The Effect of Teflon Emulsion on Hydrogen Electrode Properties and Performance in Nickel-Hydrogen Cells

Margot Wasz, Ph.D. and Albert Zimmerman, Ph.D.

Mail Stop M2-275
Energy Technology Dept./The Aerospace Corporation
P.O. Box 92957
Los Angeles, CA 90009-2957
Margot.L.Wasz@aero.org

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Concern

- T30, the Teflon emulsion used in the manufacture of hydrogen electrodes used in nickel-hydrogen cells, will soon no longer be available
  - PFOA (perfluorooctanoic acid) and Triton X-100 surfactant is being phased out in North America and Europe due to environmental concerns
  - T30, an aqueous solution of Teflon containing both of these compounds, was removed from the commercial market in 2007
  - Teflon emulsions have a short shelf life due to Teflon particle settling and coagulation

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Approach

- Establish a better understanding of the links between the properties of the Teflon emulsion, hydrogen electrode and cell performance
  - Materials characterization
  - Electrode characterization
  - Cell performance
- Put in place tools and methods of evaluation for more quickly evaluating candidate replacement emulsions when T30 is no longer available
  - TE3859, now in-use commercially as a replacement for T30, is expected to be removed from production by 2013 due to further restrictions on the use of PFOA during manufacturing

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Historical Development of the Hydrogen Electrode

- Hydrogen electrodes composed of Teflon were developed for alkaline fuel cells in the 1960s
- When nickel-hydrogen cells were proposed as an alternative to nickel-cadmium cells for satellites, the same hydrogen electrode was tested and implemented
- Hydrogen electrode composition
  - Nickel screen current collector
  - GoreTex membrane on backside to retard water loss
  - Pt/Teflon active material to reversibly catalyze the conversion of water to hydroxide and hydrogen
- Hydrogen electrode processing parameters were optimized to provide the best performance in fuel cells

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Operation of the Hydrogen Electrode

- Charge

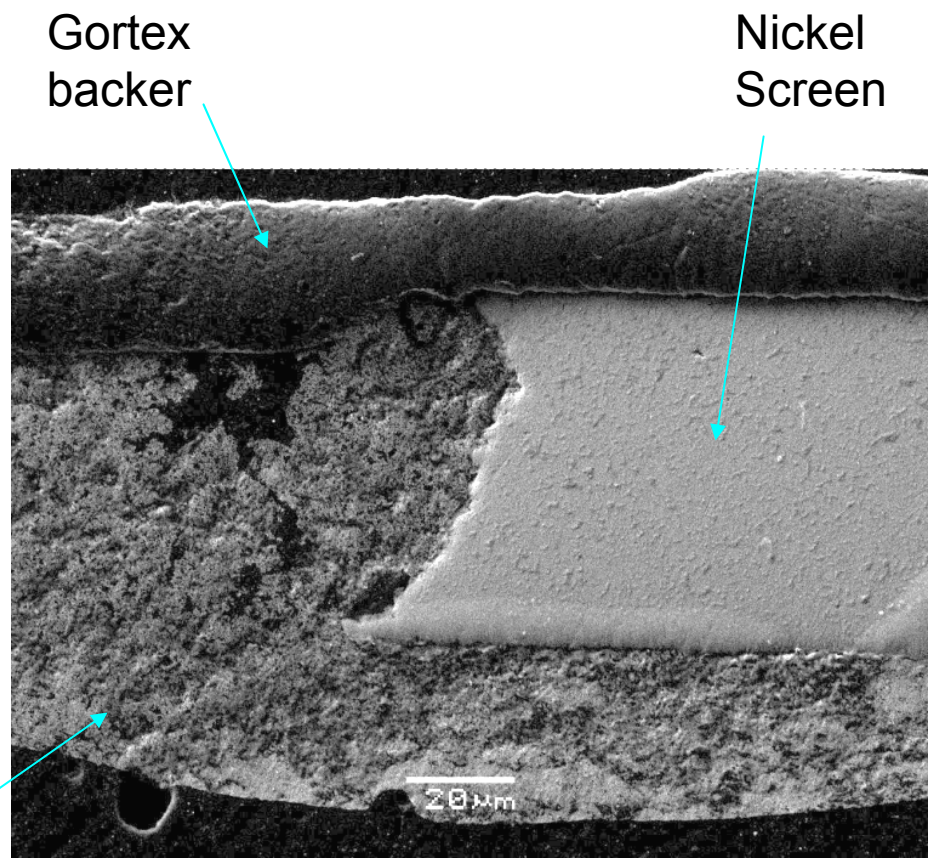
  $H_2O + e^- \rightarrow \frac{1}{2} H_2 + (OH)^-$
- Overcharge

  $2H_2O + 2e^- \rightarrow 2(OH)^- + H_2$
- Discharge

  $\frac{1}{2} H_2 + (OH)^- \rightarrow H_2O + e^-$
- Reversal (positive precharge)

  $2(OH)^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^-$
- Reversal (negative precharge)

  $\frac{1}{2} H_2 + (OH)^- \rightarrow e^- + H_2O$



SEM of the cross-section of a hydrogen electrode

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Reported Failure Modes Associated with Hydrogen Electrodes

- Alkaline Fuel Cell Applications
  - Excessive hydrophilic nature – flooding
  - Excessive hydrophobic nature – insufficient wetting
  - Flooding due to water vapor accumulation
    - More commonly a concern at higher temperatures
  - Recrystallization of Pt particles over life
    - Lowers reactivity and catalyst surface area
  - Oxidation and dissolution of platinum
  - Carbon dioxide poisoning - usually from impure reactant gases
  - Silicate build-up from asbestos wicks
- Battery Applications
  - Shorting due to Pt particle dislocation

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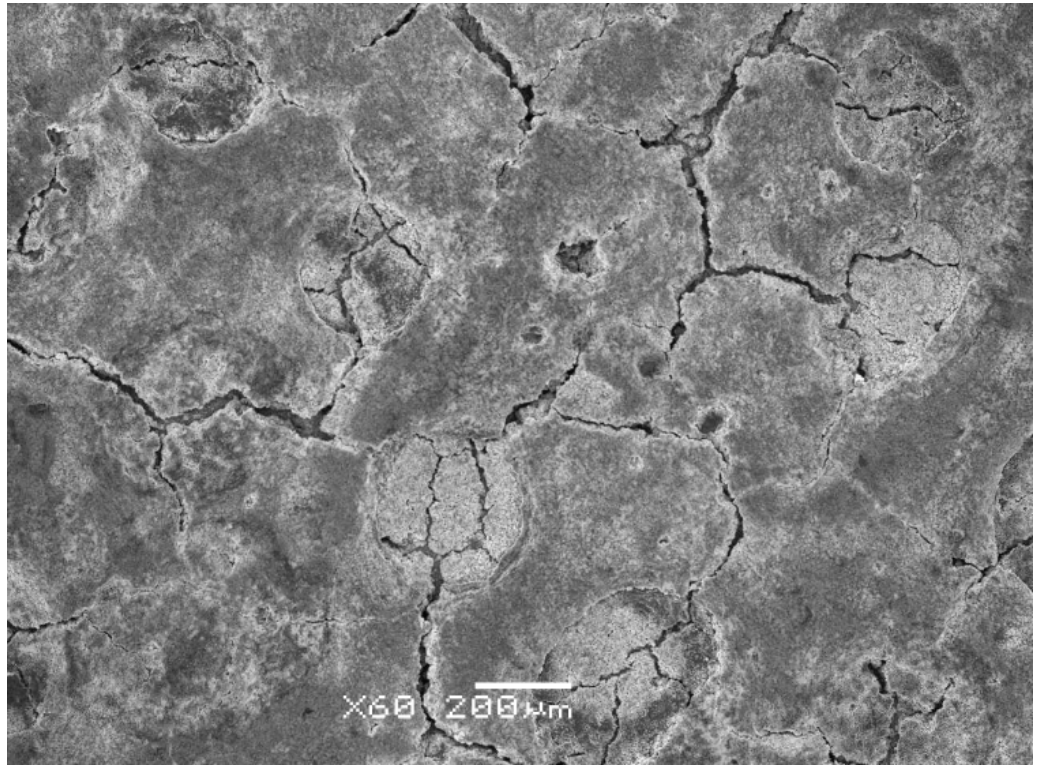
Structure of the Hydrogen Electrode

- Materials Parameters of Interest
  - Conductivity
  - Surface Area
  - Pore size distribution
  - Density
  - KOH retention
  - Gas permeability
  - Cracking
  - Adhesion of the active material
  - Phase distribution of Pt and Teflon



SEM Image of the top surface of a hydrogen electrode

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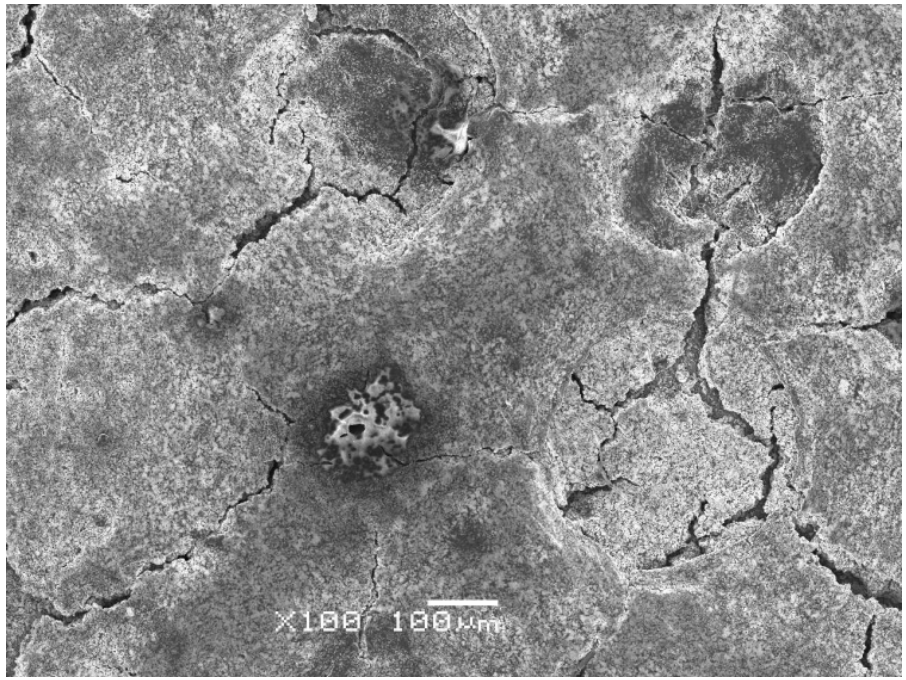
Processing Variables of Interest

- Mechanism for creating pores and surface area considered important for electrode performance…
  - Impact of the surfactant type
  - Impact of sintering temperature
  - Impact of other processing variables such as cooling rates, pressure levels, slurry composition
- ….however, how much change can be accommodated without affecting performance or life is not known



SEM Image of the top surface of a hydrogen electrode with residue left in surface crater

