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The 2002 NASA Aerospace Battery Workshop

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Preface

This CD contains the proceedings of the 35th annual NASA Aerospace Battery Workshop, hosted by the Marshall Space Flight Center, November 19–21, 2002. The workshop was attended by scientists and engineers from various agencies of the U.S. Government, aerospace contractors, and battery manufacturers, as well as international participation in like kind from a number of countries around the world.

The subjects covered included lithium-ion, nickel-hydrogen, and various advanced technologies and testing techniques.

Introduction

The NASA Aerospace Battery Workshop is an annual event hosted by the Marshall Space Flight Center. This workshop is sponsored by the NASA Aerospace Flight Battery Systems Program, which is managed out of NASA Glenn Research Center and receives support in the form of overall objectives, guidelines, and funding from Code R, NASA Headquarters.

The 2002 Workshop was held on three consecutive days and was divided into five sessions, some of which carried over from one day to the next. The first and fourth sessions covered several general topics and included some lithium-ion carry-over. The second session was a Nickel-Hydrogen Session. The third and fifth sessions were Lithium-Ion Sessions.

On a personal note, I would like to take this opportunity to thank all of the many people that contributed to the organization and production of this workshop:

> **The NASA Aerospace Flight Battery Systems Program**, for their financial support as well as their input during the initial planning stages of the workshop;
>
> **Huntsville Hilton**, for doing an outstanding job in providing an ideal setting for this workshop and for the hospitality that was shown to all who attended;
>
> **Joe Stockel, National Reconnaissance Office; George Methlie, U.S. Government; and Catherine Marsh, U.S. Government**, for 11th-hour solicitation of presentations for a couple of sessions;
>
> **Marshall Space Flight Center employees**, for their help in registering attendees, handling the audience microphones, and flipping transparencies during the workshop.

Finally, I want to thank all of you that attended and/or prepared and delivered presentations for this workshop. You were the key to the success of this workshop.

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13. ABSTRACT *(Maximum 200 words)*

This document contains the proceedings of the 35th annual NASA Aerospace Battery Workshop, hosted by the Marshall Space Flight Center, November 19–21, 2002. The workshop was attended by scientists and engineers from various agencies of the U.S. Government, aerospace contractors, and battery manufacturers, as well as international participation in like kind.

The subjects covered included nickel-hydrogen, lithium-ion, nickel-metal hydride, lithium-sulfur, lithium-iron disulfide, and silver-zinc technologies.

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AN OVERVIEW OF THE NASA AEROSPACE FLIGHT BATTERY SYSTEMS PROGRAM

2002 NASA AEROSPACE BATTERY WORKSHOP

HUNTSVILLE, ALABAMA

November 17-19, 2002

Michelle Manzo
NASA Glenn Research Center
Cleveland, Ohio 44135

NASA AEROSPACE FLIGHT BATTERY SYSTEMS PROGRAM

Unified NASA-wide program, managed by GRC, addressing battery related issues. Program goal is to ensure the availability of qualified flight hardware to support NASA's aerospace battery requirements.

Program Objectives

- Provide NASA with validation guidelines and the supporting database for technology selection of hardware and processes relating to aerospace batteries
- Develop, maintain and provide tools for the validation and assessment of aerospace battery technologies
- Disseminate validation and assessment tools, quality assurance reliability and availability information to the NASA and aerospace battery communities
- Accelerate the readiness of technology advances and provide infusion paths for emerging technologies

Major Players

NASA centers - GRC, GSFC, MSFC, JSC, JPL, LaRC, KSC, AFRL, Navy, CIA, The Aerospace Corporation

Approach

NASA-wide program, with tasks distributed among various centers, run in close coordination with other government agencies

Address battery systems level issues as well as primary and secondary cell/battery technology issues

- Maintain current battery technology
- Increase fundamental understanding of primary and secondary cells and batteries
- Establish specifications, design and operational guidelines
- Open and maintain communication lines within NASA and the aerospace community

PROGRAM TASK RESPONSIBILITIES

NASA HEADQUARTERS
CODE SM - OFFICE OF SPACE SCIENCE
ADVANCED TECHNOLOGY AND MISSION STUDIES

BATTERY STEERING COMMITTEE

PROGRAM MANAGEMENT
NASA GLENN RESEARCH CENTER
ELECTROCHEMISTRY BRANCH

NASA GSFC

VERIFICATION OF QUALITY & RELIABILITY OF Ni-CD and Ni-H2 CELLS

Li-ION BATTERY VERIFICATION

NASA JSC

Li-ION, Ni-MH, Ni-CD COMMERCIAL CELL EVALUATION

SAFETY CONTROLS FOR LITHIUM CELLS

JPL

Li-ION MODEL

CELL VERIFICATION FOR PLANETARY MISSIONS

Li-IONCHARACTERIZATION & VERIFICATION

NASA GRC

PROGRAM MANAGEMENT

DATA BASE

$Ni-H_2$ TECHNOLOGY

Li-Ion VERIFICATION

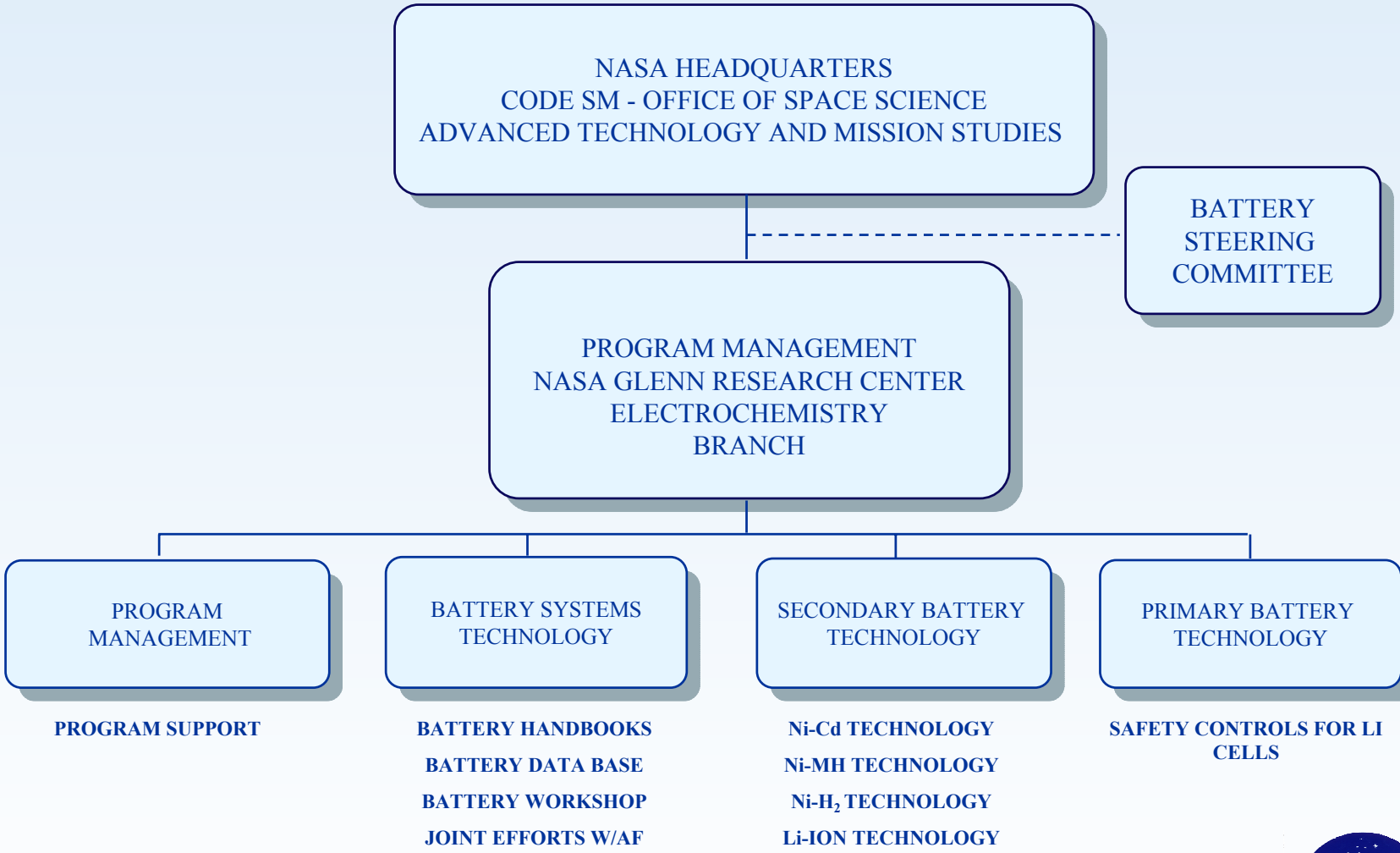
NASA MSFC

BATTERY WORKSHOP

STANDARD DPA PROCEDURES

Li-ION VERIFICATION

PROGRAM ORGANIZATION



BATTERY SYSTEMS TECHNOLOGY TASK

OBJECTIVES:

- To improve reliability of energy storage space power system design, integration, and checkout
- Address systems aspects - integration of cells into batteries and batteries into power systems

TASKS:

- NASA Battery Handbooks
- Battery Data Base
- NASA Battery Workshop
- Joint Efforts With The Air Force
- Flight Battery Operations Telecon

NASA BATTERY HANDBOOKS

OBJECTIVE:

- **Define good consistent practices for the design, integration and checkout, and testing of primary and secondary battery systems.**
- **Provide background information, guidelines and requirements related to battery systems to aid in ensuring mission success**

Approach:

- **Develop documents that serve as guidelines and checklist for the procurement of cells for flight projects**
- **Aid in development of specifications for procurement**
- **Provide rationale for selection of design features for specific applications**
- **Define representative values and ranges for technical specifications for critical design parameters**

Documents produced via combination of internal and contracted efforts - Contracts with the Aerospace Corporation, various industry consultants

Publications:

- NASA Specification for Manufacturing and Performance Requirements of NASA Standard Nickel-Cadmium Cells – NHB 8073.1, 1988
- NASA Handbook for Nickel-Hydrogen Batteries – NASA RP 1314, 1993
- Handbook for Handling and Storage of Nickel-Cadmium Batteries – Lessons Learned – NASA RP 1326, 1994
- Primary Battery Design and Safety Guidelines Handbook – NASA RP 1353, 1994
- Review and Status of Lithium-Ion Cell Technology for Aerospace Applications – JPL Internal Document D-13332, 1997
- Guidelines for the Procurement of Aerospace Nickel-Cadmium Cells – JPL Publication 97-6, 1997
- An Overview of the Design Development and Application of Nickel-Hydrogen Cells – NASA TP TBD, 2002
- Guidelines Document for Silver-Zinc Cells – NASA TP TBD, 2003

BATTERY DATA BASE

OBJECTIVE:

- **Develop data base for the dissemination of test data related to the validation of battery technologies for aerospace applications**

APPROACH/STATUS:

- **Majority of Program sponsored testing is at Crane**
- **Developed web-based system for access of operational cycle test data**
  - **Crane test data post 1990**
  - **Data from Lockheed Martin Nickel-Hydrogen Test Program**
  - **Tests sponsored at other installations being incorporated**
- **Data is available on-line to test sponsors**
  - **Real-time, processed and archived test results**
  - **Limited access can be granted as needed via approval from test sponsor**

NASA BATTERY WORKSHOP

OBJECTIVE:

- Provide forum for open communication of battery related activities
- Address technology status of established and emerging technologies

APPROACH/STATUS:

- Sponsor annual workshop
  - Started in 1968 – Goddard Battery Workshop
  - 1985 – Sponsorship assumed by Battery Program
  - Moved to MSFC in 1990
- Topics Covered
  - Research and development work on state-of-the-art aerospace battery technologies
  - Flight and ground test data
  - On-orbit operation and problem resolution efforts
  - Focused topic to address current issues relating to aerospace batteries

COOPERATIVE EFFORTS WITH THE AIR FORCE

OBJECTIVE:

- Leverage efforts by combining resources with the Air Force for efforts supporting the verification of secondary cells/batteries for aerospace applications.

APPROACH/STATUS:

- **Memorandum of Understanding**
  - **Initiated in 1996, renewed in 1999**
  - **Formal arrangement expired earlier this year**
  - **Efforts continue**
- **Areas of common interest**
  - **Common pressure vessel (CPV) nickel-hydrogen batteries**
  - **Single pressure vessel (SPV) nickel-hydrogen batteries**
  - **Individual pressure vessel (IPV) nickel hydrogen cells**
  - **Super nickel-cadmium cells**
  - **Lithium Ion Verification Testing**

FLIGHT BATTERY OPERATIONS TELECON

OBJECTIVE:

- **Provide a forum for communications among users of aerospace battery technologies to share experiences related to flight battery integration, management and operations, specifically nickel- hydrogen for the present and lithium ion technology for future missions.**

APPROACH/STATUS:

- **Convene monthly telecons on relevant topics related to flight batteries**

RECENT TELECON PRESENTERS/TOPICS

- **Fred Cohen and Penni Dalton, "Status of Nickel Hydrogen Batteries on Space Station"**
- **Tom Miller – "An Update on Design Features and Testing Status of Ni-H2 Cells/Batteries"**
- **Ray Zercher, "Status of CPV Ni-H_2 Batteries on MGS, Genesis, Mars Orbiter-05, Odyssey, and Stardust"**
- **Jon Armentrout – "HST Reliability Studies"**
- **Anisa Ahmad – "Status of GSFC Programs – MAP, Landsat, TERRA"**
- **George Methlie, "Lithium-Ion as a Replacement for Nickel Hydrogen – Progress/Status"**
- **Rob Chambers – "Nickel-Hydrogen – Oddesy Mission"**
- **Dan Debacari – "Nickel-Hydrogen Handling and Safety Considerations"**
- **Albert Zimmerman – "Nickel Hydrogen Battery Performance Signatures"**
- **Gopal Rao, Harry Wajsgras, Stanley Krol – "On-orbit Health Check of HST Nickel-Hydrogen Batteries"**

SECONDARY BATTERY TECHNOLOGY

OBJECTIVE:

- Improve performance, quality, safety and reliability of secondary battery systems.
- Maintain and improve established technologies and aid in development of emerging technologies

TASKS:

- Nickel-Cadmium Battery Technology
- Nickel-Hydrogen Battery Technology
- Nickel-Metal Hydride Battery Technology
- Lithium-ion Battery Technology
- Secondary Battery Technology Support

NICKEL-CADMIUM BATTERY TECHNOLOGY

VERIFICATION OF SECONDARY Ni-Cd CELLS

OBJECTIVE:

- Provide independent verification of manufacturing flight cells by procuring and testing representative cells from various manufacturers

APPROACH /STATUS:

- Current efforts focus on monitoring performance of cells representative of flight lots for ongoing and upcoming NASA missions.

COMPLETED EFFORTS:

- Over 200 cells tested – various temperatures, DOD
  - Evaluations of NASA Standard cells from representative flight lots
  - Advanced Ni-Cd cell designs
  - Verification testing of potential replacements for NASA Standard Ni-Cd
    - Saft, Sanyo, EP Super Ni-Cd, EP Magnum Ni-Cd, Acme
  - Cell verification testing of cells with various storage histories

NICKEL-HYDROGEN BATTERY TECHNOLOGY

IPV CELL VERIFICATION

OBJECTIVE:

- Provide independent verification of design and component variations to manufacturing flight cells. Evaluate effects of storage conditions on performance and life.

APPROACH/STATUS:

- **Over 200 cells have been tested**
- **Evaluate effects of advanced design features in flight hardware**
- **Tests run at various DOD and Temperatures**
- **Evaluate charge control methods**

NICKEL-HYDROGEN BATTERY TECHNOLOGY

IPV CELL VERIFICATION

- Verification of 26% KOH
  - Cells From Hughes, Eagle Picher, Gates, Yardney
  - Cells of ISS Design
- Advanced design features
  - Catalyzed wall wick
  - Cell stacking – Back to back vs Recirculating
  - 350AH, 5 ½" Hughes GEO Cell Evaluation
- Evaluation of cell components
  - Nickel electrode impregnation process – alcoholic and aqueous
  - Separator – Asbestos and Zircar
  - Passivation of electrode plaque
- Storage Test
  - Dry Storage
  - Wet storage

NICKEL-HYDROGEN BATTERY TECHNOLOGY

CPV Battery Evaluation

OBJECTIVE:

- Evaluate potential of CPV technology to meet NASA's needs. Develop data base to insure optimum battery management and support for missions

- **Evaluation Of 2.5" CPV Batteries**
  - **10, 2 Cell, 10AH CPV Batteries - Eagle Picher**
  - **LEO life test - 40% DOD, 10°C**
- **Characterization Of 2.5" CPV Batteries**
  - **Characterization/Mission Simulation Tests On 2.5"CPVTests**
- **Joint Task With Air Force - 3.5" CPV Batteries**
  - **21, 2-cell, 45AH CPV Batteries - Eagle Picher**
  - **3 PACKS - 2 LEO 40% DOD -5°C, 10°C, 1 GEO**
- **Evaluate CPV Ni/H2 battery technology designs –**
  - **2.5 and 3.5" Diameter Cells**
    - **Improved stack designs**
    - **26% and 31% Electrolyte concentration**
    - **Wall wick variations**

NICKEL-HYDROGEN BATTERY TECHNOLOGY

SPV BATTERY EVALUATION

OBJECTIVE:

- Evaluate potential of SPV technology to meet NASA's future needs

- **JOHNSON CONTROLS - SPV BATTERY**
  - 28 VOLT, 50 AH BATTERY
  - 35% DOD, 10°C ~44,000 CYCLES

NICKEL-METAL HYDRIDE TECHNOLOGY

OBJECTIVE:

- **Evaluate potential of Ni-MH technology to meet NASA's future needs**

APPROACH/STATUS:

- **Current efforts focus on evaluation of COTS products for EVA'S, IVA'S for space station**
- **Performance and abuse evaluation of cells from various vendors to determine best available commercial Ni-MH**
- **Develop and certify Ni-MH battery for EMU backpack, advanced helmet lights, cuff check list**

- **Completed evaluation of aerospace design cells–**
  - **Eagle Picher**
  - **Sanyo**
  - **Ovonics**

LITHIUM -ION BATTERY TECHNOLOGY

Li-ion Technology Assessment

Objective:

- **Evaluate potential of Li-Ion technology to meet NASA's future needs. Enable technology development for aerospace applications**
- **Develop performance database and user guidelines of the lithium ion battery technology**.

Approach/Status:

- **Technology review - status assessed for aerospace applications**
- **Characterize and define performance envelopes of prototype cells as related to NASA's planetary missions.**
  - **NASA/DoD Inter-agency Program**
  - **Cells developed for specific NASA missions, such as Mars Lander (MSP01) and Mars Rover (Mars Athena Rover and Mars Exploration Rover).**
  - **Cells from other sources**
- **Extensive database generated –**
  - **Rate characterization as function of charge/discharge rate and temperature**
  - **Cycle life at various temperatures and various depths of discharge**
  - **Coulombic and energy efficiencies at various temperatures**
  - **Heat evolution rates at different rates of charge and discharge**
  - **Performance in a multi-cell environment**
- **Address planetary mission requirements**
  - **Radiation tolerance / Stand time during cruise**

LITHIUM -ION BATTERY TECHNOLOGY

LITHIUM ION CELL/BATTERY CHARACTERIZATION

Objective:

- **To qualify the best lithium-ion "space" batteries in environments that mimic as closely as possible those the batteries will experience if used in the future LEO and GEO missions**

Approach/Status:

- Using the most advanced cells available, prepare battery packs that will approximate the batteries that would be used for LEO/GEO missions
- Conduct various tests over a broad range of operating temperatures (hot and cold cases, along with a nominal case), coupled with a first-cut mission profile that includes launch.
- Evaluate different charge schemes – determine optimal charge control
  - **Parallel string charging**
  - **Cell-level monitoring only to determine end of charge**
  - **"Smart" battery**
- Batteries from AEA Technologies and Saft

LITHIUM -ION BATTERY TECHNOLOGY

Li-Ion LEO/GEO Verification Test Program

Objective:

- Assess the current and developing capabilities of Li-Ion technology for LEO and GEO applications
- Develop the database that will aid in the qualification of Li-Ion for NASA's LEO and GEO missions

Approach/Status:

- Work with statistician to develop DOE to address program test goals and resource limitations
- Identify flexible matrix that will maximize use of available resources and incorporate 'incremental funding' and multiple partners in test program
- Completed initial cell purchases

LITHIUM -ION BATTERY TECHNOLOGY

Li-Ion LEO/GEO Verification Test Program

Cell Specifics

- 50 Aerospace quality cells from each of three vendors:
  - Eagle-Picher Technologies Model #SLC-16002
  - Saft America Model # G4
  - Lithion Model # INCP 95/28/154

Testing to take place at Crane, MSFC, GRC

LITHIUM -ION BATTERY TECHNOLOGY

Li-Ion LEO/GEO Verification Test Program

- **Focus on LEO with initial cell purchase**
- **Acceptance/Characterization Tests recently completed at Crane**
- **Final LEO Test conditions are being established**
- **Test Variables**
  - Vendor
  - Depth of Discharge – 3 levels
  - Test Temperature – 3 levels
  - Charge Control – 3 voltage limits
- **Additional test articles to be procured in FY03**

LITHIUM -ION BATTERY TECHNOLOGY

Li-Ion Commercial Cell Evaluation

Objective:

- **Develop an understanding of the safety issues relating to space use and qualification of new Li-Ion technology for manned applications.**
- **Enable use of new technology batteries into GFE equipment - laptop computers, camcorders**
- **Establish a data base for an optimized set of cells (and batteries) exhibiting acceptable performance and abuse characteristics for utilization as building blocks for numerous applications.**

Approach/Status:

- **Perform Evaluation – Performance and thermal characterization, evaluated abuse tolerance**
- **Typical manufacturers include Energizer, Maxell, Blue Star, Sony, Sanyo, Toshiba, Panasonic, Ultralife, and YTP**
- **Battery components such as cell voltage protection circuits, charger controls (chips), fuel gauges, miscellaneous IEEE electronic components, and commercial chargers for specific commercial equipment have been evaluated for use in flight equipment.**
- **Li-Ion batteries certified for use in Canon Camcorder, IBM Thinkpad, and a dosimeter**
- **Camcorder charger has been safety certified for flight**
- **Multiple applications are considering adaptors to allow use of the flight approved designs**

SECONDARY BATTERY TECHNOLOGY SUPPORT

Development of DPA Test Procedures

OBJECTIVE:

Define general guidelines to be followed by facilities performing DPA procedures to minimize the discrepancies that exist with DPA testing results from different facilities by defining a uniform set of guidelines by which DPA's can be conducted.

APPROACH/STATUS:

- Define guidelines that will promote stability and consistency in DPA results.
- Incorporate into an expert system software tool that can be utilized to aid in troubleshooting specific cell failures and offer suggestions as to what testing might be most appropriate on the failed cell.
  - Aerospace developed Expert Systems Approach
  - Define cell/component physical characteristics new and at failure along with signature performance – Expert System leads you to probable cause for failure
- Ni-H2 Complete and available for distribution
- Ag-Zn in Process
- Li-Ion Planned

SECONDARY BATTERY TECHNOLOGY SUPPORT

- **Battery Models**
  - Ni-Cd
  - Ni-H_2
  - Li-Ion – support efforts with NRO

- **Radiation Tolerance Testing**
  - Evaluate suitability of aerospace design cells for deep space missions
    - Li-Ion
    - Super Ni-Cd Cells

PRIMARY BATTERY TECHNOLOGY

OBJECTIVE:

- Improve performance, quality, safety and reliability of Li primary battery systems

PRIMARY BATTERY TECHNOLOGY TASK:

- Safety controls for lithium cells

SAFETY CONTROLS FOR LITHIUM CELLS

OBJECTIVE:

- Increase short circuit hazard tolerance of Li primary cells - internal cell short could result in a catastrophic failure

APPROACH/STATUS:

- Address LiBCX C, D and DD cell designs
- Reduced molarity of electrolyte - reduce capability to sustain high short circuit current for extended time
  - Determine minimum concentration to maintain capacity requirements
  - Reducing short circuit current to prevent venting or rupture
- Performance, abuse, shelf life determinations performed for qualification of cells with reduced electrolyte levels
- Levels established for C and D – unable to certify improved DD cell
- Investigate hazard controls for other Li cell chemistries (Li-CF, Li-SOCl2, Li-MnO2, Li-FeS2)
  - Shut-down separator of the Eagle-Picher Li-CF
  - Low molarity Li-SOCl2 cells
- Evaluation of Li-FeS2 AA commercial cells as replacement for alkaline AA cells
  - Better voltage control, more capacity at higher rates, lower temperature operation

SUMMARY REMARKS

- **NASA-wide, coordinated program**
  - **Promotes communication and cooperation between NASA Centers**
  - **Covers Battery Systems, Primary and Secondary Batteries**
  - **Mechanism for addressing battery and cell related issues as they arise**

- **Well integrated program complements battery related developments funded elsewhere in the agency**
  - **Battery Program integrated with mission and technology development programs**
  - **Provides verification of technology developments funded by other programs**
  - **Provides tools to aid in determining reliability of aerospace batteries and to aid in performance predictions for NASA missions**

- **Direct Benefits to NASA Missions**
  - **Battery test bed, test programs contributed to the development of operational strategies for batteries on missions such as UARS, GRO, EUVE, TOPEX**
  - **Developed database and validated technology that has been selected for numerous NASA missions**
  - **Developed safe batteries for manned applications**

NASA AEROSPACE FLIGHT BATTERY SYSTEMS PROGRAM

Program Participants

- Jeff Brewer – MSFC
- Bobby Bragg - JSC
- Ratnakumar Bugga – JPL
- Barbara McKissock – GRC
- Gopal Rao – GSFC

- Additional support from other individuals at respective centers

Performance of Li-S™ Cells :

Under USABC Dynamic Stress Test (DST) and LEO Regime

2002 NASA Aerospace Battery Workshop

November 19 -21, 2002

Joon Kim (SION POWER CORPORATION) and

Rick Kettner (**SPECTRUM**ASTRO)

Product Attributes

Rechargeable Li-S Cells

Lightweight (lithium & sulfur) : Higher specific energy density than Li-ion

Rate capability exceeds Li-Ion

Environmentally benign

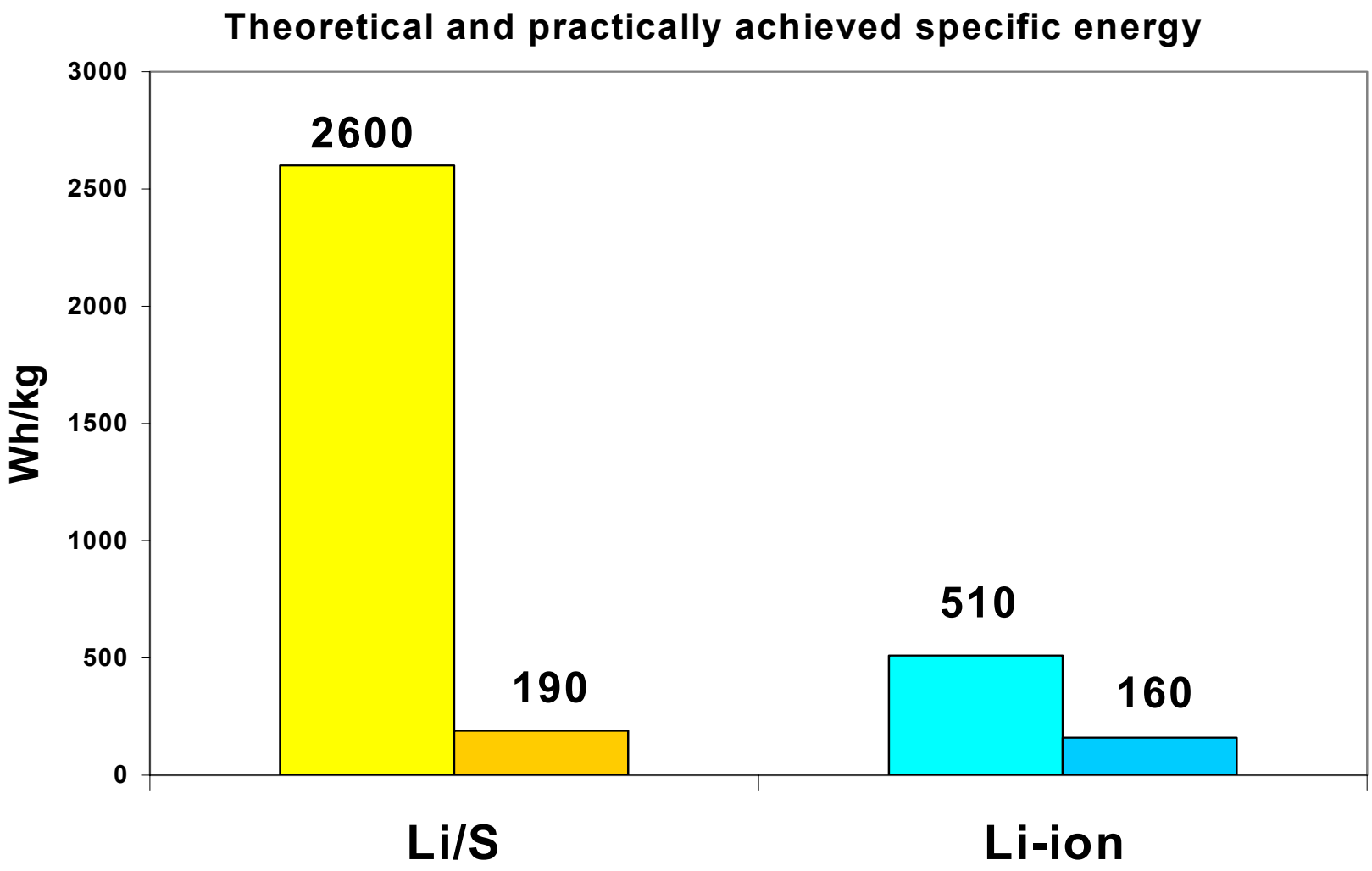
Low Material Costs

Technology Can be applied to:

Primary Batteries

Super capacitors

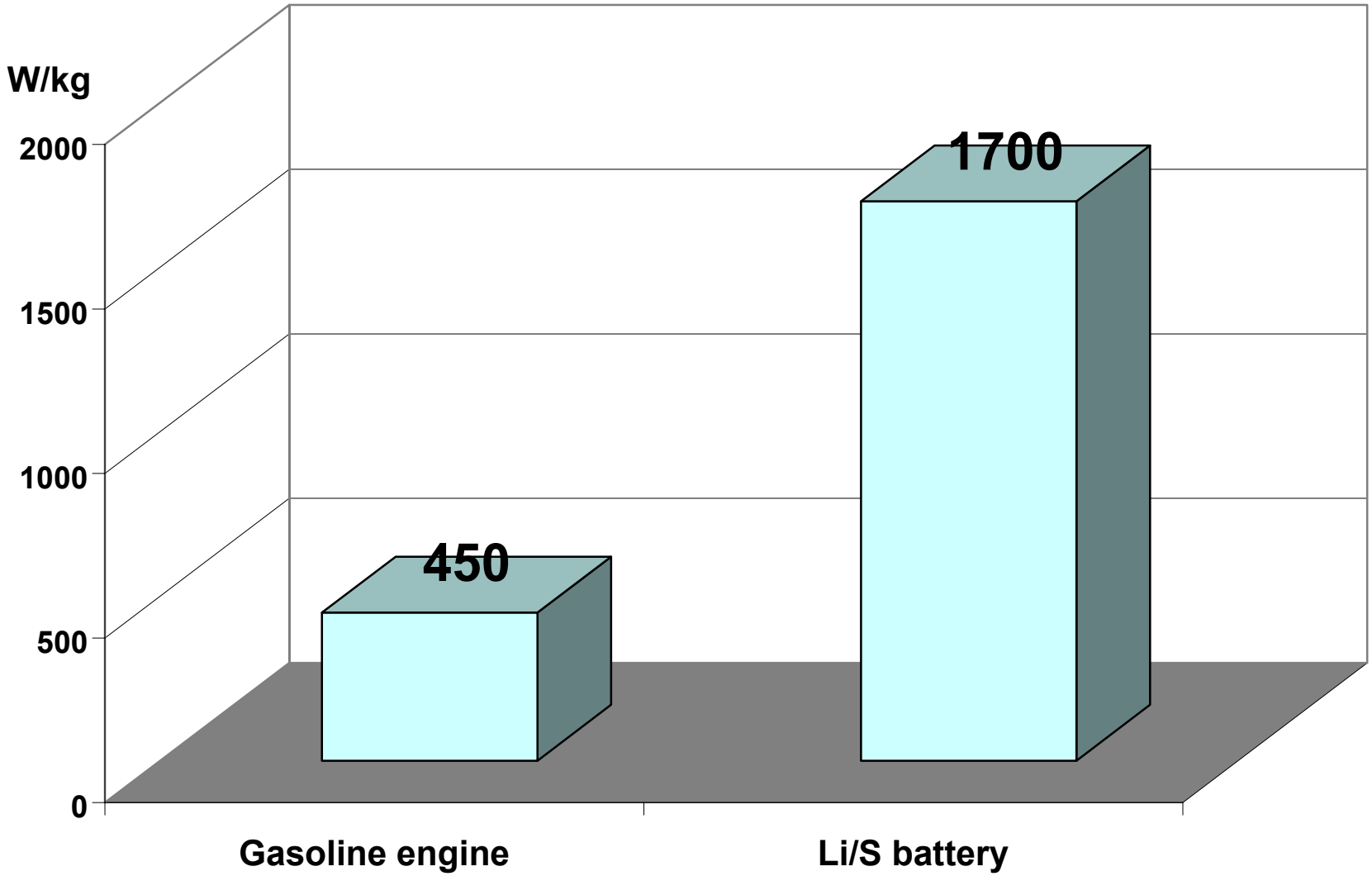
Why Li/S ?


Theoretical and practically achieved specific energy
Wh/kg
3000
2500
2000
1500
1000
500
0
2600
190
510
160
Li/S
Li-ion

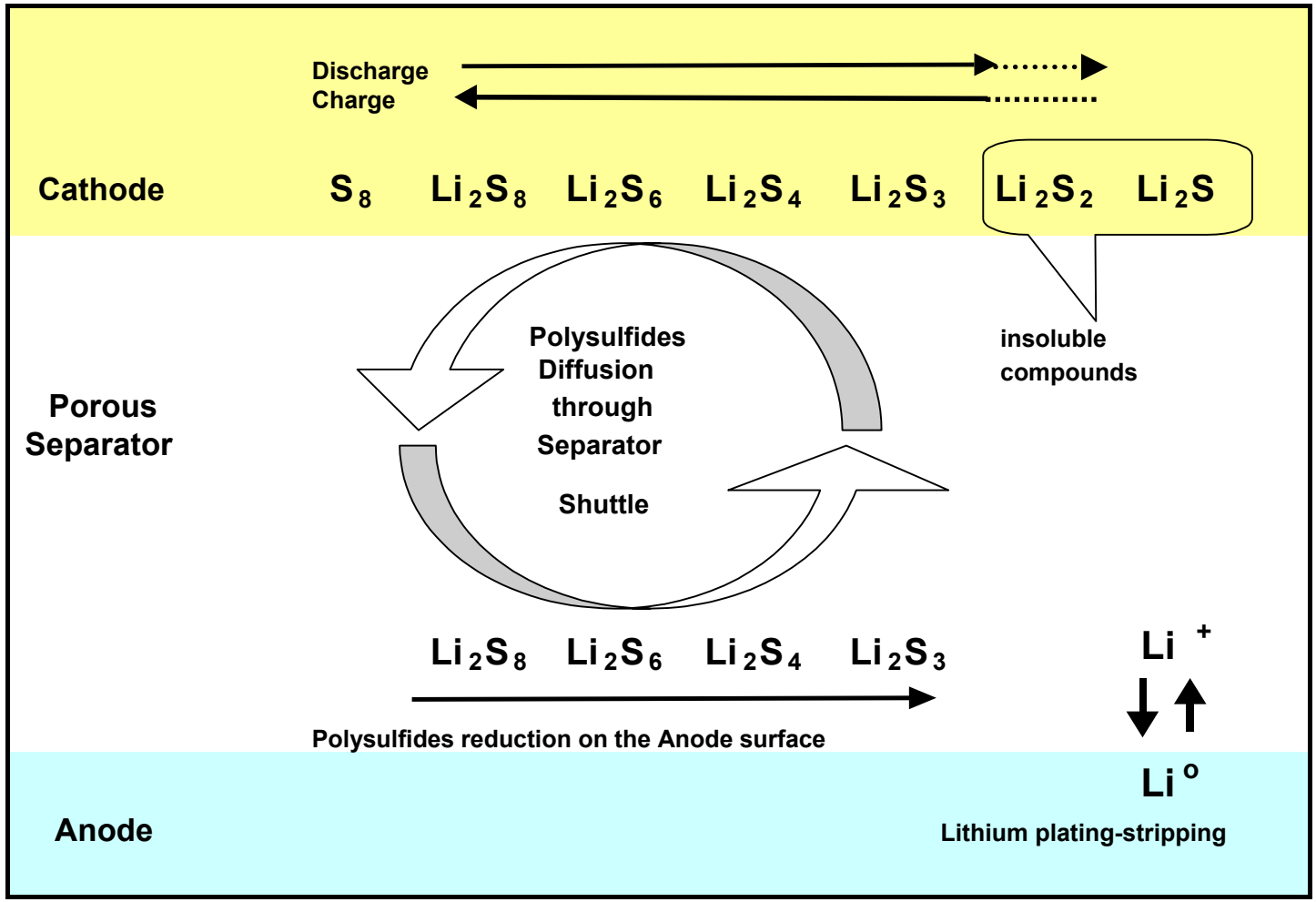
SPECTRUMASTRO

SION POWER

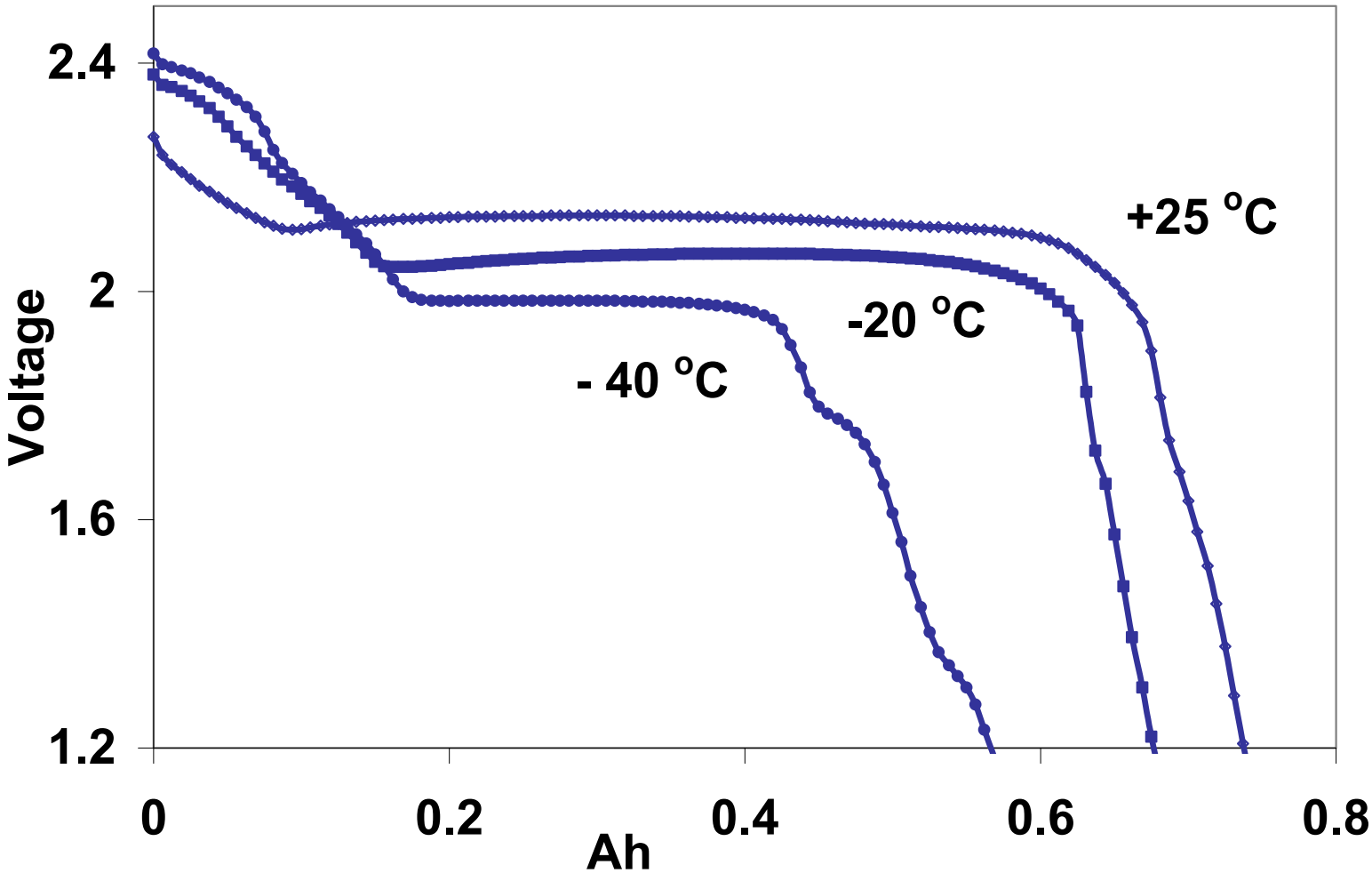
Maximum specific power, W/kg



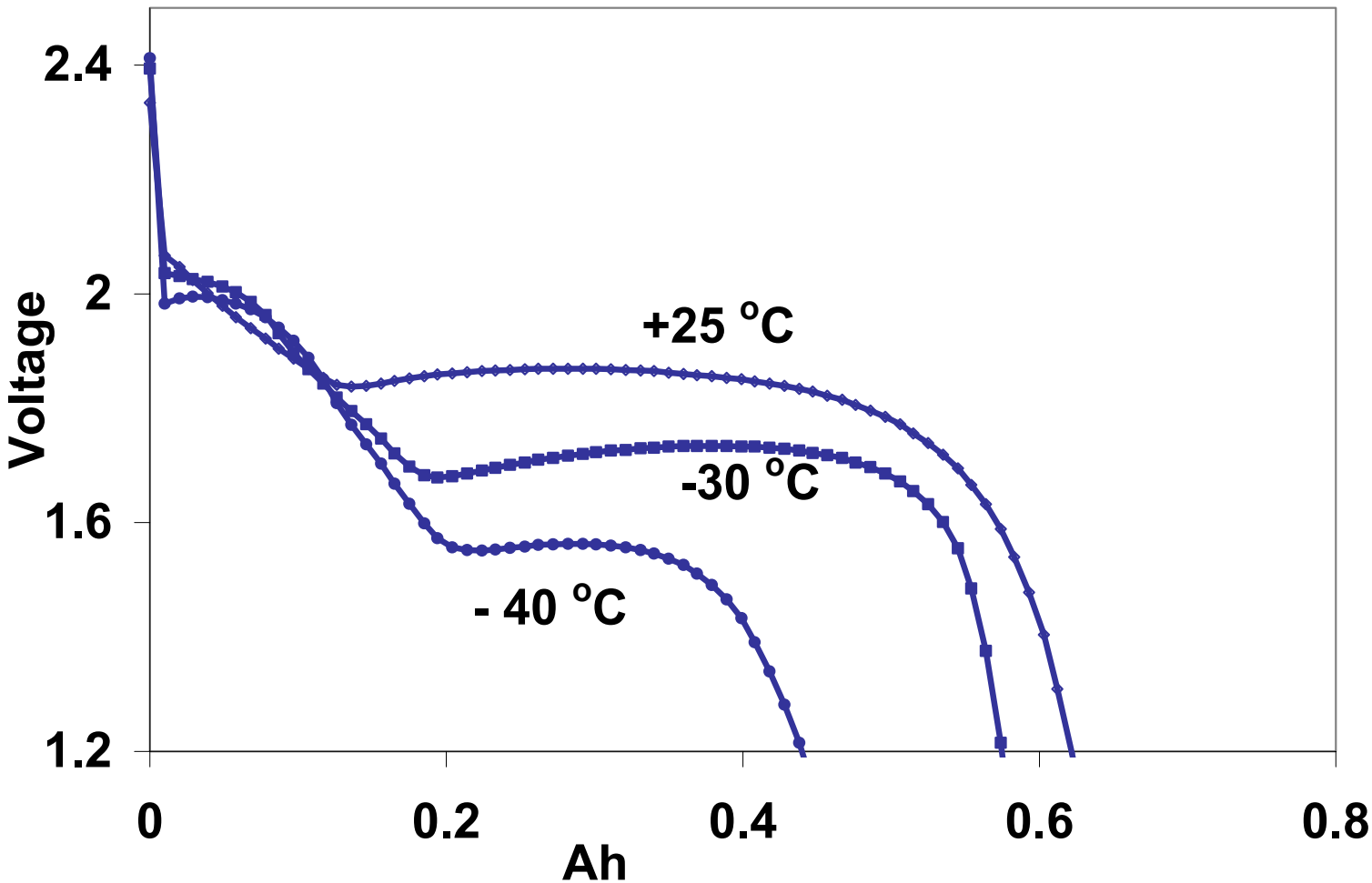
How it works?
Active Materials Transformation Diagram



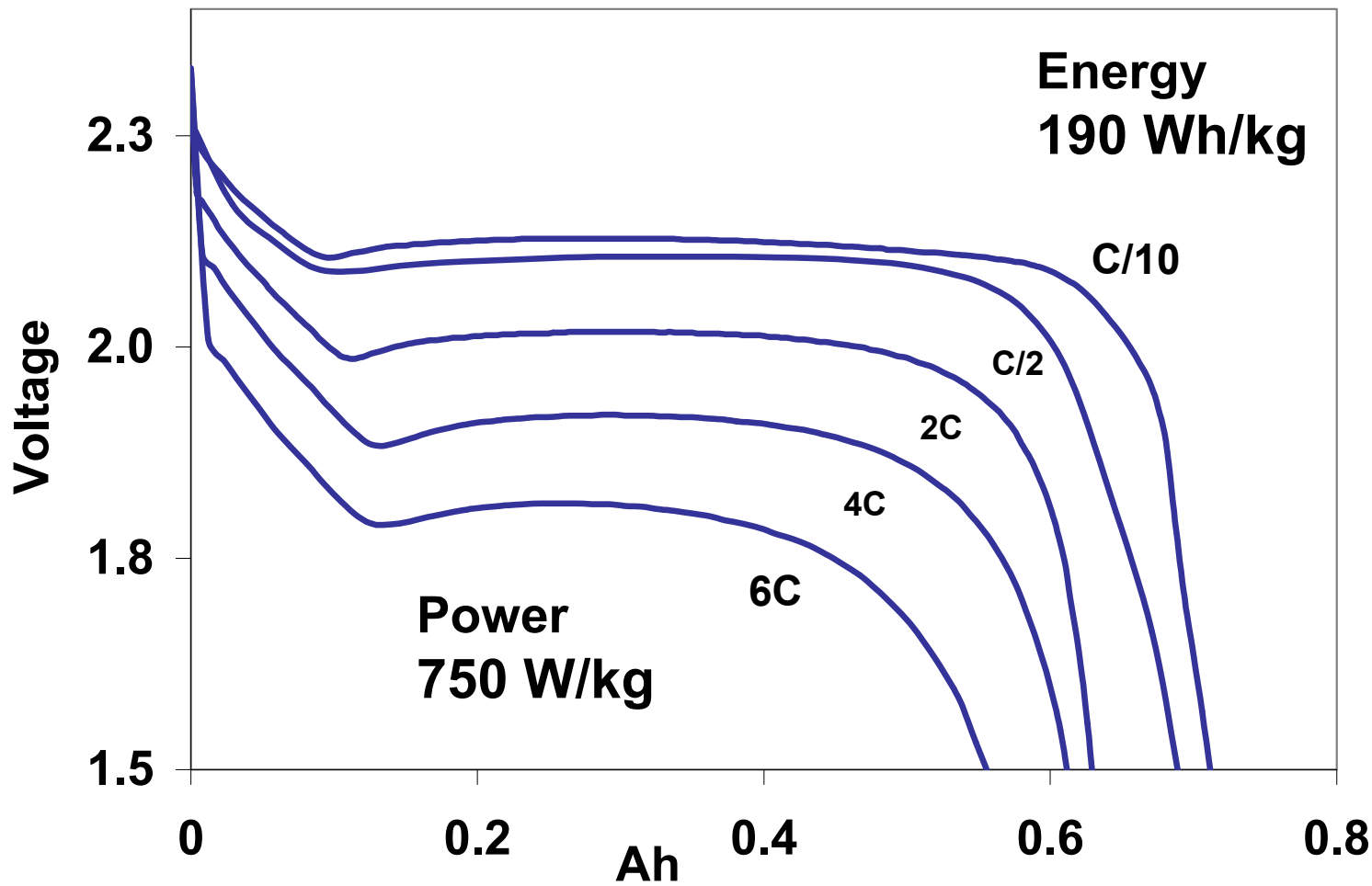
Discharge profiles at C/10 rate



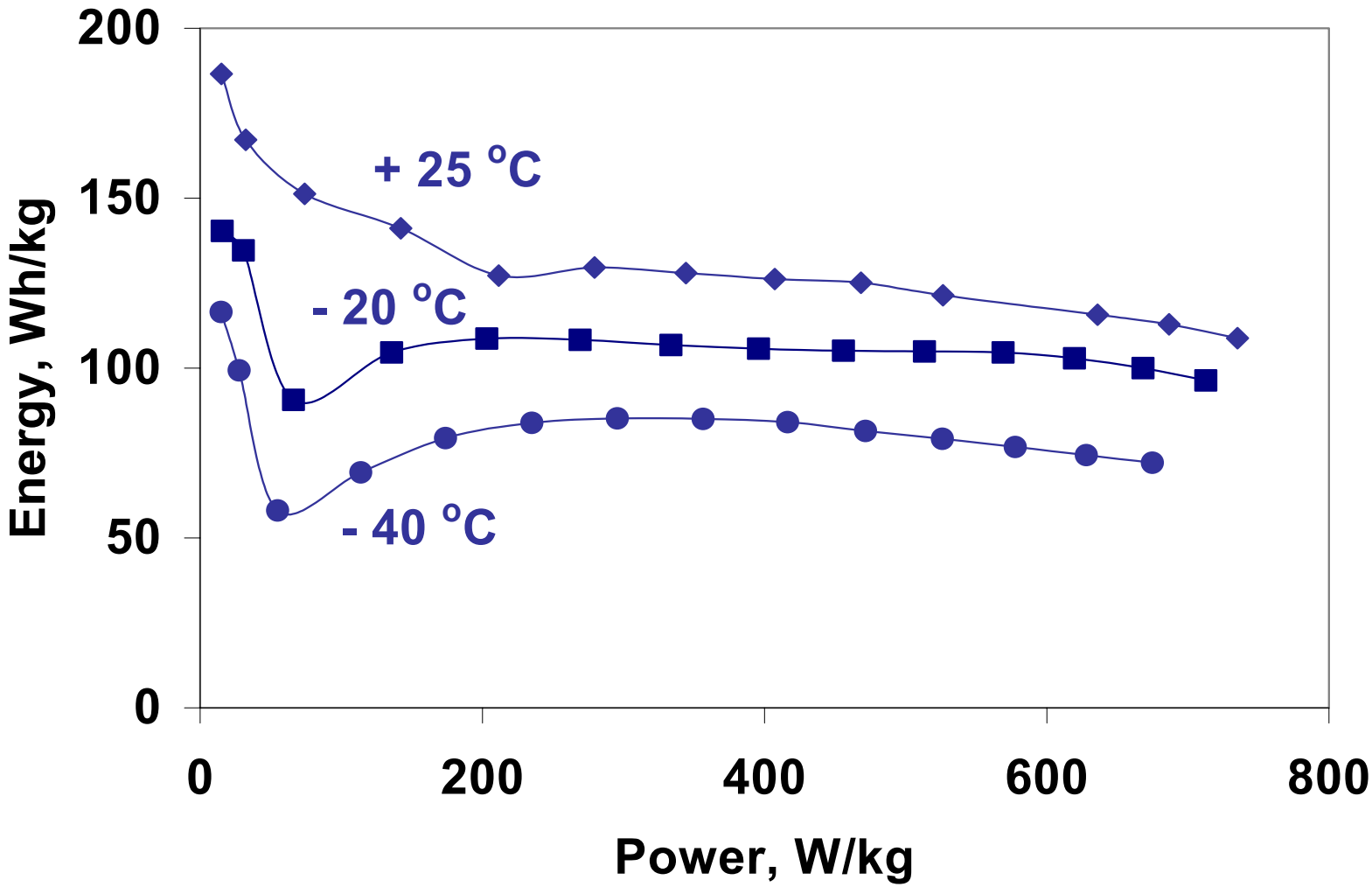
Discharge profiles at 5C rate



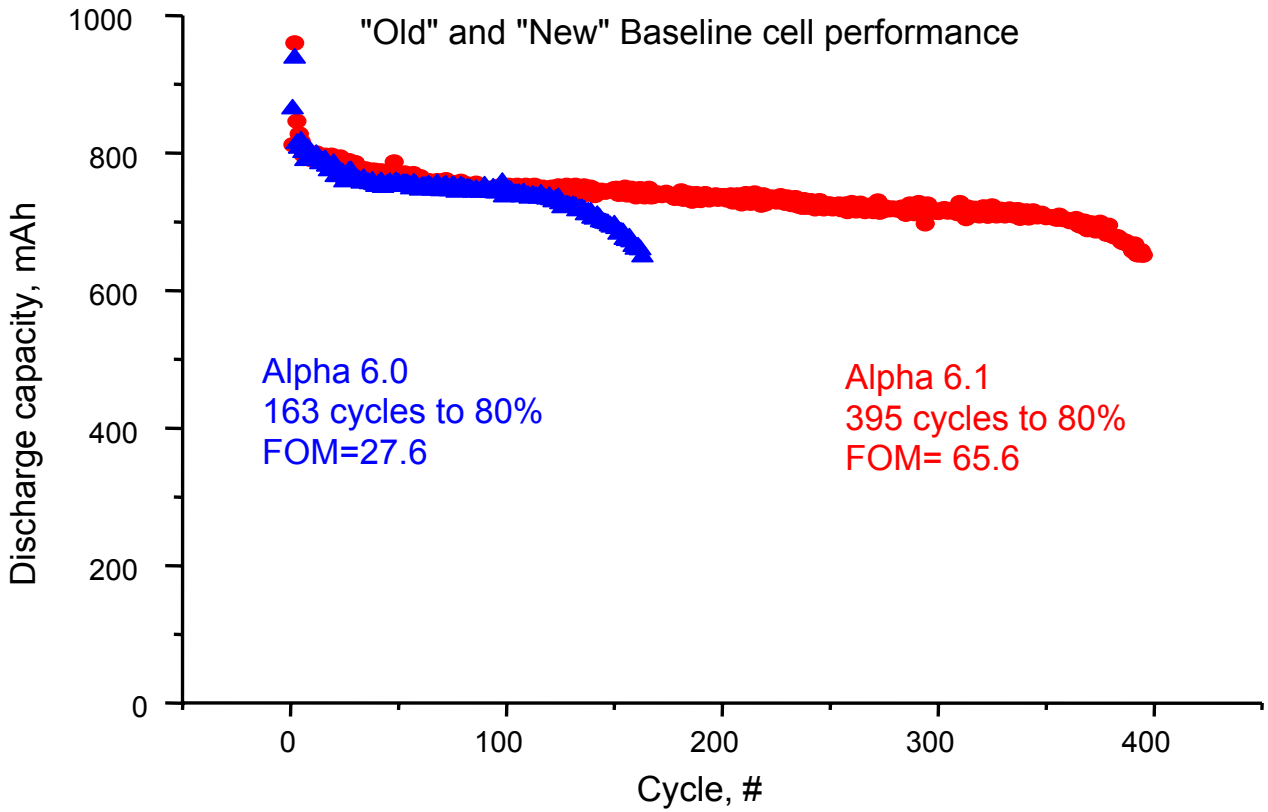
Room temperature discharge profiles at different rates



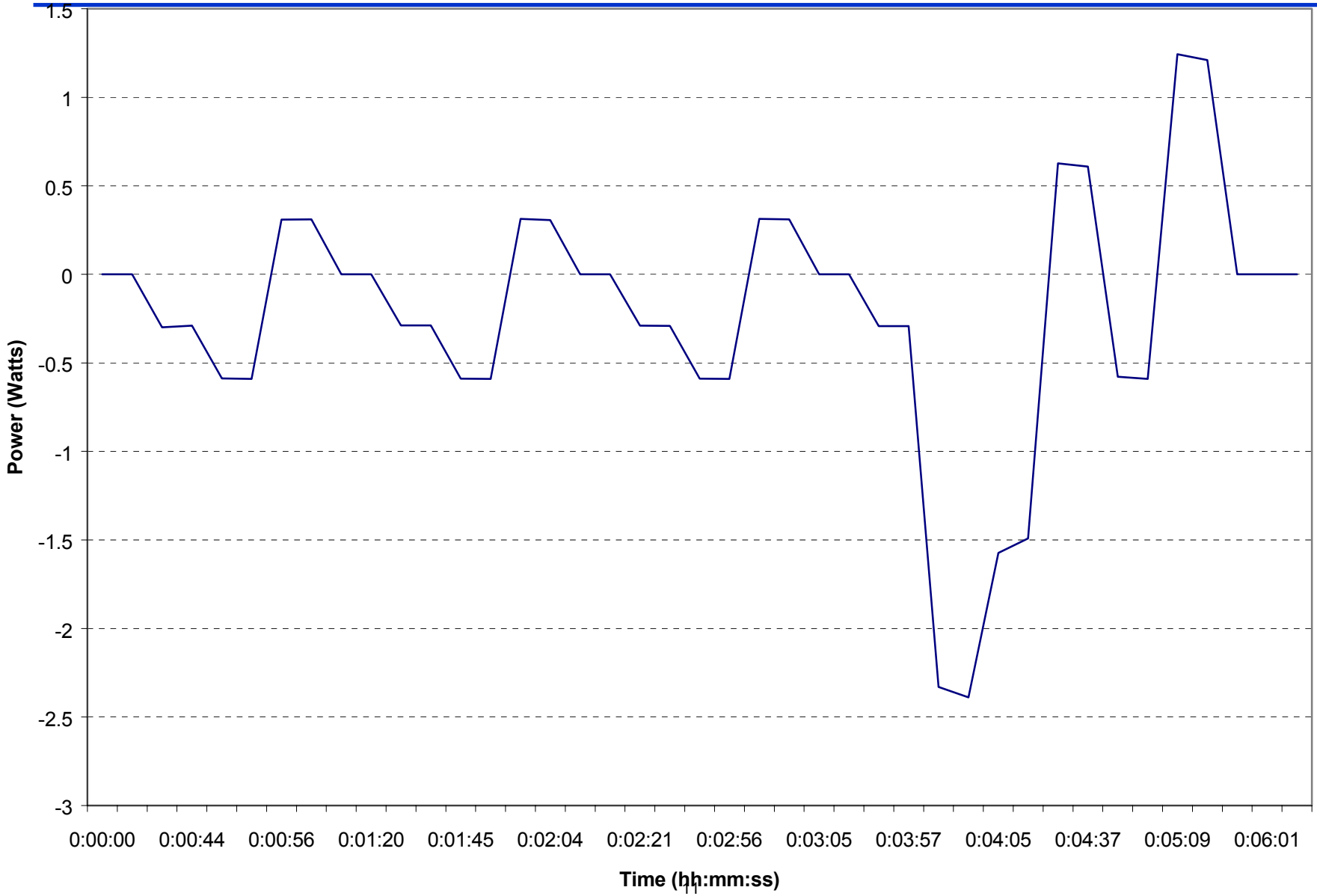
Ragone plots at different temperatures



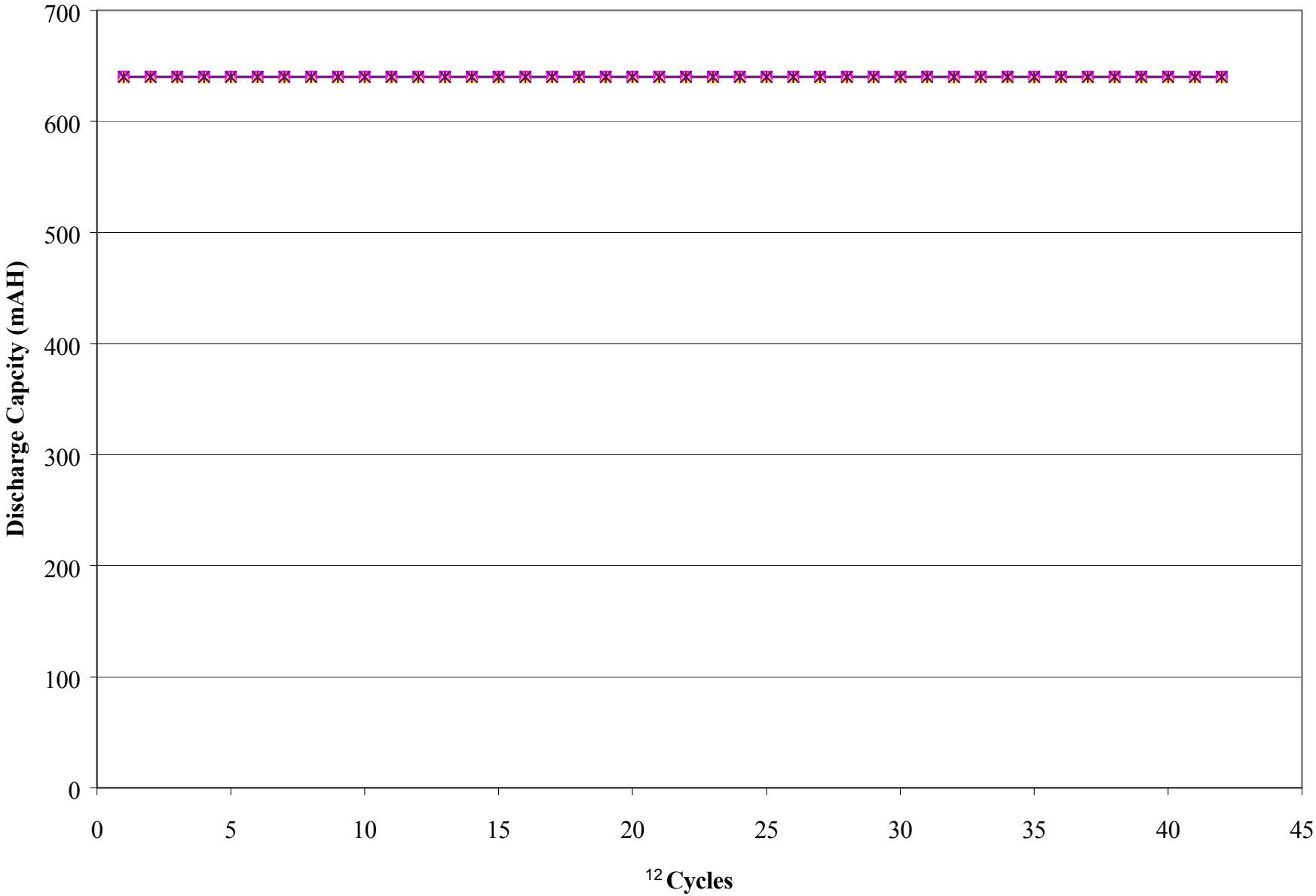
Cycle Life Evolution of Prototype Li-S Cell



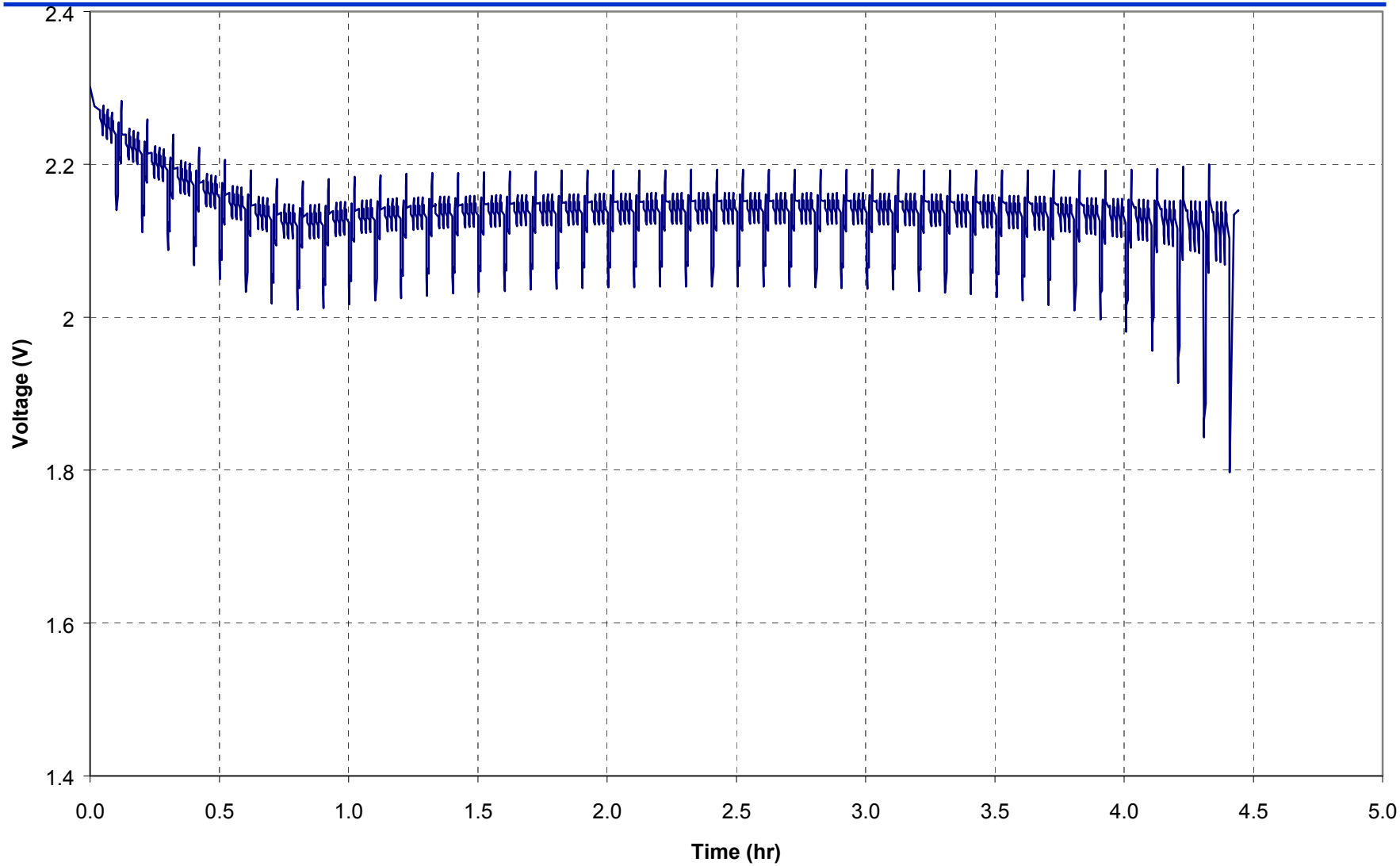
Power Profile of a Federal Urban Driving Sequence (FUDS) in a single DST240 cycle



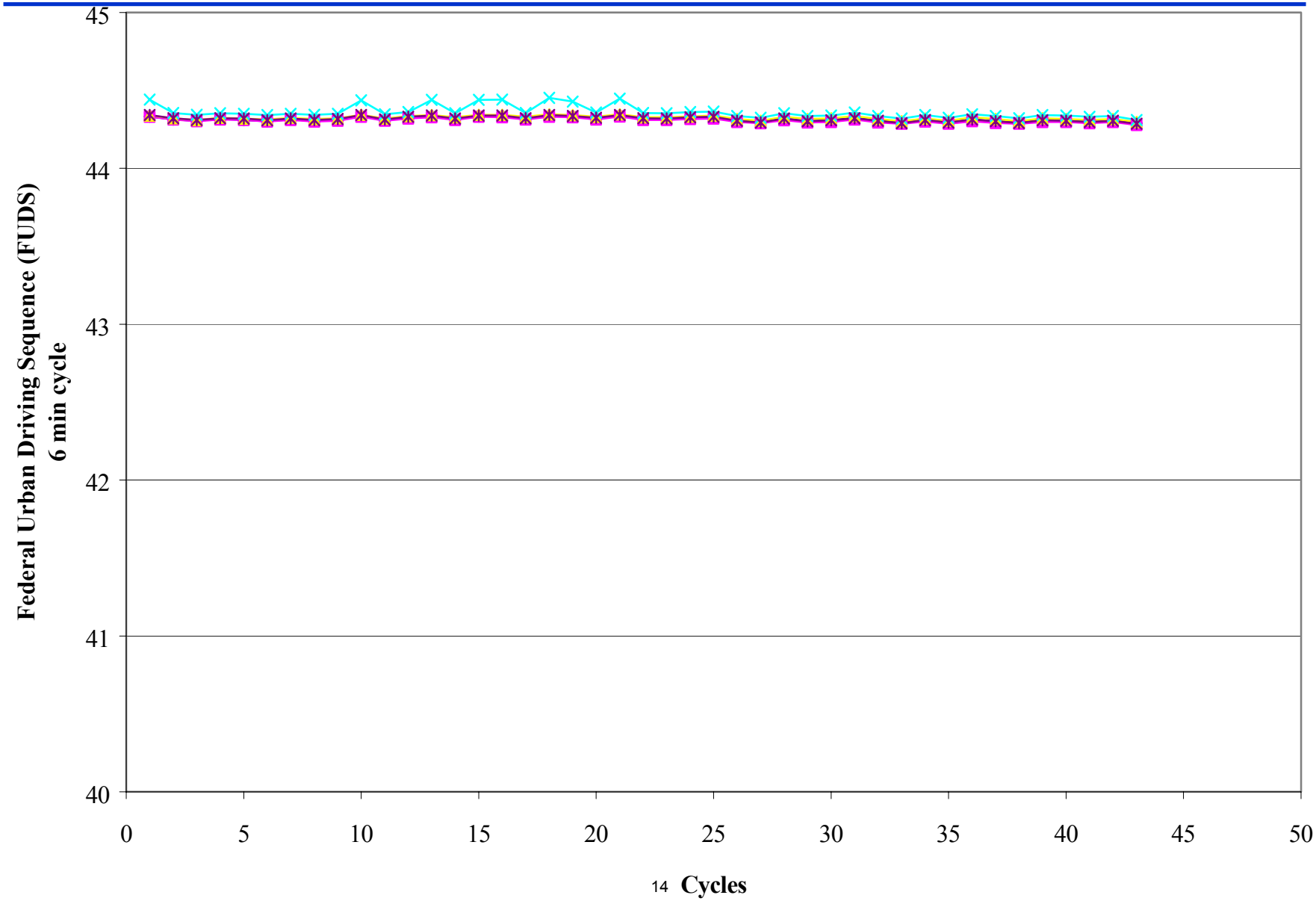
80% DoD DST_{240} Cycle Life Test (5% Over Charge)



Voltage vs. Time Curve During DST_{240} Life Cycle (at Cycle 9, 80% DOD)



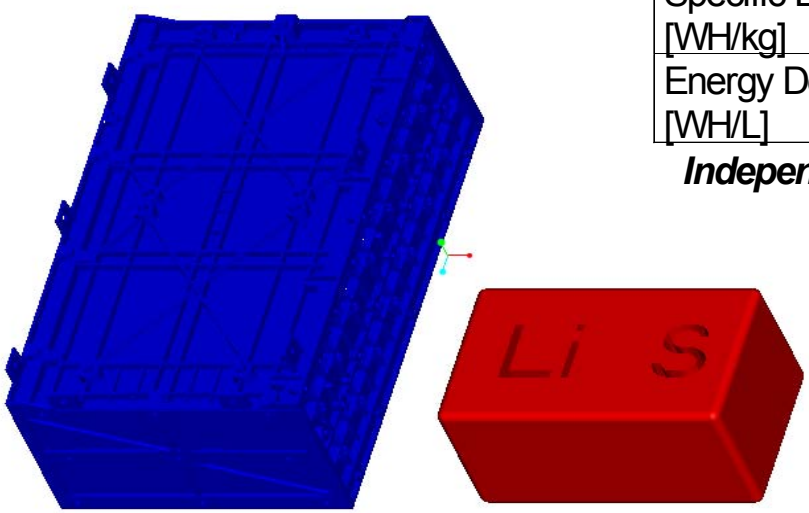
Number of FUDS vs. Cycle Life
USABC DST $_{240}$ (80%) Variable Power Test



144V HEV Battery System Comparison of NiMH vs Li-S™

Characteristic	NiMH Battery		LiS Battery Projection From Unit Cell	Advantage LiS vs Insight
	INSIGHT	MPS		
Mass [kg]	27.8	22.9	6	4.6
Volume [liters]	22.7	18.4	5.1	4.4
Specific Energy [WH/kg]	26	25	140	5.4
Energy Density [WH/L]	32	32	170	5.3

Independent test data from AeroVironment on Honda Insight



MPS Battery
Actual

Lithium Sulfur Battery
Projected

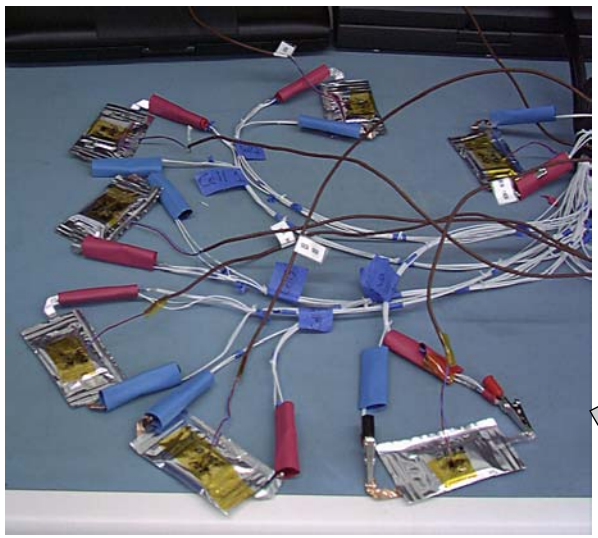
800 mAh Cell Cycling – Test Flow

- Currently 3 Cells in Test Using LEO Profile
- 800 mAh Cells Cycled
  - Using Constant Current, 25% DOD (200 mAh @ C/2)
  - Recharged Using Constant Current (C/4)
- Monitoring Cell Voltage, Current and Temperature Throughout Cycling
- After 1600 Cycles, One Cell Was Capacity Tested (Recondition Cycle)
  - Remaining Two Cells Continued Cycling
  - Reconditioned Cell Resumed Cycling

- Cells Have Completed > 2400 Cycles To Date

Li-S Cell Cycle Testing (Cont'd)

Cells Individually Instrumented With Voltage, Current, and Temperature Monitors



Cells Then Placed Into Protective Enclosure For Cycling

Li-S Cell Cycle Testing (Cont'd)

Cell Stabilization

The Cells Were Initially Stabilized Using the Following Process

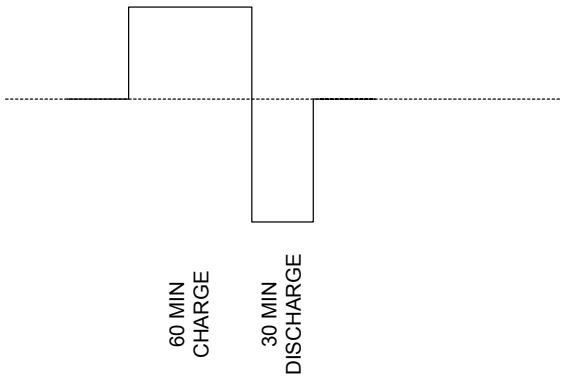
- **Charge @ 250 mA for 3.5 hours (210 min.) (875mAh)**
- **Discharge @ 350 mA until cell reaches 1.8V**
- **Measure and record capacity from this discharge**
- **Repeat steps until 800 mA-h capacity is reached**

Li-S Cell Cycle Testing (Cont'd)

Test Description

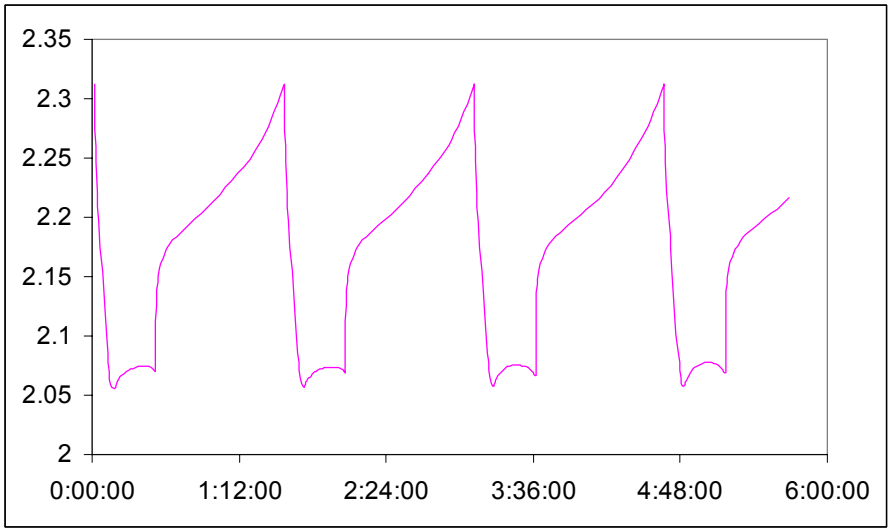
- **3 Sample Cells Were Placed in Cycle Testing**
- **Cycle Consisted of 90 Minute Period; 60 Minute Charge, 30 Minute Discharge**
  - **Roughly 25% DOD (Between 75 – 100% State-of-Charge)**

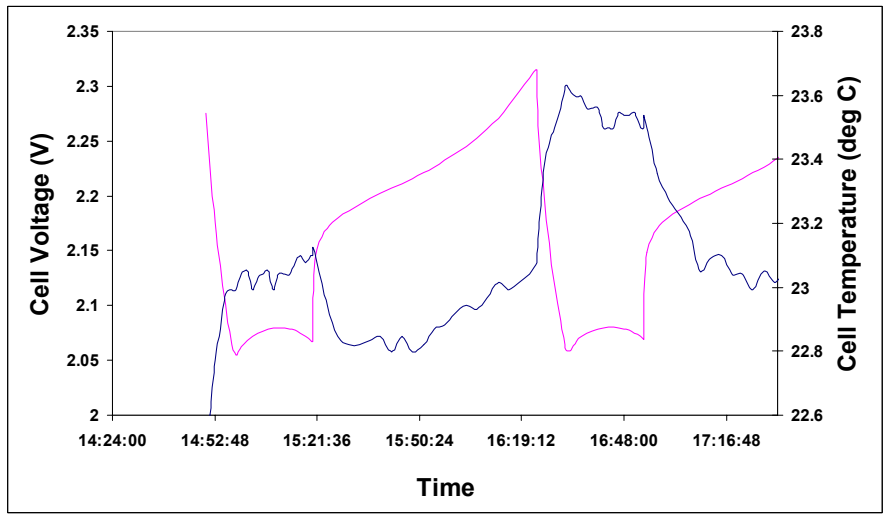
TEST PROFILE



- **Individual Cell Voltages, Currents, and Temperatures Were Captured Throughout the Cycling**

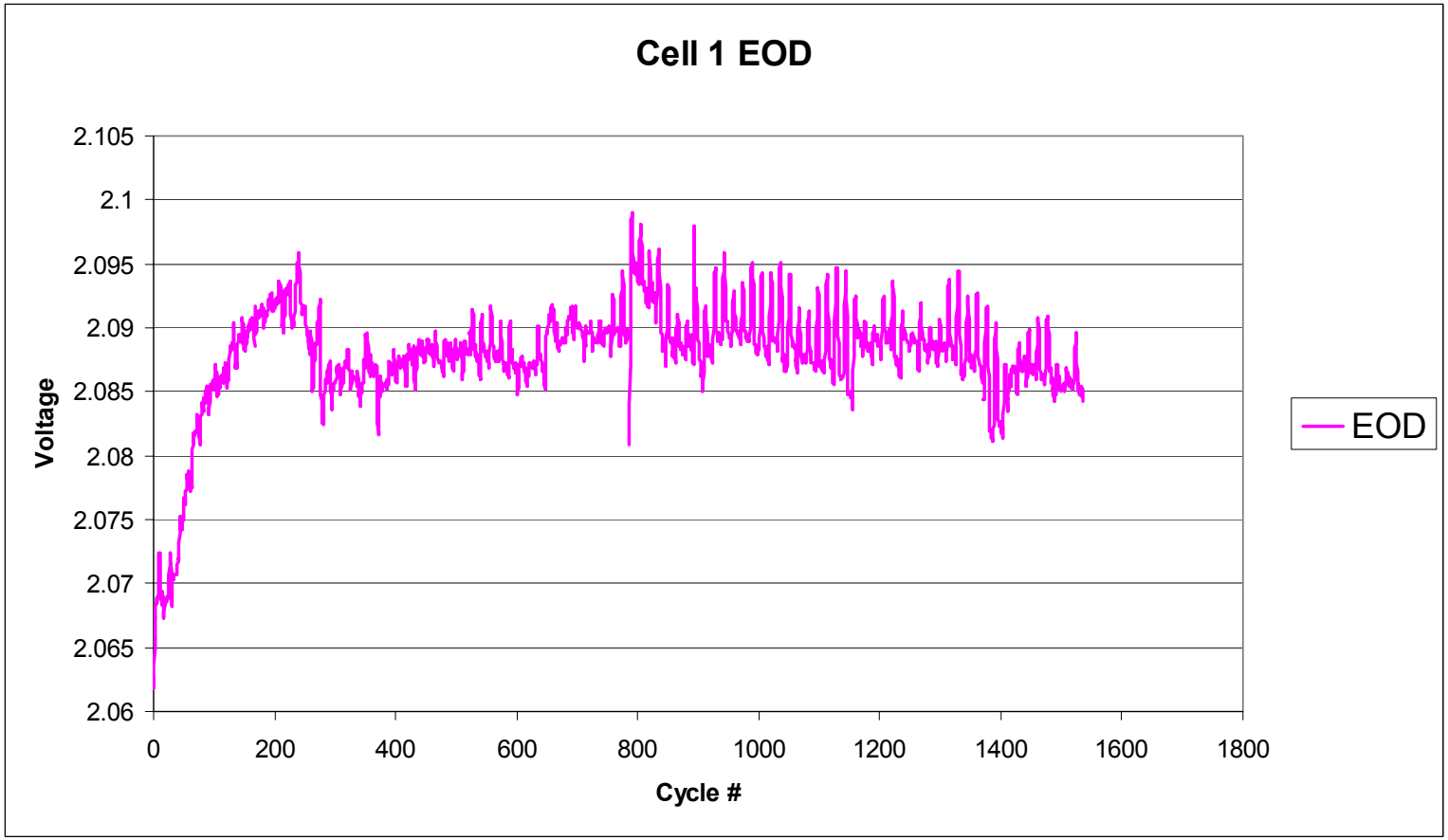
Continued Cycling of Current Cells





- **Voltage and Temperature Characteristics (~Cycle 1800)**
  - **Voltage Signature Consistent Cycle-to-Cycle**
  - **Temperature Shows Slight Decrease During Beginning of Charge (Endothermic?)**
  - **Temperature Rises Near End-of-Charge, Maintains During Discharge**

Li-S Cell Cycling – End-of-Discharge Voltage

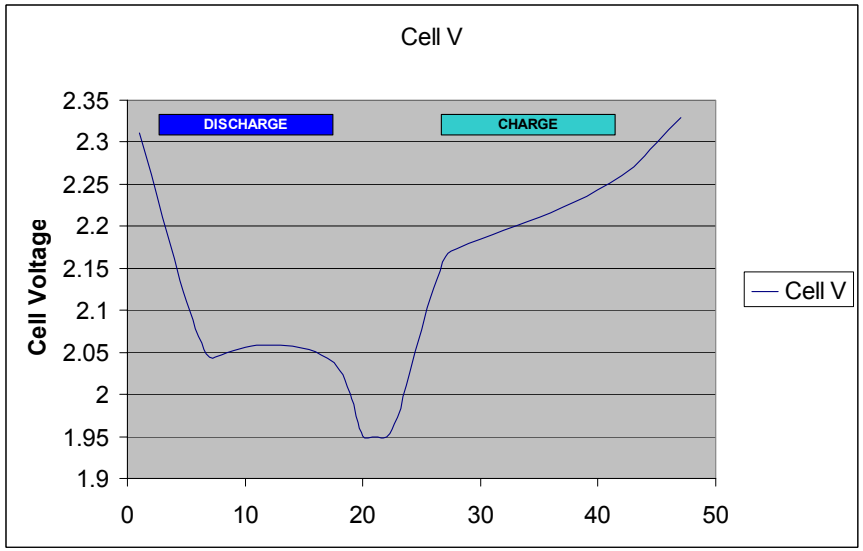


End-of-Discharge Voltage Shows Little Degradation

LiS Cell Reconditioning

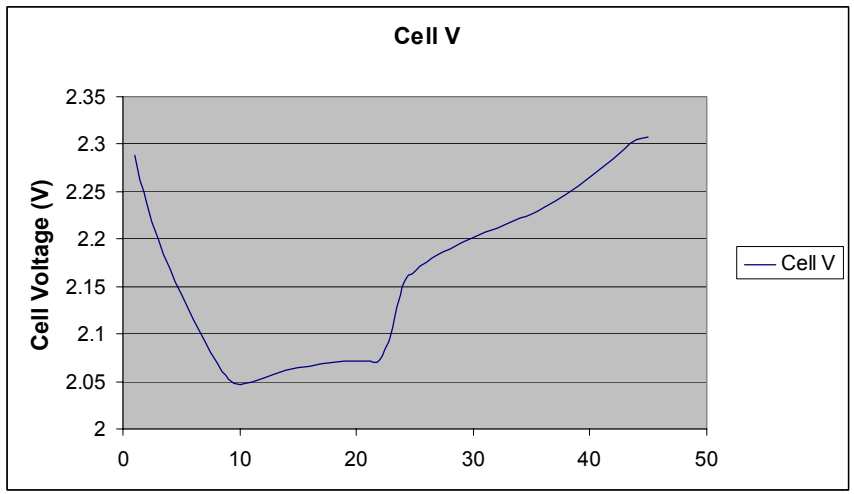
- **After Approximately 1800 Cycles, End-of-Discharge Voltage Began to Sag**

PRE-RECONDITION



- **Cell Completely Discharged, then Recharged and Cycling Resumed**
  - **Voltage Characteristic Restored**

POST-RECONDITION



Li-S Cell Cycling Observations, Plans

- **Observations**
  - **Cells Cycled To Date Have Performed Very Consistently**
  - **No Degradation Seen Until Approximately 4 Months of Continuous Cycling @ 25% DOD (1800 Cycles) except 1 cell. It was reconditioned and continued cycles.**

- **Future Plans**
  - **Continue Cell Cycling, Looking for Signs of Degradation**
    - **Voltage signature?**
    - **Temperature Rise, Drop in Efficiency?**
  - **Look at Multiple Cells in Series**
    - **What Additional Precautions should Be Taken?**
    - **Should Begin Looking at 28V Battery**
      - **Would Need Different Test Setup Including Charge Control Electronics?**
      - **Individual Cell Control? Monitors?**

Conclusions

- Sion prototype Li-S cells successfully demonstrated
  - (1) Very good power delivery capability at temperatures to -40°C
  - (2) Stable voltage profiles during DST cycle life test indicating potential electric vehicle applications
  - (3) Consistent cycle behavior under LEO test regime
  - (4) Cells can be reconditioned, if necessary
- Li-S technology offers solutions for high energy density (light weight or longer life per cycle) and high power applications

↓

We Are Targeting Opportunities

in Space and UAV (Unmanned Air Vehicle) Programs

Acknowledgement

USABC Grant to SION POWER (P.O. #103, 2002) is greatly acknowledged for partial support of this work.

