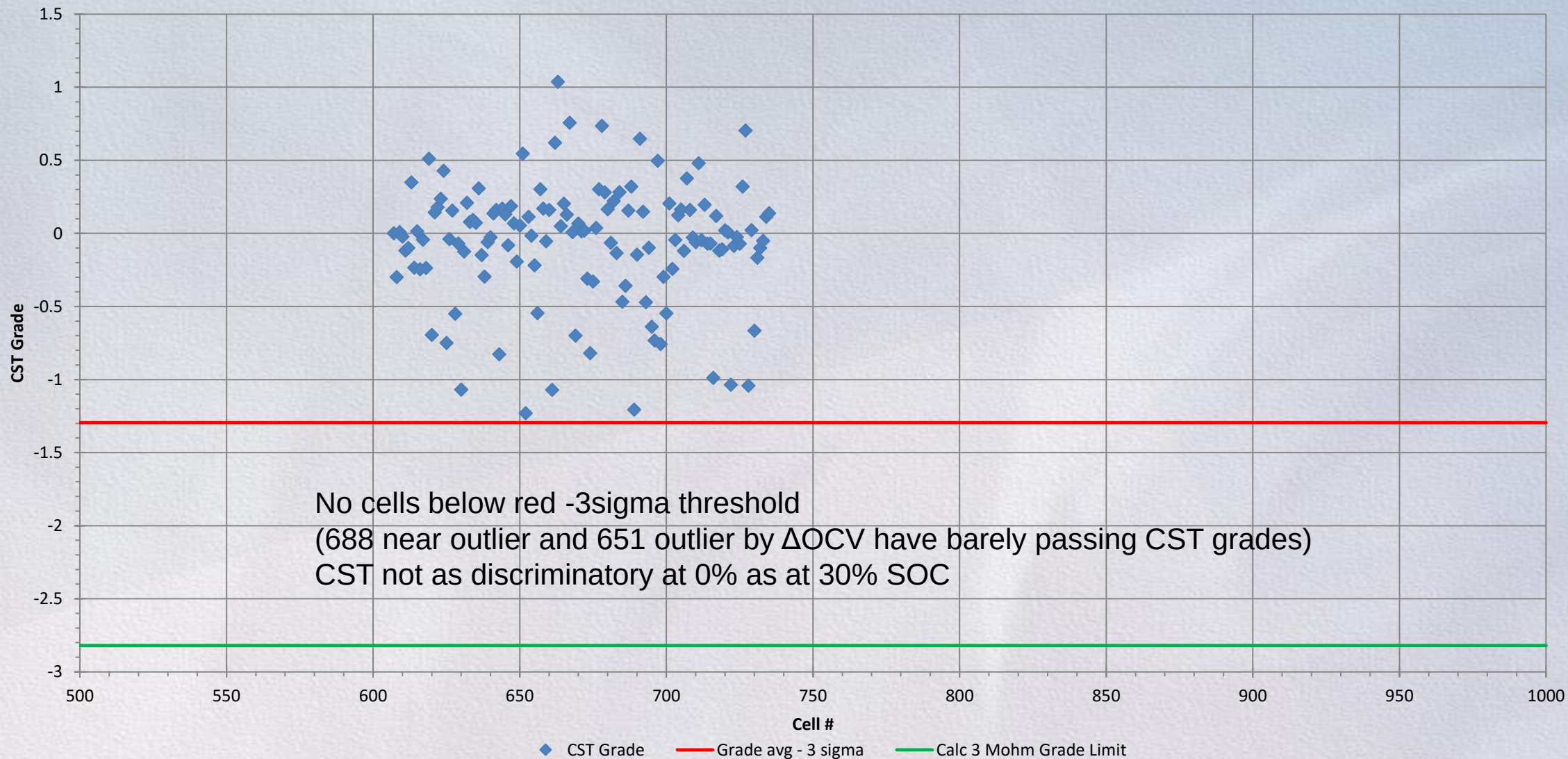
- CST rejects 5 cells for < 3 Mohm short, 10 cells $< -3\sigma$
- Including the 3 rejects from Δ OCV over 4 months
 - Including the 1 reject from 1yr wait OCV
- CST grading is more discriminatory with these M36
- With 8-hour total test time