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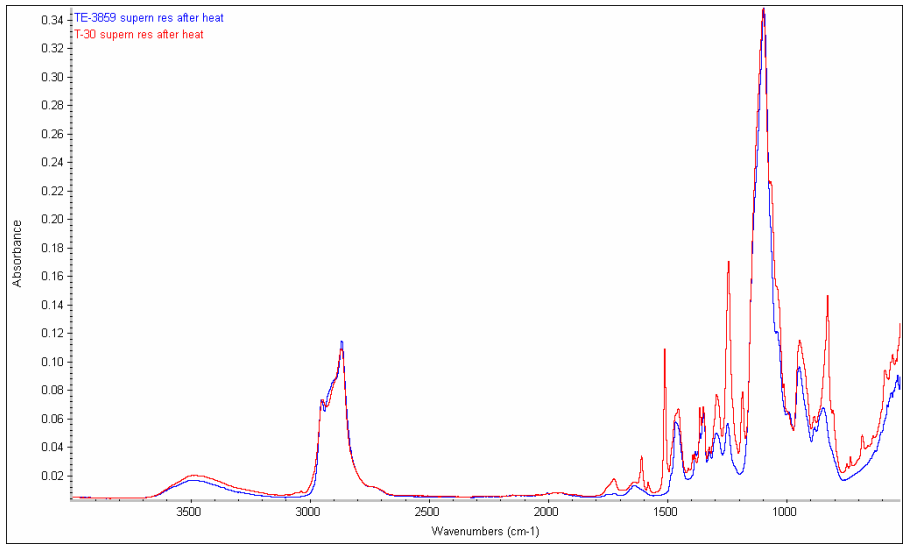
Comparison of T30 with TE3859 Replacement Emulsions

- Analysis of Trace Components
  - FTIR analysis confirmed thatT-30 contained volatiles consisting of phenol ethoxylates; octyl, nonyl and decyl phenol ethoxylates
  - FTIR analysis confirmed that TE3859 contained polyethylene glycol monomethyl ether
- Different volatility of new surfactants on likely to affect final surface area and pore size distribution for the same sintering temperatures
- Effect of different class of surfactants on electrode life is unknown
  - Ability to wash residues from electrodes also unknown



FT-IR spectra of the T-30 and TE-3859 residues of the centrifuged supernatant heated to 120°C

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Plate Characterization for T30 and TE3958 Electrodes

- In 2006, Aerospace sampled 24 electrode plates, 50% produced with T30 and 50% produced with TE3859.
- Tests included:
  - Density, thickness
  - Adhesion, surface appearance
  - KOH wettability, gas permeability, bubble pressure
  - Pt solubility, hot KOH exposure
  - Inorganic and organic contaminants
  - SEM analysis for pore, Pt particle, Teflon distribution, and cracking characteristics
  - Oxygen and hydrogen overpotential measurements

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Results of Plate Characterization for T30 and TE3958

- TE3859 electrodes were thinner and more dense, less wettable with KOH and had smoother surface
  - 20 – 50% less KOH held within pores
  - Less internal pore and void volume
  - Loss of much of the larger pores compared to T30 electrodes
  - Loss of much of the macroscopic cracking compared to T30 electrodes
  - Slightly more organic contaminates
- Slightly poorer Pt catalyst adhesion in TE3859 electrodes
  - Adhesion degraded slightly more by hot KOH exposure
- Small changes in averaged charge and discharge voltages
  - Higher H_2 evolution (recharge) voltage for TE-3859 (about 10mV at C/2)
  - Similar H_2 recombination (discharge) voltages
  - Lower O_2 recombination potential for TE-3859 (about 20mV at C/2)
  - Higher O_2 evolution potential for TE-3859 (about 10mV at C/2)

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Impact of Normal Processing Variables

- Difficult to interpret electrode test results because the normal variation of these parameters for T30 were unknown
  - Aerospace then studied 10 samples each of T30 and TE3859 electrodes where the post-sintering cool-down was varied between the allowable minimum and maximum rates
- Tests performed included:
  - Density, thickness, adhesion to substrate, surface appearance
  - KOH wettability and gas permeability
- Results found:
  - Cooling rate affected electrode density and active material adhesion
  - Range found overlapped the range seen in the prior T30 & TE3859 tests
  - Gas permeability affected by degree of compression of the Gortex layer

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Cell Testing with T30 and TE3859

- Four 90Ah cells received from EP for evaluation
  - RNH90, double zircar separator, wall wick, 31% KOH, and strain gages
  - Two made with T30 (cells 1, 4) and two with TE3859 (cells 2 & 3)
- Capacity measured at -10, 0, 10°C
  - Charge at C/10 (9A) for 16 hours followed by a C/2 (45A) discharge to 1.0V
- Voltages were slightly higher in TE3859 cells during charge and discharge

	T30 (Cell 1)	**T30 (Cell 4)**	**TE3859 (Cell 2)**	**TE3859 (Cell 3)**
Capacity (Ah)				
-10°C	104.2	105.5	105.4	104.8
0°C	106.8	107.0	107.3	107.5
10°C	98.3	97.9	98.4	98.4
EOC Voltage				
-10°C	1.604	1.603	1.606	1.605
0°C	1.561	1.560	1.561	1.562
10°C	1.519	1.519	1.520	1.520

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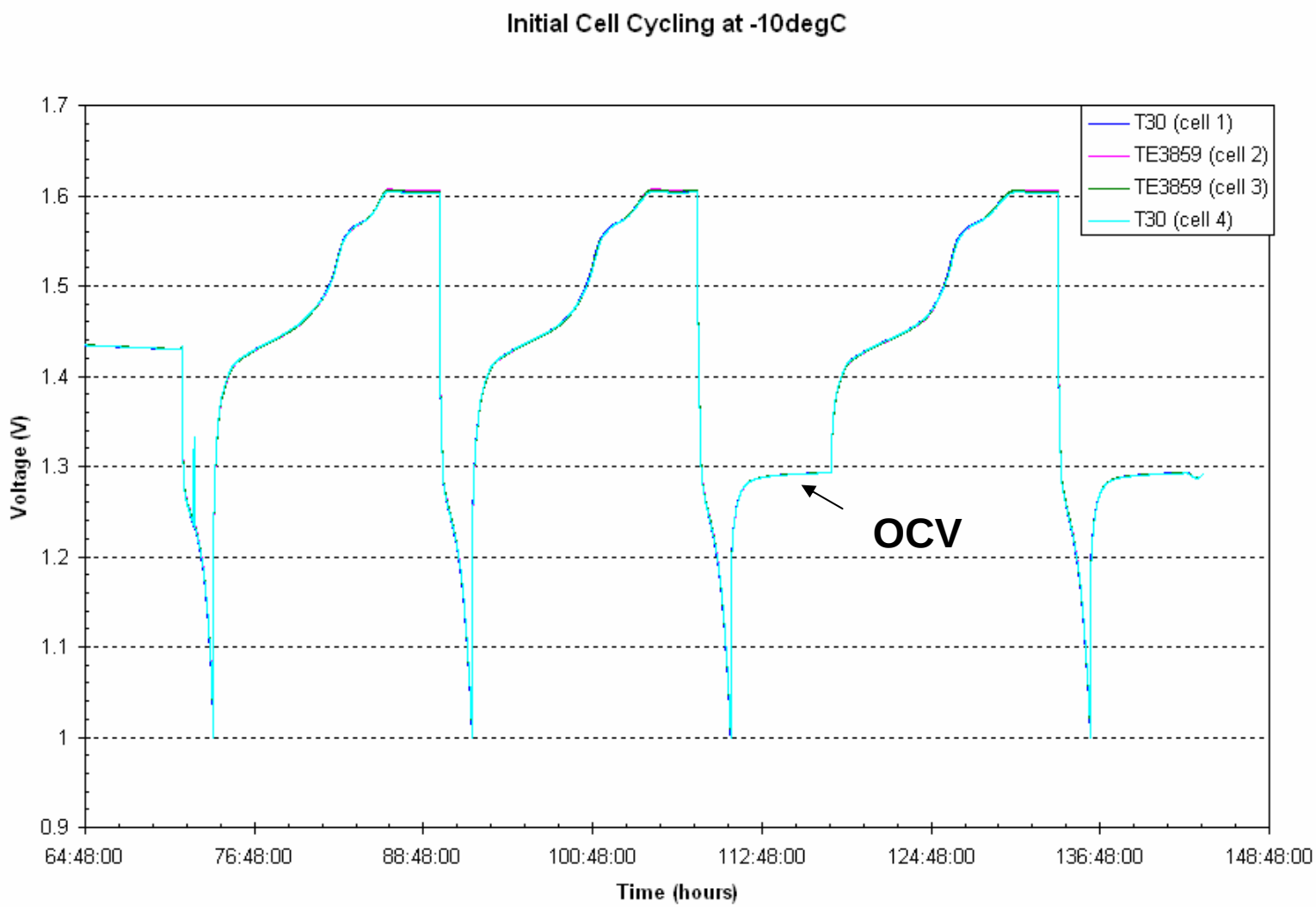
Initial Capacity Cycling of Four Cells at -10°C: Voltage



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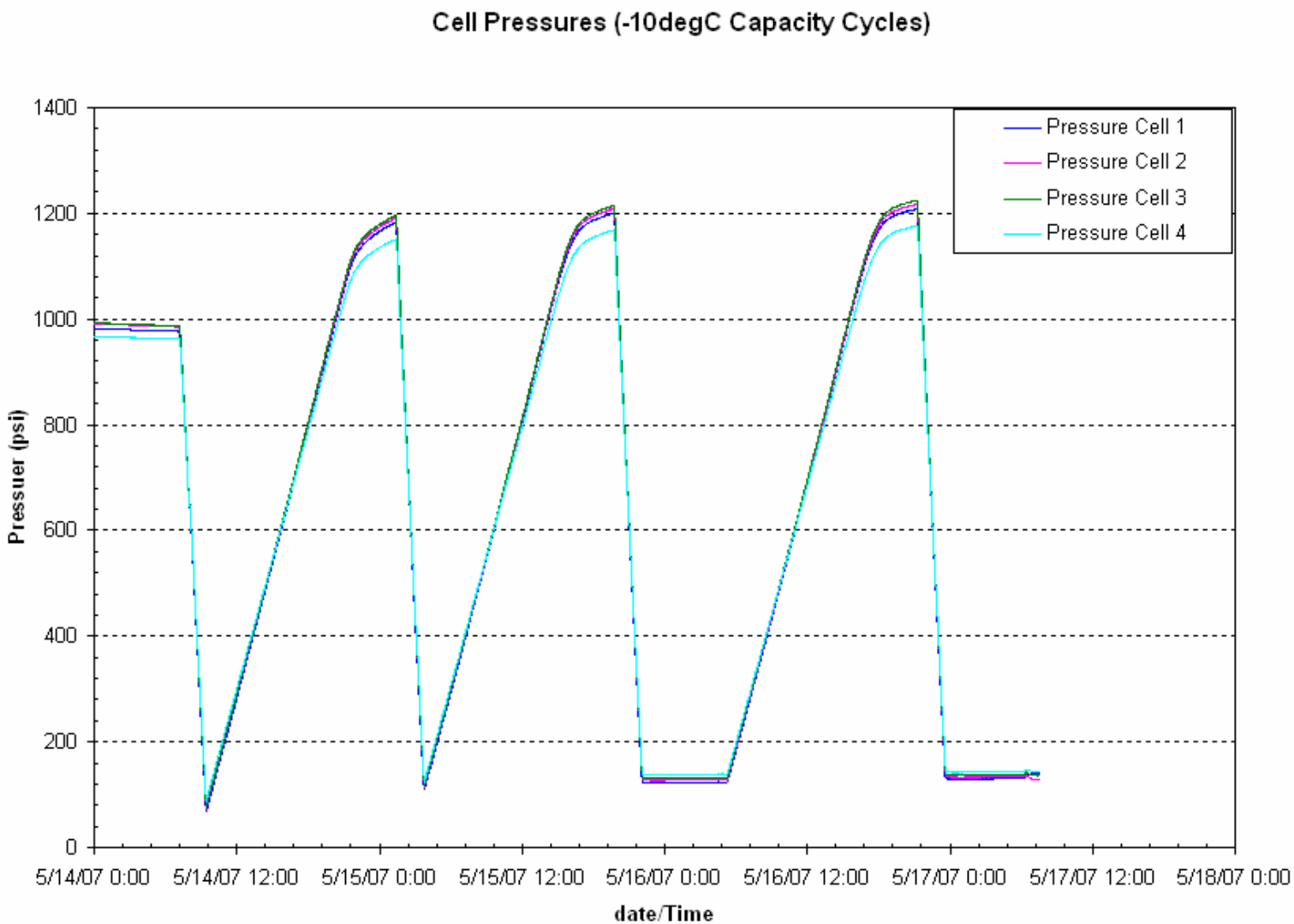
Initial Capacity Cycling of Four Cells at -10°C: Pressure