LOCKHEED MARTIN

Safety and Abuse Testing of Energizer $LiFeS_2$ AA Cells

NASA Battery Workshop

November 19-21, 2002

JUDITH A. JEEVARAJAN

Lockheed Martin/NASA-JSC

L AURA BALDWIN

Lockheed Martin/NASA-JSC

BOBBY J. BRAGG

NASA-JSC

INTRODUCTION

- The $LiFeS_2$ test program was part of the study on state-of-the-art batteries/cells available in the commercial market.
- It was carried out in an effort to replace alkaline AA cells for Shuttle and Station applications.
- A large number of alkaline cells are used for numerous Shuttle and Station applications as loose cells.
- Other government agencies reported good performance and abuse tolerance of the AA $LiFeS_2$ cells.
- In this study, only abuse testing was performed on the cells to determine their tolerance.
- The tests carried out were overdischarge, external short circuit, heat-to-vent, vibration and drop.

Energizer $LiFeS_2$ Cells

L91

e^2 Lithium

Energizer L91 Cell Characteristics

Cell:	Height	Diameter
	1.988 in.	0.5 in.

Weight: 14.5 g

OCV: 1.8 V

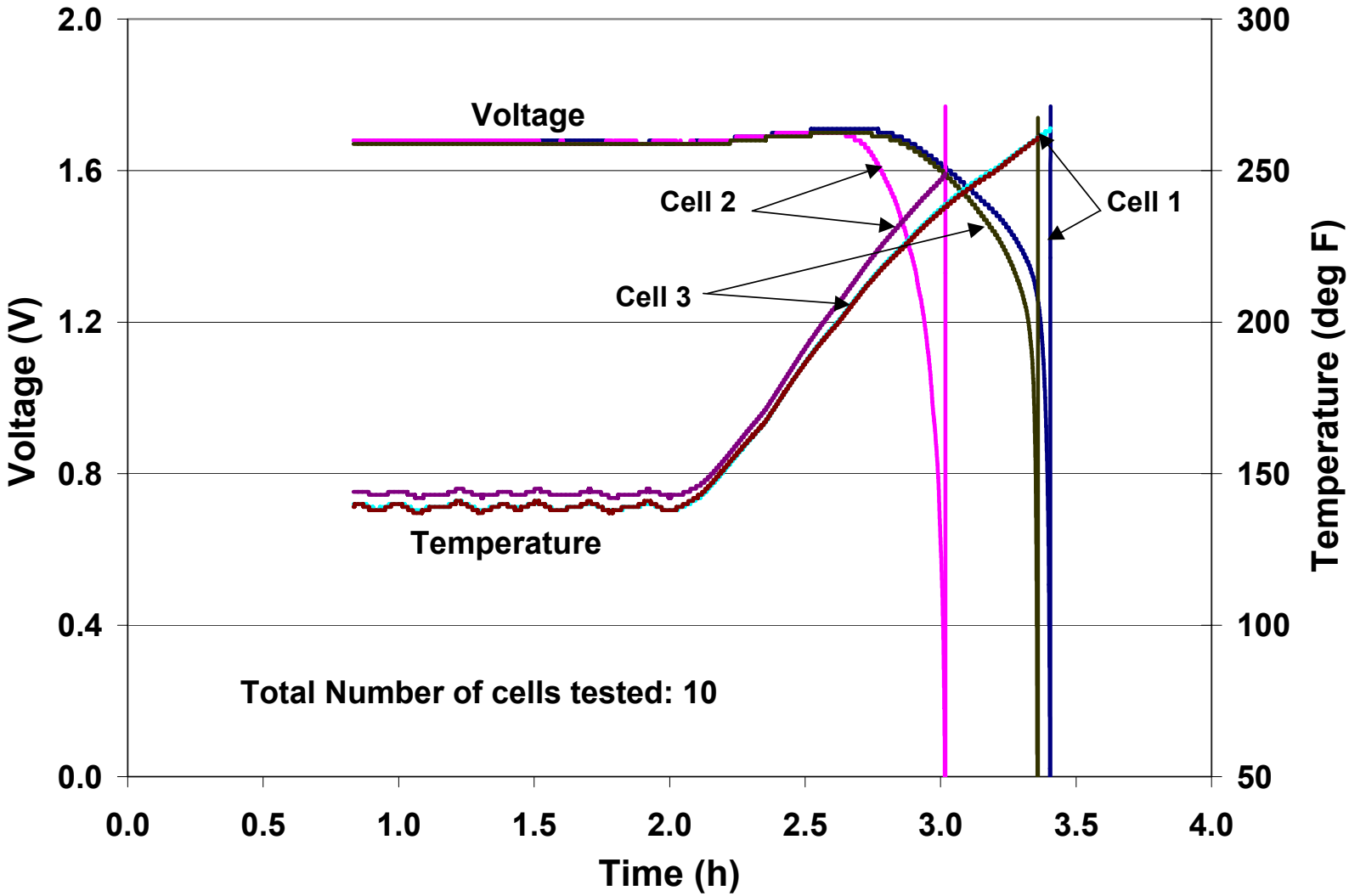
Capacity: 2.6 Ah

PTC : Operates between 85 to 95 ºC (continuous drain allowed 1.4 A)

Pressure Relief Vent: Operates between 120 to 130 ºC

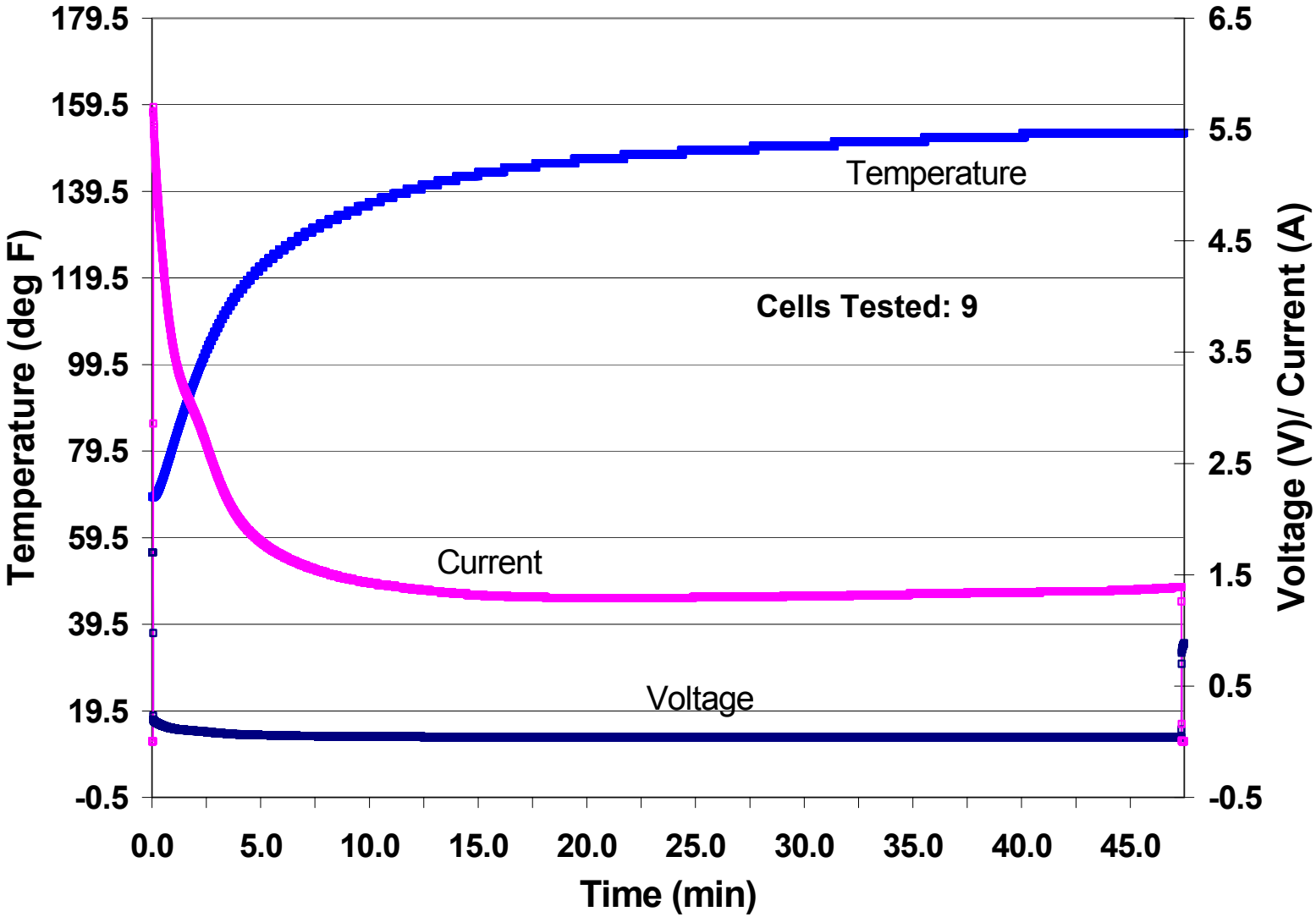
Heat-to-Vent Test Setup for the Energizer $LiFeS_2$ Cells

Heat-To-Vent Test on the Energizer L91 $LiFeS_2$ Cells



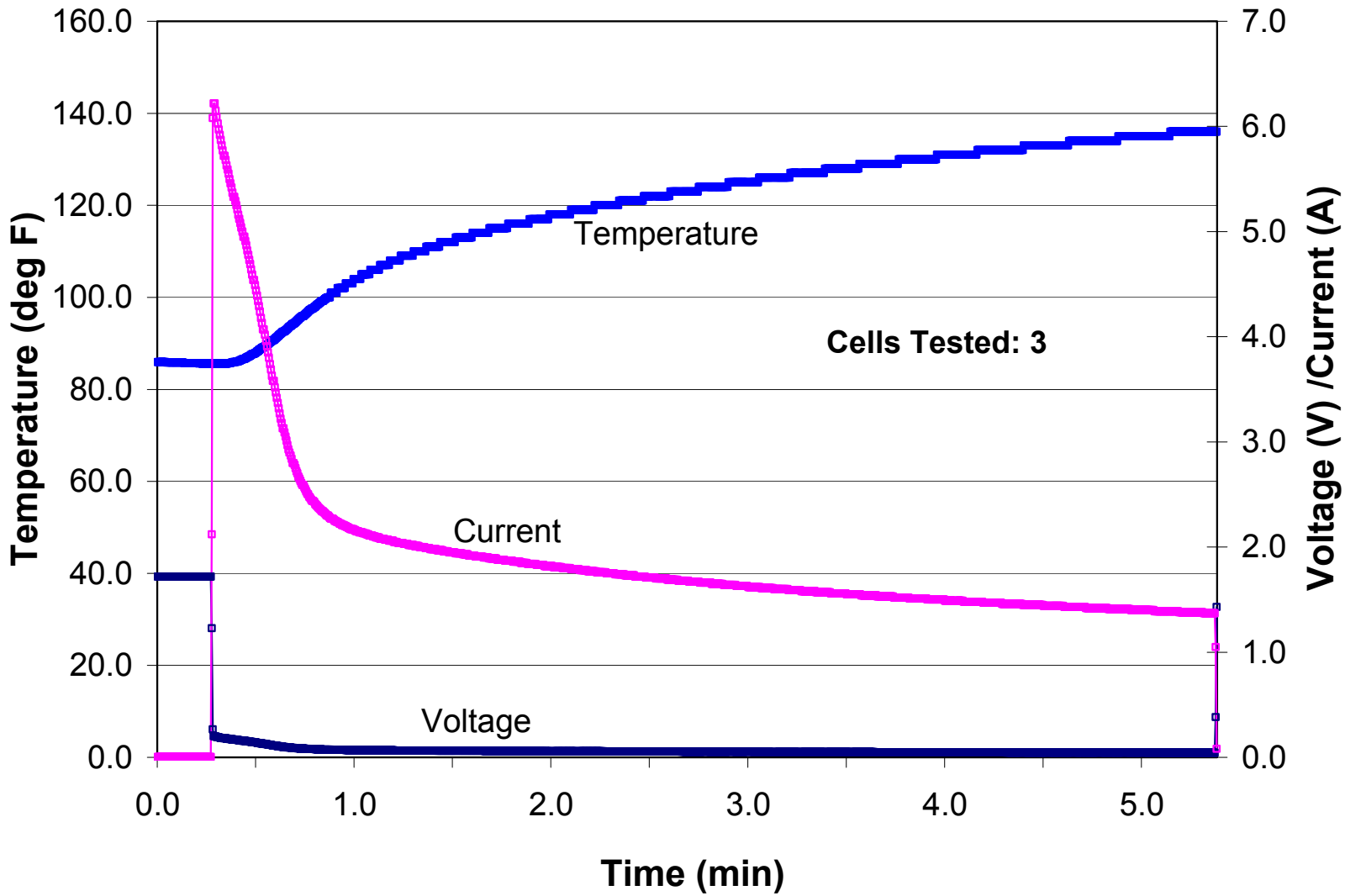
Heat-to-Vent Test on an Energizer $LiFeS_2$ Cell

Short Circuit Test on the Energizer L91 $LiFeS_2$ Cell



LOCKHEED MARTIN

Short Circuit Test on the Energizer e²Lithium $LiFeS_2$ Cell



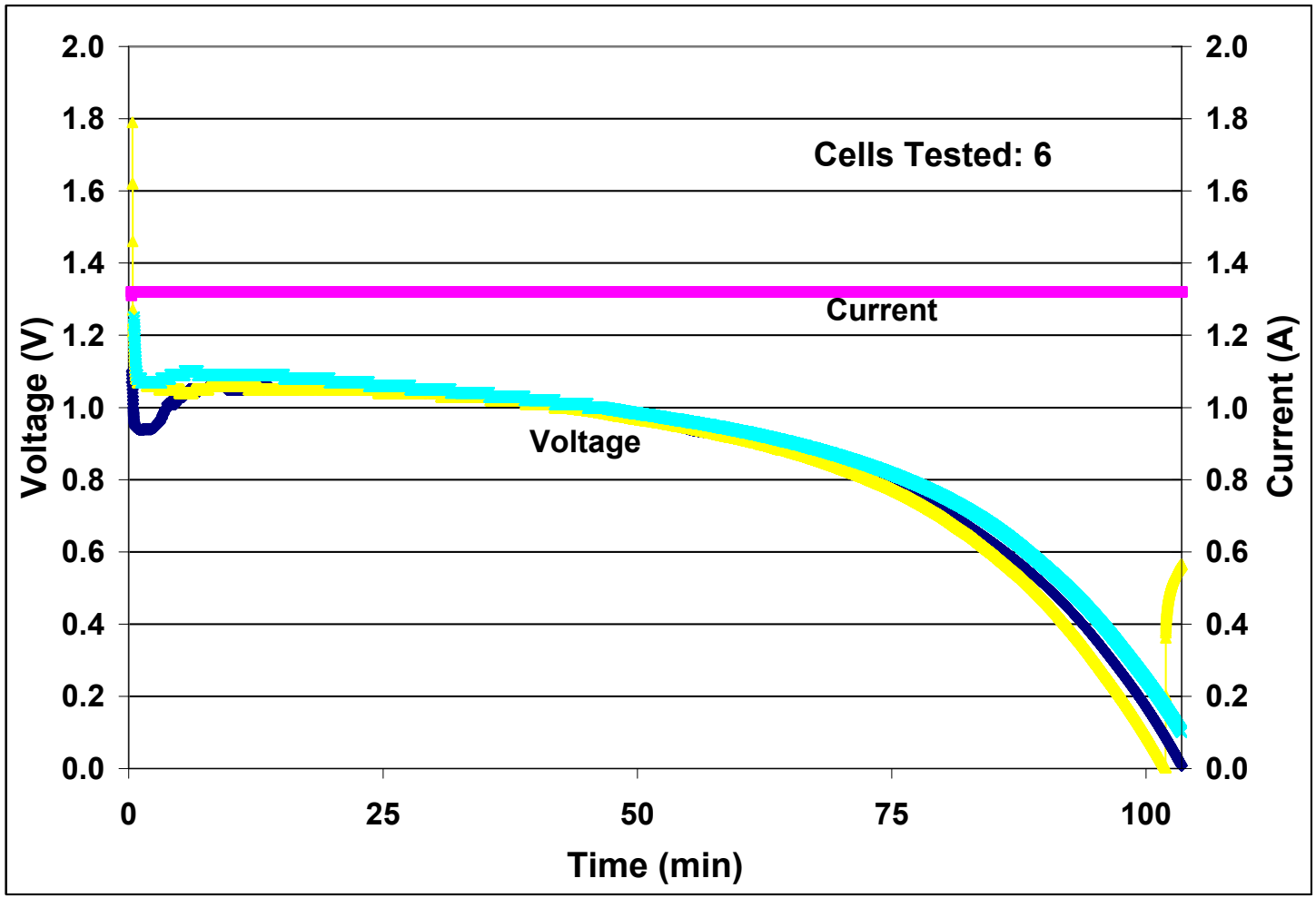
Overdischarge Test on the Energizer L91 and e^2 $LiFeS_2$ Cells

Load: 2.6 A

- Test was completed almost immediately on both models due to the activation of the PTC inside the cell.
- Six L91 cells and 3 e^2 Li cells were tested under this condition.

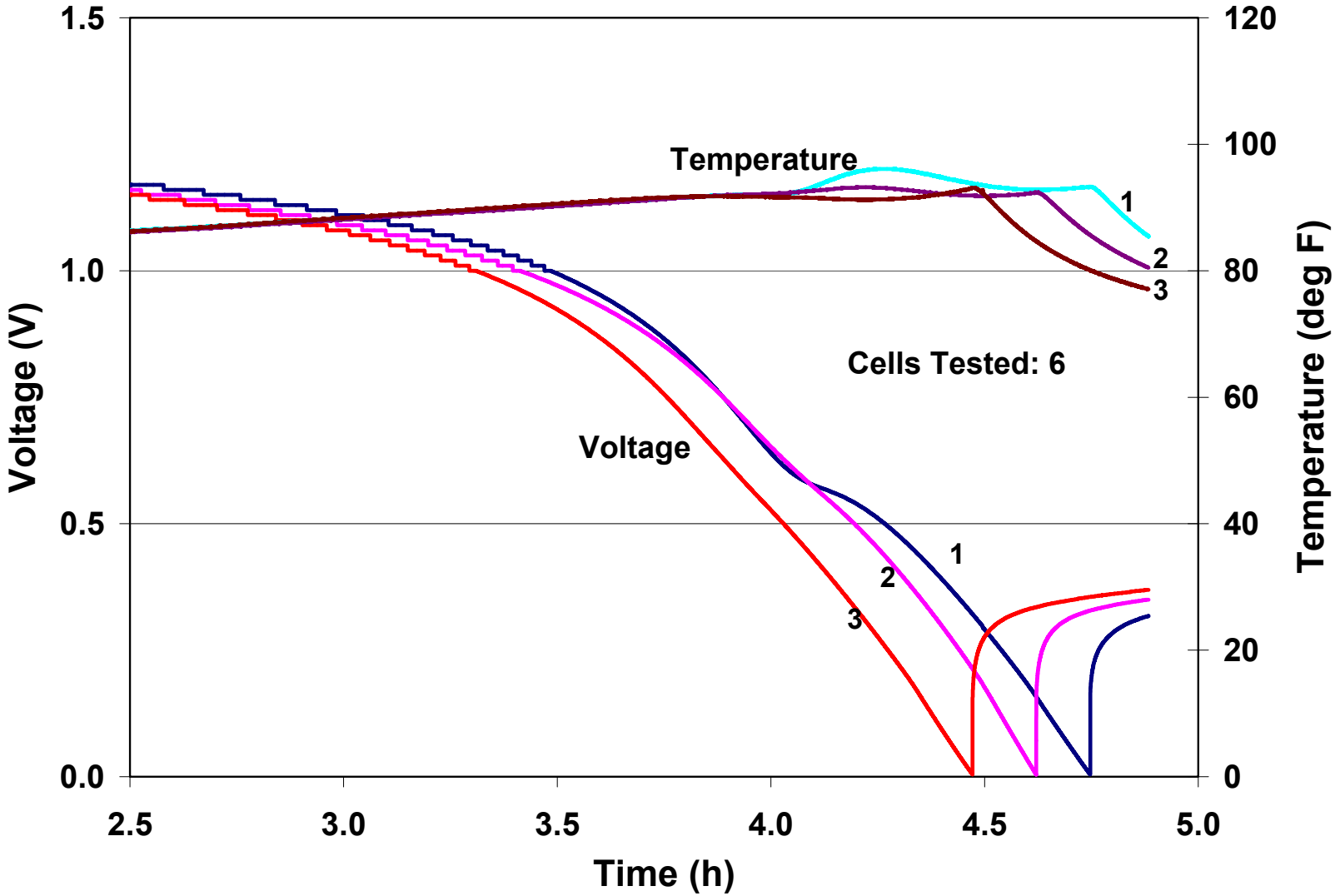
Overdischarge Test on the Energizer L91 $LiFeS_2$ Cells

Load: 1.3 A



Overdischarge Test on the Energizer L91 $LiFeS_2$ cells

Load: 0.52 A



Vibration Test for the Energizer L91 $LiFeS_2$ Cells

Frequency	Level
20-80 Hz	+3 dB/octave
80-350 Hz	0.1 g^2/Hz
350-2000 Hz	-3 dB/octave

- Four cells were vibrated for 15 minutes in each of the three independent axes.
- Post-vibration discharge was performed with 0.5 A to 0.9 V.
- Discharge capacities obtained for the four cells after the vibration in all three axes was 2.25 Ah, 1.75 Ah, 2.0 Ah and 2.0 Ah.

Drop Test on the Energizer L91 LifeS_2 Cells

- Three cells were dropped randomly from a height of 3 ft onto a concrete surface.
- Post-drop discharge was performed on the cells with 0.5 A to 0.9 V.
- Discharge capacities of 1.9 Ah, 1.95 Ah and 1.95 Ah were obtained from the three cells.

- Three cells were dropped randomly from a height of 6 ft on to a concrete surface.
- Post-drop discharge was performed on the cells with 0.5 A to 0.9 V.
- Discharge capacities of 2.1 Ah, 1.65 Ah and 2.05 Ah were obtained from the three cells.

CONCLUSIONS

- The Energizer L91 $LiFeS_2$ cells were evaluated under abusive conditions of overdischarge, heat-to-vent, short circuit, drop and high levels of vibration.
- The PTC in the cells prevents the cells from going into hazardous condition of venting or exploding during the overdischarge or short circuit test.
- The cells did not vent or explode during the heat-to-vent test.
- The cells gave reasonably good capacities after the drop test and vibration test.
- The new model of L91s which are called the e^2 Lithiums behave similar to the L91s on the short circuit and overdischarge tests.

ACKNOWLEDGMENT

Anita Thomas – LM / NASA-JSC – Cell DPA

Gerald Steward- NASA-JSC –vibration test

Long Life, High Energy Silver/Zinc Batteries

Ramesh Kainthla, Ph.D.
Brendan Coffey, Ph.D.
RBC Technologies

NASA Aerospace Workshop
Huntsville, AL
November 19, 2002

Presentation Outline

- Introduction to RBC Technologies
- Rechargeable Zinc Alkaline (**RZA™**) Systems

  MnO_2/Zn **Ni/Zn** **Ag/Zn** **Zn/Air**
- RZA Silver/Zinc Battery Developments
  - NASA Phase I and Phase II SBIR goals and results
  - Other silver/zinc opportunities

RBC Background

- Founded in 1989 to commercialize battery technology based on Ford discovery of rechargeable form of manganese-dioxide
- In 1999, RBC was awarded $3.8 million Advanced Technology Program by US Dept. of Commerce, NIST to accelerate RZA development
- Core competencies, rechargeable zinc, stable ion-blocking separator and cathode active materials
- In 2000, expanded RZA technology family to include nickel-zinc and silver-zinc
- RBC commercializes technologies through licensing and joint-venture agreements

Facilities and Staff

- College Station, Texas facility encompasses 10,000 square feet
  - full development capabilities to support the design and processing of batteries and materials
  - 400 channels of computer controlled electrical testing stations

- Battery Industry Depth - Over 110 years of professional battery industry experience: R&D, Engineering, Applications, Manufacturing, Marketing
- Extensive Corporate relationships: Electronics OEMs, battery manufacturers, materials suppliers, universities, National laboratories, agencies

Commercialization Activity Focused on Two RZA Systems

RZA System	Mn/Zn Manganese/Zinc	Ni/Zn Nickel/Zinc	
Positive electrode (cathode)	Bismuth-modified manganese-dioxide (BMD)	Nickel hydroxide	
Specific energy (wh/kg)	70-90	50-75	
Product Formats	Cylindrical AAA, AA, C and D, small (0.5 – 3 Ah) prismatic cells	15 Ah+ Ah prismatic cells and 12-volt batteries	Cylindrical sub C and D cells
Applications	Portable electronics, cameras, toys and games, radios and CD players, PDA's	42-volt hybrid and electric vehicles, standby power.	Power tools, lawn & garden tools., electric bike and electric scooter.

RBC TECHNOLOGIES

Quality Battery Solutions

Spiral Wound RZA Ni/Zn Battery

- Being developed with manufacturing partner
- Wide range of potential applications with performance/cost attributes intermediate between nickel-metal hydride and lead-acid batteries
- Higher cell voltage means fewer cells in series for a given battery voltage, (eg. 12 Volt battery uses 7 Ni/Zn cells vs 10 cells for either NiCd or NiMH)

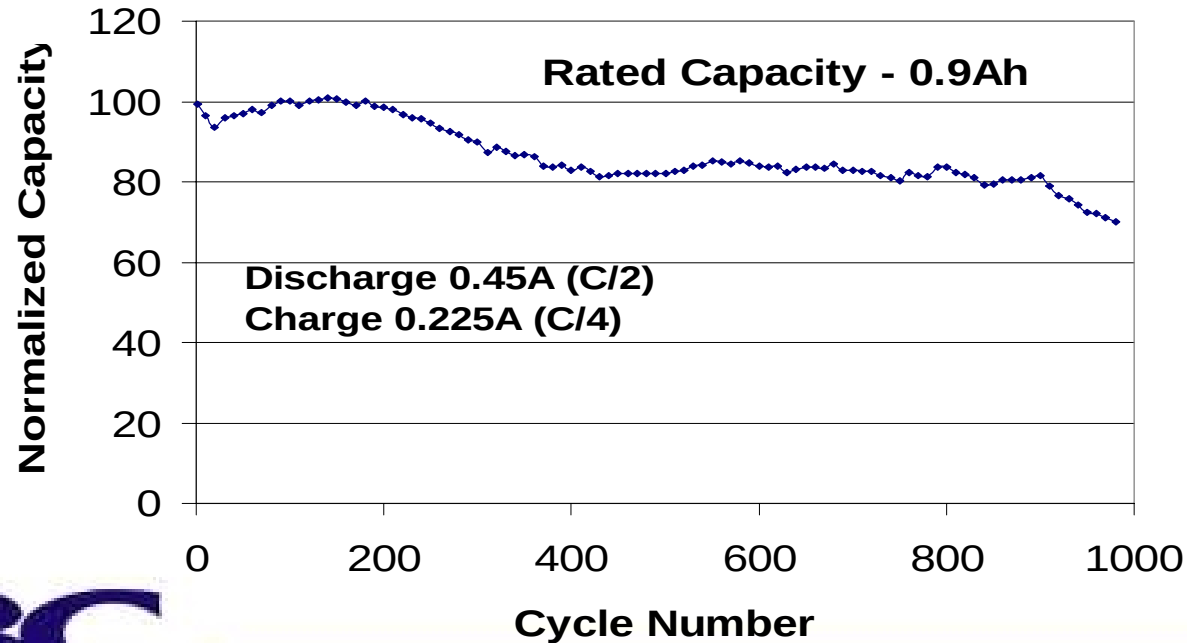
TABLE: COMPARISON OF D SIZE CELLS in 3 NICKEL ELECTROCHEMISTRIES

	NiCd	***RZA NiZn***	***NiMH***
Capacity (ampere-hours)	4.6	5.0	6.5
Operating Voltage (Volts)	1.2	1.65	1.2
Weight (g)	139	139	170
Watt-hours per kg	40	59	46
Watt-hours per liter	106	158	150

- For a given energy content an RZA Ni/Zn battery can be lighter, smaller and lower cost than the other nickel chemistries.

RBC-Ni/Zn Technical Innovation

- Anode formulation for minimal shape change, no dendrites, 1,000 cycles.
- Advanced low cost separator designs for dendrite prevention
- Charging algorithms to facilitate maintenance-free operation
- Developed innovative processes for continuous, uniform electrode manufacture



RZA Systems - Specific Energy

System	Specific Energy (Wh/kg)
Ni/Zn	55-80
$Mn0_2$/Zn	70-90
Ag/Zn	100-200

Silver-Zinc Electrochemistry

$$2AgO + H_2O + 2e \xleftrightarrow[\text{charge}]{\text{discharge}} Ag_2O + 2OH^-$$

$$Ag_2O + H_2O + 2e \longleftrightarrow 2Ag + 2OH^-$$

$$Zn + 2OH^- \longleftrightarrow Zn(OH)_2 + 2e$$

$$Zn(OH)_2 + 2OH^- \longleftrightarrow Zn(OH)_4^{2-}$$

Overall Reaction

$$AgO + Zn + H_2O \longleftrightarrow Ag + Zn(OH)_2$$

Silver-Zinc Applications

(primary as well as secondary)

Space	Launch-vehicle guidance and control, telemetry, NASA vehicles Lunar Rover and Mars Rover, space shuttle payload launch and power for the life-support equipment used by the astronauts during EVA's.
Military	Missle systems, Navy: mines, buoys, deep submergence and rescue vehicles, torpedo propulsion, drones and submarines.

Silver/Zinc Problems and Opportunities

- Highest specific energy and energy density
- High discharge rate capability
- Good charge retention
- Flat discharge voltage curve

BUT

- **Relatively low cycle life**
- **Limited wet life (3-18 months, fill/activate prior to use)**
- Sensitivity to overcharge

Technical Issues

- Zincate migration from electrode following discharge, non uniform charging leading to shape change
- Zinc dendrite formation which can penetrate the separator causing shorting
- Cellophane separators chemically attacked by colloidal silver and KOH
- Silver goes into solution and can pass through the separator

Note:

- RBC has developed separator system which inhibits cross over of selective ions in alkaline electrolyte (U.S. 5,952,124)

NASA SBIR Phase I, Technical Objectives

- Collaborate with Eagle-Picher Technologies, an established supplier of mission-critical silver/zinc batteries to:
  - construct silver/zinc cells using RBC's advanced anode and separator components
  - evaluate the ability of these components to render improvements in: specific energy, cycle life and wet-life of rechargeable silver/zinc batteries

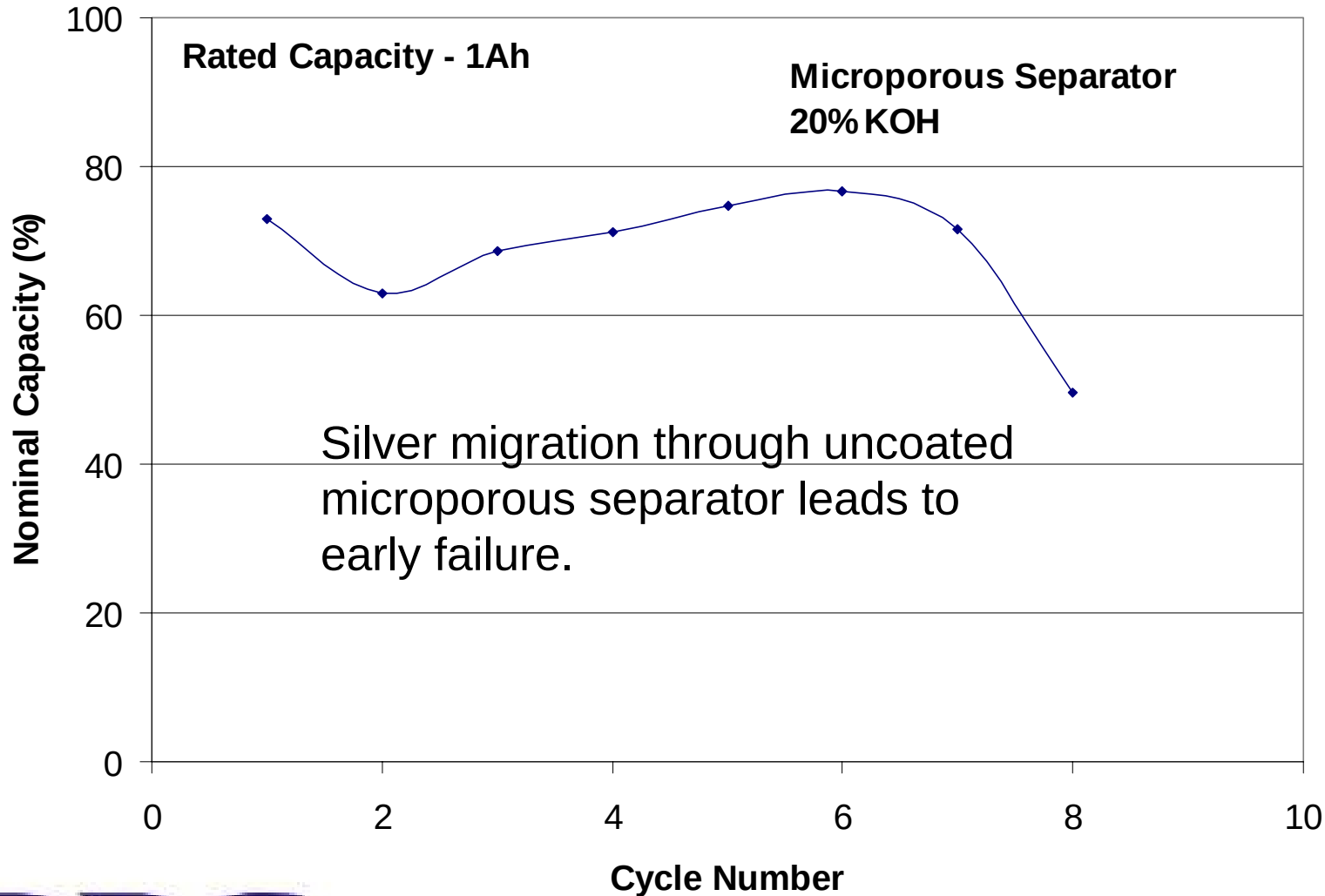
Design Variables

– ***Separators Evaluated:***

Separator Type	***Description***
Microporous polyolefin separator	Continuous polyolefin membrane, approximately 1 mil thick, with carboxylic surface functionality
SPPO coated microporous polyolefin separator	As above, but dip-coated with sulphonated polyphenylene oxide per U.S. 5,952,124
Cellophane laminate	Cellophane laminated to a non-woven polyamide, approximately 6 mils thick
AMS	A mineral filled polyolefin supplied by Advanced Membrane Systems.

- ***Electrolyte compositions evaluated:***
  - 20%KOH 45%KOH

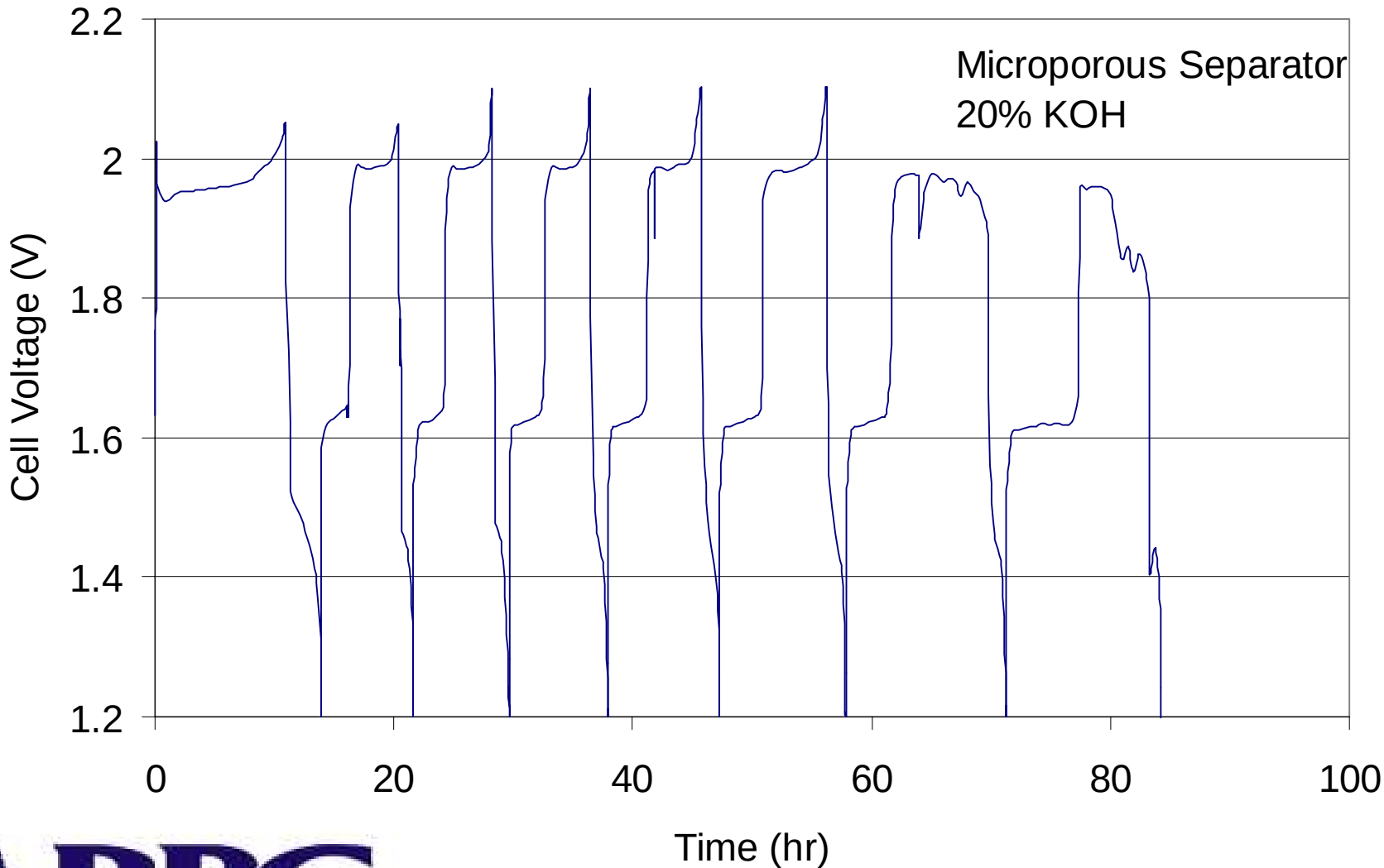
1Ah Cell - Standard RZA Separator & Electrolyte



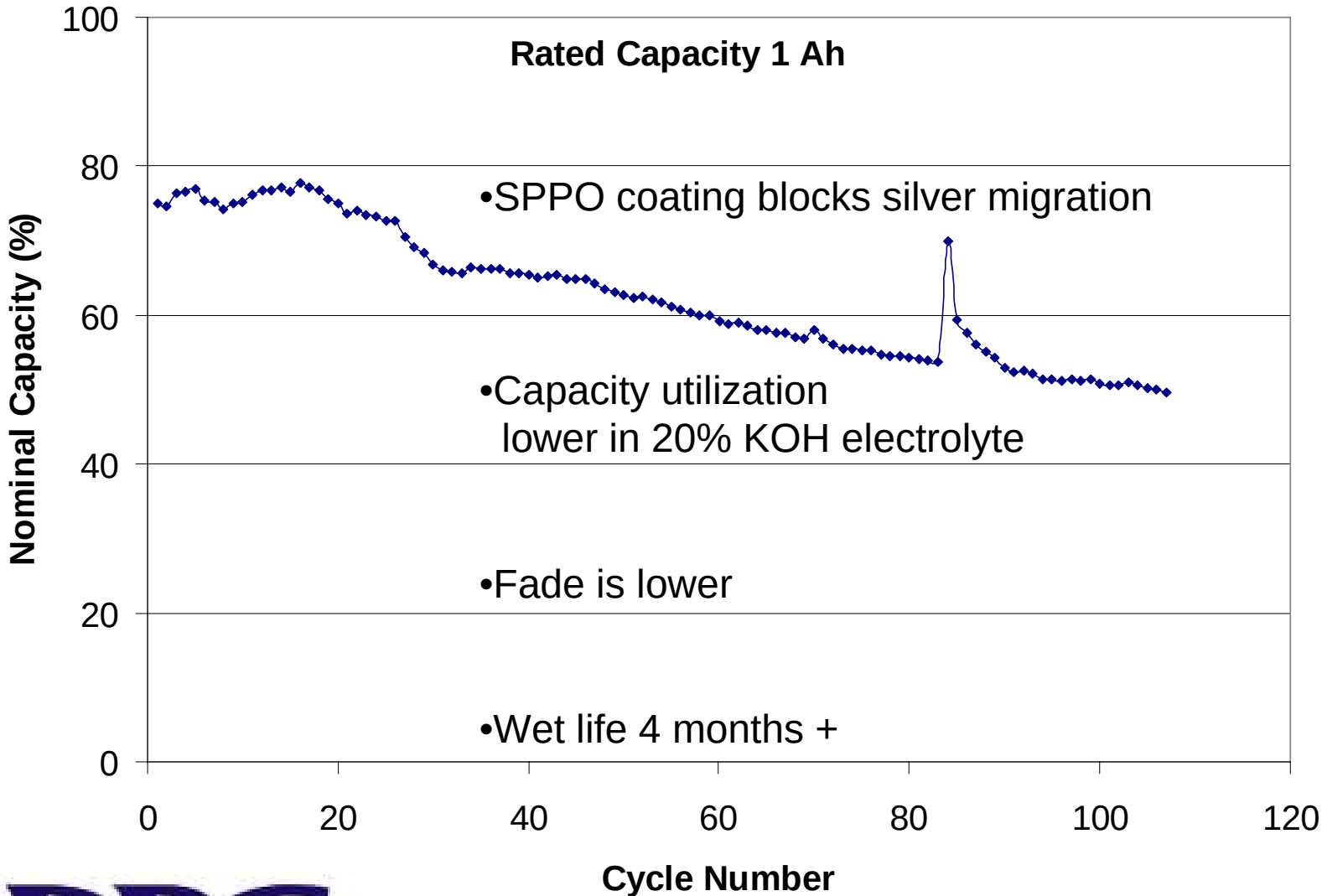
RBC TECHNOLOGIES

Quality Battery Solutions

1Ah Cell - Standard RZA Separator & Electrolyte



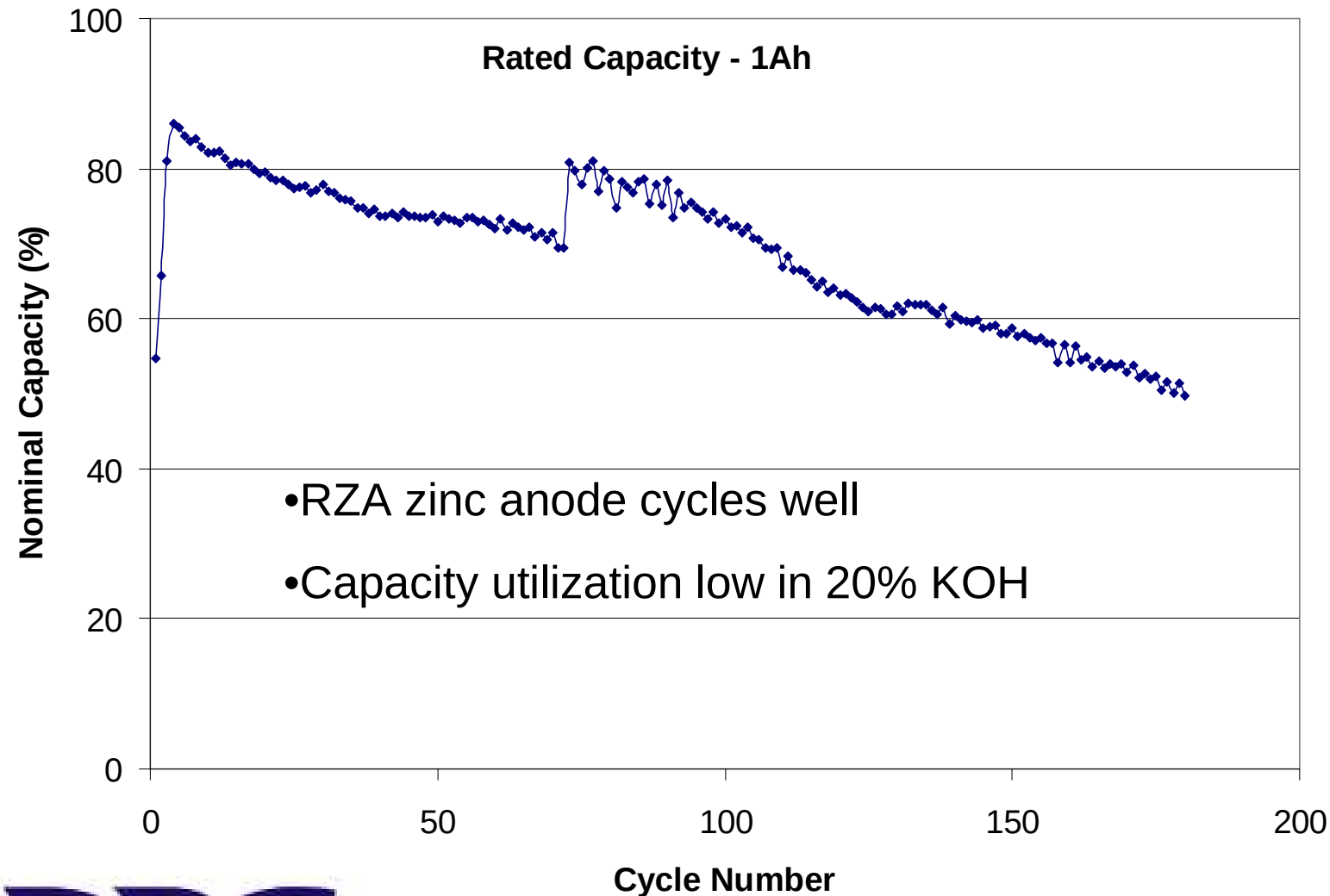
1 Ah Cell - SPPO Coated Separator 20% KOH



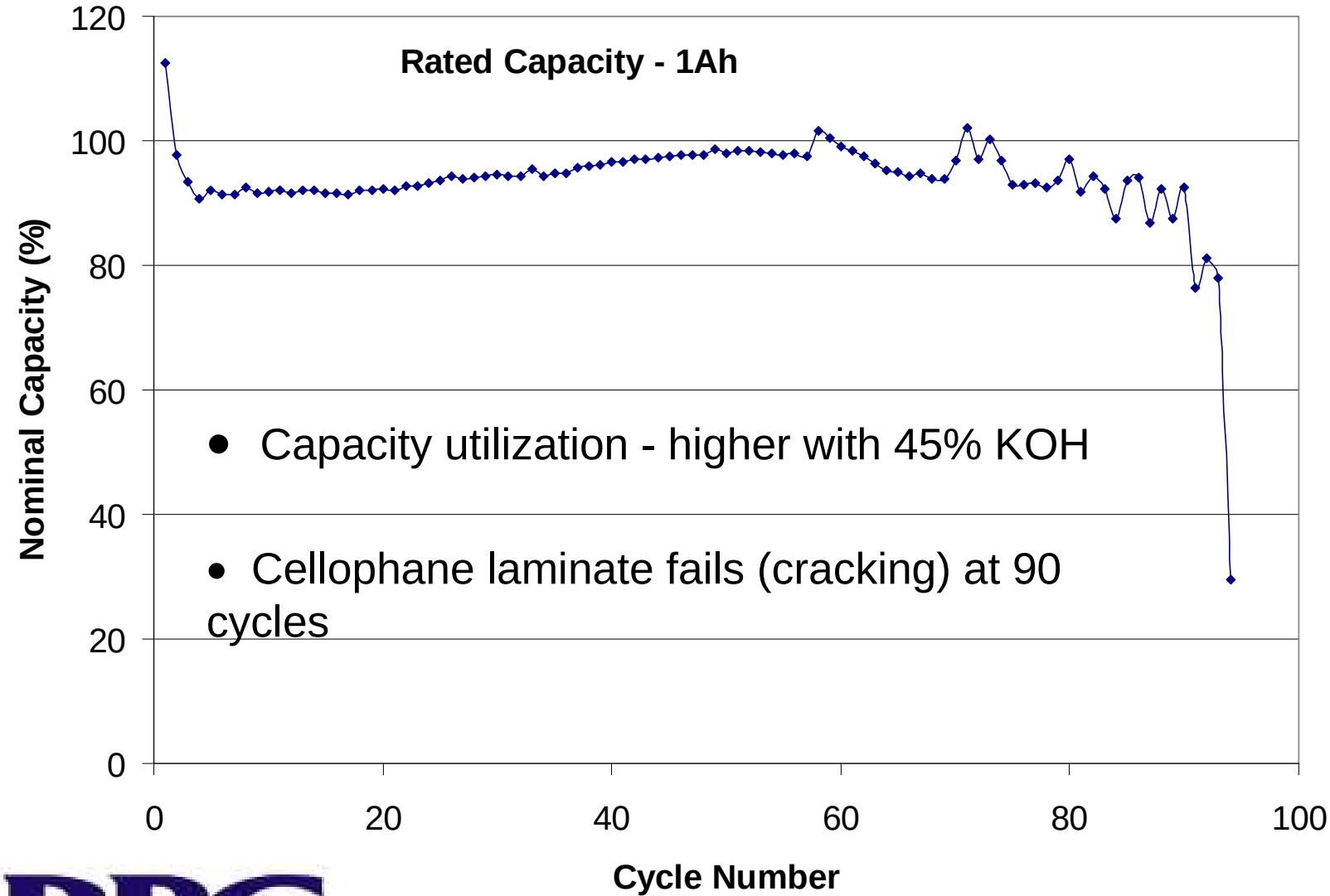
RBC TECHNOLOGIES

Quality Battery Solutions

1 Ah-Cellophane Laminate Separator, 20% KOH

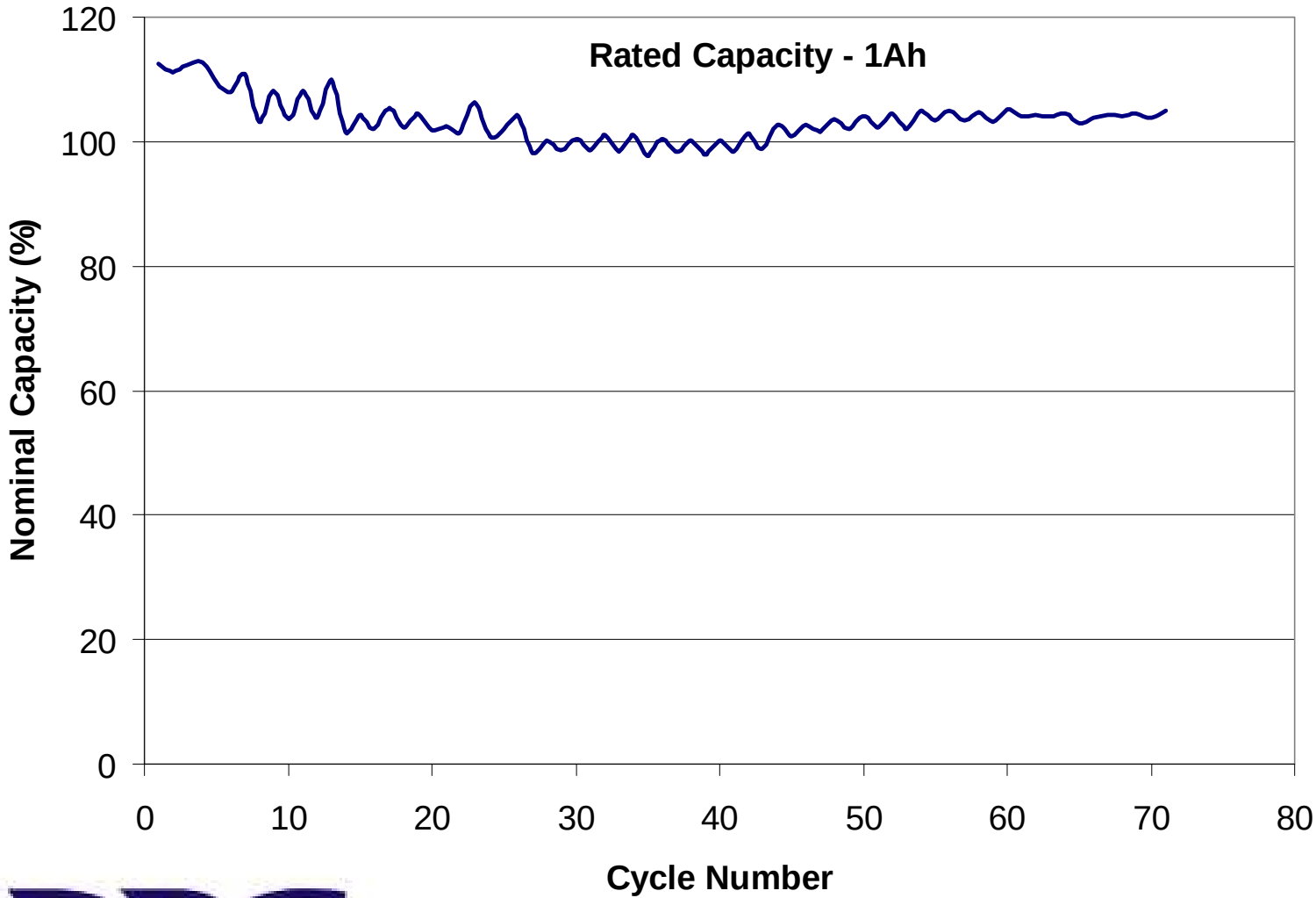


1 Ah Cell - Cellophane Laminates, 45% KOH

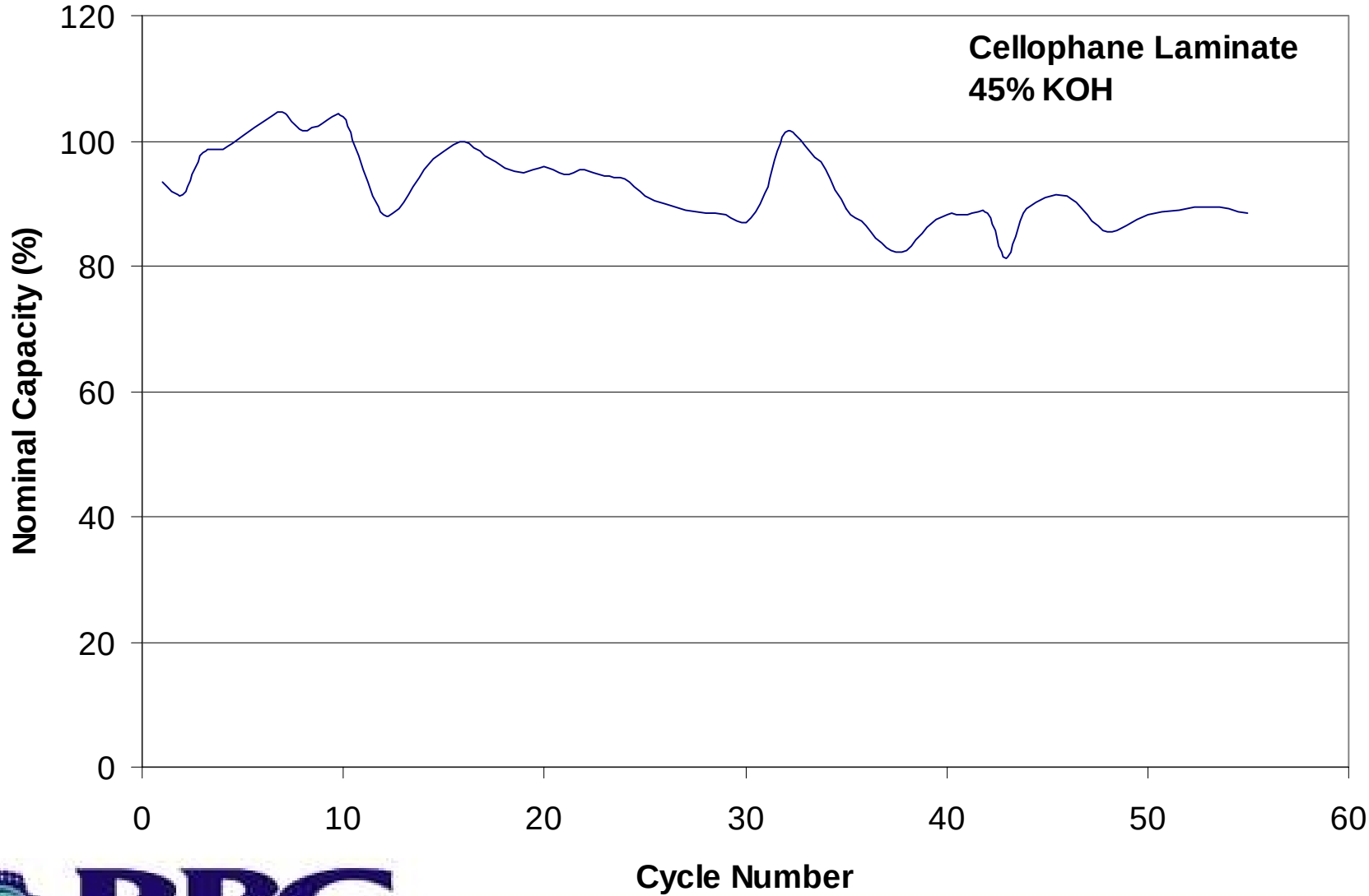


- Capacity utilization - higher with 45% KOH
- Cellophane laminate fails (cracking) at 90 cycles

1Ah Cell - AMS Separator, 45% KOH



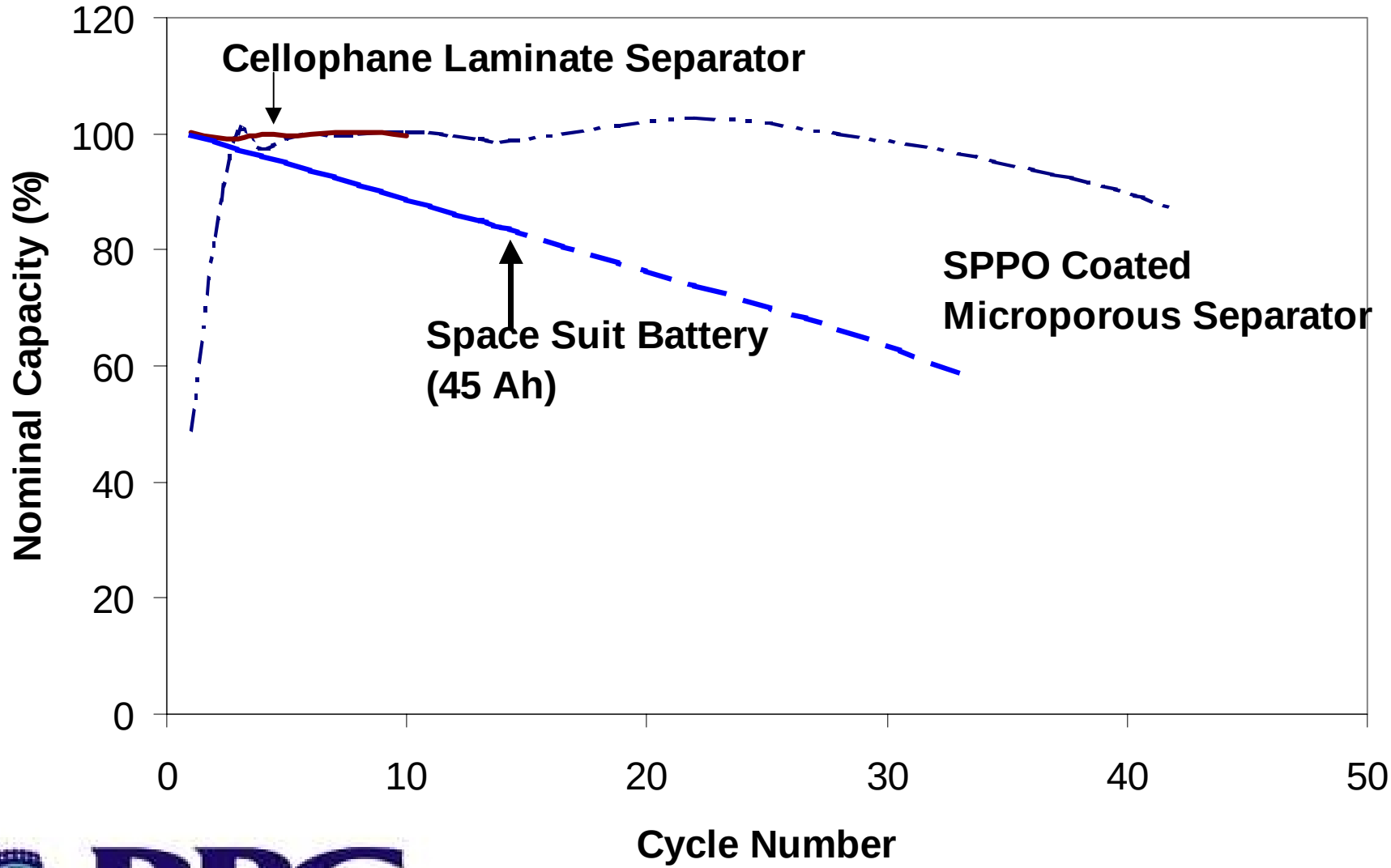
Silver-Zinc 10 Ah Cell



RBC TECHNOLOGIES

Quality Battery Solutions

5 Ah Silver-Zinc Cells, 45% KOH



RBC TECHNOLOGIES

Quality Battery Solutions

Phase I Conclusions

- Use of RBC anode in Silver-Zinc cells enhanced cycle life substantially.
- Within the limited time period of the project, wet life exceeding 4 months was demonstrated with the cell still operating satisfactorily.
- Coated microporous separators inhibit silver migration. Coated and filled polyolefin separators allow for greater wet-life stability then cellulose and cellulose laminates.
- All the cells were assembled in the charged state and did not need formation.
- KOH concentration must be optimized for cycle life, capacity and wet life.

NASA SBIR PHASE II
Technical Objectives

Application Demonstration: EMU-PLSS Battery

- Optimize separator and electrolyte for wet life/cycle life
- Scale to 5Ah, 17V battery (11 cells in series)
- Scale to 40Ah cells and a 17V battery
- Deliver two (2) 17V, 40Ah equivalent batteries to NASA, which will exceed the performance of current batteries.

Phase II SBIR Goals

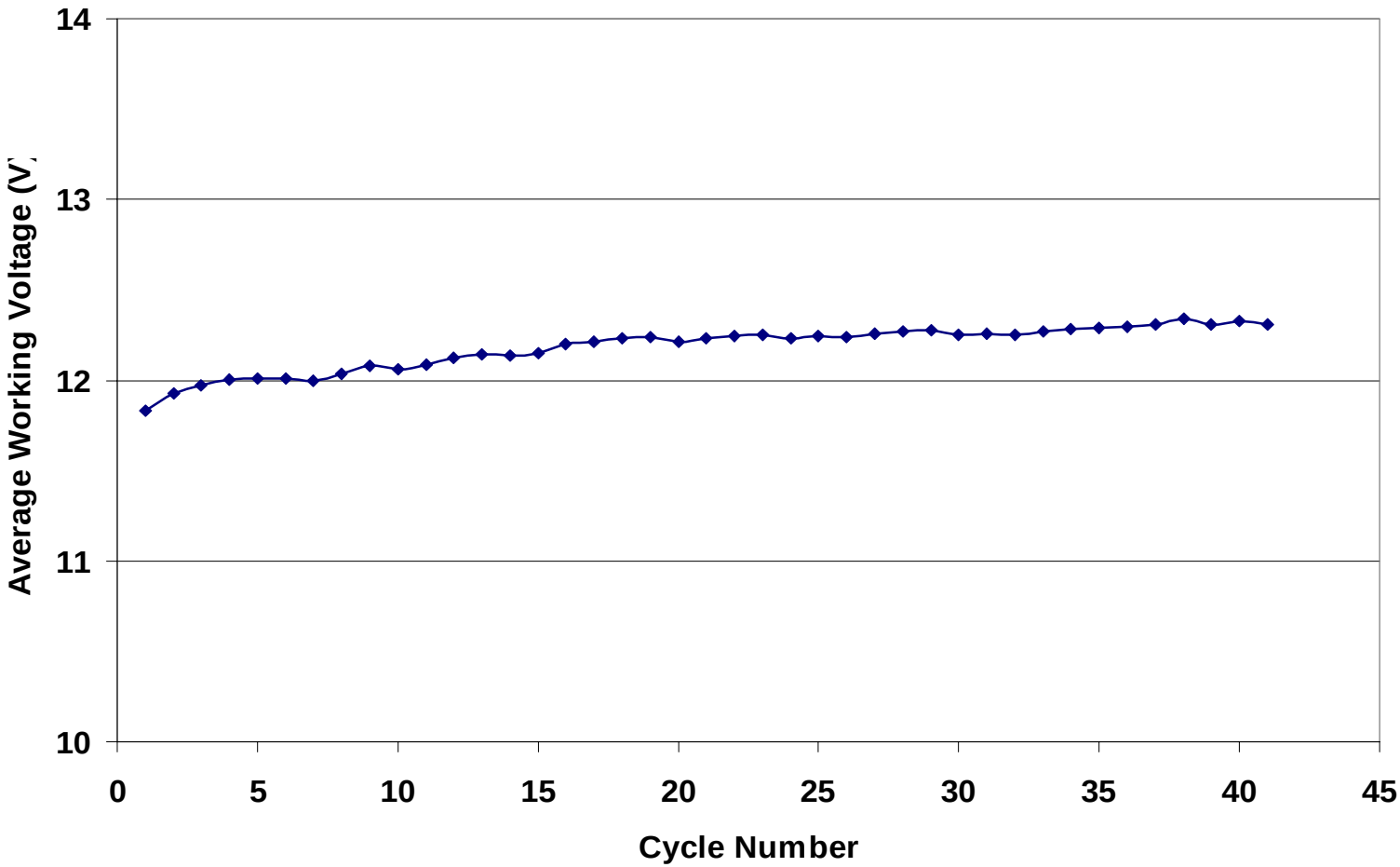
Application Demonstration: EMU-PLSS Battery

Item	***Existing***	***Phase II Goal***
Conditioning	Fill and electrically charge	Fill and go
Volume (L)	2.27	2.12
Weight (Kg)	4.4-6.4	5.2
Capacity	26.6 Ah minimum @3.8A	26.6 Ah minimum @3.8A
Number of cycles to 26.6 Ah cut-off	7-32	50 minimum
Operation	Rugged, Vented maintenance free	Rugged, vented maintenance free
Charging	With existing charger	Ability to interface with existing charging systems
Wet-life	170-420 days	450 days minimum
Electrical	16.5 volts	16.5 volts

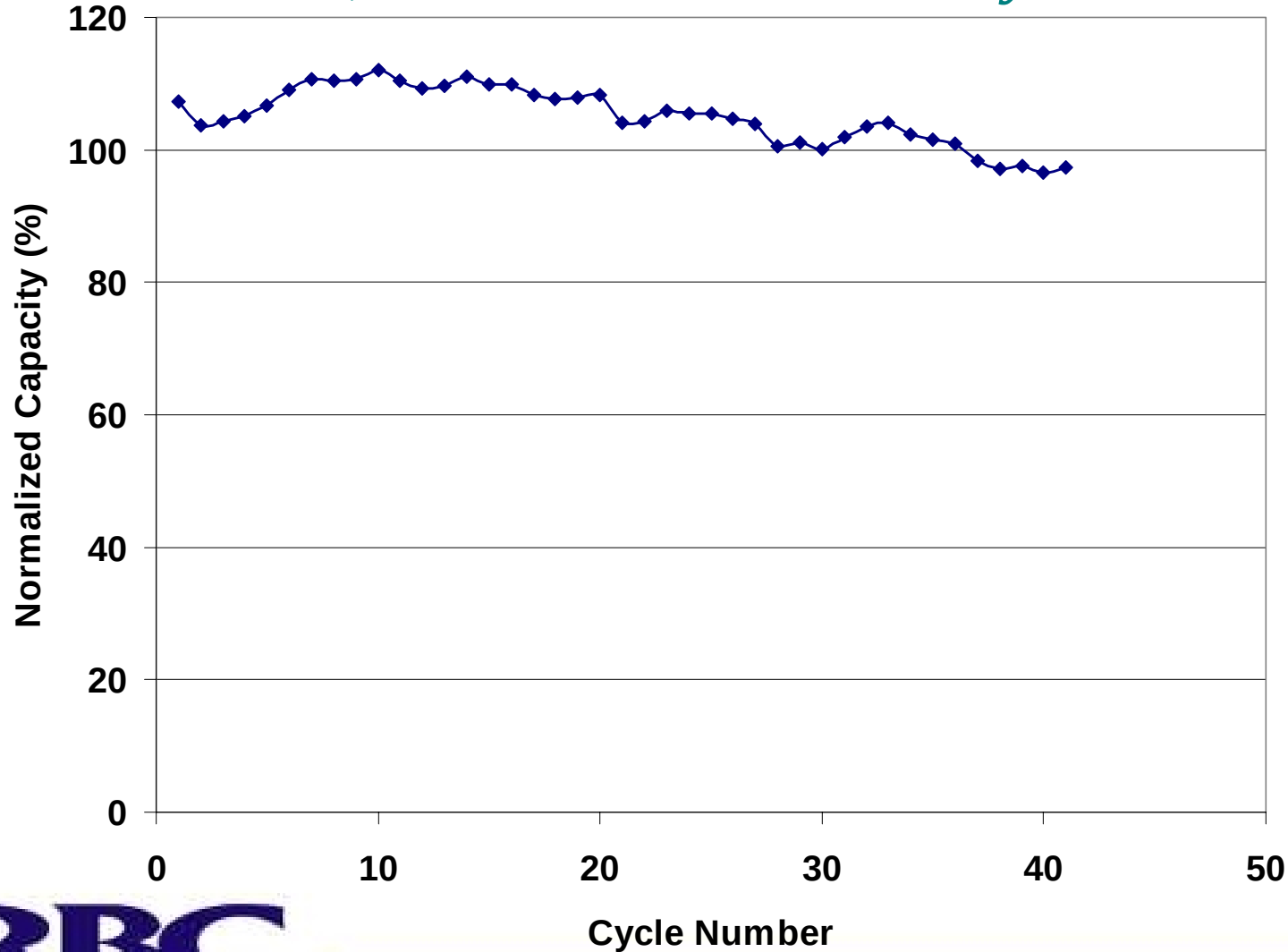
Phase II -Current Status

- Program started Sept. 2002
- Evaluating separators,absorbers and electrolytes to optimize wet/cycle life
- 12V batteries have been assembled and are being tested
- More than 40 cycles and at least two months wet life demonstrated

Average Working Voltage vs Cycle number for 1 Ah, 12V Silver/Zinc Battery



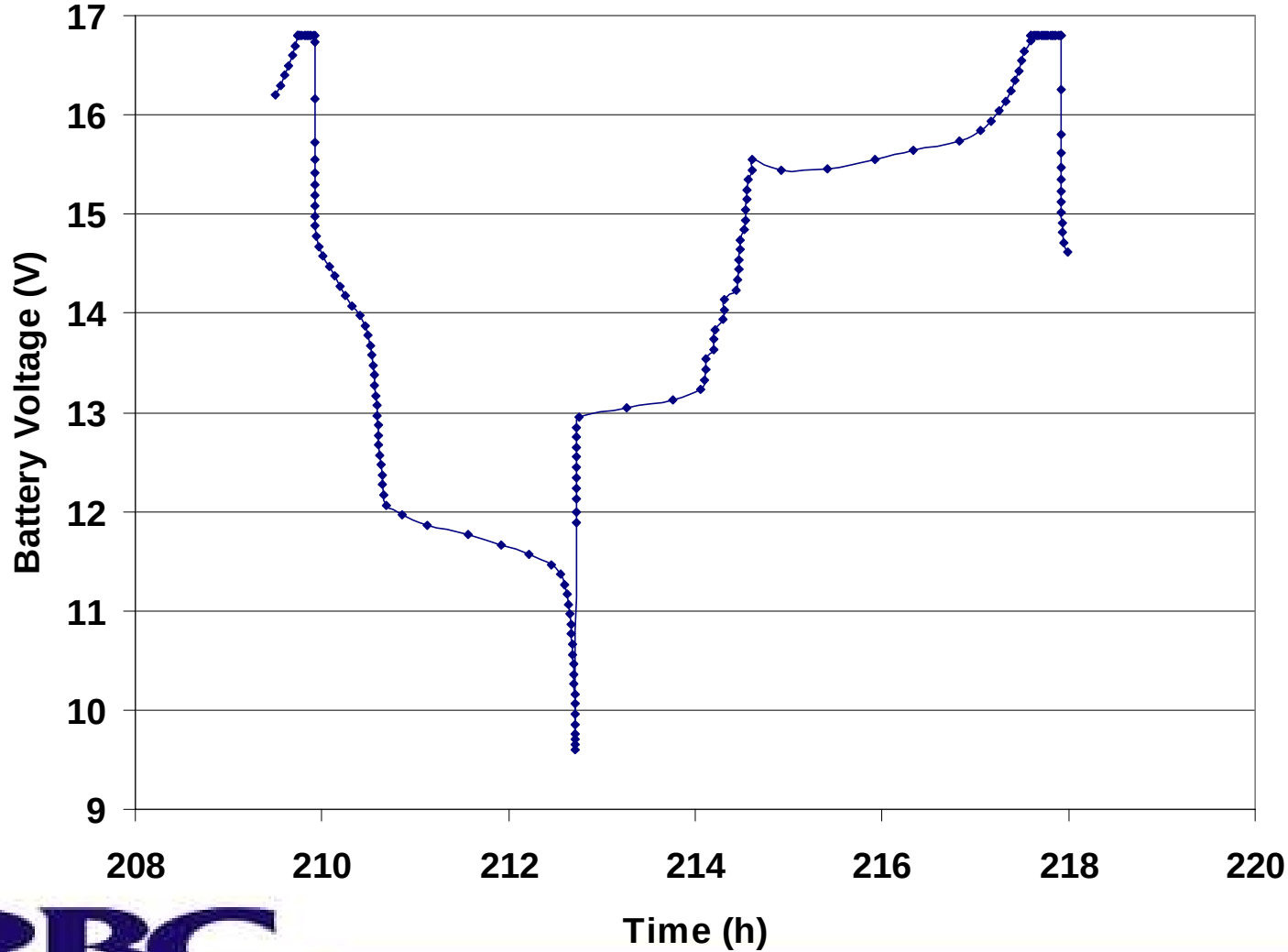
Capacity vs Cycle number for 1 Ah, 12V Silver/Zinc Battery



RBC TECHNOLOGIES

Quality Battery Solutions

Discharge/Charge Profile for 1 Ah, 12V Silver/Zinc Battery



RBC TECHNOLOGIES

Quality Battery Solutions

Opportunity- Spiral Wound RZA Silver/Zinc Battery

TABLE: Comparison of Cylindrical Cells in Various Rechargeable Electrochemistries

Chemistry	Cell config.	Capacity (Ah)	Cell voltage	Wh/kg	Wh/l
NiCd	D	4.6	1.2	40	106
RZA-NiZn	D	5.0	1.65	59	158
NiMH	D	6.5	1.2	46	150
Li-ion	18650	2.0	3.7	130	410
RZA-Ag/Zn	D	10.2	1.5	110	300

Conclusions

- Issues with long term wet life and cycle life of the silver/zinc battery system are being overcome through the use of new anode formulations and separator designs

- Performance may exceed 200 cycles to 80% of initial capacity and ultimate wet-life of > 36 months

- Rechargeable silver/zinc batteries available in prismatic and cylindrical formats may provide a high energy, high power alternative to lithium-ion in military/aerospace applications

Acknowledgements

NASA, SBIR S4.07-0679

US Dept of Commerce, NIST

Advanced Technology Program
#70NANB9H3031

Lithylene™

free form battery technology

Space applications
Hybrid Electric Vehicles
Notebook PC's

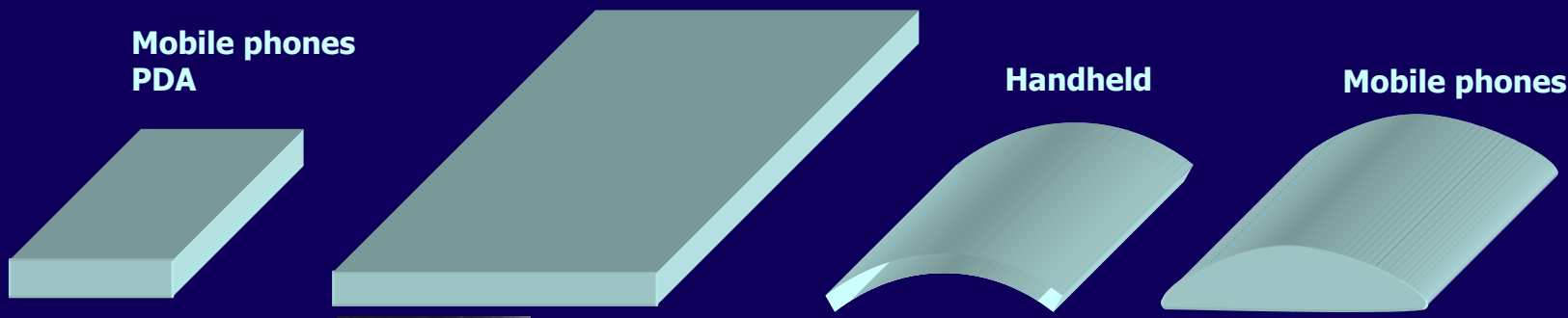
Lithylene™ ‘free forms’

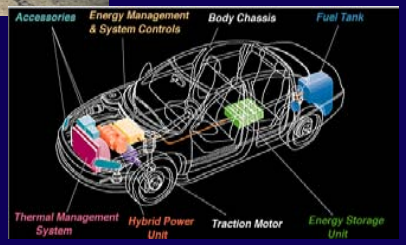
Hybrid Electric Vehicle (HEV)
Space
Notebook PC’s

Mobile phones
PDA

Handheld

Mobile phones



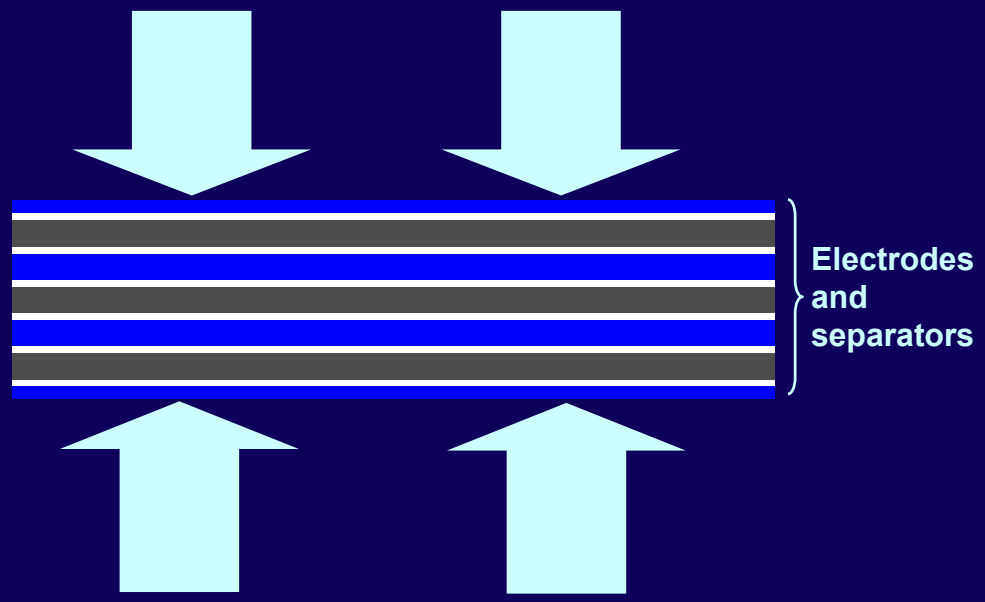


Issues on battery life

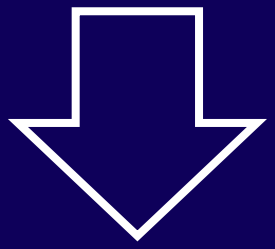
Rechargeable Li-ion (polymer) batteries

general

Stack pressure



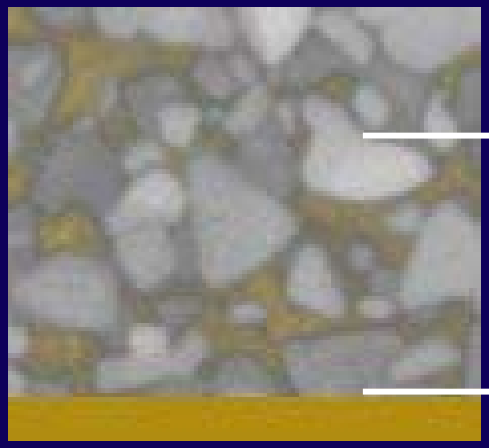
Stack pressure/integrity



low impedance
high cycle-life

Stack pressure and stack integrity

microscopic scale



electrical contact between particles

electrical contact with current collectors

electrode

Li-ion

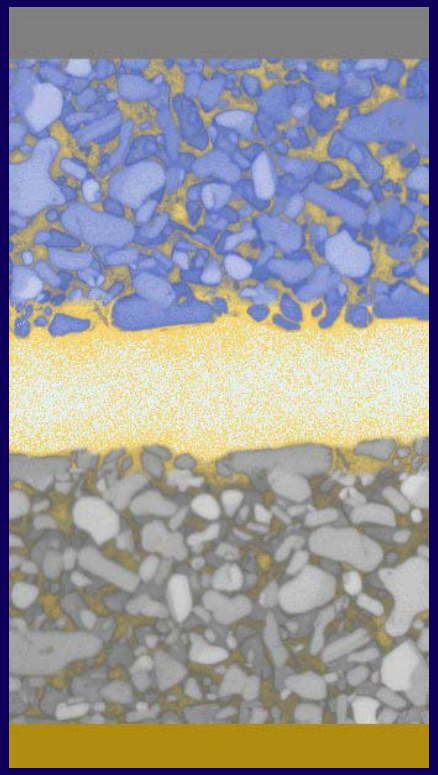
Current collector

Li_xCoO_2

Separator
liquid electrolyte

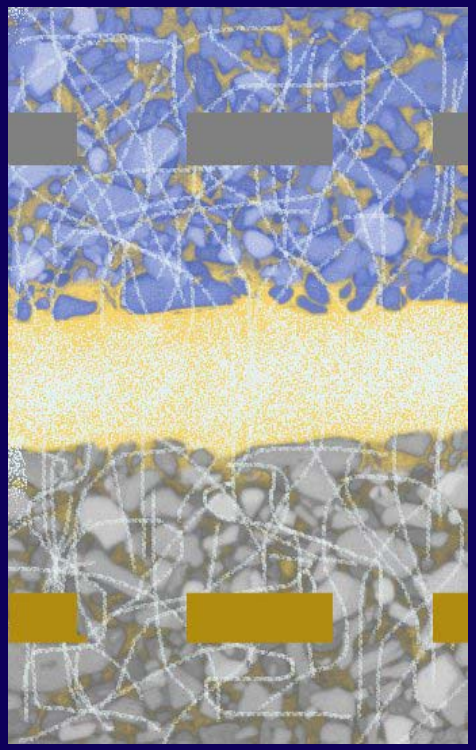
C_6Li_y

Current collector



outside pressure required

Li-ion-polymer

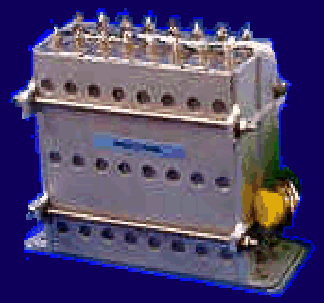


Polymer gel
electrolyte

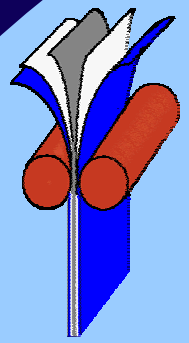
No outside pressure required

Stack pressure methods

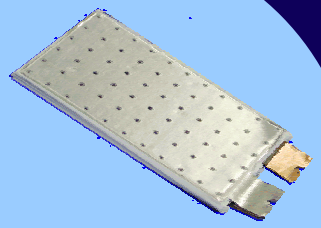
Metal can



External rods



Lamination



rivets

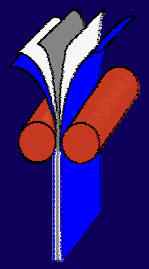
in softpack

Atmospheric pressure

Stack pressure methods in softpack

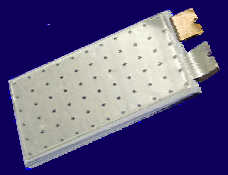
Spiral-wound or free-stacked

- use of mature Li-ion electrodes
- stack pressure loss when vacuum not maintained