500 M36 Cells Screened by Δ OCV at 0% SOC



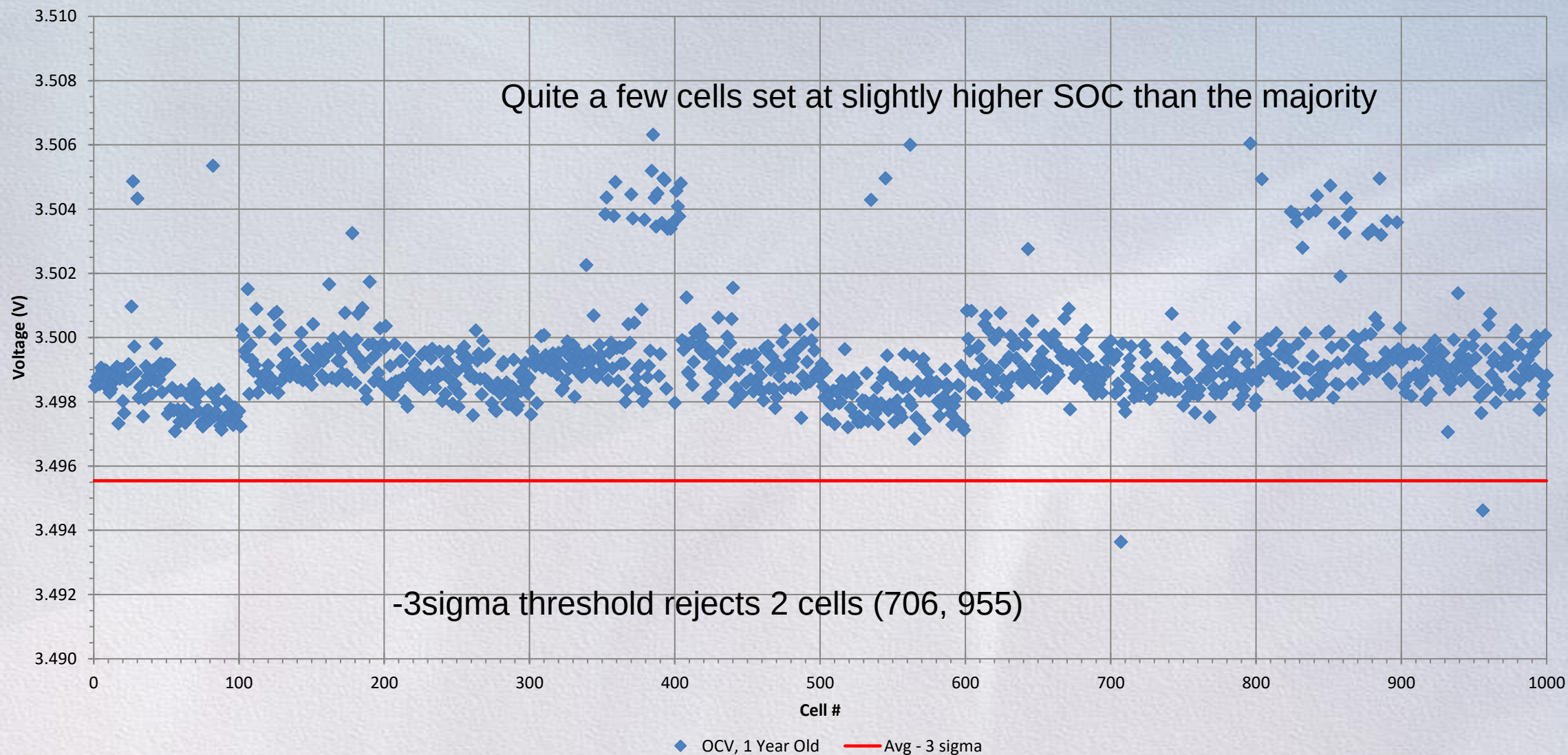
128 M36 Cells CST Graded at 0% SOC

LG M36 Cells; Raw CST Grades; 3 months after discharge



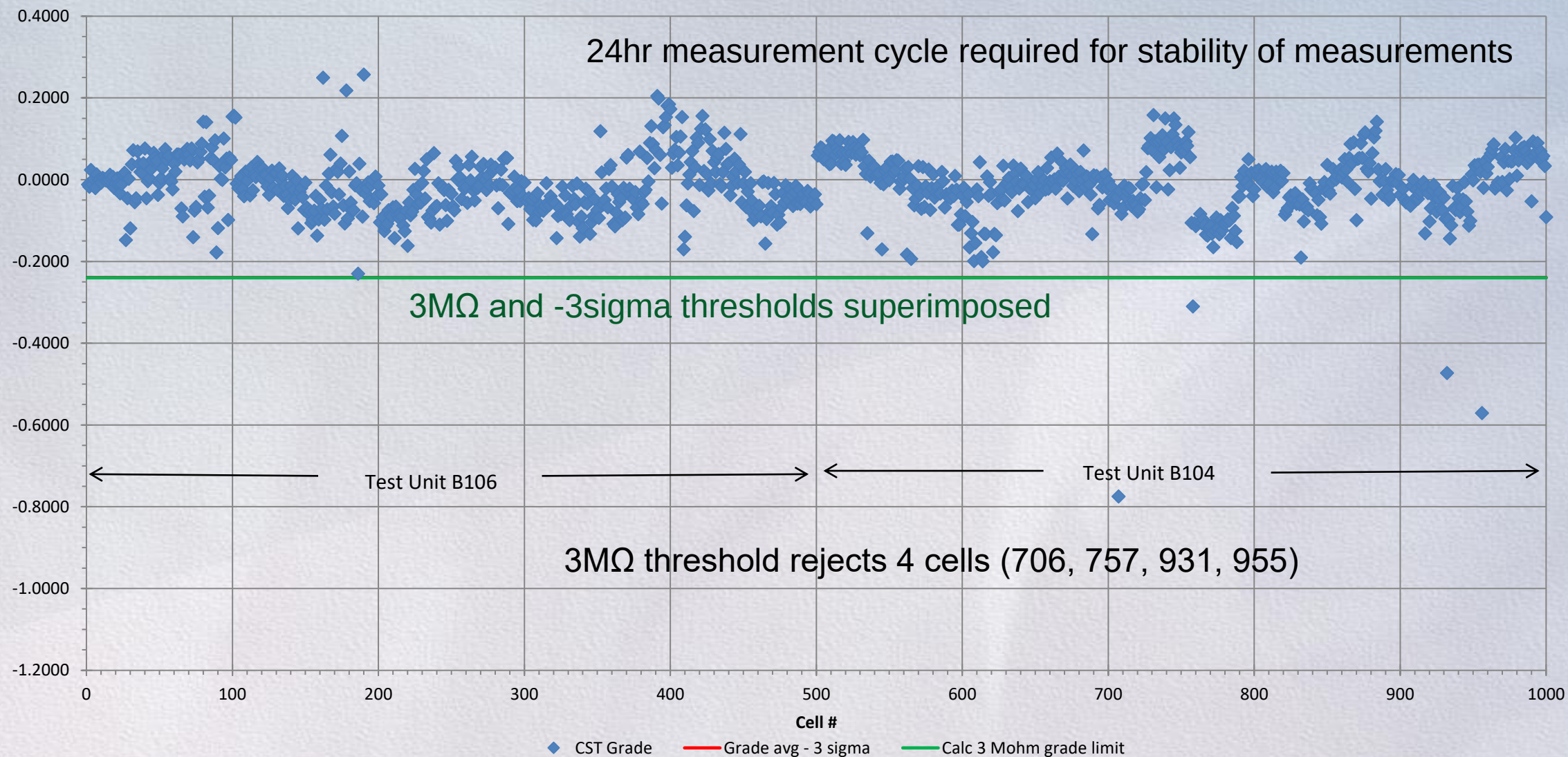
1000 M35A OCV at 1-yr past BOD

OCV ~1 Year Old, Room Temp Storage



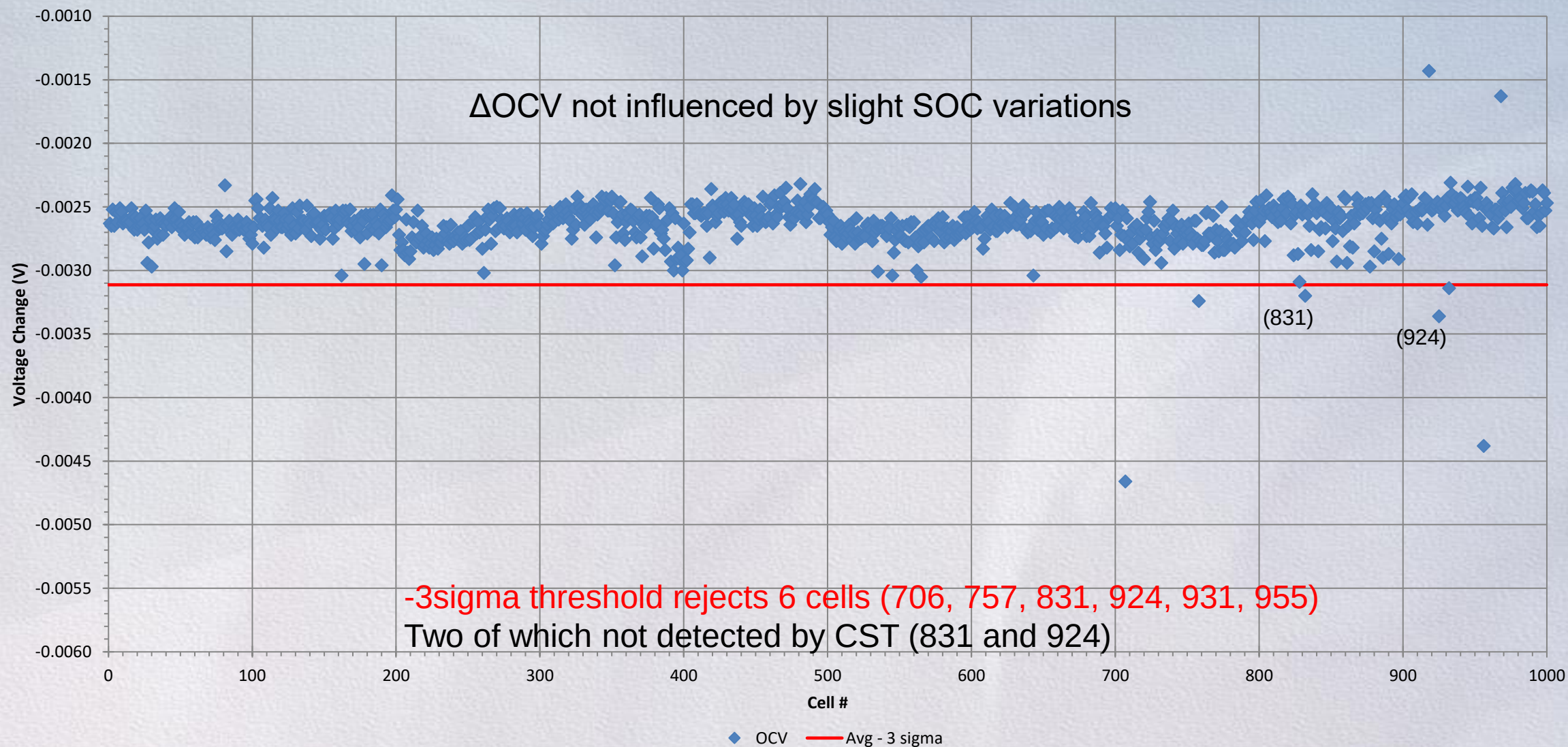
CST Grades on same 1000 M35A Cells

Moli M35A Cells; Raw CST Grades