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Cell-Level Testing of Cells made with T30 and TE3859

- Problem: How to test NiH_2 cells to best compare the capability of the different hydrogen electrodes?
  - The nickel electrode is usually the life-limiting electrode when cycling NiH_2 cells
- Typically, life tests and stress tests defined for NiH_2 cells are designed to stress the nickel electrode
  - Higher depth of discharge
  - Increased temperature
  - Increased amount or rate of overcharge
  - Increased frequency of cycles (throughput)
- Stress factors appropriate to the H_2 electrode were proposed
  - Increased rates for charge and discharge
  - Reduced temperatures to evaluate liquid and gas transport processes
  - Overcharge to evaluate O_2 recombination tolerance

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Hydrogen Electrode Stress Test Cycle

- Low temperature operation: -10ºC at end of charge
  - Enables operation with minimal overcharge to stress the nickel electrodes
  - Worst case for transport processes
  - Relatively abrupt onset for oxygen evolution at full charge
- 90-minute cycle profile
  - 30 minutes discharge, 60 minutes recharge
- 40% DOD with periodic high rate discharge pulses
  - Three cycles of 8 minutes discharge at 0.5C followed by 2 minutes at 2C for a 40 DOD
  - High rate pulses expected to stress the H_2 electrode transport capabilities
  - Pulse periodicity expected to allow H_2 pressure dependence to be studied
- High peak recharge rate (C-rate)
  - Current taper at a peak cell charge voltage limit
  - One set of cells run at 1.02 RCF, other set at a 1.04 RCF target (1.03 – 1.05 actual)
    - Lower RCF cells go to open circuit conditions while the second set of cells obtain their higher RCF during the 60 minute charge

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P/F Criteria and Parameters Trended

- Tests will run until cell voltage falls below 0.7 V during 2C discharge or 1.0 V at 0.5C
  - To date, over 1880 cycles had been applied

- Parameters trended for possible sensitivity to the type of emulsion used in the hydrogen electrodes
  - Voltages signatures during charge and discharge
  - EOCV and EODV
  - Current taper
  - Recharge ratios (RCF)
  - Thermal signatures
  - Pressure signatures

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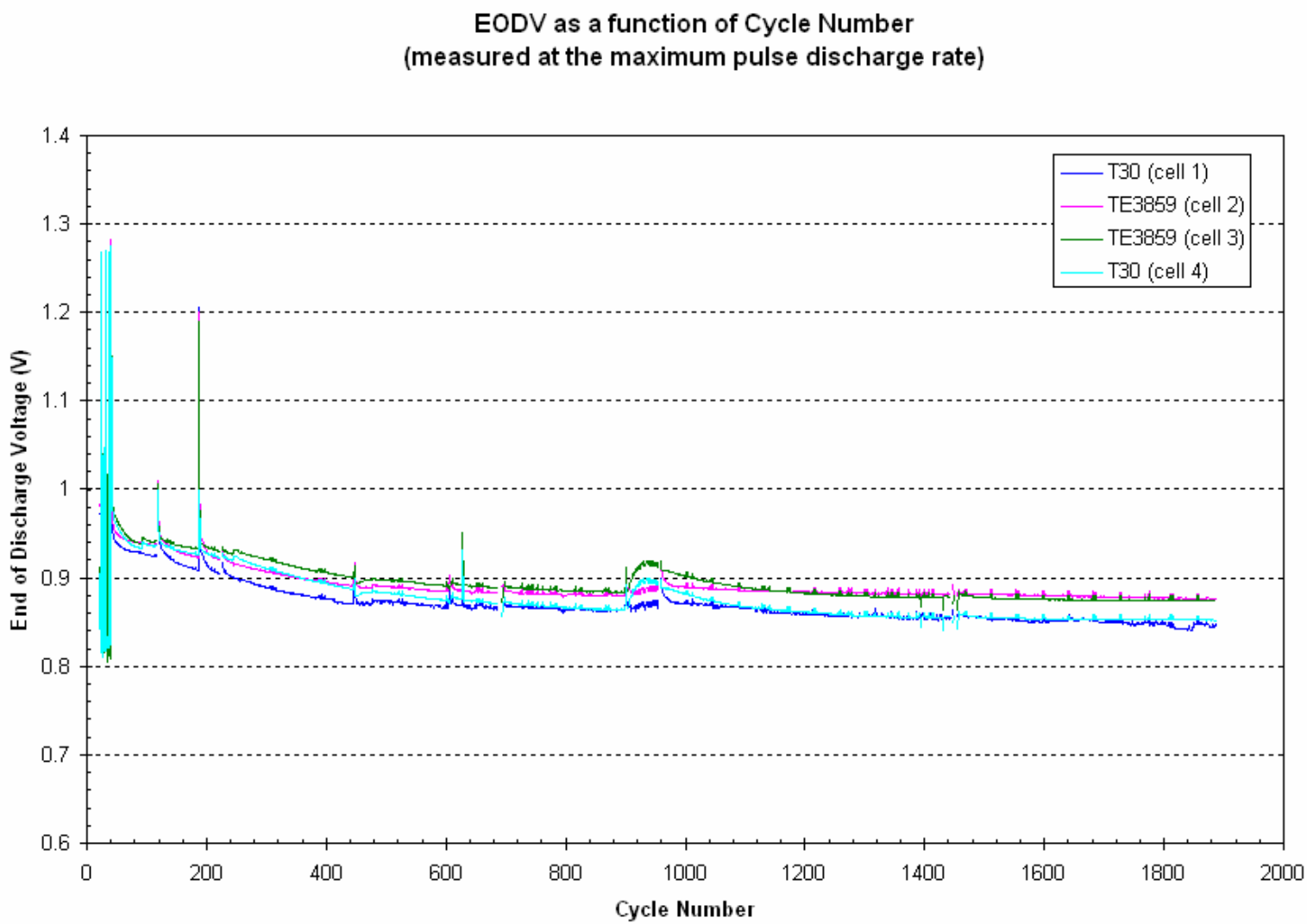
Stress Test Results to Date: End of Discharge Voltage



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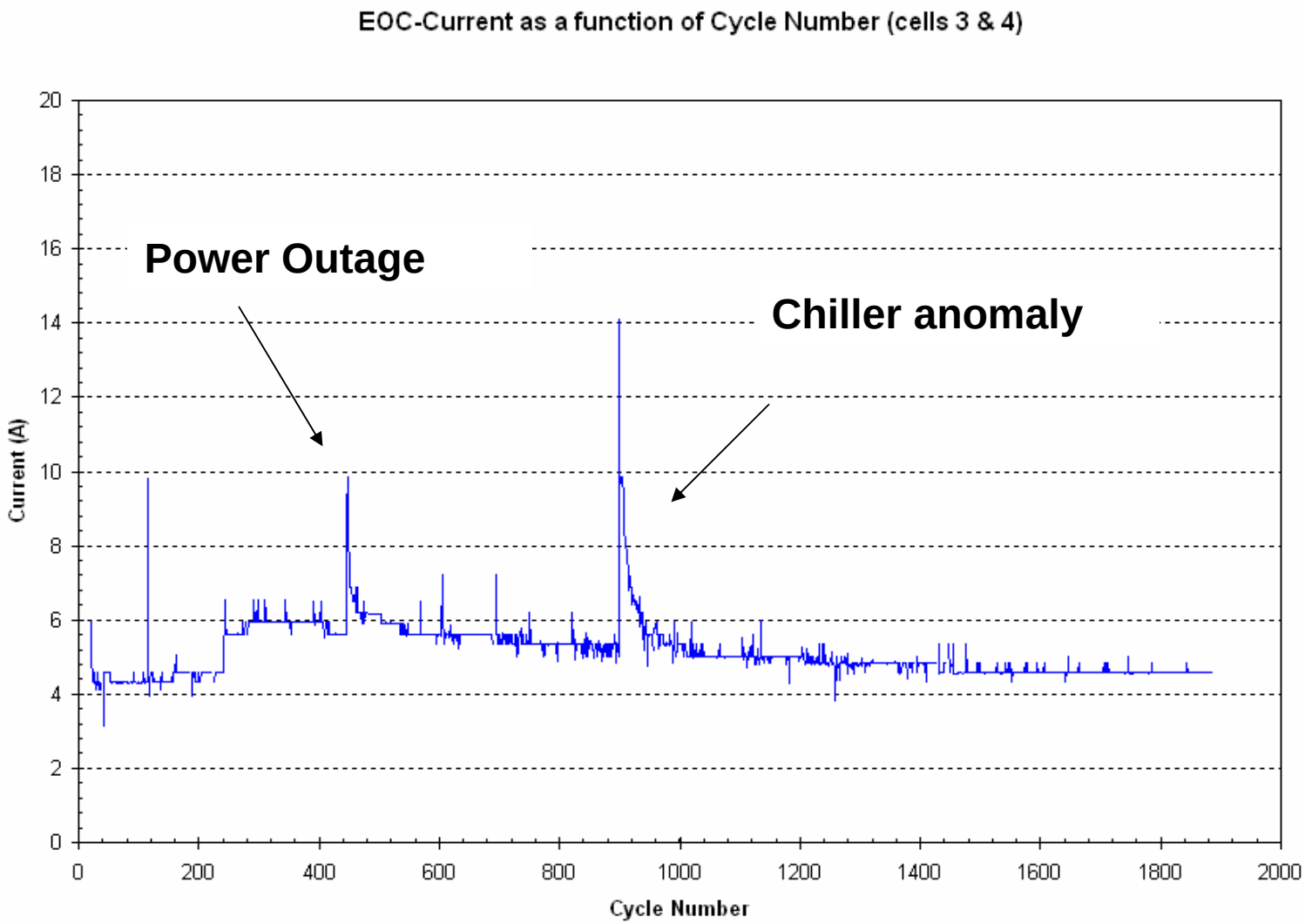
Stress Test Results to Date: Current Taper (cells 3 & 4)