Lamination of Polymer electrodes

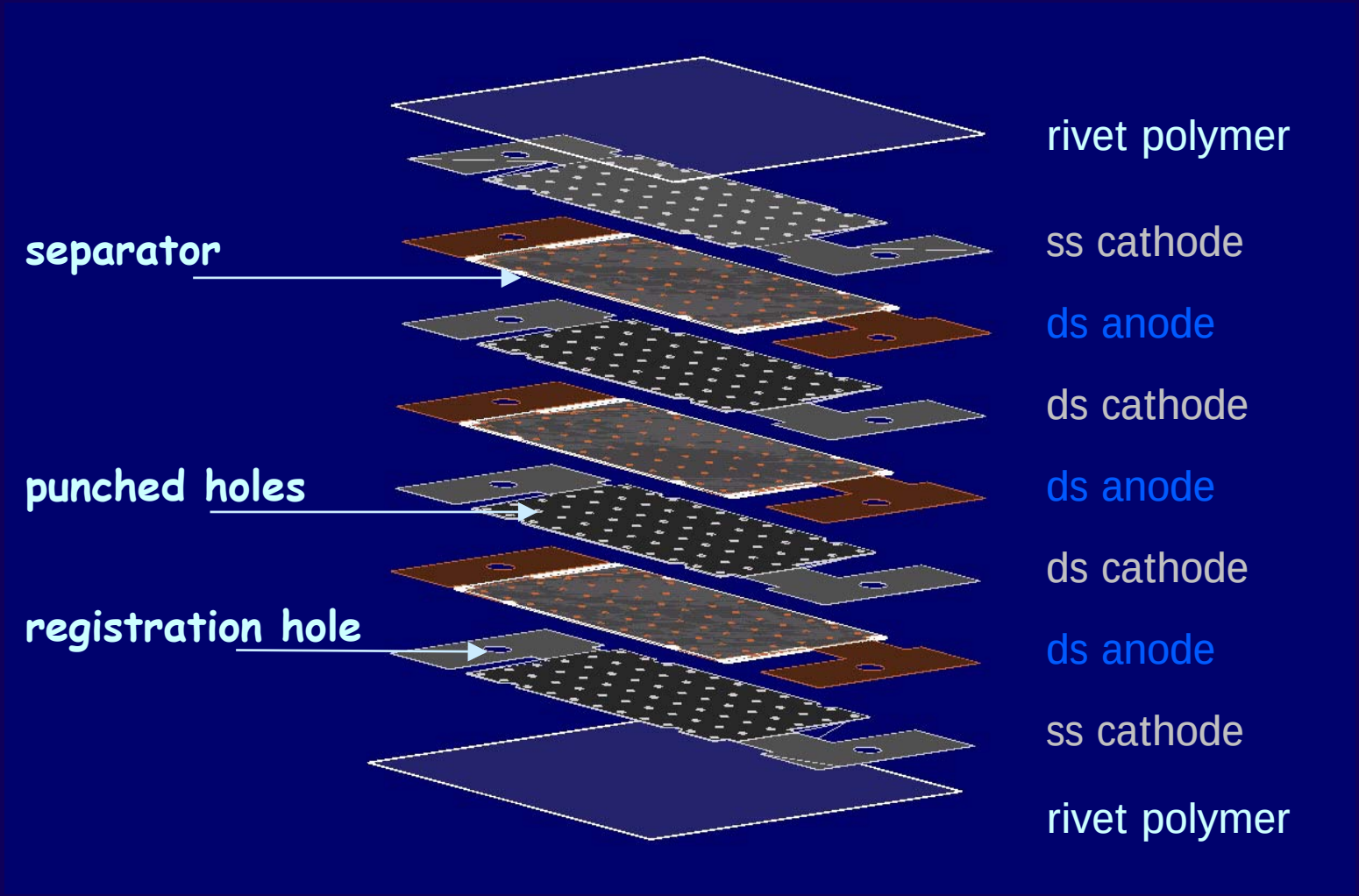
- requires adapted electrode chemistry
- reduced energy density



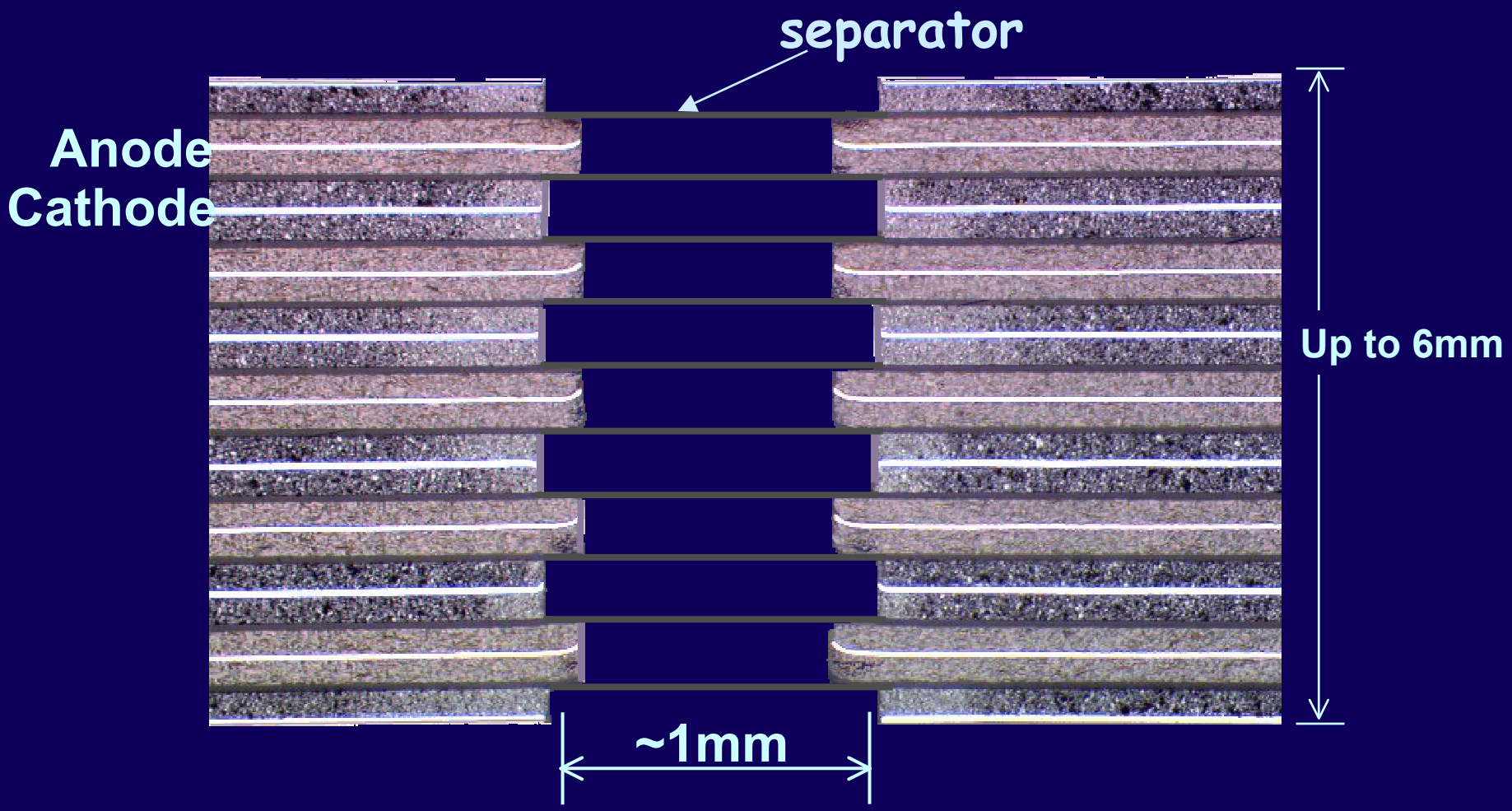
Lithylene™ with polymer rivets

- use of mature Li-ion electrodes
- high energy density
- stable structure does not rely on vacuum

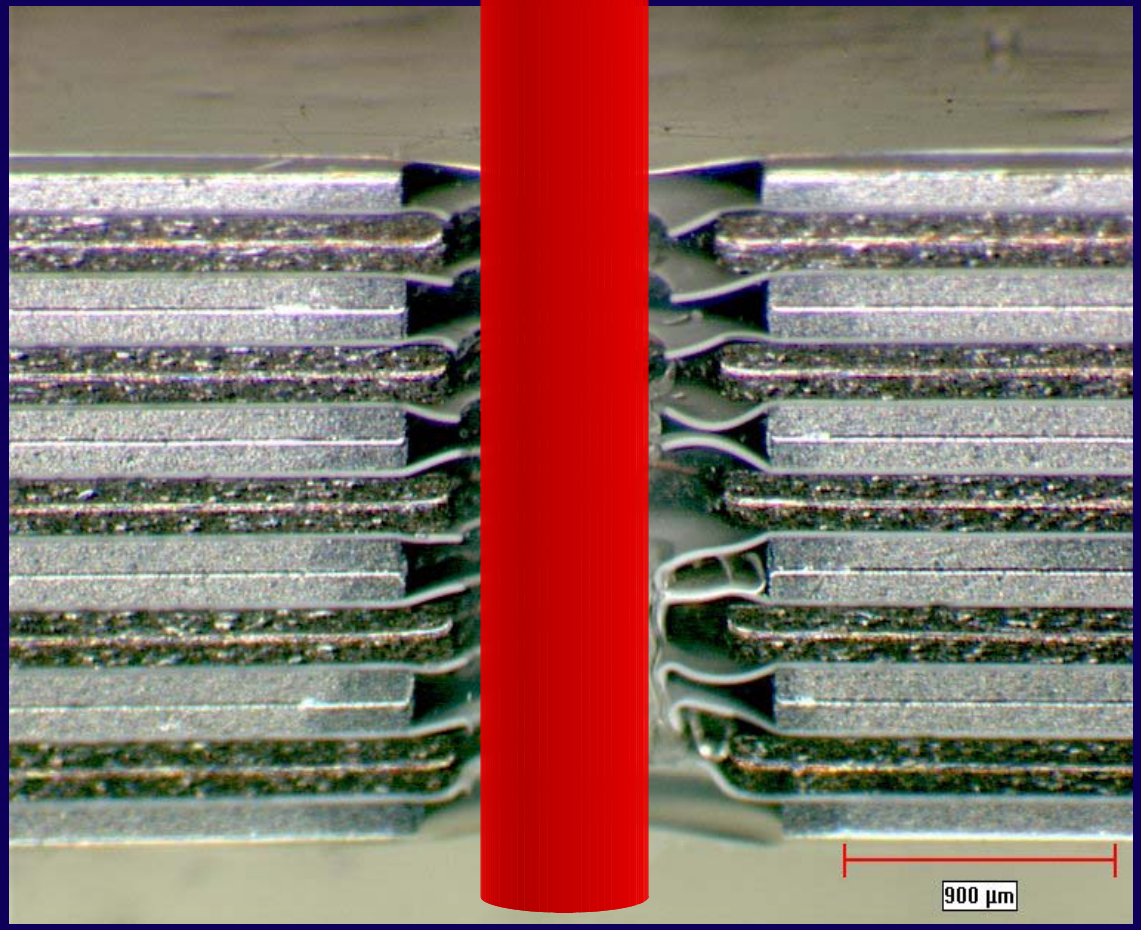
Lithylene™ stack



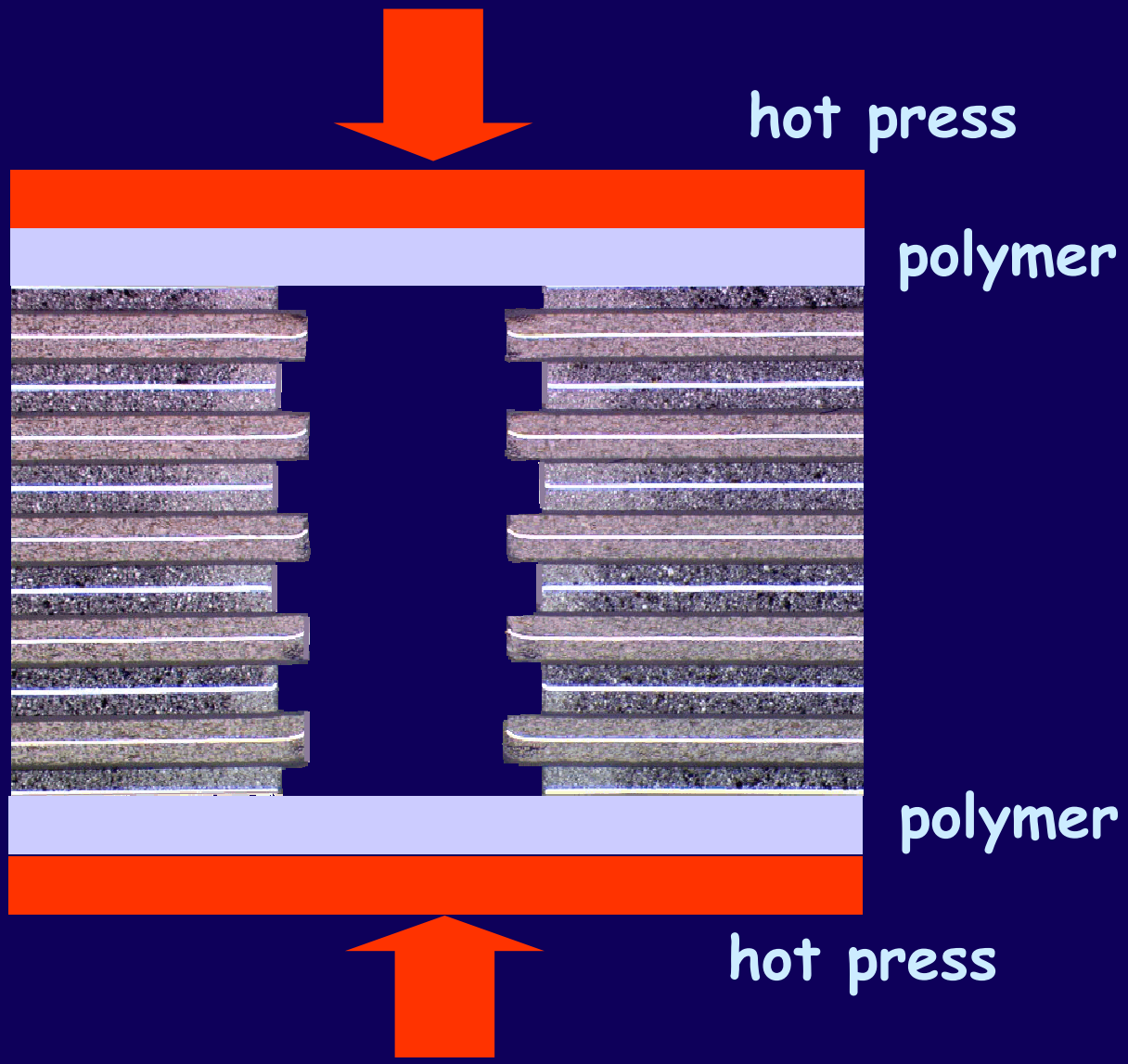
Cross section

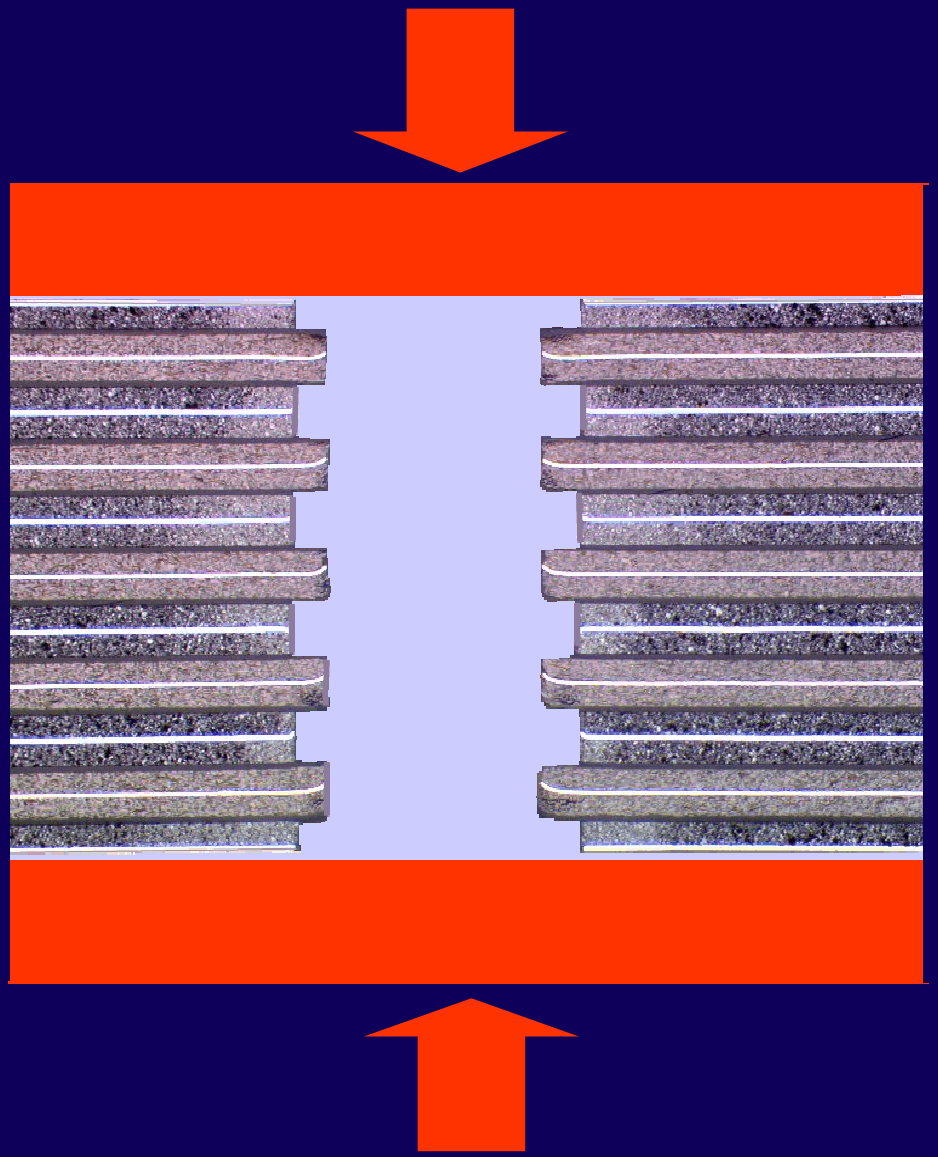


Melting holes in separator

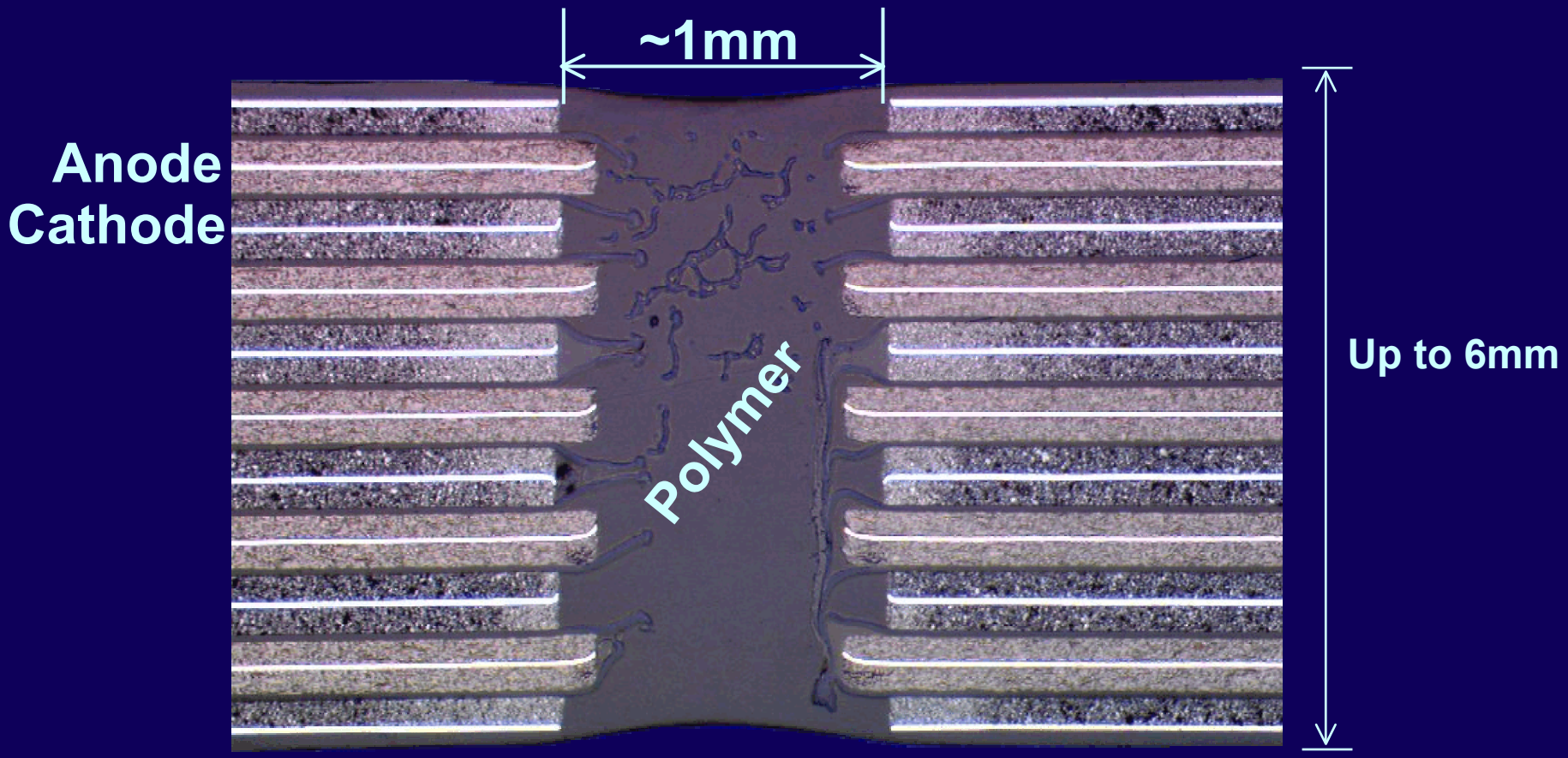


Riveting

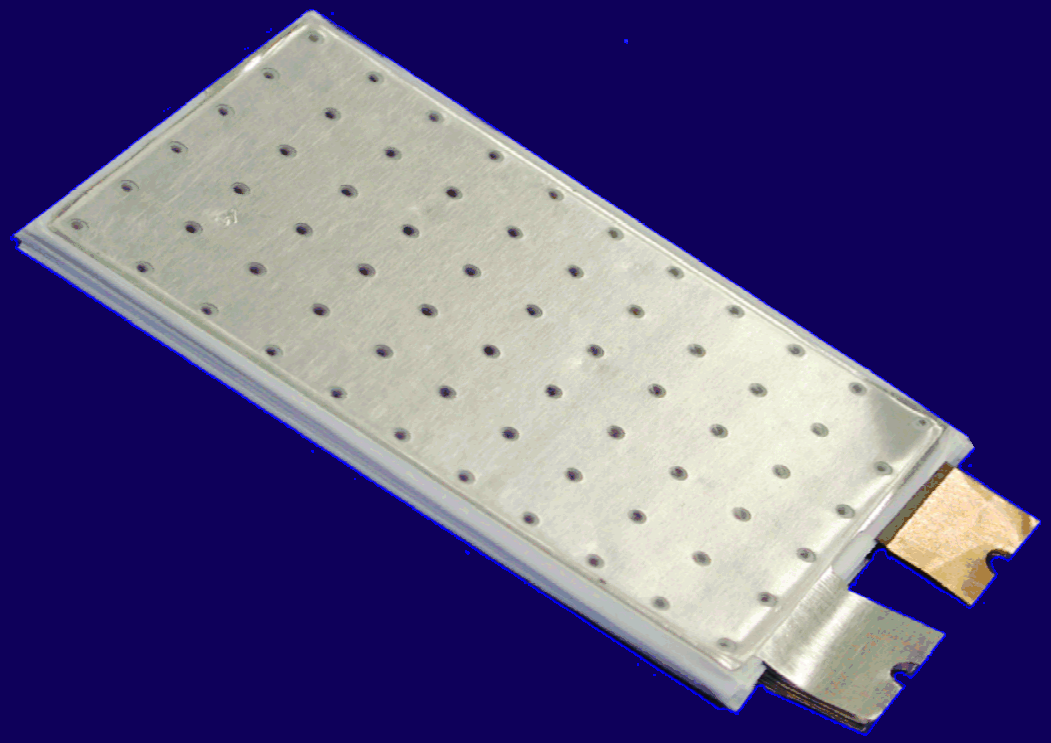




Lithylene™ stack



Lithylene™ stack



Space

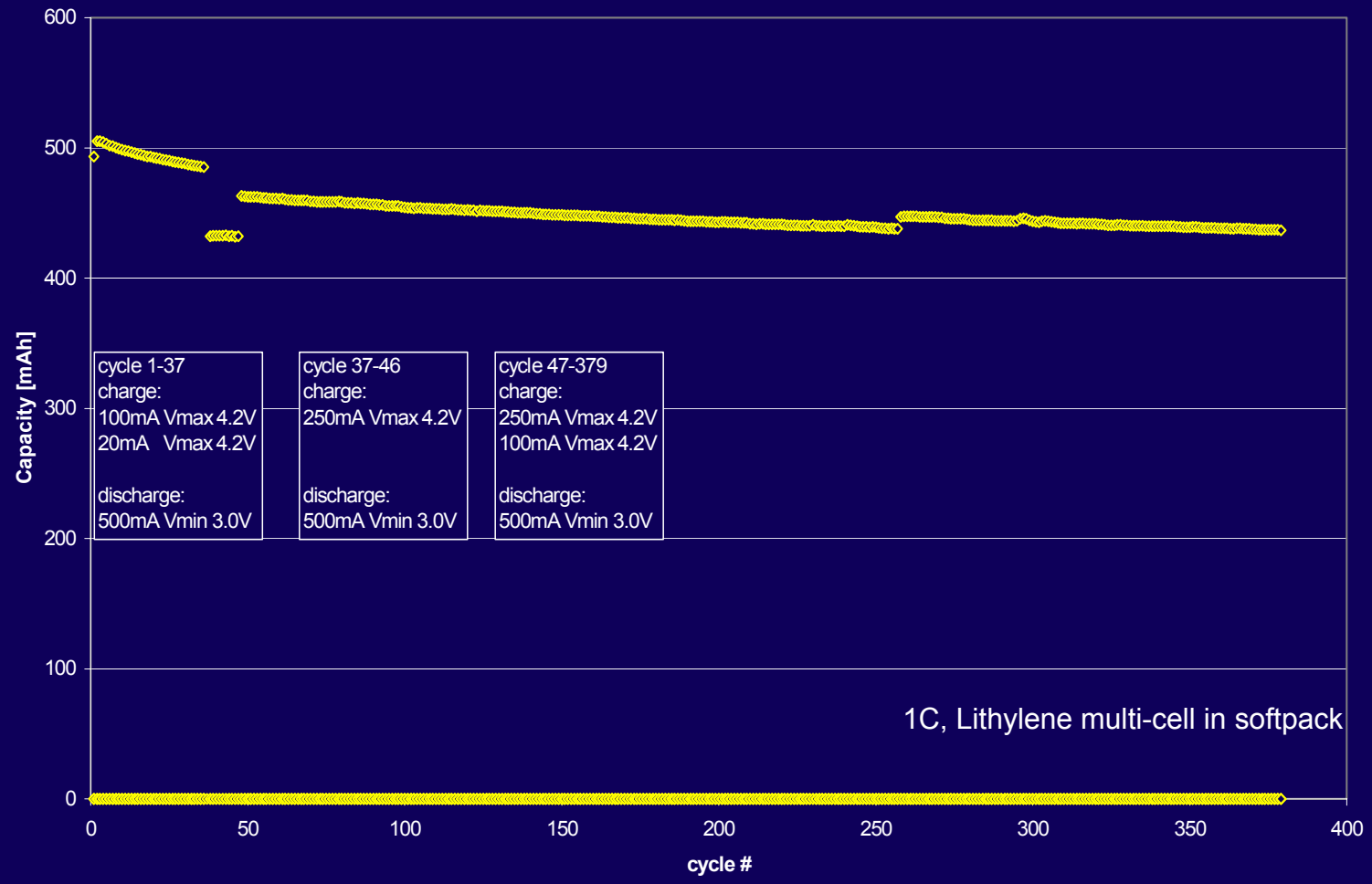
Trends

- Low weight, high energy density
- Acceptance of Li-ion battery
- Low magnetic signature

Lithylene™ benefits

- Lightweight prismatic shape
- Low magnetic signature
- Performance under vacuum conditions

Lithylene™ cycle life softpack not vacuumed



Competition

Technologies

- Other Softpack Li-ion batteries
  - cannot operate under vacuum conditions (space)
- Cylindrical Li-ion
  - High weight
  - High magnetic signature

Large prismatic Li-ion batteries

External support structure

Large cylindrical Li-ion batteries

thermal management

Water cooled

Lithylene™ key advantages

- High Energy Density > 350 Wh/l
- Thin and flat or curved
- Scalable mobile phone, PDA, Notebook PC's, (H)EV, Space
- Standard Li-ion electrodes and separators
- Does not rely on vacuum in softpack

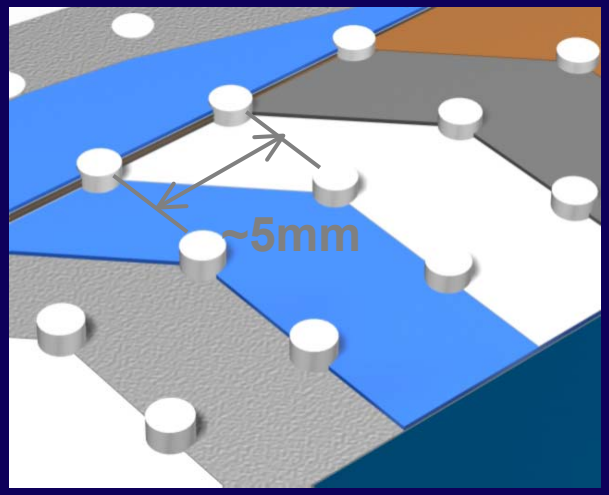
Independence of cell-chemistry

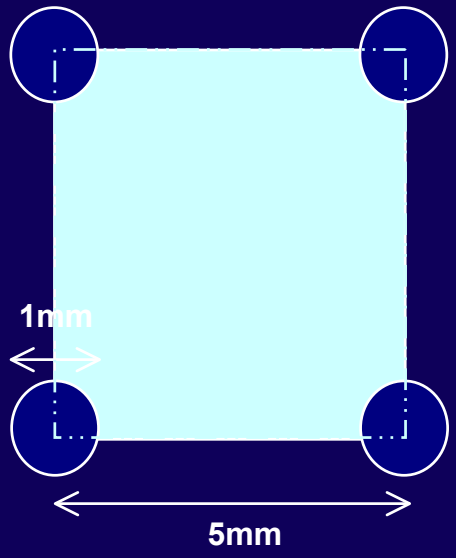
Hundreds of samples, made with different electrode/electrolyte combinations, proof that the electrochemical properties of cells are not affected by the polymer rivets.

Capacity loss due to the rivets ~ 3%

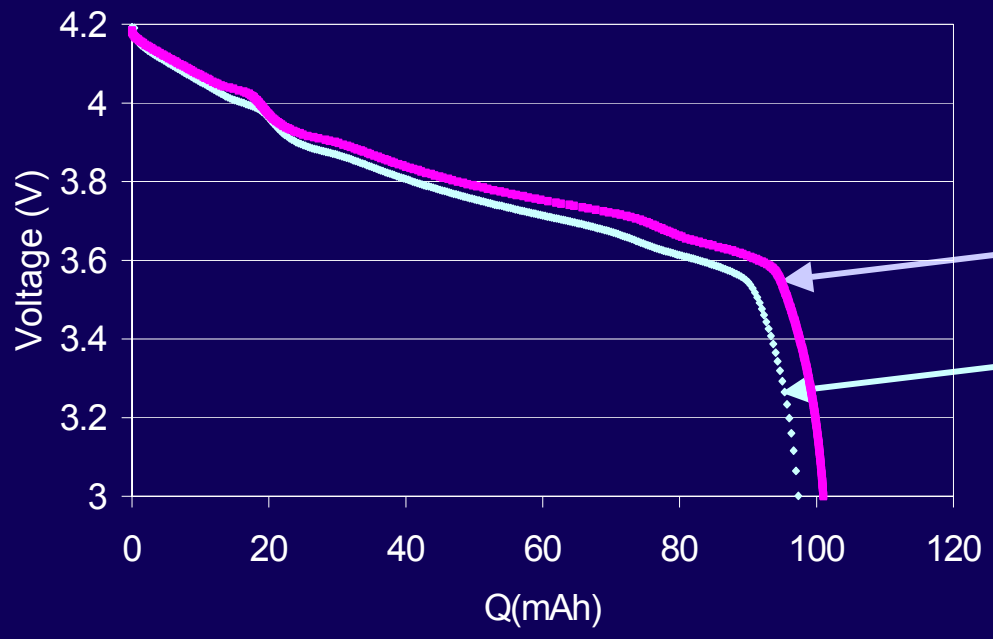
$$\frac{Area(hole)}{Area(total)} = \frac{\pi * r^2}{l * w} \cong \frac{\pi * (0.5mm)^2}{5 * 5mm^2} = 0.0314$$

dimensions



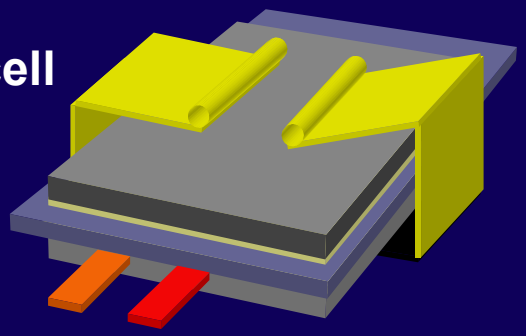


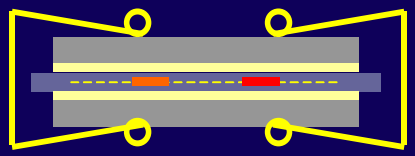
Capacity loss due to the rivets(2)



Reference cell without rivets

Lithylene cell





Lithylene™ qualities

- **Mechanical construction independent of electro-chemical properties**
- **Use of state-of-the-art Li-ion battery components, and inert polymer rivets with high temperature stability**
- **Safety: thermal fuse type separators**
- **Suitable for both small and large area batteries (for mobile telephone as well as for notebook PC's, (H)EV and Space)**

Philips *Lithylene*™

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PHILIPS

Manufacturing

Equipment development by
Philips Centre for Industrial Technology (CFT)

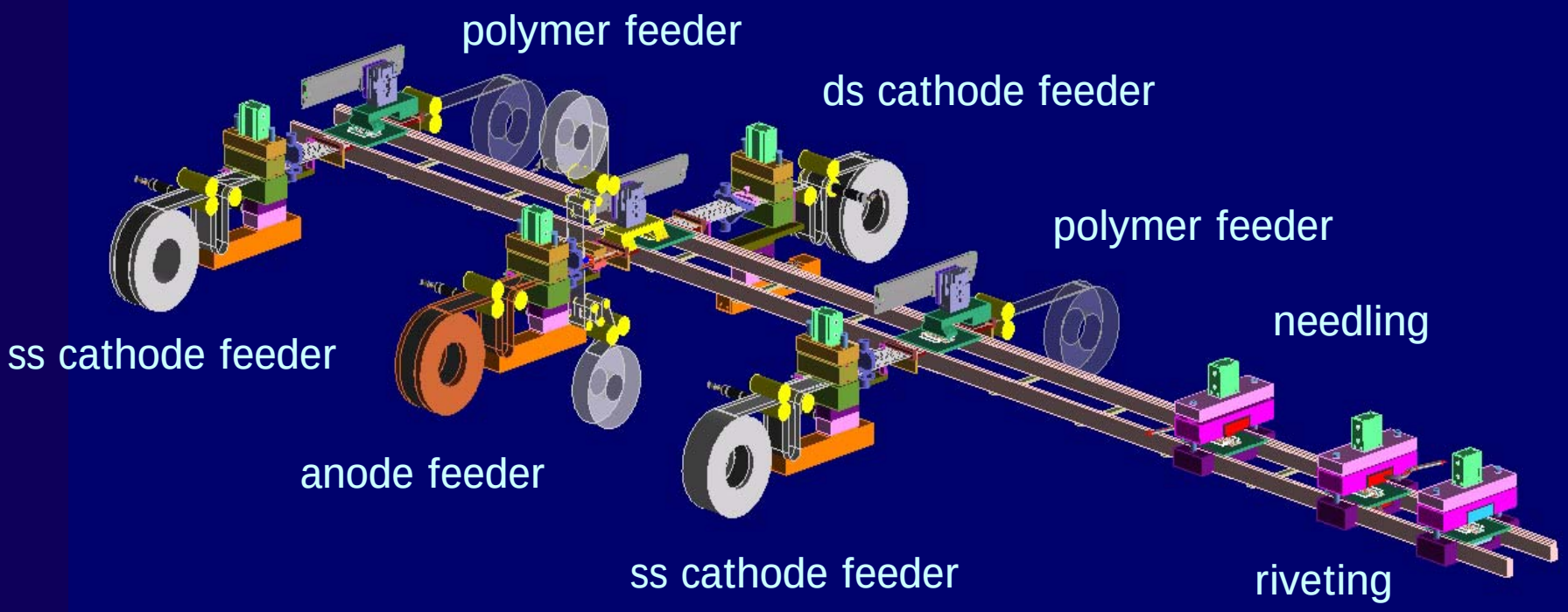
Production

Pilot production 1-5 multi-cells/min
Mass production 15 multi-cells/min

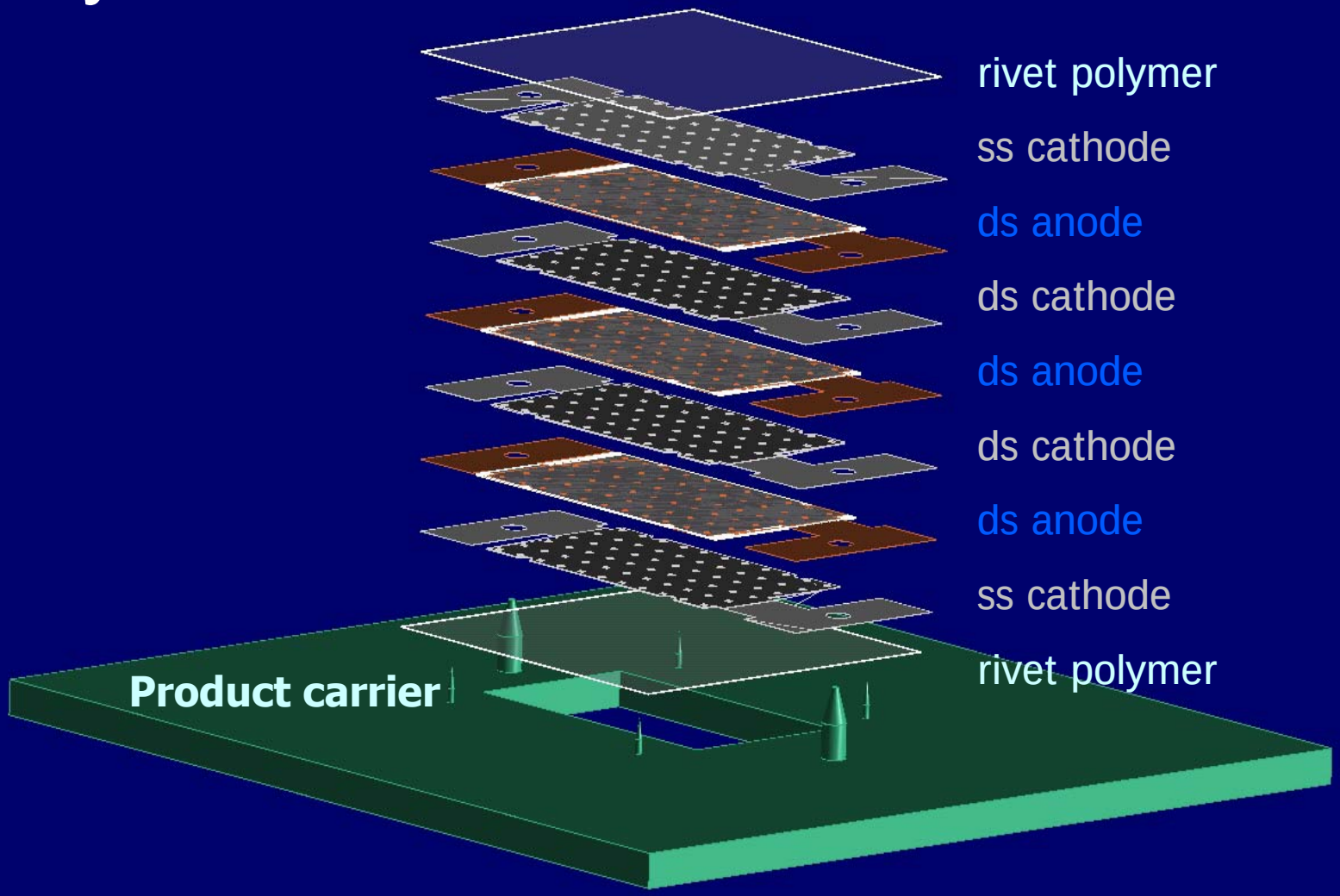
Evaluation kit

50 multi-cells/day

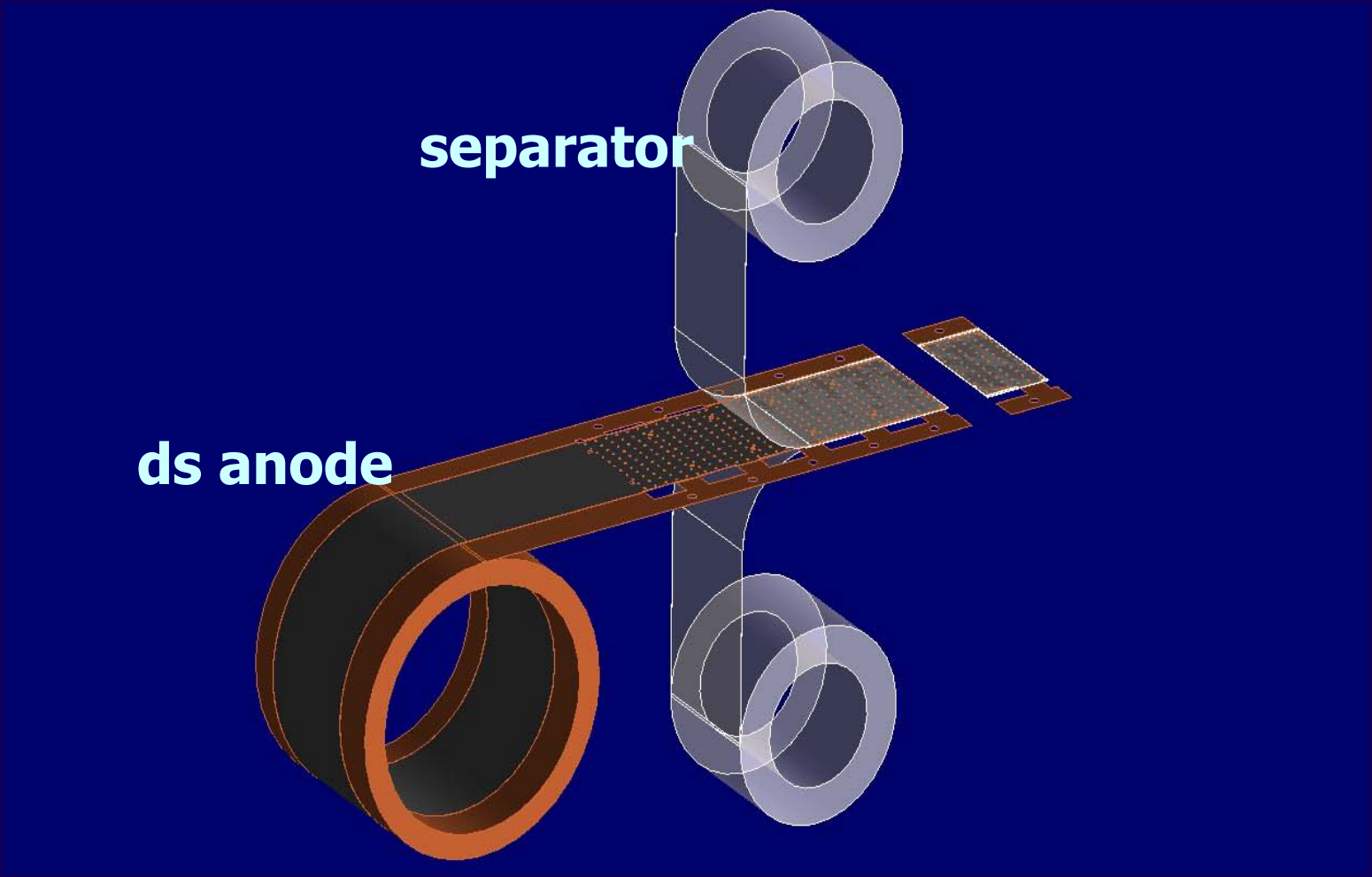
Manufacturing line



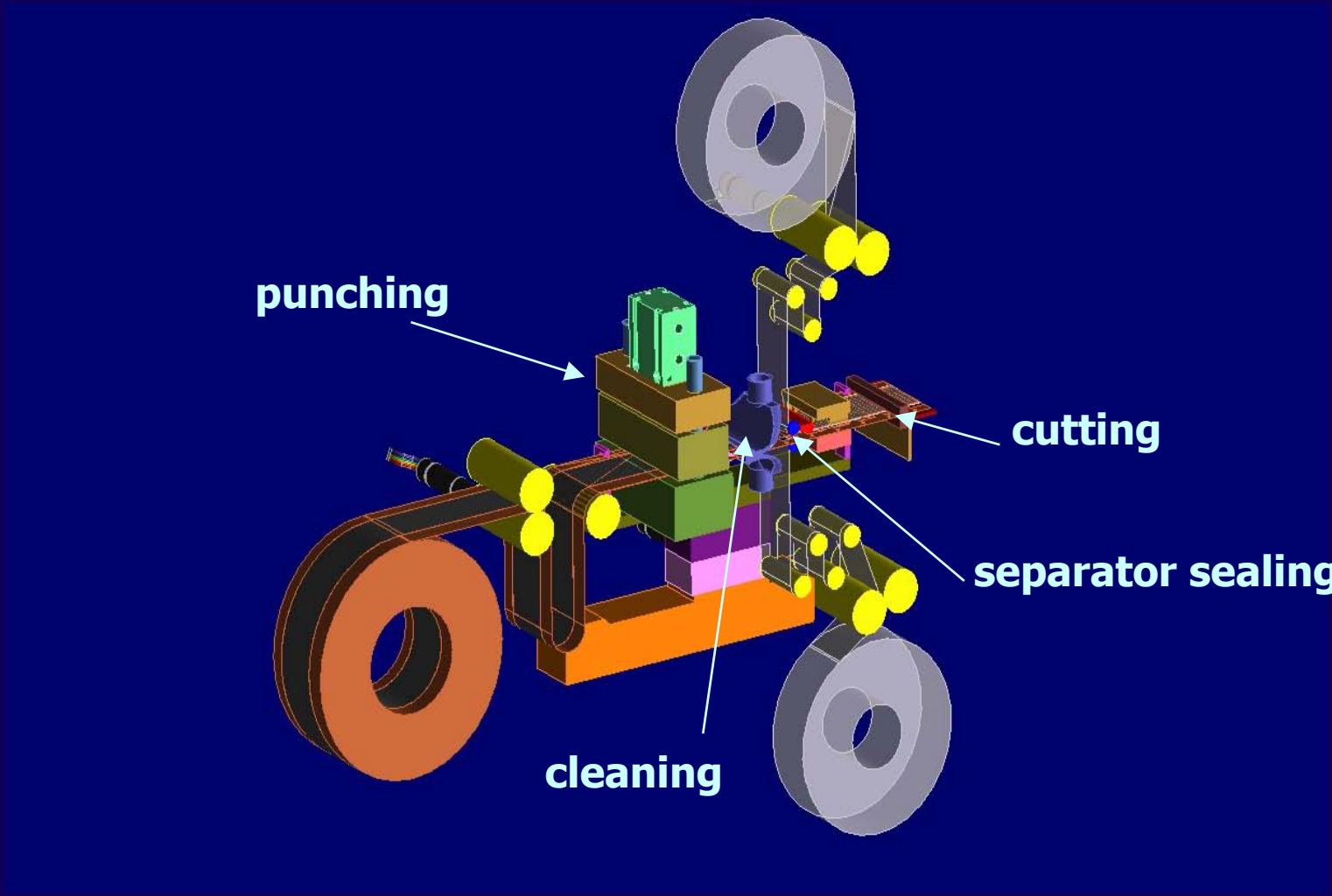
Lithylene stack



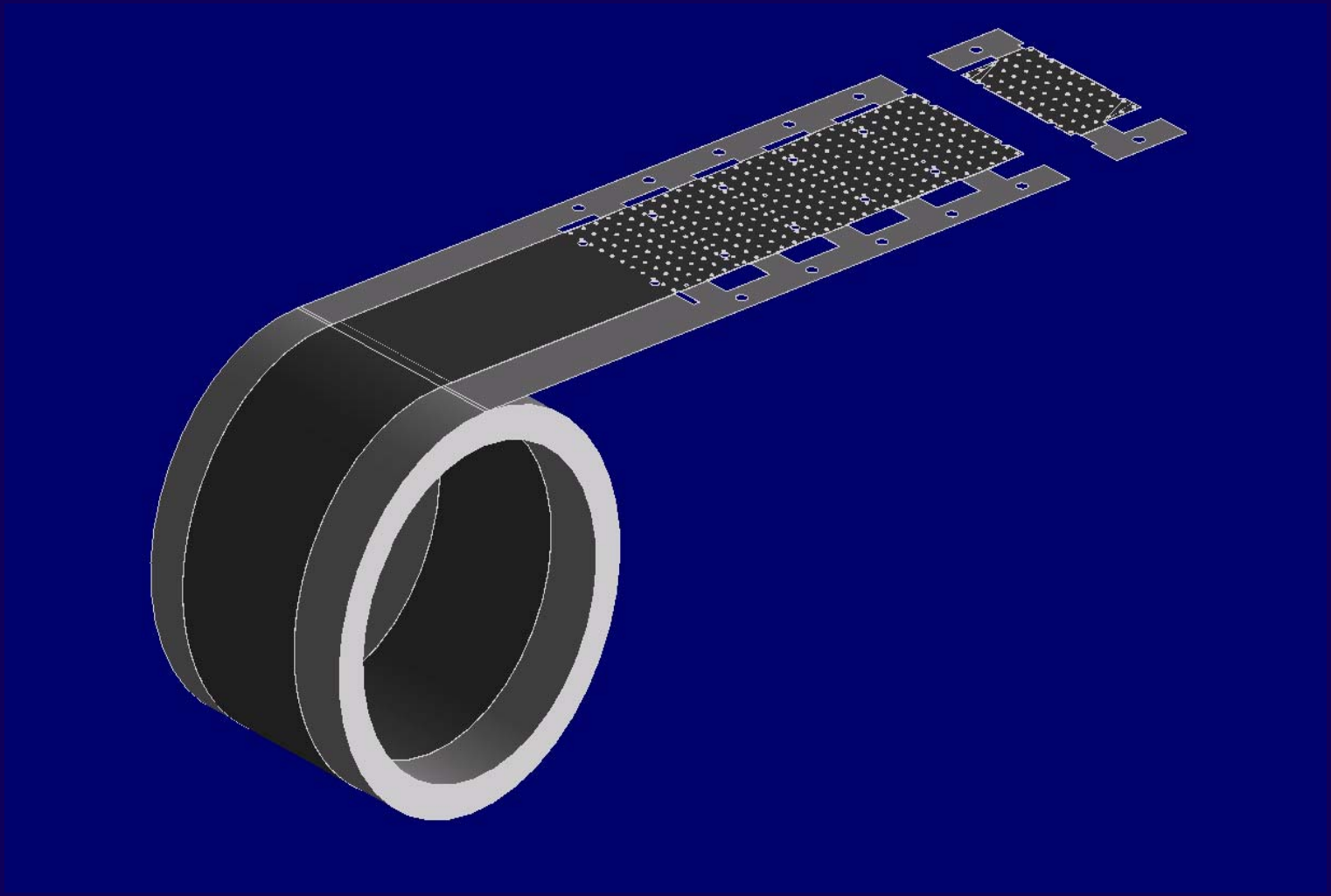
Anode



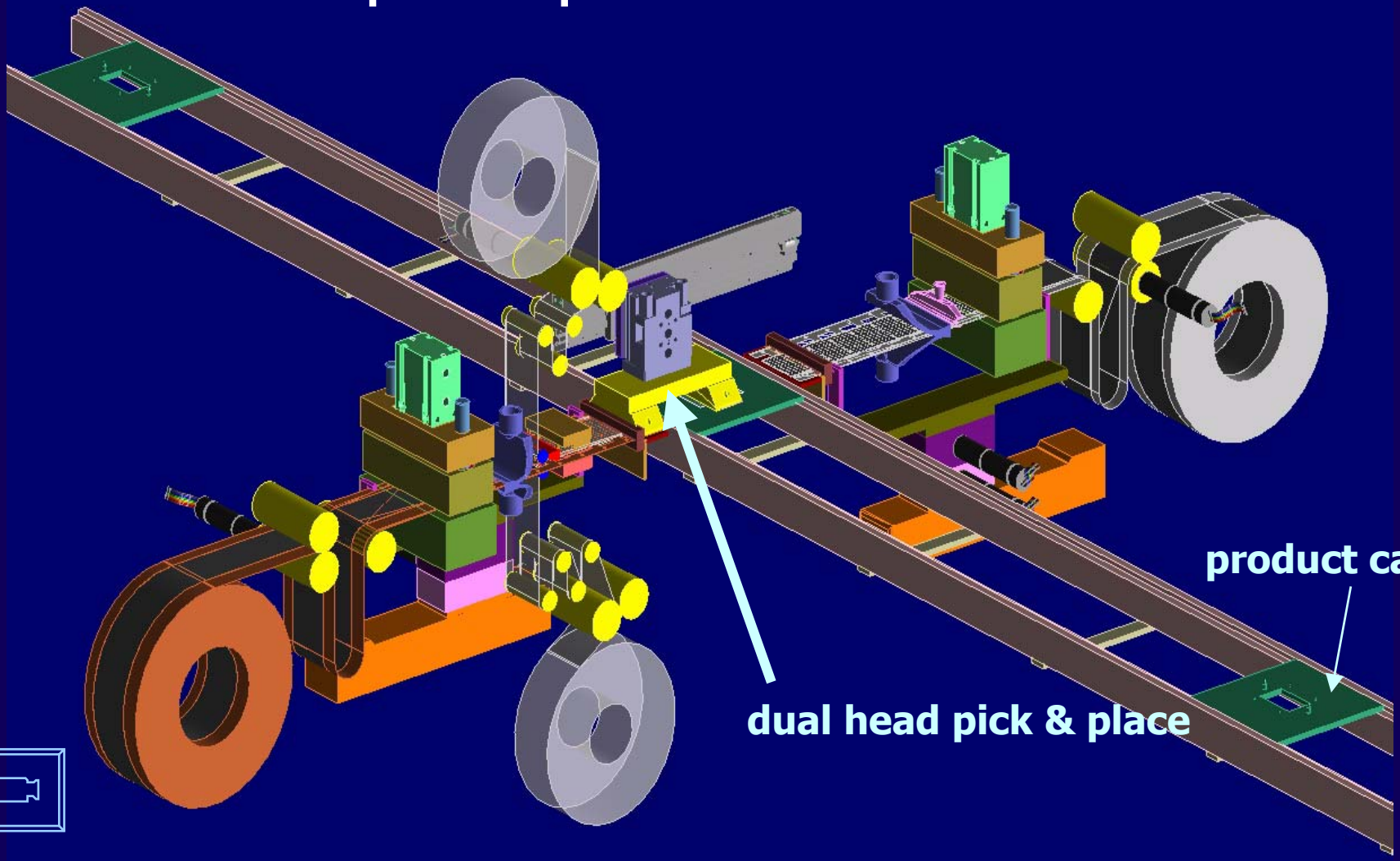
Anode feeder



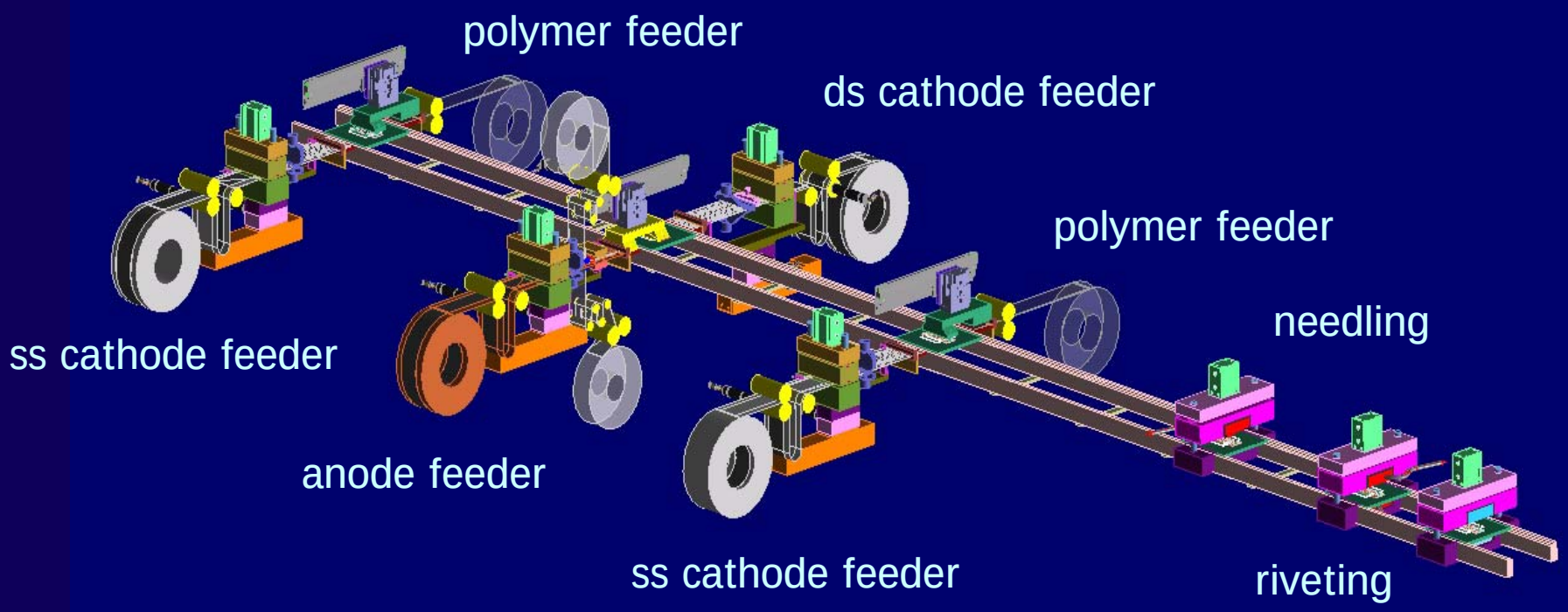
Cathode



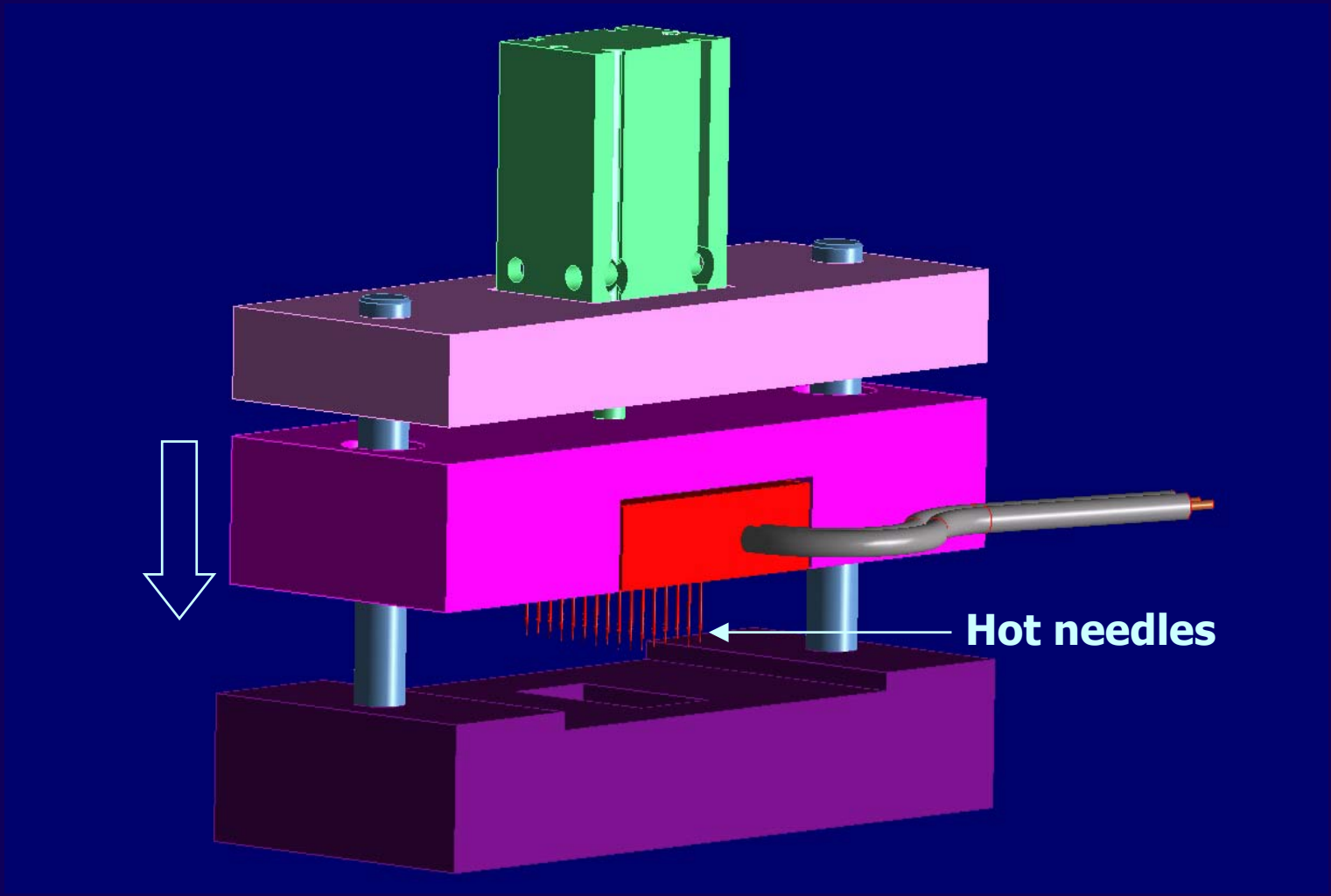
Electrode pick&place



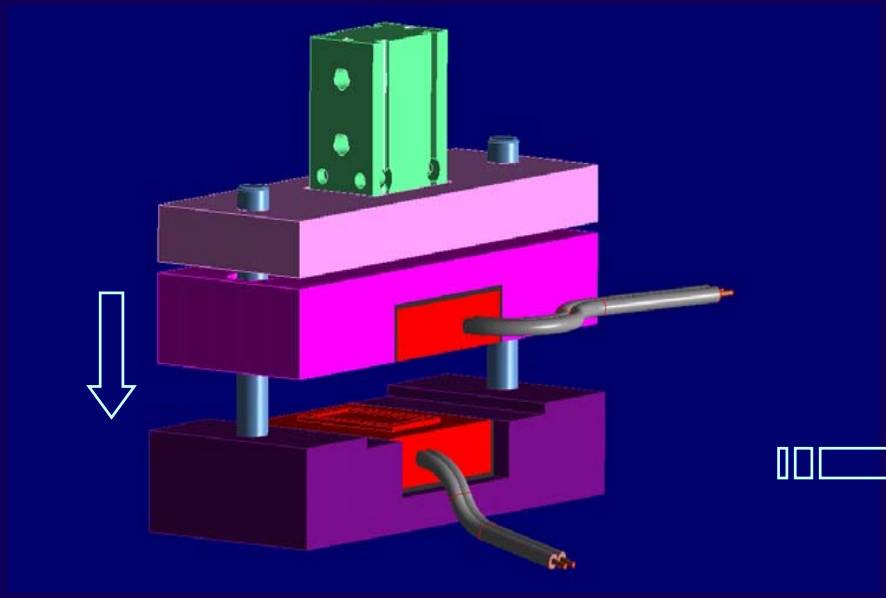
Manufacturing line



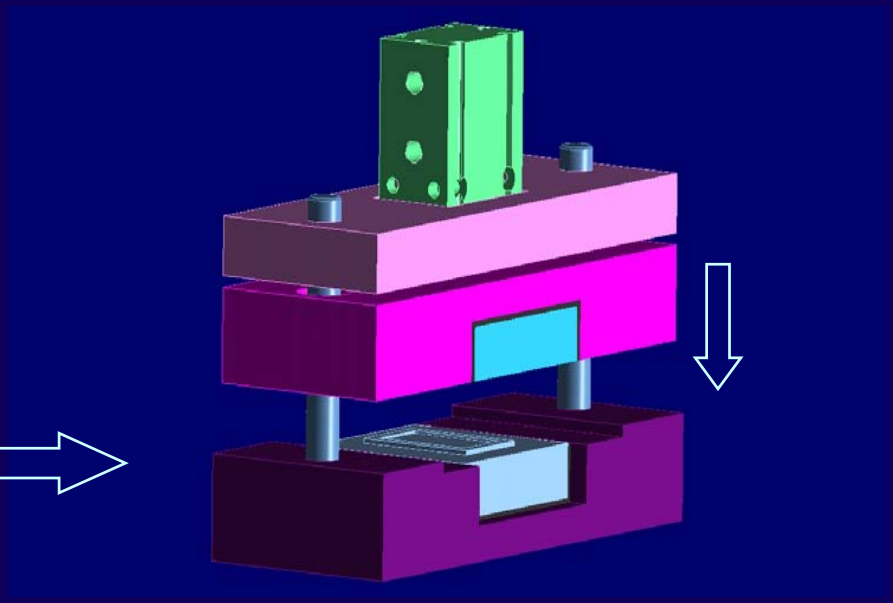
Needling



Riveting

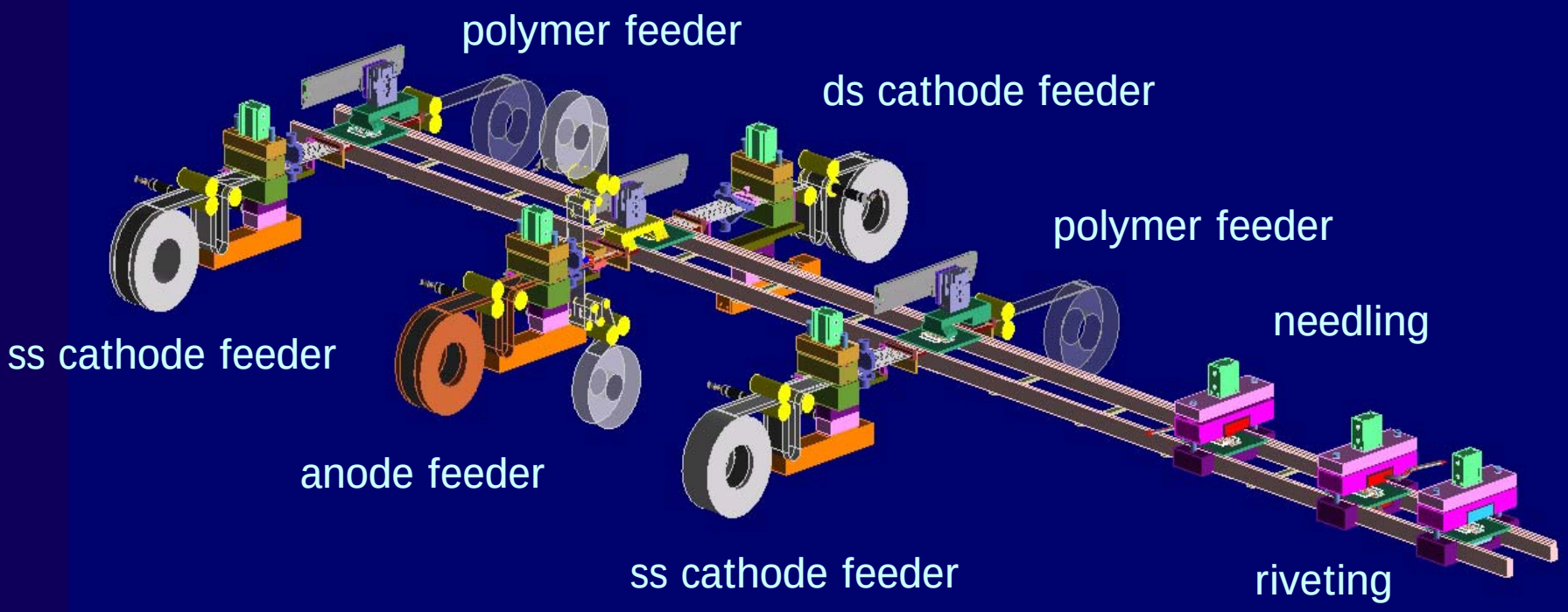


Hot press



Cold press

Manufacturing line



Philips *Lithylene*™

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cyril.chiang@lithylene.com

Update of LEO and GEO Cycling on Lithium-ion Cell and Batteries

R. Gitzendanner, F. Puglia, C. Deroy, S. Santee
Lithion - Yardney Technical Products
Pawcatuck, CT 06379
www.lithion.com

MSP01 Lander Battery

Fully Space-Qualified Lithium-ion Battery

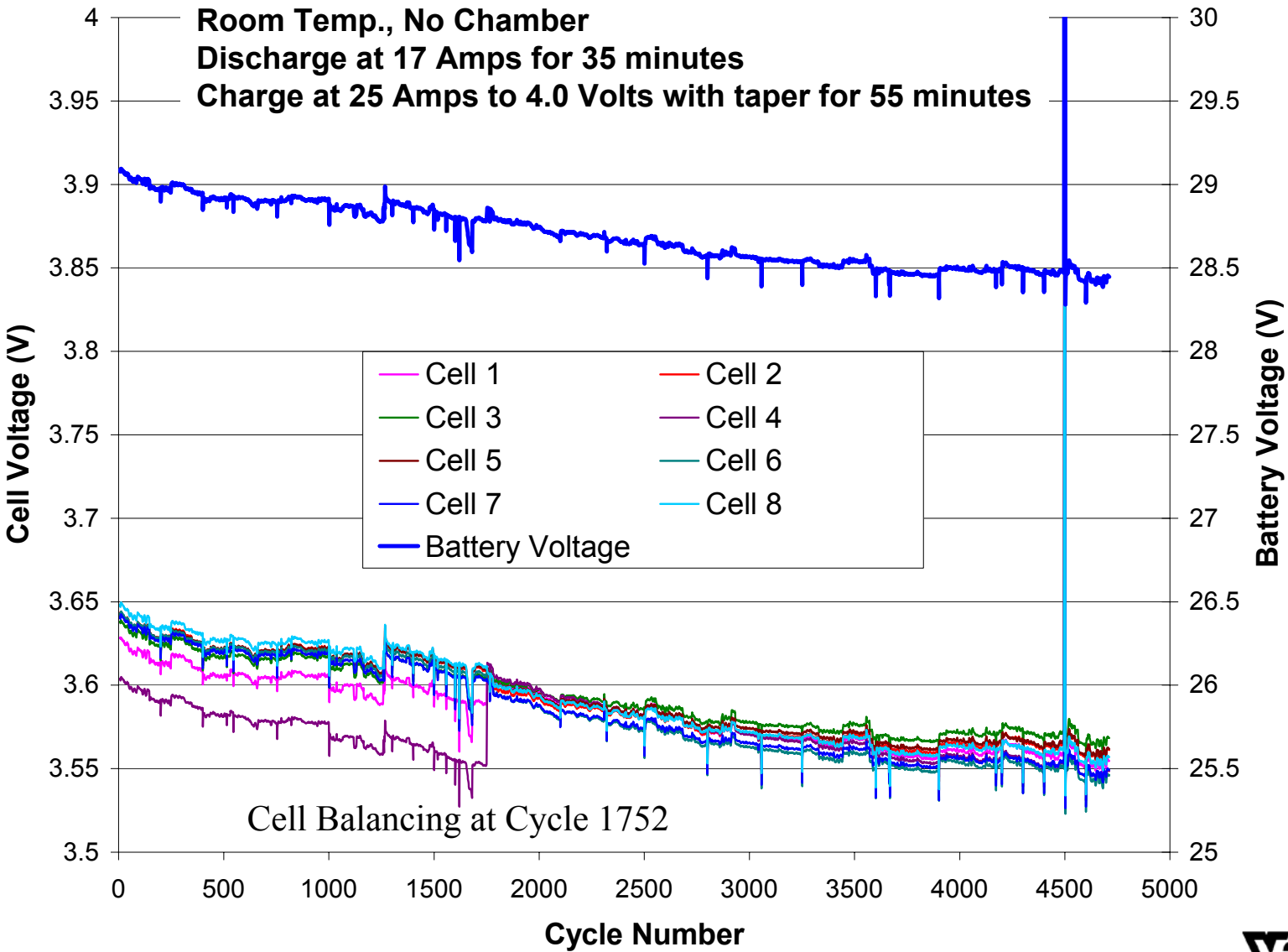
Lithion Inc.

MSP01 Lander Batteries

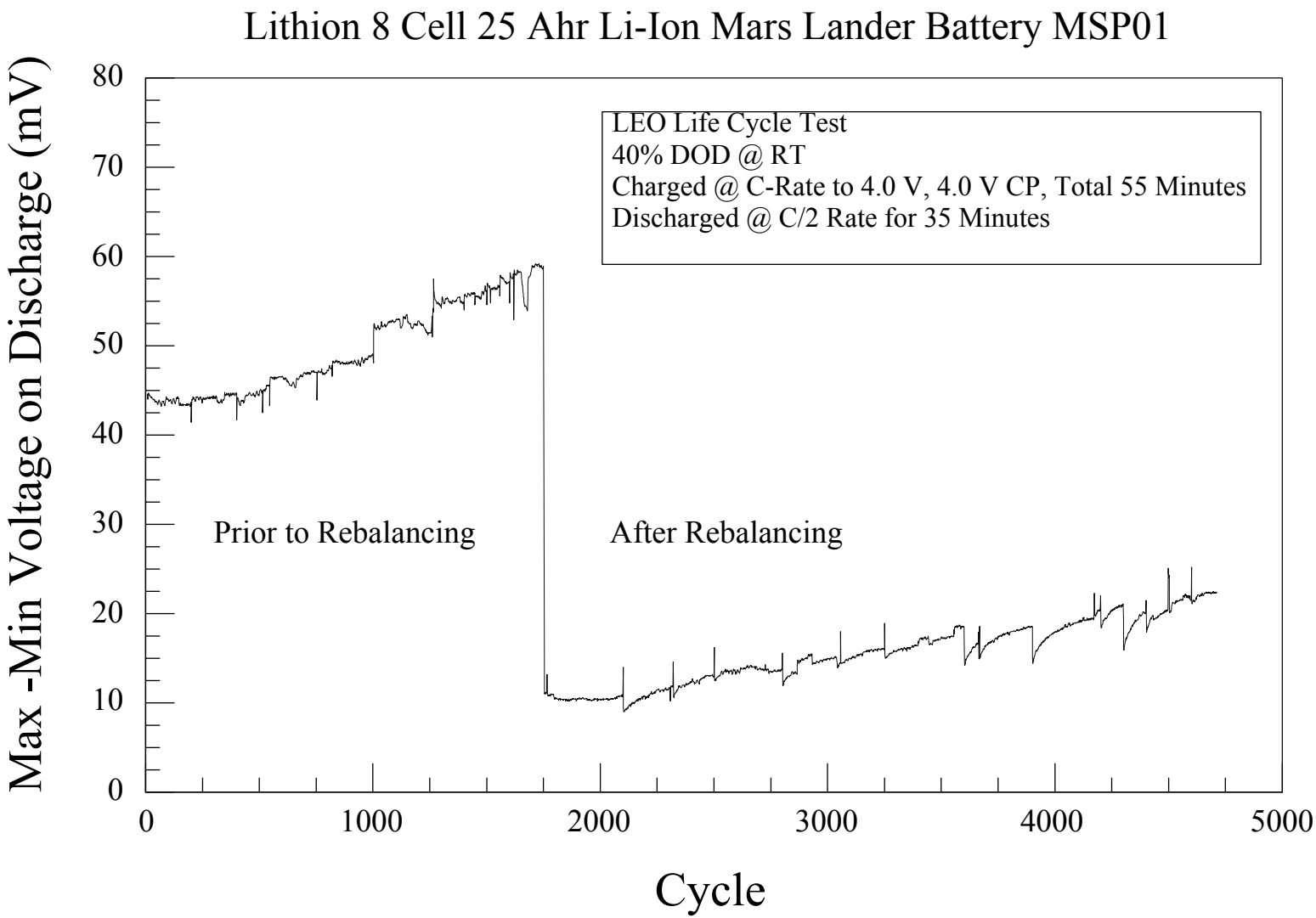
- *5 Batteries developed for the MSP01 Mars Lander Program*
  - *JPL - Further Mars Mission Simulation Testing*
  - *NRL - Full Sky Astrometric Mapping Explorer (FAME)*
    - *Slightly elliptical GEO-type mission*
    - *Scheduled for launch in 2005*
  - *NASA Glen*
    - *LEO cycling at low temperatures*
  - *Wright Patterson Air Force Base*
    - *LEO cycling at Room Temperature (continuation of pack-level tests*
  - *Lockheed Martin Astronautics (Returned to JPL)*
    - *LEO cycling at reduced charge voltages*

Yardney TECHNICAL PRODUCTS, INC.