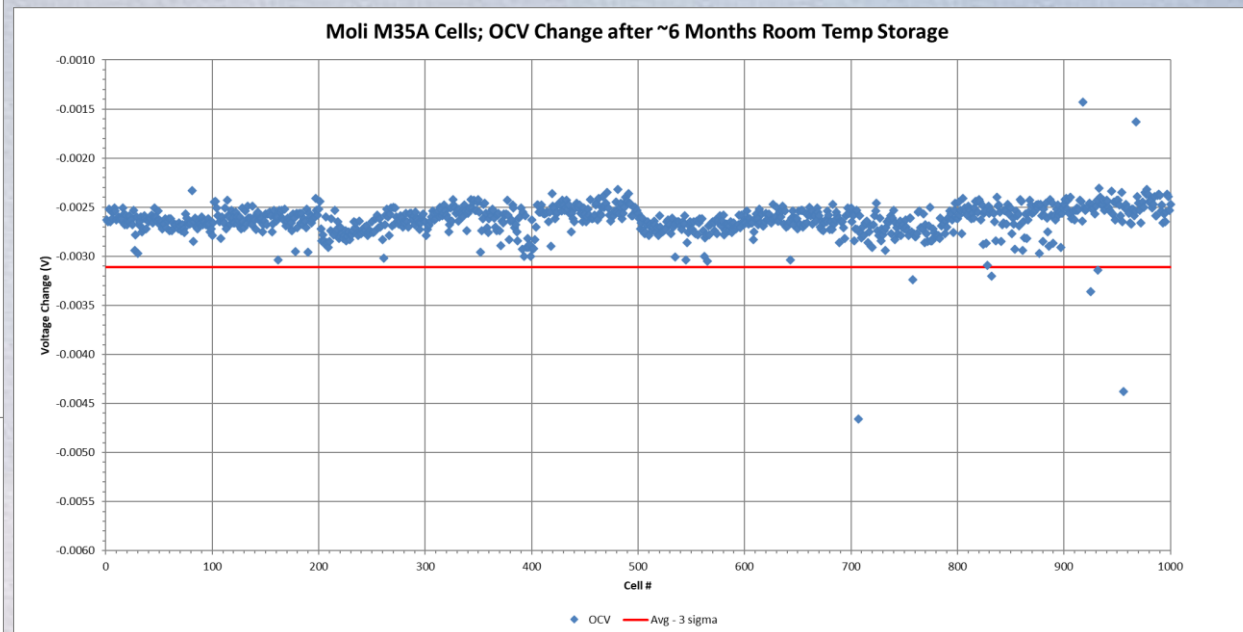
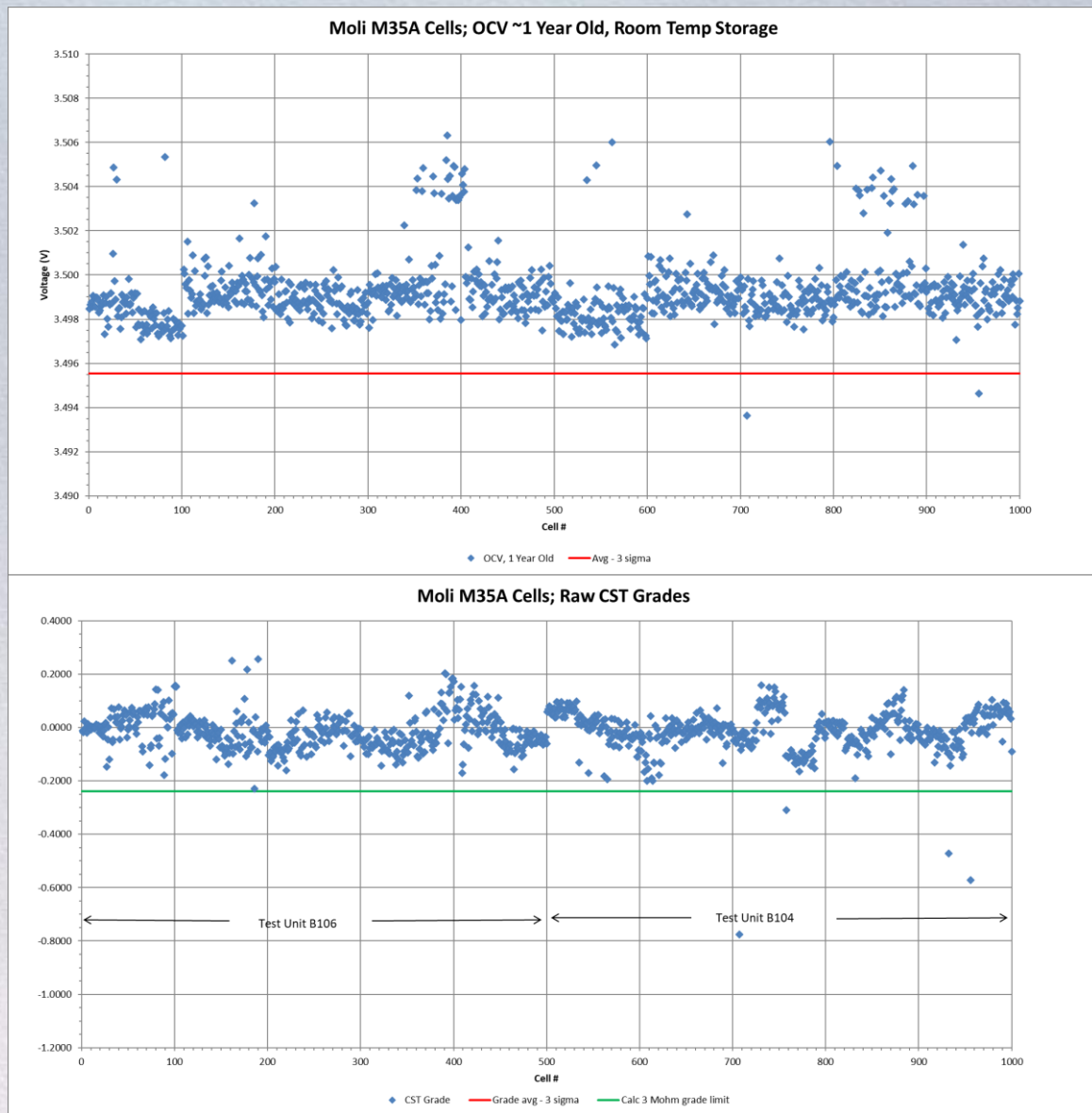


6-month Δ OCV on same M35A Cells

Moli M35A Cells; OCV Change after ~6 Months Room Temp Storage



M35A 1yr OCV vs CST Grades vs 4-month Δ OCV



Δ OCV after 6 months rejects 6 cells

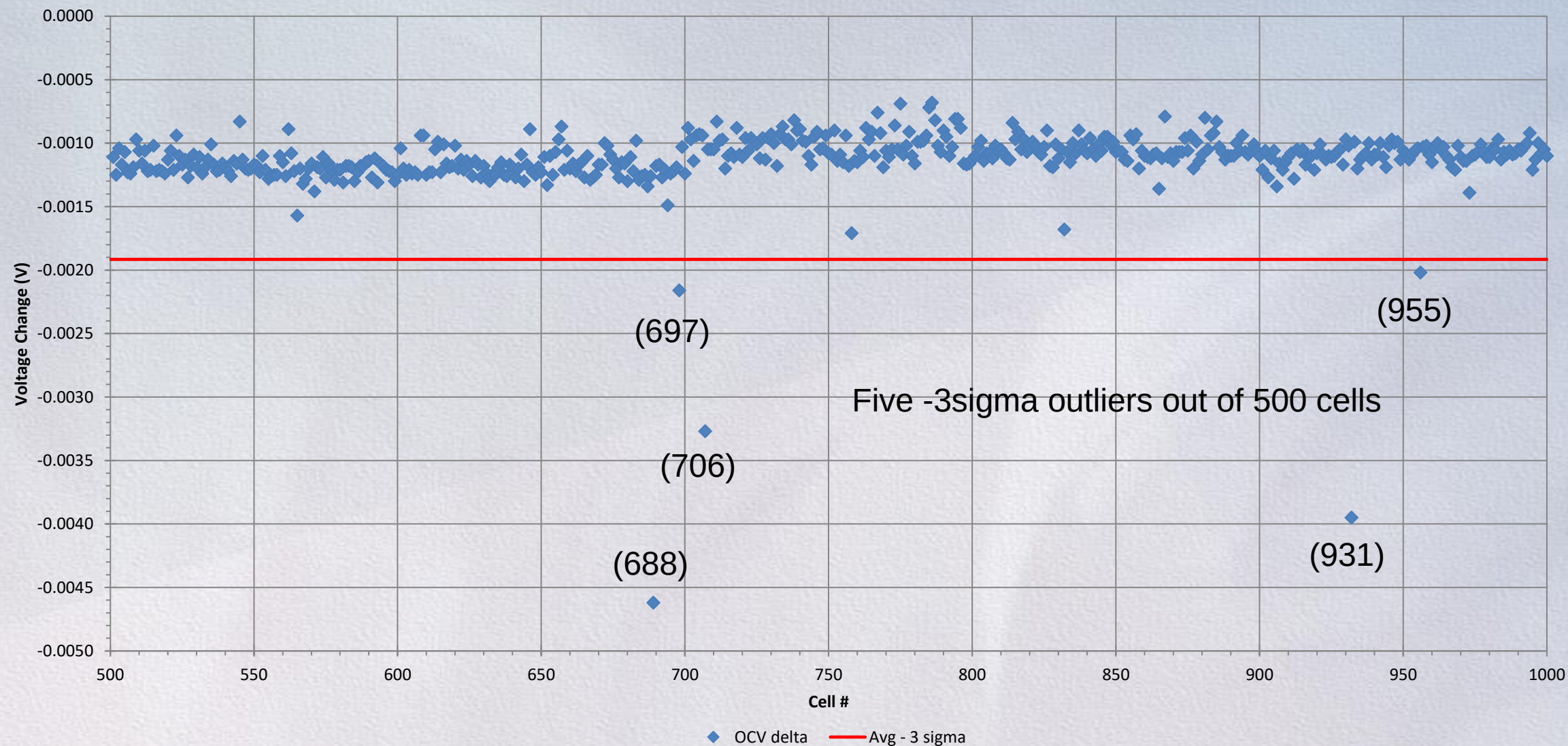
- Including 2 rejected by wait 1-yr OCV method
- Including 4 rejected by CST grading