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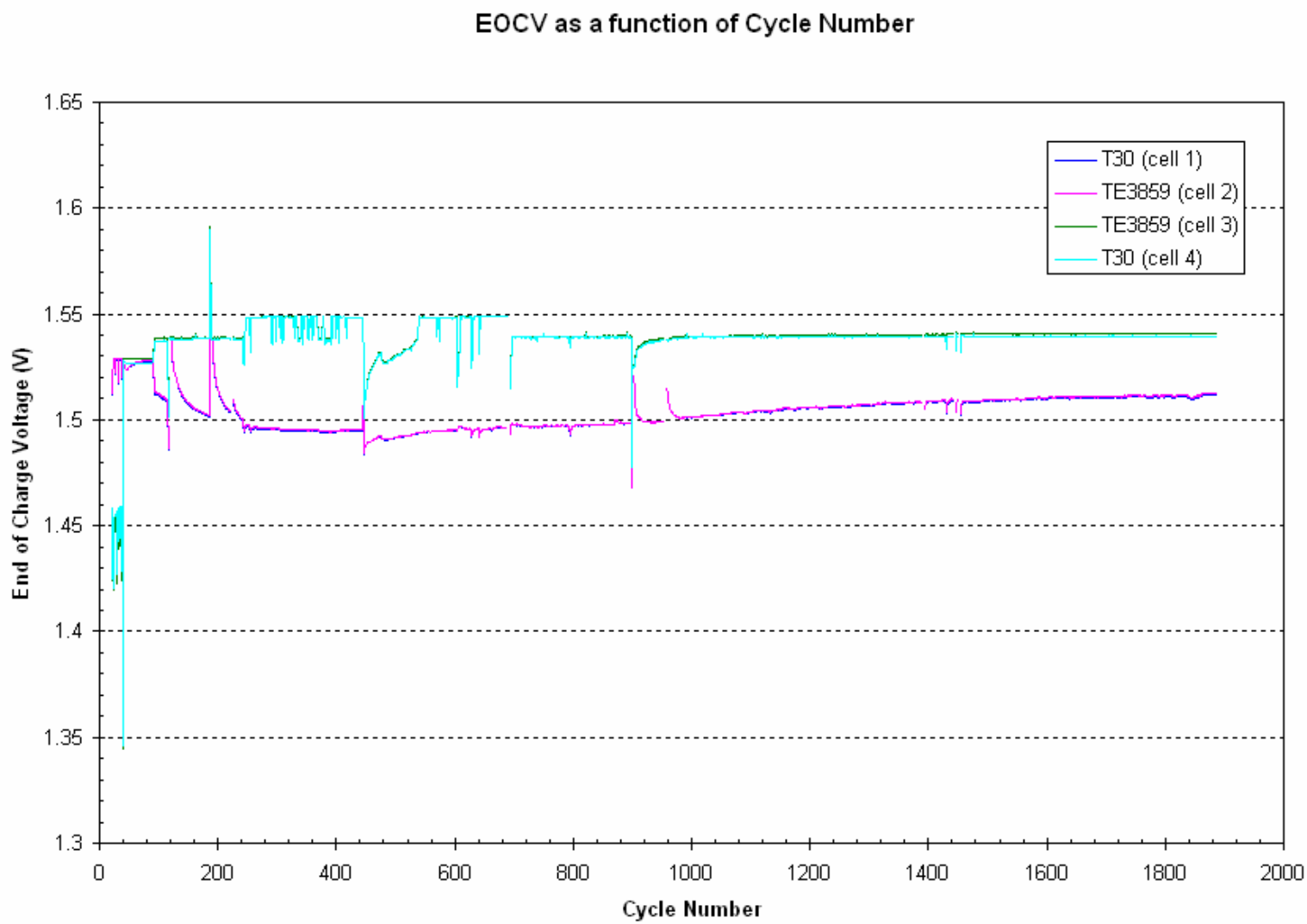
Stress Test Results to Date: End of Charge Voltage



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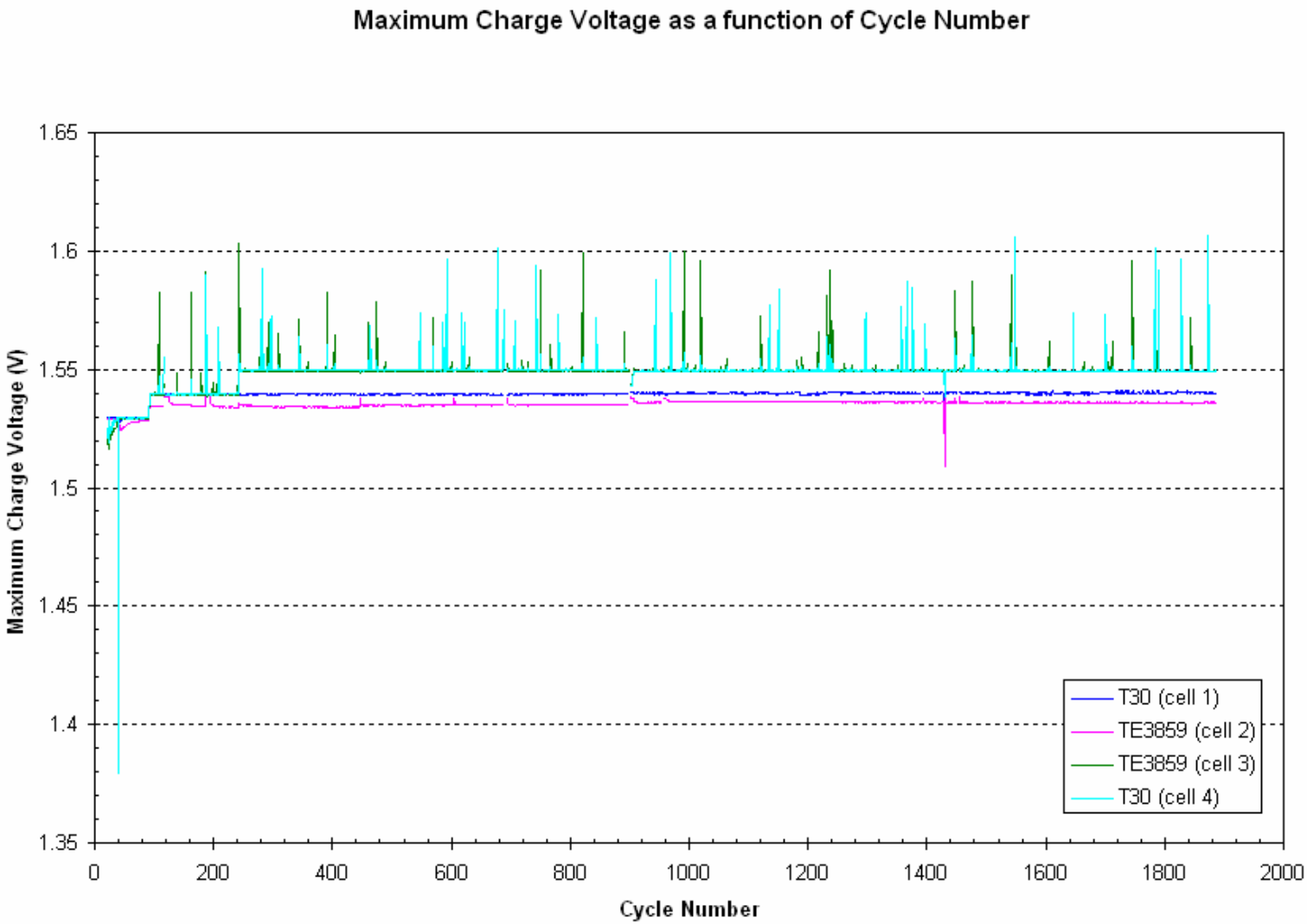
Stress Test Results to Date: Max Charge Voltage prior to Taper



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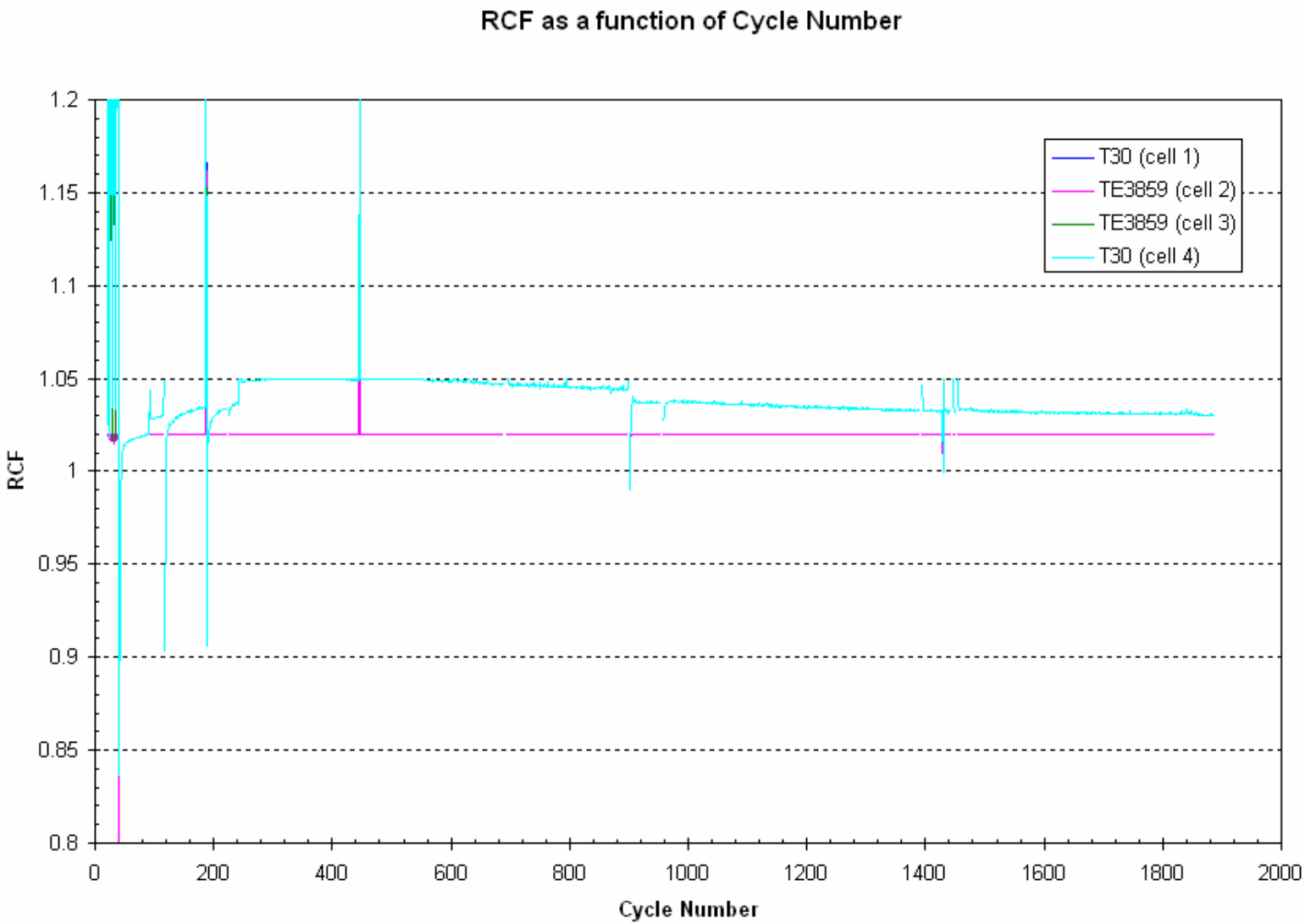
Stress Test Results to Date: Recharge Fraction (RCF)