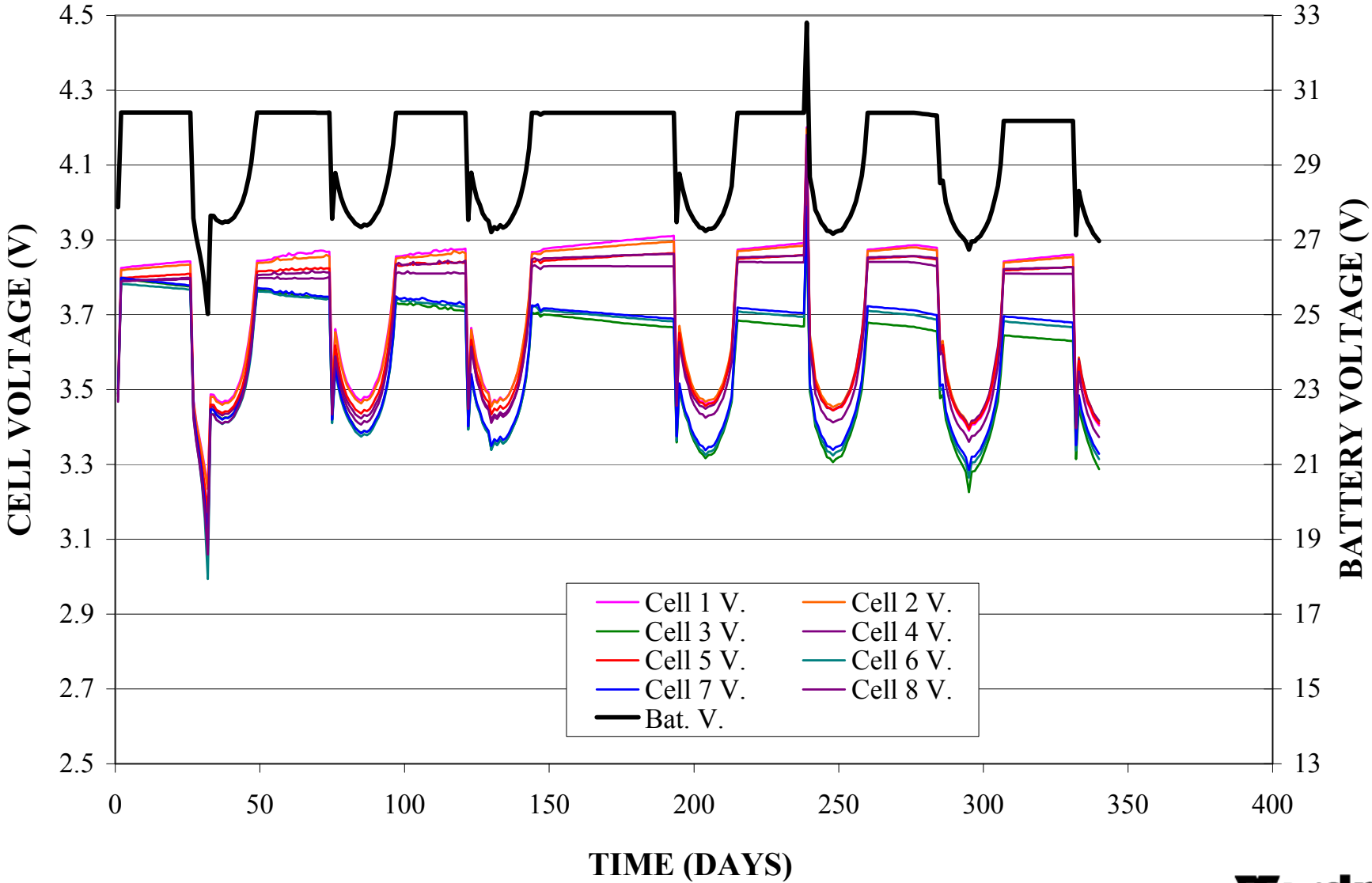
LEO Testing at WPAFB



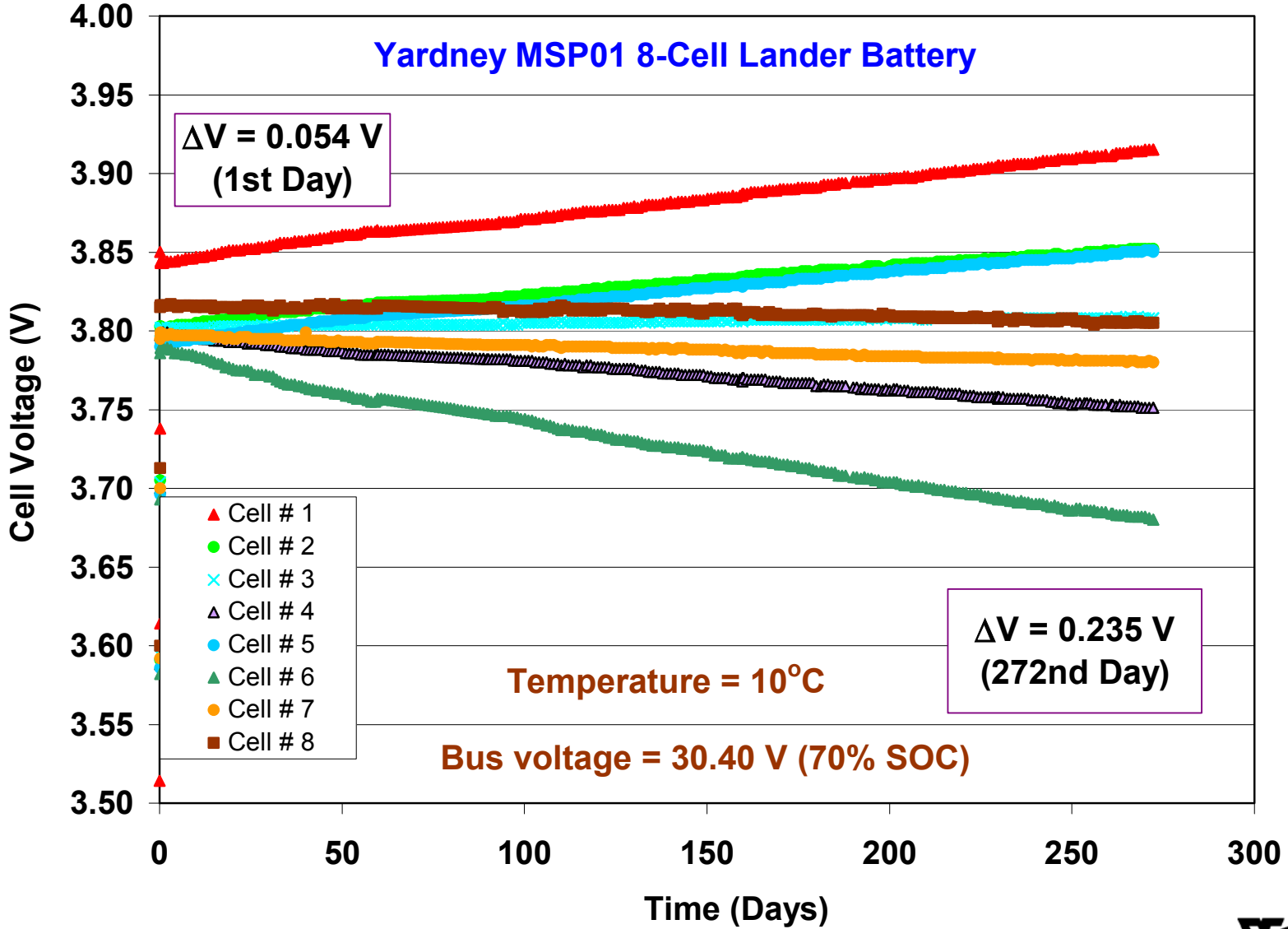
Cell Voltage Difference



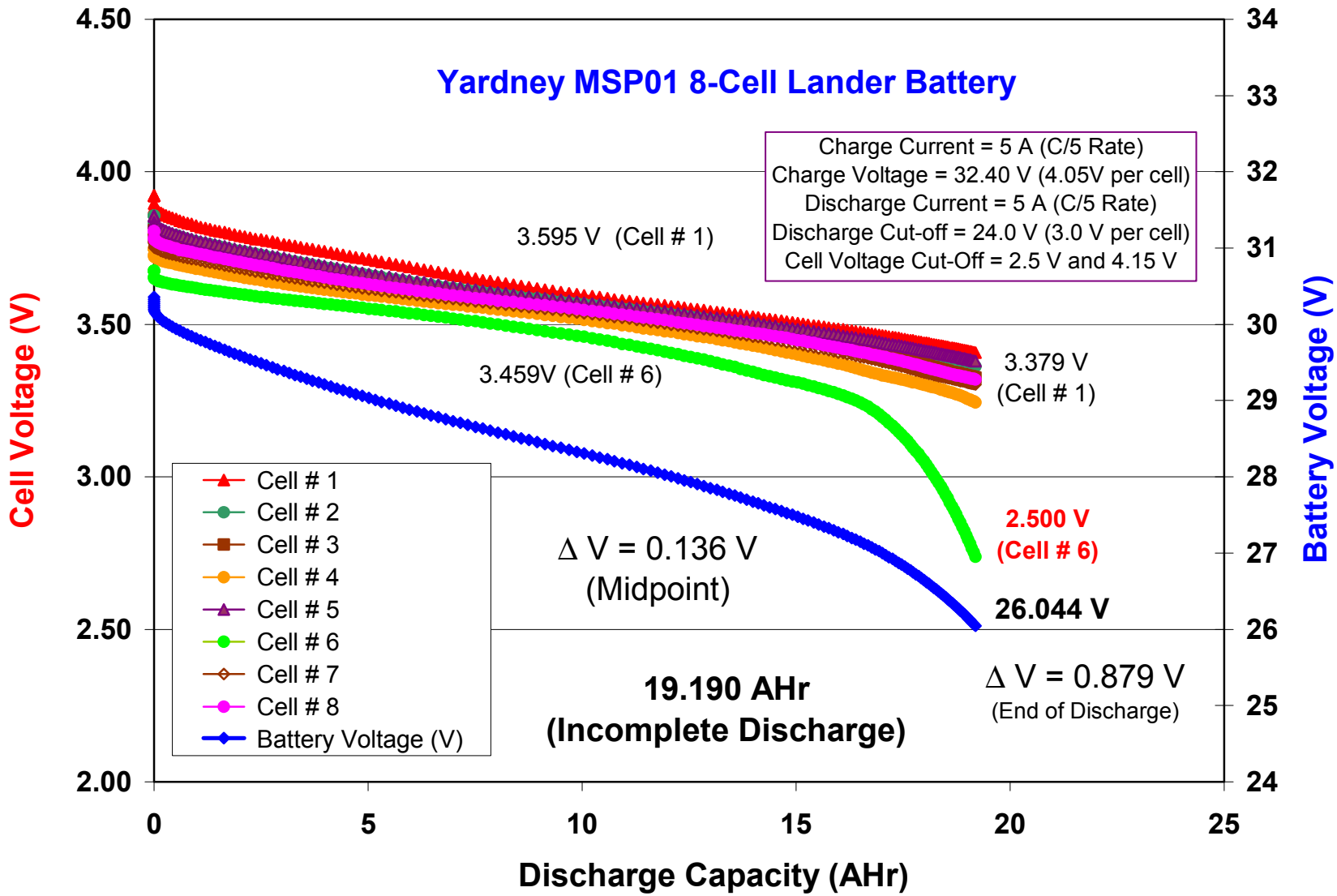
NRL - FAME Tests



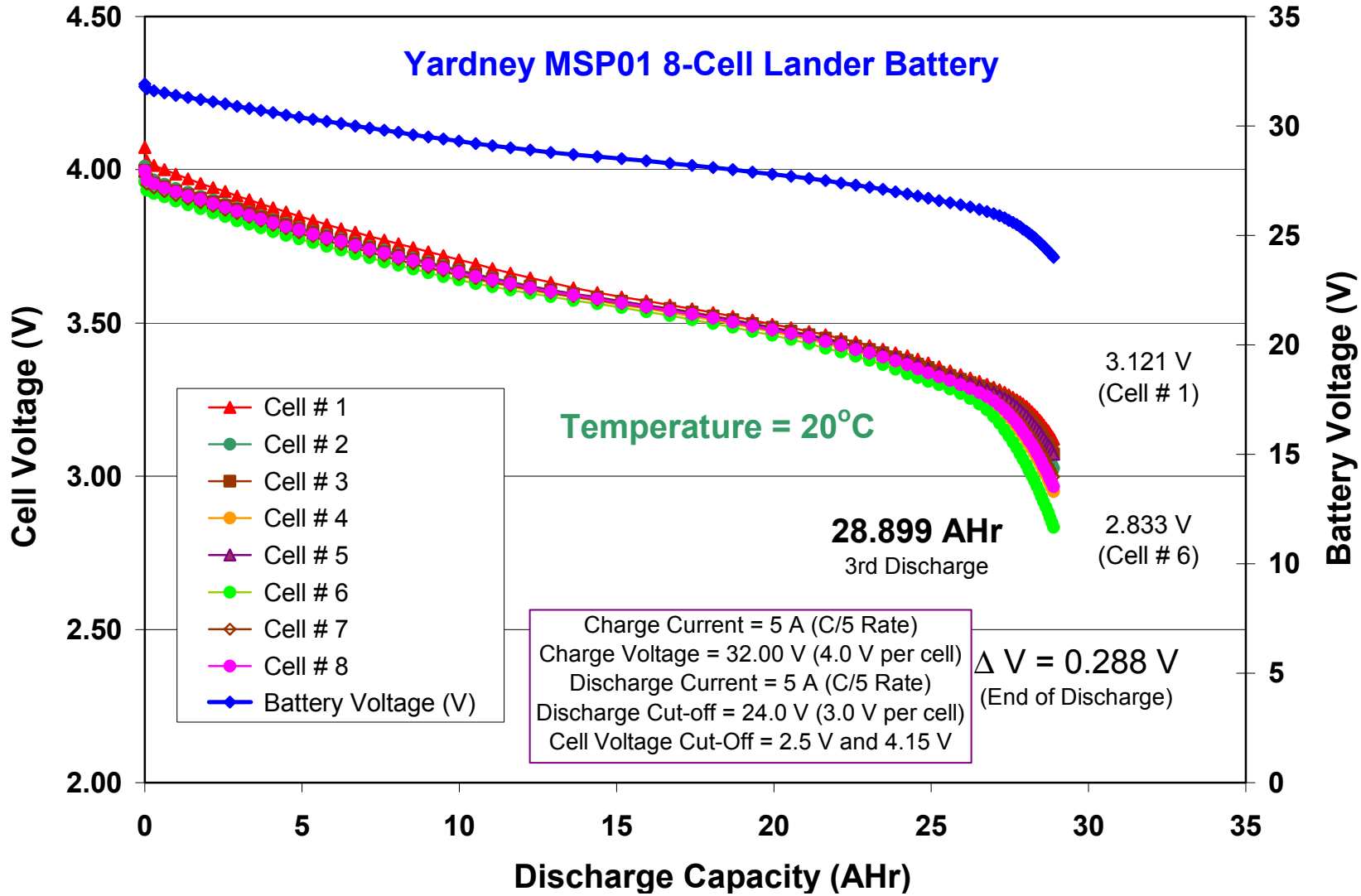
JPL - Cruise Storage Simulation



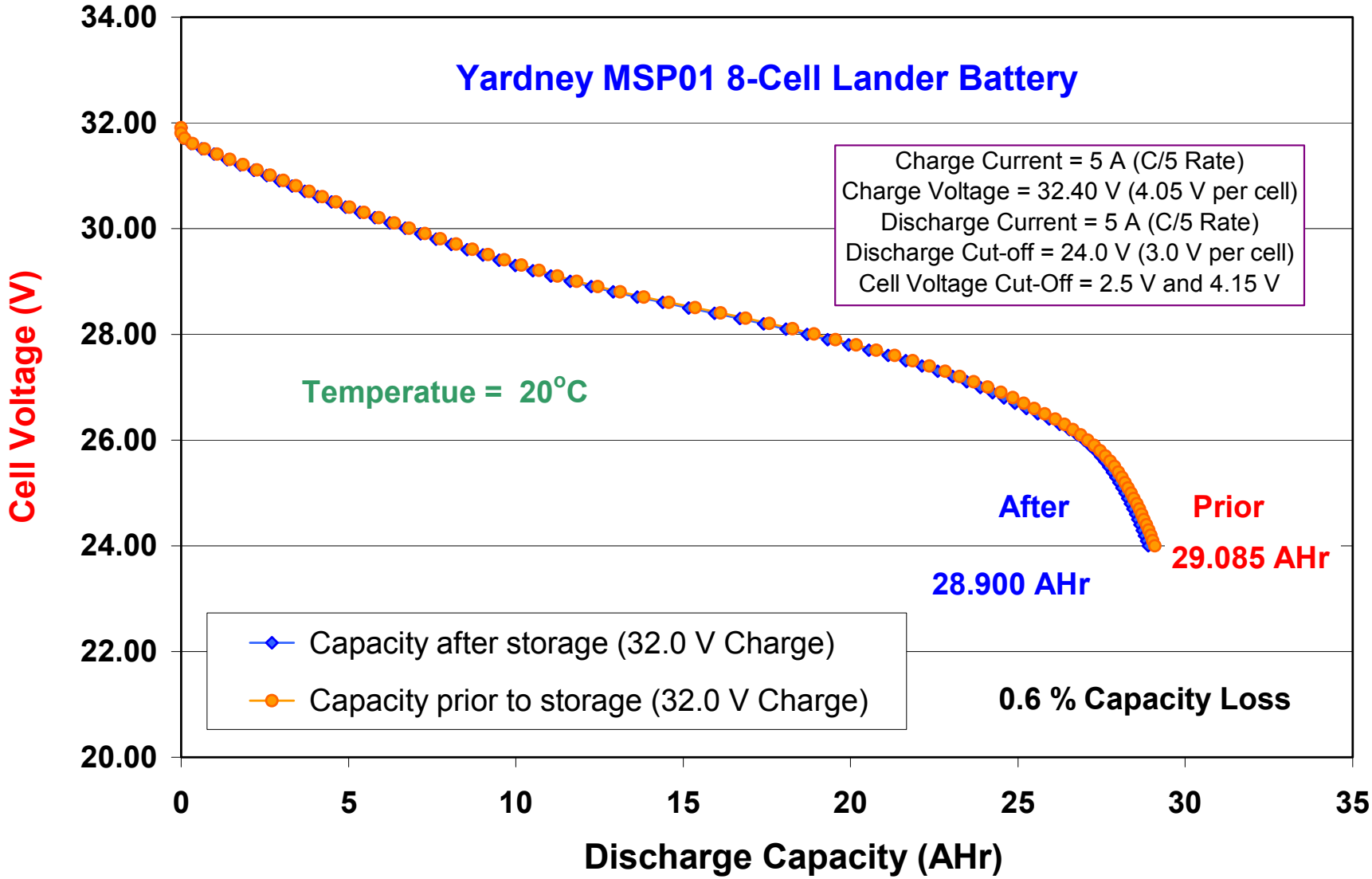
Post-Cruise Discharge



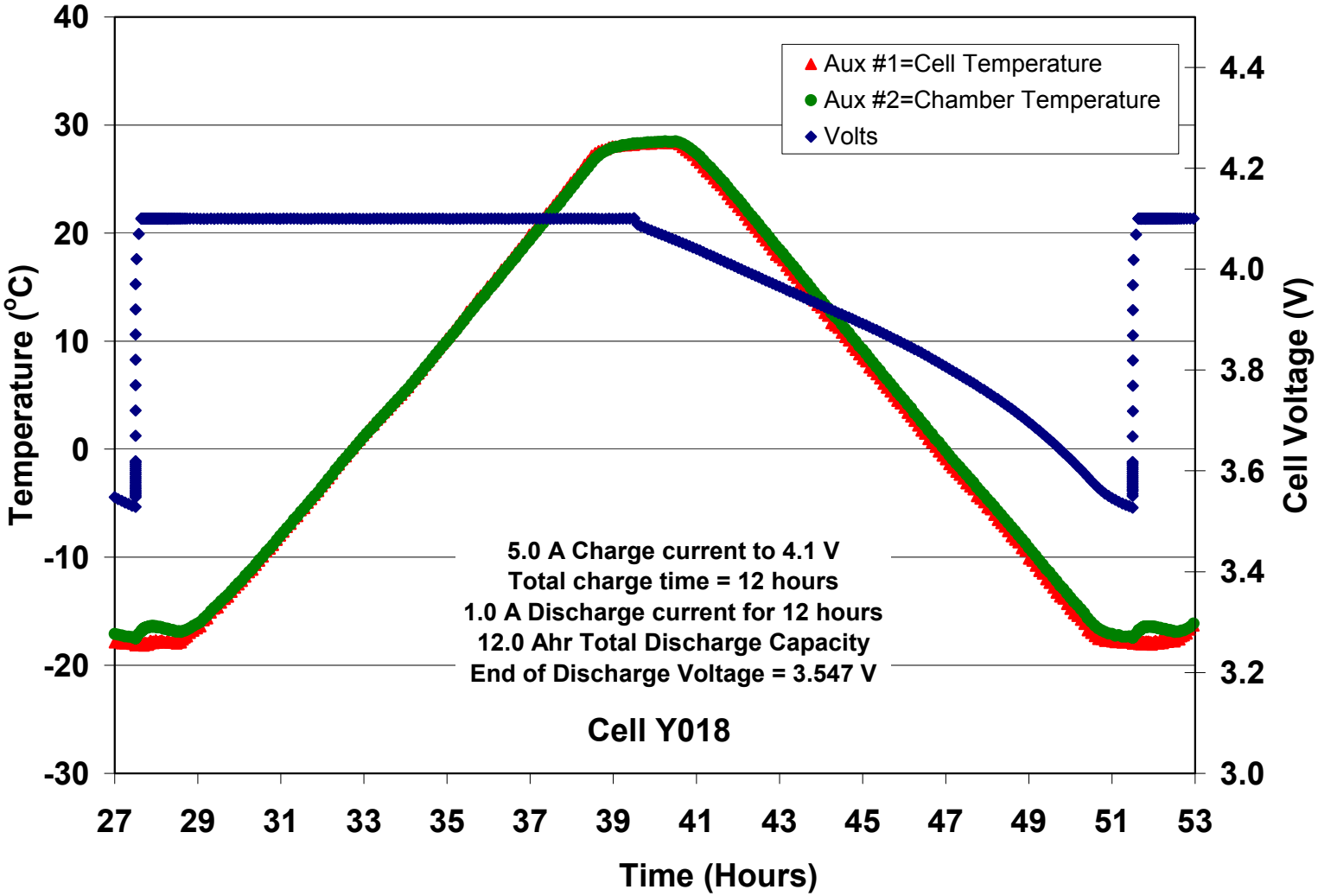
After Balancing



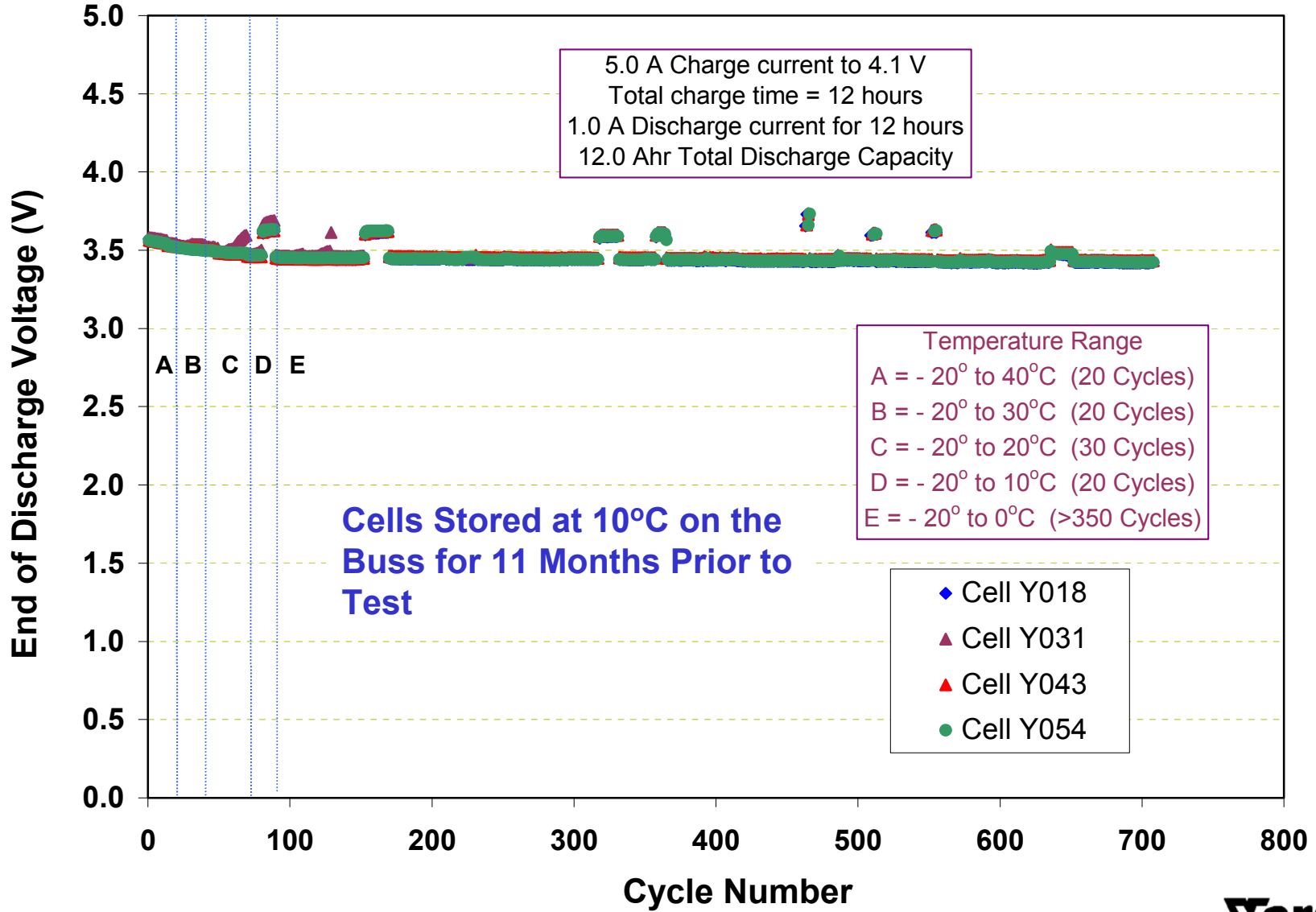
Before and After 9 Month Cruise



Mission Simulation

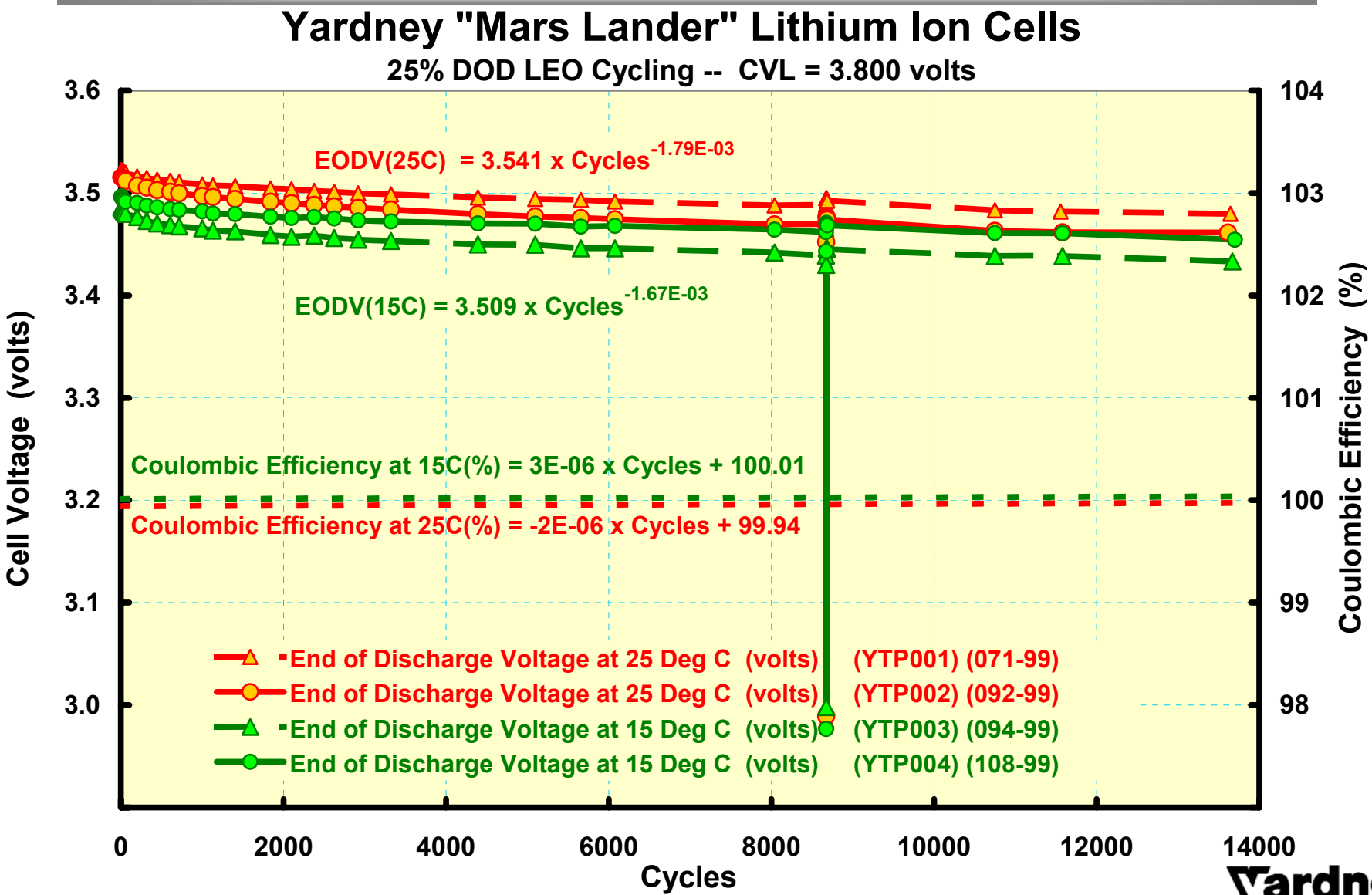


Cell-level Mission Simulation

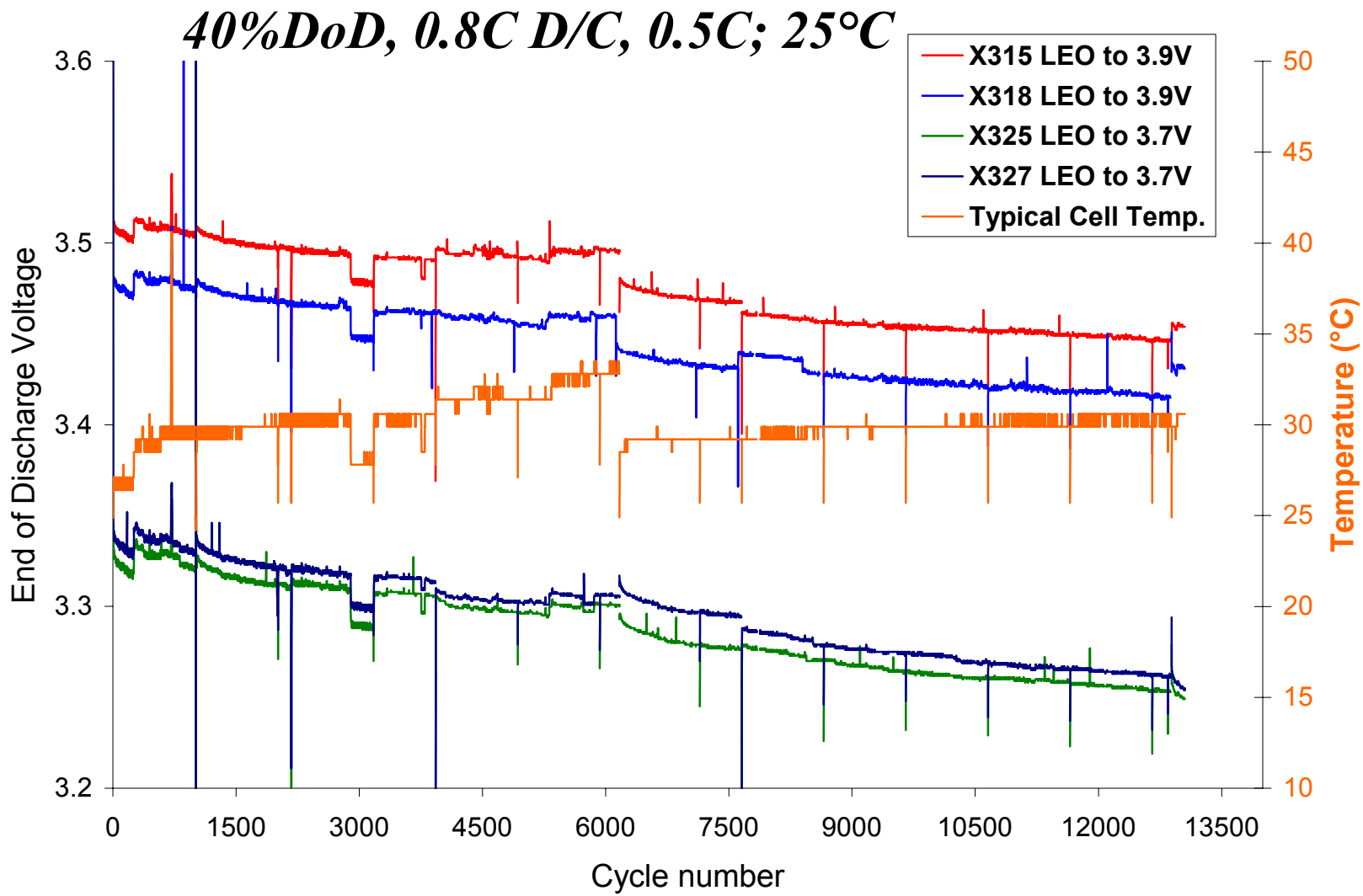


Cell-Level Testing

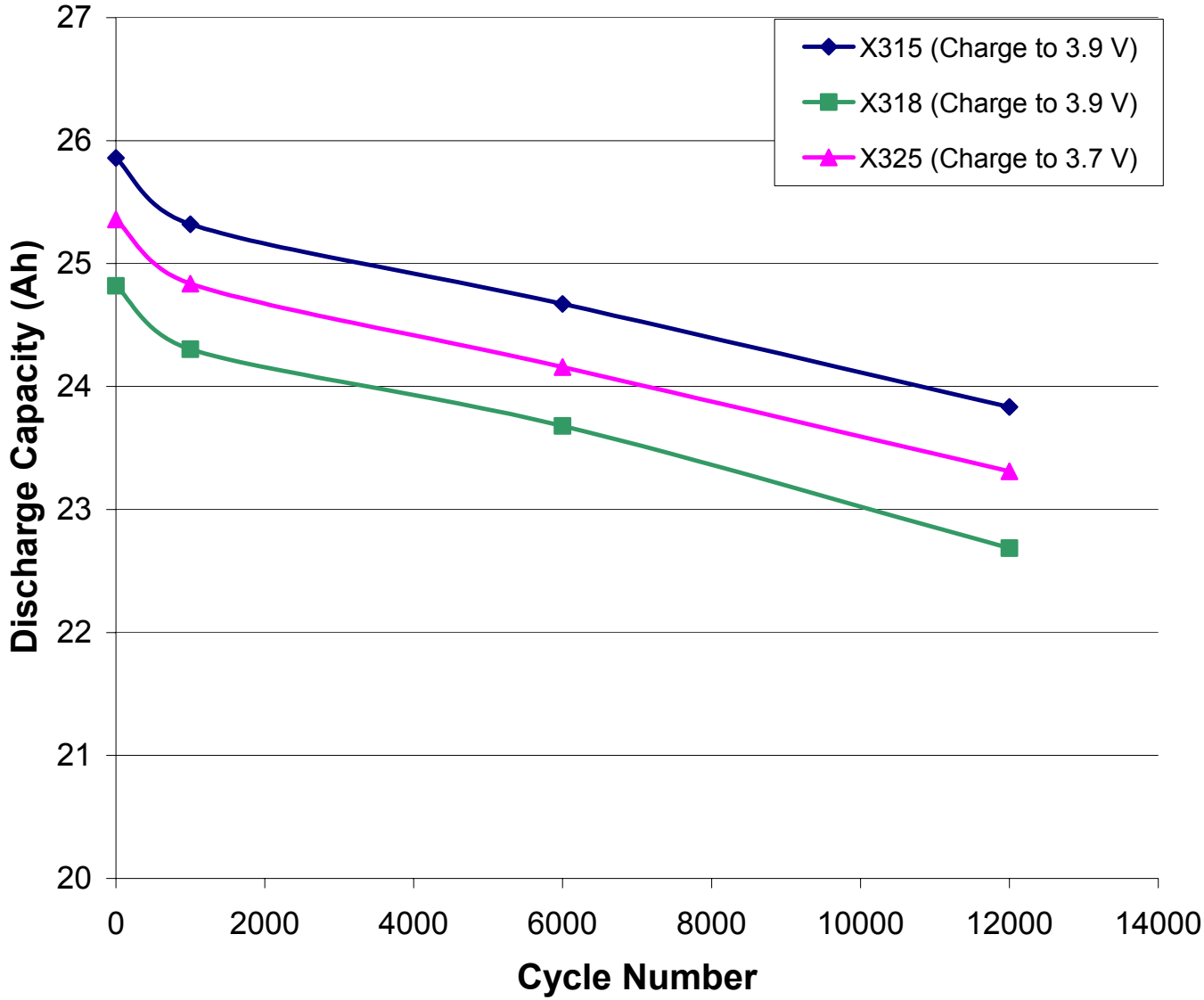
LEO Cycling at TRW



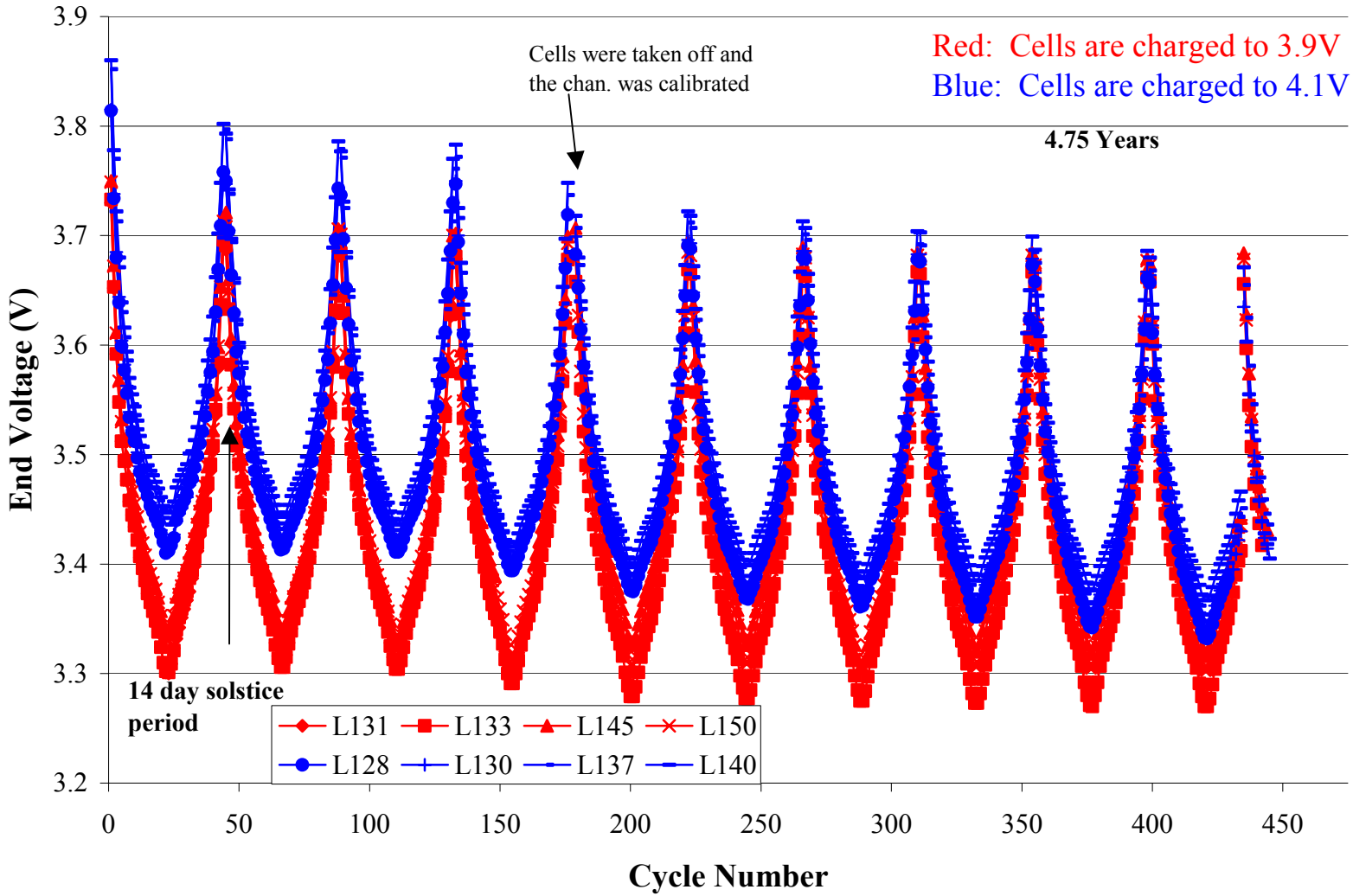
LEO Cycling at Lithion



Capacity Check Cycles



GEO Cycling

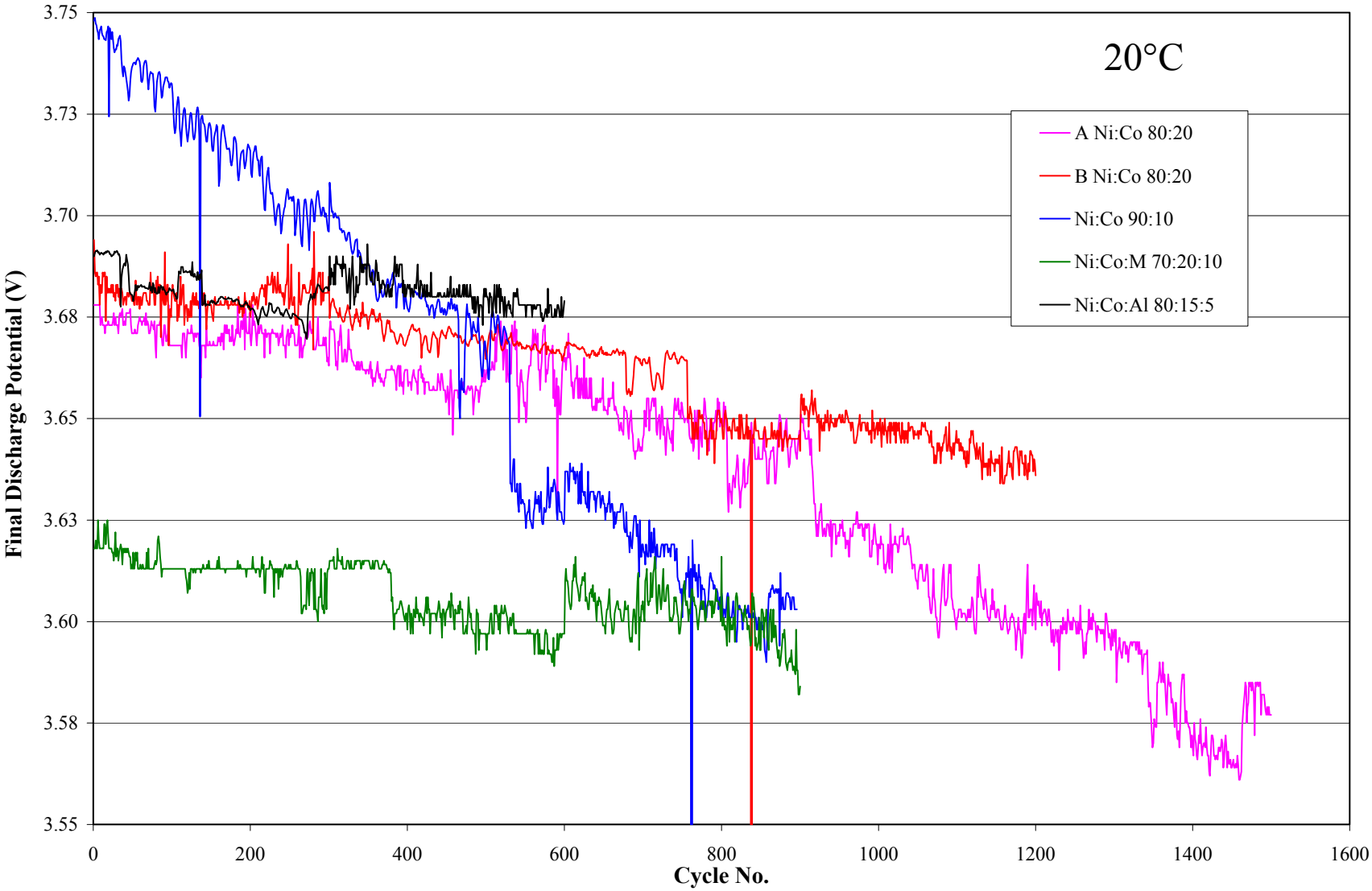

Cells were taken off and the chan. was calibrated
Red: Cells are charged to 3.9V
Blue: Cells are charged to 4.1V
4.75 Years
14 day solstice period
L131
L133
L145
L150
L128
L130
L137
L140
End Voltage (V)
Cycle Number
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
0
50
100
150
200
250
300
350
400
450

Investigation of New Materials

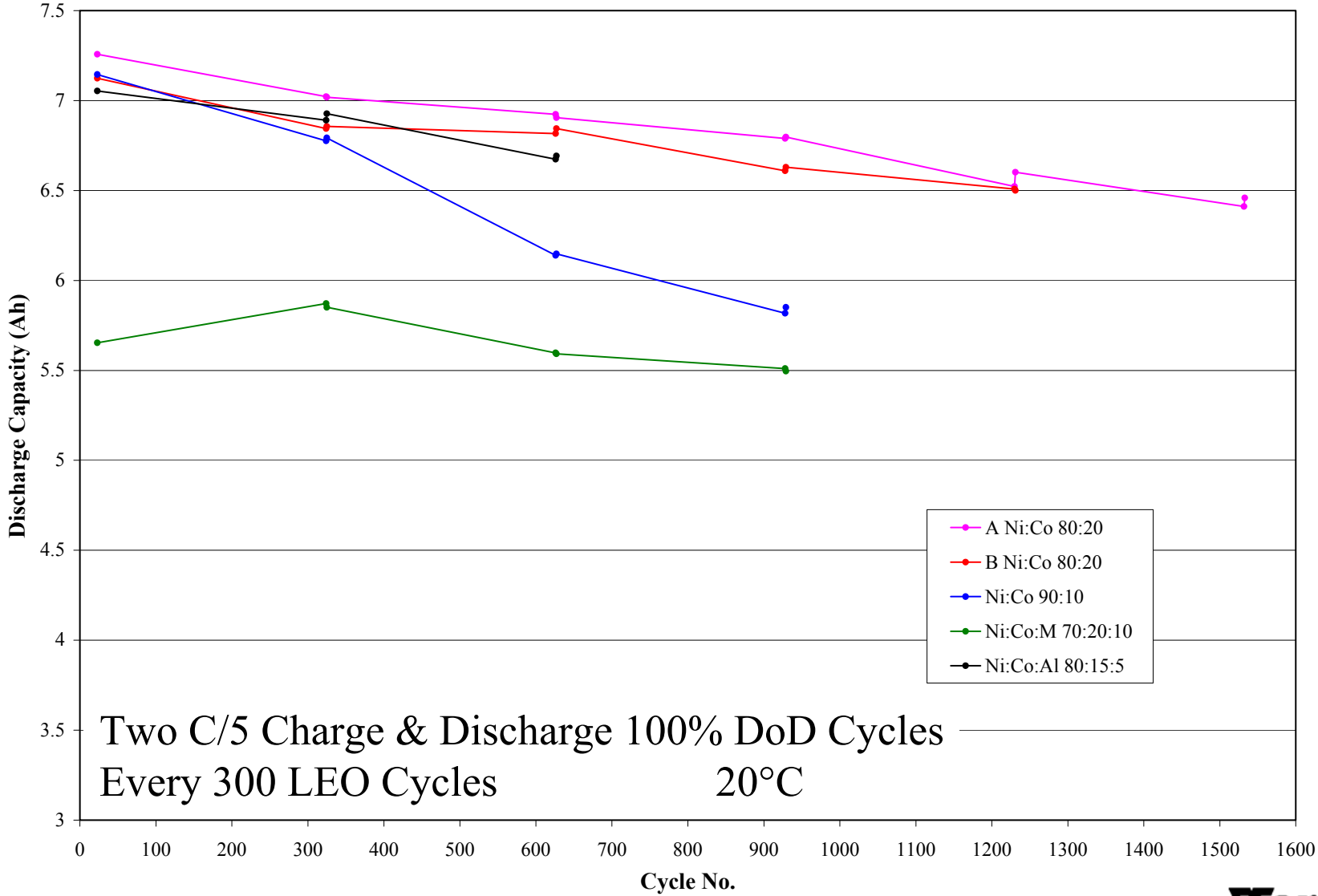
Continued Development

- *Current Baseline technology still available*
- *Investigating new materials for next generation designs*
  - Improved $LiNiCoO_2$
    - Aluminum Doped
    - Doping with other metals
  - Enhanced $LiCoO_2$
- *Beginning program to investigate Anode materials*

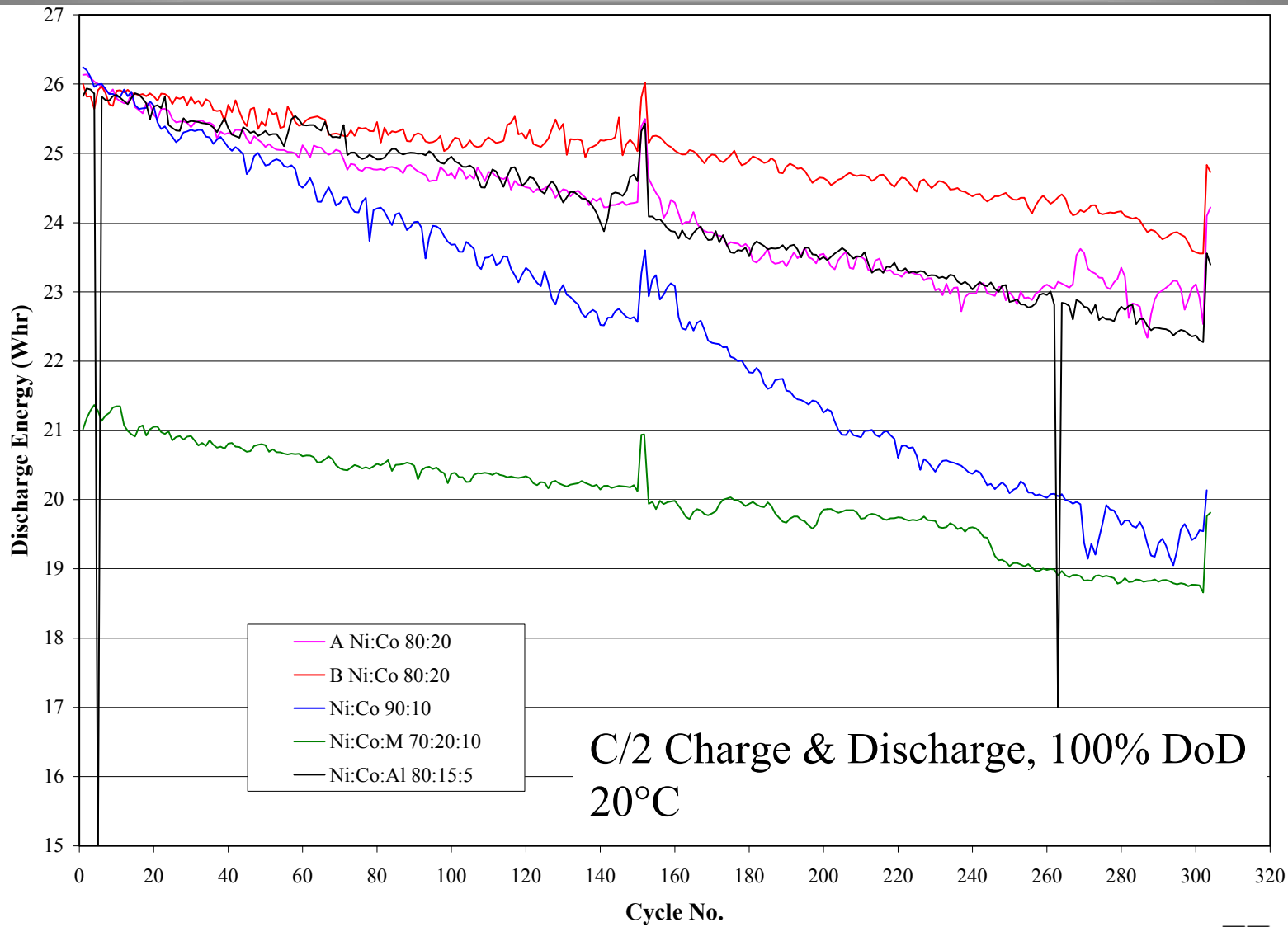
40% DoD LEO Cycling



Capacity Check Cycles



100% DoD Life Cycling



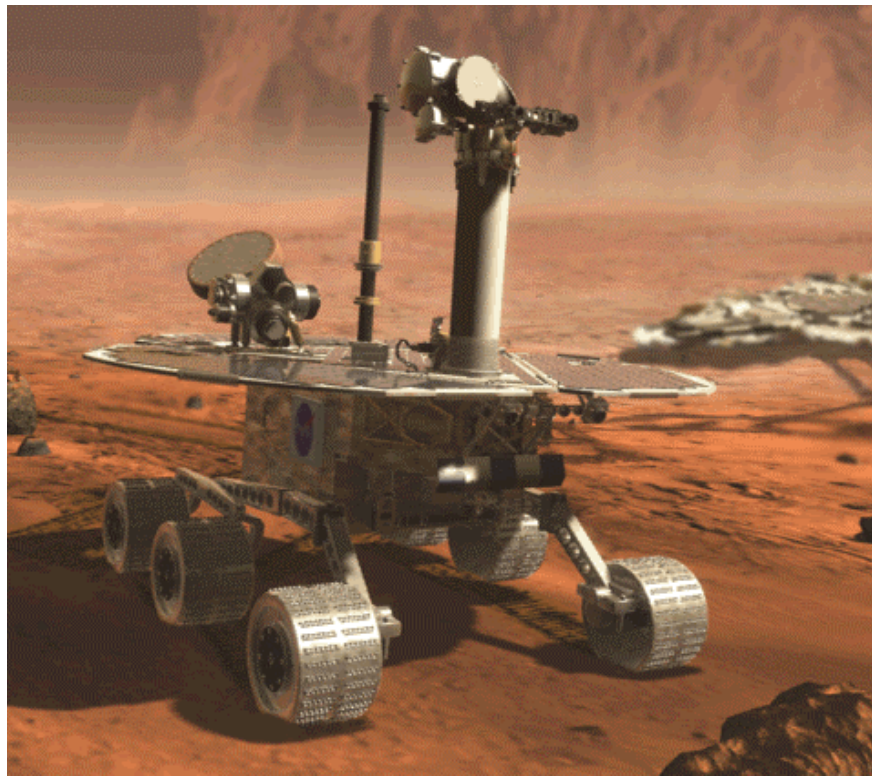
MER Rover

"Son of Lander"

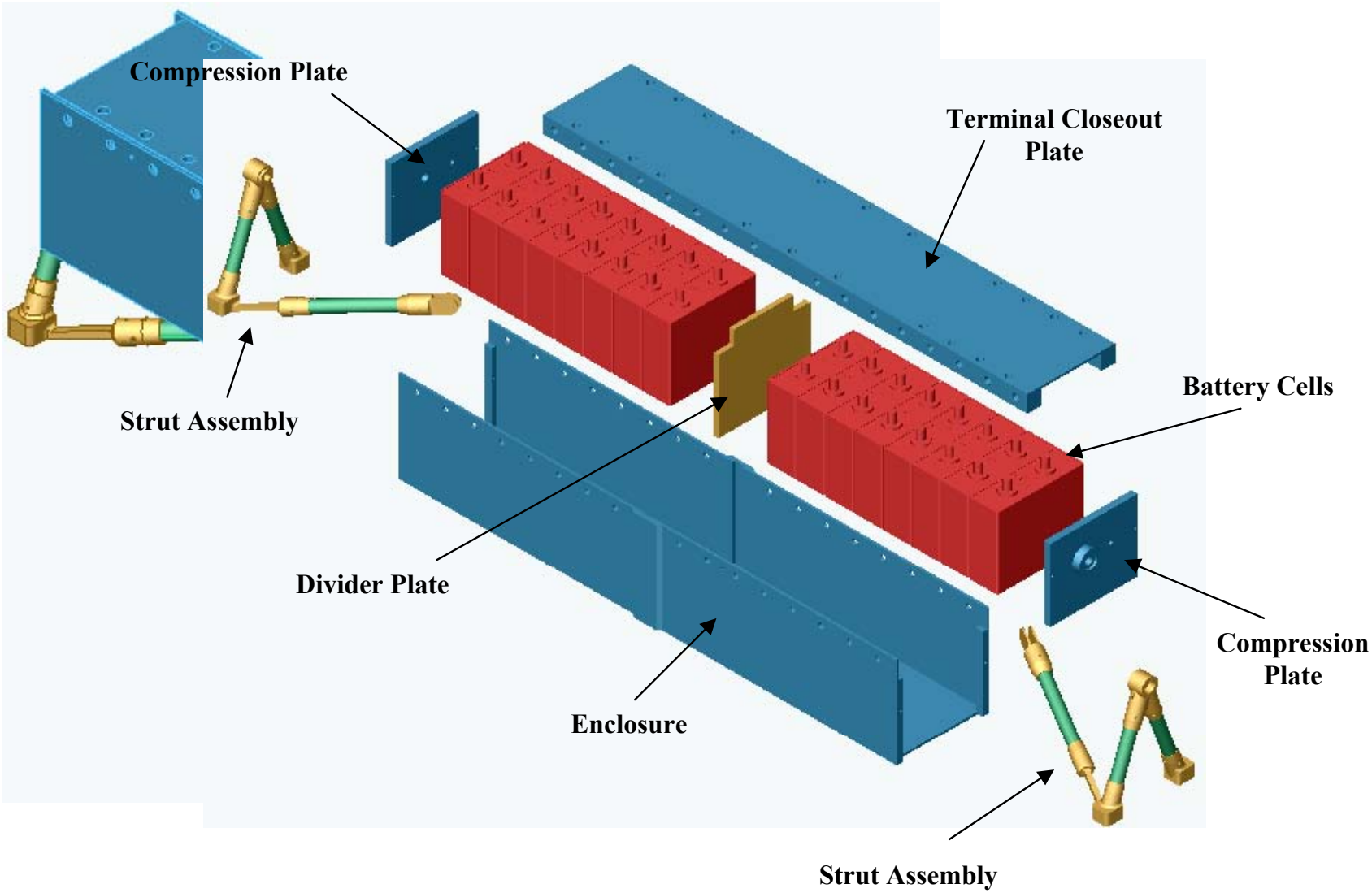
Short Marketing Segue

MER Rover

- *2003 Mars Exploration Rover*
- *NASA JPL Program*
- *Battery Power Supply for "Must Not Fail" Mission*
  - High Reliability
  - Fast Turn Around
- *2 x 28V, 10Ah Batteries*
- *Launching Two Rovers*
- *Must Survive 50g Landing Impact*
- *Flight Batteries delivered Nov '02*



Battery Design



Conclusions

- *Extensive Database of Cell and Battery Level performance to Aerospace Application Regimes*
- *LEO and GEO cycle data to date extrapolates to meeting Mission Requirements with substantial margin*
- *Battery-level testing continuing to show most important "real-world" data*
  - Take home message: Cell balancing is an important consideration in battery design.

Acknowledgements

- *This effort is funded by the Air Force Research Labs at Wright Patterson Airforce Base, contract number F33615-98-C-2898*
- *Data Supplied by*
  - Gary Loeber – WPAFB
  - Marshall Smart – JPL
  - Chris Garner – NRL
  - Chuck Lurie – TRW
- *Co-Workers and other staff at Lithion*

NiH_2 LEO Cycle Life Study

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Sunnyvale, CA

Gopalakrishna M. Rao
NASA/Goddard Space Flight Center
Greenbelt, MD

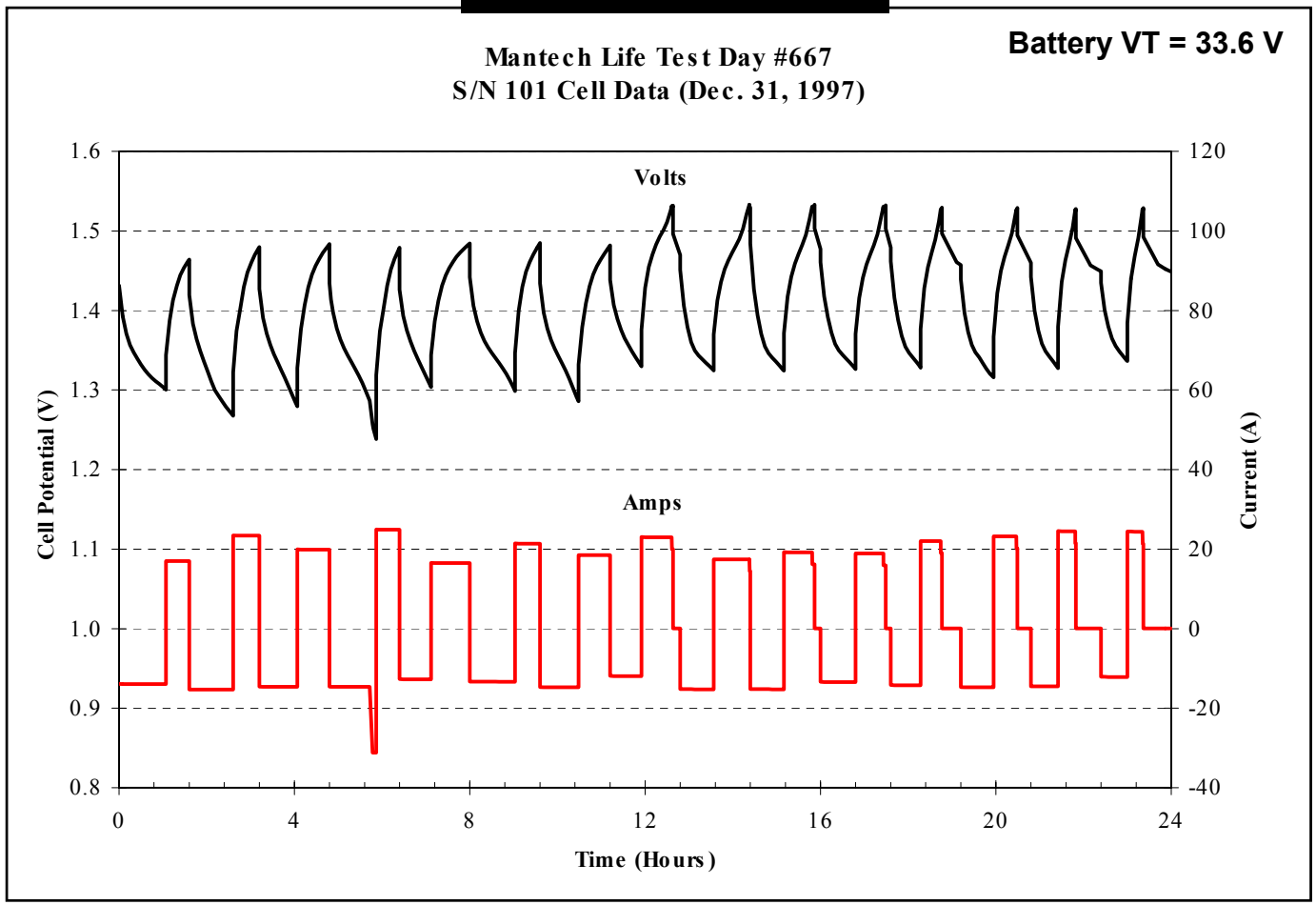
Mantech Cell Cycle Test History

- Mantech Cells on Duty Cycle Test at 41 °F at Various Load Levels Since 1996
  - Generic LEO Load Profile with Peak Load Test for Minimum Voltage Test
  - Concern With Spacecraft is Low Bus Voltage Trip into Safe-Mode
  - Reconditioning Scheduled Annually During Cycling
  - Also Perform Reconditioning to Maintain Voltages Above Minimum Requirement
    - 19 - 22 Cells in Series Configuration
- Lot 1 Slurry Process Cells Added 3/96 - Completed 35.2K Cycles
- Lot 2, 3 Slurry Process Cells Added 9/97 - Completed 26.7K Cycles
- HST Dry Sinter Cells (3) added 9/97
  - Previously Cycled 6 Years at MSFC (~33K Cycles) - Unknown Storage History
  - Removed From Test 10/00 (16K + ~33K Cycles) - Cold Storage @ EPT
- Lot 5 Slurry Process Cells Added 10/98 - Completed 21.0K Cycles
- Lot 6 Slurry Process Cells Added 10/00 - Completed 10.5K Cycles

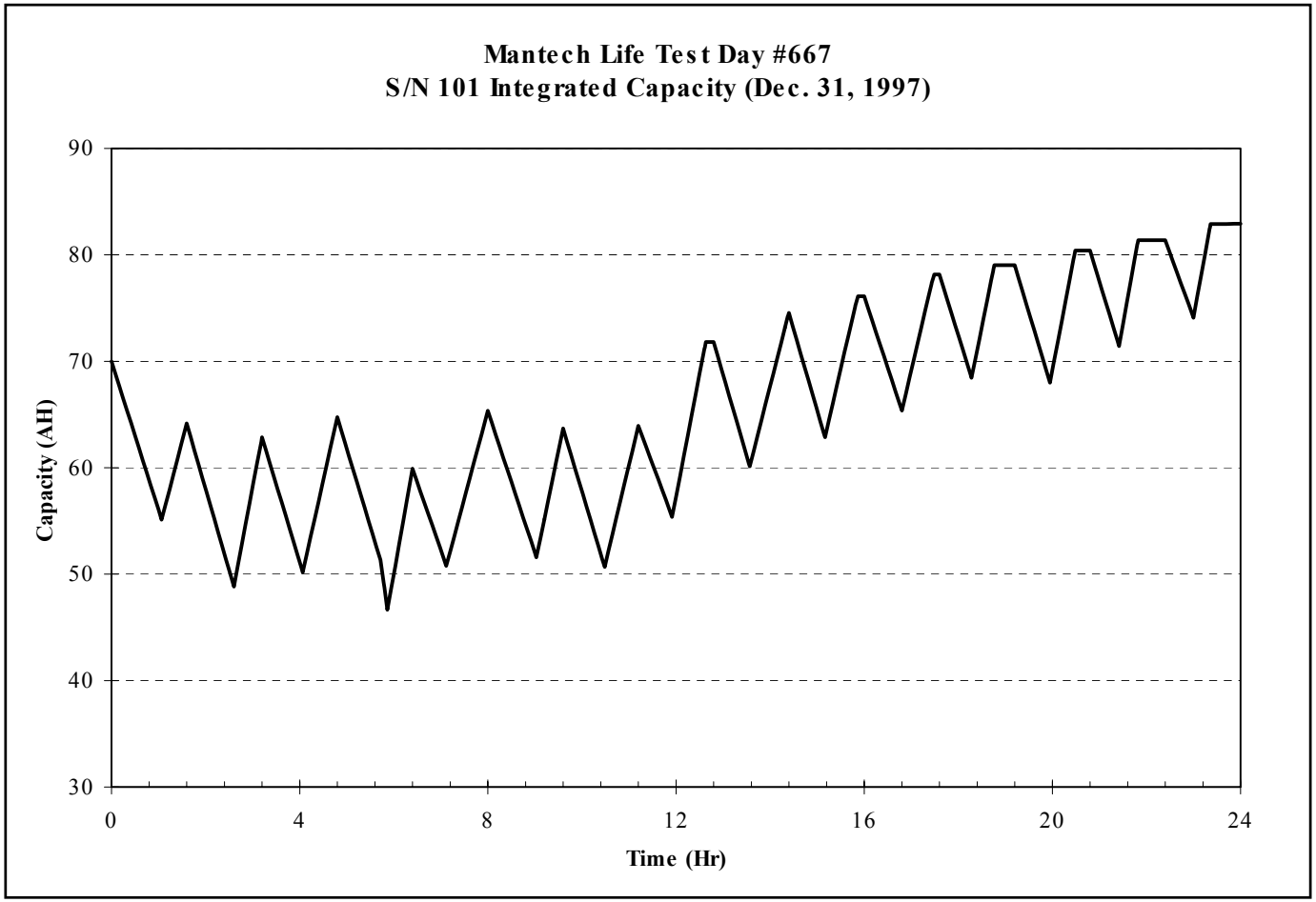
Eagle Picher Cell Life Test Load Profiles

Test Profile	Ave. Dischg. Amps	Ave. Dischg. Minutes	Ave. Batt. Load Ahout/rev	Max. DOD AH	Peak Load Amps	Battery Max V	Profile Dates	Comments
ML1	12.8	52.3	11.2	28.8	15.2	33.1	3/14/96 -	Lot 1 Cells (3/96)
ML2	12.8	52.3	11.2	33.0	25.0	33.1	- 4/26/97	
HL1	16.2	49.3	13.3	32.4	32.4	33.1/33.6	4/26/97 - 8/18/97	
HL7	14.8	49.3	12.2	25.1	31.2	33.6	8/18/97 - 9/13/97	
HL8	14.2	49.3	11.7	22.0	31.2	33.6	9/13/97 - 1/28/98	Lot 2, 3, HST Cells Added (9/97)
UHL	11.7	47.3	9.2	40.8	27.3	33.2	1/28/98 - 5/23/98	
HL8	14.2	49.3	11.7	22.0	31.2	33.2	5/23/98 - 10/9/98	
HL10M	15.0	49.3	12.4	30.0	32.3	33.2/33.6	10/9/98 - 8/9/99	Lot 5 Cells Added (10/98)
HL12M	13.9	49.3	11.4	25.7	29.4	32.8/33.0	8/9/99 - 6/22/01	HST Cells Removed Lot 6 Added (10/00)
HL14R	10.8	47.4	8.6	14.1	30.0	32.8	6/22/01 - 3/21/02	
HL15R	10.8	47.4	8.6	17.1	30.0	32.8/33.0	3/21/02 -	

Cell Life Study
HL8 Test Profile



Cell Life Study
HL8 Test Profile



Cell Life Study
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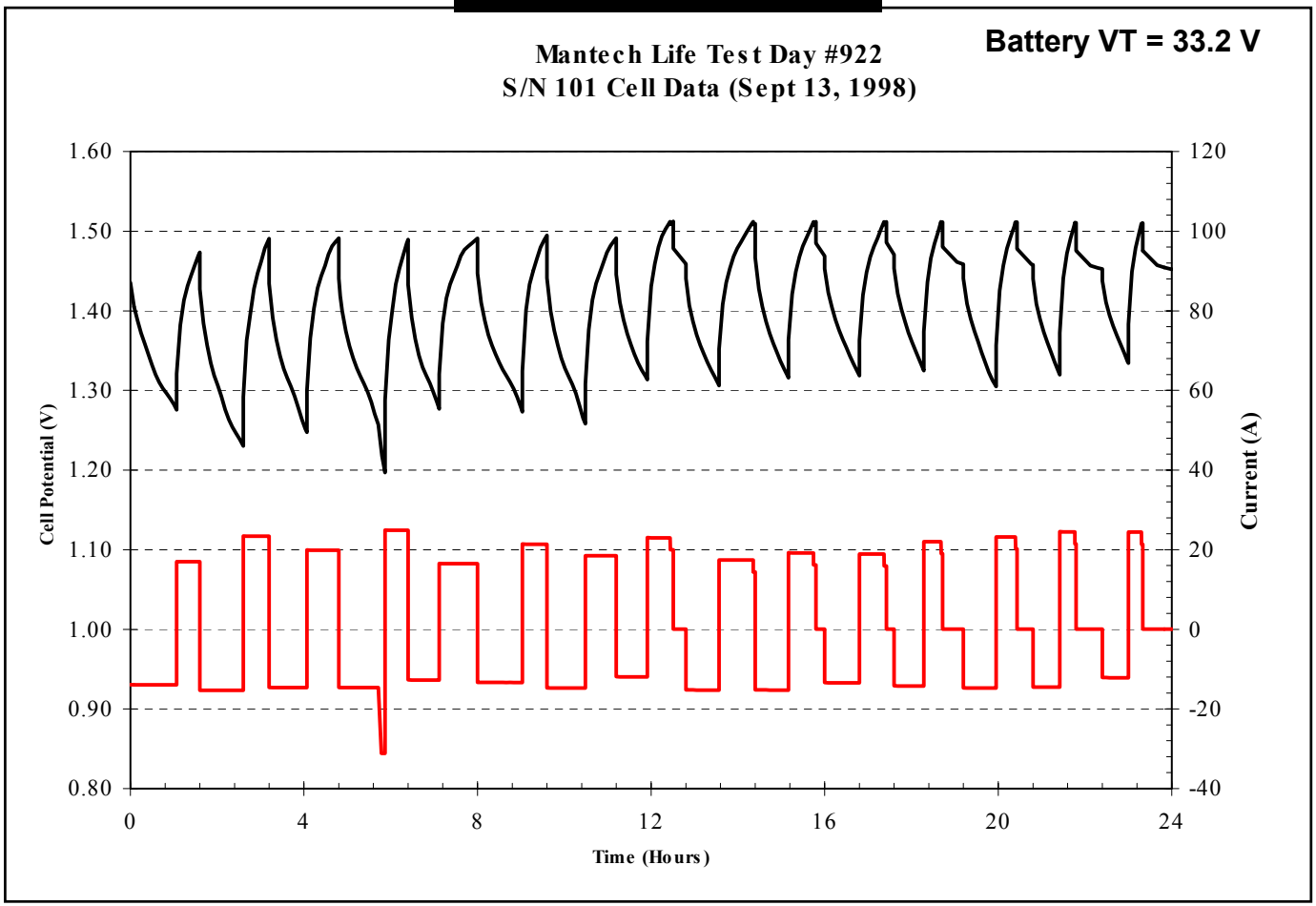
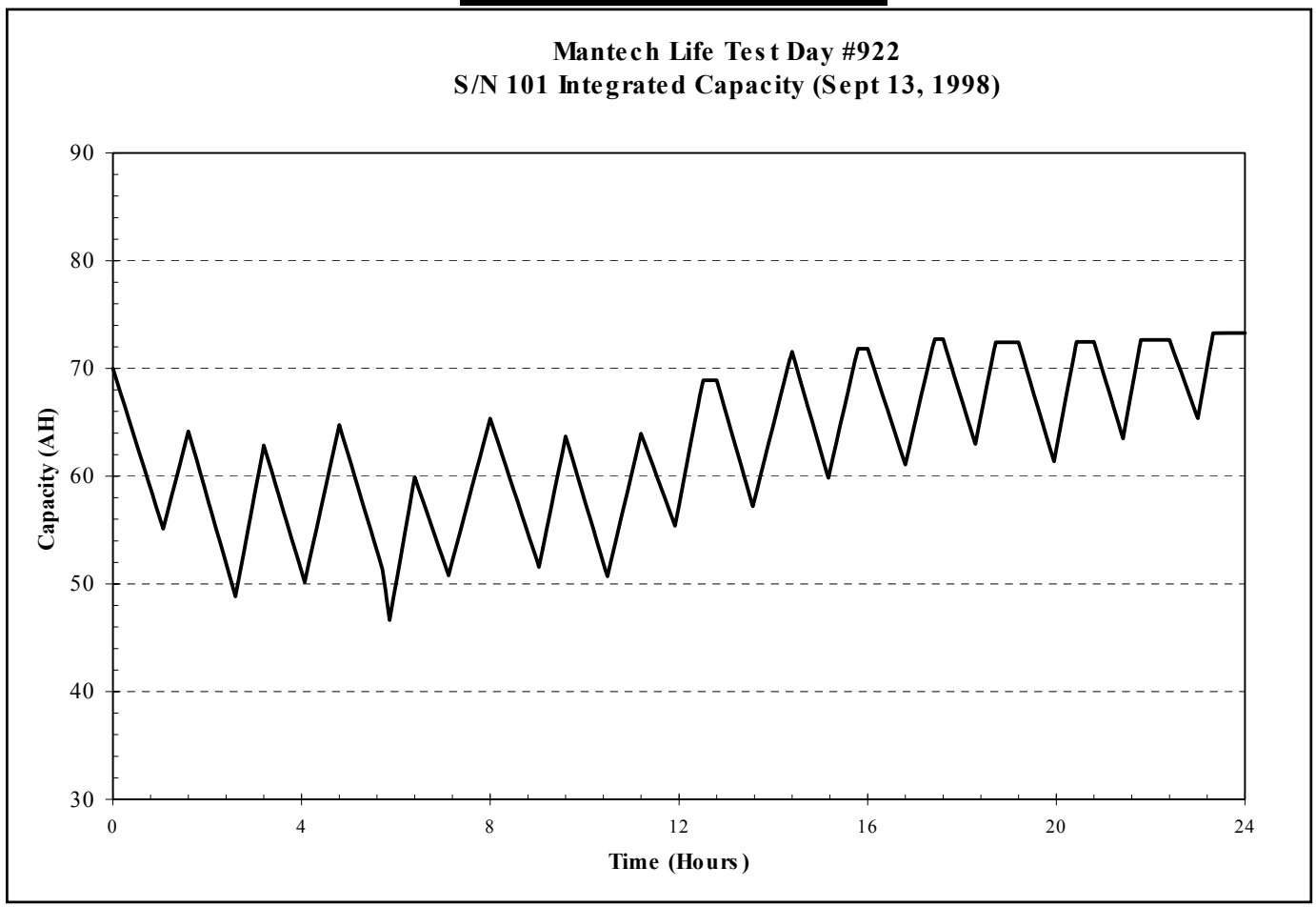
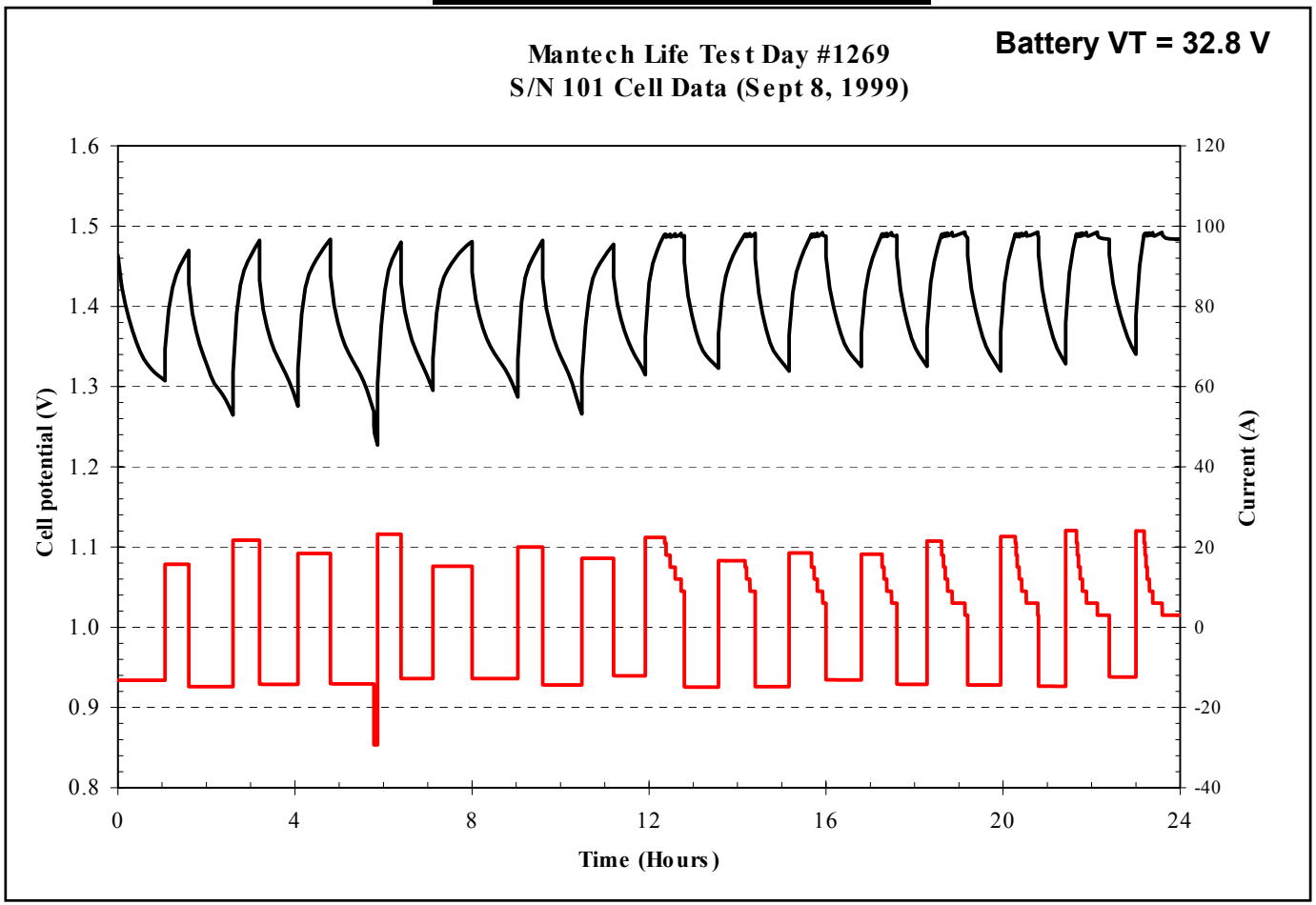


Cell Life Study
HL8 Test Profile



Cell Life Study
HL10M Test Profile



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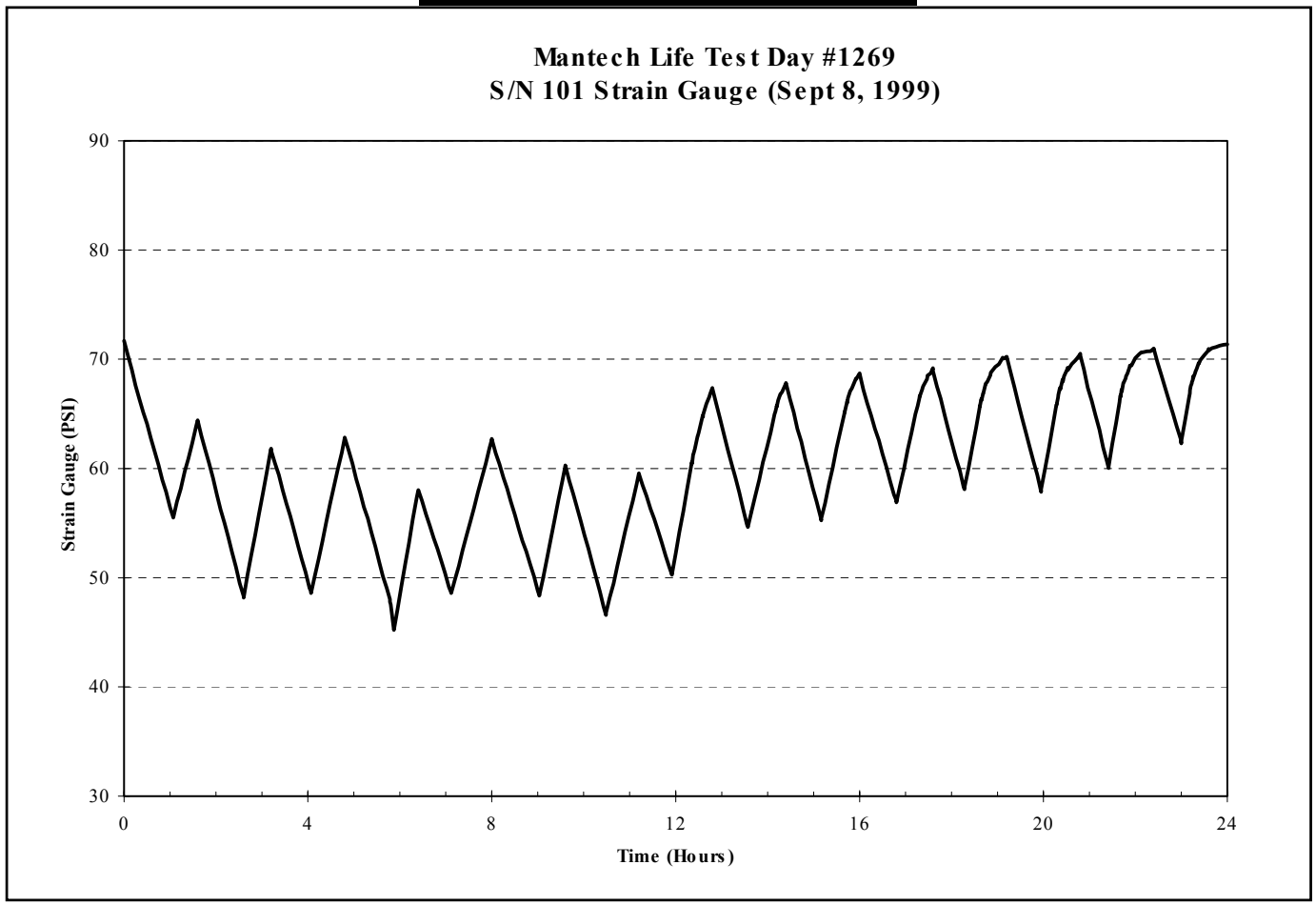
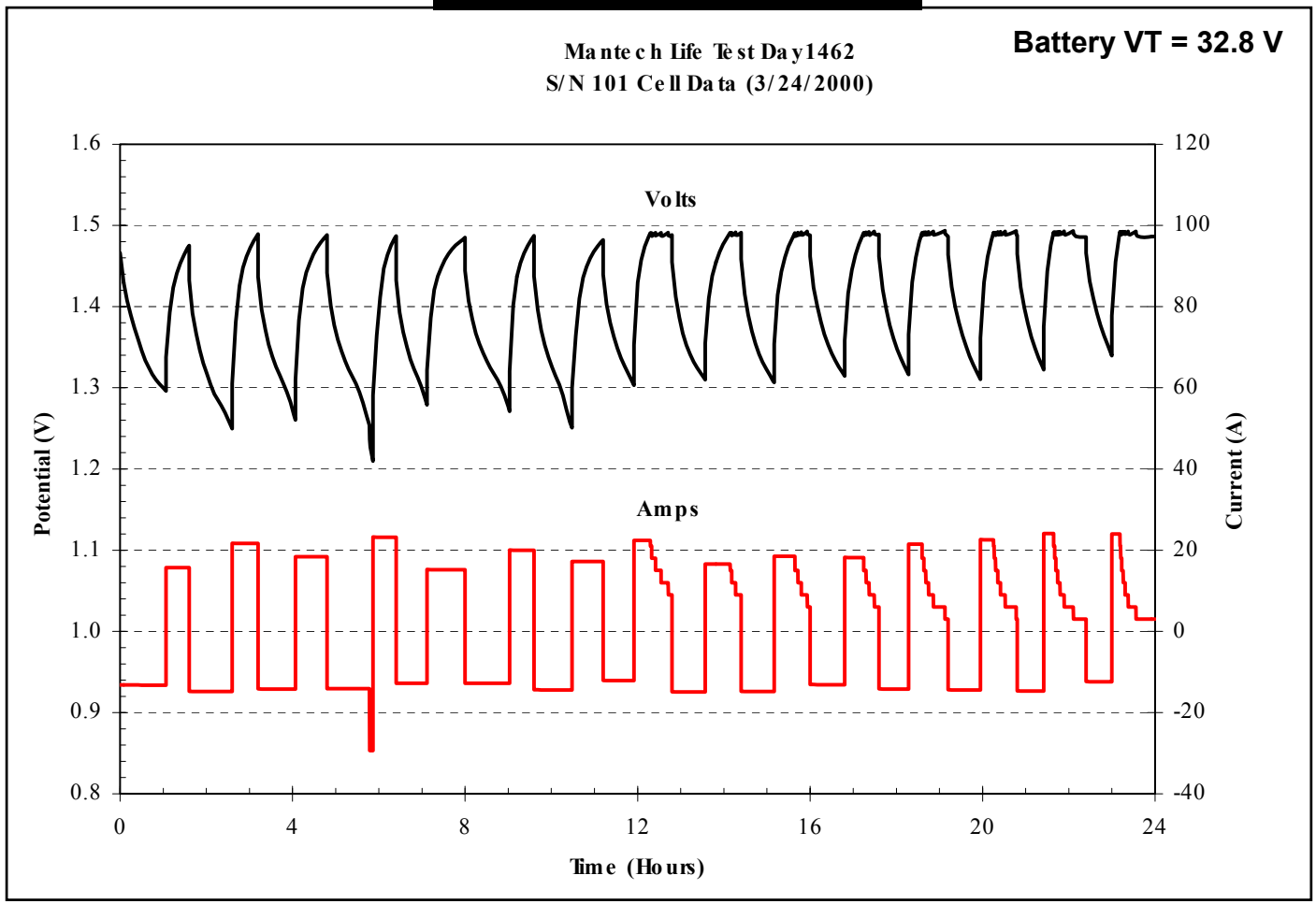
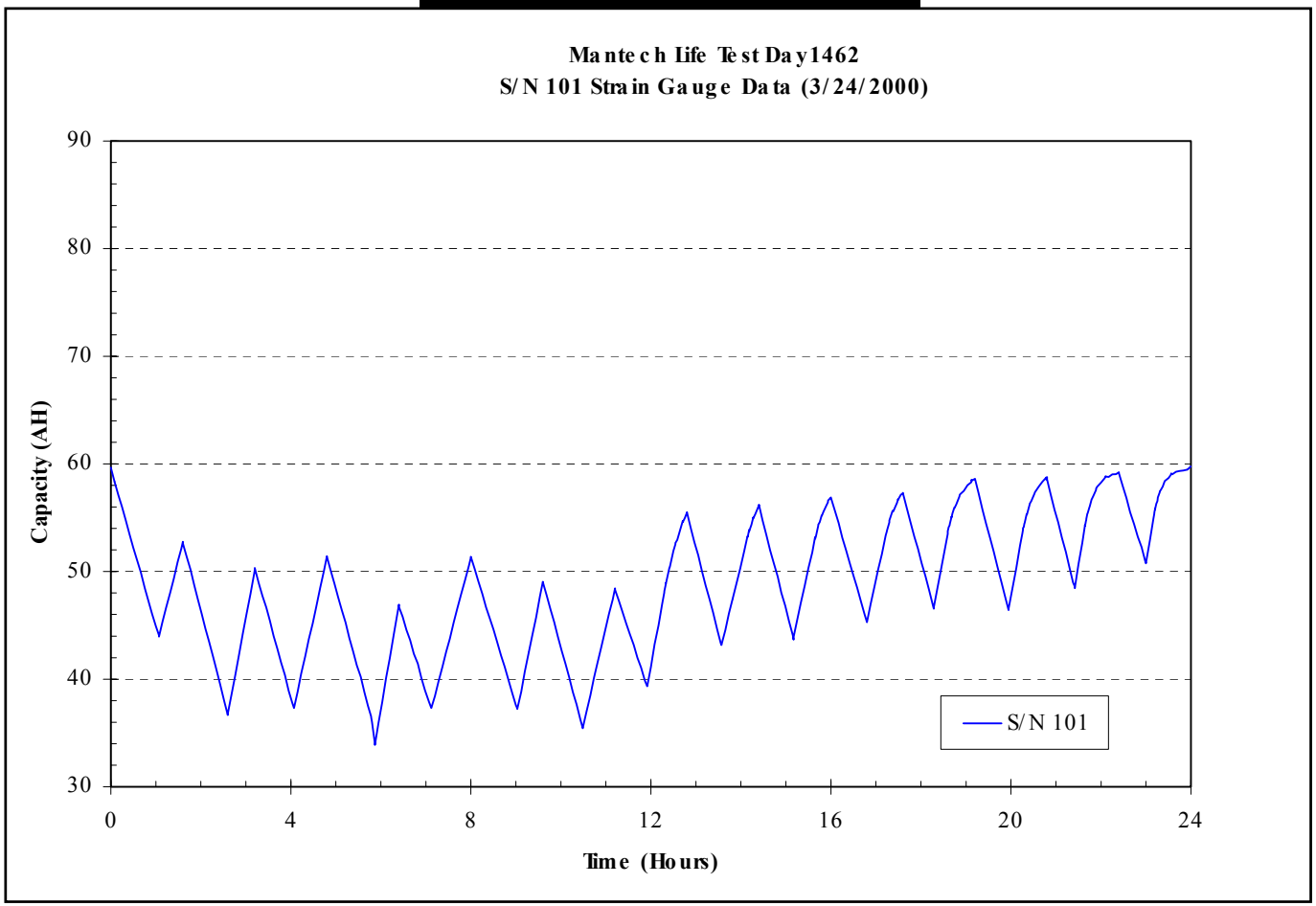
HL10M Test Profile