Δ OCV after 6 months is more discriminatory in this case

- Picks out two more subtle outlier cells

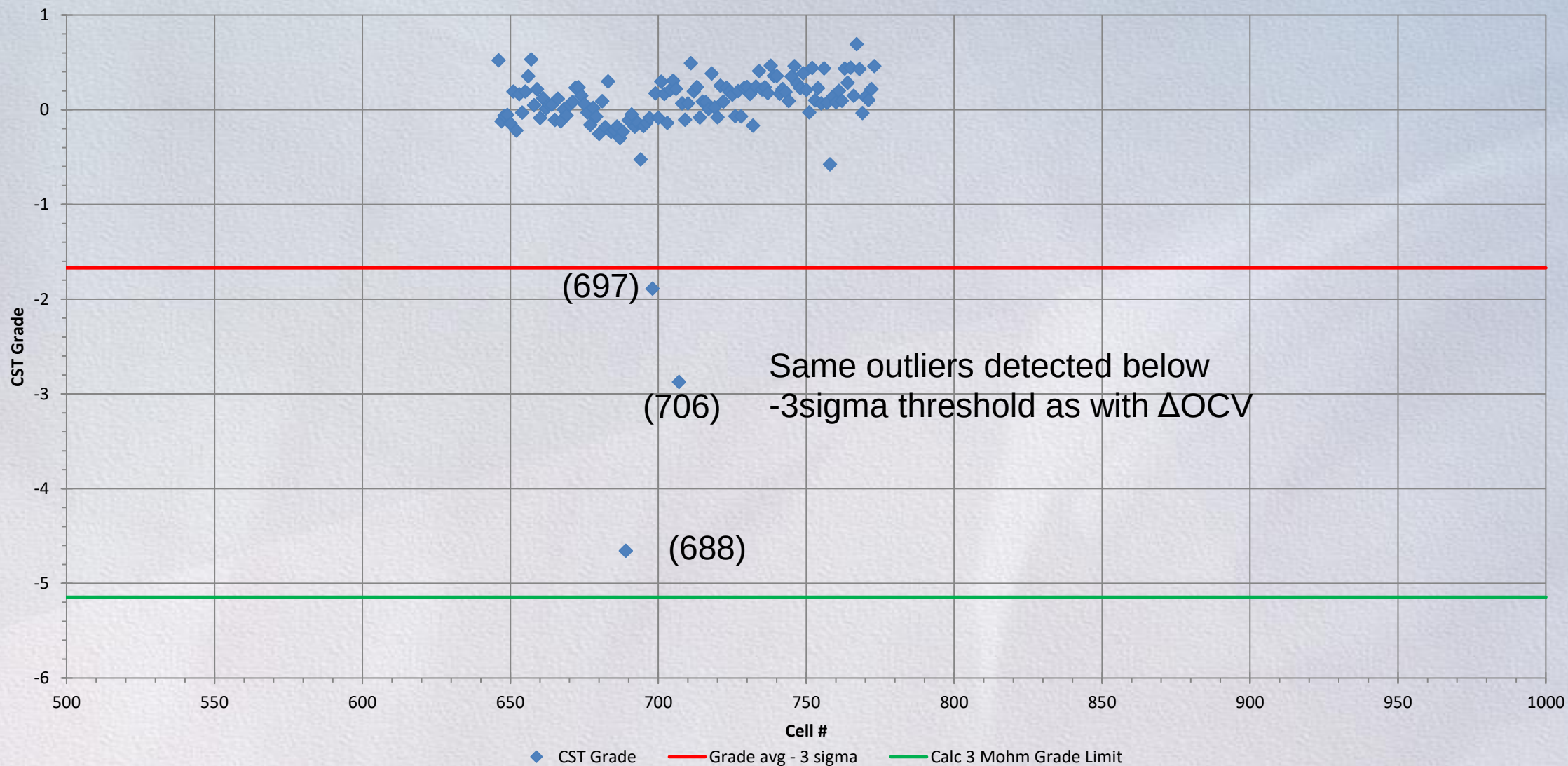
500 Moli M35A Cells at 0% SOC by ΔOCV

M35A Cells; OCV Change Months 2 to 3 After Discharge



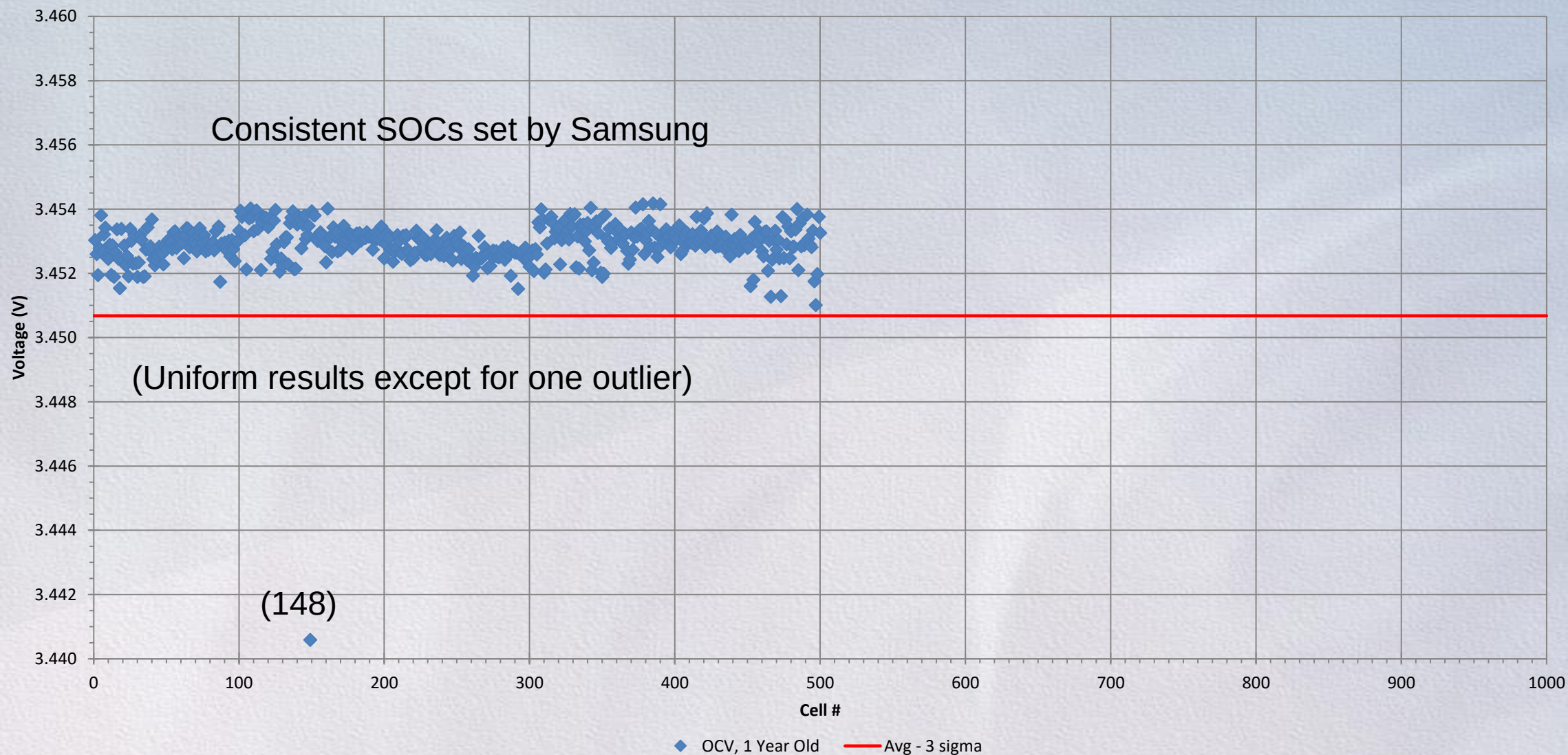
CST Grading 128 Moli M35A Cells at 0% SOC