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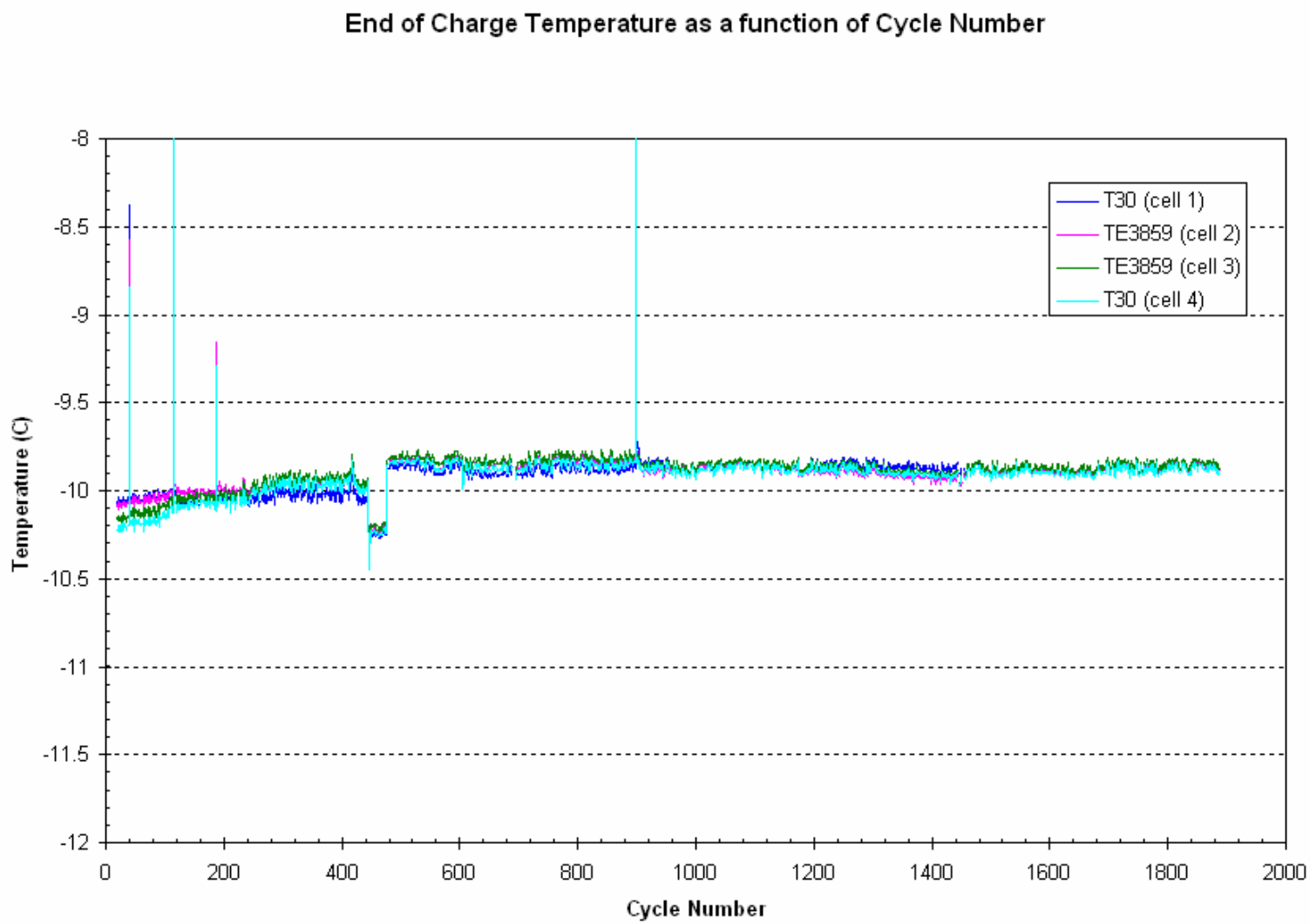
Stress Test Results to Date: End of Charge Temperature



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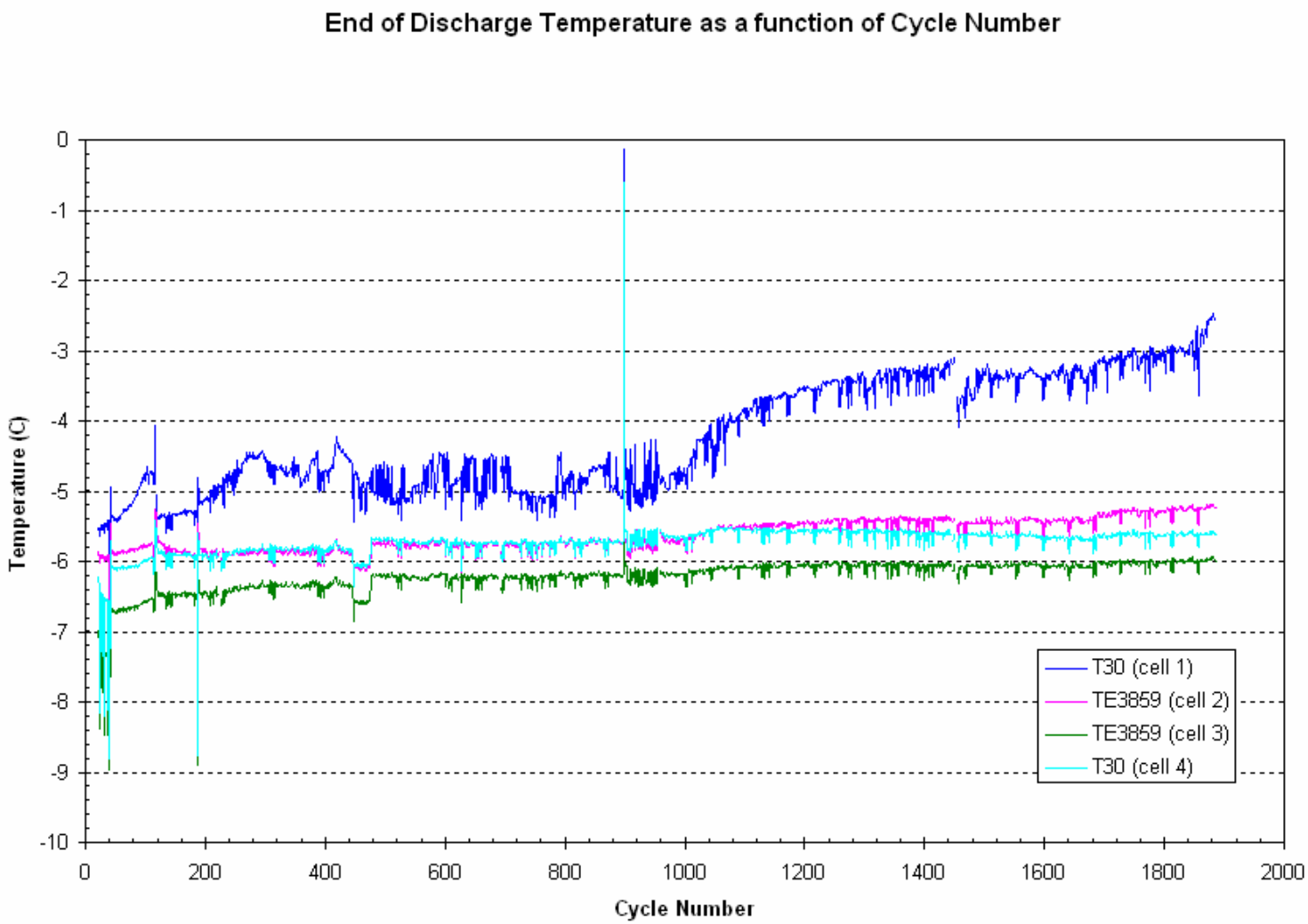
Stress Test Results to Date: End of Discharge Temperature



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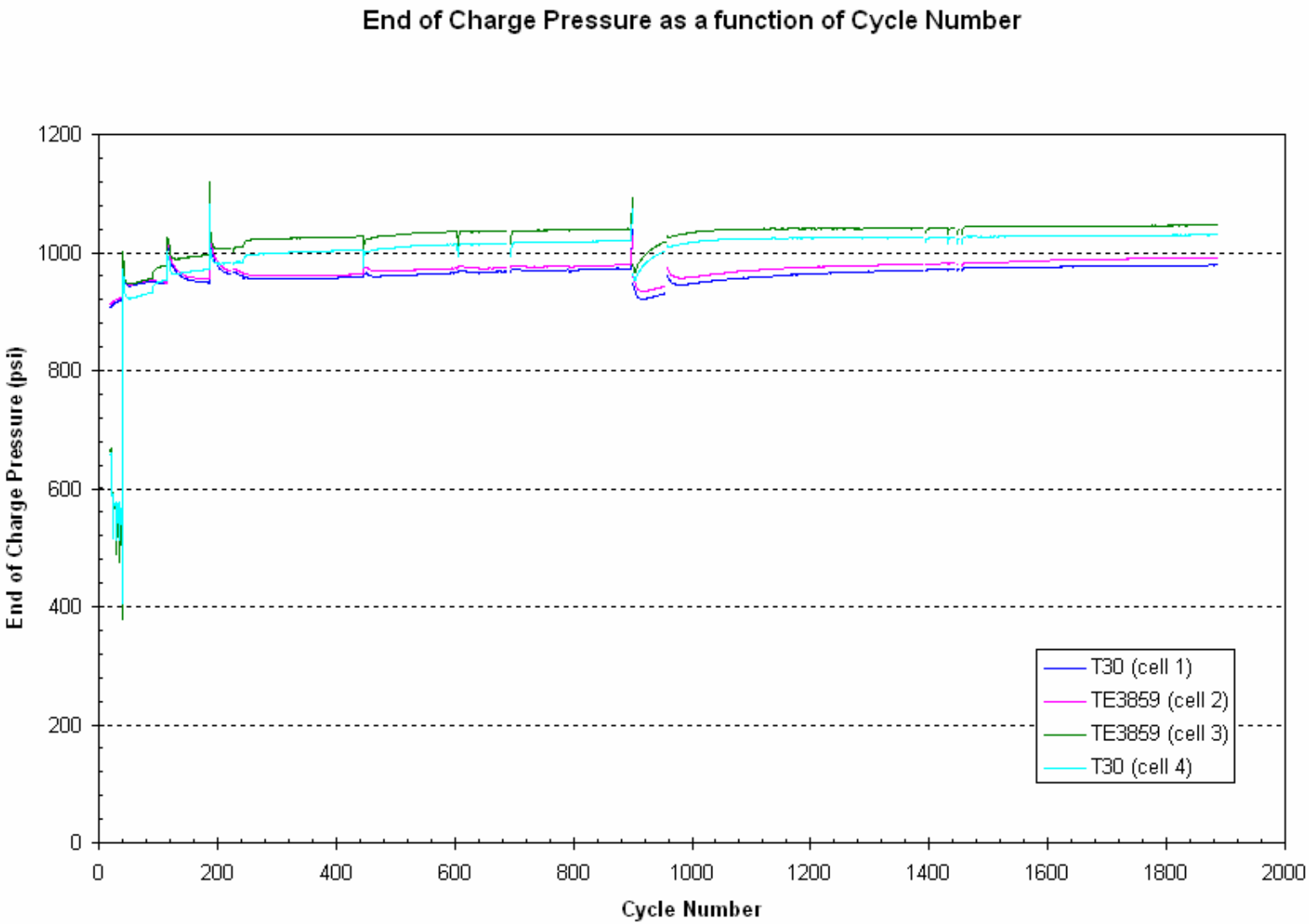
Stress Test Results to Date: End of Charge Pressure