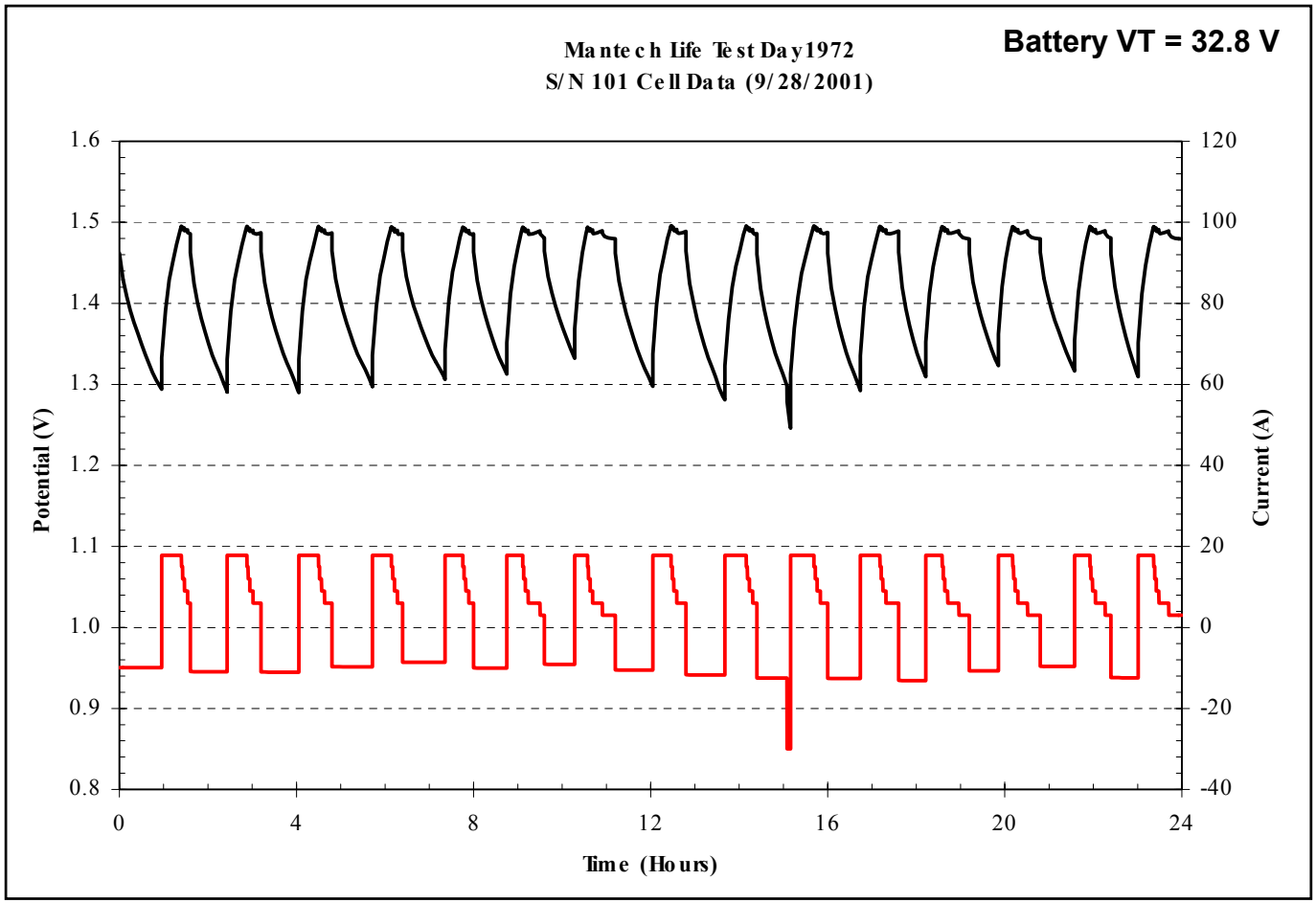
Cell Life Study
HL12M Test Profile



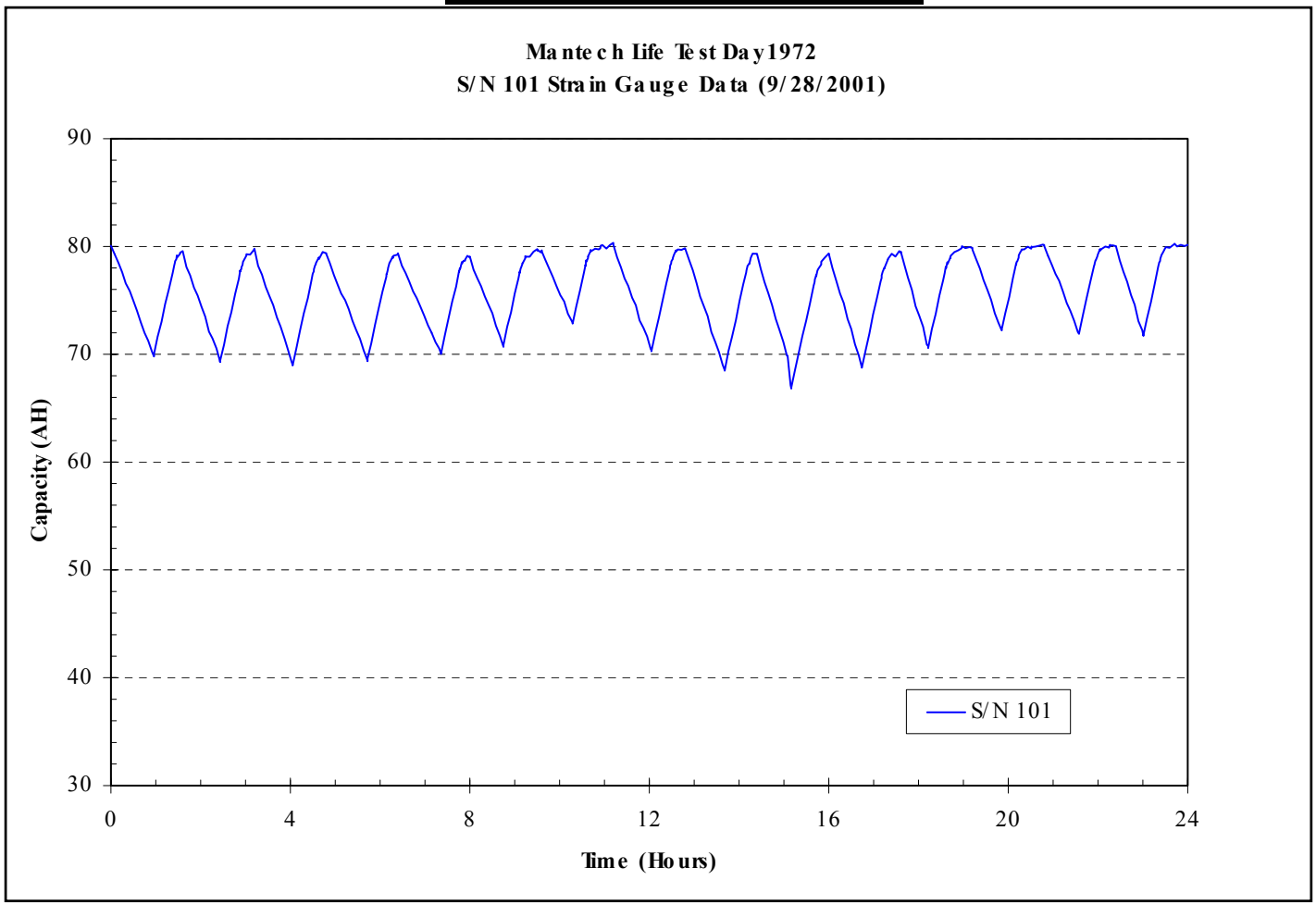
Cell Life Study
HL12M Test Profile



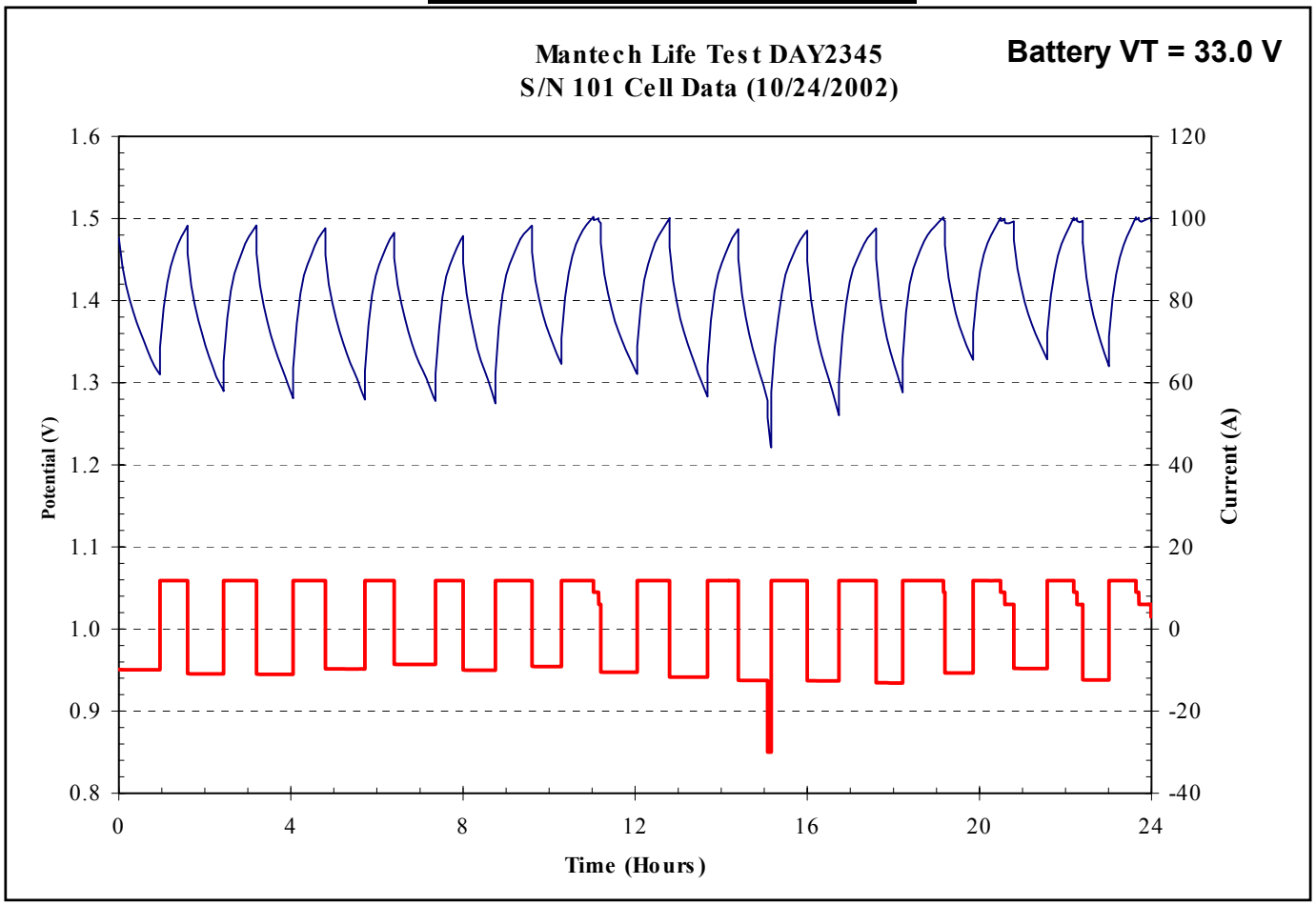
Cell Life Study
HL14R Test Profile



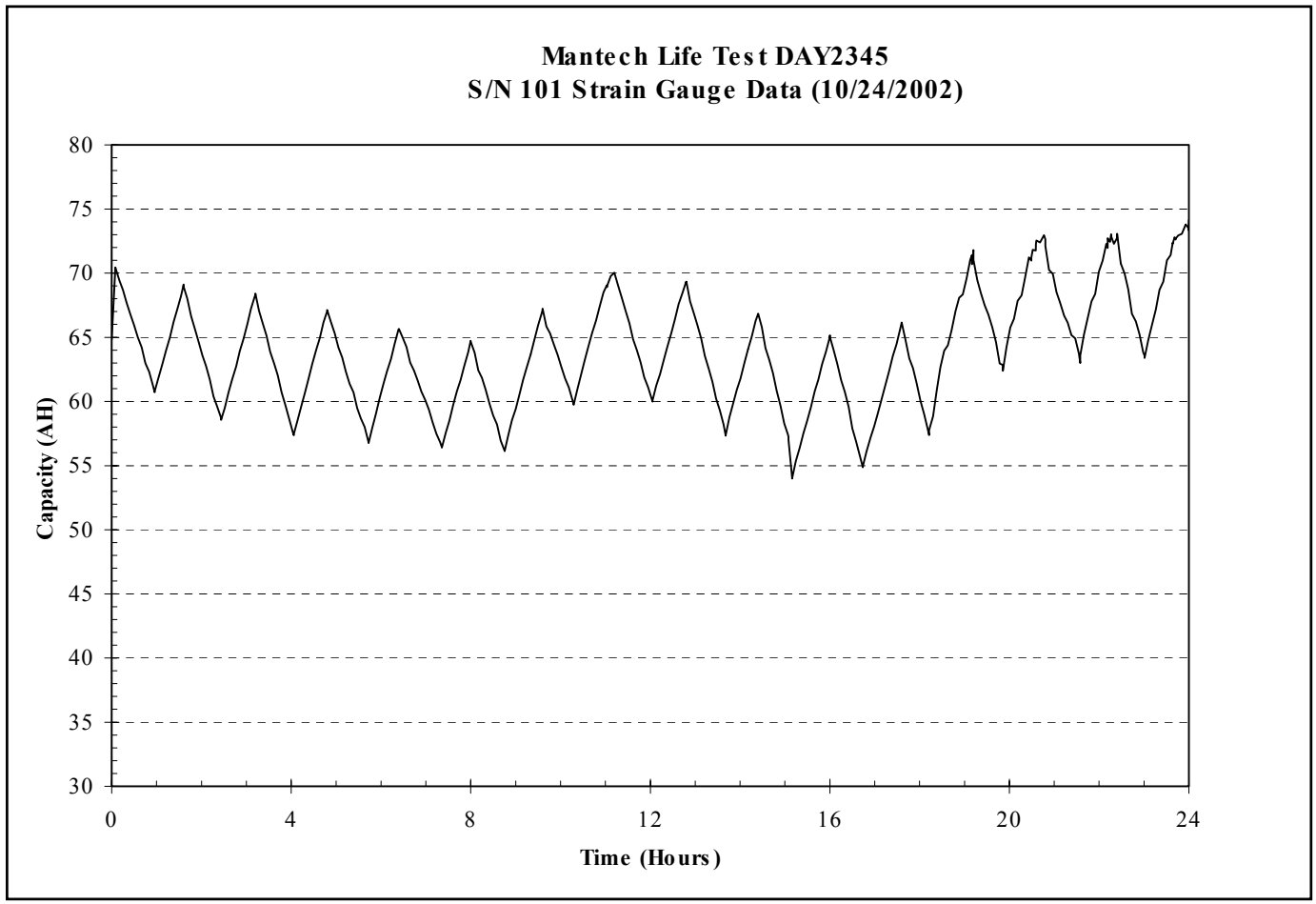
Cell Life Study
HL14R Test Profile



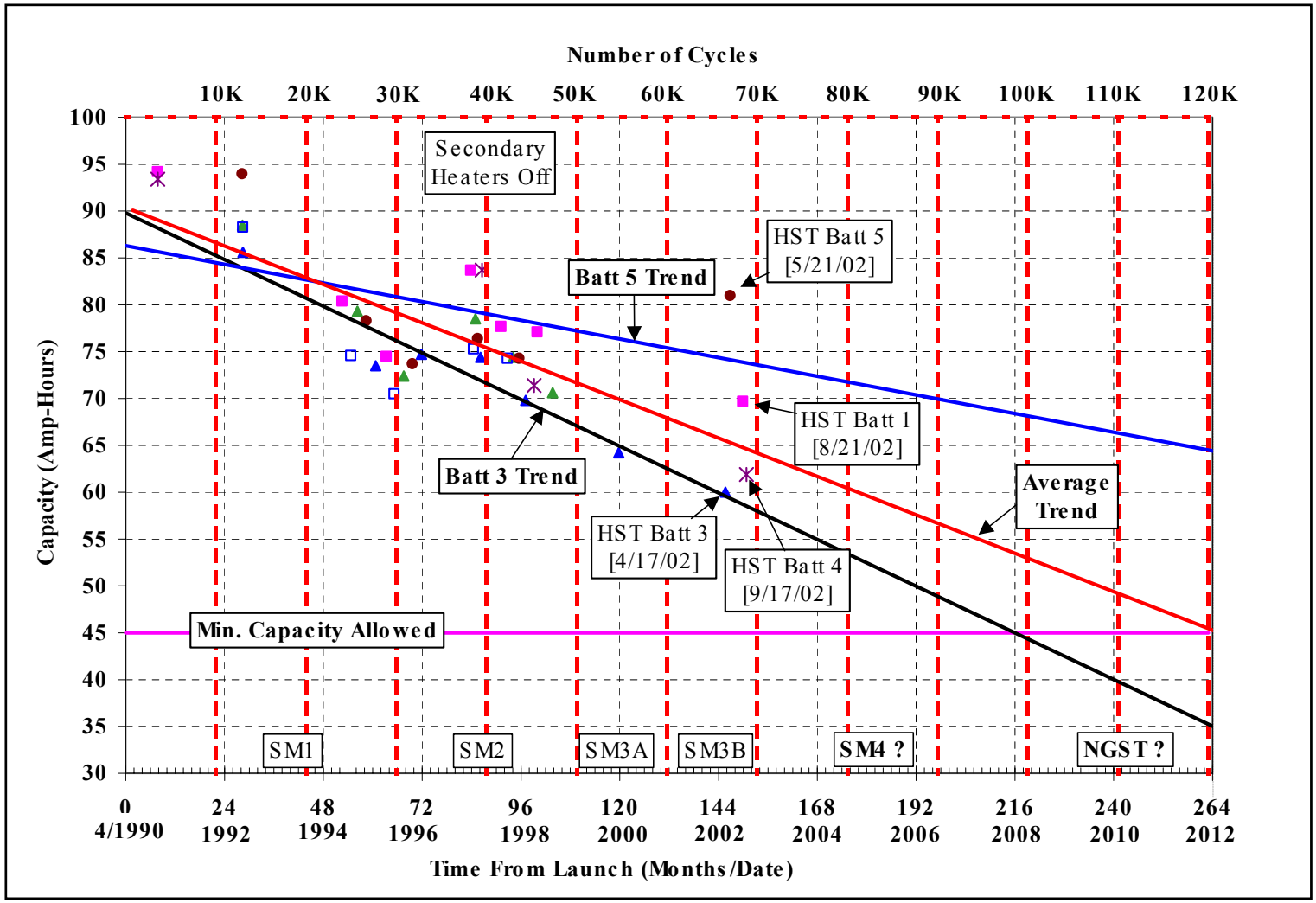
Cell Life Study
HL15R Test Profile



Cell Life Study
HL15R Test Profile



HST Orbital Capacity Trend



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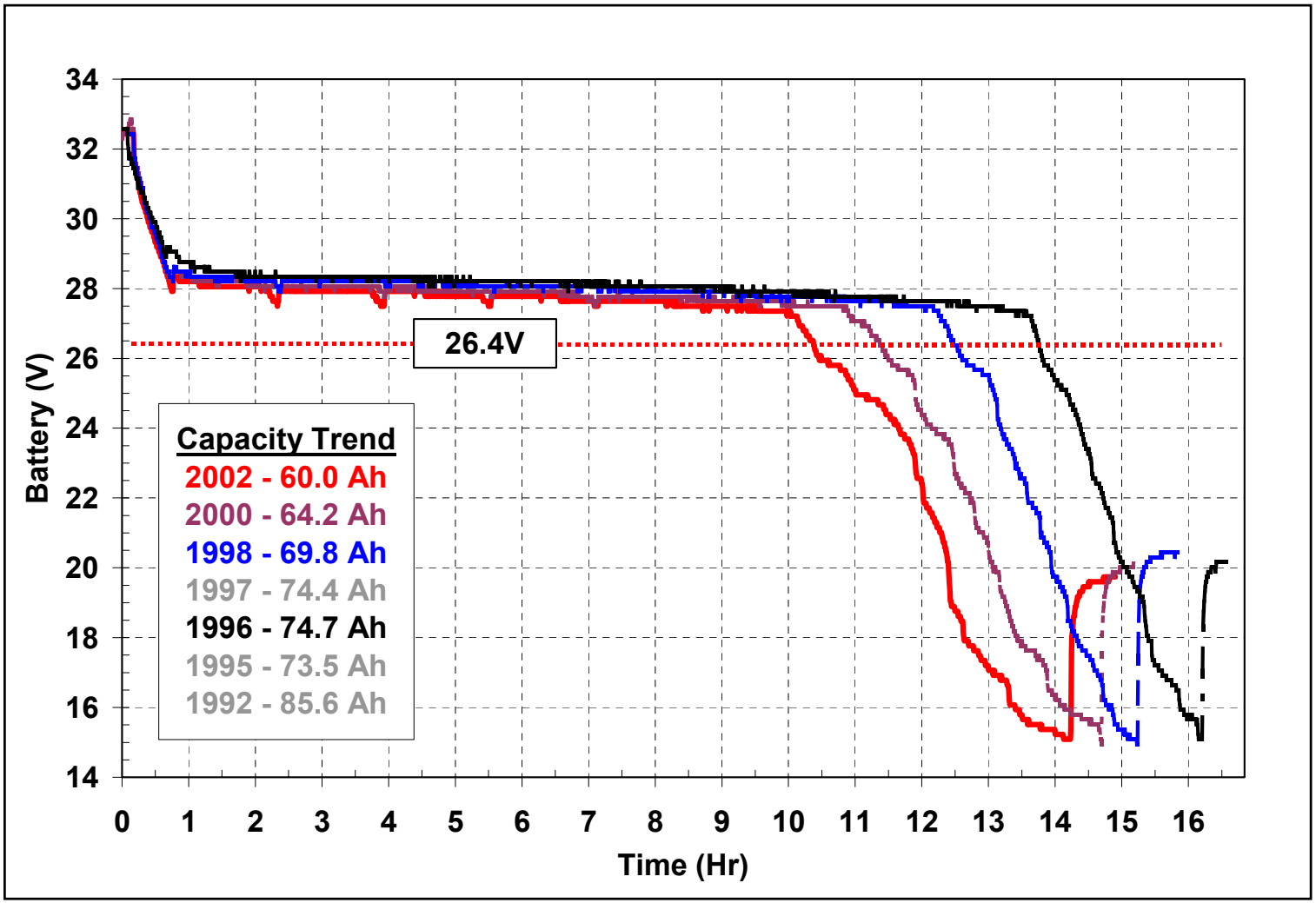
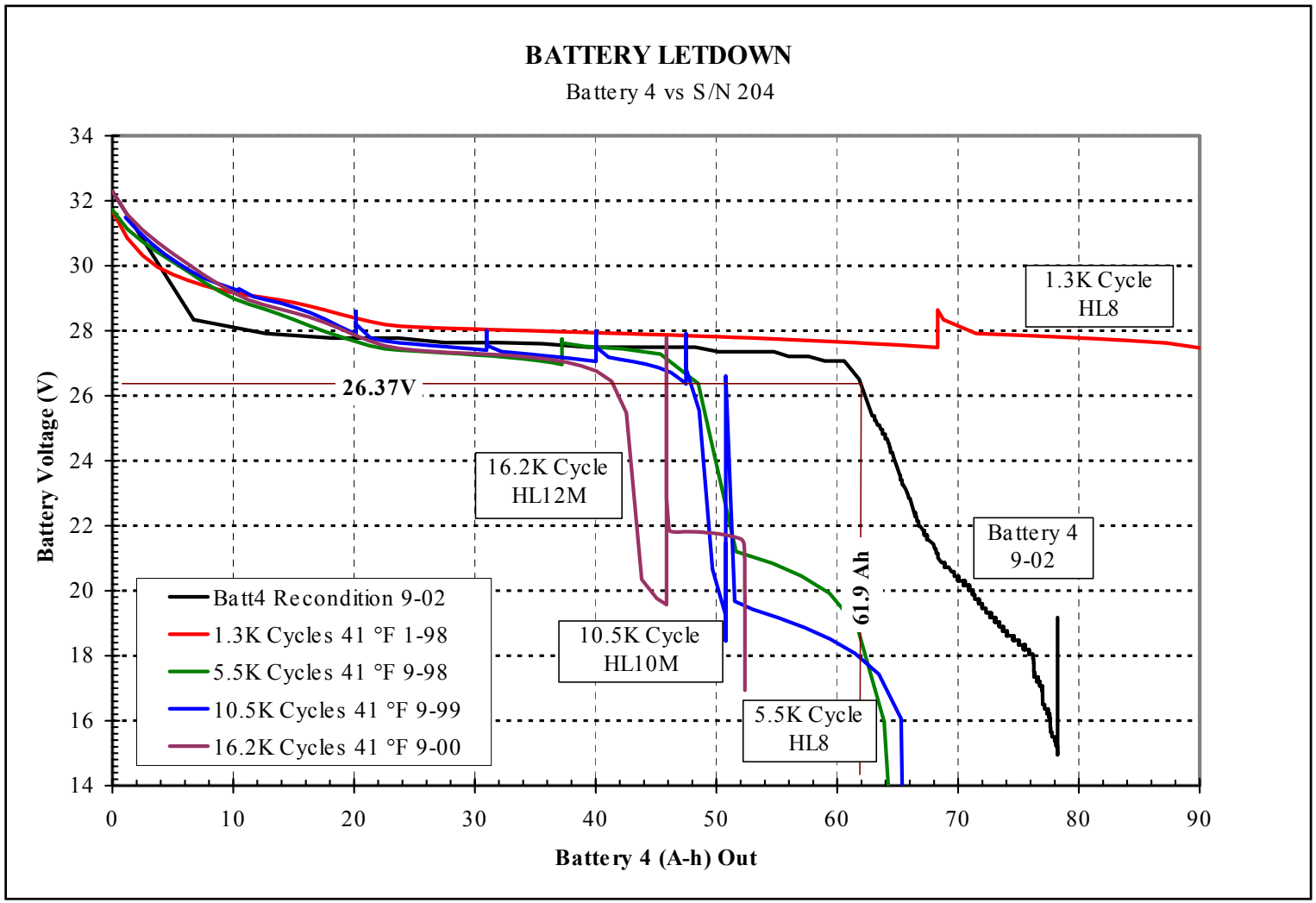
HST Orbital Recondition Capacity Trend Battery 3

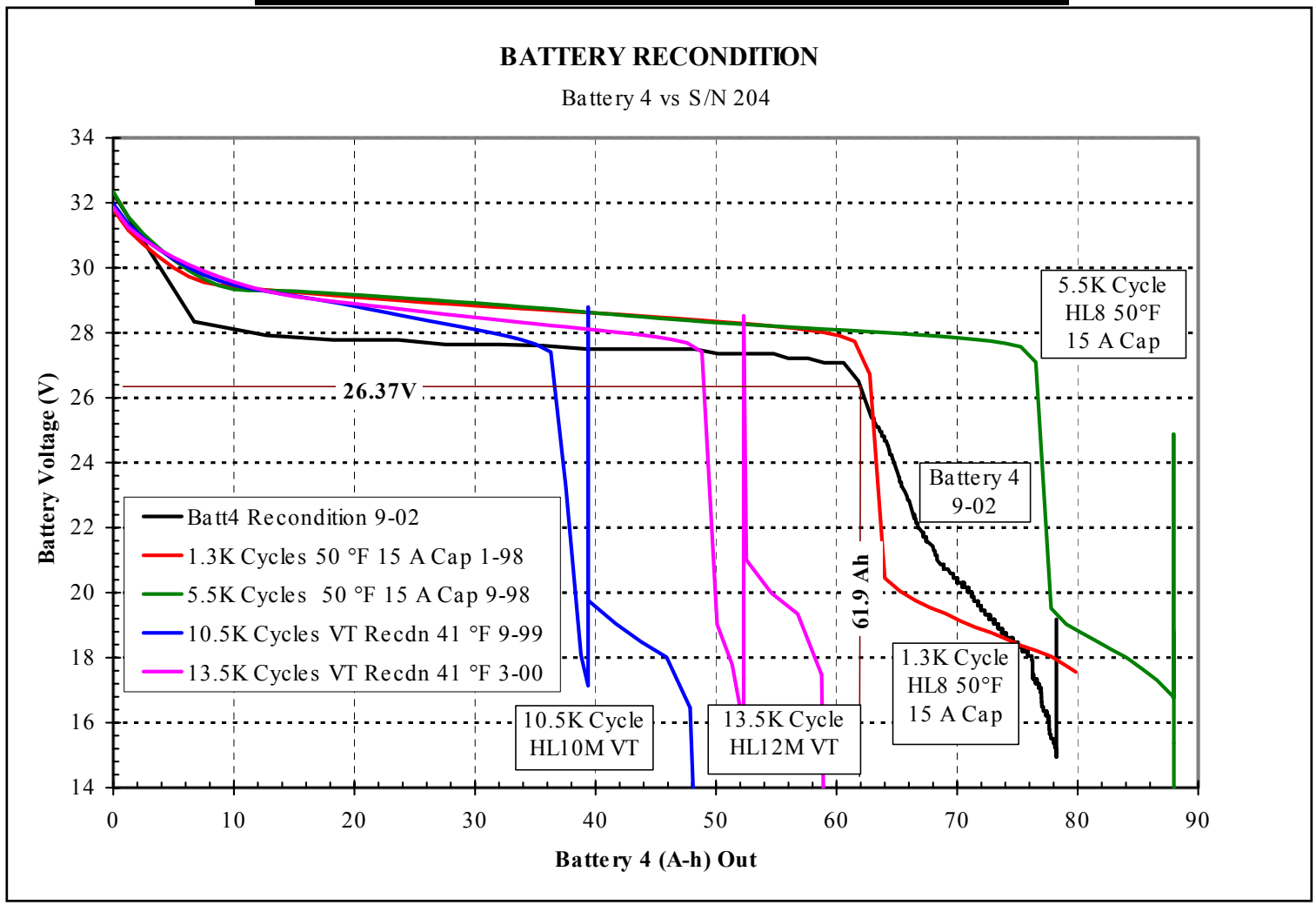


IECEC-2002

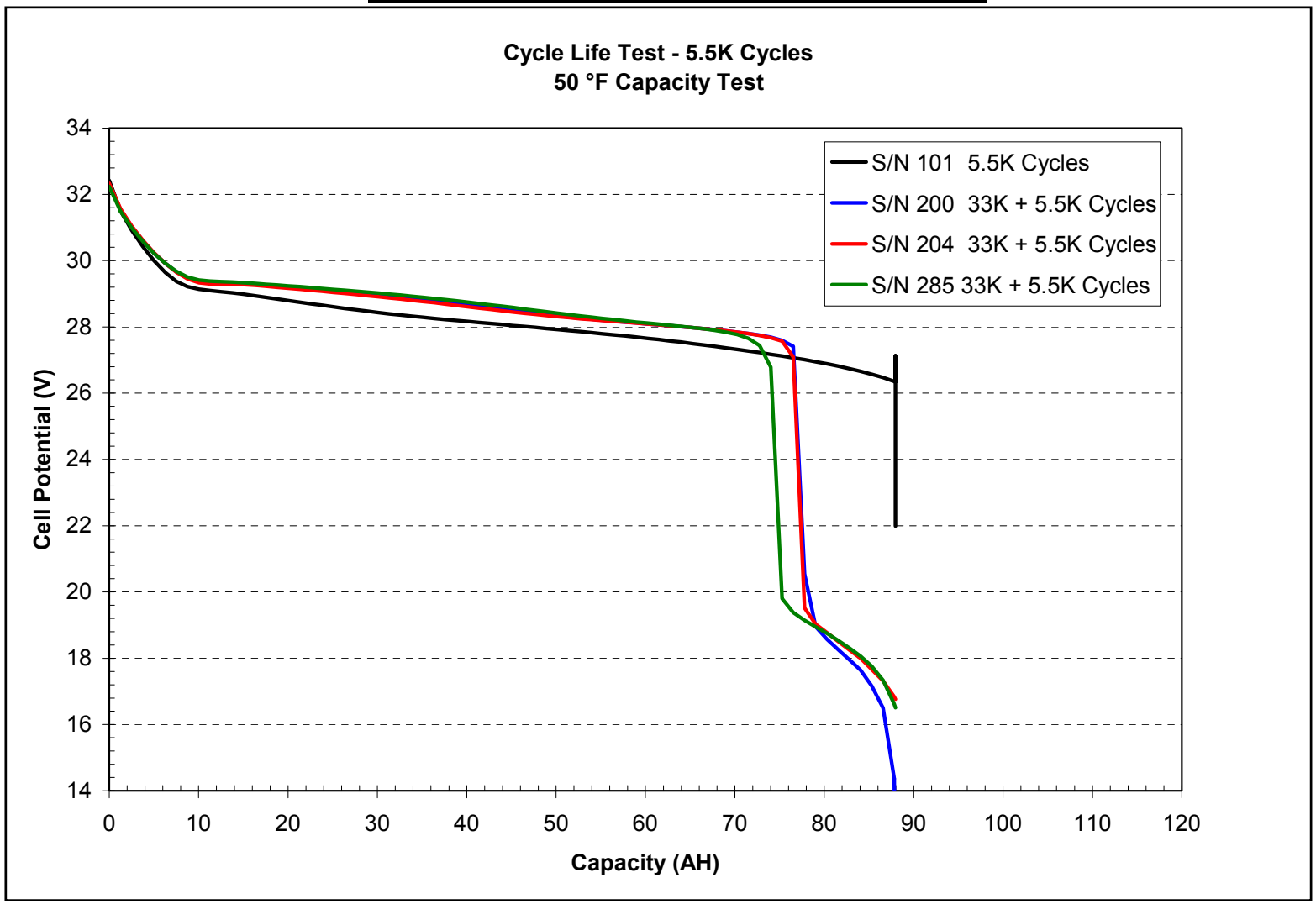
HST Recondition Capacity Comparison
Battery 4 Orbital vs S/N 204 Ground



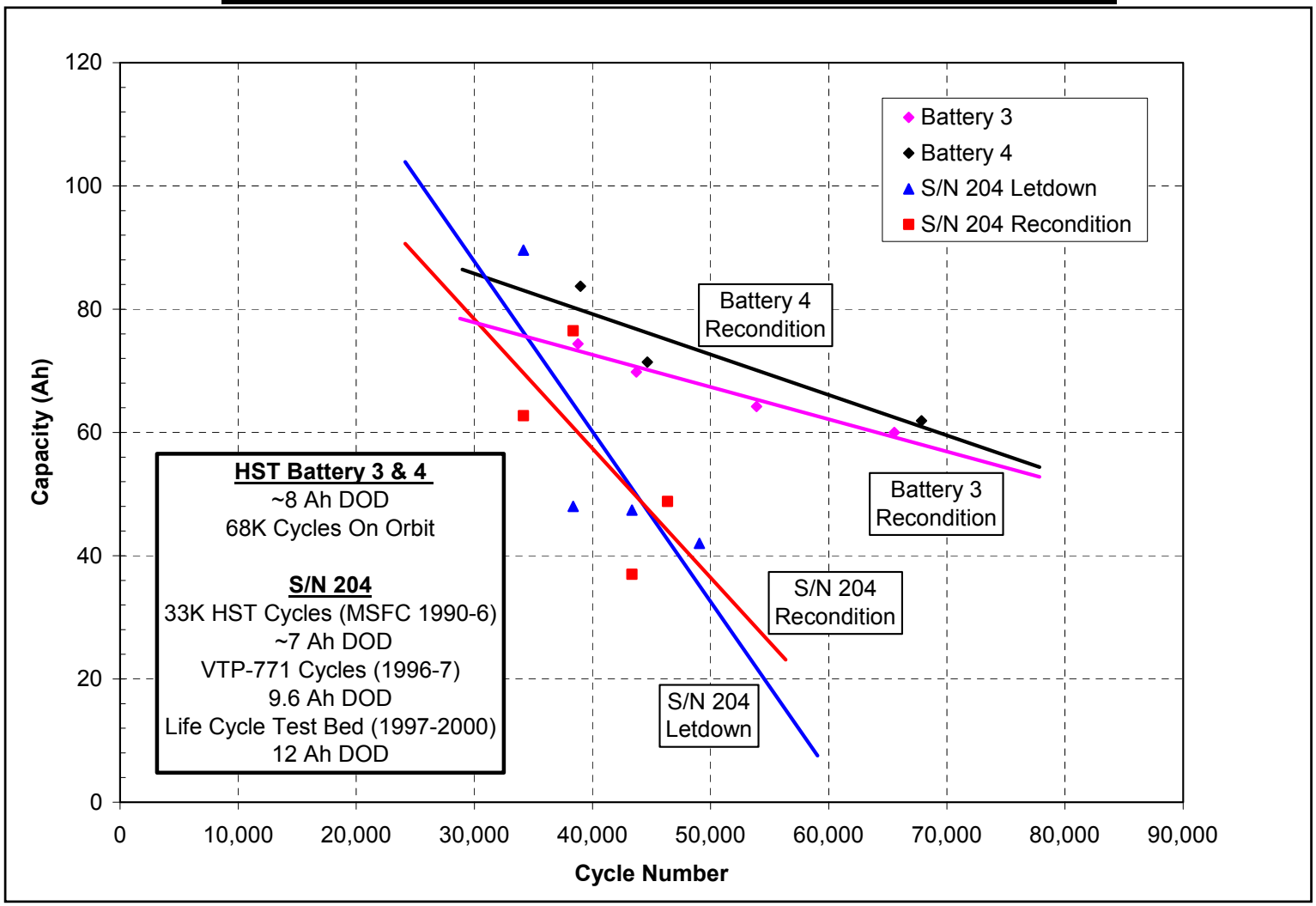
HST Recondition Capacity Comparison Battery 4 Orbital vs S/N 204 Ground



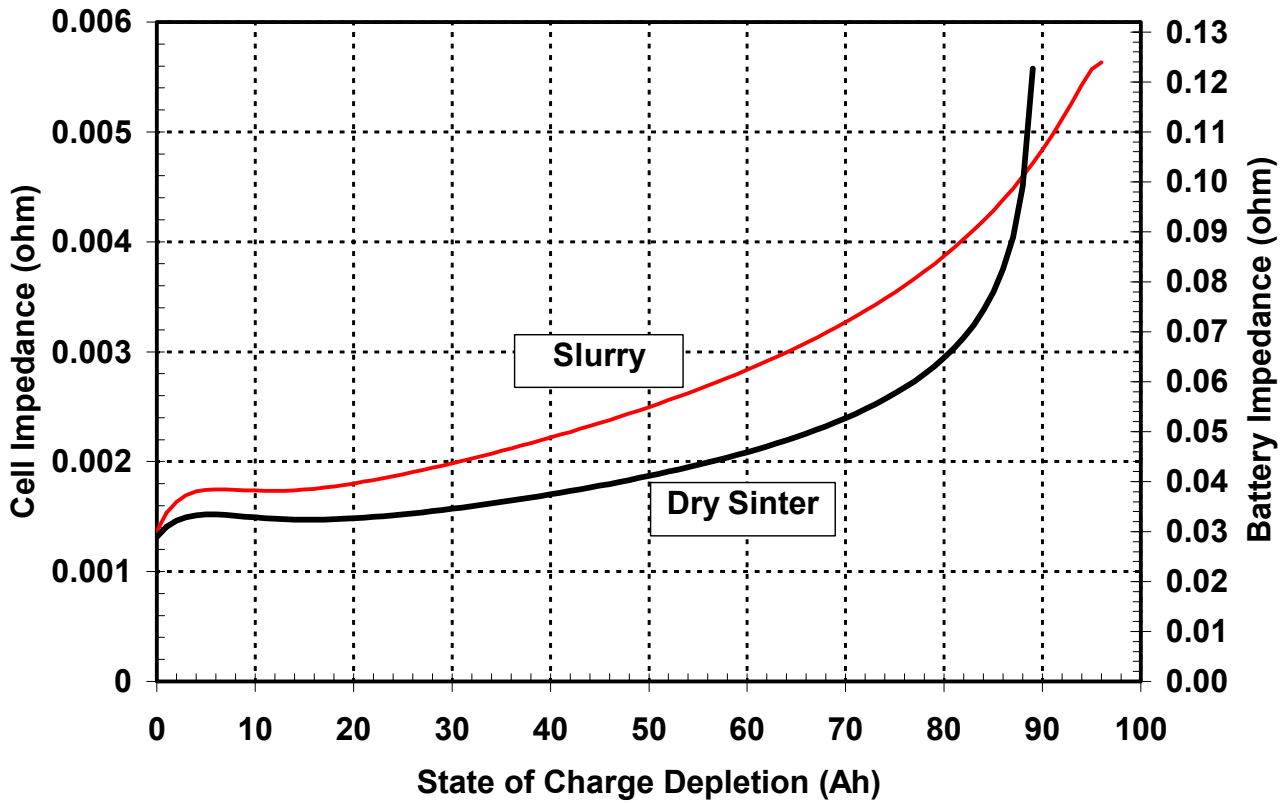
50 °F Capacity Test Comparison
Cycle Life Test



HST Recondition Capacity Comparison
Battery 3 & 4 Orbital vs S/N 204 Ground



Battery Model Impedance Prediction



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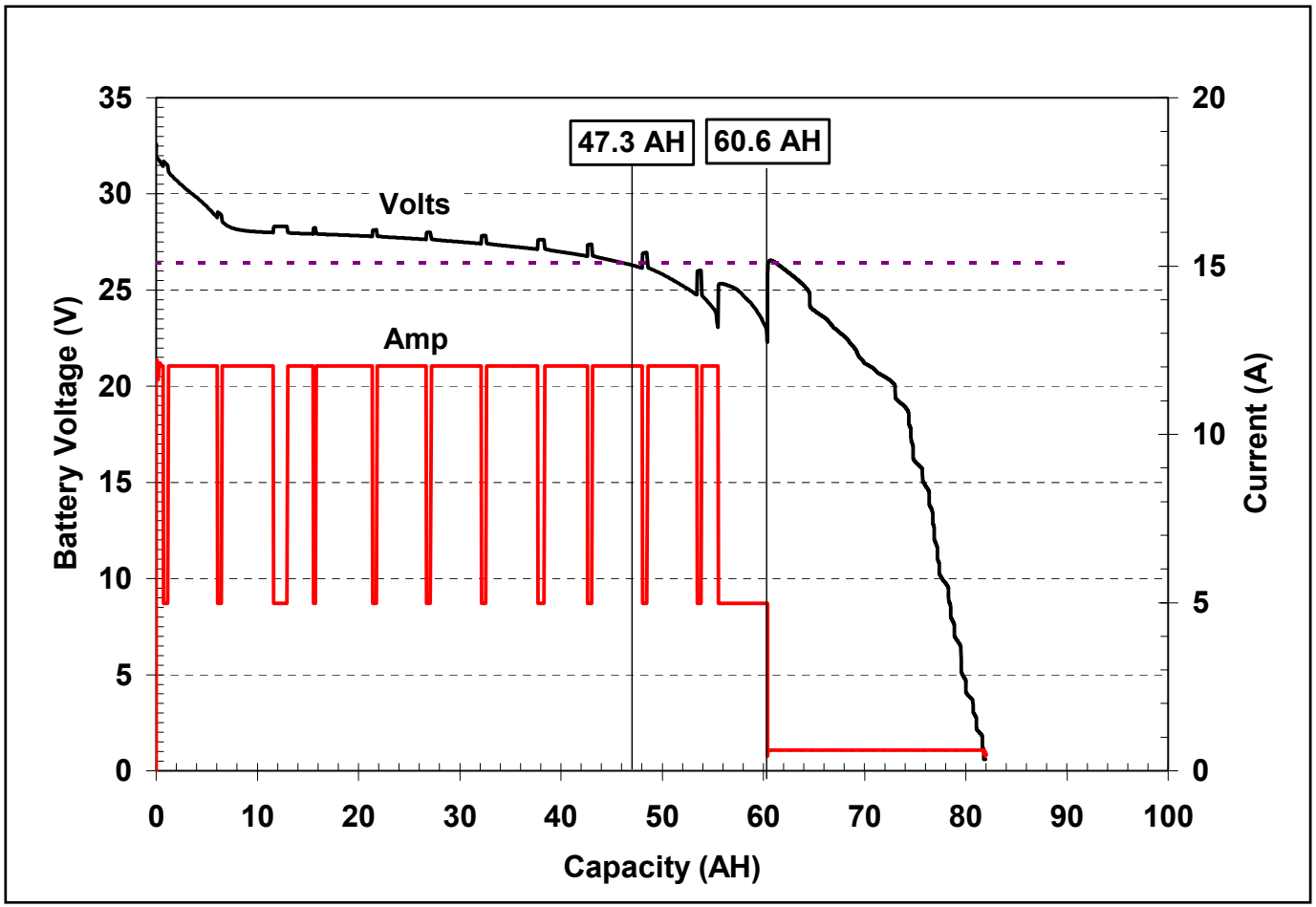
Flight Spare Battery Pulse Discharge



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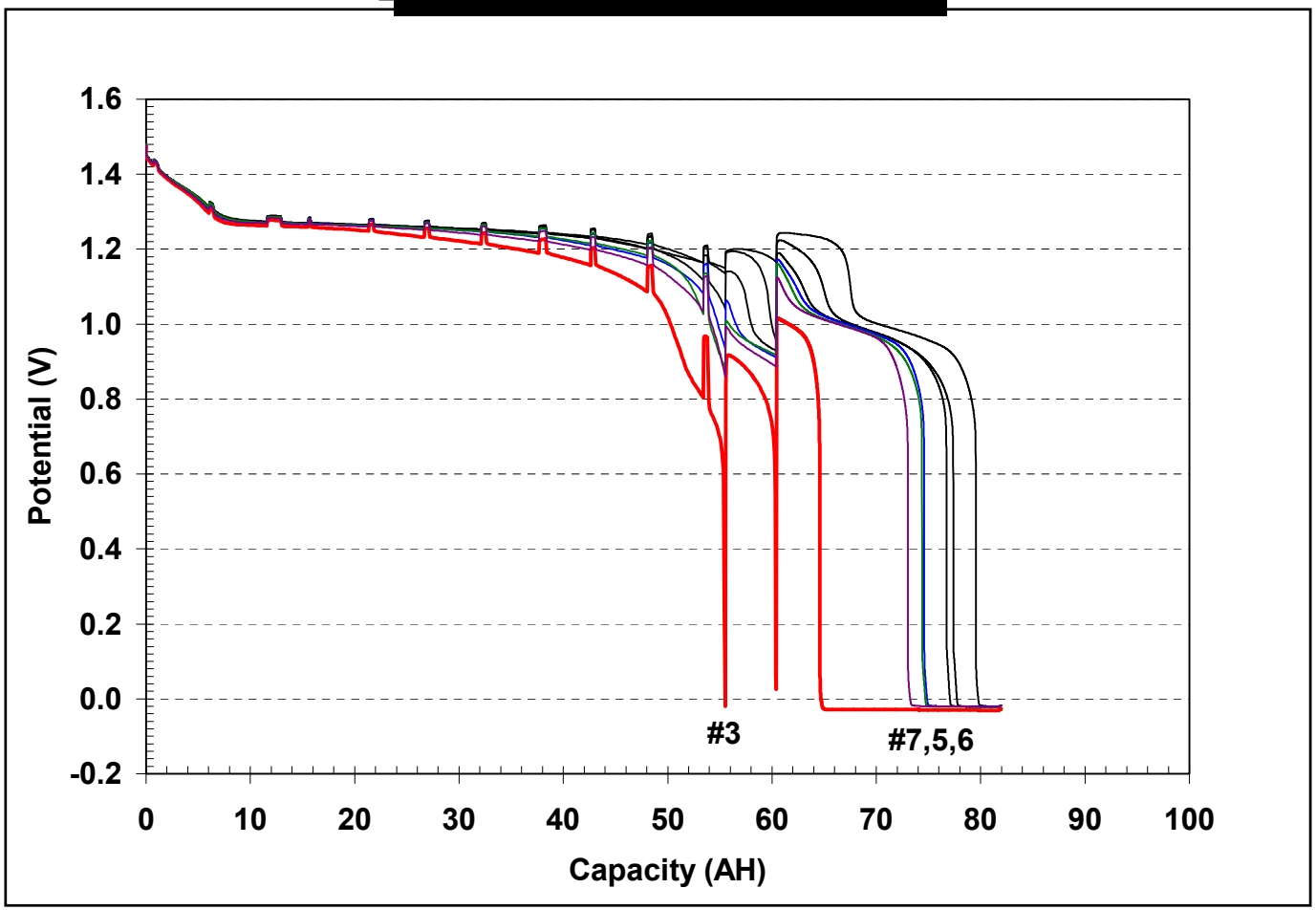
Flight Spare Battery Cell Potential Distribution



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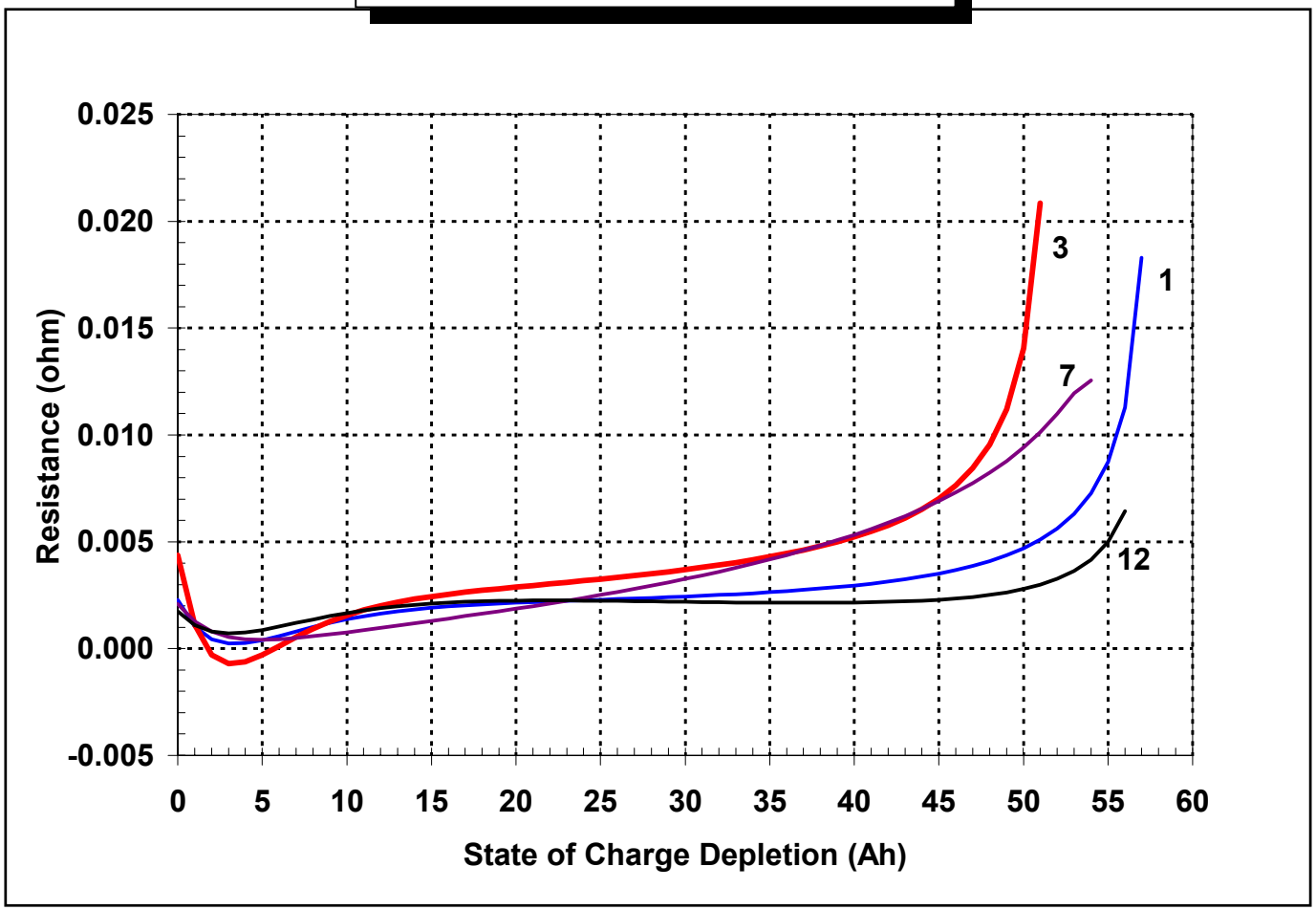
Flight Spare Battery Cell Impedance Distribution



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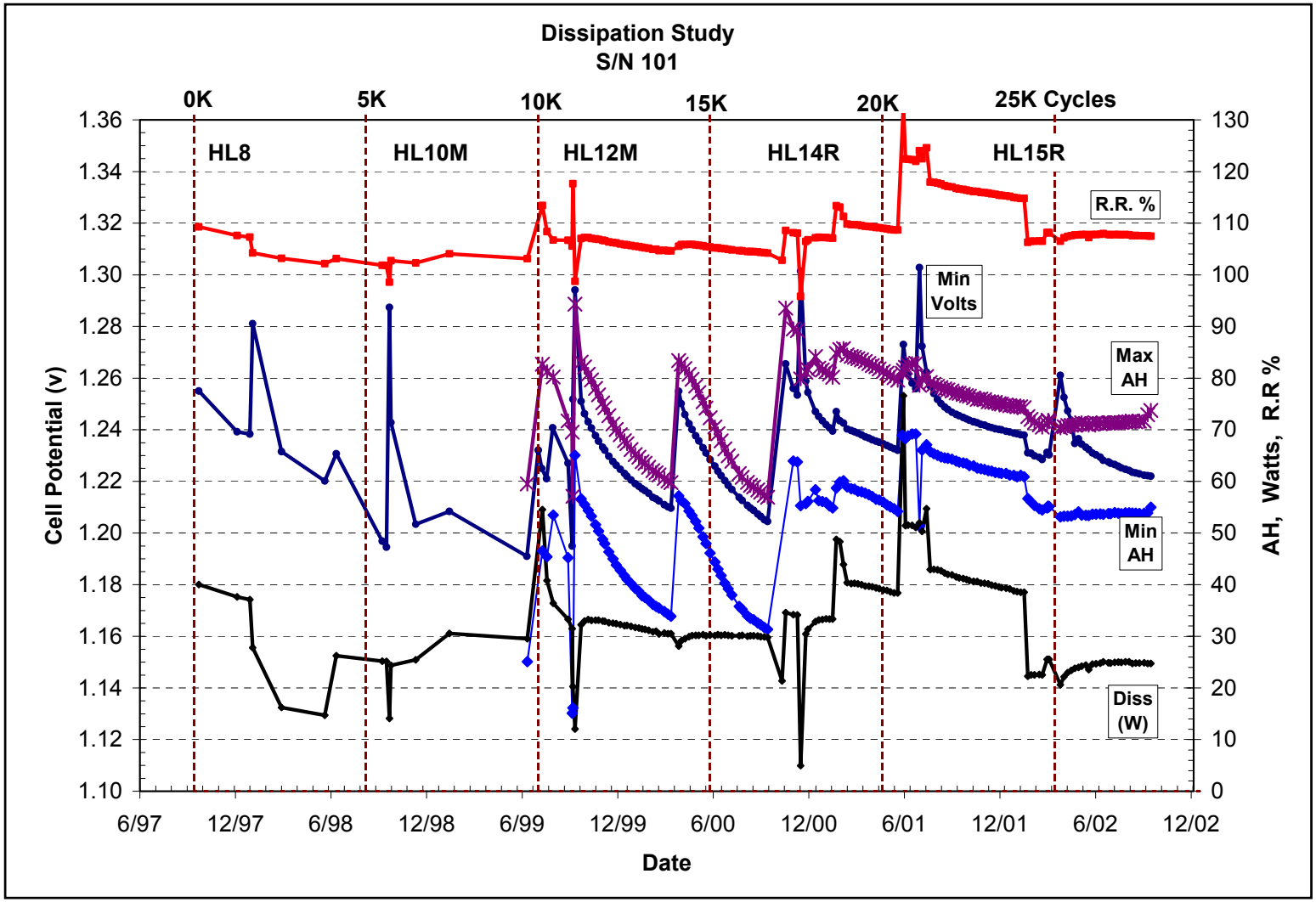
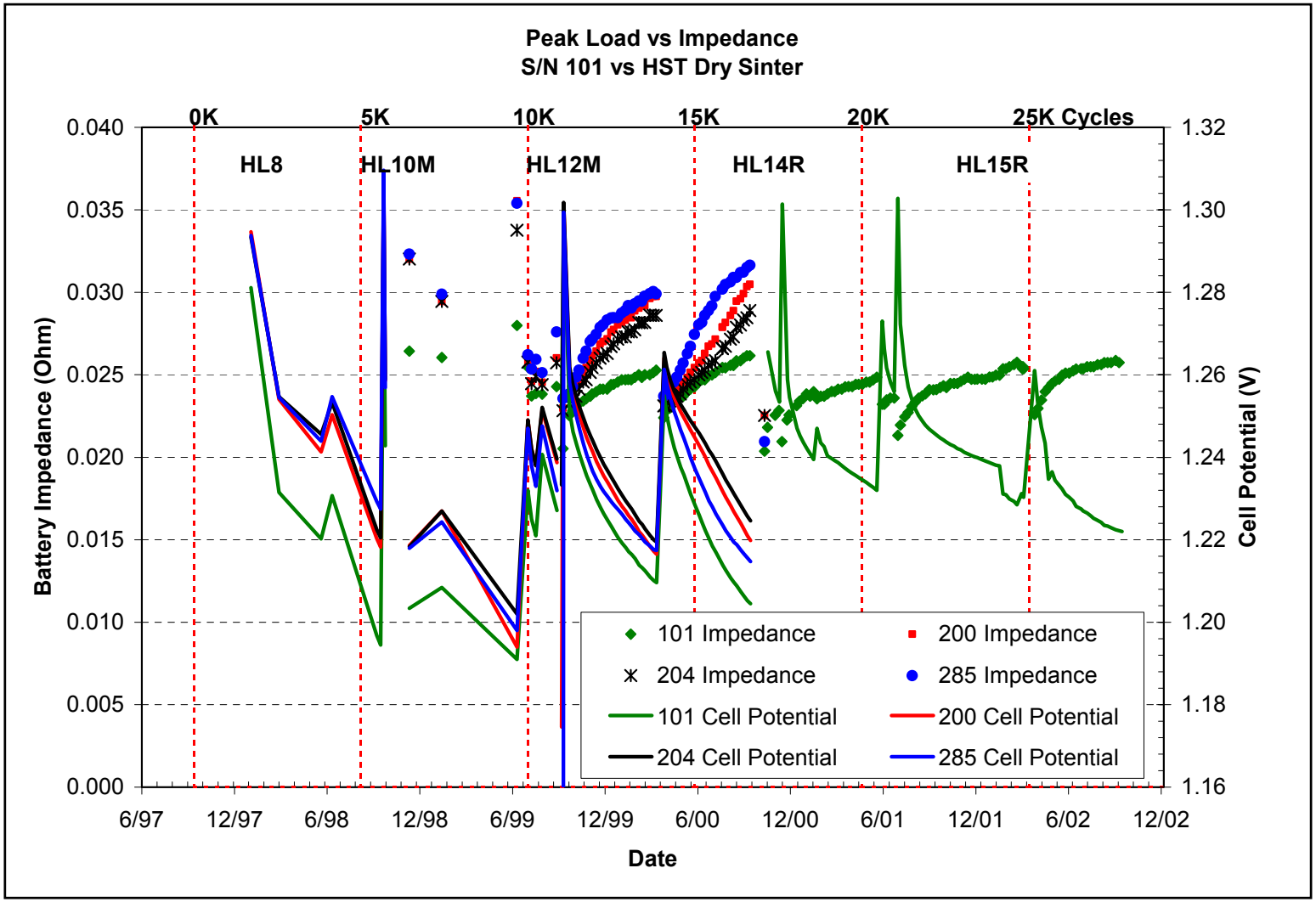
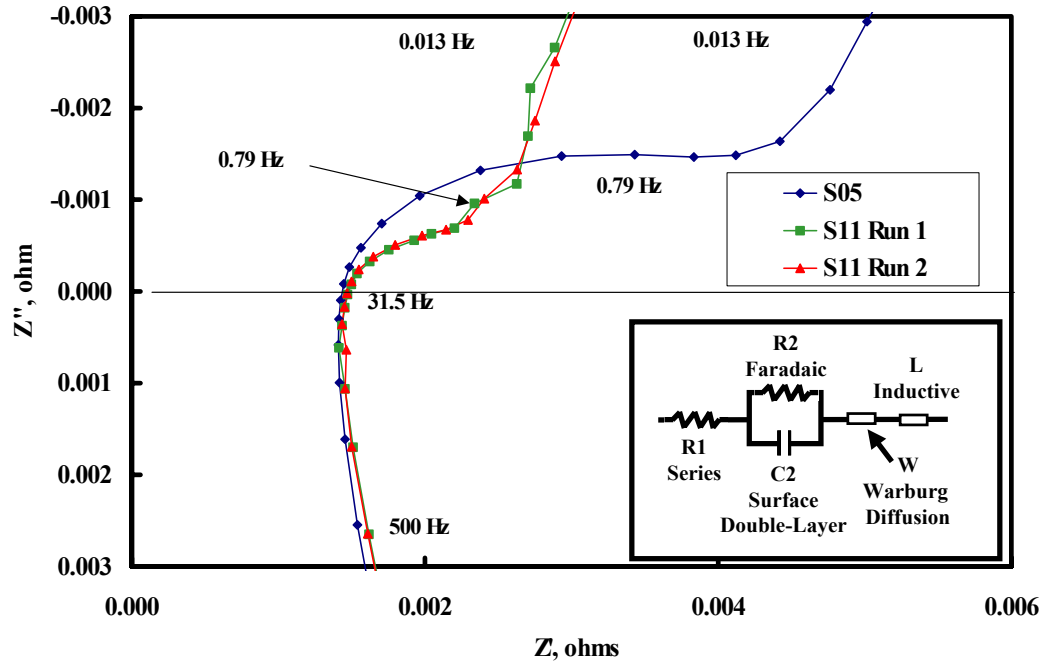
Cell Life Study
9/1/97 - 11/1/02



Cell Life Study
9/1/97 - 11/1/02



AC Impedance - GEO Ground Cycling (RNH 76-11 Dry Sinter)



	S/N 11	S/N 05
Seasons	15 (Real)	58 (Accel.)
R1, milliohms	1.4	1.4
R2, milliohms	0.8	2.4
C2, farads	44	26

Interpretation of Results

- Decrease in Active Surface (R2, C2)
- Electrode Surface Effect (R2, C2)
- No Difference at High-Frequency (R1 - No Separator Difference)
- Inductive Effects Ignored

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- Jon Armantrout & Doug Hafen, 1996, "NiH2 Battery Reconditioning for LEO Applications," *Proceedings 1996 NASA Aerospace Battery Workshop*

- Douglas P. Hafen, 1998, "NiH_2 Battery Reliability Update," *Proceedings 1998 NASA Aerospace Battery Workshop*

- Jon Armantrout & Dale Gordon, 2000, "Effects of Dry Storage on NiH_2 Slurry Electrode Cells," *Proceedings 2000 NASA Aerospace Battery Workshop*

- Roger P. Hollandsworth, Jon D. Armantrout & Gopalakrishna M. Rao, July, 2002, "NiH_2 Reliability Impact Upon Hubble Space Telescope Battery Replacement", *Proceedings of the 37th IECEC*, Paper # 20034

ACKNOWLEDGEMENTS

- **This Work Was Supported by NASA Contract Mod 593 Dated 2 June 1987**
  - Directed LMSC to Design, Develop and Deliver Nickel-hydrogen Battery Modules
  - For the Hubble Space Telescope Low Earth Orbit Mission
    - Per NAS 8-32697 and NAS 5-5000.

- **LMMSO Wishes to Acknowledge the Technical Support From**
  - HST Program Office for Orbital Data
  - NASA/MSFC for Ground Test Data.

60% LEO Life Cycle Data

For Large Capacity Ni-H2 Cells

Jeff Dermott, Jack Brill

Eagle-Picher Technologies, LLC

Joplin, Missouri

Background

- Requirements for higher power satellites have created a demand for large capacity cells running at high DOD's.
- Most LEO test on smaller cells are performed at 15%-40% DOD.
- EPT developed two cell designs to accumulate Life Test data on Large capacity cells at 60% DOD.

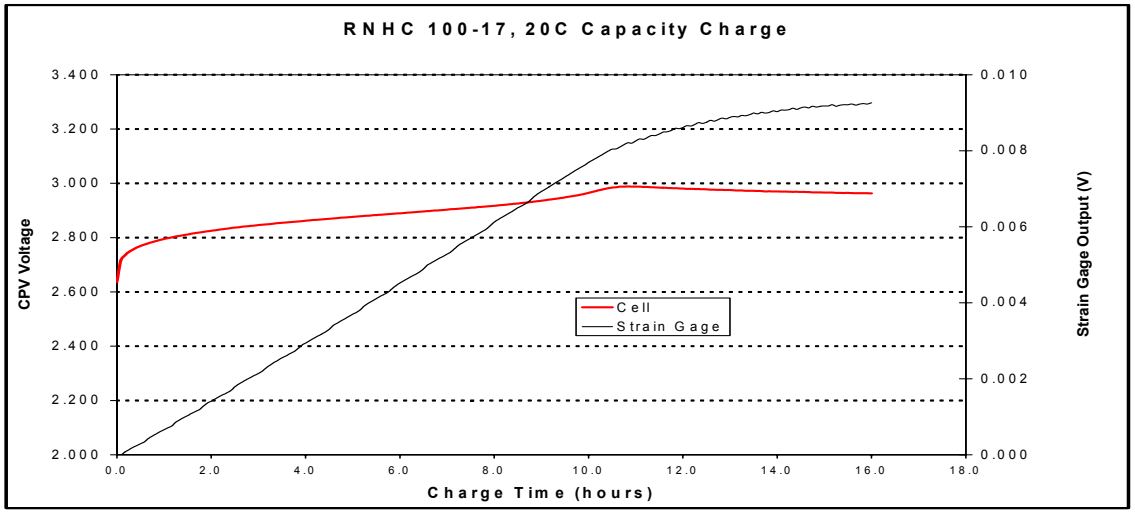
Cell Design Features

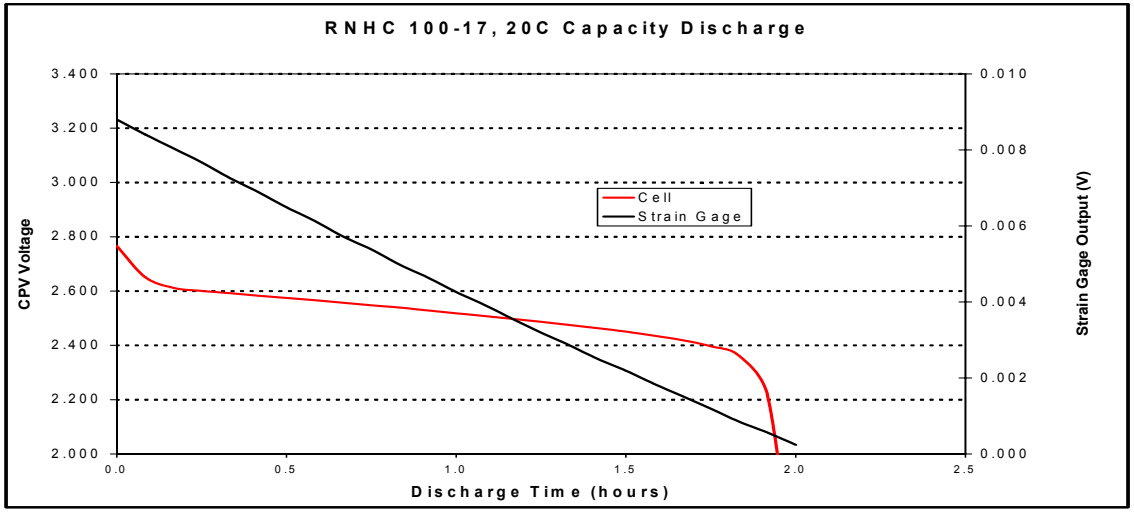
- Stack Configuration - Two stacks in series (CPV)
- Stack Support - Plastic center core (MANTECH)
- Terminal Configuration - Rabbit ear
- Pressure Vessel - 4.5” Dia., 0.030” thick
- Positives - Water base slurry, aqueous impregnation
- Electrolyte - 31% KOH
- Wall Wick - yes
- Cell Capacities - 60AH and 100AH (2.5V)

Cell BOL Performance Summary

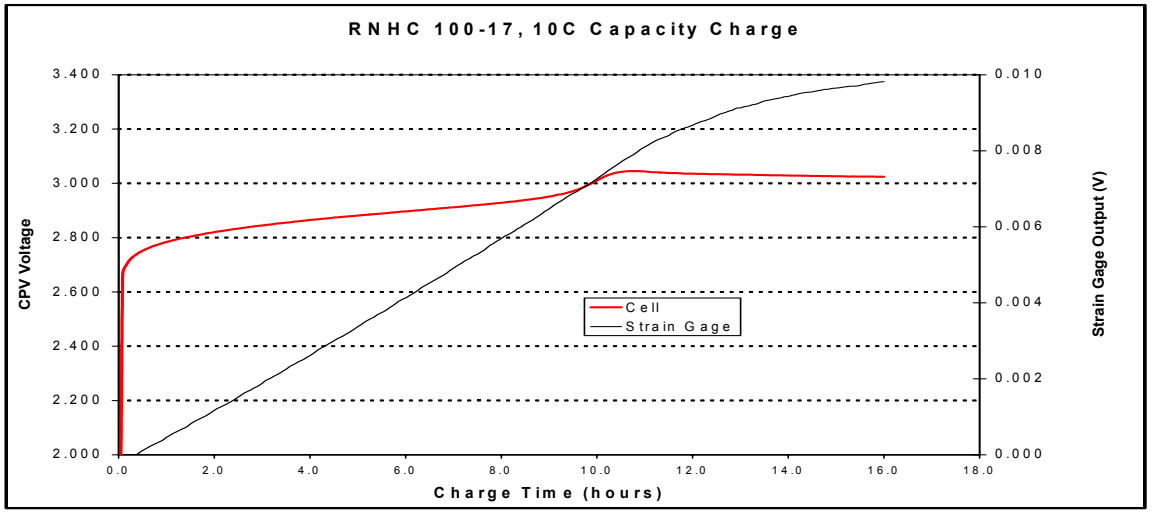
	RNHC 60-11	RNHC 100-17
Cell Voltage	2.5V	2.5V
Operating Press. (psig)	900	950
20°C Capacity (AH)	64	96.8
10°C Capacity (AH)	69.7	109.5
0°C Capacity (AH)	74.5	117.8
Cell Length (inches)	12.4	16.5
Cell Diameter (inches)	4.64	4.64
Weight (grams)	3350	4357
Specific Energy (Whr/kg)	52	62.8
Energy Density (Whr/l)	86	85

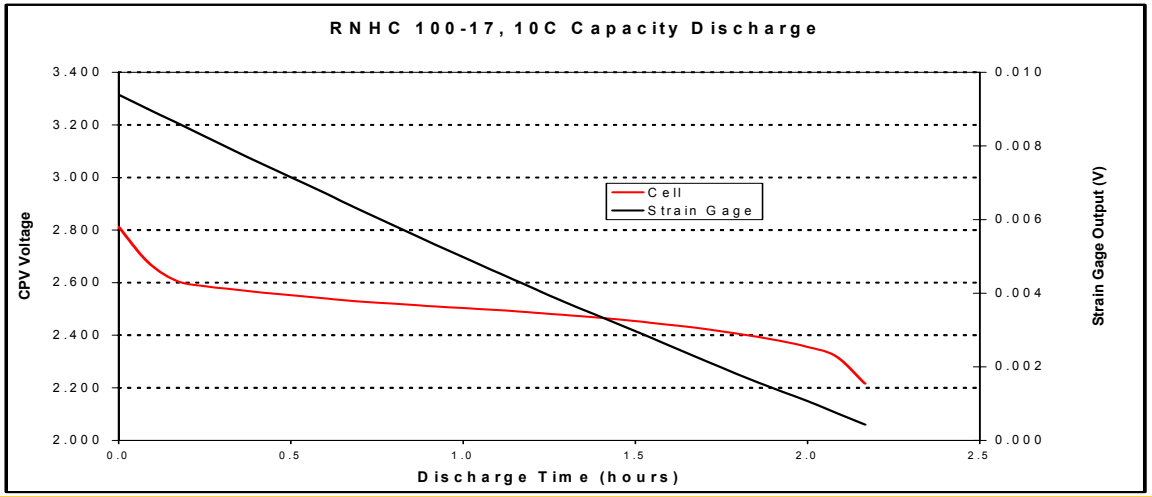
BOL Cell Performance



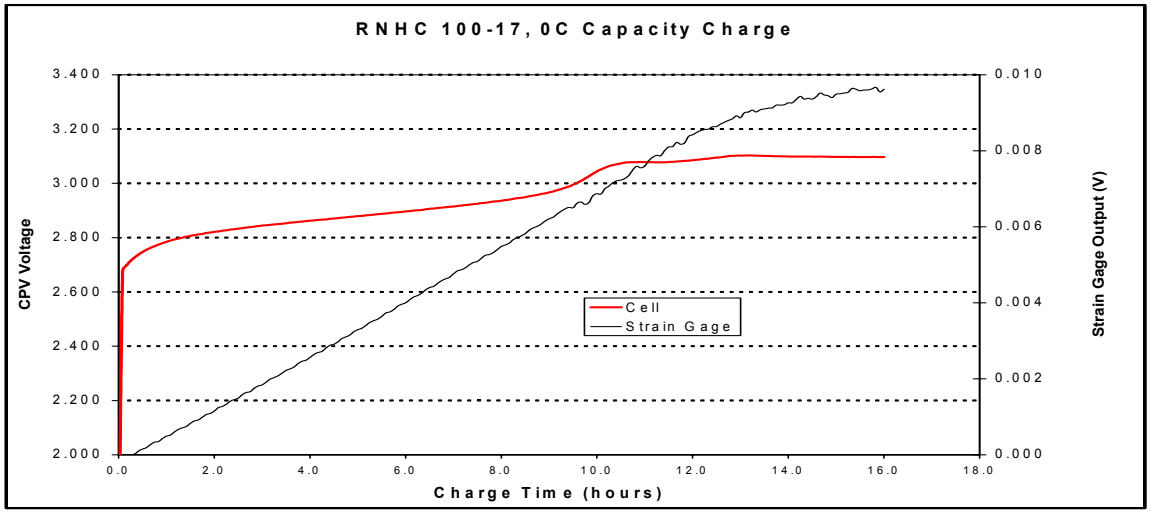


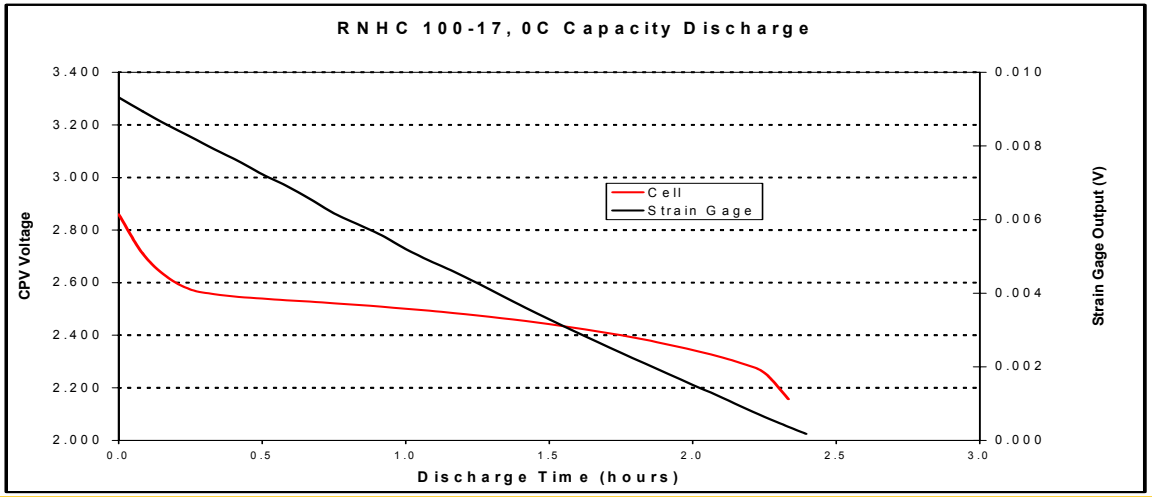
BOL Cell Performance





BOL Cell Performance





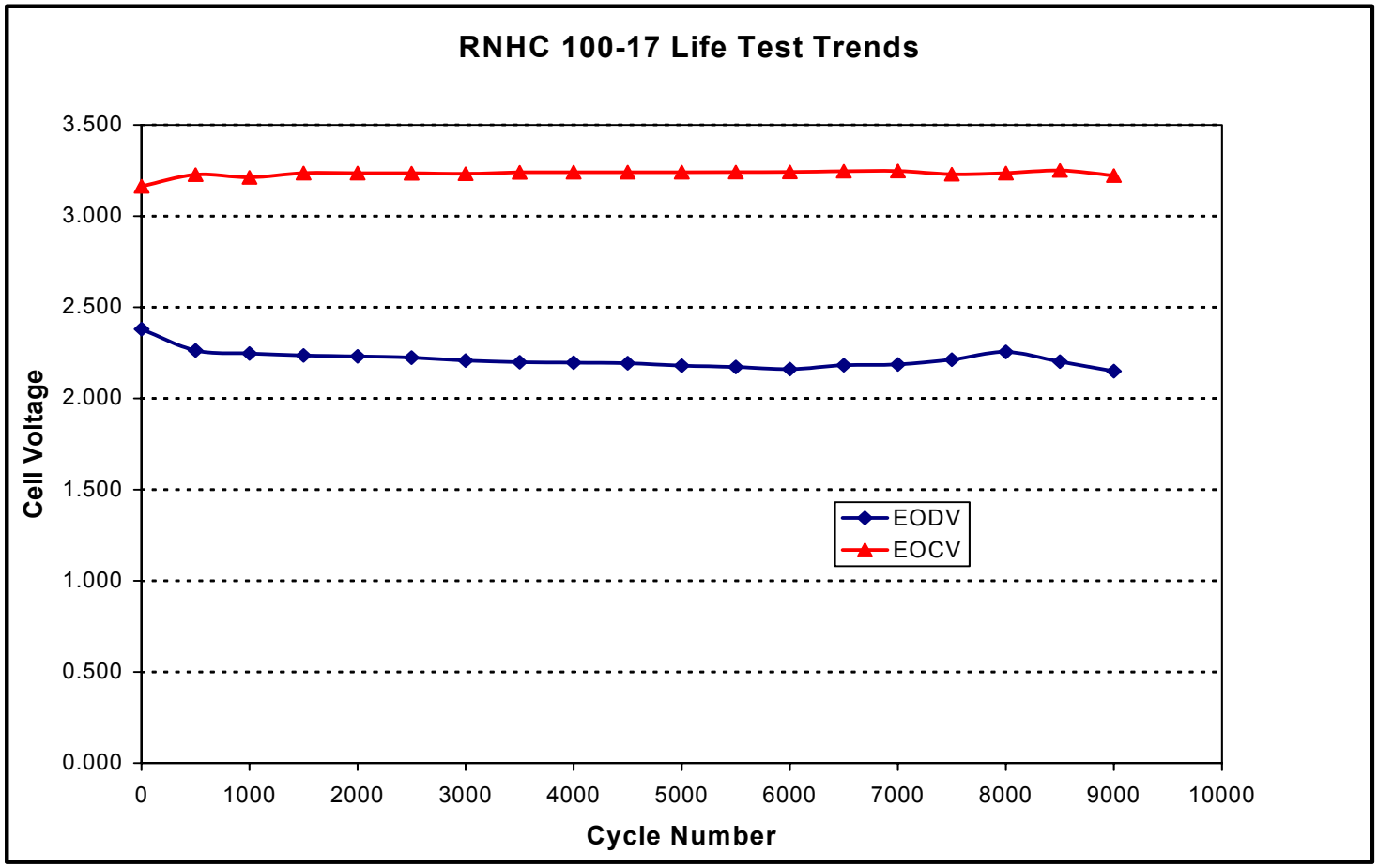
Life Test Cycle Regime

- **RNHC 100-17** **Charge @ 70A for 54 min.**
  Discharge @ 100A for 36 min.
- **RNHC 60-11** **Charge @ 42A for 54 min.**
  Discharge @ 60A for 36 min.