M35A Cells; Raw CST Grades; 3 months after discharge

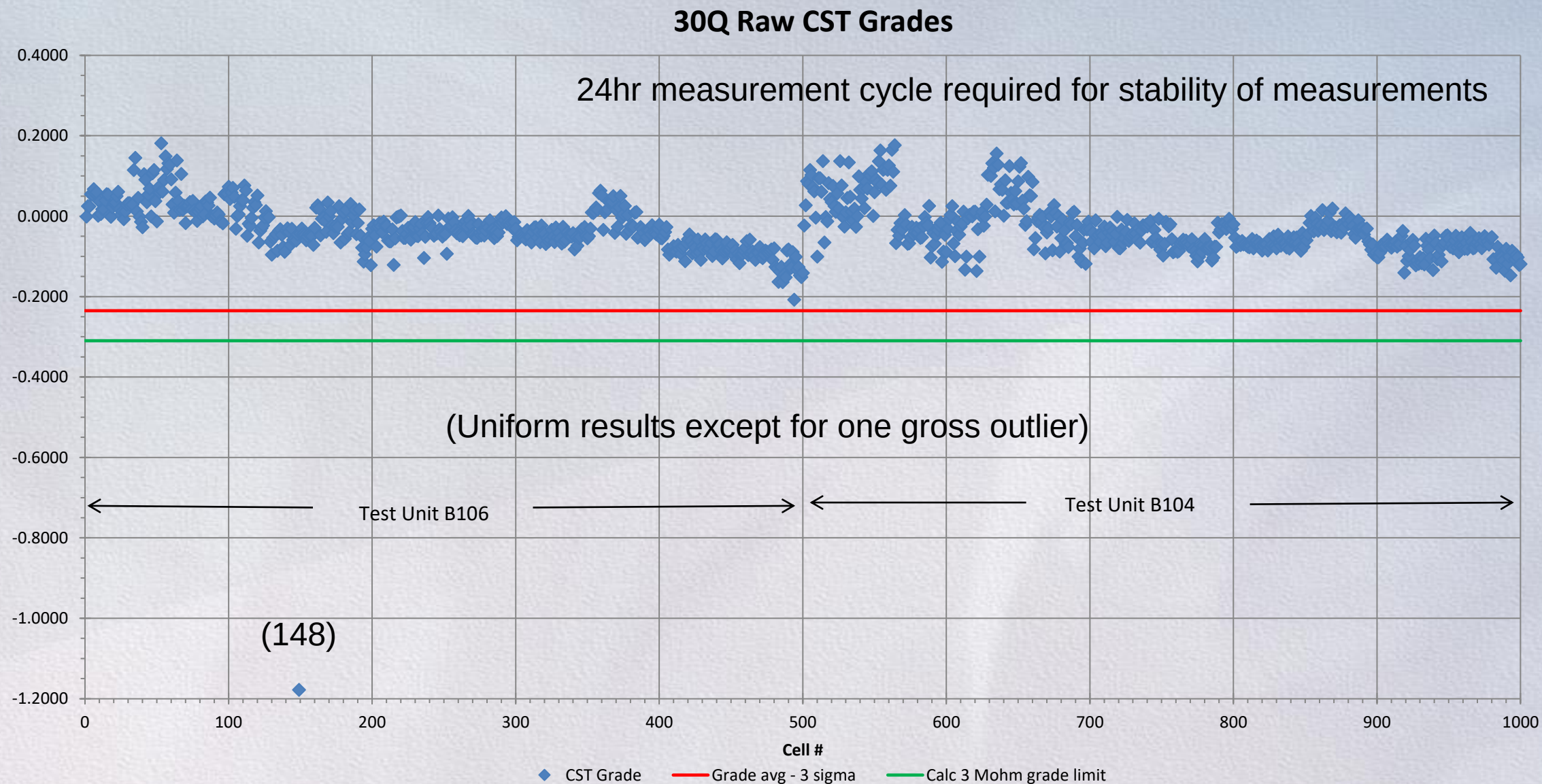


500 Samsung 30Q Cells > 1-year past BOD

Samsung 30Q Cells; OCV ~1 Year Old, Room Temp Storage

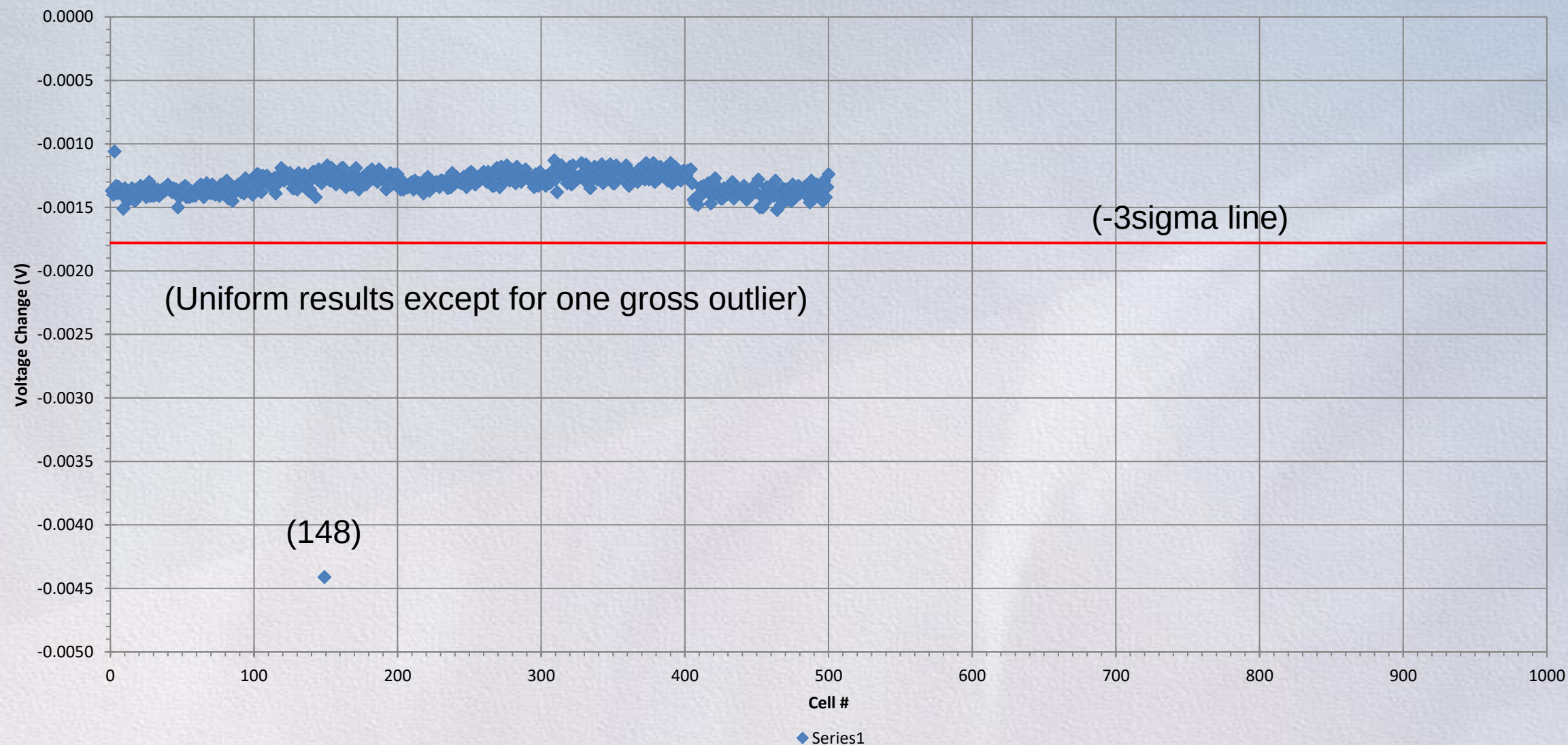


1000 Samsung 30Q CST Grades



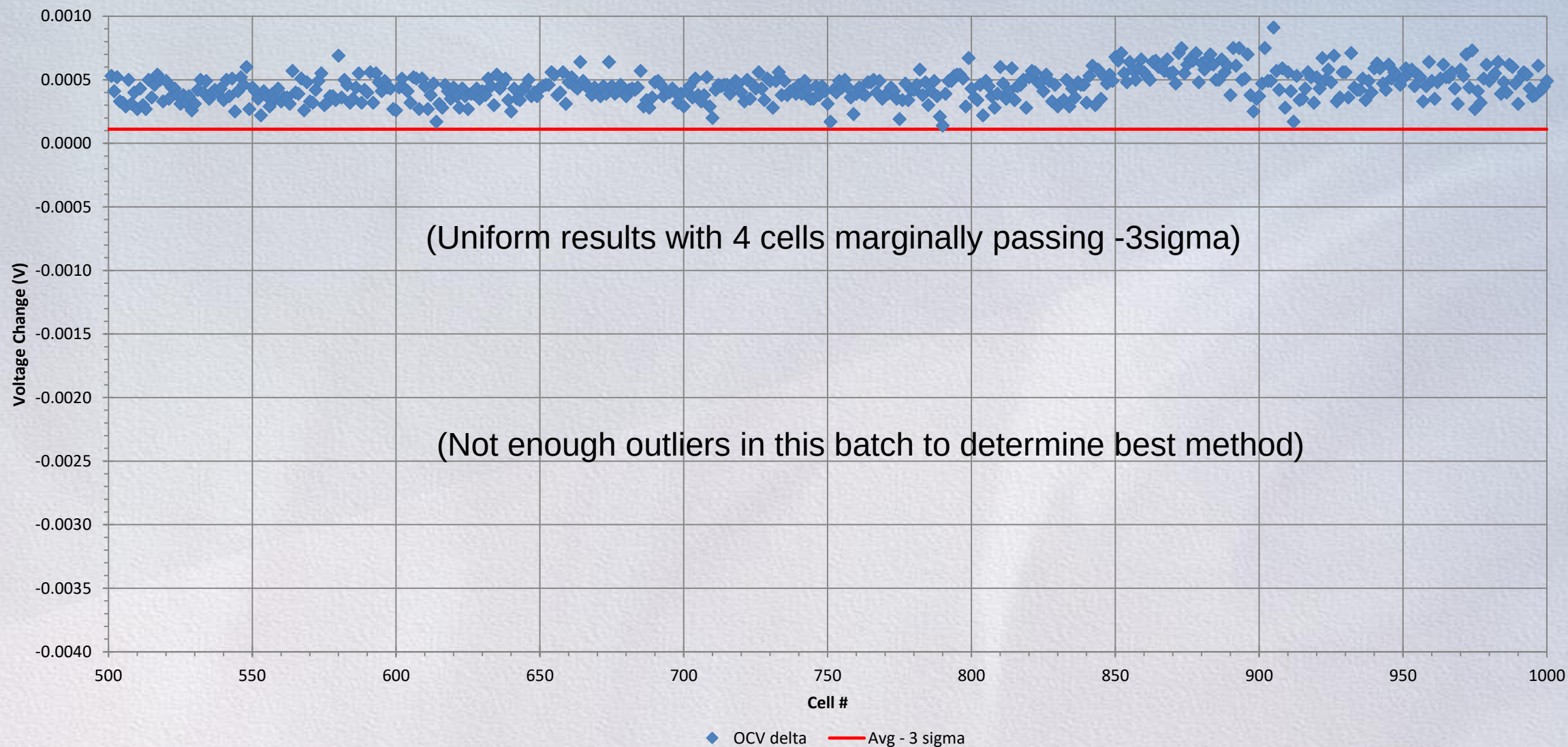
500 Samsung 30Q by Δ OCV at 30% SOC