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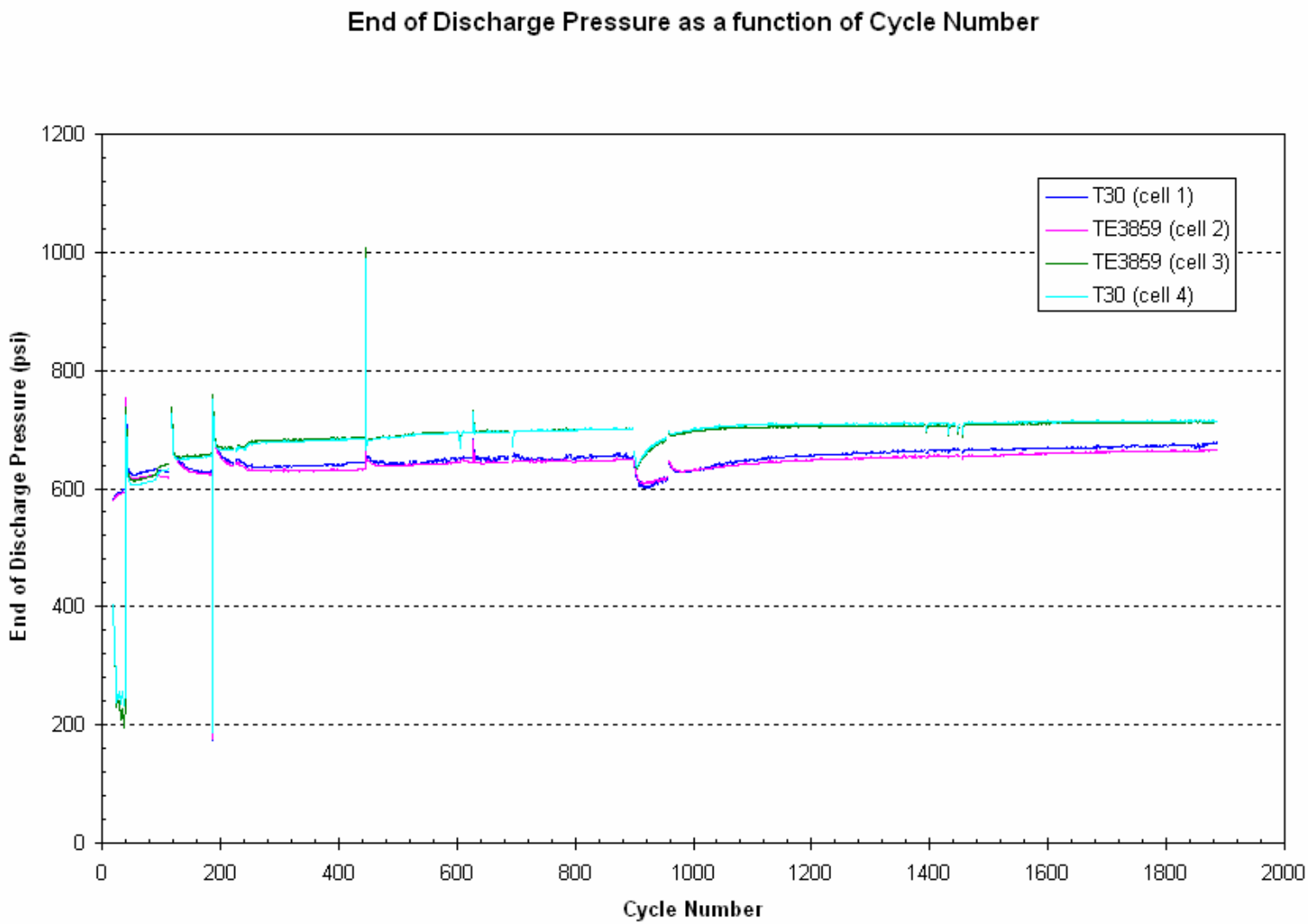
Stress Test Results to Date: End of Discharge Pressure



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Summary of Findings to Date

- Differences in surfactants used in electrodes expected to impact microstructure of electrodes produced due to differences in volatility, however, processing variables may have as strong of an impact
  - Expect to need to vary some processing parameters for follow-on replacement emulsion for T30
  - Need to develop the allowable range for critical parameters based on existing T30 production lots
- Different Teflon emulsions expected to show small impacts in charge and discharge voltages
- Low temperature, high pulse cycling of cells containing T30 electrodes and other cells containing TE3859 electrodes are presently showing greater end-of-discharge voltage losses in the cells containing the T30 electrodes
  - About 1850 cycles applied so far

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Next Directions

- Continue four-cell low temperature cycling tests
- Continue baseline effort for existing T30 electrodes
- Study variation of processing parameter on hydrogen electrode material characteristics
  - Surface area, porosity
  - Hydrophobicity
  - KOH retention
- Study variation of processing parameter on hydrogen electrode material characteristics
  - Plate-level stress tests
- Evaluate candidate replacement emulsions when they become available

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Acknowledgments

- The author is grateful for the assistance and contributions of the following personnel:
  - The Aerospace Corporation: Lindsay Berger, Boyd Carter, Myriam Easton, Tom Giants, Warren Hwang, Michael Quinzio, Larry Thaller, and Gloria To
  - Boeing: Ken Jennings
  - Eagle-Picher: Jeff Dermott

- The Aerospace Corporation is gratefully acknowledged for supporting this work as part of the Aerospace Mission Oriented Investigation and Experimentation (MOIE) program.

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Additional Data

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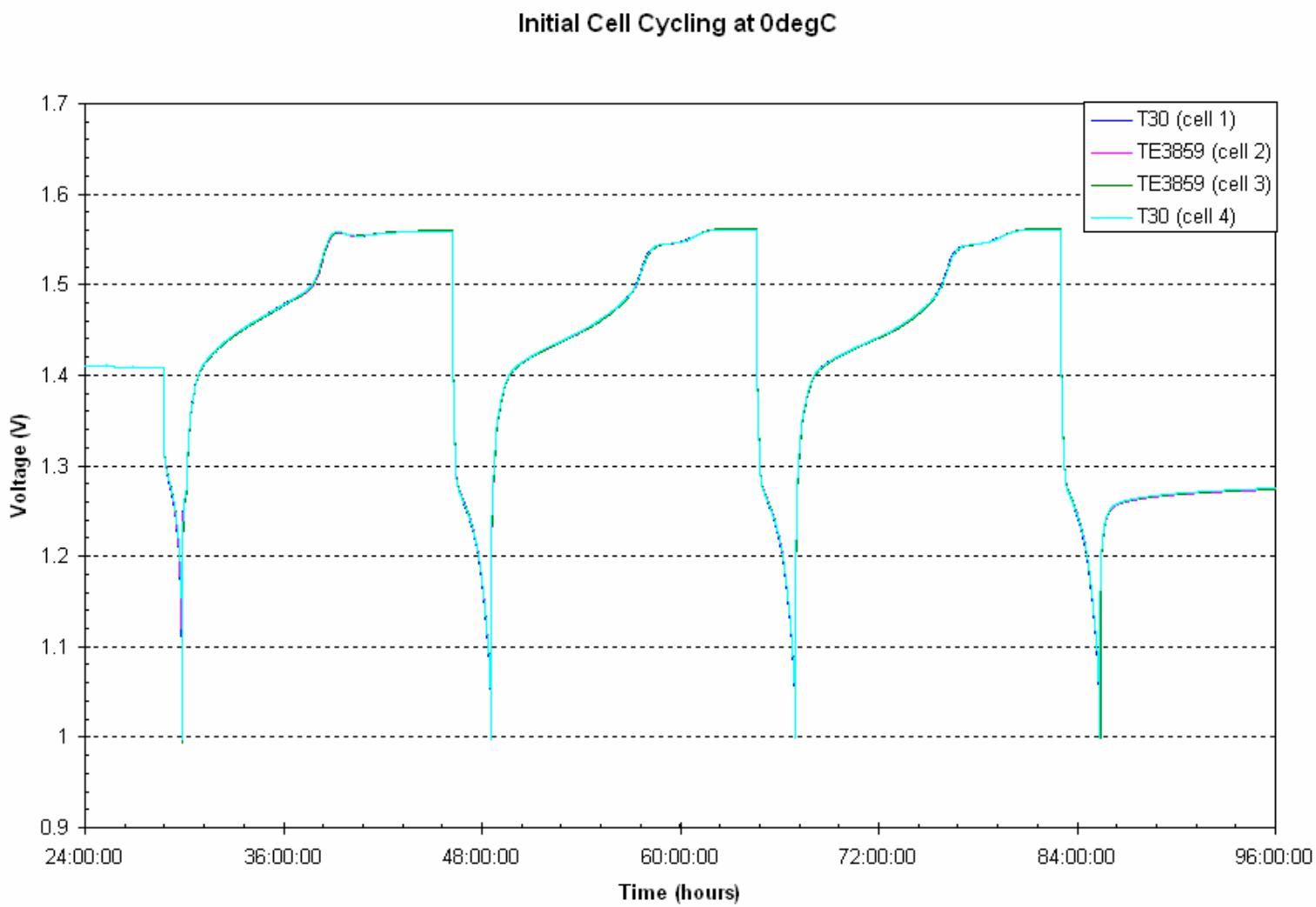
Initial Capacity Cycling of Four Cells at 0°C



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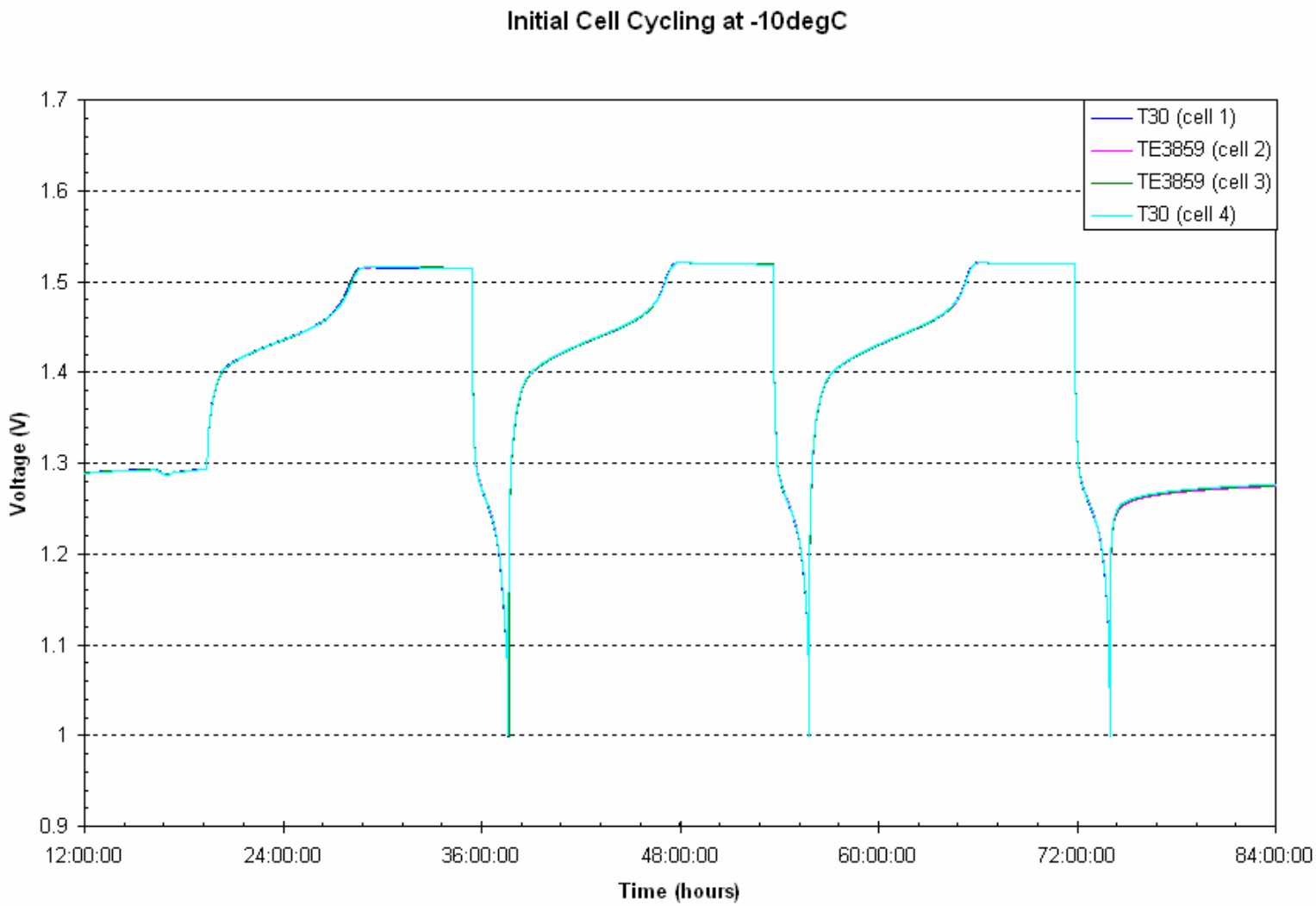
Initial Capacity Cycling of Four Cells at 10°C