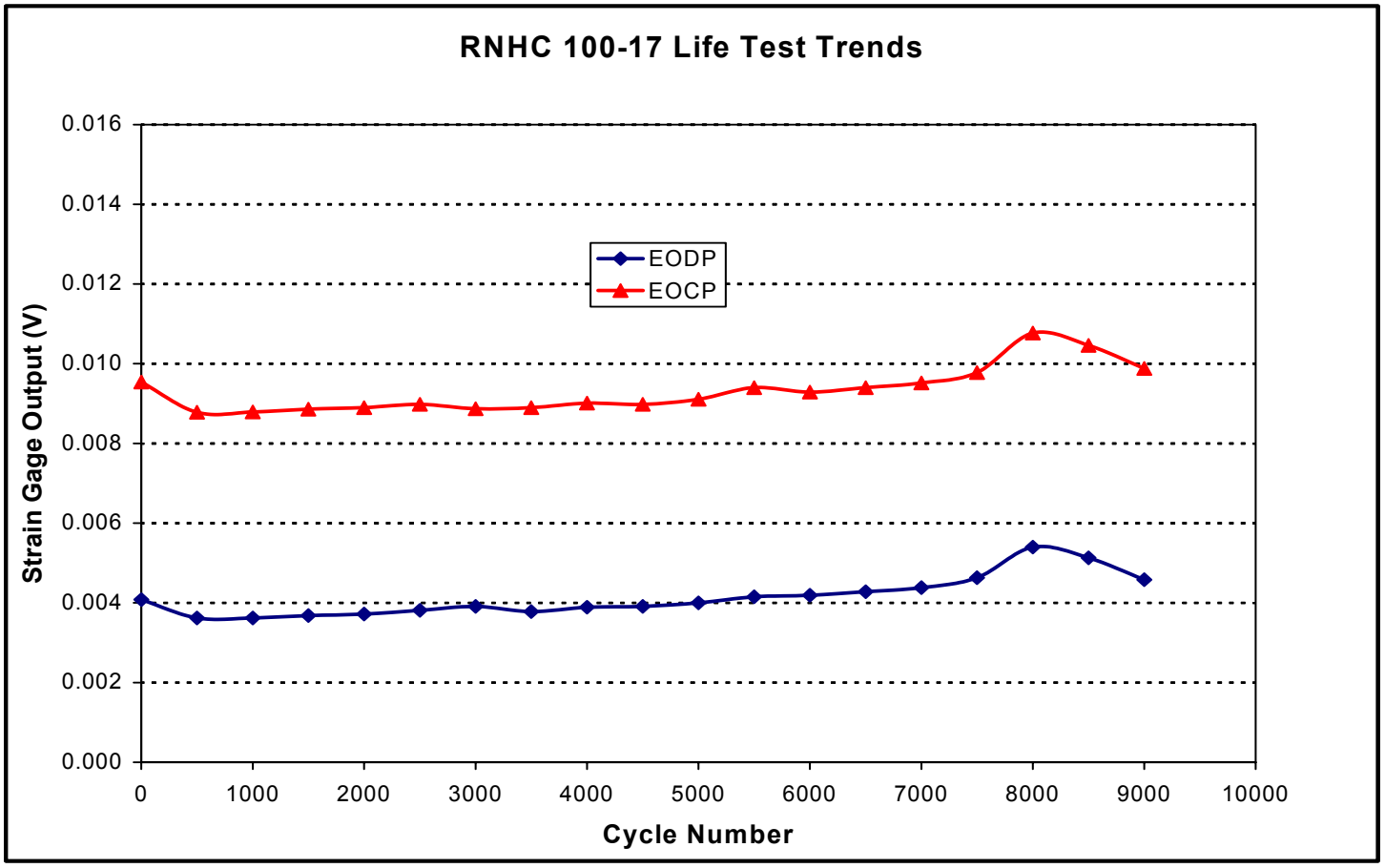
Life Test Set-up

- Cells installed in cooling cart that uses air flow to maintain cell temperature.
- Cart design minimizes dome to dome thermal gradients.
- Test temperature controlled at 10ºC based on average upper dome temperature.

Life Test Data



Life Test Data



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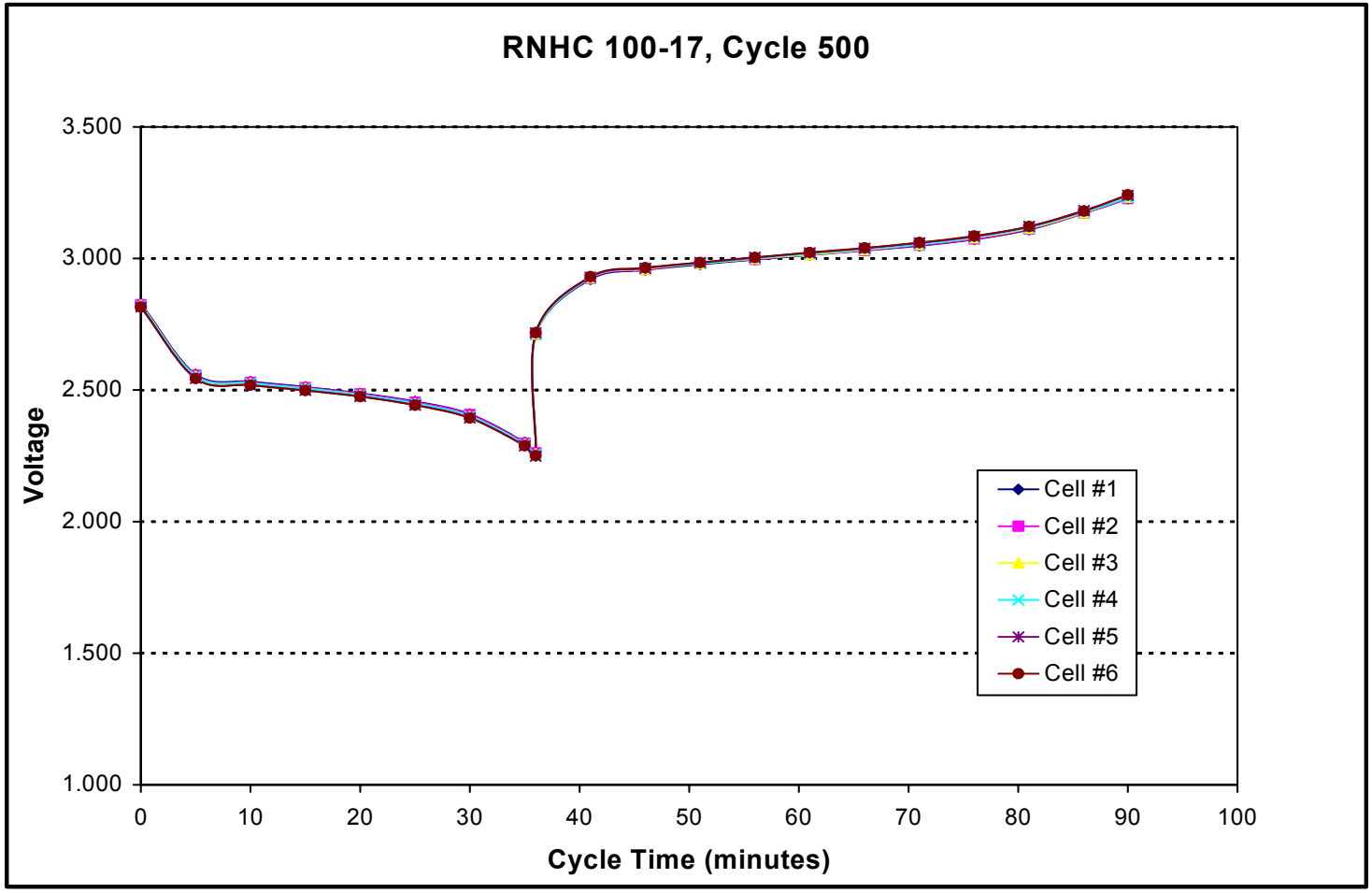
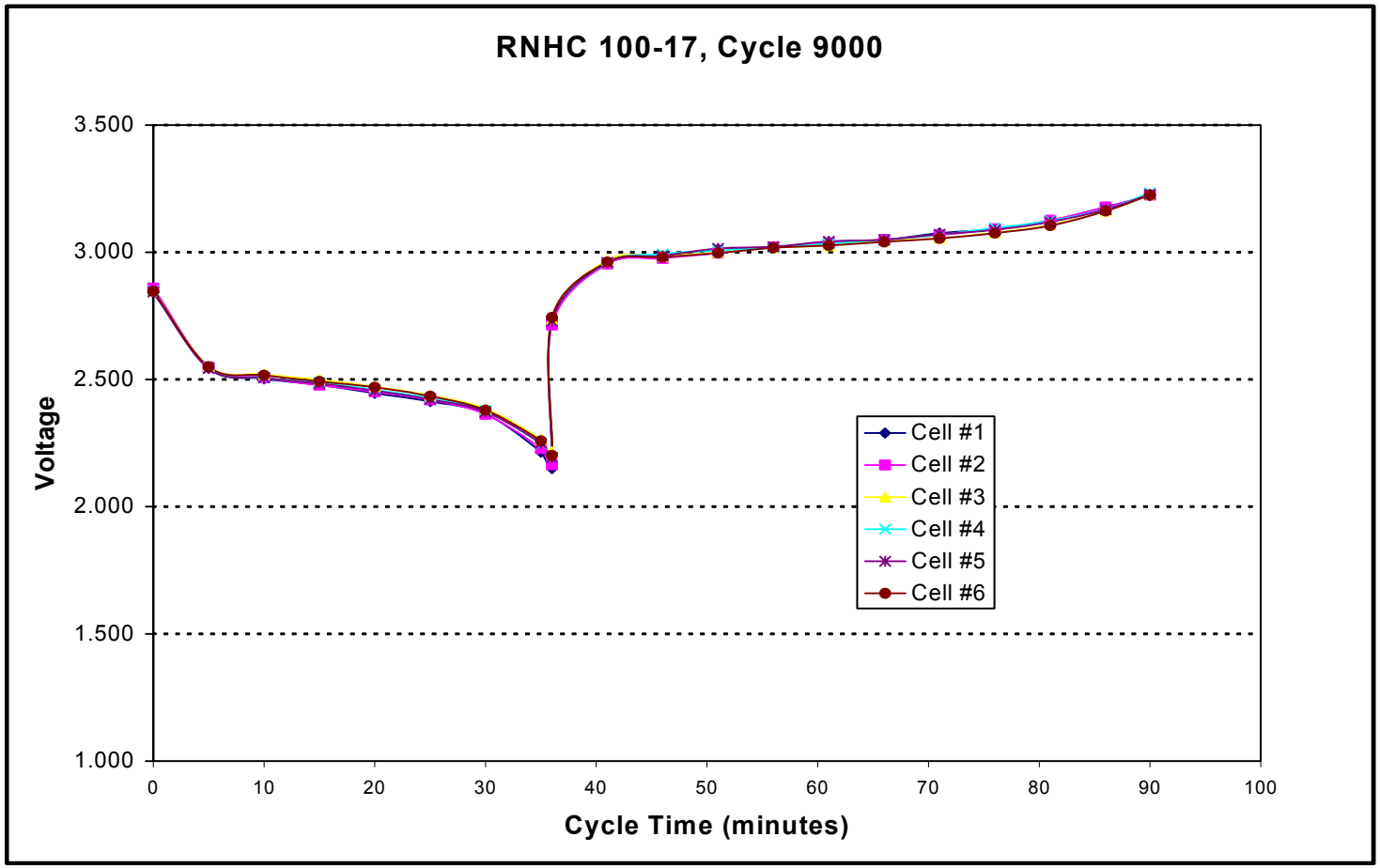
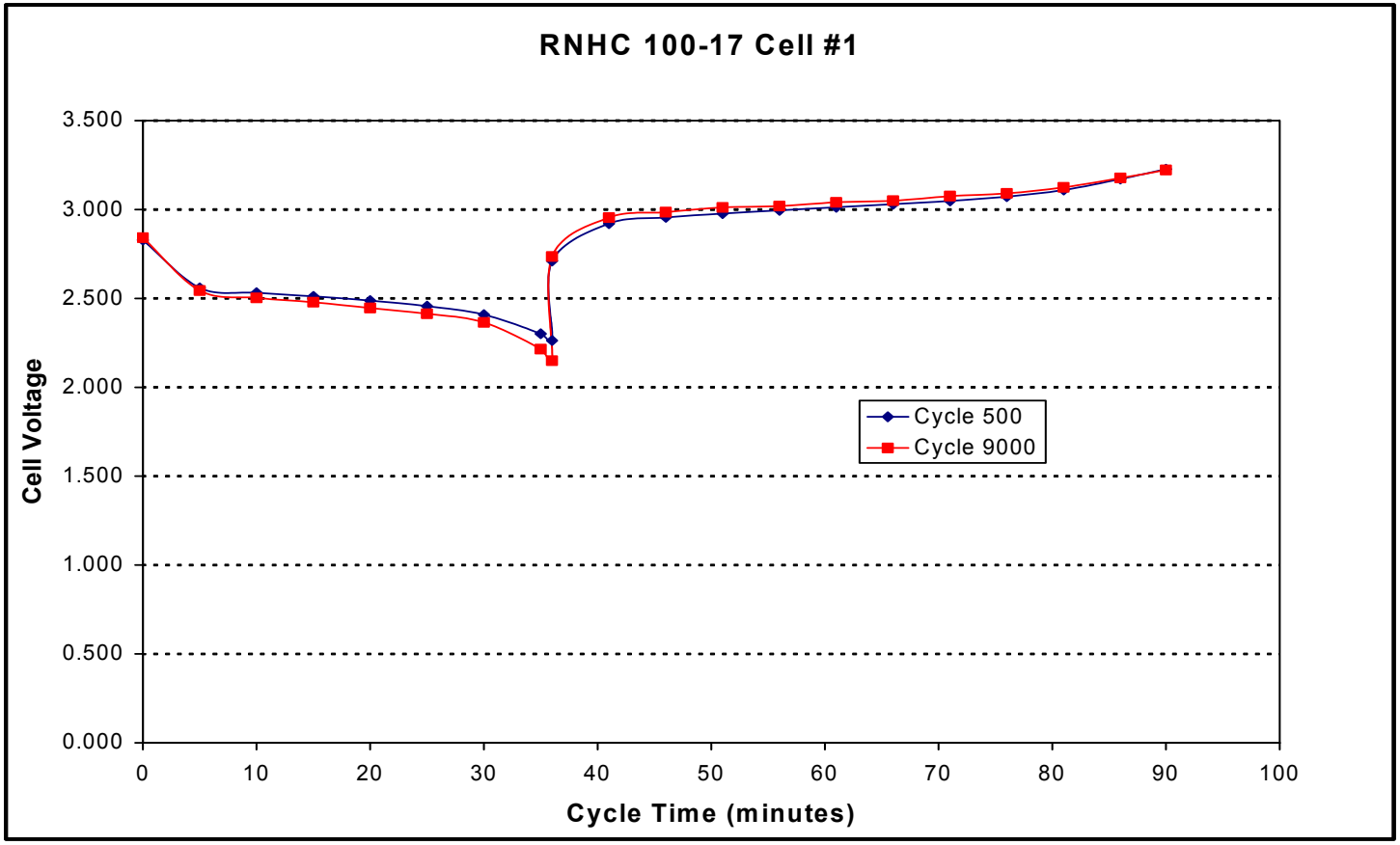


Life Test Data



Life Test Data



Summary

- Currently all cells in the test are performing as expected.
- Data for the RNHC 60-11 cell is similar to that presented for the RNHC 100-17 cell.
- Testing on both designs will continue in an attempt to accumulate significantly more cycles.

Optimal Battery Charging for Damage Mitigation

NASA Grant NCC3-820

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November 2002

Electrical and Computer Engineering

Control Philosophy

Two Phases of Control System Design:

Phase I is the design of optimal trajectories and associated inputs, that move a given plant from one operating condition to another, while minimizing some performance measure. Requires a nonlinear dynamic model of the specific system.

Phase II is the design of a trajectory following controller (sometimes called a regulator or tracker) that provides a real-time control input perturbation to keep the plant operating near the designed optimal trajectory. Usually uses a linearized dynamic model of the specific system.

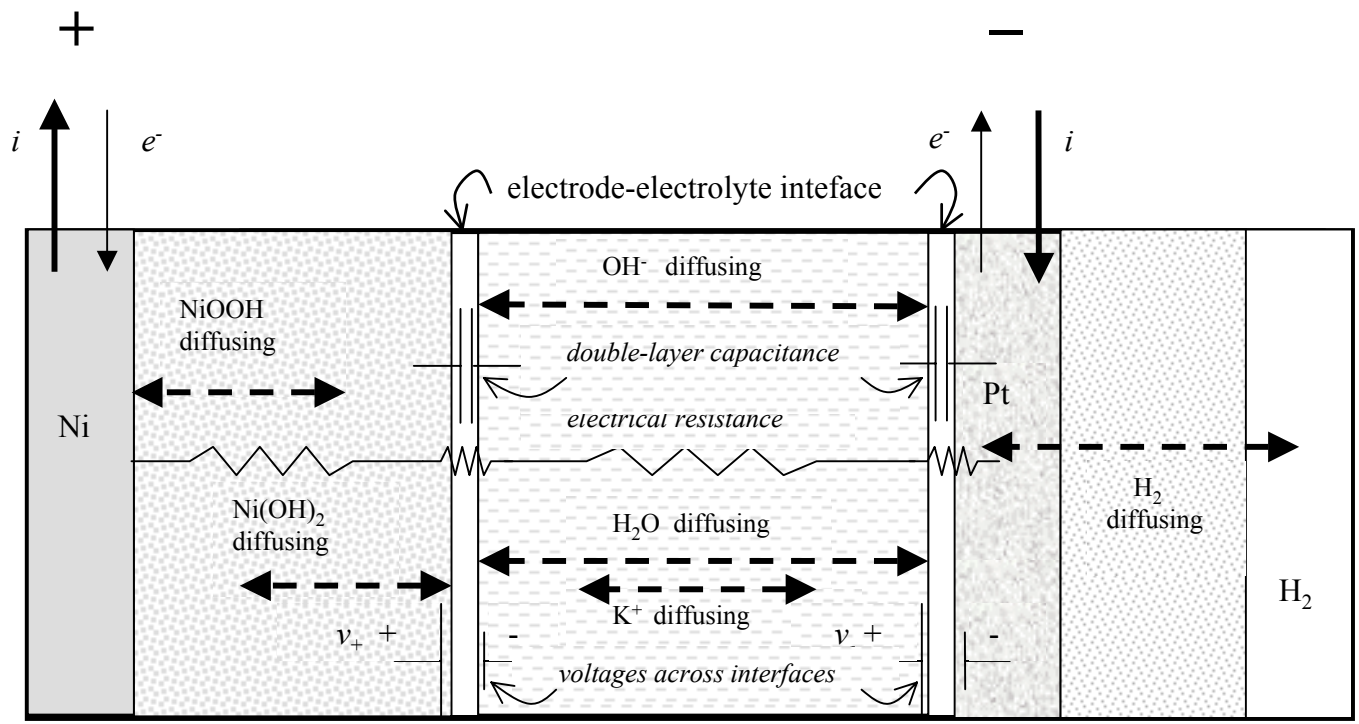
Phase I:

Our control philosophy is to charge the NiH2 cell in such a way that the damage incurred during the charging period is minimized, thus extending its cycle life. Requires nonlinear dynamic model of NiH2 cell and a damage rate model. We must do this first.

This control philosophy is generally considered damage mitigating control or life-extending control.

Electrical and Computer Engineering

Overview of NiH2 Electrochemistry



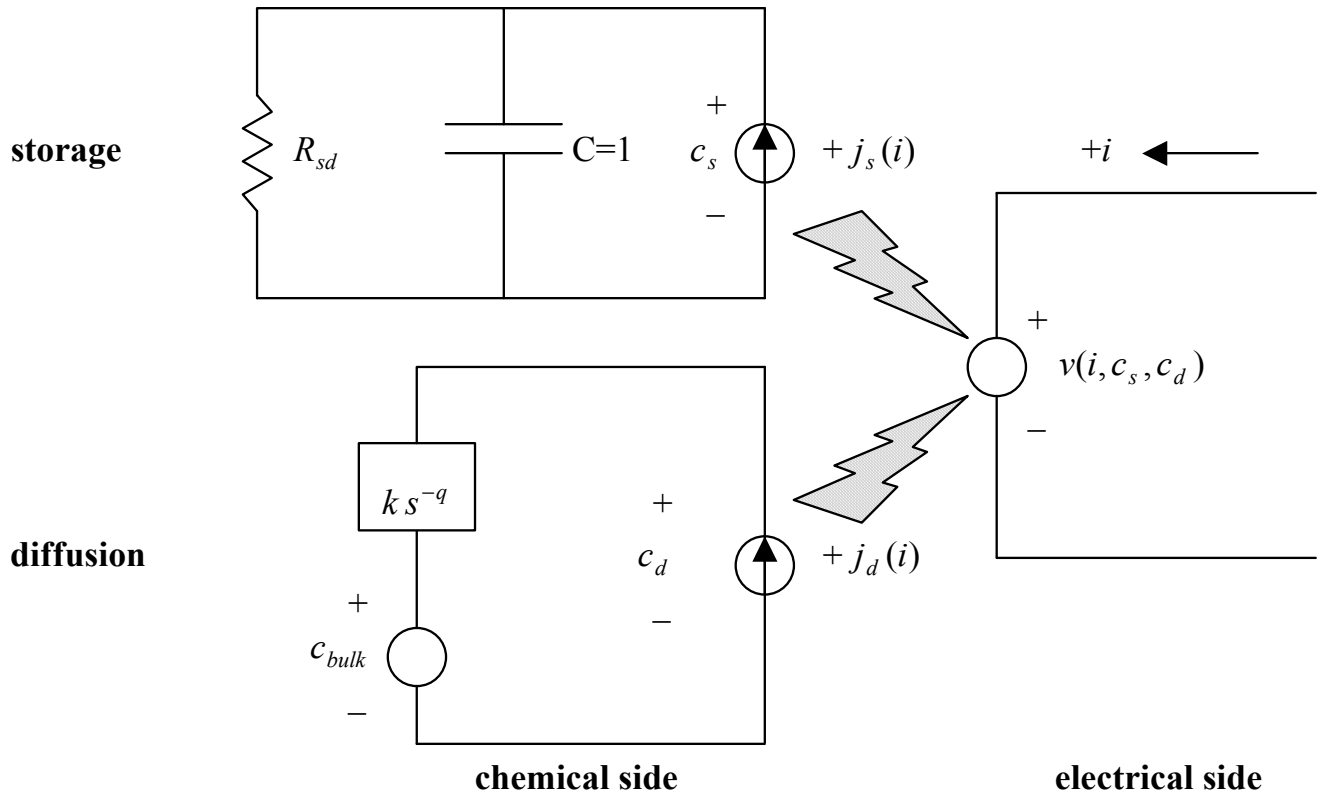
Normal charge-discharge operation of a nickel-hydrogen cell:

positive nickel electrode: $NiOOH + H_2O + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Ni(OH)_2 + OH^-$

negative hydrogen electrode: $\frac{1}{2} H_2 + OH^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} H_2O + e^-$.

Electrical and Computer Engineering

Essentialized performance model of NiH2 cell.



$$S + D + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{reaction products}$$

Electrical and Computer Engineering

Electrode Behavior: Faraday's Law

- For the discussion of the next two sections, consider the electrode process :

$$a\mathrm{A} + b\mathrm{B} \longleftrightarrow c\mathrm{C} + d\mathrm{D} + ne^{-}.$$

- This equation represents both a chemical process and an electrical process.
- The reaction rates can be completely determined using the electrical process by seeing that the chemical conversion can only occur if electrons are either arriving or leaving.
- Thus, the chemical conversion rates are controlled by, or measured by, the electrical current passing through a given electrode.
- Then recognizing that the rate of electron production is related to electrical current *i*, the following rate equations result :

$$-i \equiv \frac{dq_{e^-}}{dt} = -\frac{d}{n}\frac{d\mathrm{D}}{dt} = -\frac{c}{n}\frac{d\mathrm{C}}{dt} = +\frac{a}{n}\frac{d\mathrm{A}}{dt} = +\frac{b}{n}\frac{d\mathrm{B}}{dt}$$

where q_{e^-} is the charge of a single electron.

Electrode Behavior: Electrode Equation

Consider the fluxes, *j*, of the species in the forward and reverse reactions at the electrode,

$$i = j_f - j_r .$$

Assuming that the species fluxes are proportional to concentrations, yields

$$i = k_f c_A^a c_B^b - k_r c_C^c c_D^d .$$

The rate constants, *k*, can be related to the electrical potential across the electrode-electrolyte interface using free energy considerations,

$$k_f = k_0 e^{(F/RT)(1-\alpha)(v-v_0)}$$

$$k_r = k_0 e^{(F/RT)(-\alpha)(v-v_0)}$$

Inserting these gives the electrode equation,

$$\boxed{i = k_0 \left(c_A^a c_B^b \, e^{(F/RT)(1-\alpha)(v-v_0)} - c_C^c c_D^d \, e^{(F/RT)(-\alpha)(v-v_0)} \right).}$$

The approach used is often referred to as the Butler-Volmer approach.

Linear-in-the-parameters Electrode Equation

We propose a linear-in-the-parameters approximate solution to the electrode equation;

$$\boxed{v = k_1 + k_2 \ln\left(1 + |i|\right)\mathrm{sgn}(i) + k_3 \ln(c_d) + k_4 \ln(1 - c_s)}$$

where the *k*'s are parameters to be determined from data.

This represents a compromise between the Tafel and the Nernst solutions of the electrode equation:

The Nernst solution assumes that the current is so small as to be negligible

$$v = v_0 + \frac{RT}{nF} \ln\left(\frac{c_s}{c_d}\right).$$

The Tafel solution assumes that the current is large in one direction or the other, which means that one of the two exponential terms is negligible

$$v = v_0 + \frac{RT}{\alpha nF} \ln(k_0) - \frac{RT}{\alpha nF} \ln(i).$$

Electrical and Computer Engineering

Essentialized Model Overview

Terminal behavior: **current into the battery is +*i***,
the terminal voltage is +*v*,

stored material with self-discharge:

$$\frac{dc_s(t)}{dt} = i(t) - \frac{1}{R_{sd}} c_s(t) ,$$

diffusing material:

$$c_d(t) = c_{bulk} - k_d \; {}_0d_t^{-q} i(t) ,$$

electrode-equation:

$$v(c_s, c_d, i) = k_1 + k_2 \ln\left(1 + |i|\right)\mathrm{sgn}(i) + k_3 \ln(c_d) + k_4 \ln(1 - c_s) .$$

Electrical and Computer Engineering

Parameter Determination

The cell chosen is the NSWC Crane Pack ID 3602G (Gates):

- rated at 65 AHr
- uses 31% KOH concentration
- maintained at 10 degrees C
- charge-discharge profile is a square wave
  - with 35% depth-of-discharge (DOD)
  - 104% recharge ratio
  - current is 26.29 A for 54 minutes charging
  - –37.92 A for 36 minutes during discharge
- note that 65 AHr = 3900 AMin, 35% of 65 AHr = 1365.1 AMin .

Electrical and Computer Engineering

Essentialized Model with Identified Parameters

Terminal behavior: **current into the battery is +*i***,
the terminal voltage is +*v*,

stored material with self-discharge:

$$\frac{dc_s(t)}{dt} = i(t) - 0.0002085 c_s(t),$$

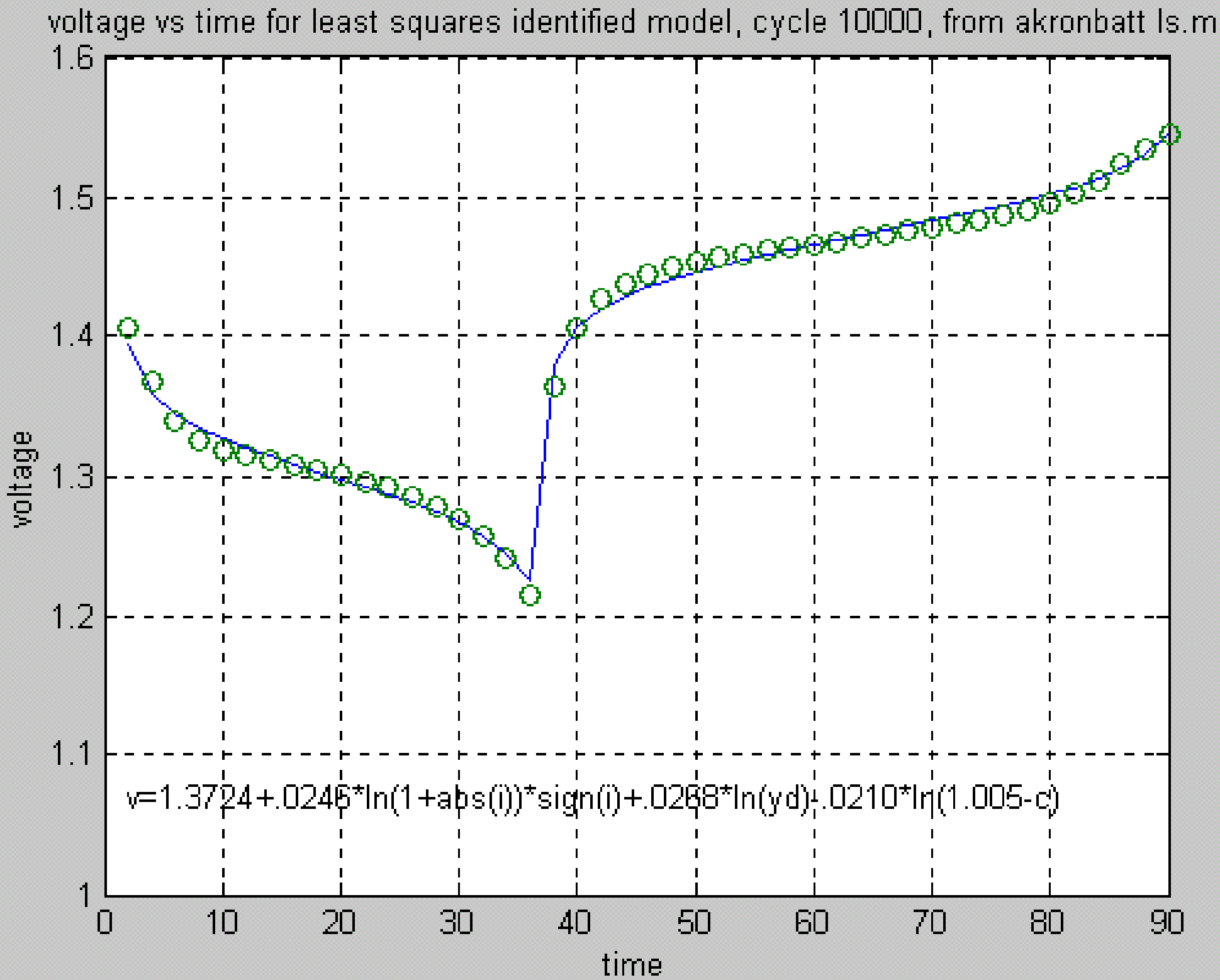
diffusing material:

$$c_d(t) = 1 - 0.001036\, {}_0d_t^{-0.9034} i(t),$$

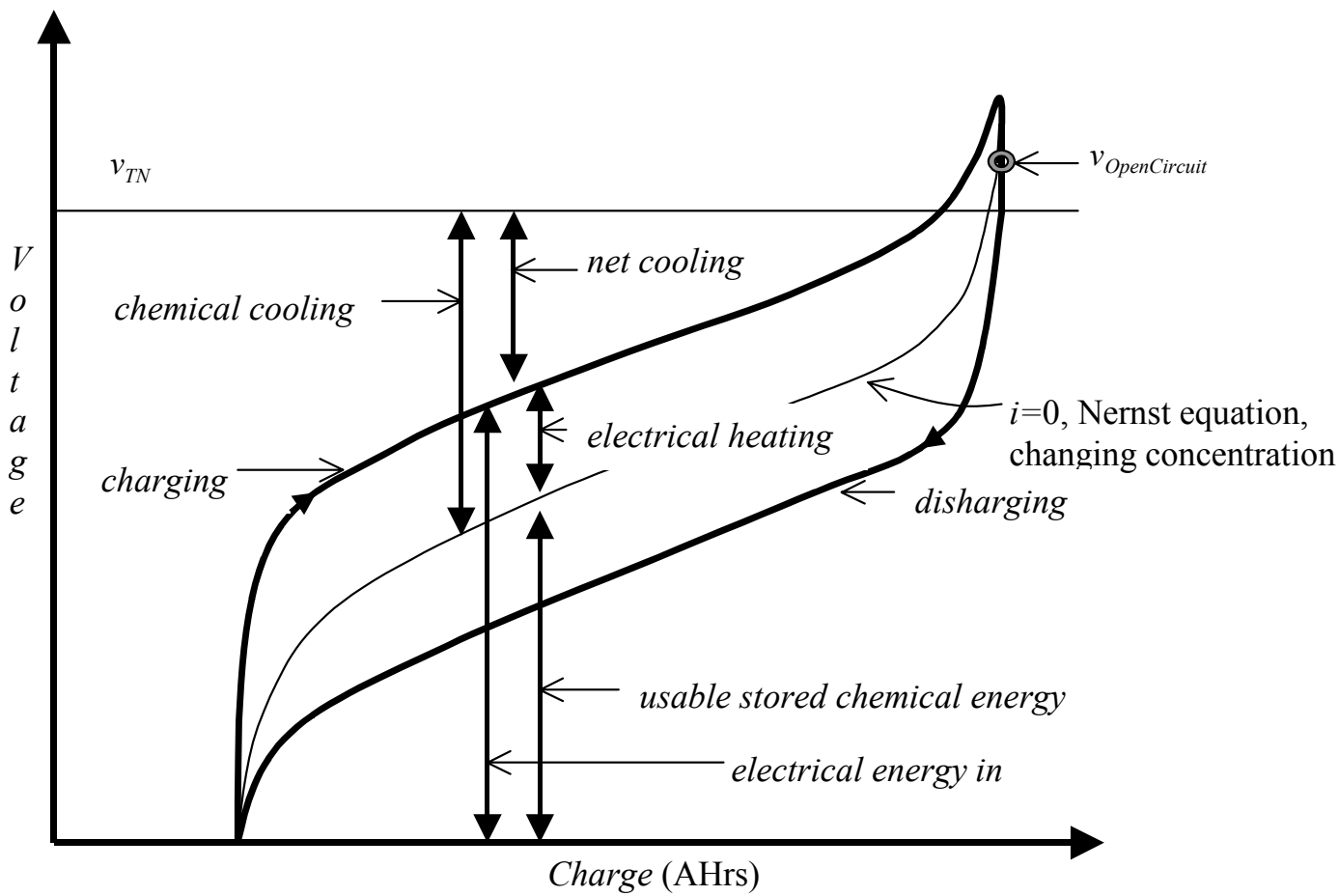
electrode-equation:

$$v = 1.3656 + 0.0265 \ln(1 + |i|)\operatorname{sgn}(i) + 0.0229 \ln(c_d) - 0.0262 \ln((1.005 * 3900 - c_s)/3900)$$

Electrical and Computer Engineering


voltage vs time for least squares identified model, cycle 10000, from akronbatt ls.m
1.6
1.5
1.4
1.3
1.2
1.1
1
voltage
0
10
20
30
40
50
60
70
80
90
time
v=1.3724+.0246*ln(1+abs(i))*sign(i)+.0268*ln(yd)-.0210*ln(1.005-c)

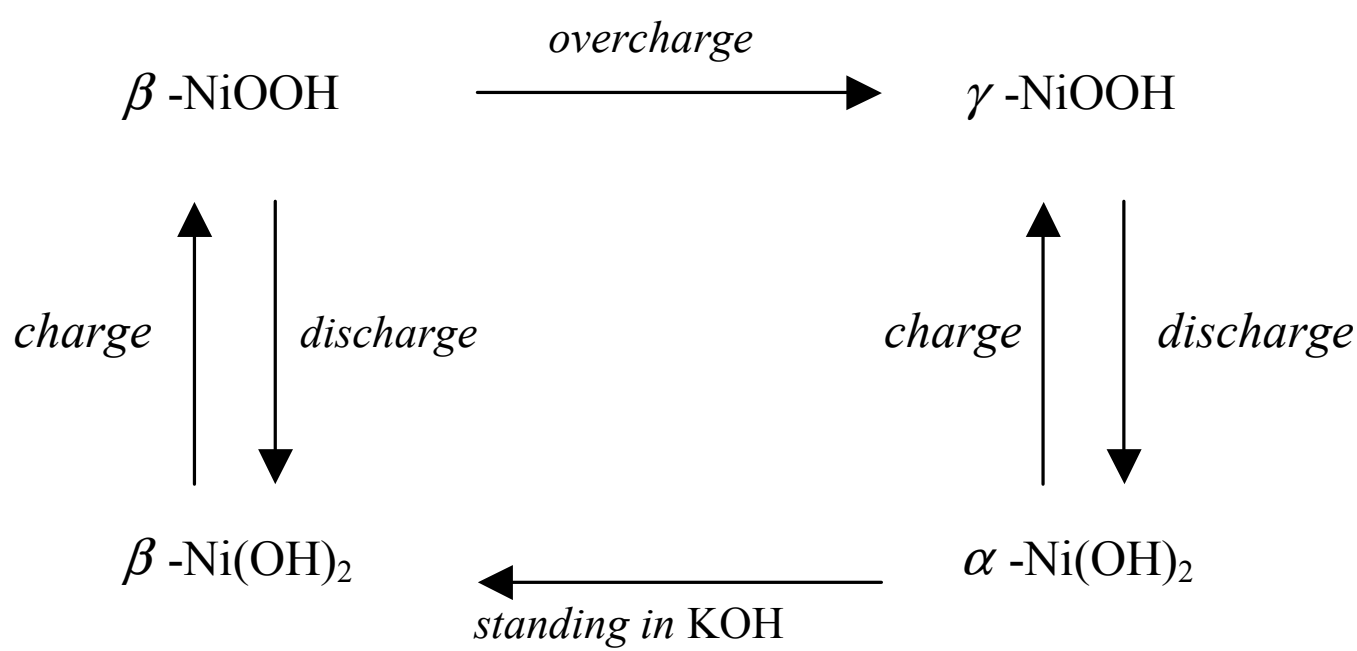
A typical charge-discharge cycle, charging.



Electrical and Computer Engineering

Damage Mechanisms for NiH2 Batteries

Formation of γ - phase NiOOH:



Bode's Solid phase relationships for a NiOOH electrode.

Electrical and Computer Engineering

Damage Mechanisms for NiH2 Batteries

Formation of O2:

Overcharge: 1) continuing to charge the cell after all the β-$Ni(OH)_2$ has been converted

2) the charging current is too large

The effect of this is the formation of O_2 at the nickel electrode, along with heating.

Damage Mechanisms for NiH2 Batteries

Heating:

Sources: 1) heat of reaction
2) formation of O_2
3) electrical current

Results in: 1) the formation of γ-NiOOH:
which a) reduces cell capacity
b) does physical damage to the cell

Results in an increase in self-discharge reaction rates.

Battery Continuum Damage Modeling

- Many Possible Damage Mechanisms
  - Hard to model all these
- Overall Birth to Death Data will be Used Instead
- Crane Database Provides much Information
- Green-Hoffman Data Taken as Starting Point

Electrical and Computer Engineering

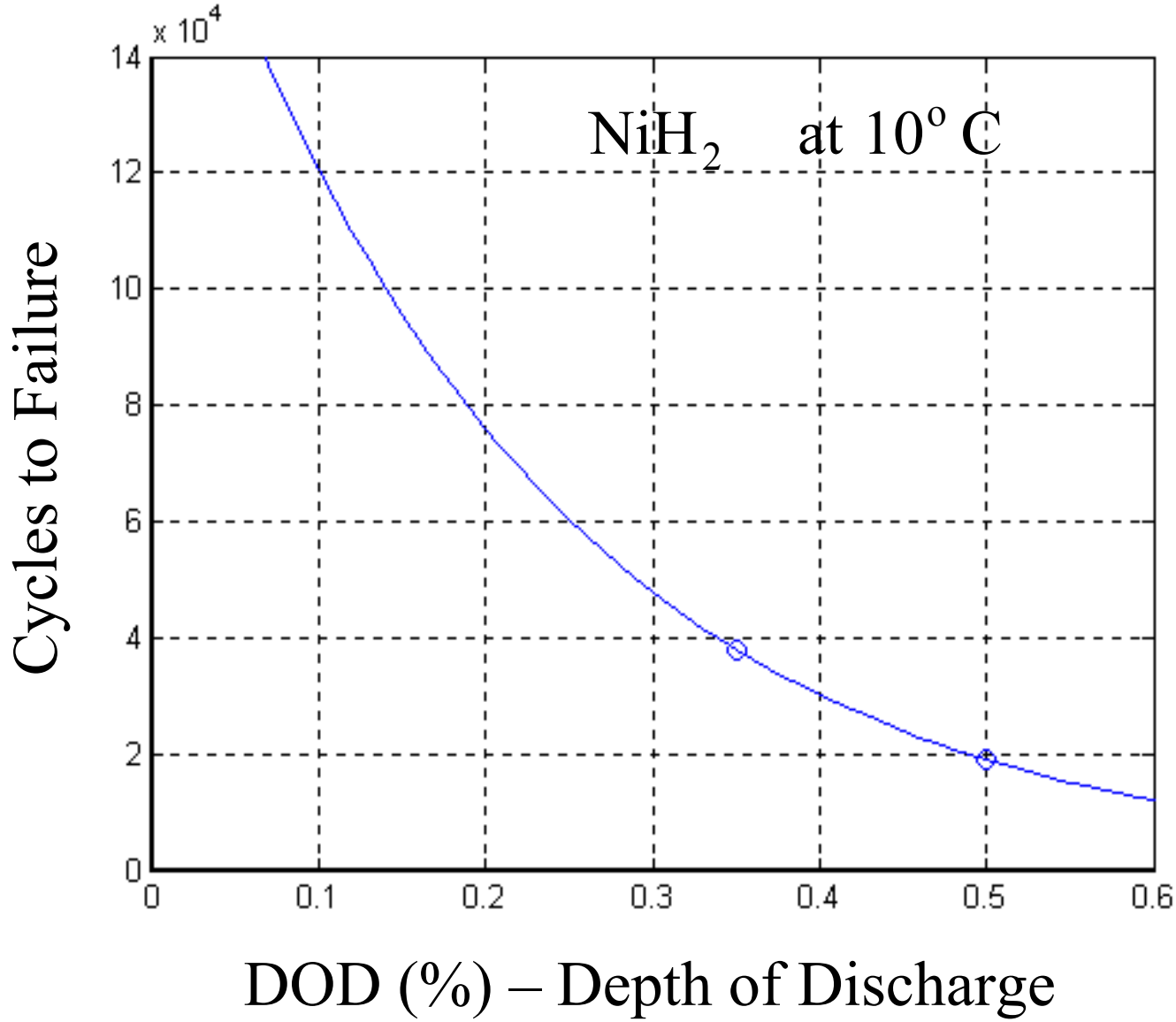
Battery Continuum Damage Modeling

Green-Hoffman Data NiH_2 at $T = 10\ ^{o}C$

DOD	Cycles To Failure
35%	38,000
50%	19,000

Electrical and Computer Engineering

Green-Hoffman Battery Life Model



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Continuum Damage Model

Based on G-H Data

$$N_{f_{GH}} = 1885.04 e^{4.621(1-DOD)}$$

$$= 191511.73 e^{-4.621 DOD}, \quad \text{at } 10^{\circ}\text{ C}$$

For constant damage per cycle

$$D_{cyc} = \frac{1}{N_{f_{GH}}} = 5.222 \times 10^{-6} e^{4.621\, DOD}$$

$$DOD = c_1 v_a$$

$$D_{cyc} = 5.222 \times 10^{-6} e^{4.621 c_1 v_a}$$

Electrical and Computer Engineering

Continuum Damage Model

$$\int_{cycle} \hat{\delta}(v)\,dv = D_{cyc} = 5.222\times10^{-6}\, e^{4.621 c_1 v_a}$$

where $\hat{\delta}(v) = \dfrac{dD}{dv}$ = voltage referred damage rate

For damage on charging only

$$\int_{v_{\min}}^{v_{\max}} \hat{\delta}(v)\,dv = D_{cyc} = 5.222\times10^{-6}\, e^{4.621 c_1 v_a}$$

Electrical and Computer Engineering

Continuum Damage Model

$$\int_0^{v_{\max}-v_{\min}} \hat{\delta}(v+v_{\min})\,dv = 5.222\times10^{-6}\,e^{4.621c_1 v_a}$$

$$= 5.222\times10^{-6}\,e^{4.621c_1(v_{\max}-v_{\min})}$$

Thus inferring

$$\hat{\delta}(v+v_{\min}) \cong 5.222\times10^{-6}\,4.621\,c_1\,e^{4.621c_1 v}$$

$$= 2.4131\times10^{-5}\,c_1\,e^{4.621c_1 v}$$

Hence

$$\boxed{\hat{\delta}(v) = 2.4131\times10^{-5}\,c_1\,e^{4.621c_1(v-v_{\min})}}$$

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Continuum Damage Model

Instantaneous Damage Rate

$$\dot{D}(t) \equiv \frac{dD}{dt} = \frac{dD}{dv}\frac{dv}{dt} = \hat{\delta}(v(t))\,\dot{v}(t)$$

Requiring Positive Damage

$$\dot{D}(t) \equiv \frac{dD}{dt} = \frac{dD}{dv}\left|\frac{dv}{dt}\right| = \hat{\delta}(v(t))\,\left|\dot{v}(t)\right|$$

$$\dot{D}(t) = 2.4131\times10^{-5}\,c_1\,e^{4.621\,c_1\,(v-v_{\min})}\,\left|\dot{v}(t)\right|$$

$$\boxed{\dot{D}(t) = 2.4131\times10^{-5}\,c_1\,e^{4.621\,c_1\,(v-1.2)}\,\left|\dot{v}(t)\right|}$$

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Modified Continuum Damage Model

For zero damage at zero DOD

$$D_{cyc} = c_2 \left(e^{c_3 DOD} - e^{c_3 0} \right)$$

$$D_{cyc} = c_2 \left(e^{c_3 DOD} - 1 \right) = \frac{1}{N_f}$$

c_2 and c_3 are determined to match G-H Data

$$D_{cyc} = 1.0404 \times 10^{-5} \left(e^{3.602 DOD} - 1 \right) = \frac{1}{N_f}$$

Repeating the previous process gives

$$\boxed{\dot{D}(t) = 3.7475 \times 10^{-4} c_1 e^{3.602 c_1 (v - 1.2)} \left| \dot{v}(t) \right|}$$

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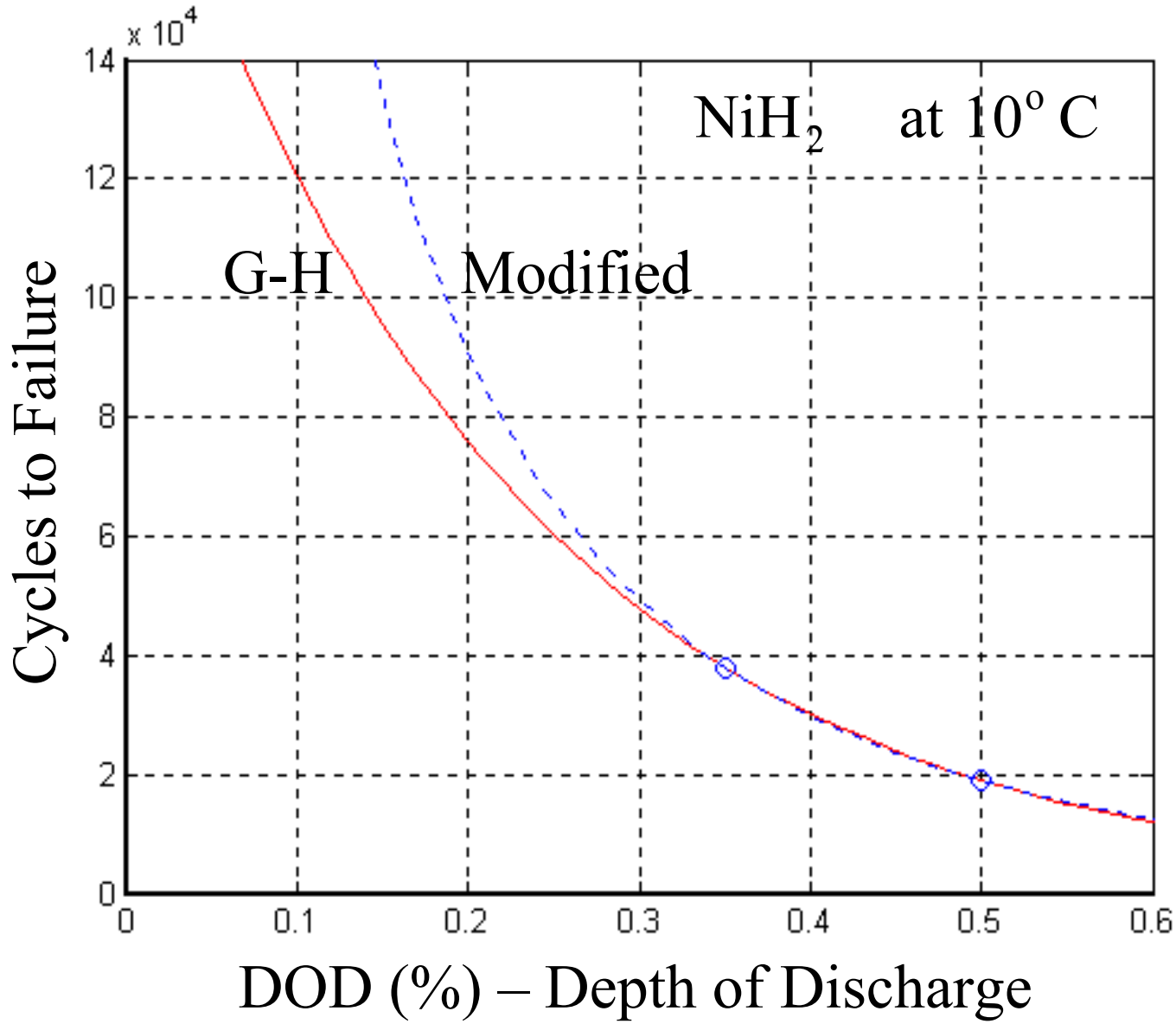
Battery Life Models



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Modified Continuum Damage Model

In terms of current

$$\dot{D}(t) \equiv \frac{dD}{dt} = \frac{dD}{dv}\left|\frac{dv}{dq}\right|\left|\frac{dq}{dt}\right| = \hat{\delta}(v(t))\left|\frac{dv}{dq}\right|\left|i(t)\right|$$

where $\frac{dv}{dq}$ is slope of charging curve

<u>For zero damage when voltage rate goes negative</u>

$$\boxed{\begin{array}{ll} \dot{D}(t) = 3.7475\times10^{-4}\, c_1\, e^{3.602 c_1 (v-1.2)}\, \dot{v}(t), & \dot{v}(t) \geq 0 \\ \dot{D}(t) = 0, & \dot{v}(t) < 0 \end{array}}$$

Control Philosophy

Two Phases of Control System Design:

Phase I is the design of optimal trajectories and associated inputs, that move a given plant from one operating condition to another, while minimizing some performance measure. Requires a nonlinear dynamic model of the specific system.

Phase II is the design of a trajectory following controller (sometimes called a regulator or tracker) that provides a real-time control input perturbation to keep the plant operating near the designed optimal trajectory. Usually uses a linearized dynamic model of the specific system.

Phase I:

Our control philosophy is to charge the NiH2 cell in such a way that the damage incurred during the charging period is minimized, thus extending its cycle life. Requires nonlinear dynamic model of NiH2 cell and a damage rate model. Now that we have this we can begin the control design process. The specific control philosophy is employed is generally considered damage mitigating control or life-extending control.

Electrical and Computer Engineering

Performance Measure

The **performance measure** to be minimized is the accumulated damage per recharge cycle:

$$J = w_{fs}\left(c_s^*(t_f) - c_s(t_f)\right)^2 + \int_0^{t_f} \frac{dD(t)}{dt} dt$$

$c_s^*(t_f)$ is the desired stored charge at the end of charge,

w_{fs} is the cost weighting ,

$\frac{dD(t)}{dt}$ is obtained from the damage model,

t_f for our problem is 54 Min.

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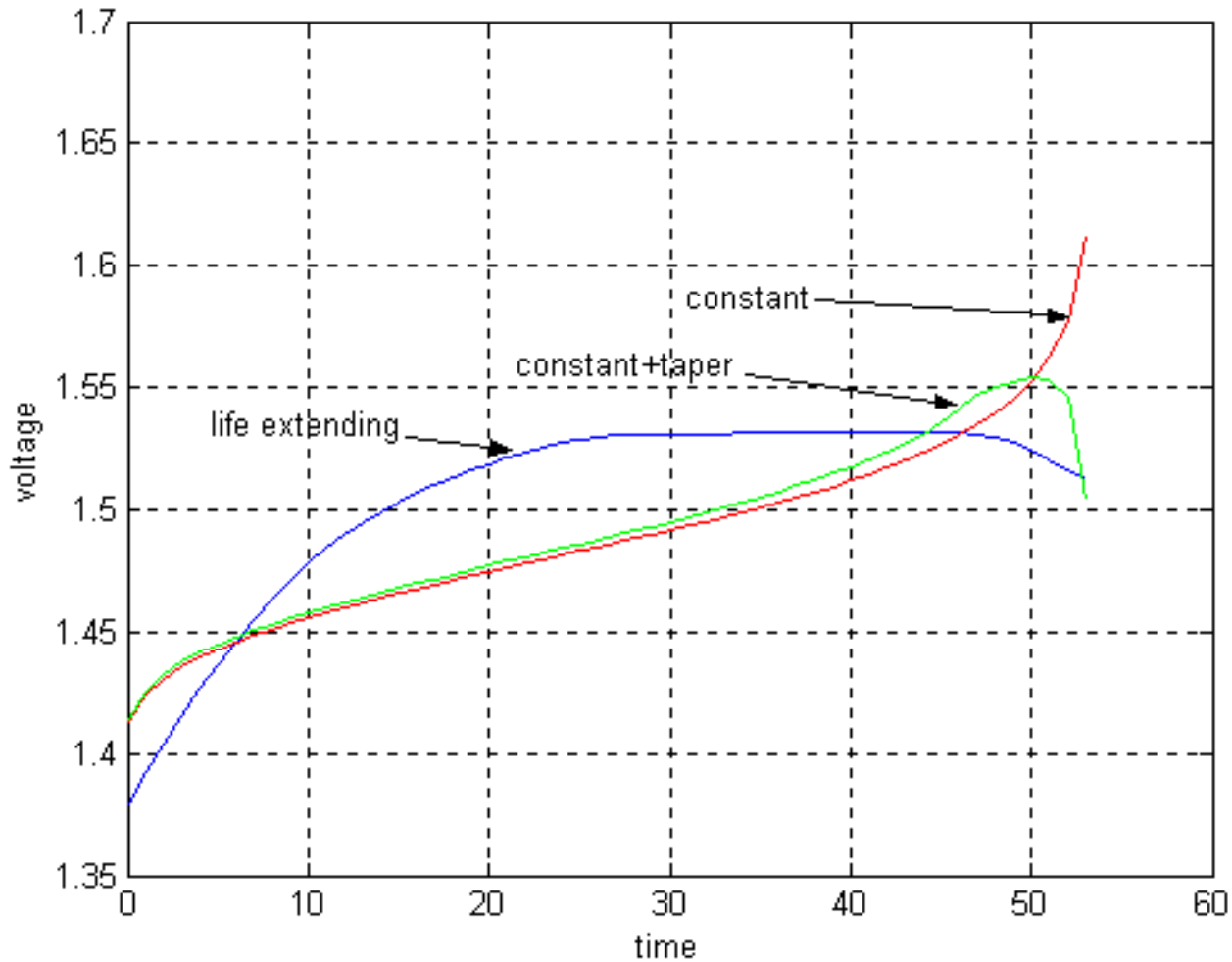
65%-100% recharging, voltage profile



Comparison of 65%-100% charging methods, voltage

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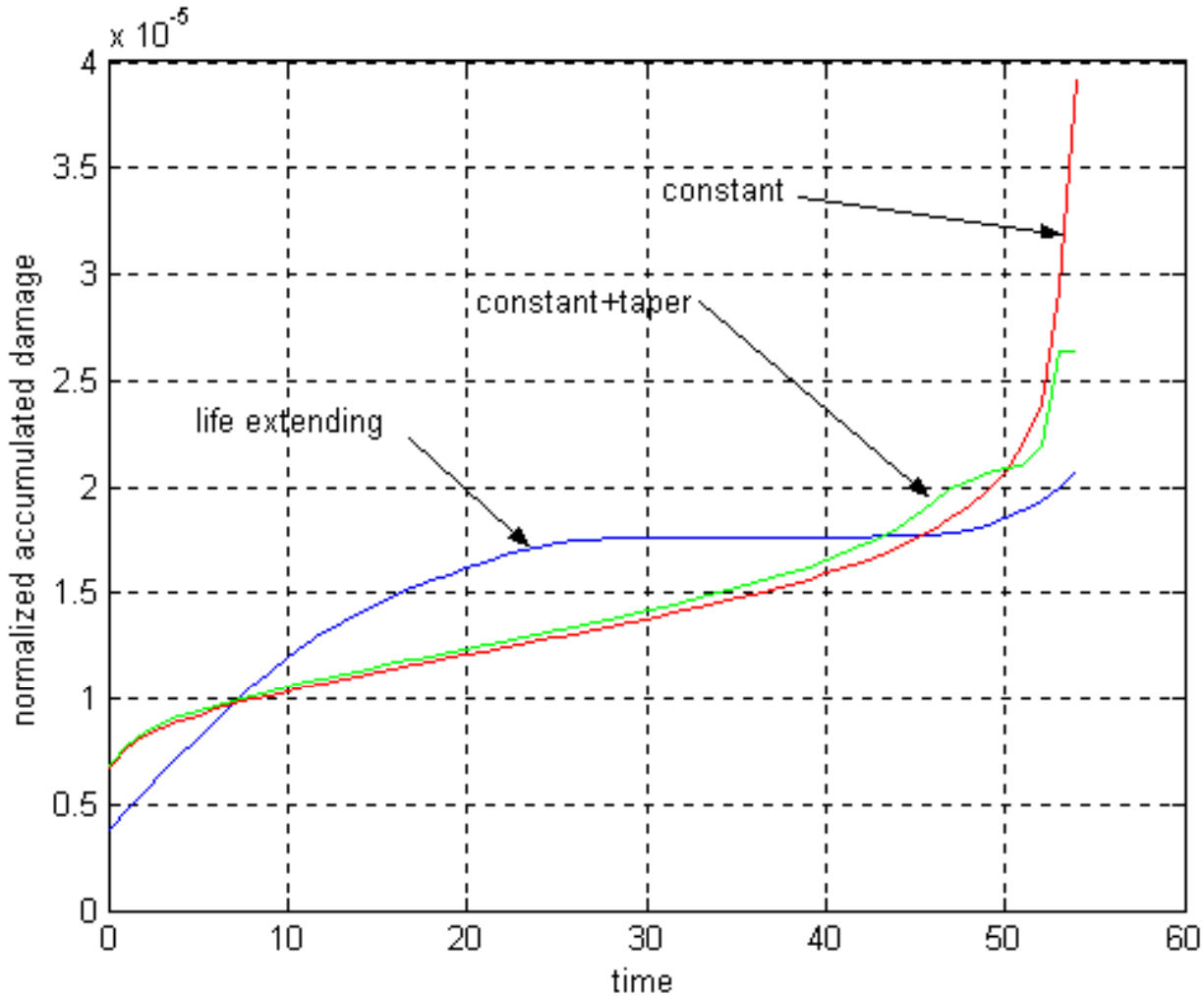
65%-100% recharging, damage profile



Comparison of 65%-100% charging methods, damage.

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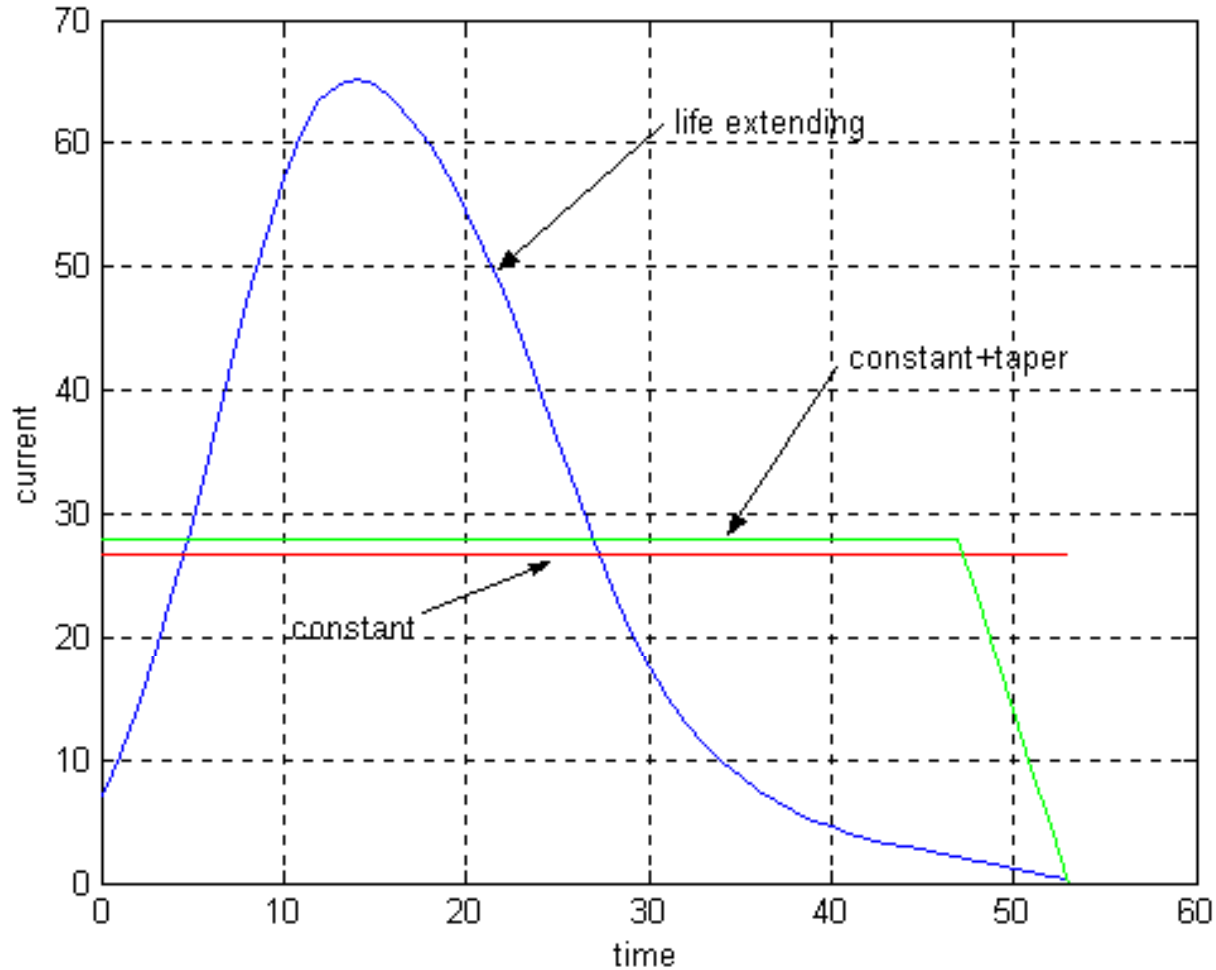
65%-100% recharging, current profile



Comparison of 65%-100% charging methods, current.

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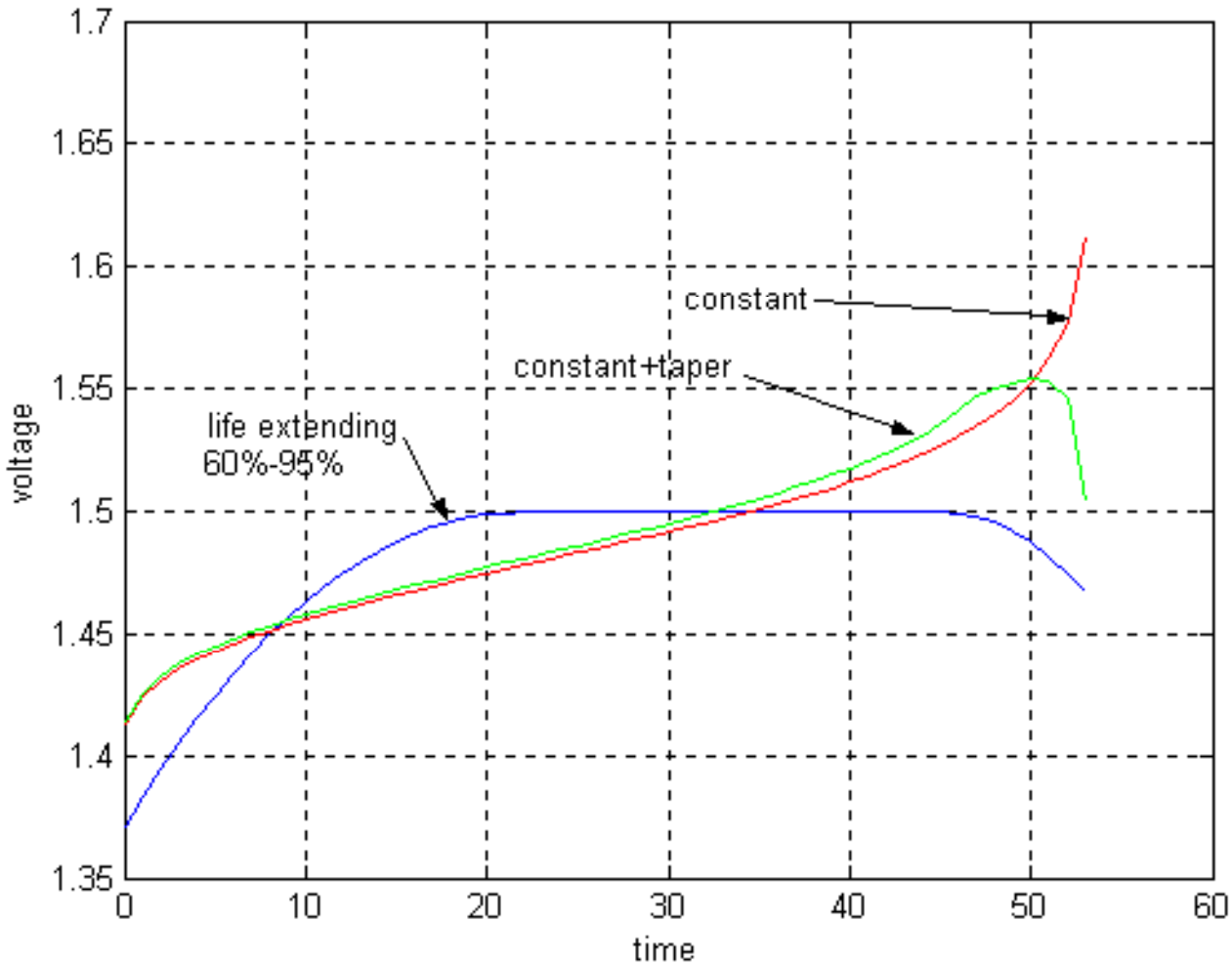
60%-95% recharging, voltage profile



Comparison of 60%-95% and standard charging methods, voltage.

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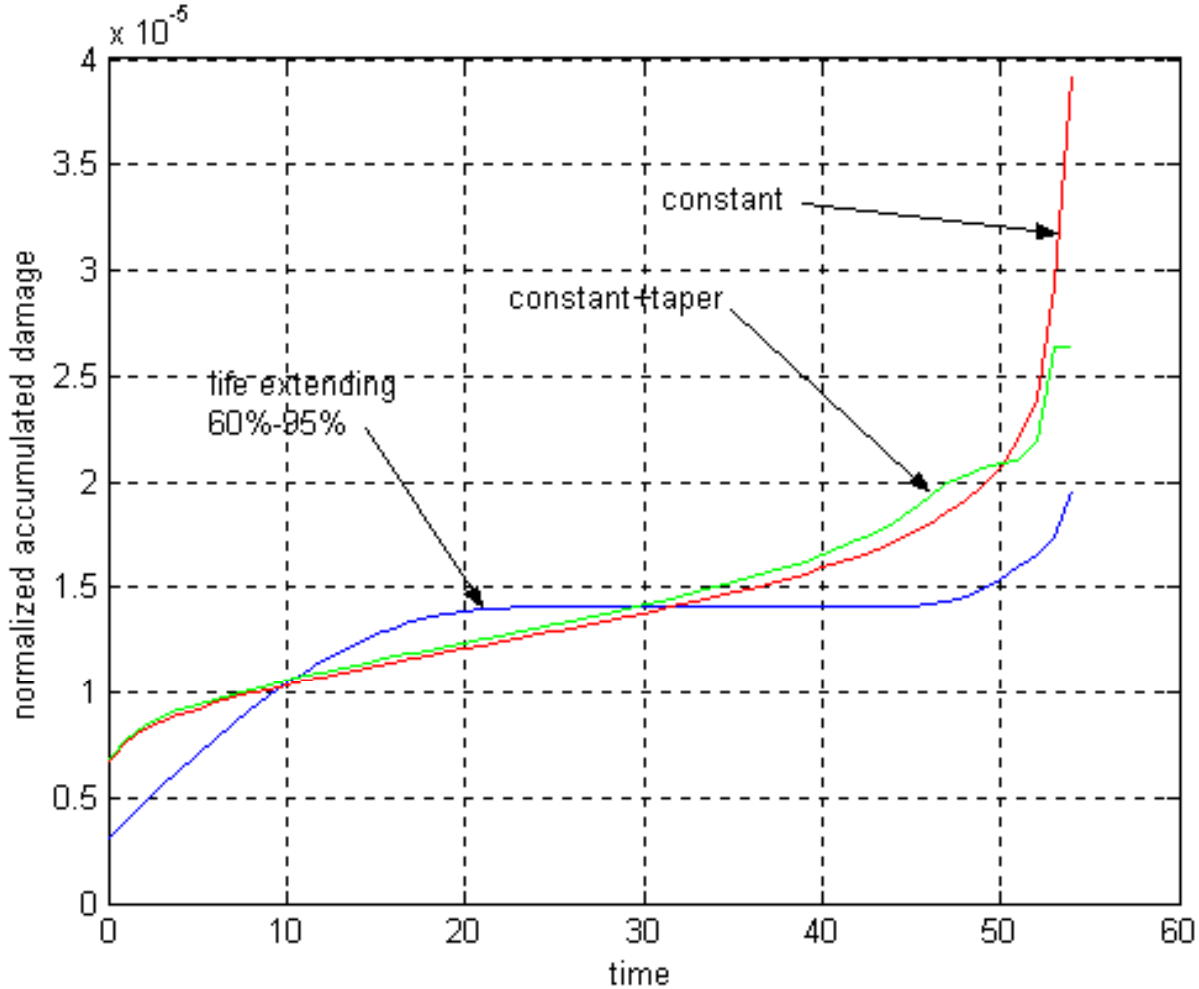
60%-95% recharging, damage profile



Comparison of 60%-95% and standard charging methods, damage.

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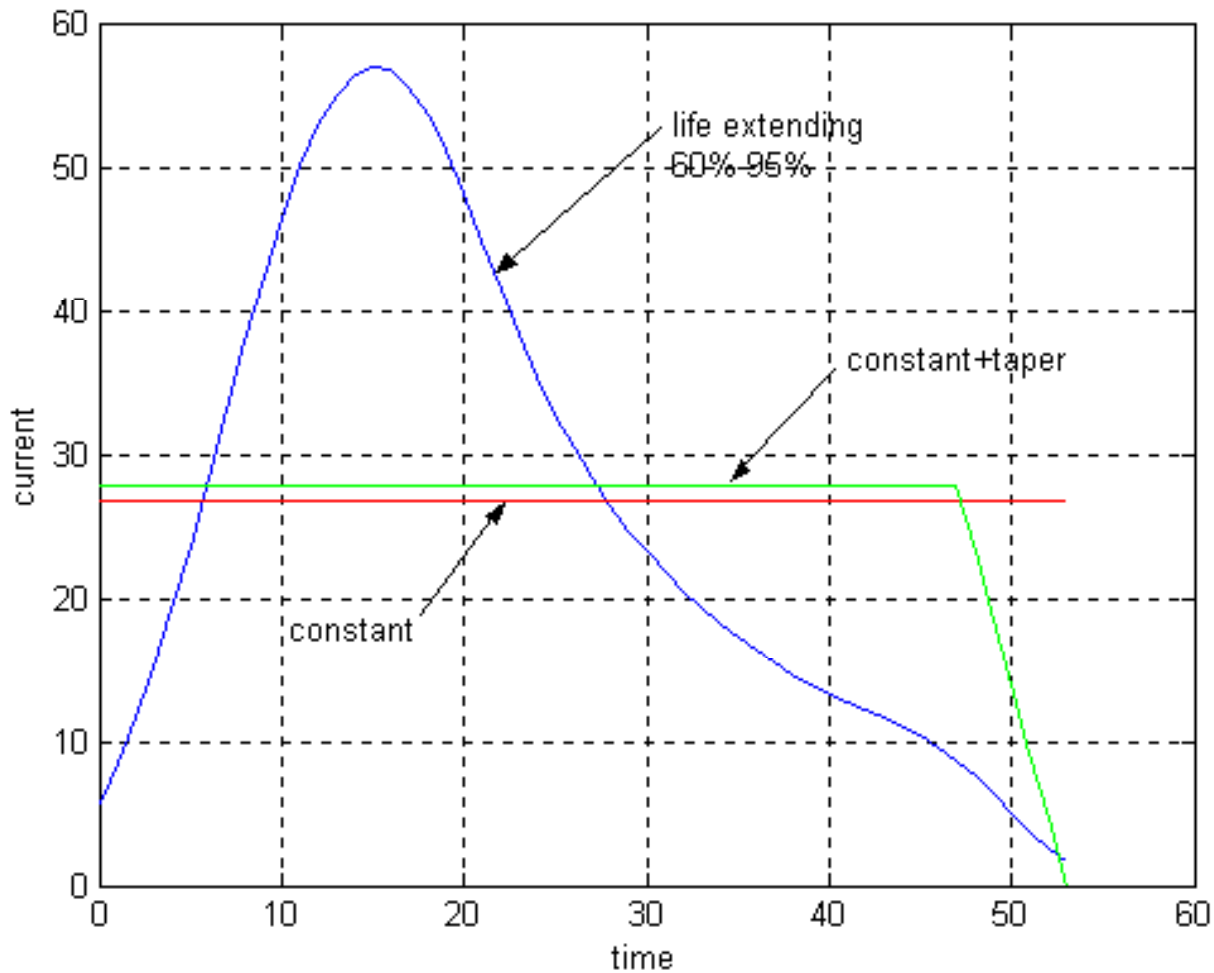
60%-95% recharging, current profile



Comparison of 60%-95% and standard charging methods, current.

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Optimal Charging Summary

	Damage per Cycle	Cycles to Failure	% Life Extension relative to constant current	% Life Extension relative to constant current-plus-taper
Constant-Current Charging	0.000039269	25465	0%	not applicable
Constant + Taper Charging	0.000026316	38000	49.22%	0%
Life Extending Charging 65%-100% Cycle of Figure 5.4 with abs(dv/dt) damage rate	0.000020780	48123	88.98%	26.64%
Life Extending Charging 60%-95% Cycle of Figure 5.5 with abs(dv/dt) damage rate	0.000019535	51190	101.02%	34.71%
Life Extending Charging 65%-100% Cycle of Figure 5.6 with only +dv/dt damage rate	0.000022080	45290	77.85%	19.18%

Comparison of damage for various charging methods, assumes damage only during charge. Percentage life extension is reduced proportionately for damage during discharge.

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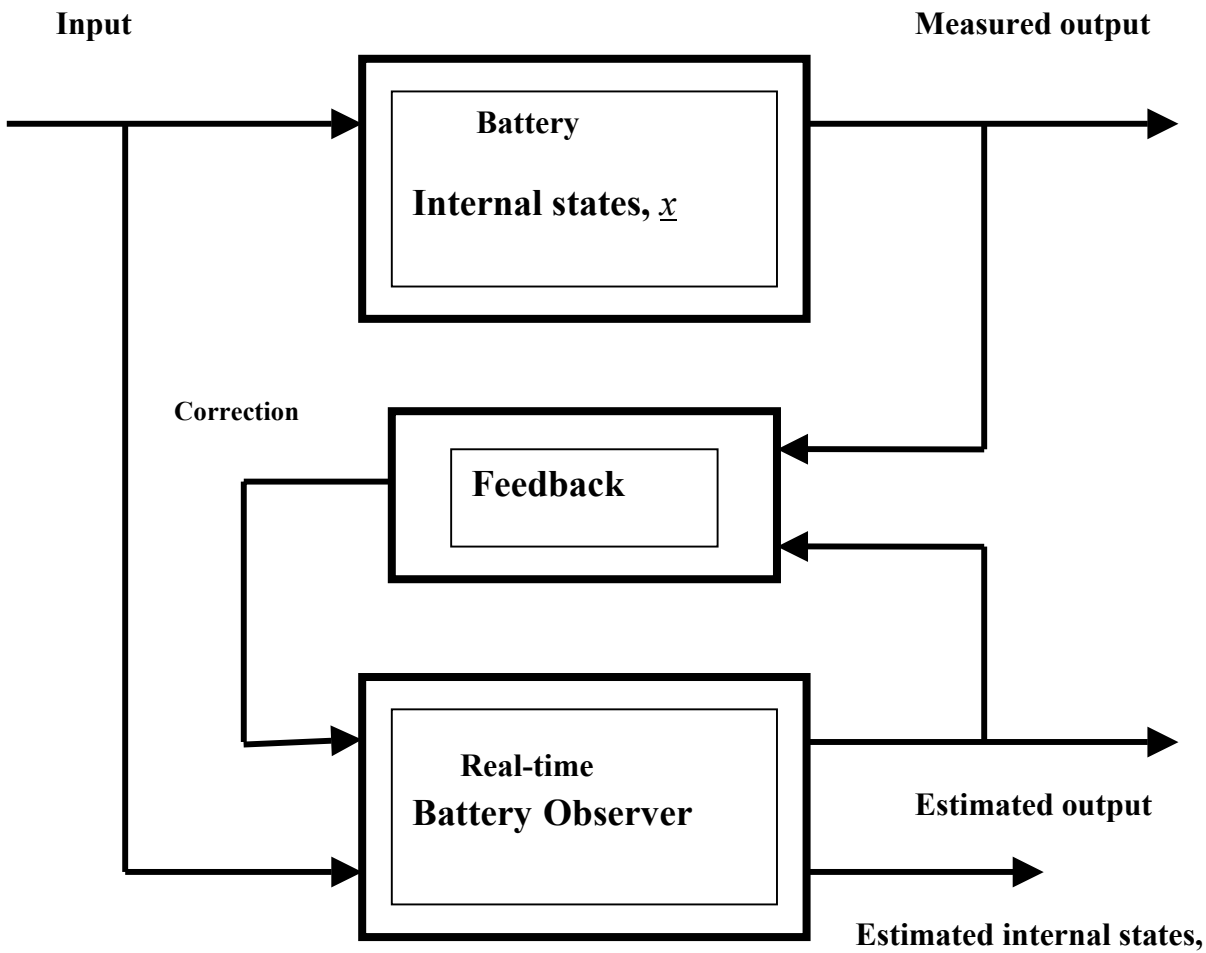
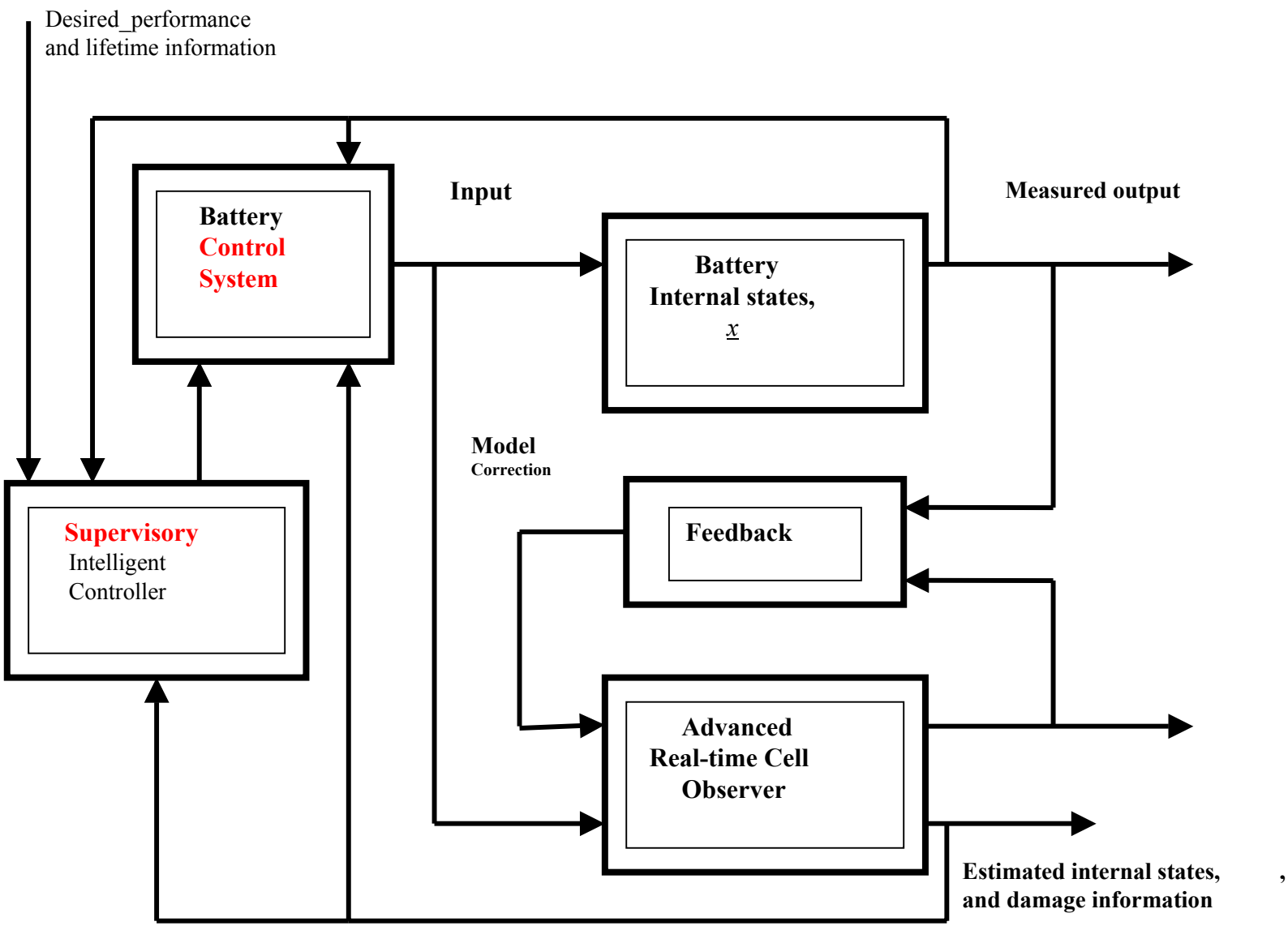
Control Design - Phase II: Tracking



Real-time observer structure.

Electrical and Computer Engineering

Control Design - Phase II: Tracking



Advanced control system using advanced real-time observer.