Samsung 30Q Cells; OCV Change after ~3.5 Months Room Temp Storage



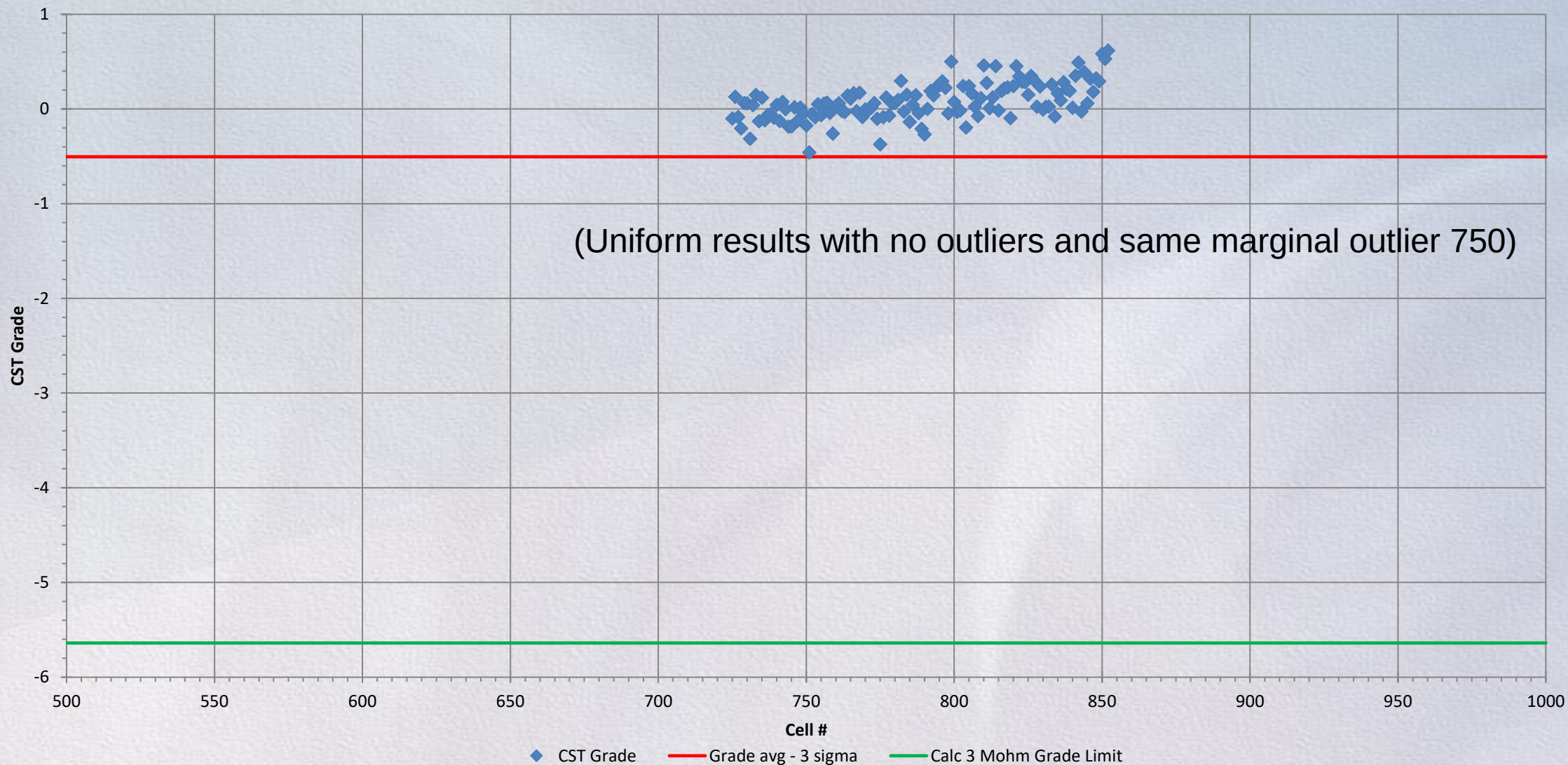
500 Samsung 30Q Cells by Δ OCV at 0% SOC

30Q Cells; OCV Change Months 2 to 3 After Discharge

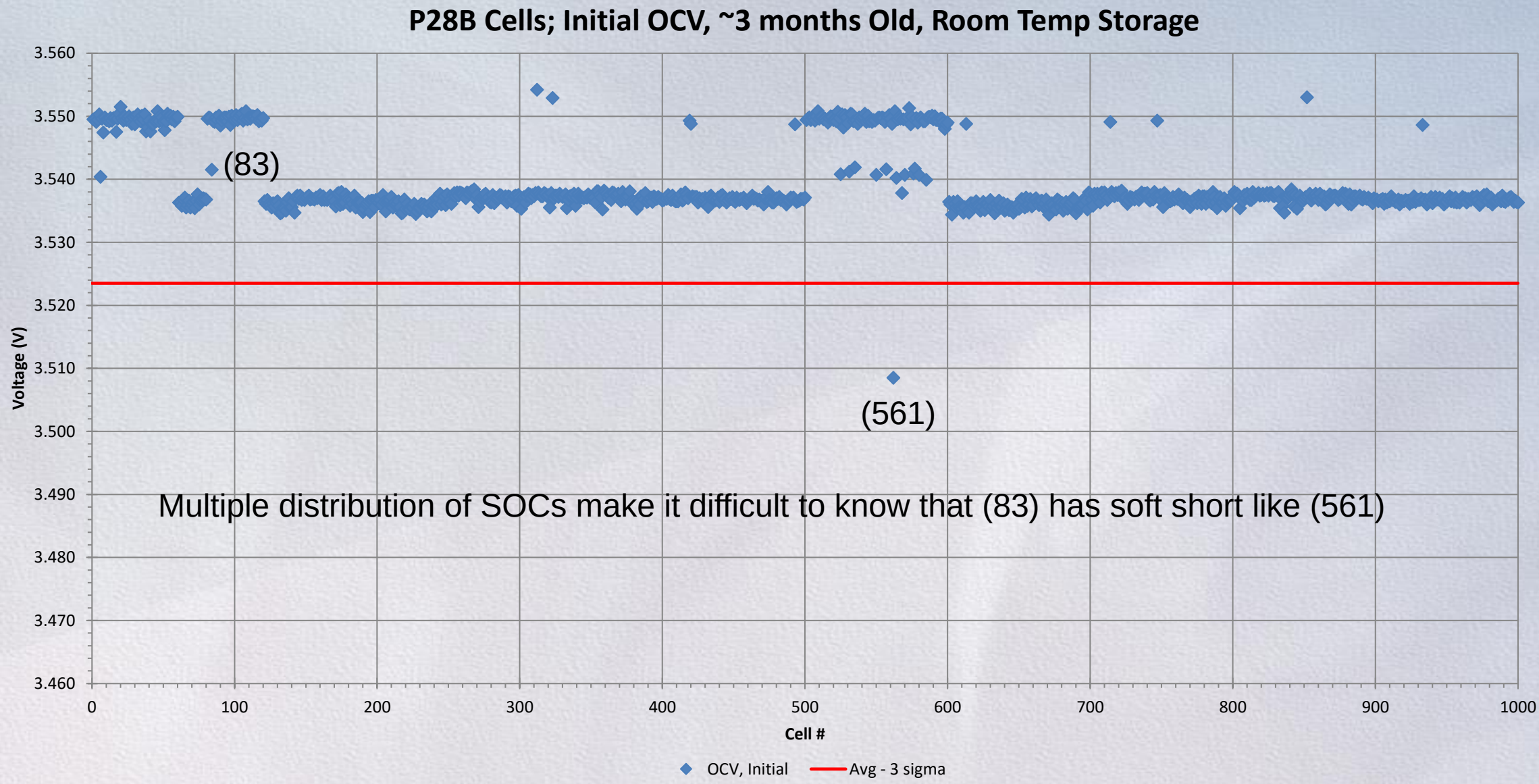


CST Grades of 128 30Q Cells at 0% SOC

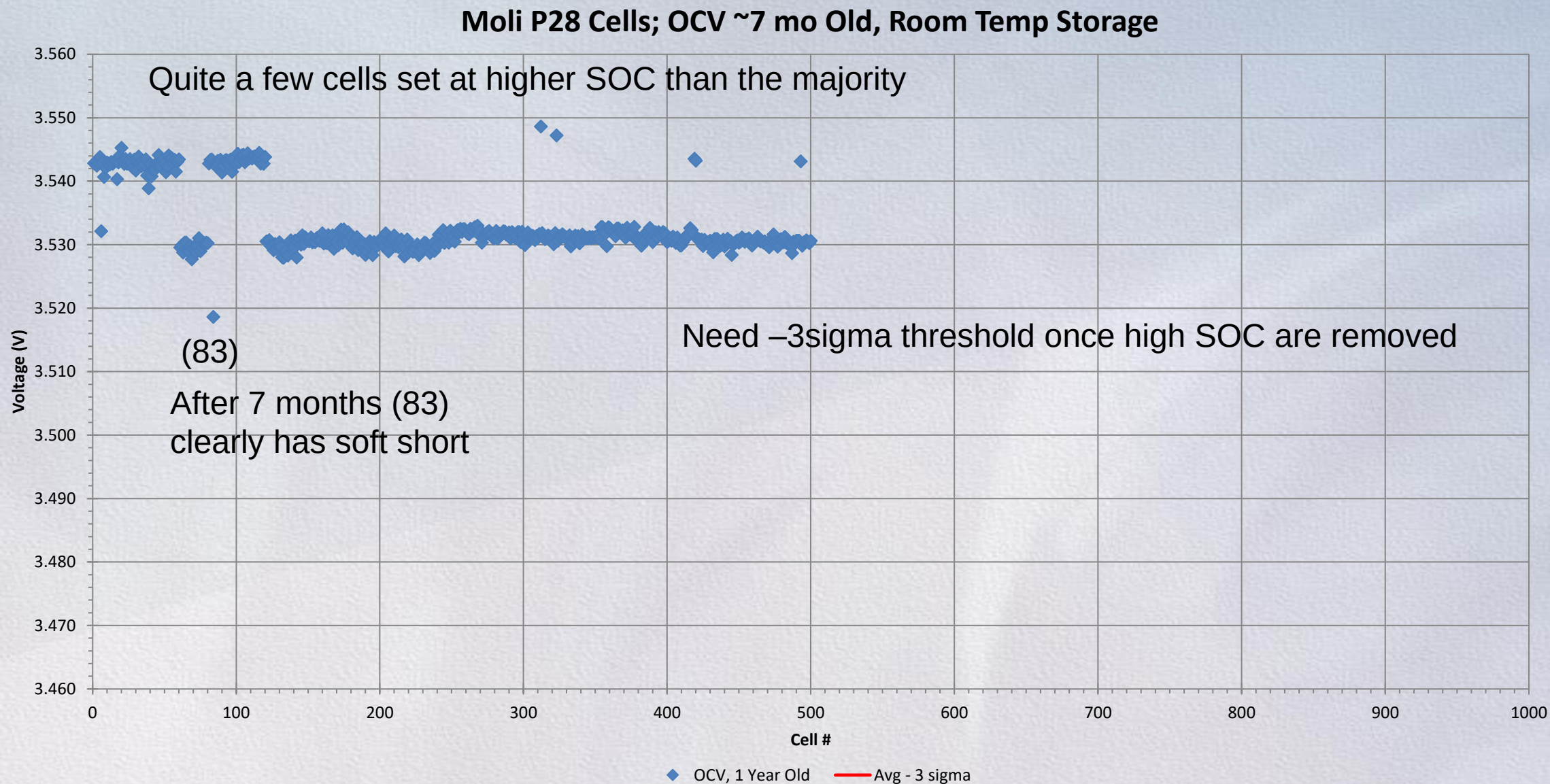
Samsung 30Q Cells; Raw CST Grades; 3 months after discharge