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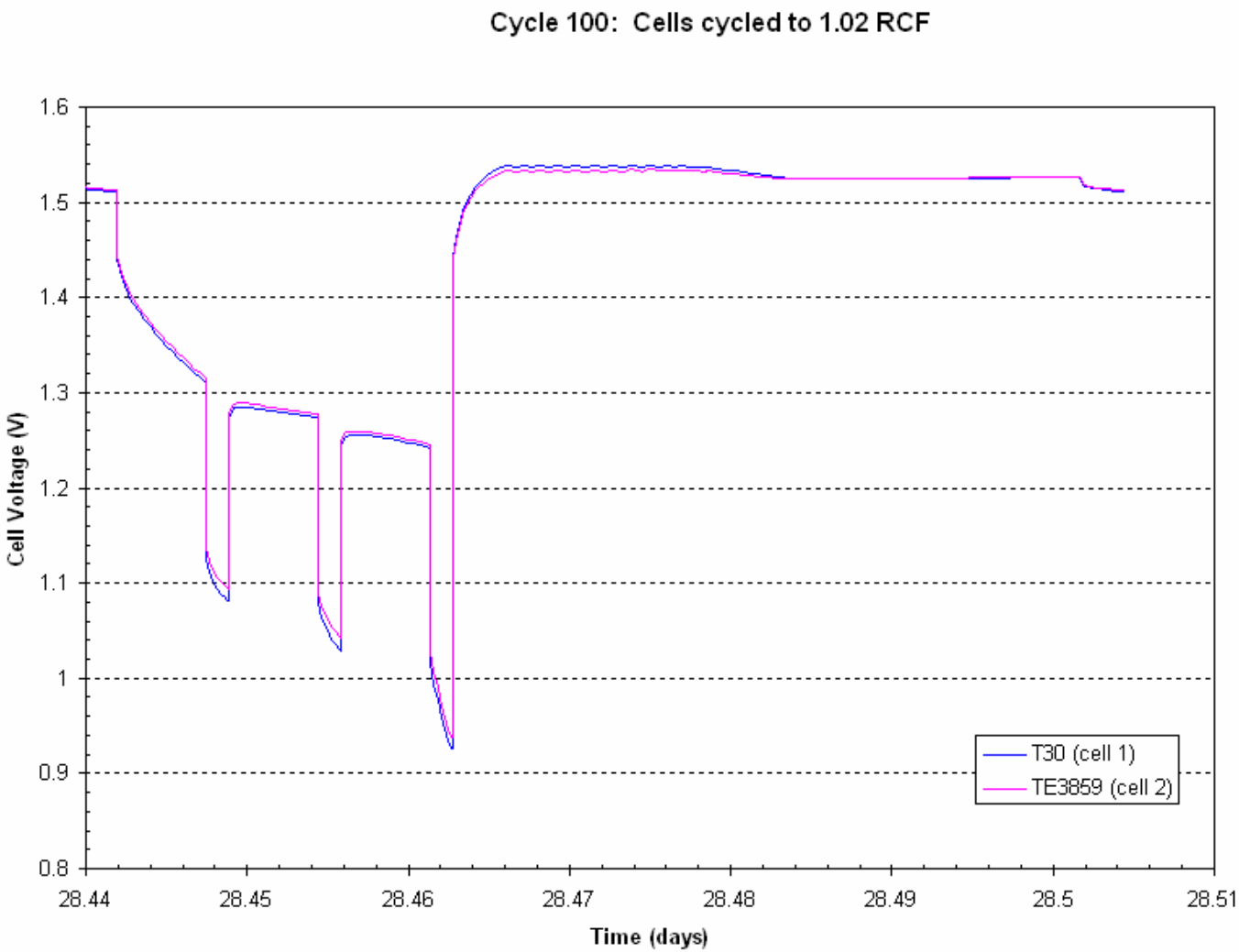
Cycle 100 Curves for 1.02 RCF



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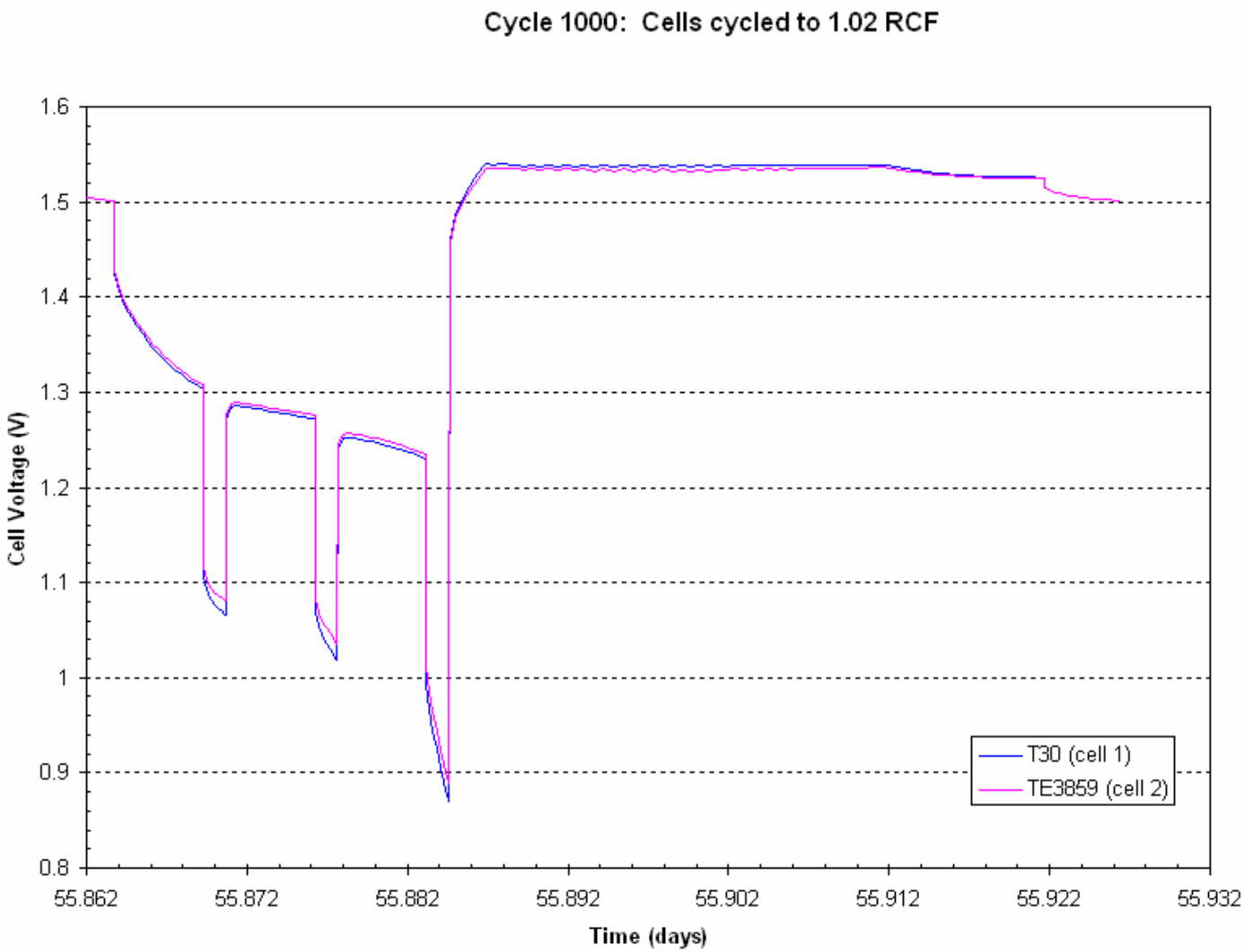
Cycle 1000 Curves for 1.02 RCF



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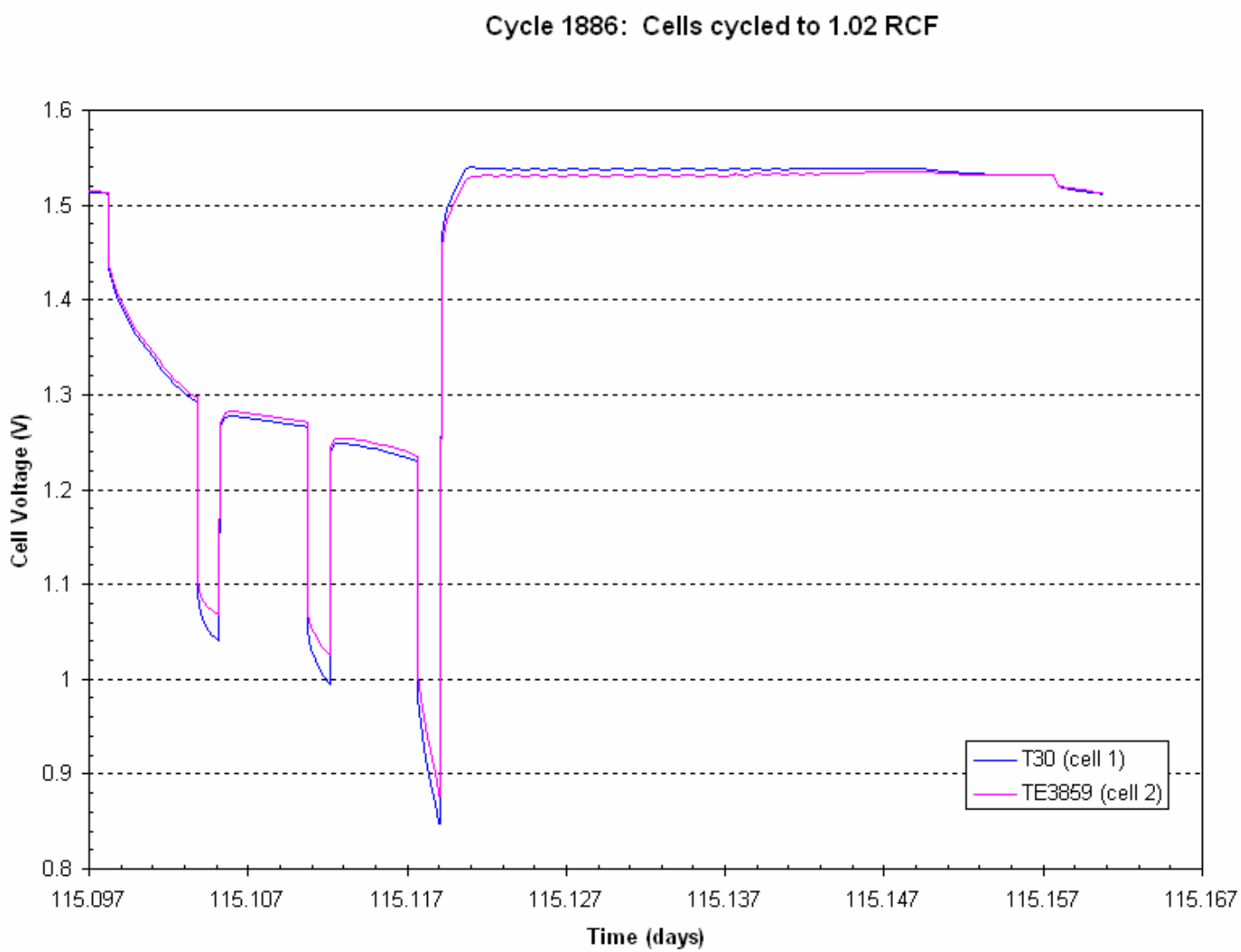
Cycle 1886 Curves for 1.02 RCF