Electrical and Computer Engineering

Summary

- Control Philosophy
- Essentialized Model Development
- Damage Model
- Optimal Life-Extending Charging
- Tracking Controller
- Real-time Parameter Identification Development
- Application to Lithium based cells

Electrical and Computer Engineering

Nickel-Hydrogen Positive Plaque Comparison

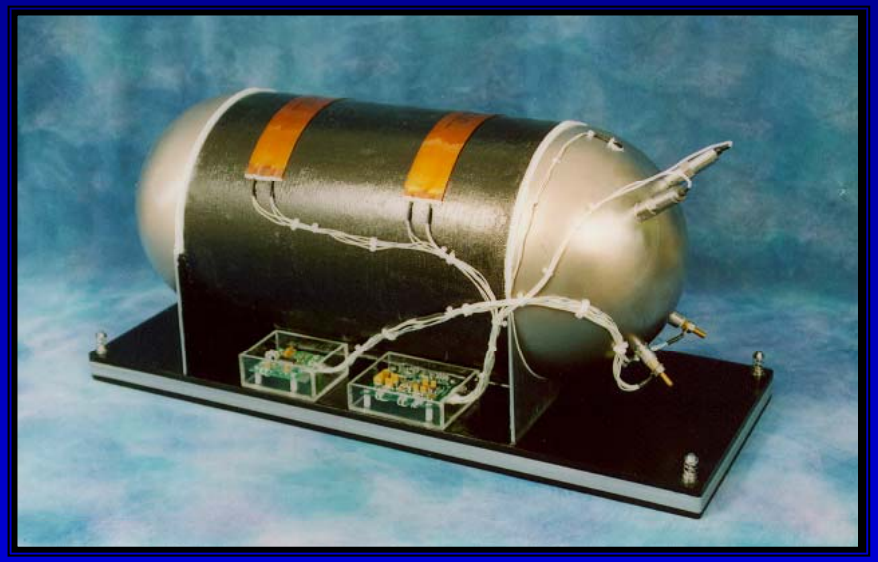
Water Based vs. Alcohol Based Slurry

Eagle-Picher Technologies, LLC

Joplin, Missouri

Outline

- Background
- Water Based Slurry History
- Electrode/Plaque Data
- Cell Data
- Life Test Data
- Flight Data
- Summary



Background

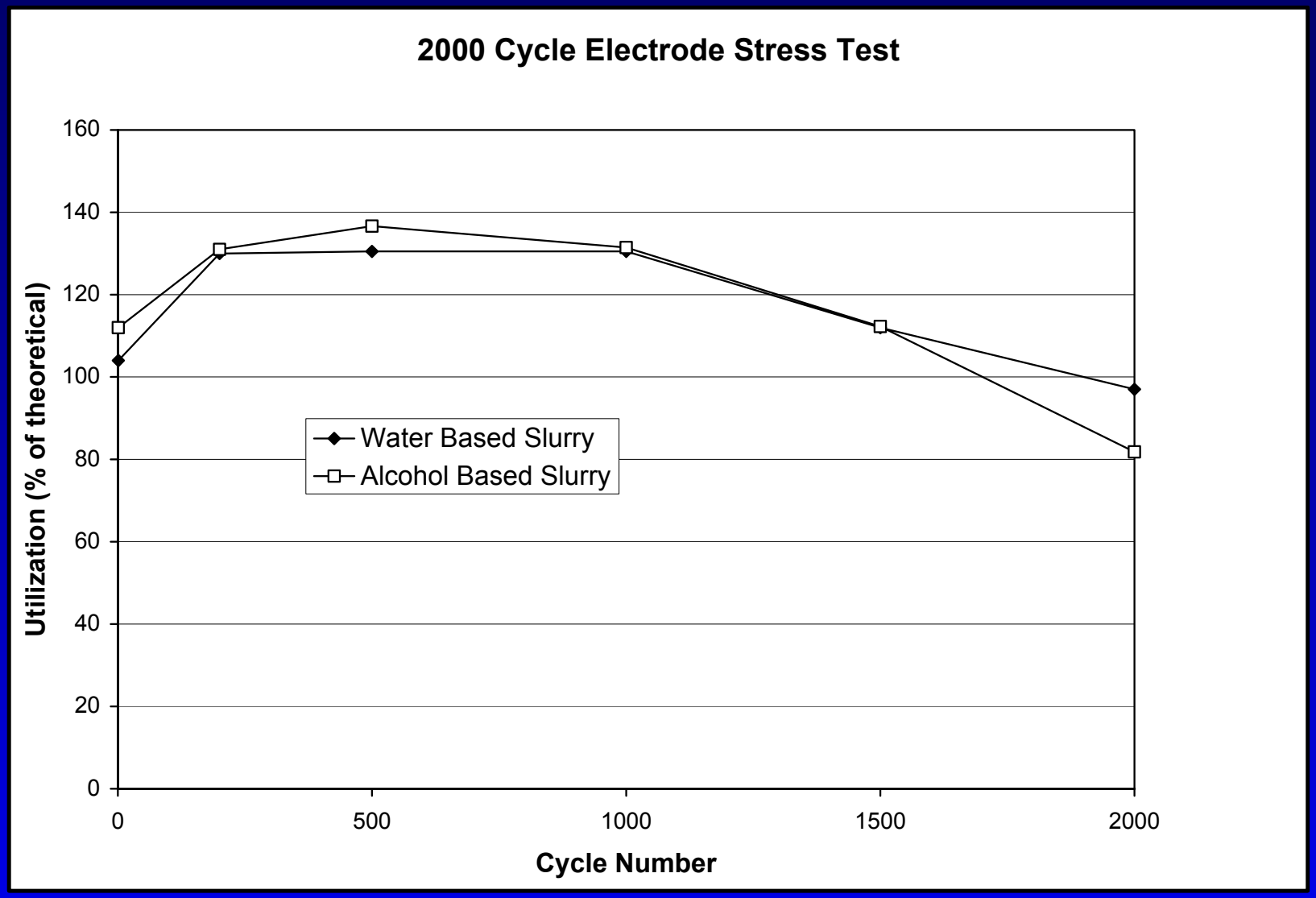
- Alcohol Based Slurry Mfg. at Co. Springs Facility was the Only Plaque used in EPT Ni-H2 Cells.
- Increased Demand for Cells and Batteries Required a Second Plaque Source.
- Production and Use of Water Based Slurry Over the Last 8 Years has Provided a Good Data Base for Comparison with the Alcohol Based "Standard".

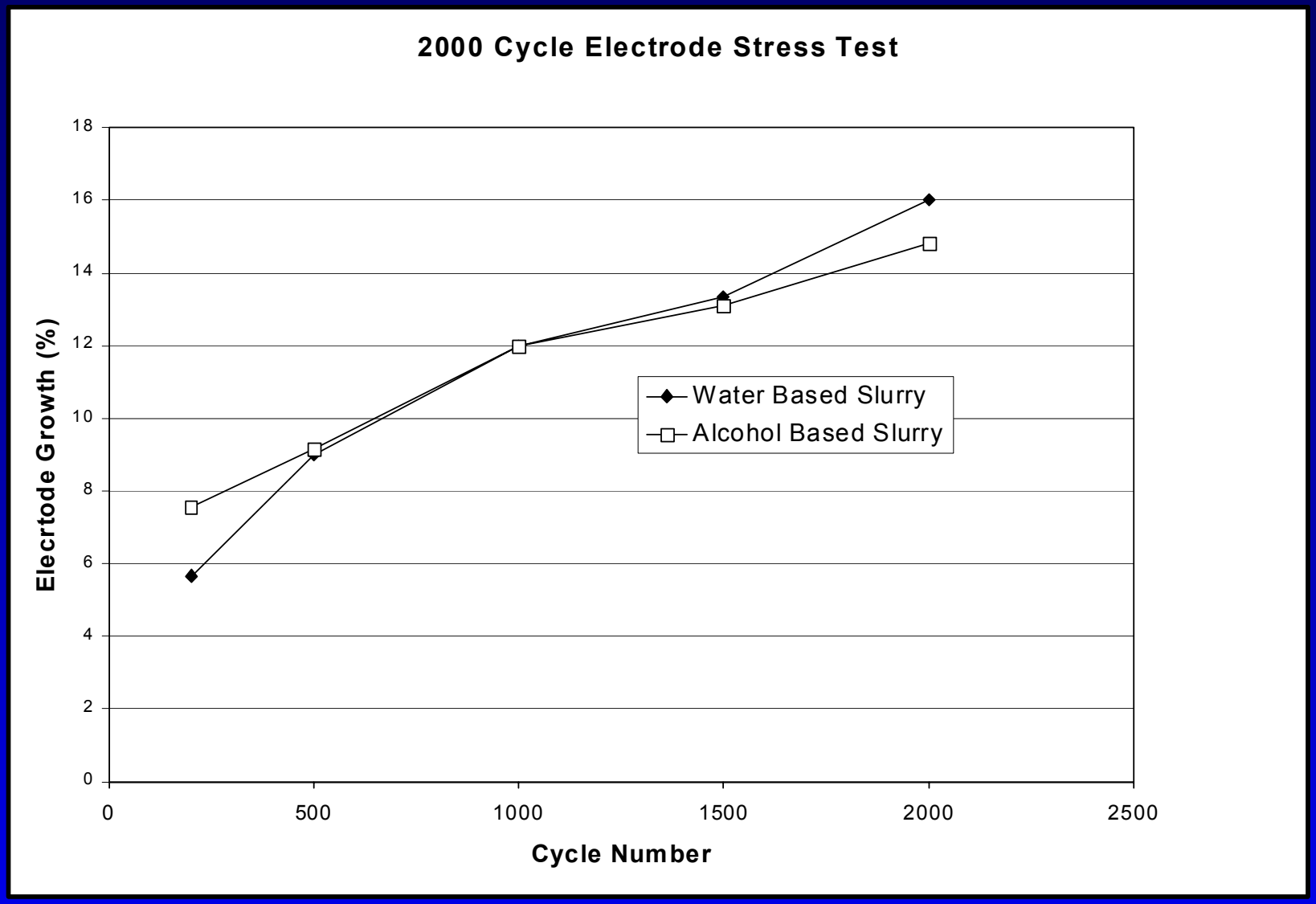
Water Based Slurry History

- Began Water Based Slurry Production in 1990 for Nickel-Iron (Ni-Fe)Automotive Batteries.
- Produced Approximately 75,000 Pieces of 80 mil Thick, 80% Porous, Water Based Slurry Plaque for Ni-Fe Batteries.
- Conversion to Nickel-Hydrogen Production Began in 1994.
- To Date Have Produced Approximately 90,000 Pieces of Water Based Slurry Plaque for Ni-H2 Cells.
- Plaque has Ranged in Thickness from 30 to 35 mil and Porosity from 80% to 84%.

Electrode Stress Test

- Typical Stress Testing of Electrodes Involves 200 Cycles at 10C Charge and Discharge Rates.
- Stress Testing at These Same Rates was Extended to 2000 Cycles.
- Water Based and Alcohol Based Slurry Electrodes Were Periodically Evaluated for:
  - Utilization (Capacity of Electrode)
  - Thickness Growth


2000 Cycle Electrode Stress Test
Utilization (% of theoretical)
160
140
120
100
80
60
40
20
0
0
500
1000
1500
2000
Cycle Number
Water Based Slurry
Alcohol Based Slurry

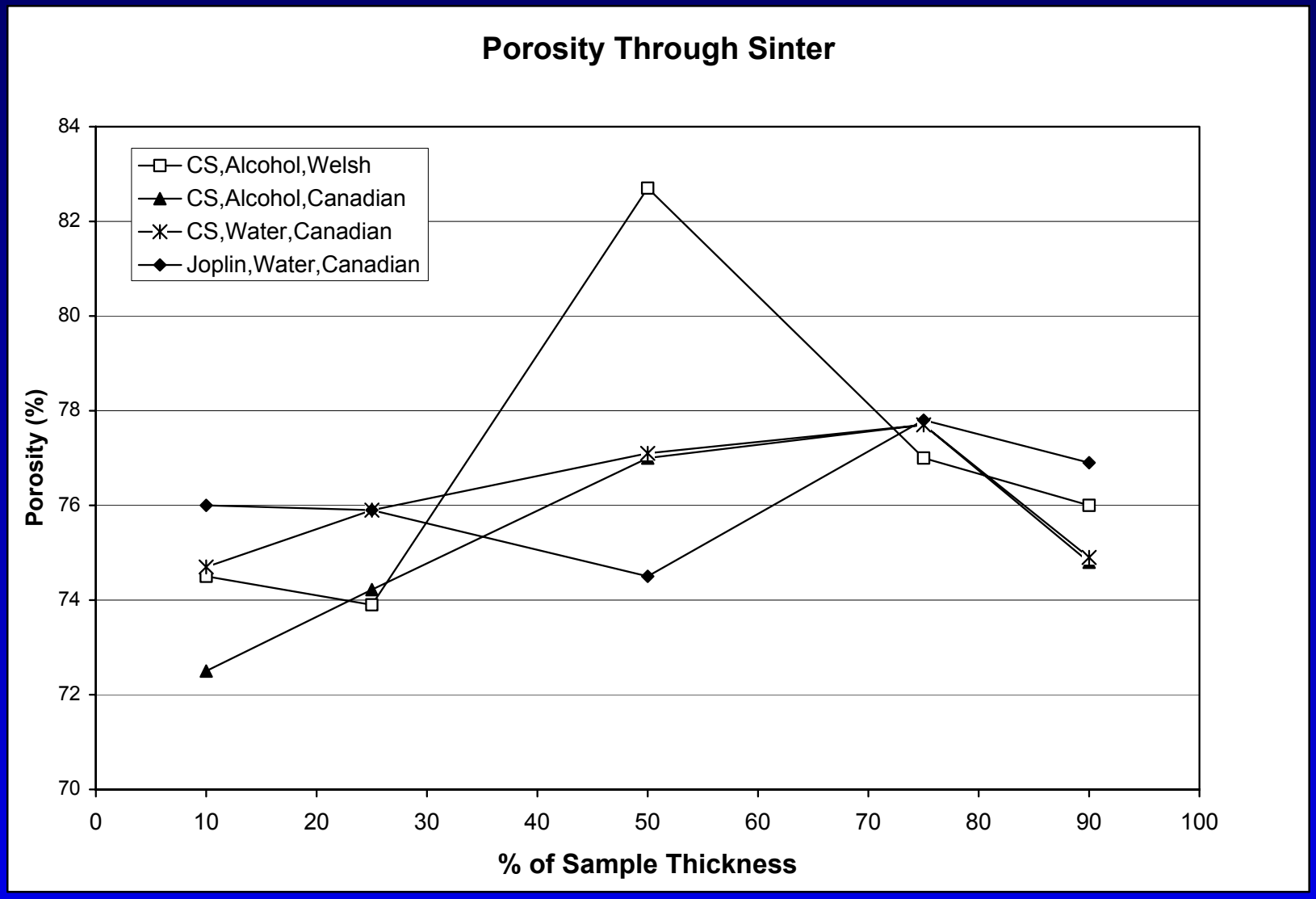

2000 Cycle Electrode Stress Test
Elecrtode Growth (%)
18
16
14
12
10
8
6
4
2
0
0
500
1000
1500
2000
2500
Cycle Number
Water Based Slurry
Alcohol Based Slurry

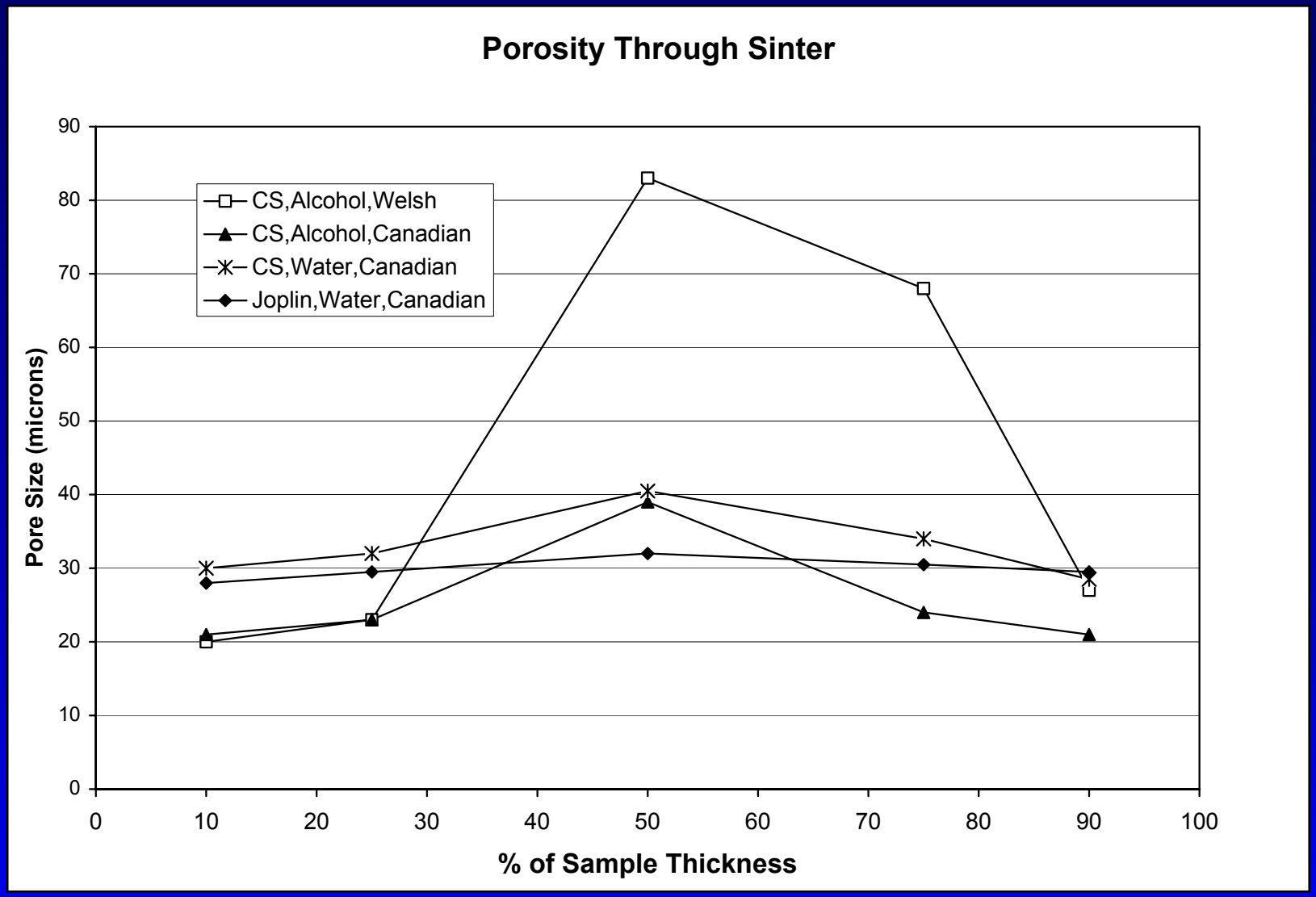
Plaque Porosity Analysis

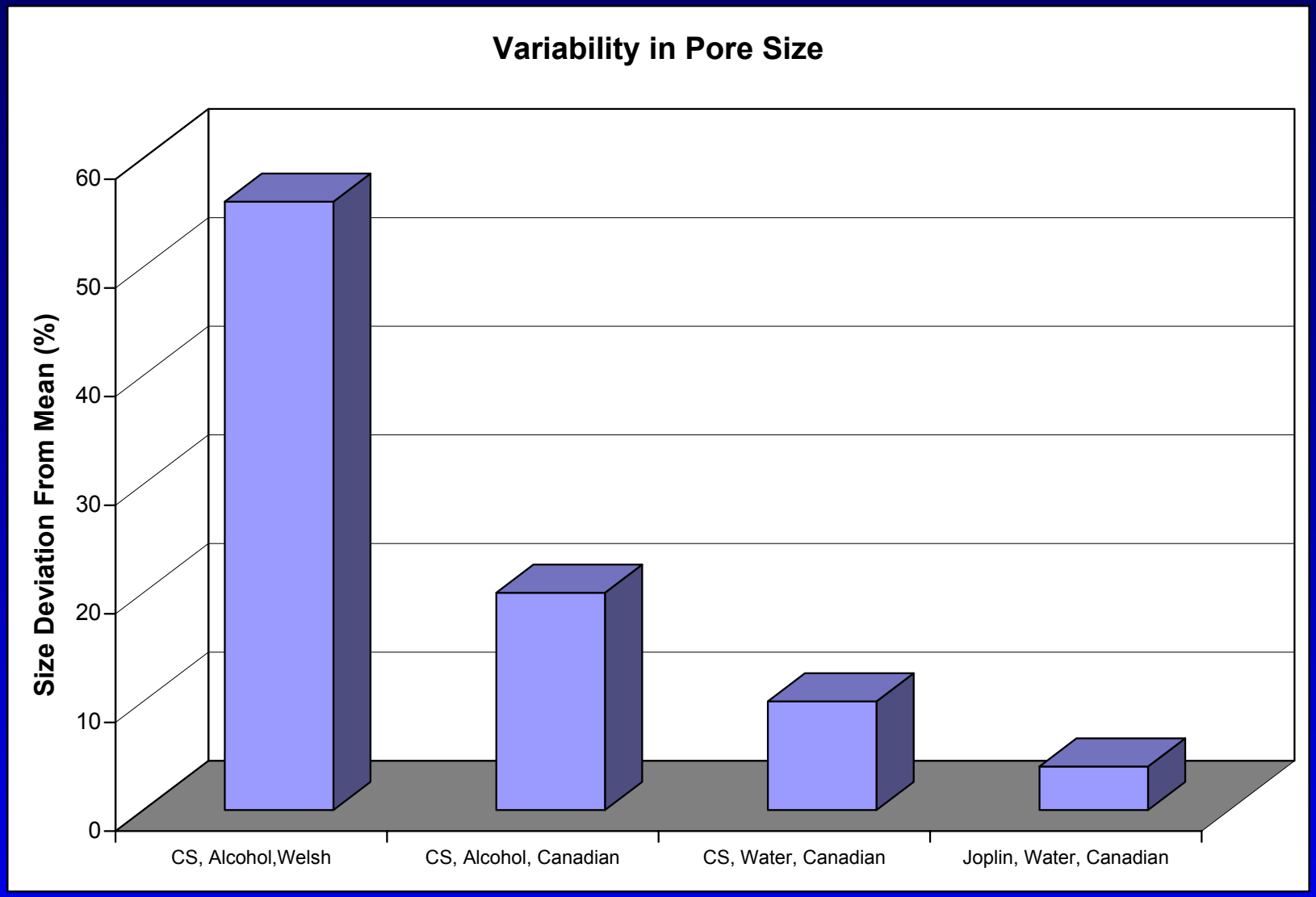
- Porosity Uniformity in Plaque is an Important Characteristic
- Study Conducted by Independent Lab Characterized Porosity of Plaque Samples Using the Scanning Porosity Method.
- Four Samples Analyzed were:
  - Co. Springs, Alcohol Based Slurry, Welsh Powder
  - Co. Springs, Alcohol Based Slurry, Canadian Powder
  - Co. Springs, Water Based Slurry, Canadian Powder
  - Joplin, Water Based Slurry, Canadian Powder

Plaque Porosity Analysis

- Four Properties of Plaque Porosity were Characterized
  - Porosity Variation Through the Sinter Thickness
  - Pore Size Variation Through the Sinter Thickness
  - Pore Uniformity
  - Pore Size Distribution
- In All Categories the RLF Water Based Slurry was Found to be Superior to the Other Samples.

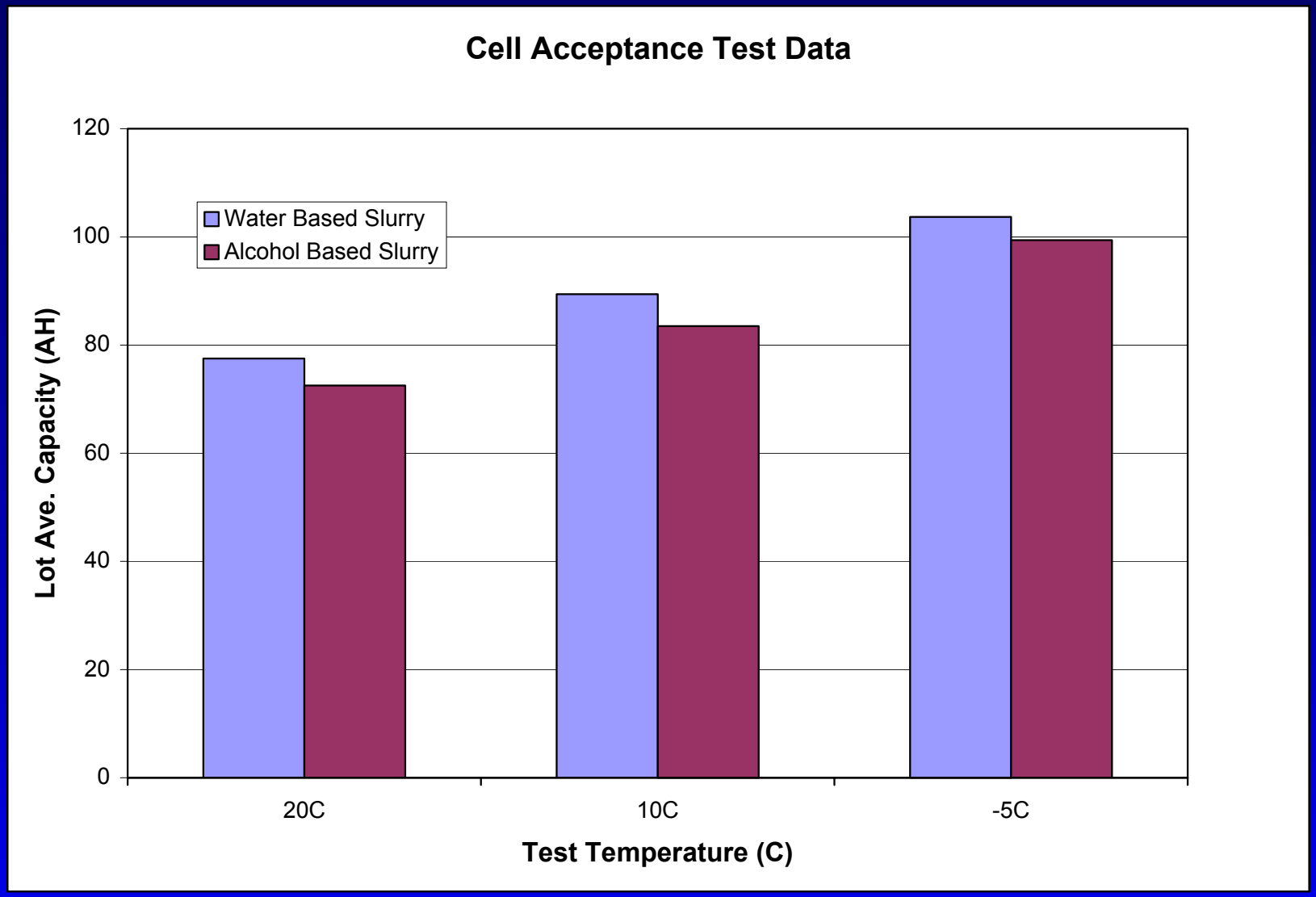

Porosity Through Sinter
CS,Alcohol,Welsh
CS,Alcohol,Canadian
CS,Water,Canadian
Joplin,Water,Canadian
Porosity (%)
84
82
80
78
76
74
72
70
0
10
20
30
40
50
60
70
80
90
100
% of Sample Thickness

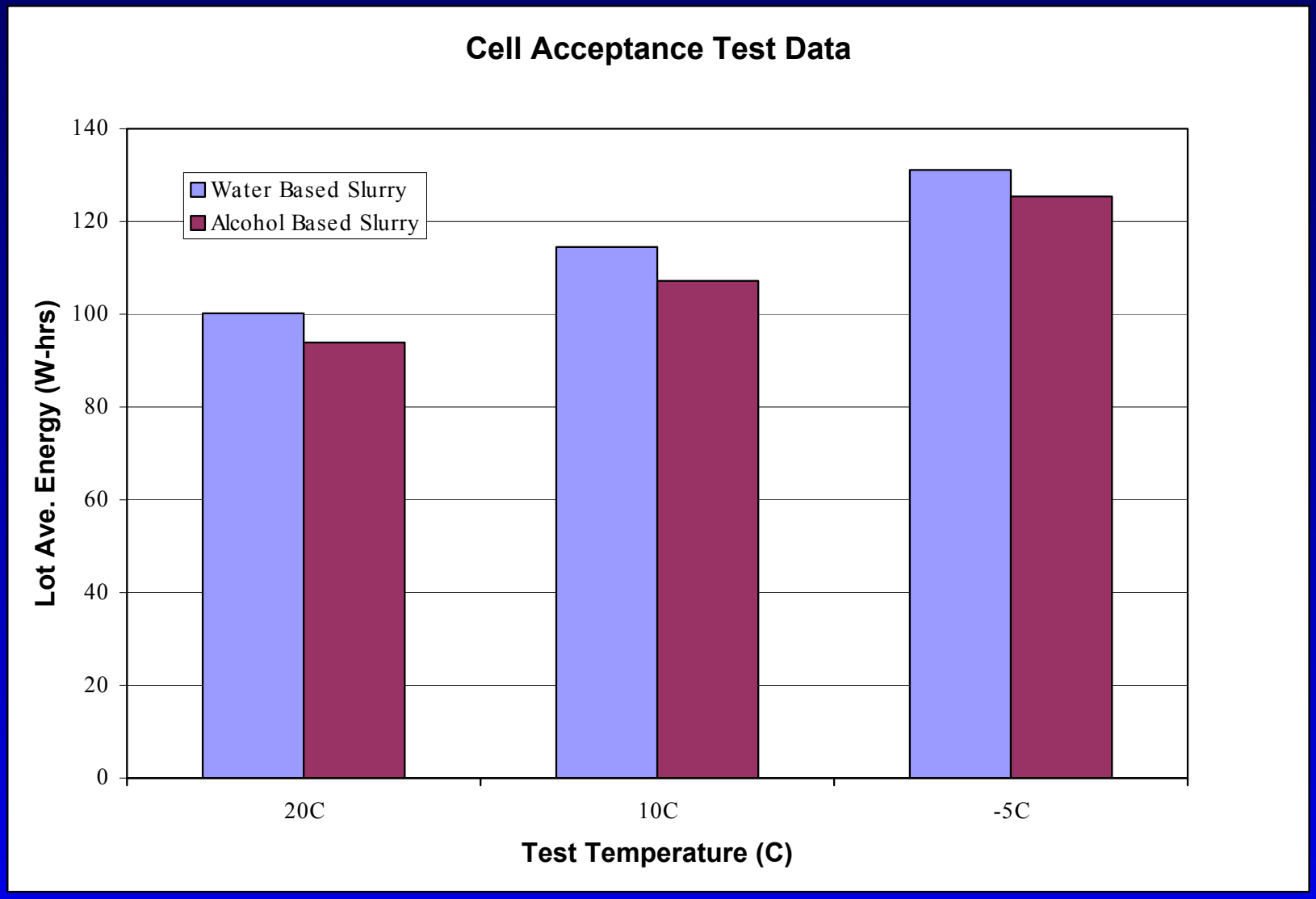

Porosity Through Sinter
CS,Alcohol,Welsh
CS,Alcohol,Canadian
CS,Water,Canadian
Joplin,Water,Canadian
Pore Size (microns)
% of Sample Thickness
0
10
20
30
40
50
60
70
80
90
100

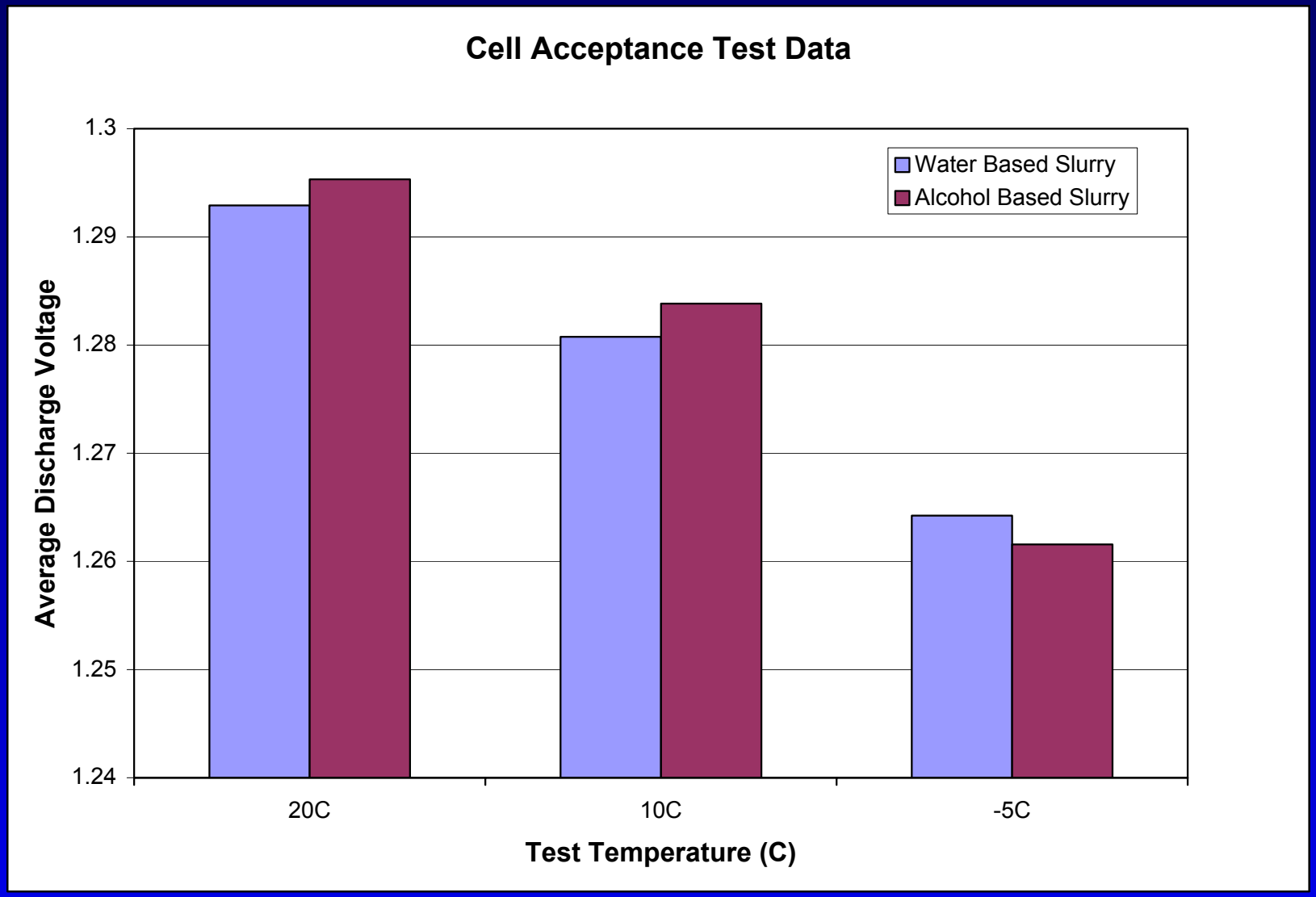

Variability in Pore Size
Size Deviation From Mean (%)
60
50
40
30
20
10
0
CS, Alcohol,Welsh
CS, Alcohol, Canadian
CS, Water, Canadian
Joplin, Water, Canadian

Cell Test Data

- Several Programs have Already Switched from Alcohol to Water Based Slurry.
- The Following Data was Generated From One Such Program.
- This Data Compares the Same Cell Design with Water vs. Alcohol Slurry.
- Each Lot was Accepted for Flight and Built into a Battery.


Cell Acceptance Test Data
Water Based Slurry
Alcohol Based Slurry
Lot Ave. Capacity (AH)
120
100
80
60
40
20
0
20C
10C
-5C
Test Temperature (C)


Cell Acceptance Test Data
Water Based Slurry
Alcohol Based Slurry
Lot Ave. Energy (W-hrs)
140
120
100
80
60
40
20
0
20C
10C
-5C
Test Temperature (C)

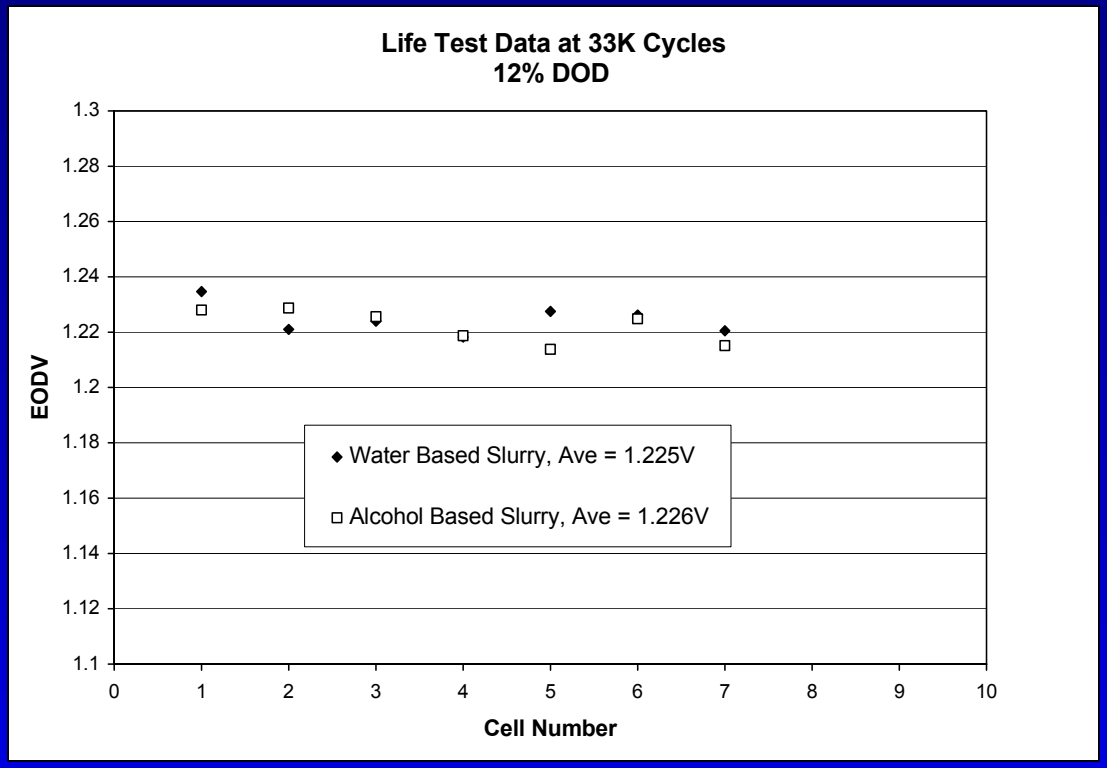

Cell Acceptance Test Data
Average Discharge Voltage
1.3
1.29
1.28
1.27
1.26
1.25
1.24
Water Based Slurry
Alcohol Based Slurry
20C
10C
-5C
Test Temperature (C)

Life Test Data

RNH 56	IPV	56	3.5	0.030	80	31	ACC LEO	70	13,000	1.000	EP-RLF
RNH 56	IPV	56	3.5	0.035	80	31	ACC LEO	70	15,400	1.000	EP-RLF
RNH 56	IPV	56	3.5	0.035	80	26	ACC LEO	70	20,900	1.045	EP-RLF
RNH 56	IPV	56	3.5	0.035	84	26	ACC LEO	70	20,900	1.022	EP-RLF
SAR-10065	SPV	50	10	0.033	82	31	LEO	30	25,000	27.068	EP-RLF
SAR-10065	SPV	50	10	0.033	82	31	LEO	40	33,950	25.500	Customer
SAR-10081	SPV	60	10	0.033	82	31	LEO	25	21,800	27.743	EP-RLF
RNH-90-9	IPV	90	3.5	0.035	80	31	LEO	12	32,000	28.050	EP-SP
RNH-90-9Y	IPV	90	3.5	0.033	82	31	LEO	25-60	3,000	N/A	EP-SP
CRNH 131-1	IPV	131	4.5	0.035	80	31	GEO	83	450	?	Customer
CRNHC 50-63	CPV	50	3.5	0.035	80	31	Mod. LEO	75	1500	?	Customer
RNH 50	IPV	50	3.5	0.030	80	31	LEO	40	26,000	1.222	EP-SPP
RNHC 60	CPV	60	4.5	0.035	80	31	LEO	60	9,000	2.212	EP-SPP
RNHC 100	CPV	100	4.5	0.035	80	31	LEO	60	9,000	2.202	EP-SPP

Life Test Data

- A Life Test at EP is Running a Direct Comparison of Water vs. Alcohol Slurry.
- Currently All Cells are Performing Equally.



Flight Data

BATTERY	PROGRAM NAME	VEHICLE LAUNCH DATE	VEHICLE YEARS IN SPACE	TOTAL OPERATIONAL CELL HRS	NOM CAP	CYCLES/ YEAR	TOTAL CYCLES	DOD	CELL TOTAL
CRNHC-50-63	GE-7	14-Sep-00	1.86	912,043	50	88	164	75%	56
CRNH-100-11	GE-1A	1-Oct-00	1.81	1,333,792	100	88	160	75%	84
CRNH-100-11	N-SAT-110	6-Oct-00	1.80	1,197,644	100	88	158	75%	76
CRNHC50-63	GE-8	19-Dec-00	1.60	783,019	50	88	140	75%	56
CRNH-131-3	ECHOSTAR	21-Feb-02	0.42	287,545	131	88	37	75%	78
CRNH-131-3 &	NEWSKIES 7	16-Apr-02	0.27	200,800	131	120	33	80%	84
SAR-10065	Iridium*	05-May-97	5.22	72,121,733	50	5,256	27,455	31%	2090
SAR-10065	STEX	03-Oct-98	3.81	734,249	50	5,256	20,025	26%	22
SAR-10065	Ikonos	24-Sep-99	2.83	546,281	50	5,256	14,899	26%	22
RNH-64-1	Globalstar**	14-Feb-98	4.44	23,368,818	64	4,874	21,654	20%	832

- * IRIDIUM Data Represents 93 Batteries Launched.
- ** GLOBALSTAR Data Represents 52 Batteries Launched.

Summary

- Electrode Level Test Shows that the Water Based Slurry is Capable of Meeting the Alcohol Based Slurry Performance.
- Flight and Life Test Data Bases Have Been Established for the Water Based Slurry.
- Current Trends Show Similar Performance Between the Two Technologies.

Commercial NiMH Cells in LEO Cycling

Thermal Vacuum Life Test Performed for the Floating Potential Probe (FPP)

By

Eric Darcy, NASA-Johnson Space Center

Brad Strangways, Symmetry Resources, Inc.

For

2002 NASA Aerospace Battery Workshop

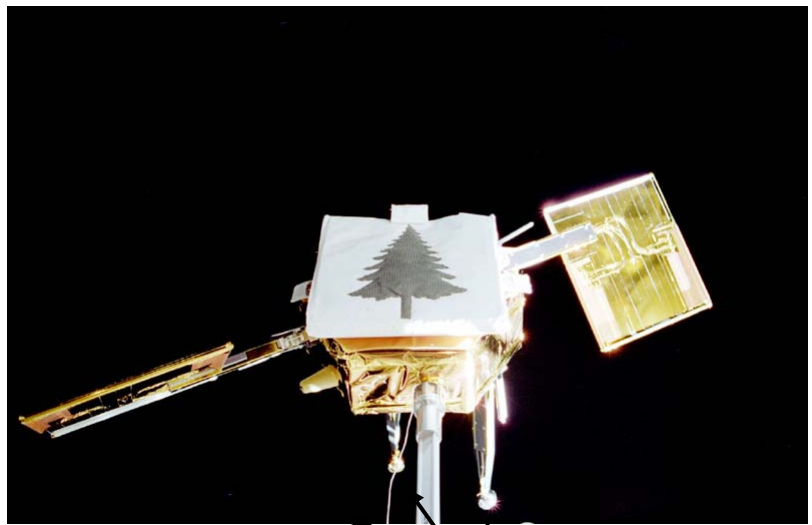
Outline

- Introduction
  - What is the (Floating Potential Probe) FPP?
  - Why was a NiMH battery selected?
  - How well would crimped seal cells performed in long term vacuum exposure?
- Verification Tests
  - Battery description
  - Test Methods
  - Results
  - Main Findings
  - FPP Status

Introduction

- Purpose of FPP
  - Determine the bonding effectiveness of the Plasma Contacting Unit (PCU) to mitigated large electrical fields that could induce a hazardous plasma environment for EVAs (spacewalks) on the international Space Station (ISS)
  - Essentially, it is a fancy voltmeter powered by solar arrays and a 12V battery

Floating Potential Probe



V_{ref} cable

V and T Probes

Introduction (cont.)

- Selected Battery
  - Schedule pressure precluded any battery development
  - EVA Helmet Interchangeable Portable (EHIP) light battery was best match
  - 3P-5S array of 4/3A NiMH cells (3.5Ah nameplate) from Toshiba and Sanyo
  - Using only two 5S strings in series to get 12V output, leaving the middle string unused

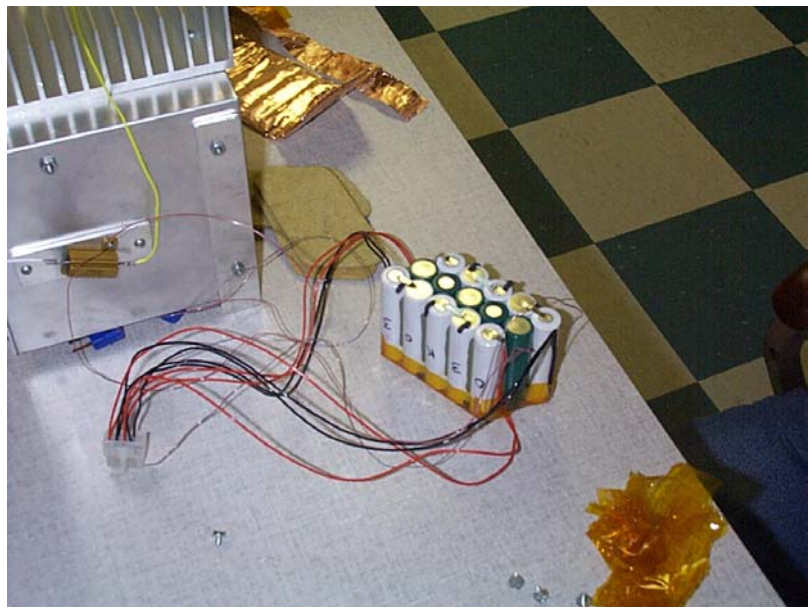
EVA Helmet Interchangeable Portable (EHIP)
Battery Brick Assembly
SEG39130224

Introduction (cont.)

- Problem
  - FPP needed a battery with 2-year LEO cycle
  - That's >17,520 hours of vacuum exposure
  - EHIP light battery was certified for 260 spacewalks (or 1820 hours of vacuum) over 5 years
  - Would the crimp seal be compatible with vacuum LEO cycling?
  - Seal must hold hydrogen partial pressure and some water vapor pressure

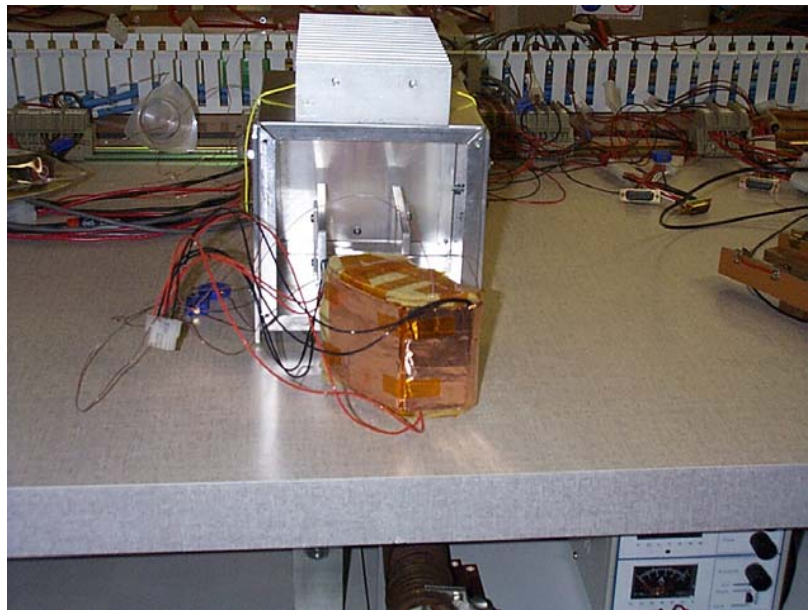
Verification Test Program

- Performed by Symmetry Resources, Inc., in Arab, AL
- Cell Acceptance
  - Cells were spares from EHIP flight lots that had passed all acceptance tests
  - Pre-Test - 2 charge/discharge cycles for capacity and resistance measurements, phenolphthalein leak test, and weighing
- Test Battery Assembly
  - 2 prototype EHIP light battery bricks assembled
  - In each battery, one string of Toshiba and one string of Sanyo
  - Bricks insulated in Durrette felt



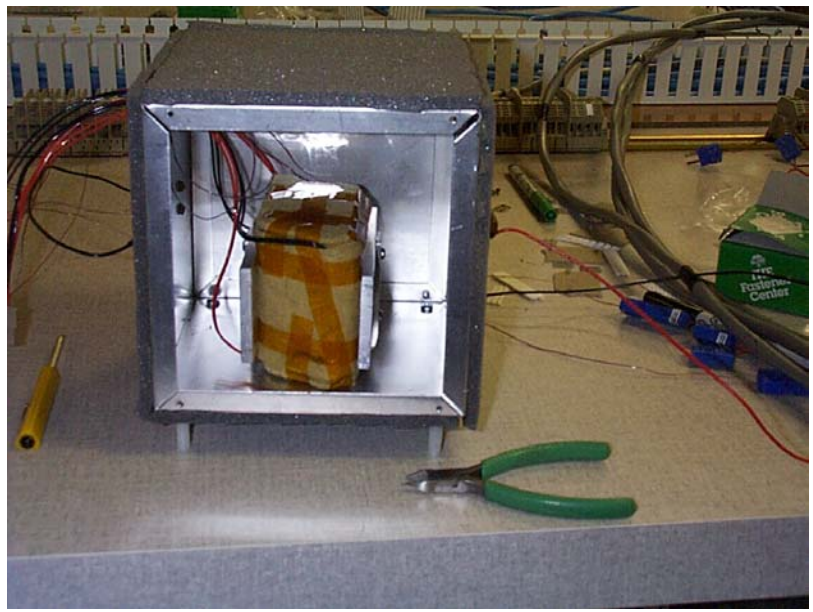
Test Method

- Battery Assembly
  - No EHIP battery housing available
  - Test bricks were modified to include copper tape to encapsulate the felt and provide better thermal conduction after 66 cycles
  - Same configuration for both batteries
  - One thermocouple and one voltage sense per string

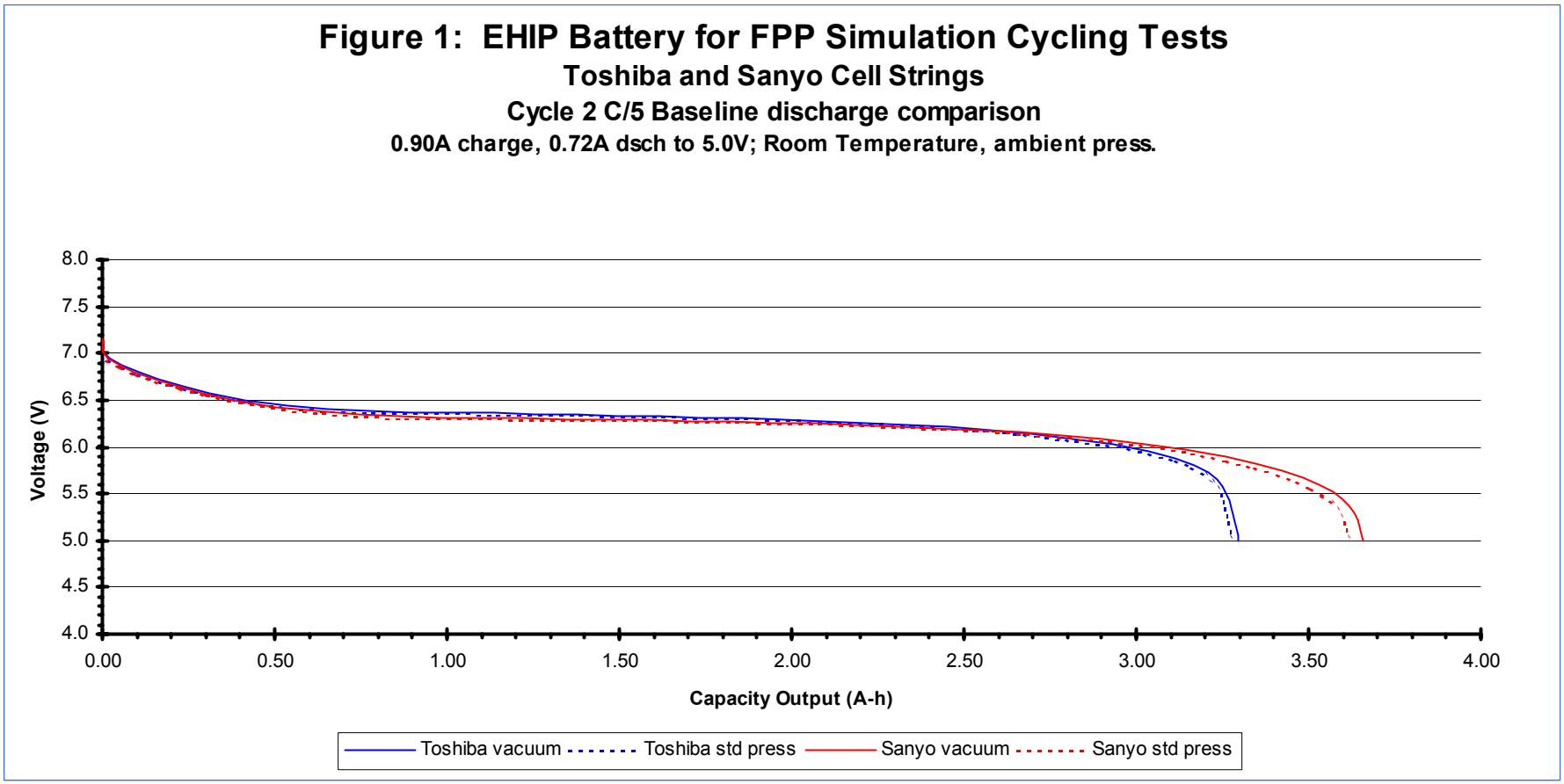


Test Method (cont.)

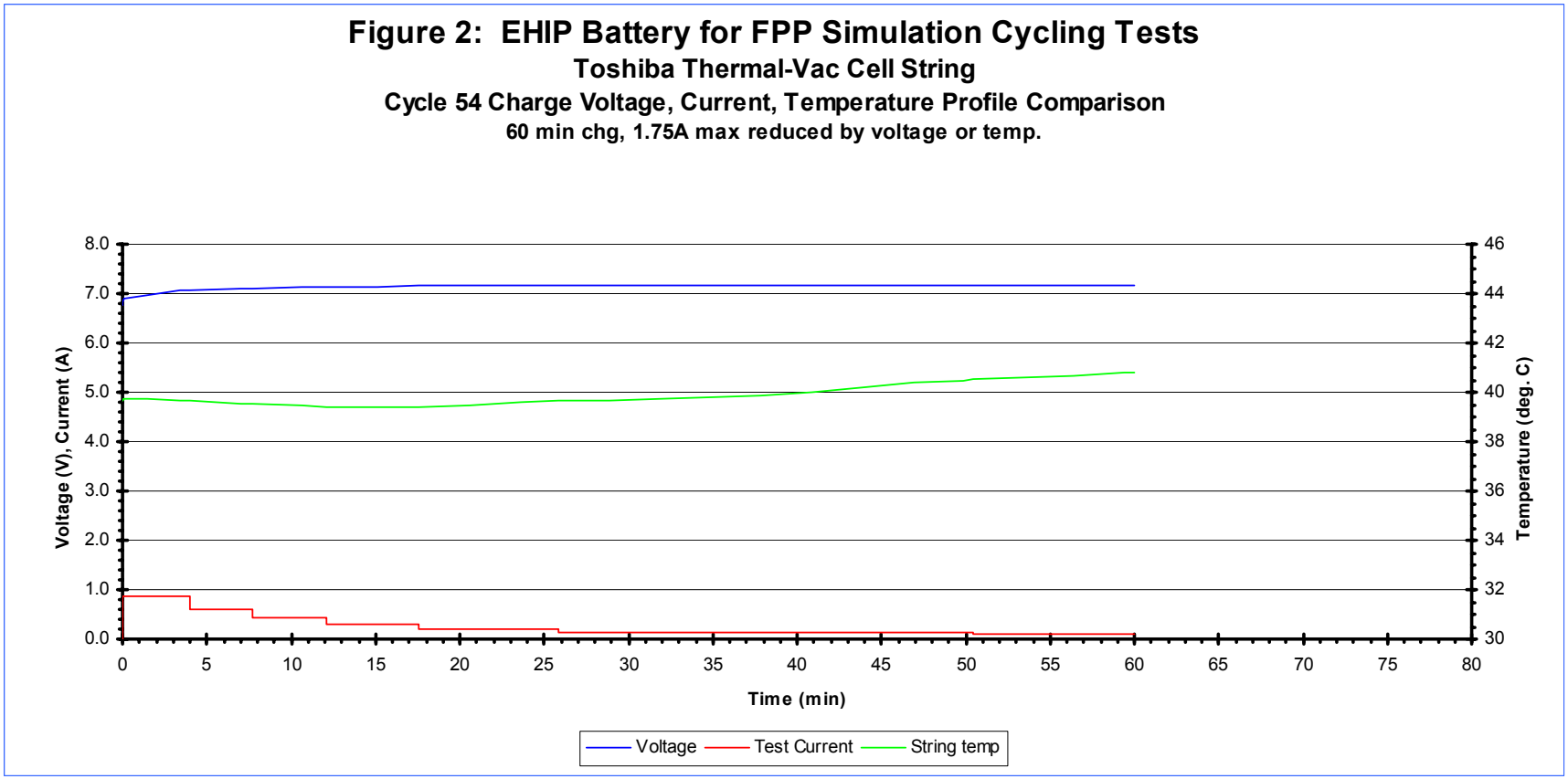
- Batt#1 in a thermal chamber set at 32°C
- Batt#2 in a thermal vacuum chamber set at 32°C, < 0.5 torr
- Each string controlled independently w/ a Maccor system
  - Discharge: 2.125W for 30 min
  - 60 min Charge: stepwise simulation of FPP charge algorithm
    - 1.75A start with reductions based on OCV and temperature
    - Taper from 1.75A at 6.5V to 0.58A at 6.8V then to 0.04A at 7.2V
    - Taper from 1.75A at 38°C to 0A at 45°C



Cycle 2 Capacity Baseline



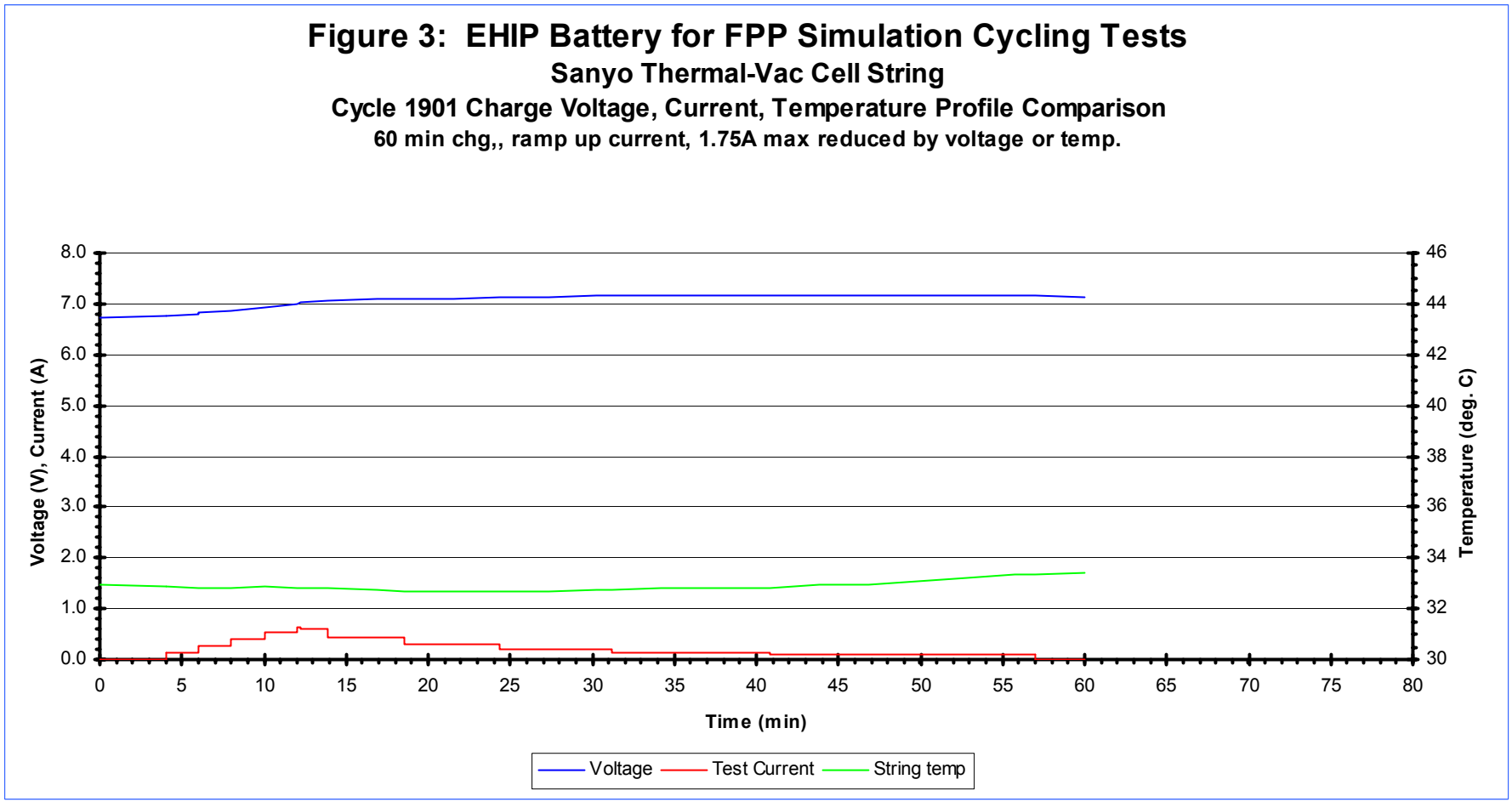
Initial Thermal Profile: Getting too hot!



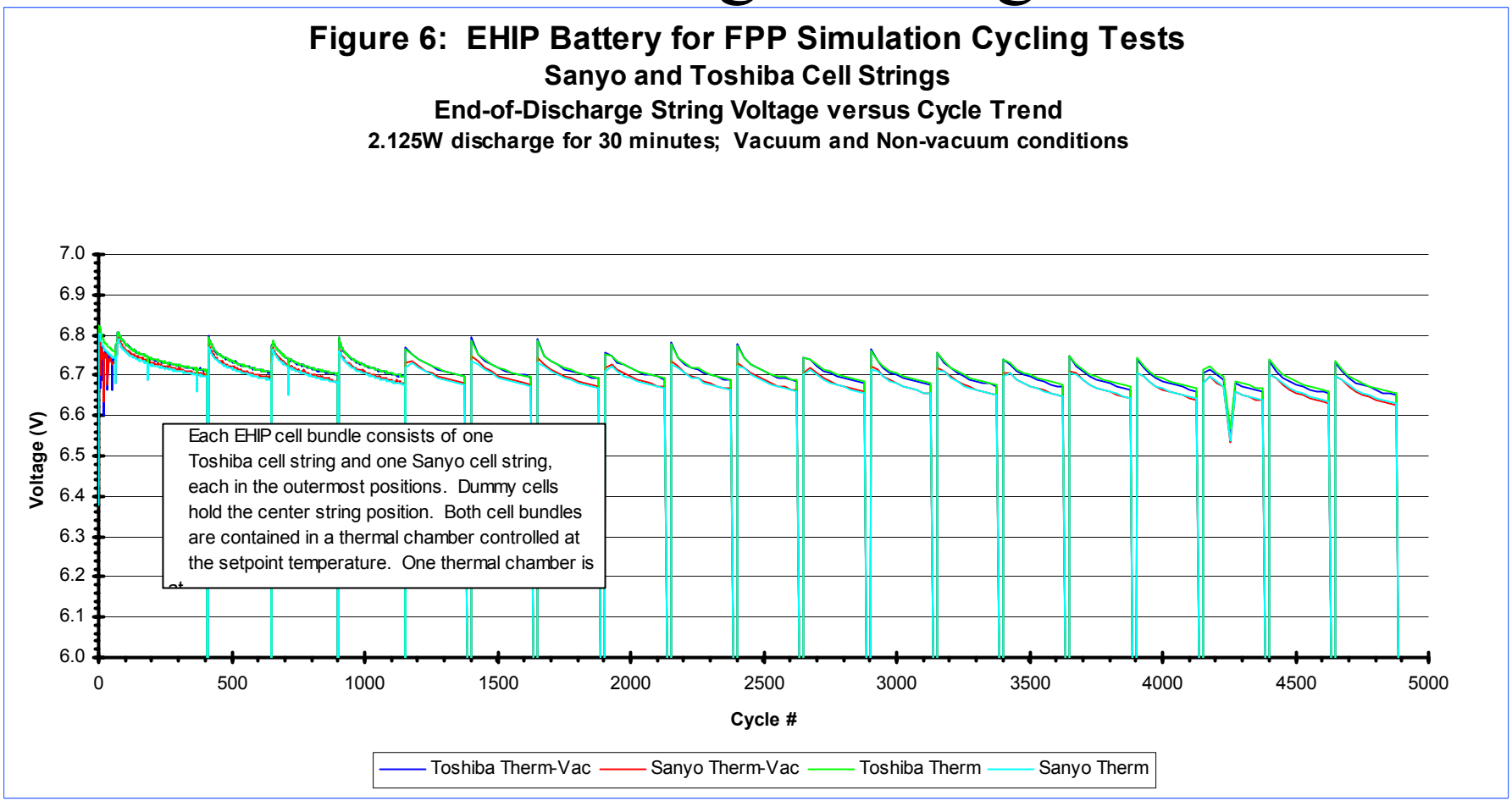
Test Method (cont.)

- First 66 cycles results
  - Batteries operating temperature drifted to > 40 °C
- Modifications to better simulate actual FPP
  - Changed initial temperature setting from 32 to 30°C
  - Add a delay followed by a gradual current increase at beginning of charge
  - Made adjustments to voltage based current limits to compensate for increased wire resistance present in actual FPP
- Modifications to the test article
  - Removed the Durette felt on the cylindrical side of the cells
  - Encapsulated the felt with copper tape

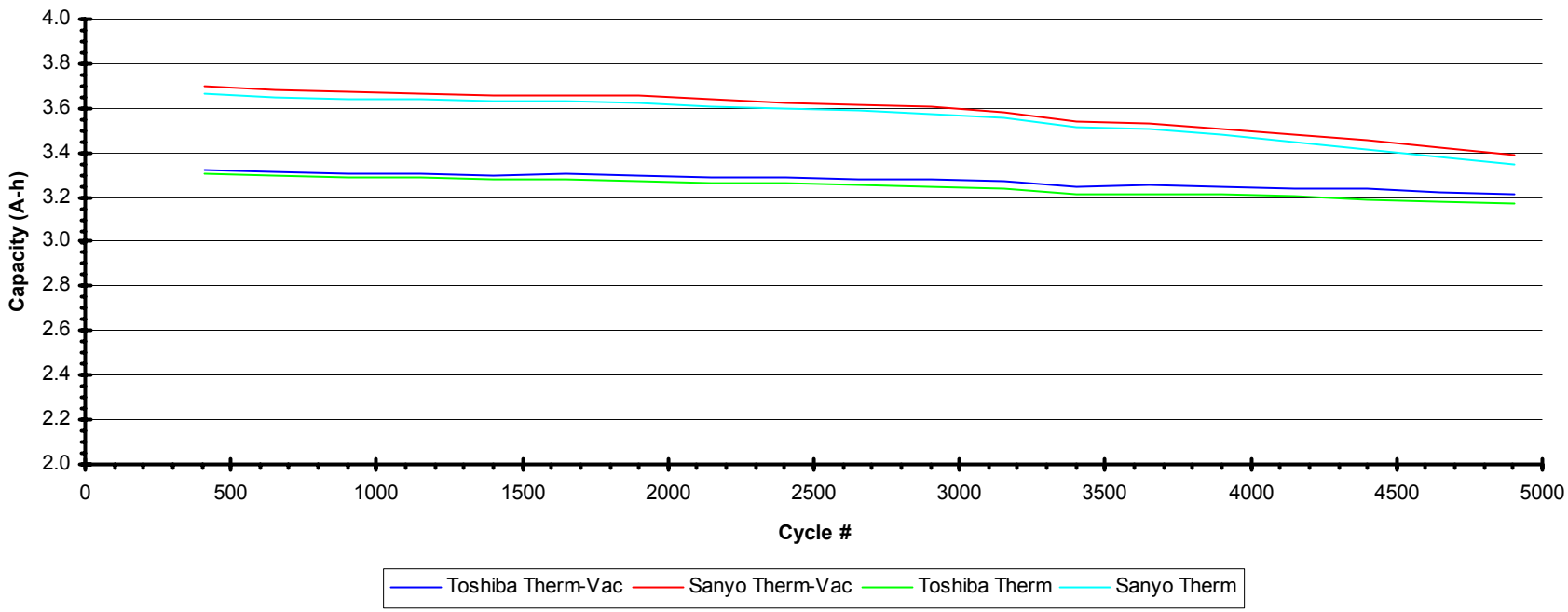
After the Modifications



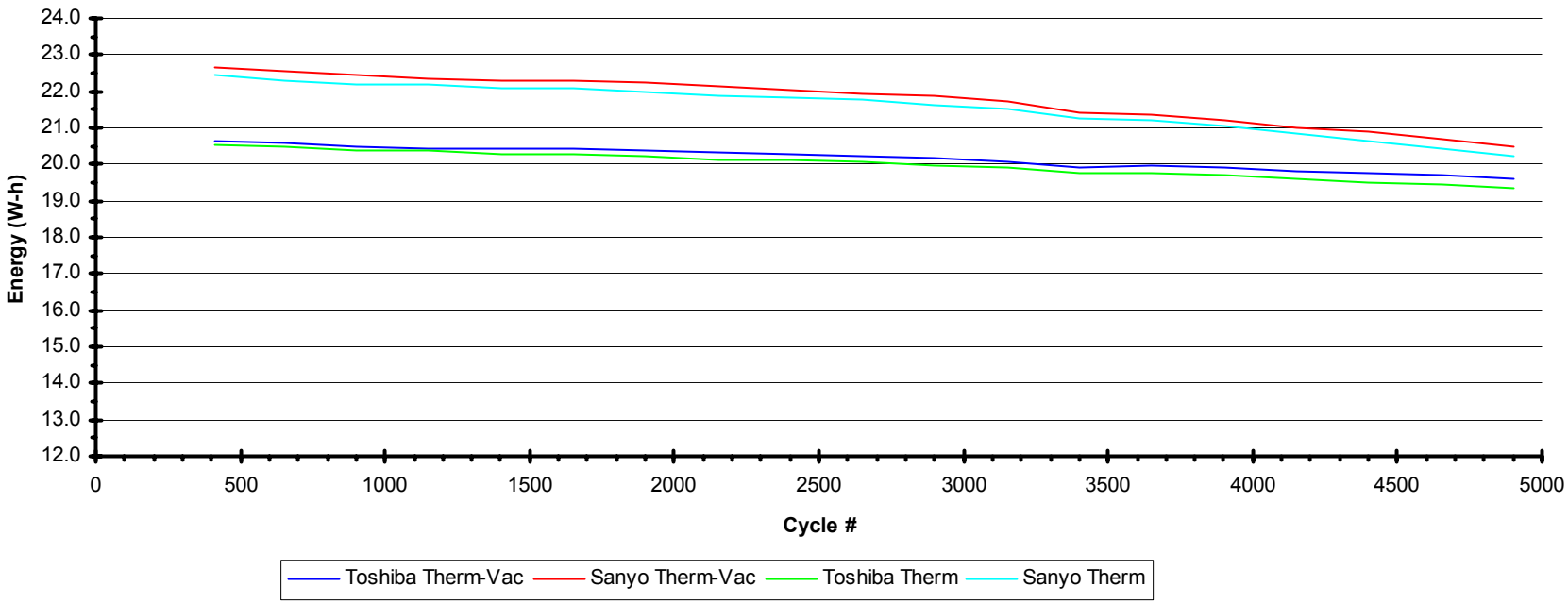
End of Discharge Voltage Trend



Test Results



Test Results (cont.)



Test Results after 10 months

- Capacity and internal resistance degradation occurred
  - Sanyo
    - 85% increase in internal resistance
    - 9% loss in capacity
  - Toshiba
    - 75% increase in internal resistance
    - 2% loss in capacity
- Very little difference between vacuum & ambient P
  - Post test mass loss are very low
    - Sanyo: <23 mg/cell (Vac) vs < 22 mg (1 atm)
    - Toshiba: <14 mg/cell (Vac) vs < 6 mg (1 atm)
  - Capacity and resistance changes are independent of pressure
    - Losses and increases were due to the aggressive charge and warm conditions

FPP Status

- FPP was launch in Dec 2000
- It work for some months, then LOS occurred
- About several months later, its communication was re-established
  - It provided excellent data
  - the PCU is doing its job
  - the electrical fields are less of a concern than anticipated
- A later, we lost signal again
- Funding was discontinued after 10 months of testing because program decided to no longer attempt to talk to it
- FPP is still up there and it may be brought back on a summer 2003 mission

Nickel-Hydrogen IPV LEO Life Tests at NSWC/Crane

Jean Marie Baer and Warren Hwang

The 2002 NASA Aerospace Battery Workshop

Marshall Space Flight Center

Electronics & Photonics Laboratory
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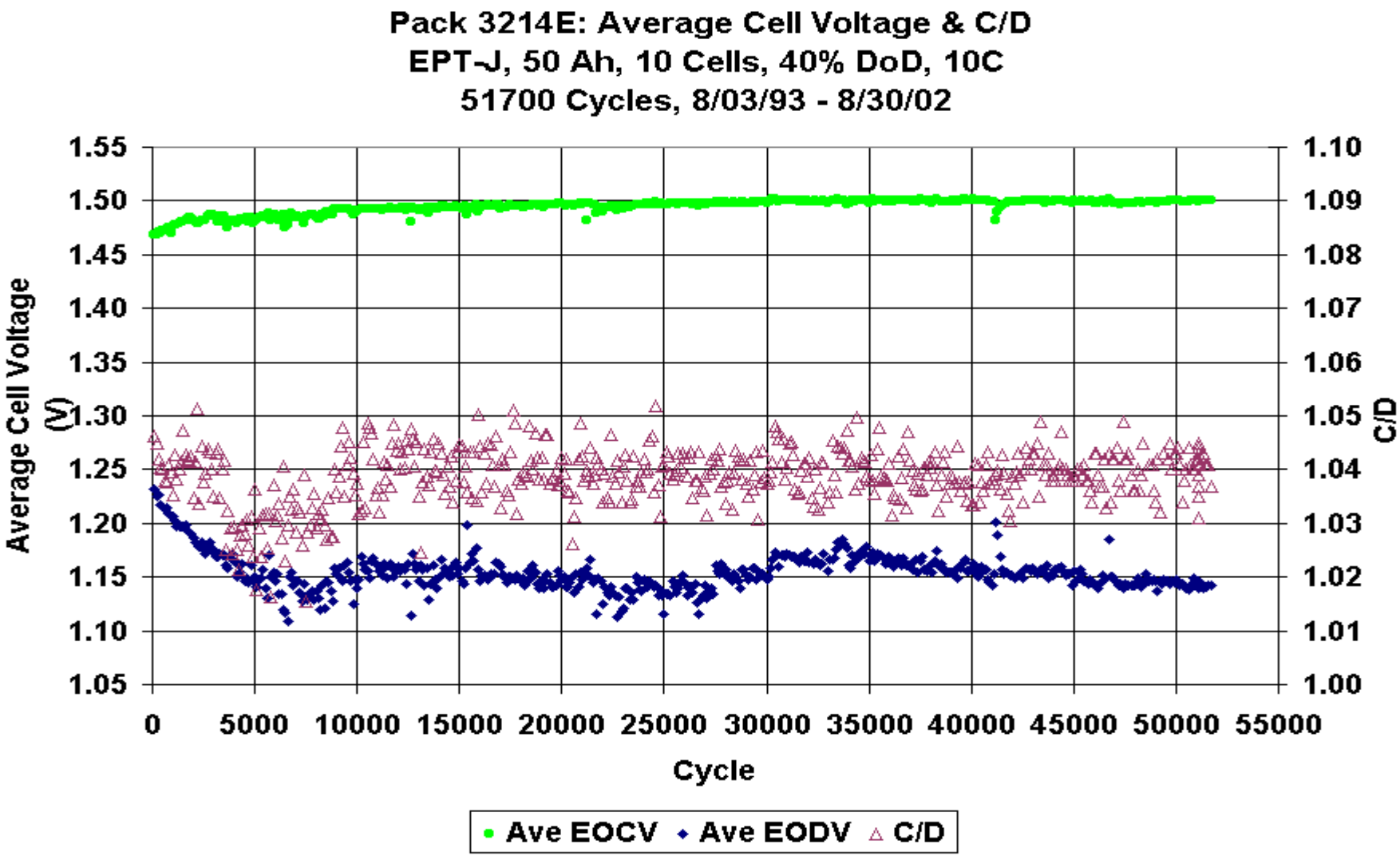
NiH_2 Cell Life Tests

- **NiH_2 Air Force qualification battery cells**
  - **Assembled into seven IPV packs and LEO life tested at the Naval Surface Warfare Center, Crane Division**
    - **A typical life cycle simulates a 90-min orbit, using a 2-step constant current charge control.**
    - **Testing duration ranges from approximately 51,000 to 80,000 cycles**
    - **Life tests provide valuable information in understanding the long-term distribution of failures of various cell designs.**

NiH_2 Cell Life Tests

- **Pack 3214E: 3.5" 50-Ah cell (EPT-J), 26% KOH, back-to-back stack design, dual-layer Zircar, 10-cell pack, 10^0 C, 40% DoD, average C/D = 1.039**
  - **1993 test start-up; 51700 cycles as of 8/30/02. Cells 1 and 2 were removed from test after cycle 38587 and sent to The Aerospace Corporation to study capacity walk-down and permanent capacity loss.**
  - **No cell failures to-date**

NiH_2 IPV Pack



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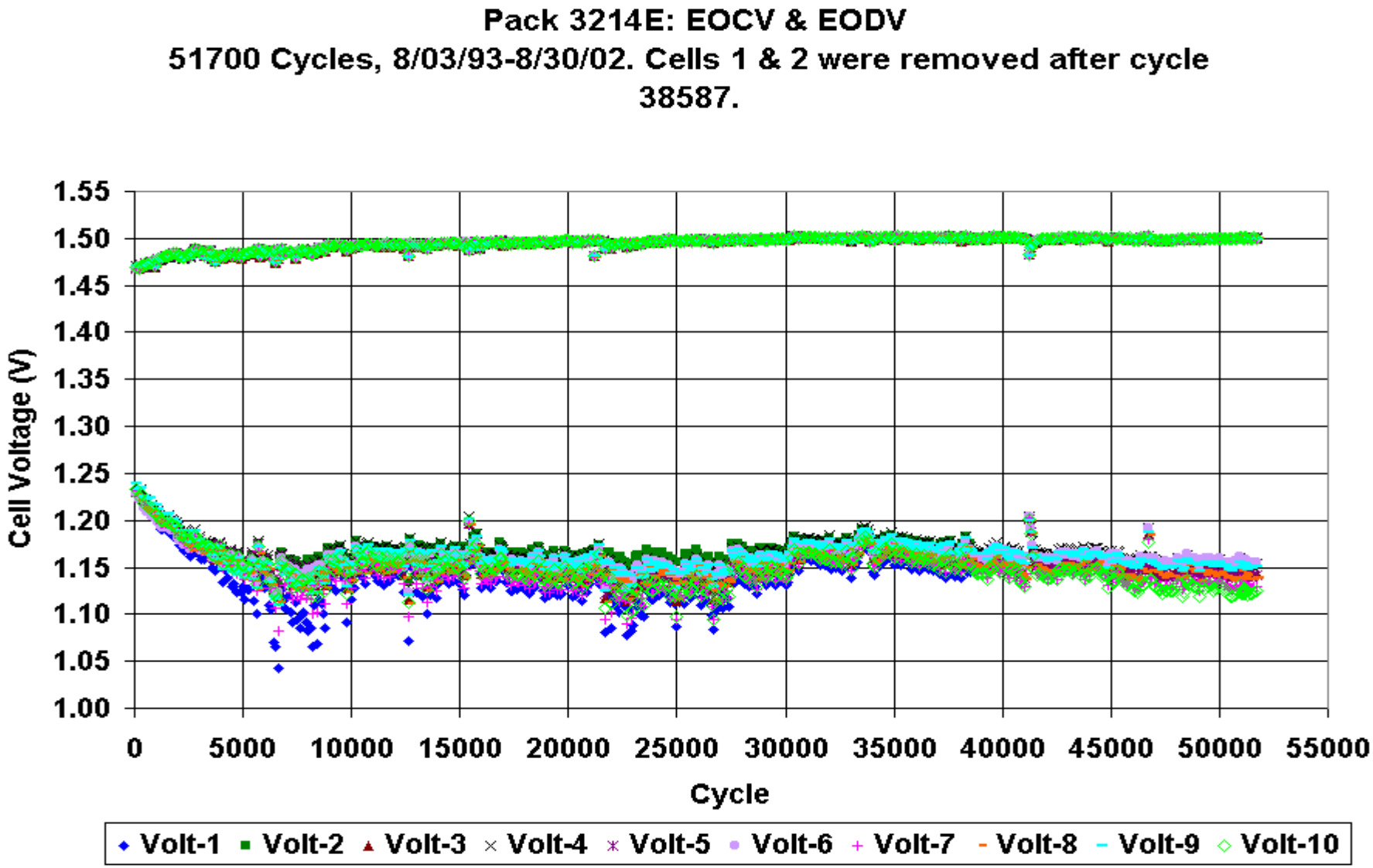
NiH_2 IPV Pack



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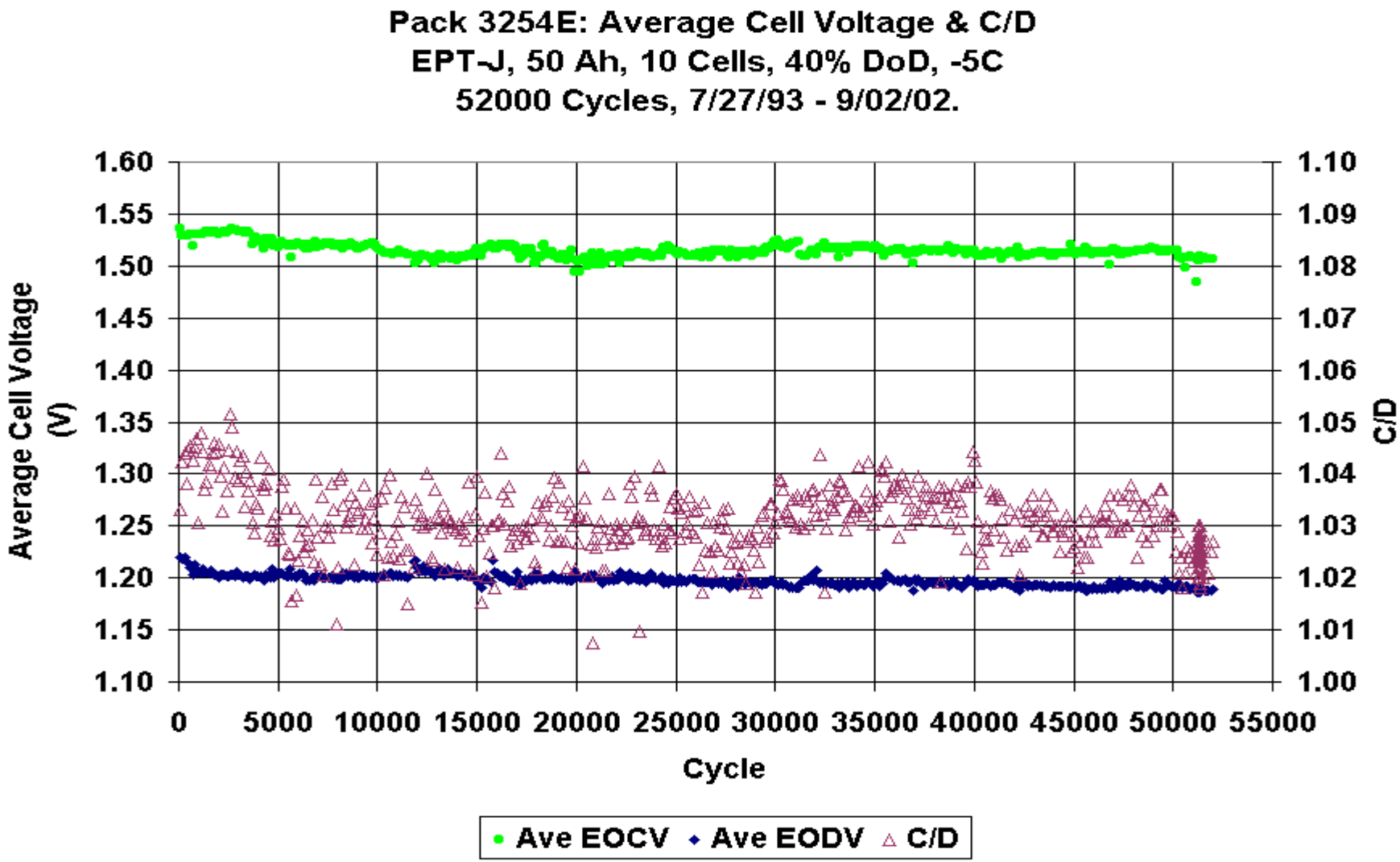
NiH_2 Cell Life Tests

- **Pack 3254E: 3.5" 50-Ah cell (EPT-J), 26% KOH, back-to-back stack design, dual-layer Zircar, 10-cell pack, -5^0 C, 40% DoD, average C/D = 1.031**
  - **1993 test start-up; 52000 cycles as of 9/2/02. Cells 1 and 2 were removed after cycle 39045 for the same Aerospace study as cited with pack 3214E.**
  - **No cell failures to-date.**