1000 Moli P28B Cells OCVs at 30% SOC and 3 months³²

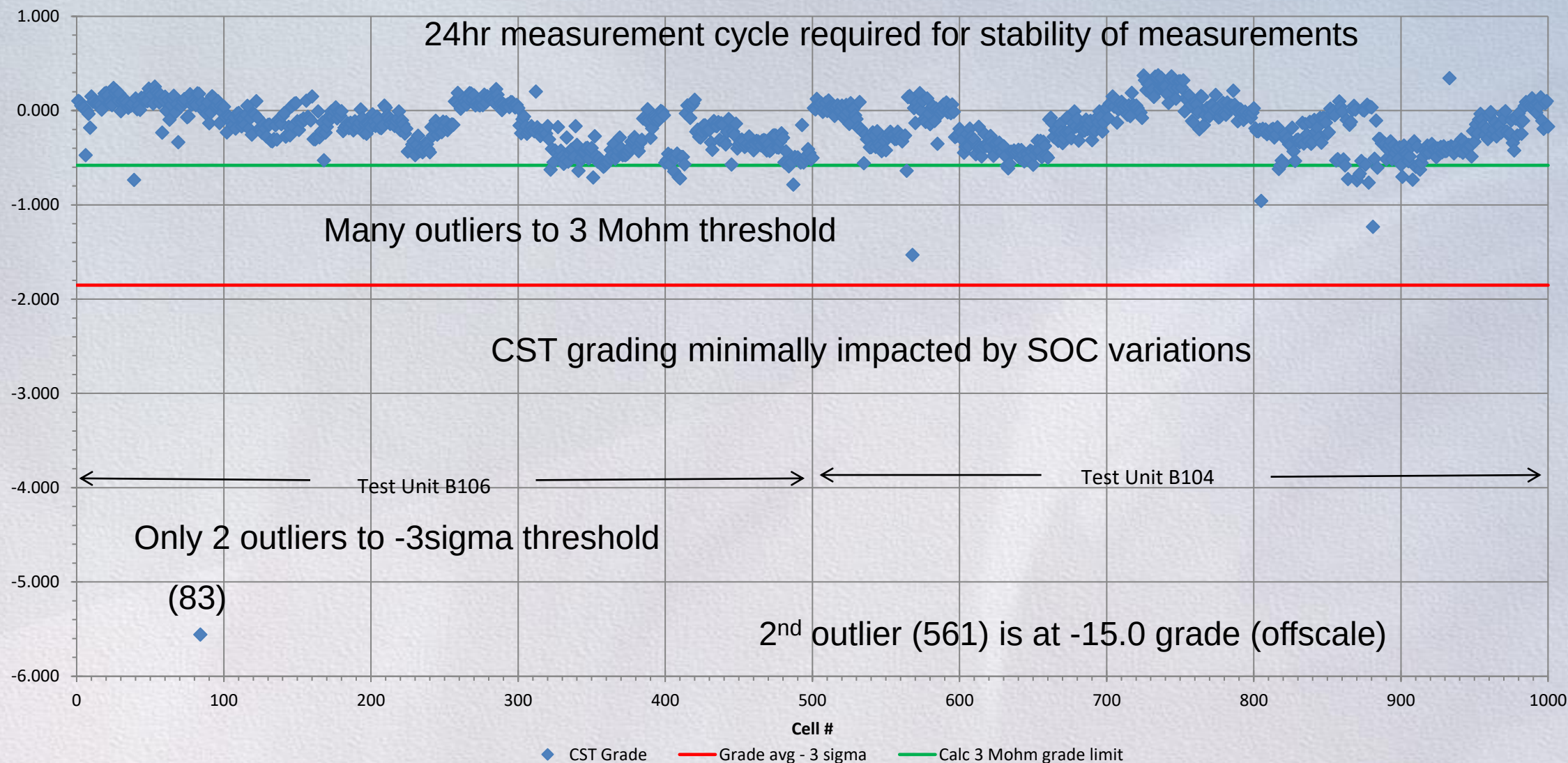


500 Moli P28B with OCVs 7-month past BOD



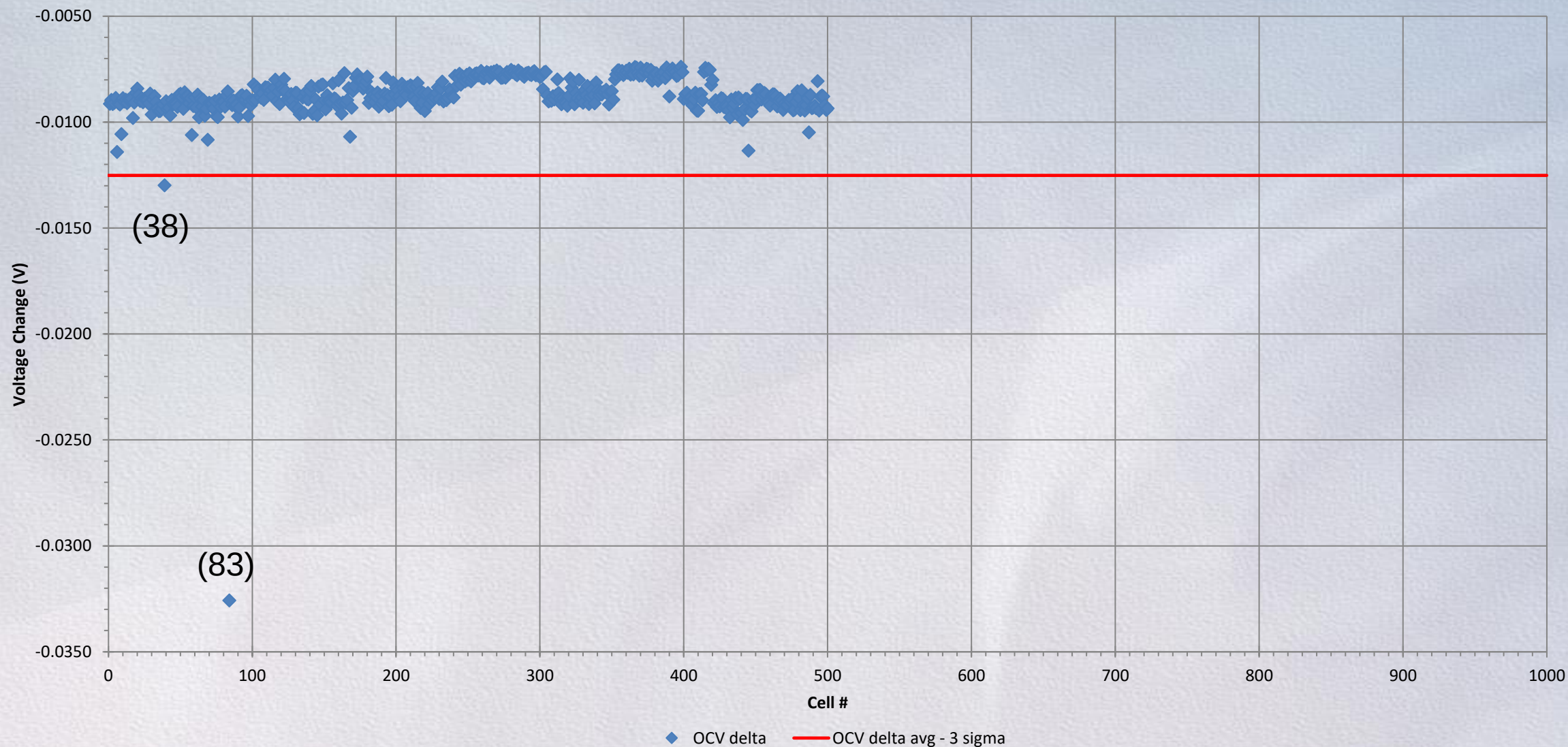
CST Grades on 1000 P28B Cells at 30% SOC