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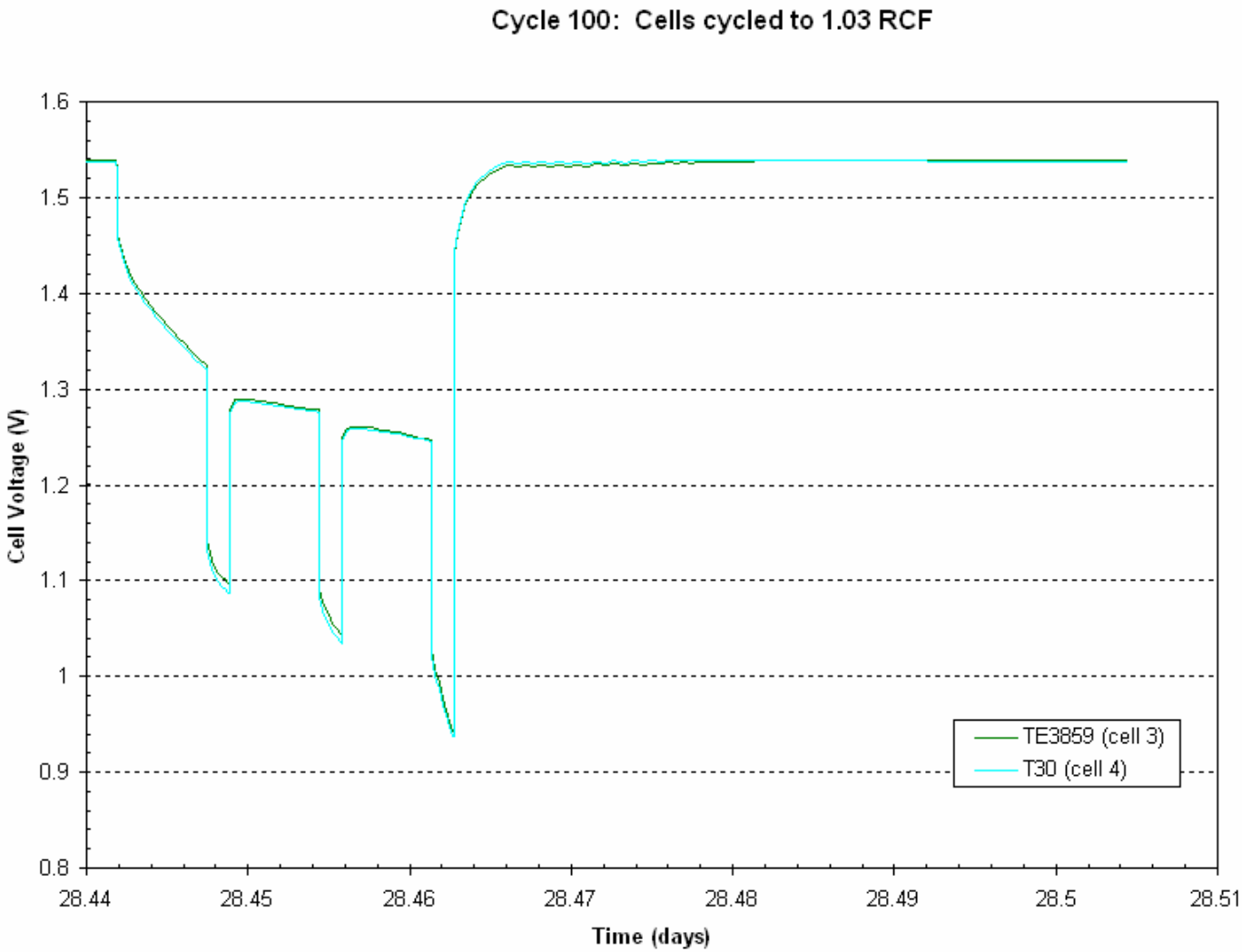
Cycle 100 Curves for 1.03 – 1.05 RCF



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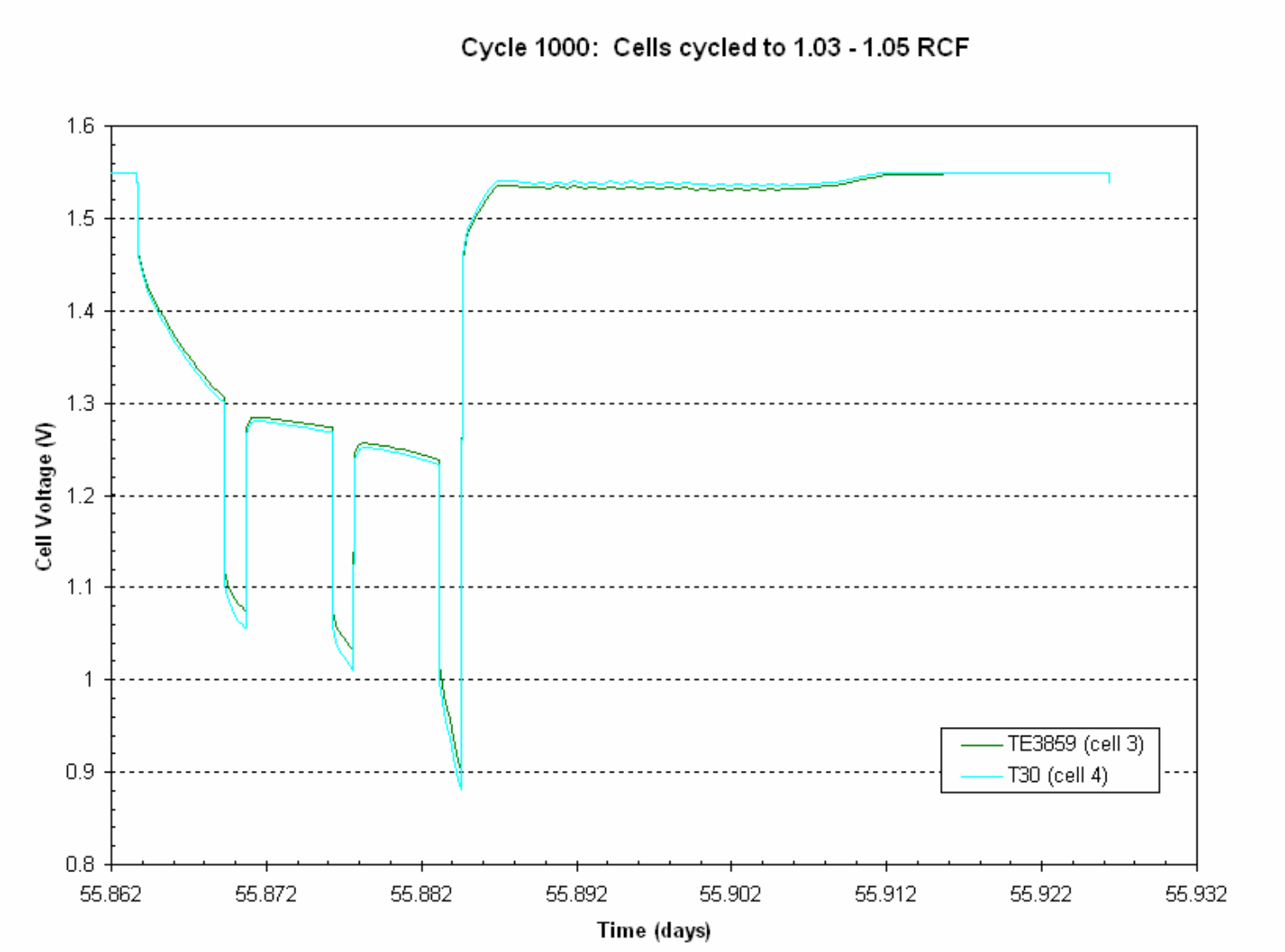
Cycle 1000 Curves for 1.03 – 1.05 RCF



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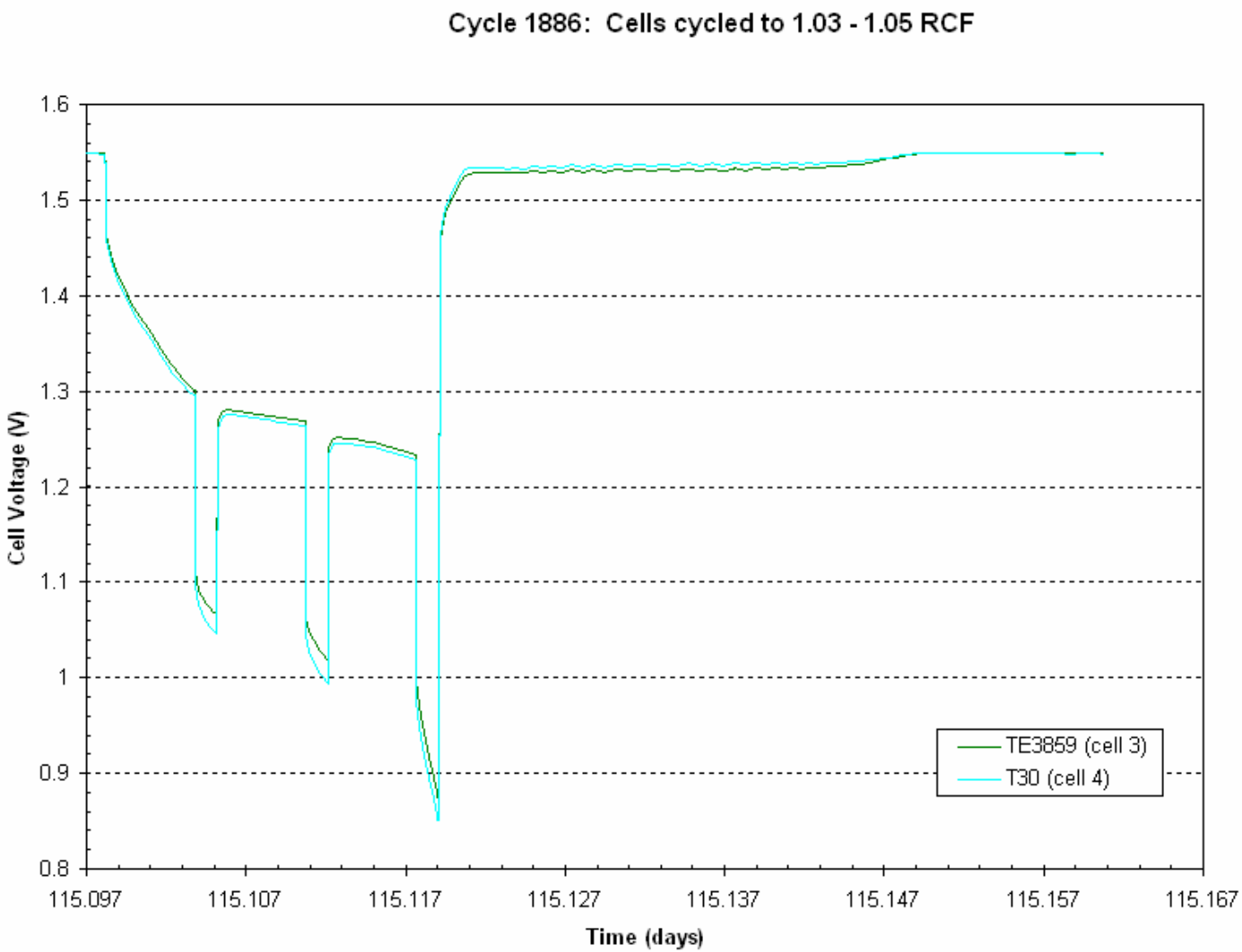
Cycle 1868 Curves for 1.03 – 1.05 RCF



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