Moli P28B Cells; Raw CST Grades



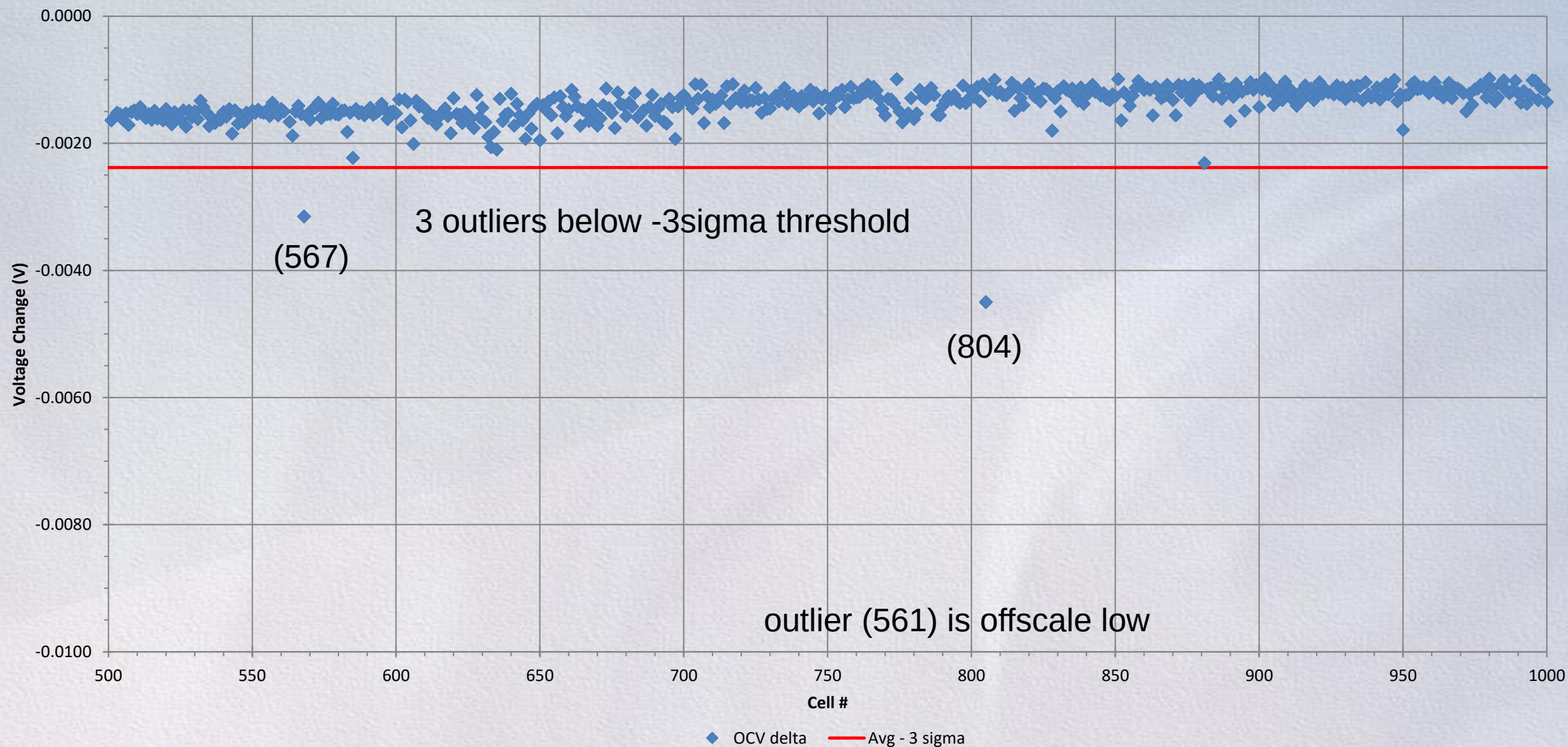
500 Moli P28B Cells with Δ OCV at 30% SOC

Moli P28B Cells; OCV Change after ~6 Months Room Temp Storage



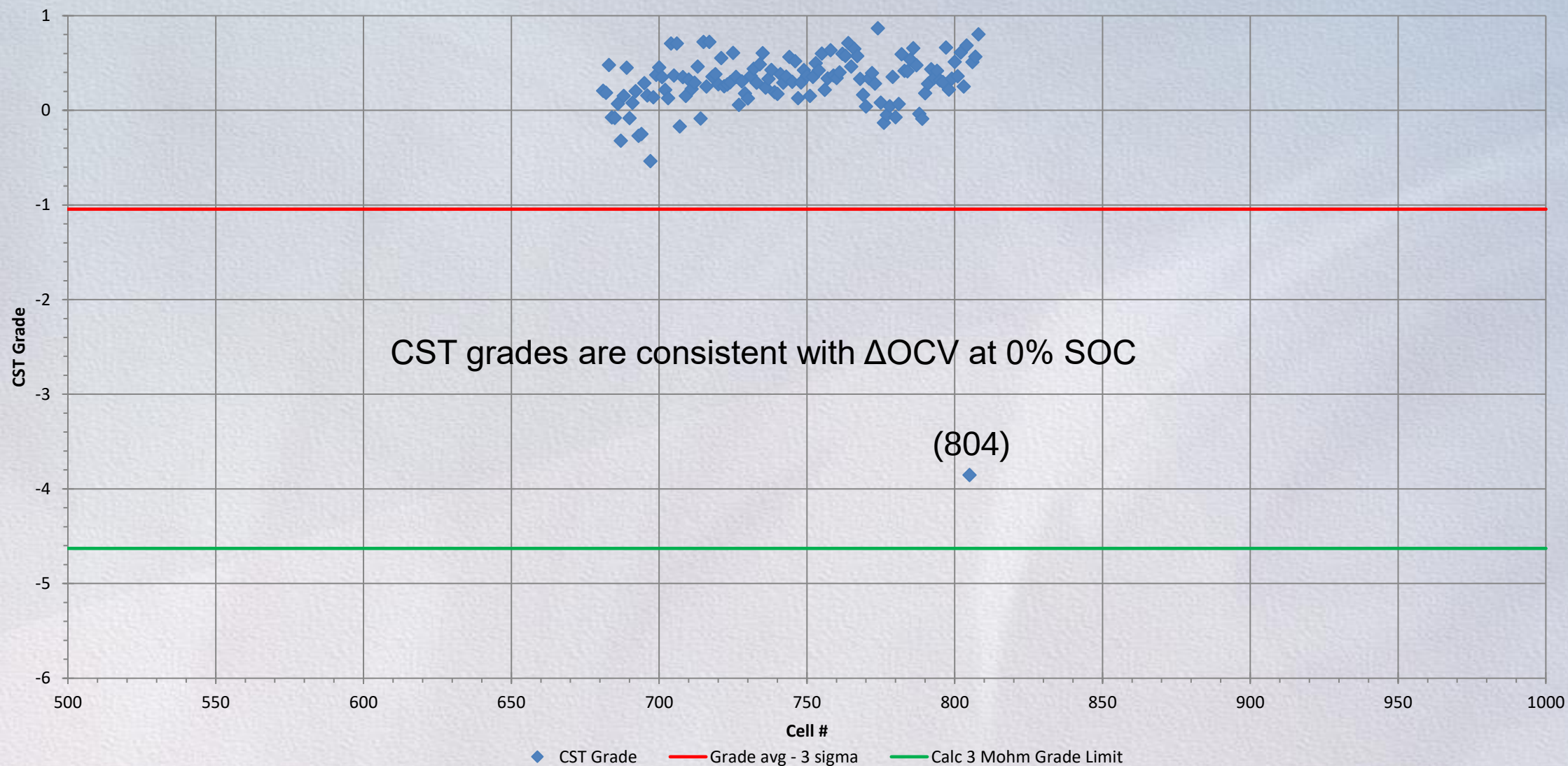
500 P28B Cells with ΔOCV at 0% SOC

Moli P28B Cells; OCV Change Months 2 to 3 After Discharge



129 Moli P28B Cells Graded by CST at 0% SOC

P28B Cells; Raw CST Grades; 3 months after discharge



Findings to Date

- The wait 1-year at as received SOC can't be used with even slight multimodal SOC distributions set by the manufacturer **and is least discriminatory** with M36, M35A, and P28B
- CAMX CST grading is not influenced by slight SOC variations
- CAMX CST grading of comparative self-discharge values **is most discriminatory** for LG M36
- Δ OCV over 4 months at as received SOC is more discriminatory for the Moli M35A and P28B design than CST grading or wait 1-year
 - Better yet, 5 of 500 cells (1%) detected with Δ OCV at 0% SOC for M35A
- Δ OCV at 0% SOC has to be measured between 2 and 3 months to remove bounce back bias and requires the most steps
- CAMX CST grading shows promise for speedy and discriminatory detection of subtle soft shorts and deserves more maturation testing with many more cells
 - Some cell designs require more equilibration time (~1 week) prior to valid scans to remove charge/discharge settling bias and temperature induced changes to electrode potentials

Method	M36	M35A	30Q	P28B
OCV > 1 yr BOD at 30% SOC	0.10%	0.20%	0.20%	0.20%
CST grading at 30% SOC	1.00%	0.40%	0.10%	0.20%
Δ OCV at 30%, 3.5-6 months	0.30%	0.60%	0.20%	0.40%
Δ OCV at 0%, 2 vs 3 months	0.40%	1.00%	0.00%	0.30%