NiH_2 IPV Pack



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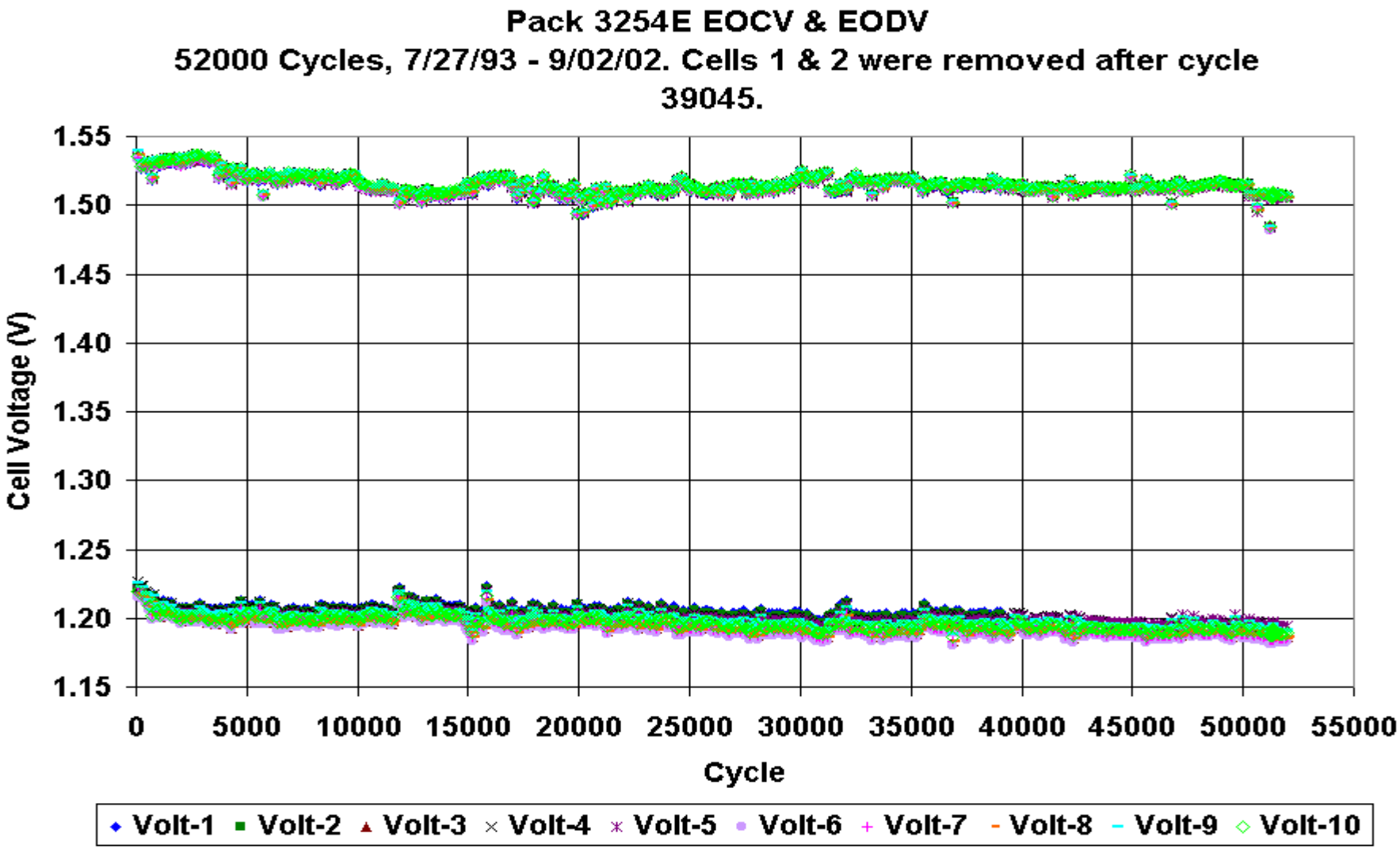
NiH_2 IPV Pack



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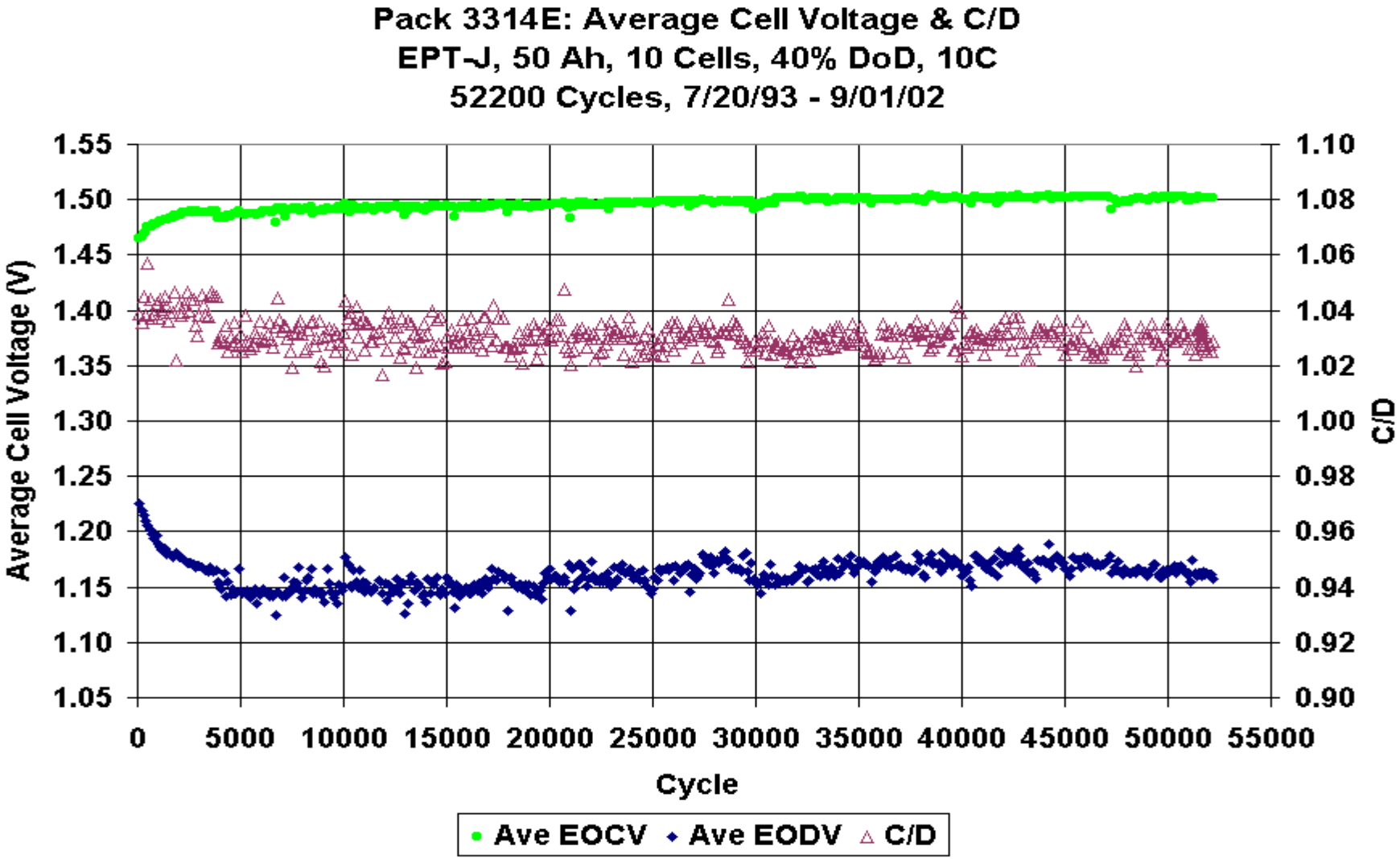
NiH_2 Cell Life Tests

- **Pack 3314E: 3.5" 50-Ah cell (EPT-J), 31% KOH, alternating stack design, dual-layer Zircar, 10-cell pack, 10^0C, 40% DoD, average C/D = 1.031**
  - **1993 test start-up; 52200 cycles as of 9/1/02. No cell failures to-date.**
- **Pack 3316E: 3.5" 50-Ah cell (EPT-J), 31% KOH, back-to-back stack design, dual-layer Zircar, 10-cell pack, 10^0C, 60% DoD, average C/D = 1.038**
  - **1993 test start-up; 51000 cycles as of 8/31/02. No cell failures to-date, although this pack was temporarily put off-line after 50500 cycles because, during charge, it exceeded the pressure safety limit of 1200 psig set by Crane.**

NiH_2 Cell Life Tests

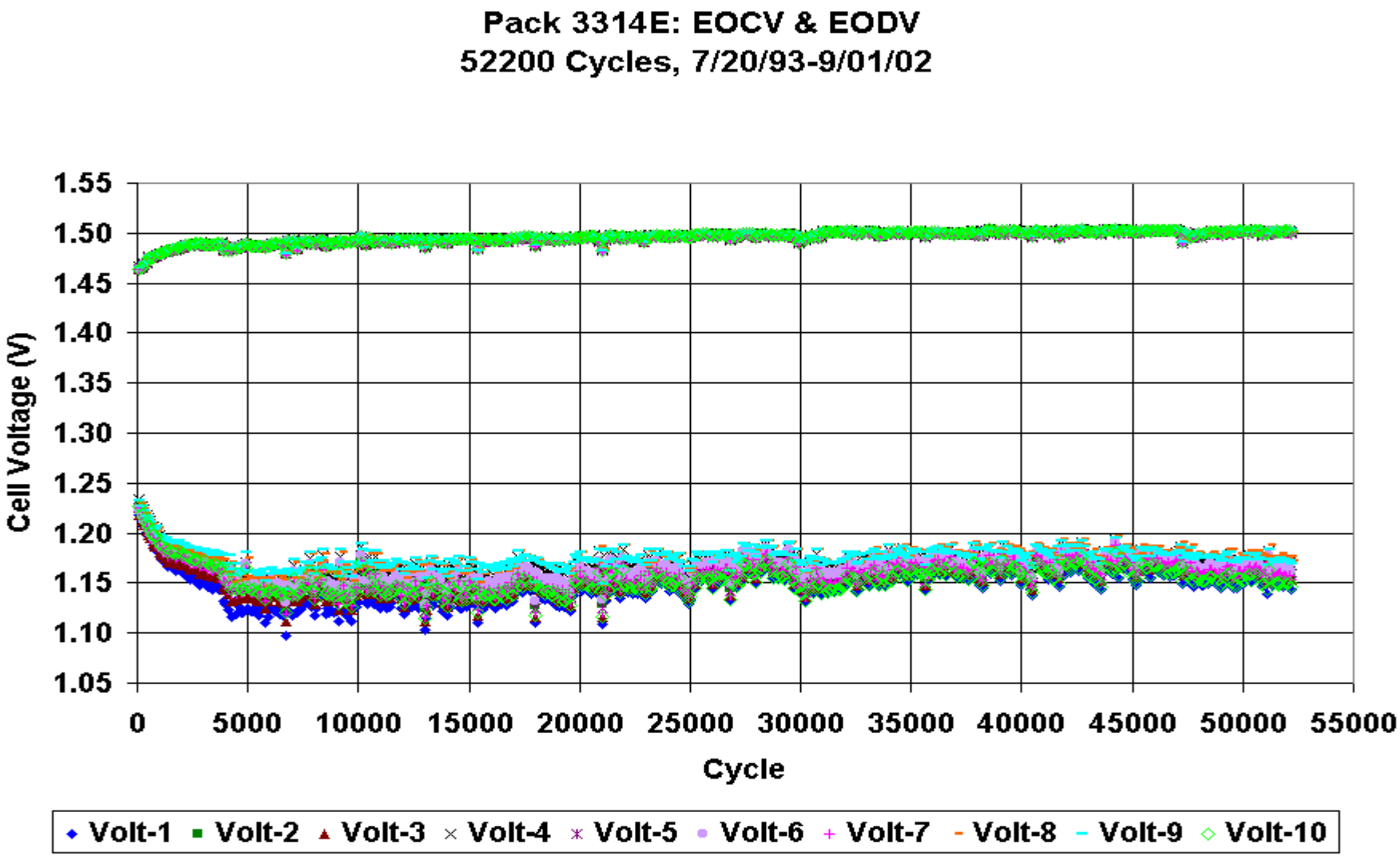
- **(The end-of-discharge pressure was about 950 psig.) After consultations with the cell manufacturer, it was decided to increase the pressure limit to 1250 psig.**

NiH_2 IPV Pack



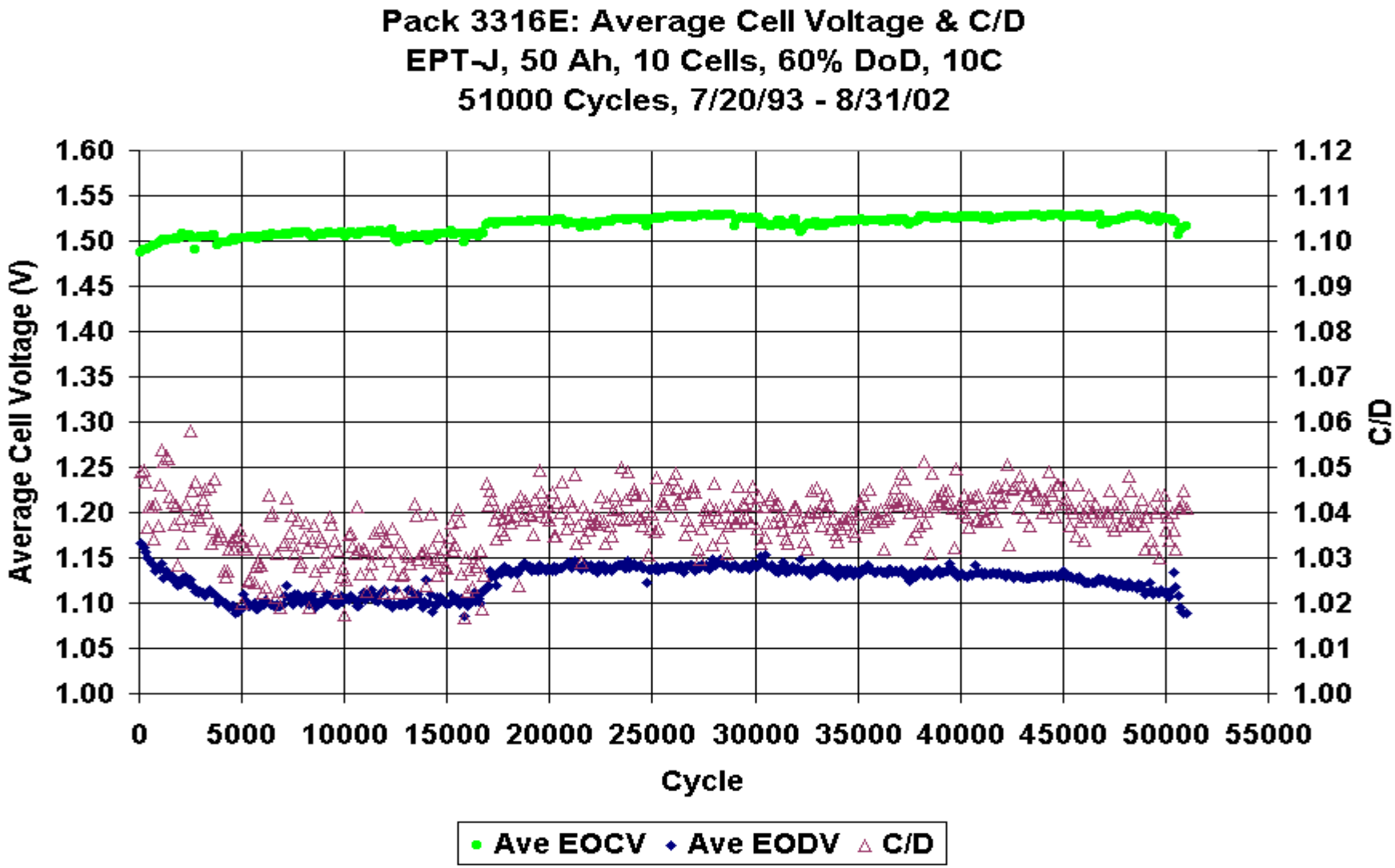
THE AEROSPACE CORPORATION

NiH_2 IPV Pack



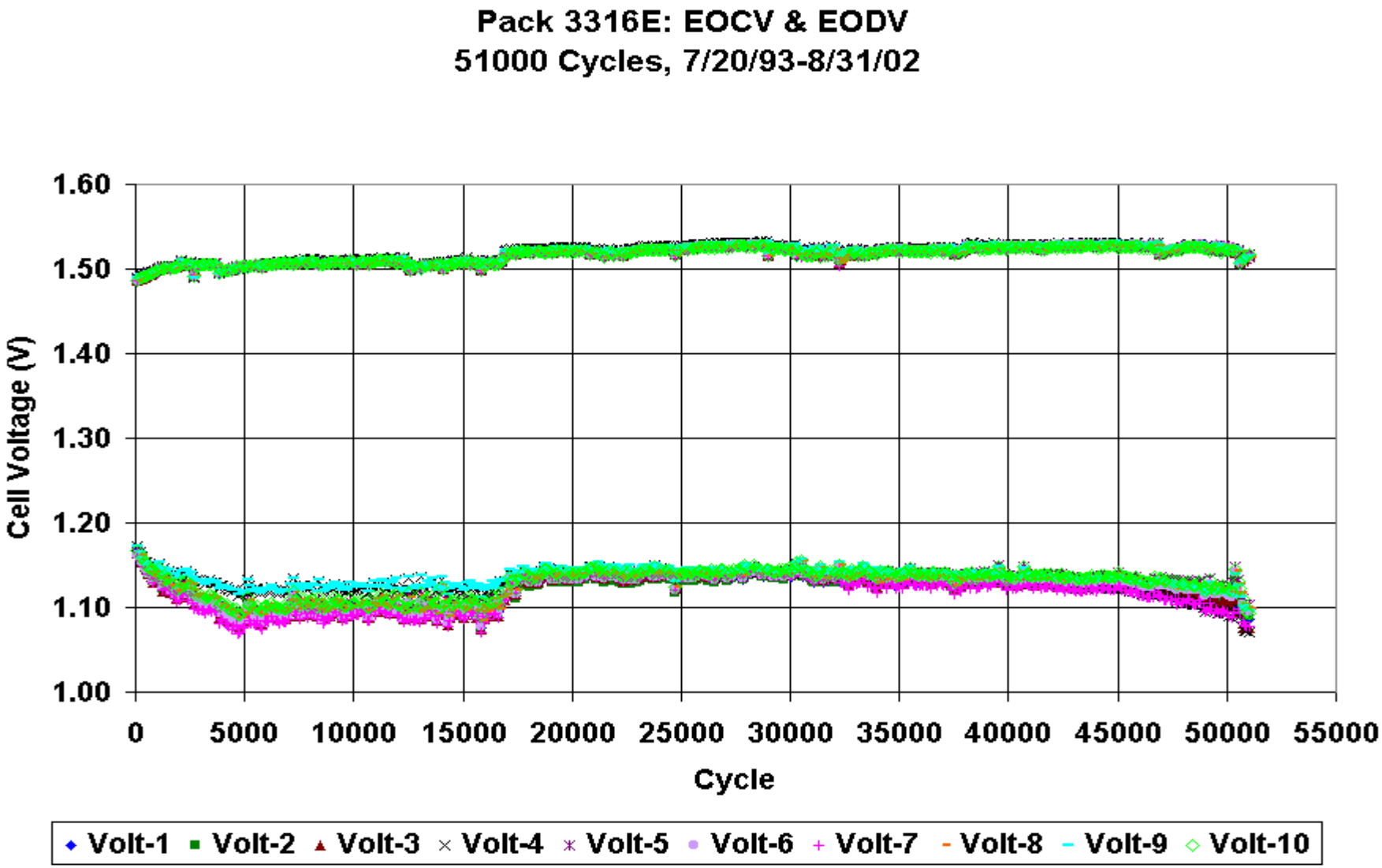
THE AEROSPACE CORPORATION

NiH_2 IPV Pack



THE AEROSPACE CORPORATION

NiH_2 IPV Pack



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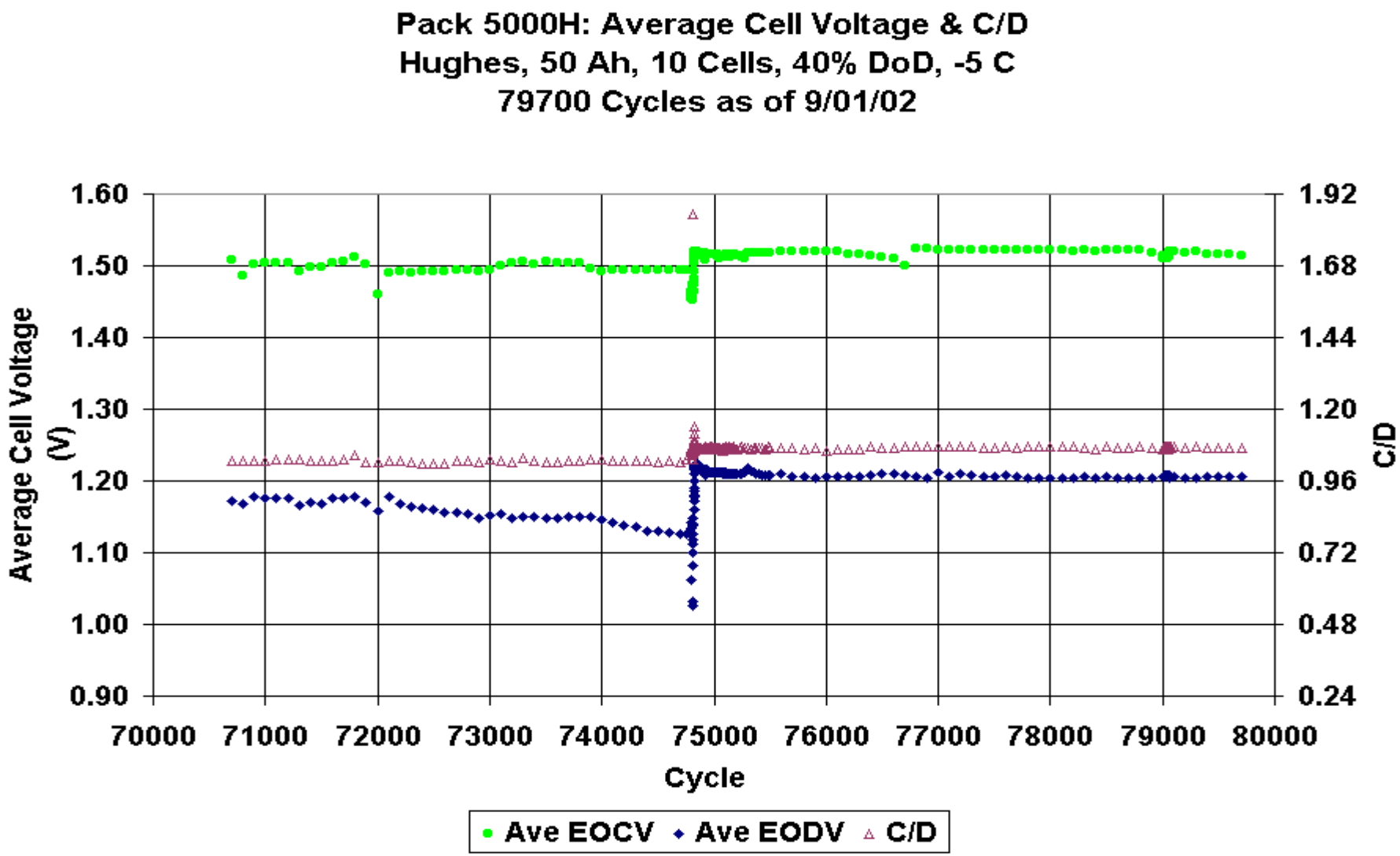
NiH_2 Cell Life Tests

- **Pack 5000H: 3.5" 50-Ah cell (HUGHES), 31% KOH, back-to-back stack design, Zircar separator, 10-cell pack, -5^{0}C, 40% DoD**
  - **1988 test start-up; 79700 cycles as of 9/1/02. No cell failures to-date, although the pack could not complete a full discharge after about 74800 cycles due to one cell's low voltage (cell 5). Therefore, the C/D was increased from an average of 1.032 to its present average value of 1.070. This resulted in an increase in the cells' state-of-charge, as seen in their higher charge and discharge voltages. Cell 5 remains in the pack. Note: The life test data presented for this pack begins with cycle 70700.**

NiH_2 IPV Pack



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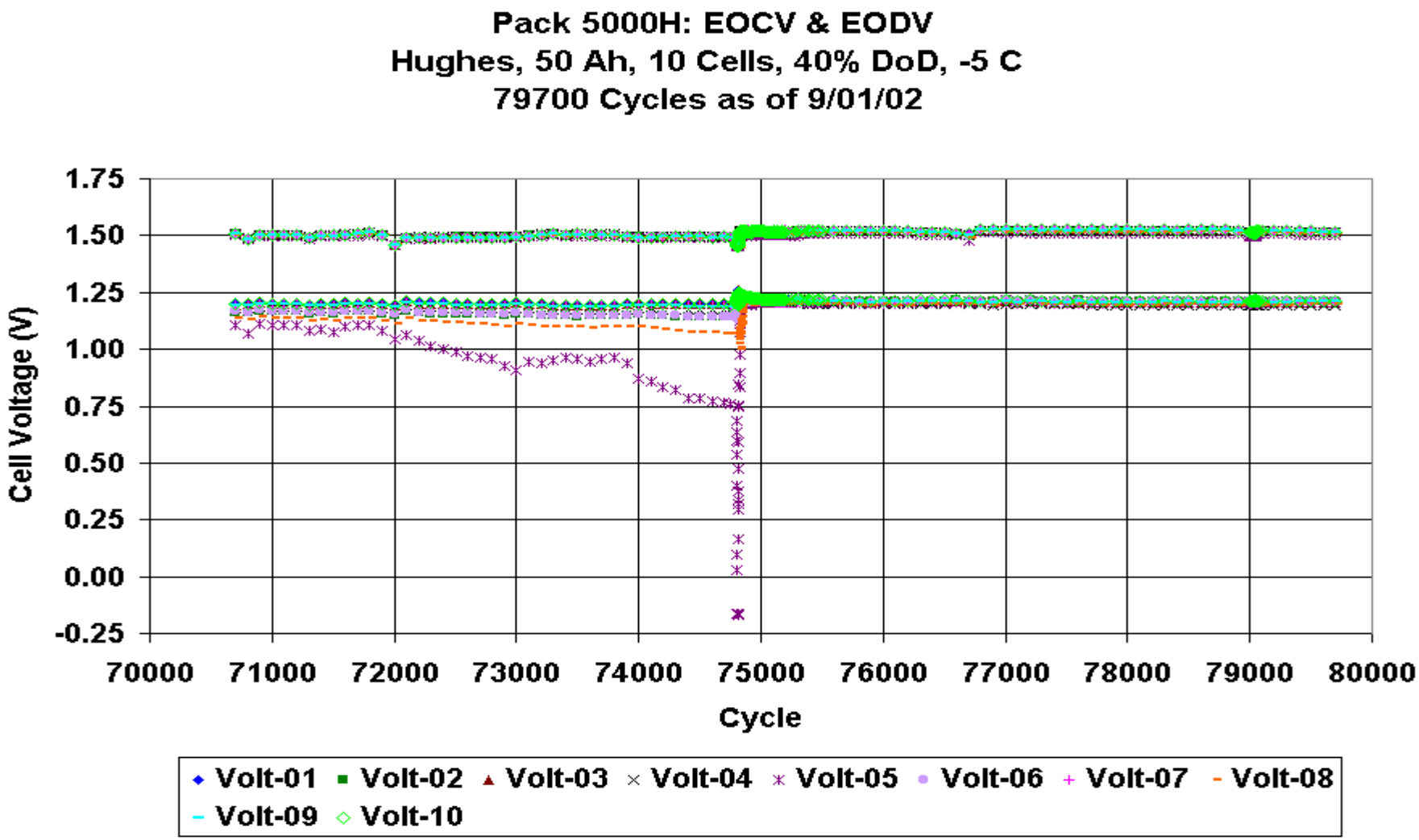
NiH_2 IPV Pack



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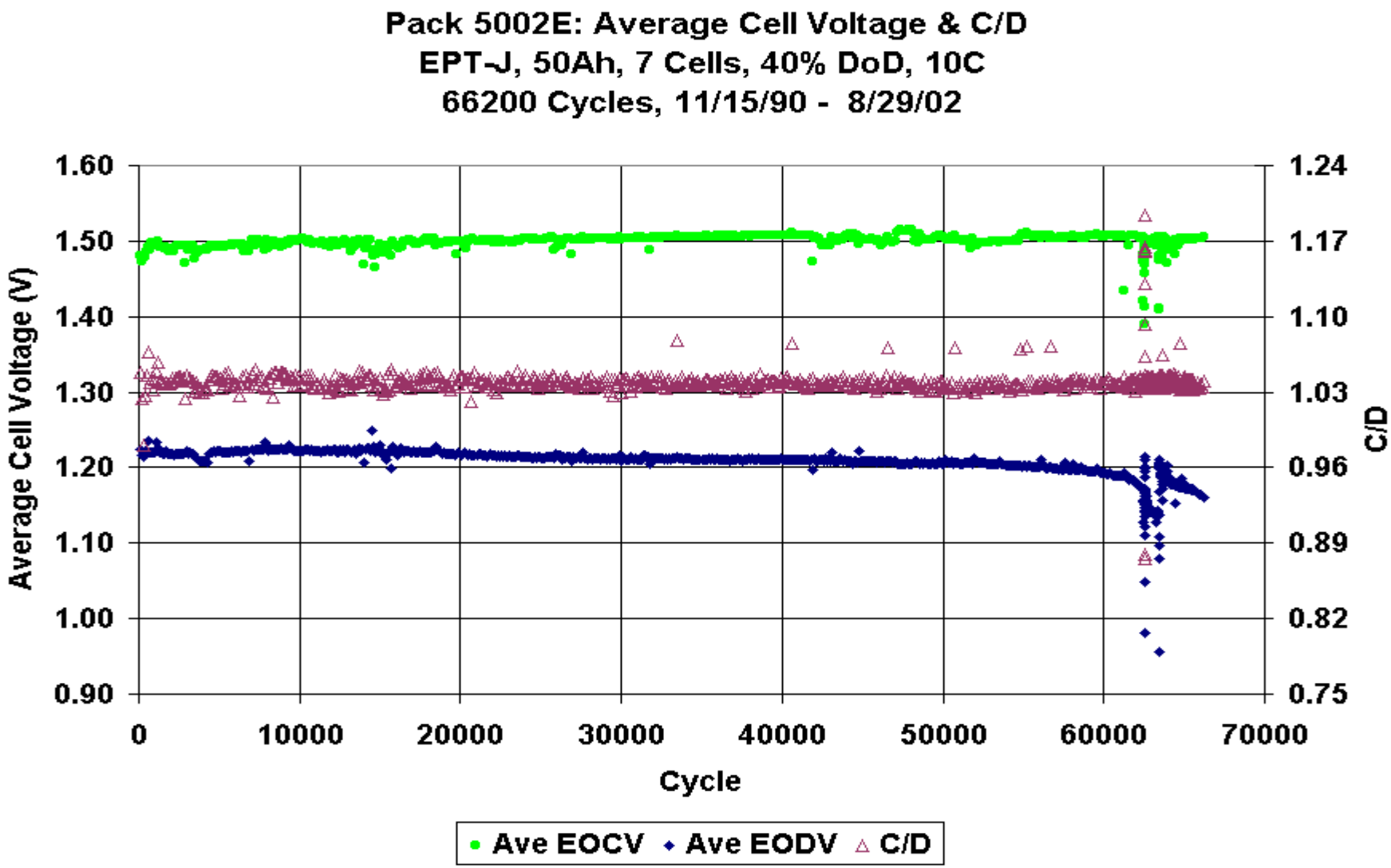
NiH_2 Cell Life Tests

- **Pack 5002E: 3.5" 50-Ah cell (EPT-J), 31% KOH, back-to-back stack design, dual-layer Zircar, 7-cell pack, 10^0C, 40% DoD, average C/D = 1.037**
  - **1990 test start-up; 66200 cycles as of 8/29/02. There has been a single cell failure: Cell 3 was physically removed from the pack during cycle 63484. It had exhibited high voltage during the high-rate portion of the charge (>1.675 V limit) and low discharge voltage (<0.5 V limit). Note: The voltages obtained during high-rate charge are not shown on the graphs; only EOC voltages are shown.**

NiH_2 Cell Life Tests

- **The remaining cells continue to test under the same prior operating conditions without failure. However, there is a decline in end-of-discharge voltages, particularly those of cell 5.**

NiH_2 IPV Pack



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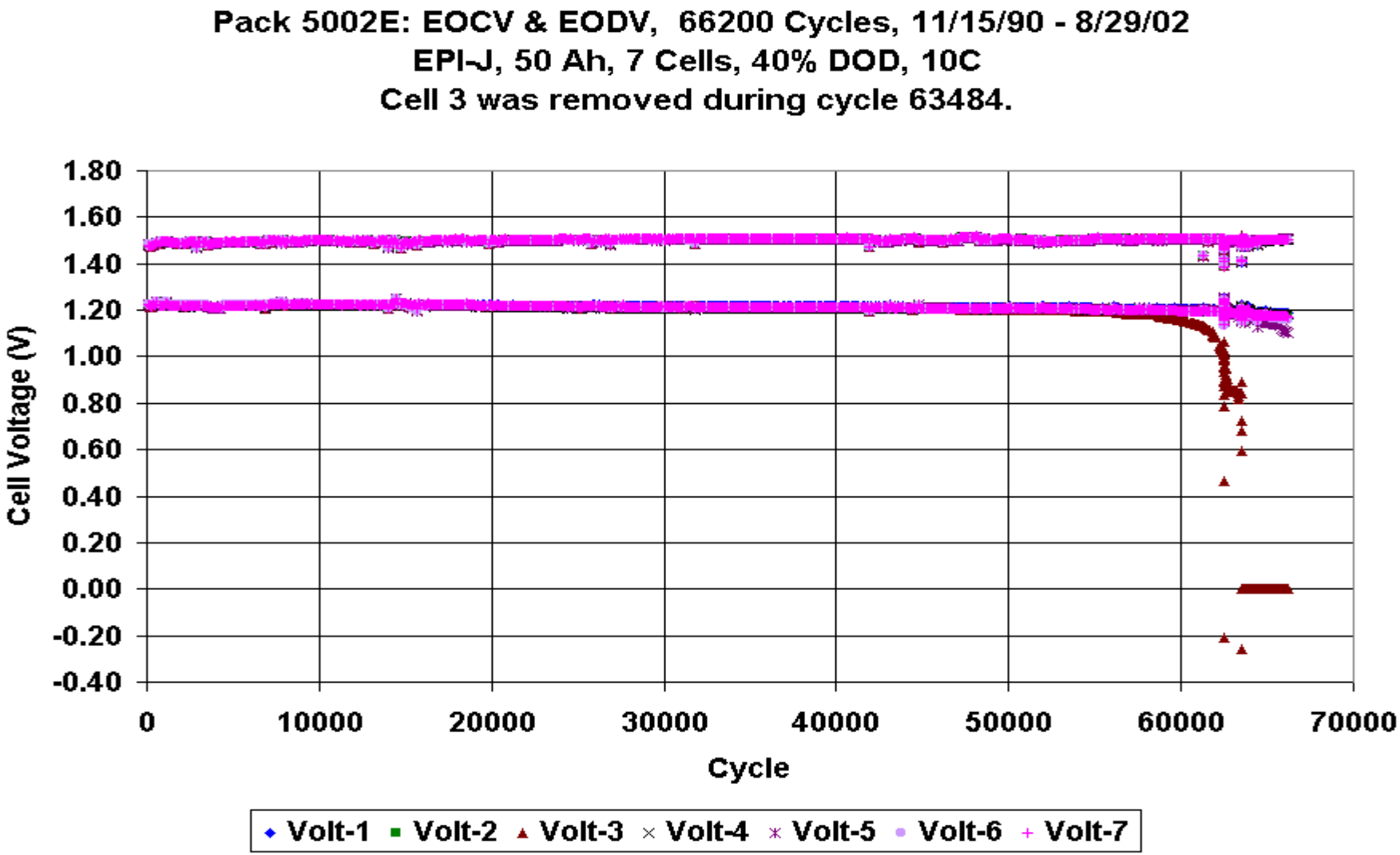
NiH_2 IPV Pack



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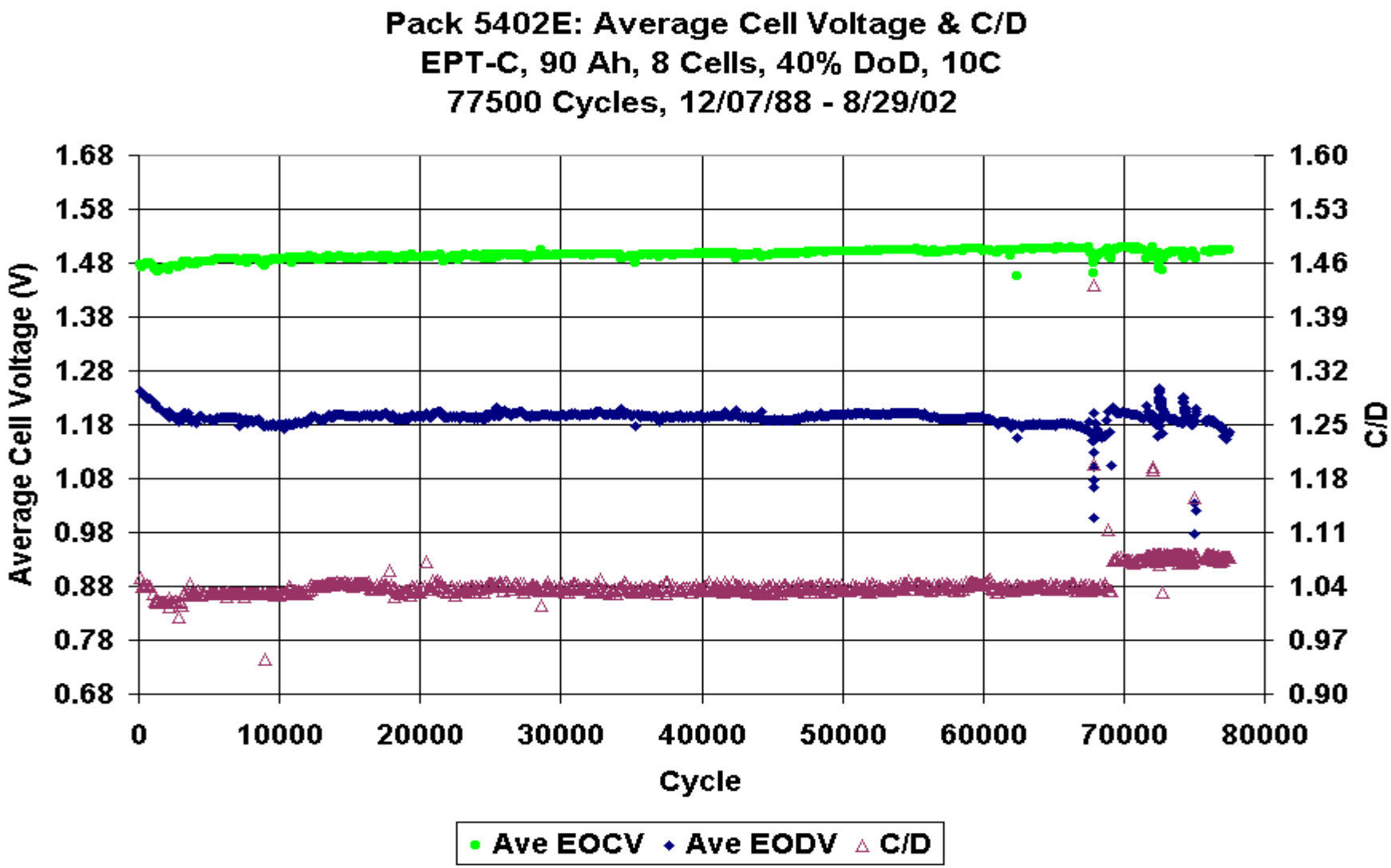
NiH_2 Cell Life Tests

- **Pack 5402E: 4.5" 90-Ah cell (EPT-C), 31% KOH, alternating stack design, dual-layer Zircar, 8-cell pack, 10^0C, 40% DoD**
  - **1988 test start-up; 77500 cycles as of 8/29/02. Two cell failures have occurred to-date. Both cells were electrically removed from the pack because of low discharge voltages (<0.5 V limit) during cycles 67839 (cell 4) and 75078 (cell 3). The remaining cells were placed back on-test. Cell 4 was subsequently sent to The Aerospace Corporation for DPA.**

NiH_2 Cell Life Tests

- **After cycle 69,100, the C/D was increased from an average of 1.038 to its present average value of 1.078.**

NiH_2 IPV Packs



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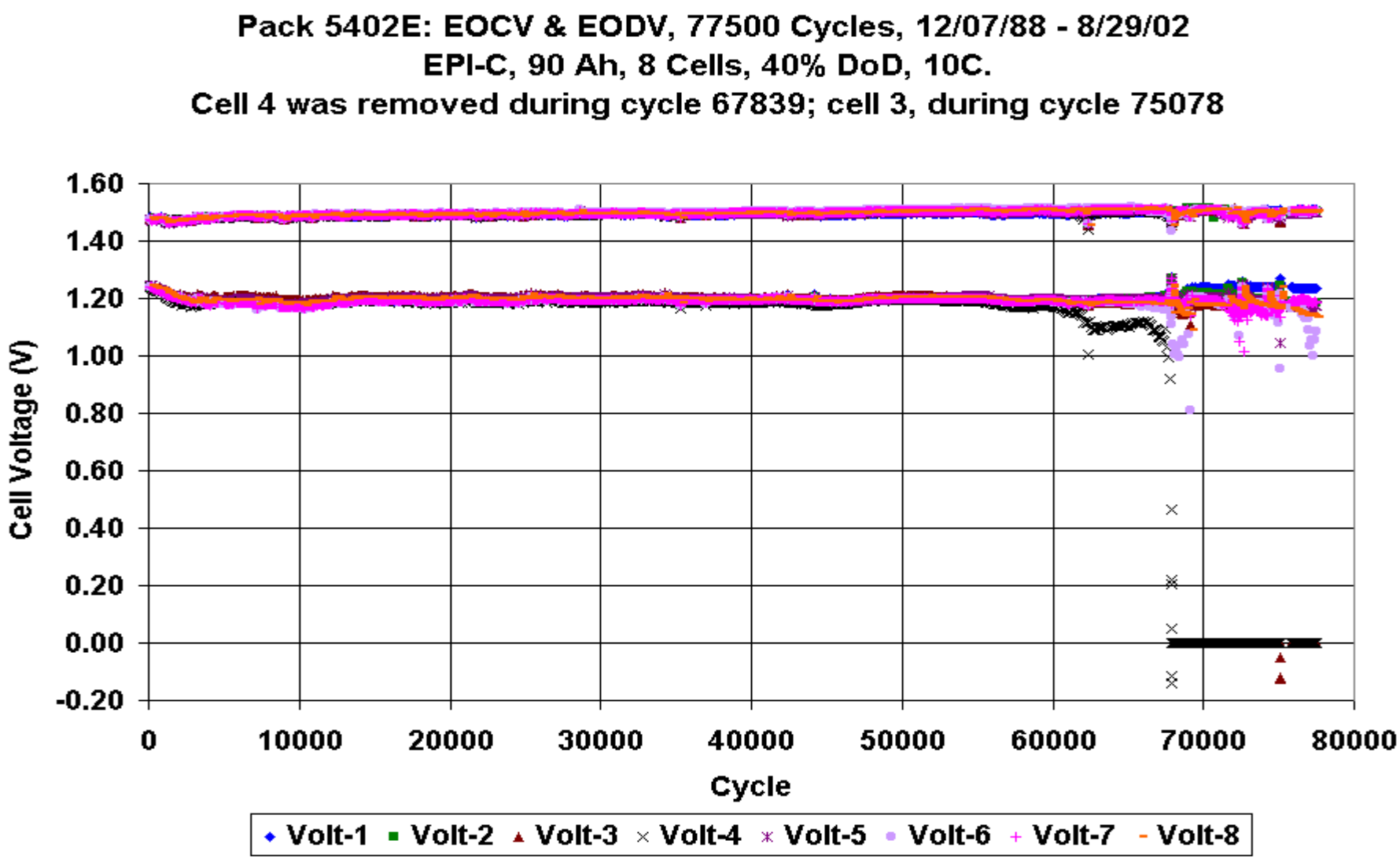
NiH_2 IPV Packs



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Summary

Pack	Cell Description	Temp (^{0}C)	DOD (%)	Cycles	Cells in Test	Cycles at Failure
3214E	EPT-J 50-Ah 26% KOH	10	40	51700	8/10*	none
3254E	EPT-J 50-Ah 26% KOH	-5	40	52000	8/10*	none
3314E	EPT-J 50-Ah 31% KOH	10	40	52200	10/10	none
5002E	EPT-J 50-Ah 31% KOH	10	40	66200	6/7	63484
5402E	EPT-C 90-Ah 31% KOH	10	40	77500	6/8	67839, 75078
5000H	Hughes 50-Ah 31% KOH	-5	40	79700	10/10	none
3316E	EPT-J 50-Ah 31% KOH	10	60	51000	10/10	none

* **Note: 2 cells were removed from both packs 3214E and 3254E as part of an Aerospace Corporation study, and not because of any failure.**

These seven IPV packs are amongst the longest running LEO life tests; overall, it is assessed that the cells are performing very well.

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Acknowledgement

The support of the Air Force Research Laboratory and the SBIRS Low program is gratefully acknowledged.

Understanding the Impact of Electrolyte and Cobalt Additive Concentrations on the Performance of Nickel-Hydrogen Cells

L. H. Thaller, A. H. Zimmerman and G. A. To
The Aerospace Corporation
El. Segundo, CA

For Presentation at
The 2002 NASA Aerospace Battery Workshop
November 19-21, 2002
Huntsville, AL

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Outline of Presentation

- Background
- Data Bases Relevant to Study
- Factors that Were Considered
- Findings Relative to 26% vs. 31% KOH
- Findings Relative to 5% vs. 10% Cobalt
- Summary Statements

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Background

- Early NASA-LeRC (GRC)-funded studies with Hughes-Malibu of cycle life vs. electrolyte concentration via accelerated cycling tests, showed significant improvements in cycle life when 26% KOH solutions were used as the electrolyte[1].
- Later studies carried out at Hughes showed that electrodes cycled in 31% KOH solutions had slightly higher levels of total capacity compared with electrodes cycled in 26% KOH solutions[2].
- Other NASA-funded studies with Hughes in flight-type cells showed that cells filled with 26% KOH had slightly higher discharge and charge voltages compared with cells filled with 31% KOH[3].

1. "KOH concentration effects on the cycle life of nickel-hydrogen cells", Lim, H. S., Vol. 1, pp. 165-170, Proceedings of the 20th Intersociety Energy Conversion Engineering Conference, Miami Beach, FL, Aug. 18-23, 1985.

2. "Effect of KOH concentration on LEO cycle life of IPV nickel-hydrogen flight battery cells", Smithrick, J. J., Vol.. 3., pp. 16-21, Proceedings of the 25th Intersociety Energy Conversion Engineering Conference, Reno, Nevada, Aug. 12-17, 1990.

3. "Electrochemical behavior of heavily cycled nickel electrodes in nickel-hydrogen cells containing electrolytes of various KOH concentrations", Proceedings of the 16th International Power Sources Conference, pp. 471-484, Bournemouth, UK, September 1998.

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Background (cont.)

- An extensive study by Hughes on the capacity fading phenomenon revealed that boiler plate cells that were built with electrodes made using the alcoholic process (~11% cobalt additive level in the active material) had a noticeably lower mid discharge voltage than boiler plate cells that were built with electrodes made using the aqueous process (~7% cobalt level in the active material). The lower voltage ranged from ~ 30 to - 50 mV[4].

4. "Effects of electrode and cell design variables on capacity fading of a nickel-hydrogen cell on storage", Lim, H. S. and Verzwyvelt, S. A., Vol. 3., pp. 7-15, Proceedings of the 25th Intersociety Energy Conversion Engineering Conference, Reno, Nevada, Aug. 12-17, 1990.

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Data Bases Available For Review

- Life cycle testing programs supported by NASA and the AF carried out at the Navy facility located in Crane, IN.
- Results of an extended Aerospace study on a set of representative nickel electrodes.
  - Electrodes studied were both new and well cycled
  - Both powder and slurry plaque material
  - Cells that had been cycled +10°C and -5°C
  - Cells that had been cycled with 26% KOH and 31% KOH
- Samples of material tested using the flooded utilization (FU) and electrochemical voltage spectroscopy (EVS) techniques.
  - Samples of all 6 electrodes tested using both techniques
  - Samples of all 6 electrodes tested in 26% KOH and 31% KOH solutions
  - Samples of all 6 sample tested at +24, +10, 0, and -5°C
- The results have been compiled in a series of Aerospace reports that are available.

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Data Bases Available for Review (cont.)

- The references listed below contain the details of the material to be presented in the following charts.

1. Thaller, L. H., Zimmerman, A. H., and To, G. A., "Techniques to Improve the Usability of Nickel-Hydrogen Cells", Aerospace Report No. TR-2002(3397)-2, 1 May 2002.
2. Thaller, L. H., Zimmerman, A. H., and To, G. A., "Understanding and Managing Capacity Walkdown in Nickel-Hydrogen Cells and Batteries", Aerospace Report No. TR-2002(3000)-2, 31 May 2002.
3. Thaller, L. H., Zimmerman, A. H., and To, G. A., "Flooded Utilization and Electrochemical Voltage Spectroscopy Studies on Nickel Electrodes", Aerospace Report No. TR-2002(3397)-3, 1 July 2002.
4. Thaller, L. H., Zimmerman, A. H., and To, G., "Capacity Trends in Nickel Electrodes as Affected by Temperature and Electrolyte Concentration", Aerospace Report No. TR-2002(3397)-4, 30 September 2002.
5. Thaller, L. H. and Zimmerman, A. H., "A Critical Review of Nickel-Hydrogen Life Testing", Aerospace Report No. ATR-2001(8466)-2, 15 May 2001.

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Factors that were Considered

- Structural factors of the nickel active material.
  - The lattice constants of the different phases present
- The potential and kinetics of the oxygen evolution reaction..
  - The co-evolution of oxygen as the end-of-charge is approached reduces the charge efficiency and thus the amount of stored capacity
- The potential of the beta charging peak during EVS testing.
  - The voltage at which the beta material is charged is impacted by several factors
- The potential of the gamma charging peak during EVS testing.
  - A separate charging peak for the gamma material is not always seen due to its closeness to the potential when large amounts of oxygen are evolved
- The impact of temperature on these reactions.
  - The temperature impacts both the kinetics and the potential at which these reactions take place

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Structural Features of the Nickel Active Material

- Nickel electrodes are known to expand during cycling.[1]
- Unconstrained electrodes can grow in thickness as much as 70%.
- Constrained electrodes can break the plastic core piece on which the electrodes are stacked.[2]
- Plate expansion has been more of a problem at lower temperature and when using higher concentrations of KOH.
  - These conditions favor the formation of gamma NiOOH, and a large active material volume change
  - Repetitive cycling of the material causes nickel plate expansion

1. Thaller, L. H. and Zimmerman, A. H., "A Critical Review of Nickel-Hydrogen Life Testing", Ch. 20, Aerospace Report No. ATR-2001(8466)-2, 15 May 2001.

2. Mueller, V. C., "Failure Analysis of Nickel-Hydrogen Cell Subjected to Simulated Low Earth Orbit Cycling", Proceedings of the 1983 Goddard Space Flight Center Battery Workshop, pp. 523-535, NASA-MSFC, Greenbelt, MD, November 15-17, 1983, NASA CP 2331.

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Structural Features of the Nickel Active Material

- The lattice constants of the different phases associated with the active material help explain these observations.
- The "C" spacings are as follows:[2]
  - alpha $Ni(OH)_2$ - 8-9 Angstroms
  - beta $Ni(OH)_2$ - 4.6 Angstroms
  - beta NiOOH - 4.7 Angstroms
  - gamma NiOOH - 7.2 Angstroms

2. Faure, C., Delmas, M., and Fouassier, J., Power Sources, vol. 35, p. 279, 1991.

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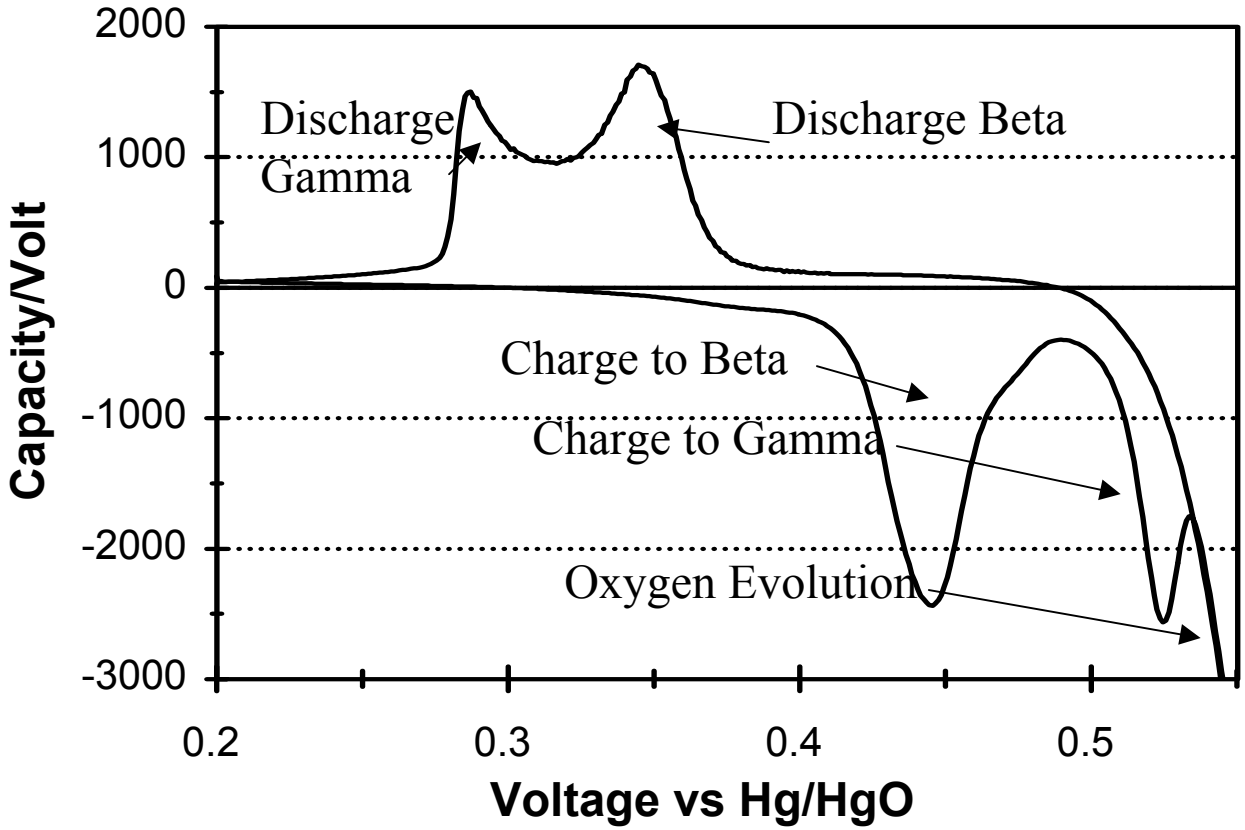
Charging and Discharging Potentials in Nickel Electrodes During an Illustrative EVS Scan



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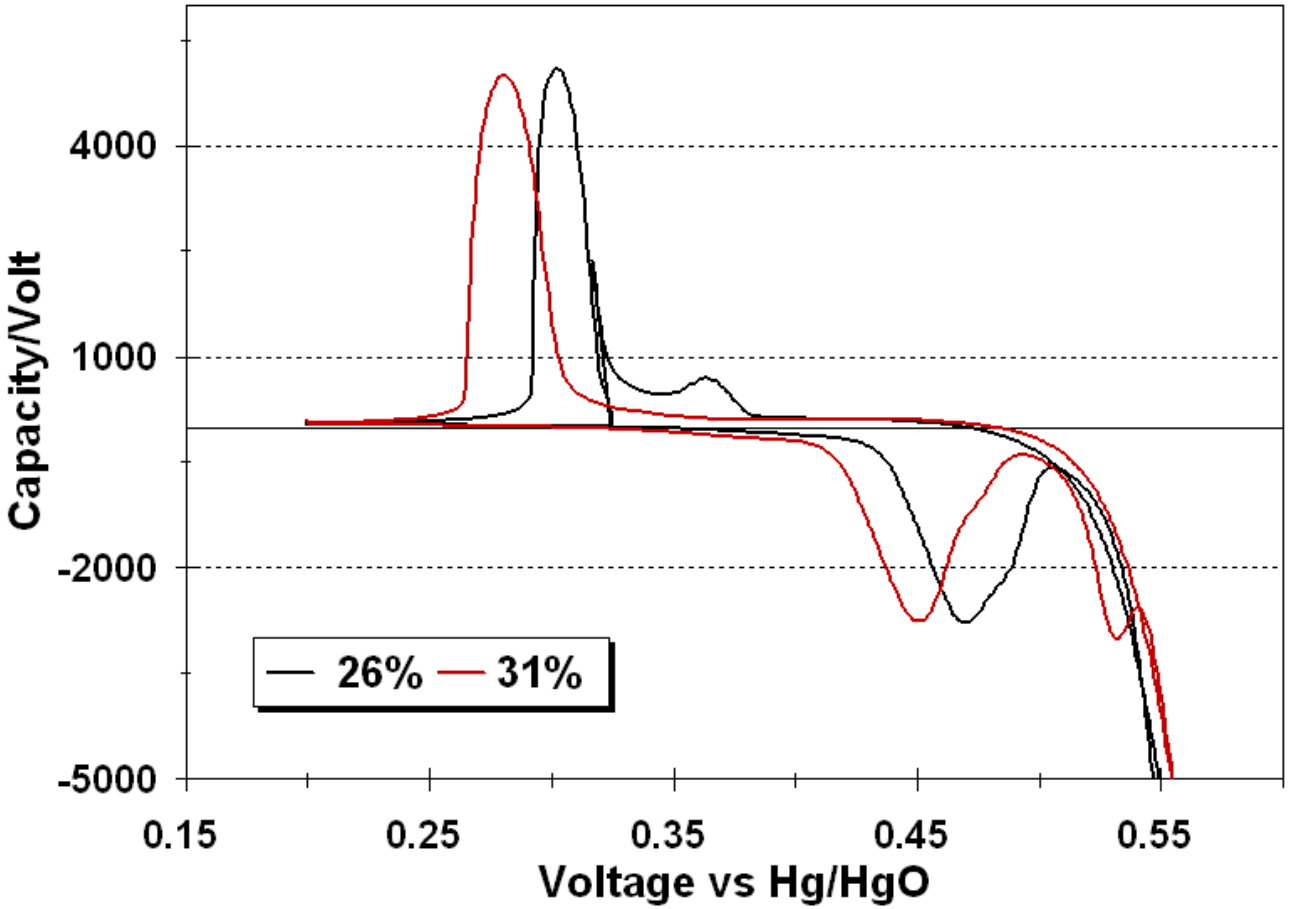
Higher Charging Potentials are Associated with 26% KOH Solutions vs. 31% KOH



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Lower Charge Efficiencies of 26% KOH Results in Larger Amounts of Capacity Walkdown Compared to 31% KOH Solutions[1]

Pack	Concentration of KOH - %	Max. BOL Press. - psi	Estimated Capacity Walkdown - %
1-a	31	606	33
1-b	26	567	42
2-a	31	685	20
2-b	26	605	31
3-a	31	725	31
3-b	26	680	43
4-a	31	787	14
4-b	26	700	23
5-a	31	795	11
5-b	26	697	35
6-a	31	705	16
6-b	26	660	29

1. Thaller, L. H., Zimmerman, A. H., and To, G. A., "Understanding and Managing Capacity Walkdown in Nickel-Hydrogen Cells and Batteries", Aerospace Report No. TR-2002(3000)-2, 31 May 2002.

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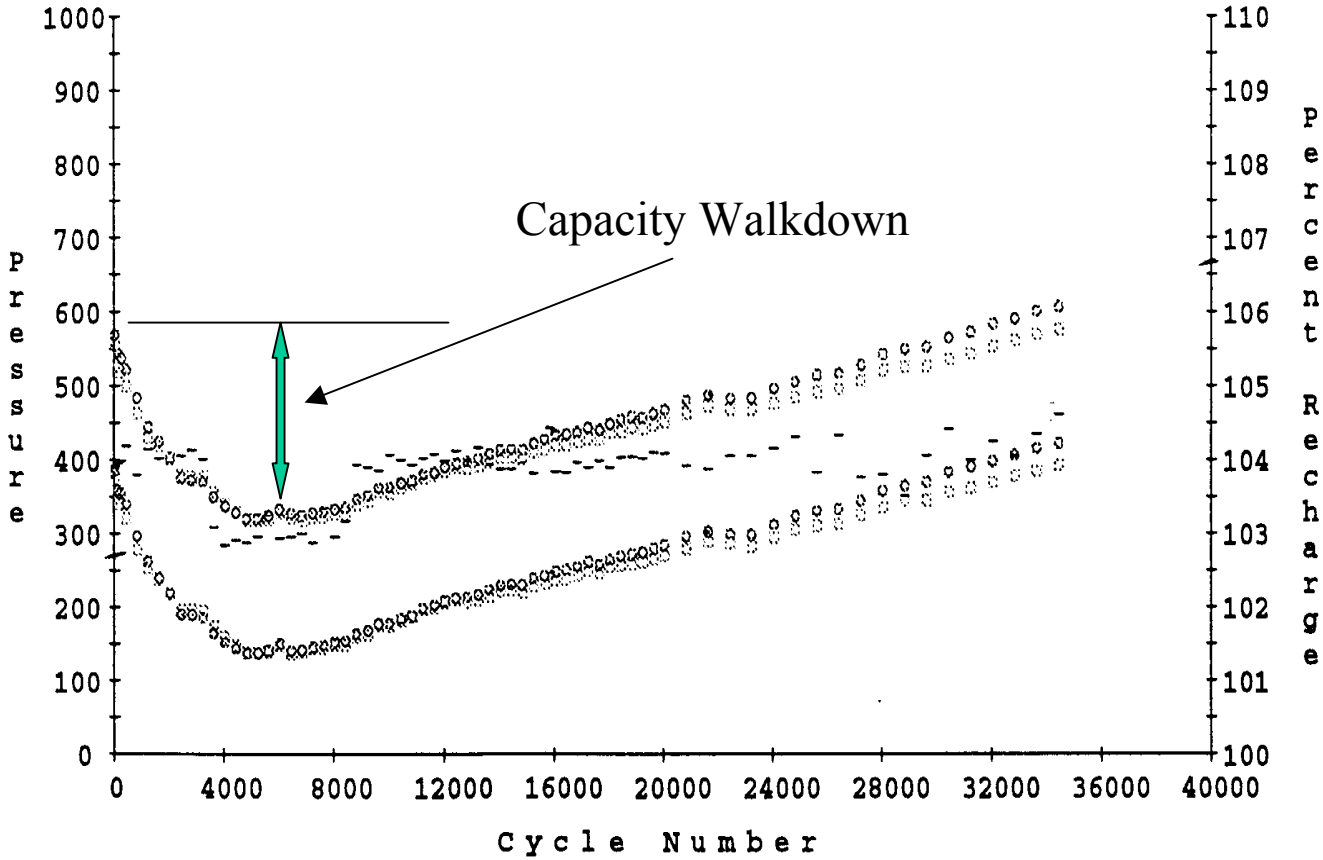
LEO Cycling Often Results in Different Amounts of Capacity Walkdown



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Capacity Gains are Available When Fully Charging Electrodes in 31% KOH vs. 26% KOH[1]

Plate No.	After 10 hours of charge	After 14 hours of charge
1	22.6%	56.4%
2	74.5%	77.8%
3	39.6%	72.9%
4	19.9%	61.4%
5	37.6%	58.6%
6	42.6%	55.1%

Comparisons at -5°C from electrode samples charged using the standard charging current (4 mA/ cm^2) in 26% KOH vs. 31% KOH solutions.

1. Thaller, L. H., Zimmerman, A. H., and To, G., "Capacity Trends in Nickel Electrodes as Affected by Temperature and Electrolyte Concentration", Aerospace Report No. TR-2002(3397)-4, 30 September 2002.

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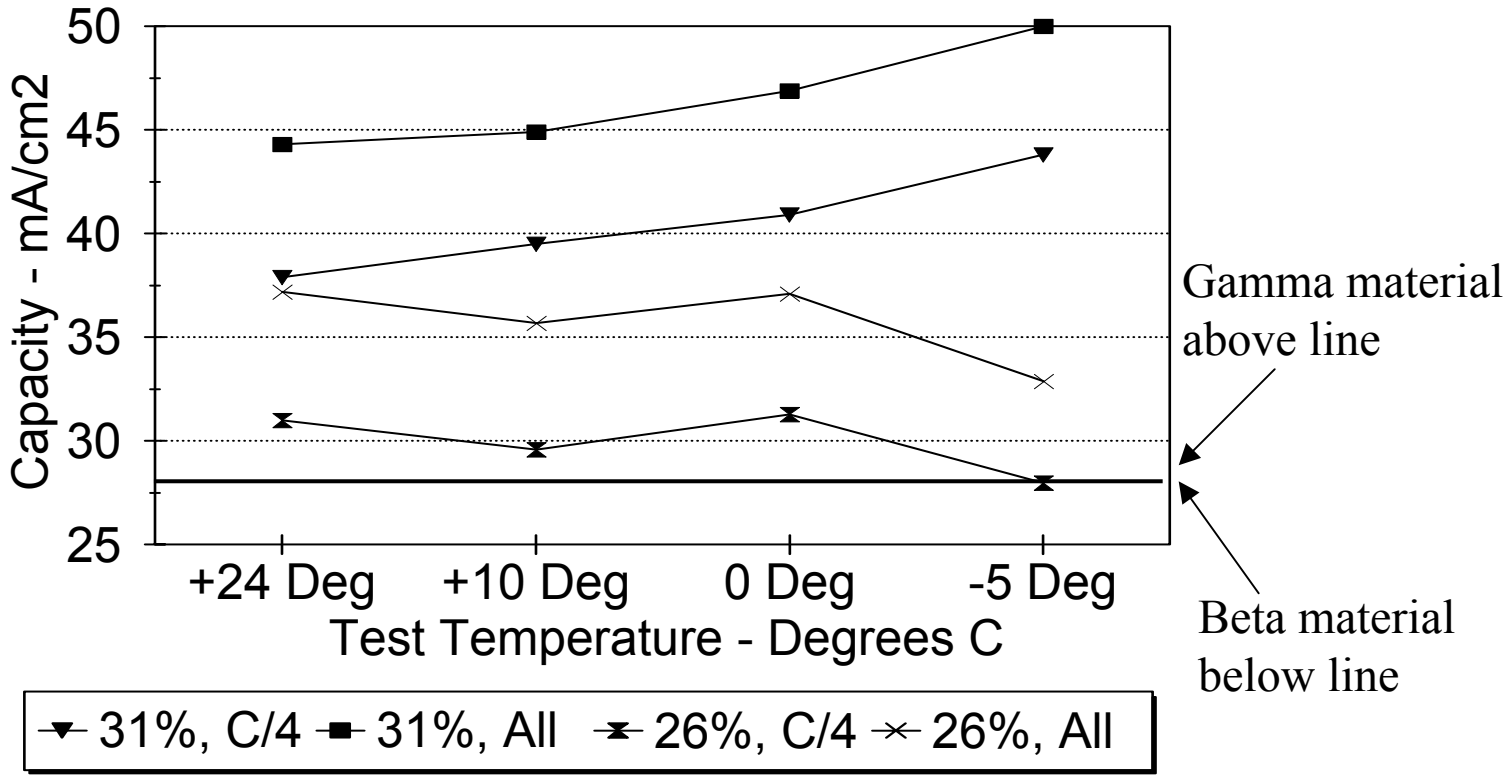
Electrodes are More Difficult to Charge to the Gamma Phase in 26% KOH vs. 31% KOH



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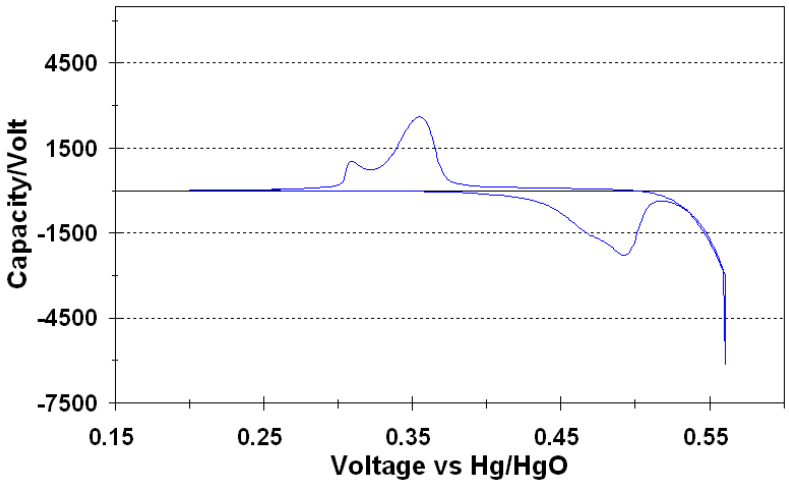
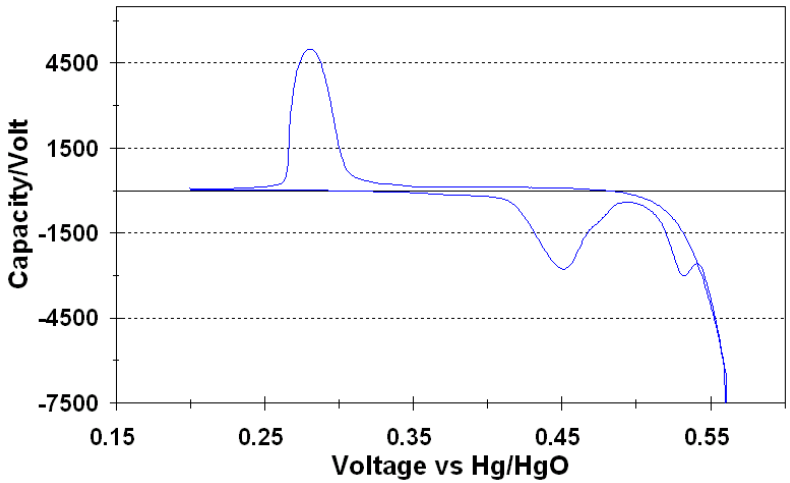
EVS Scans Support Flooded Results that 26% KOH Electrodes are More Difficult to Charge at -5°C

26% KOH



31% KOH



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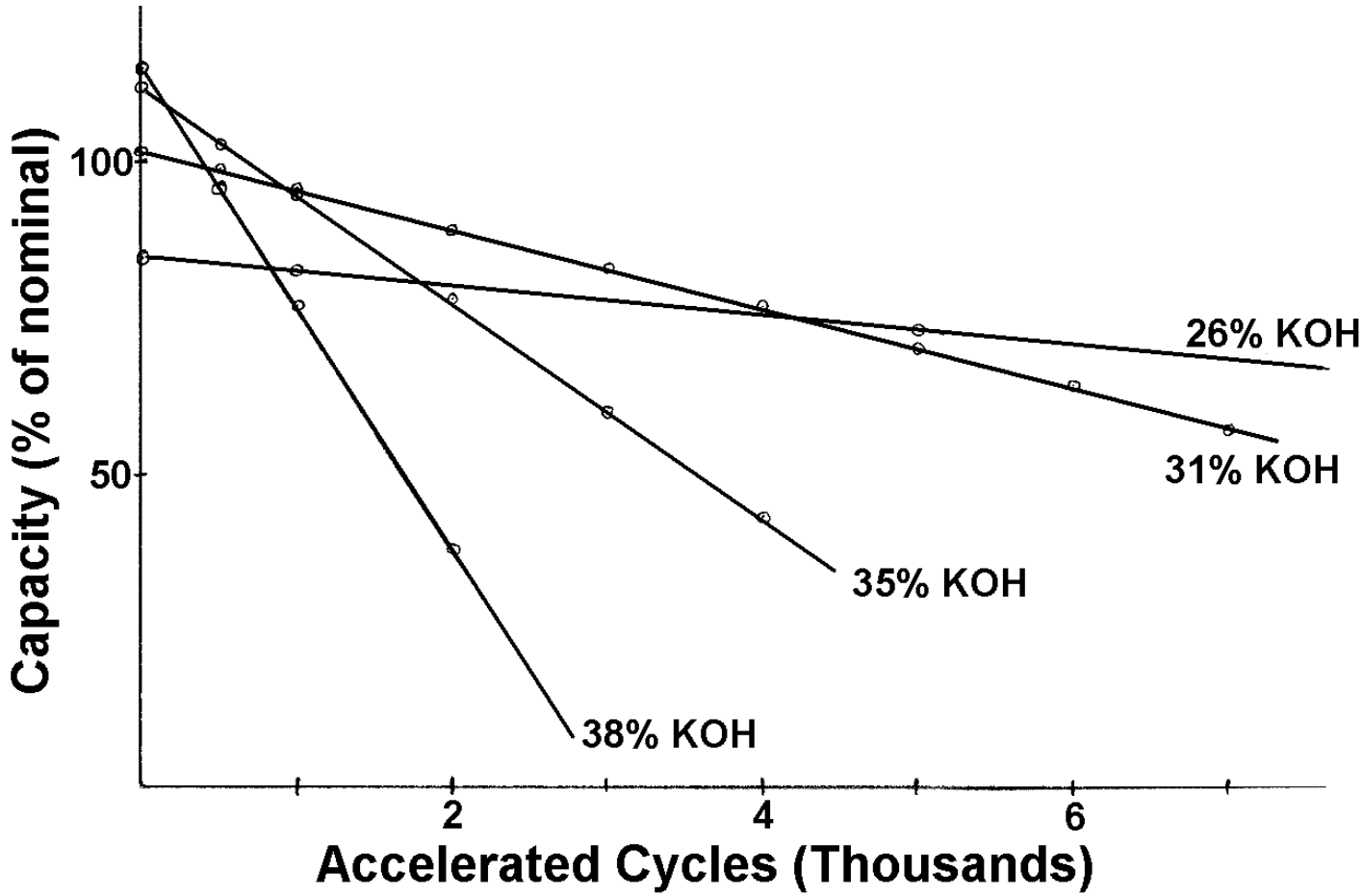
Higher KOH Concentrations are Associated with Higher Capacities and Shorter Cycle Lives



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Findings Related to the 26% vs. 31% KOH Issue

- The electrode potentials are higher in 26% solutions by about 20-40 mV.
- In 26% KOH solutions, the span between charging to the beta phase and oxygen evolution is narrower. This results in:
  - Larger amounts of capacity walkdown
  - Smaller amounts of usable capacity
  - Lower charging efficiencies
  - It is more difficult to form the gamma phase
- At -5°C there is a significant drop in the usable capacity in 26% solutions relative to 31% KOH solutions.
- However, every side-by-side test of 26% KOH vs. 31% KOH has shown the 26% KOH cells to result in longer cycle lives.
  - Stresses related to repeated gamma phase formation are a dominant life controlling factor

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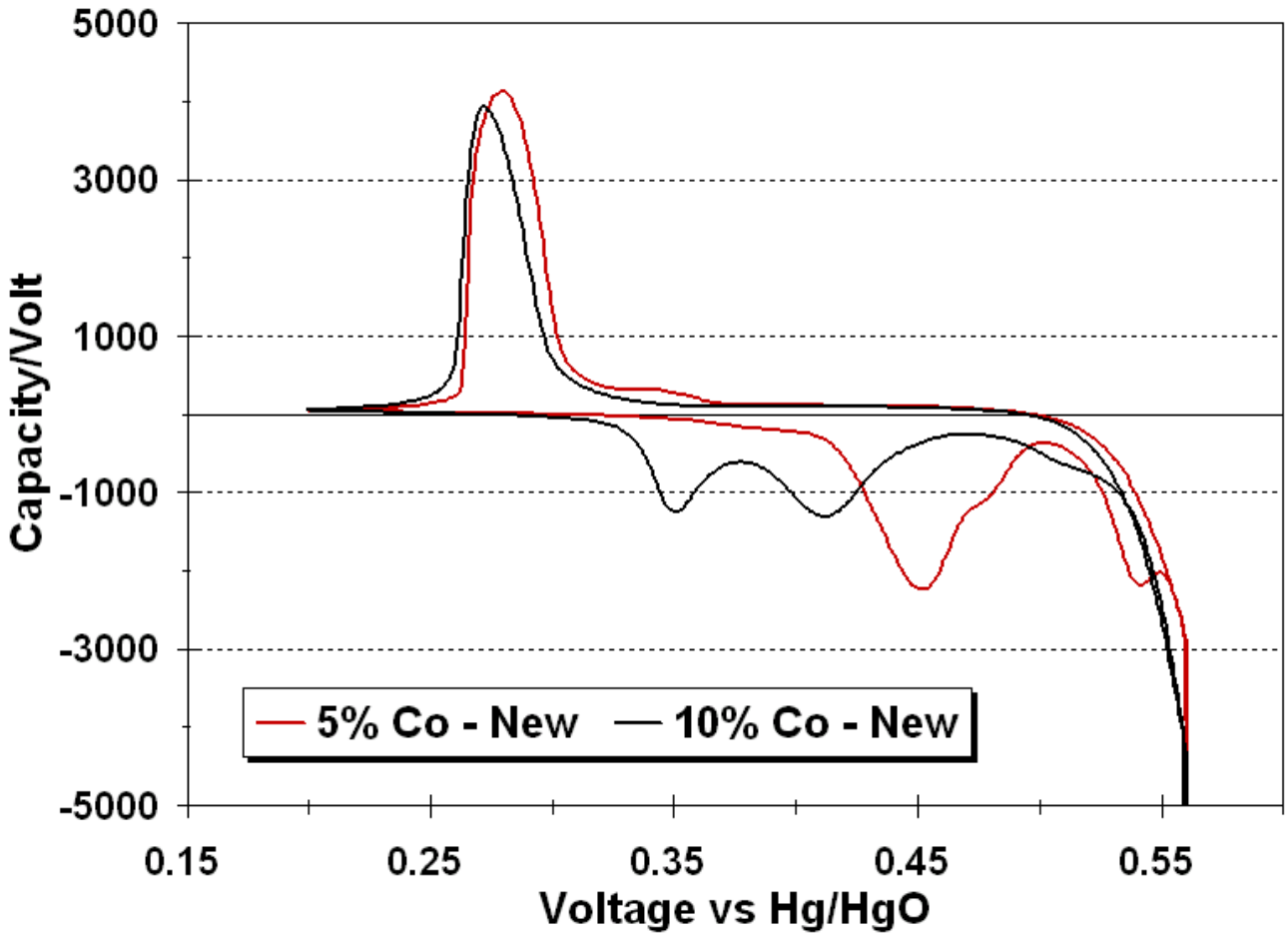
Electrodes With 10% Cobalt Charge at Lower Potentials Compared With 5% Cobalt Electrodes



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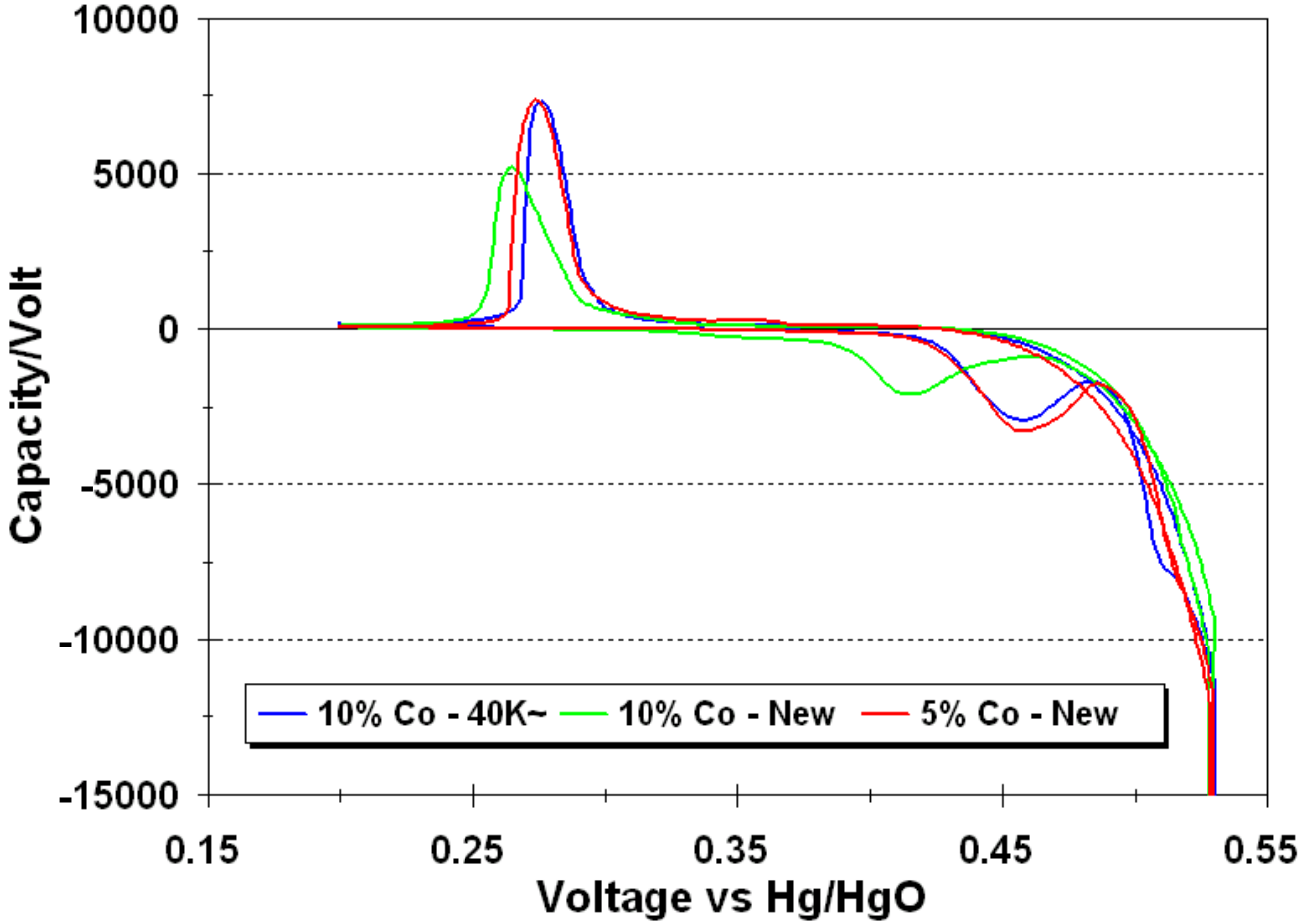
After Many Cycles, 10% Co Electrodes Resemble 5% Co Electrodes



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Findings Related to the 5% vs. 10% Cobalt Issue

- The electrode potential are higher in 5% cobalt electrodes by about 20-40 mV compared to 10% cobalt electrodes. This results in less separation between charging the electrode and the co-evolution of oxygen as thus lower charging efficiencies when using 5% cobalt electrodes.
- There is evidence that it is easier to charge to the gamma phase when using 10% cobalt electrodes due to the lower charging voltage.
- There is evidence that 10% cobalt electrodes are structurally more stable than 5% cobalt electrodes due to the active material being softer.[1]
- There is evidence that 10% cobalt electrodes are more susceptible to capacity fading in cells that are hydrogen precharged.[2]

1. Fritts, D. H., J. Electrochem. Soc., 129, 118-122, January 1982.

2. "Effect of KOH concentration on LEO cycle life of IPV nickel-hydrogen flight battery cells", Smithrick, J. J., Vol.. 3., pp. 16-21, Proceedings of the 25th Intersociety Energy Conversion Engineering Conference, Reno, Nevada, Aug. 12-17, 1990.

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Summary Statements

- In General
  - 26% KOH cells are suggested for longer cycle lives and 31% KOH cells are suggested when optimum energy density is required and life is not as critical.
  - 26% KOH, 10% cobalt cells are suggested for higher charging efficiencies and lower plate expansion and 31% KOH, 5% cobalt cell are suggested for higher levels of total capacity and greater long term stabilities.
    - Electrolyte quantities, cell dryout, and temperature effects are also important factors impacting the cycleability of these cells.
  - The two major cell designs, 26% KOH - 10% Co and 31% KOH - 5% Co have both produced excellent cycling results

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Summary Statements

- Therefore:
  - The selection of KOH concentration and cobalt level depends on the cycling conditions and the mission objectives.
  - It is helpful to understand the factors that impact the cycleability, charge efficiency, electrode expansion, and temperature effects on the nickel electrode.
  - By applying this understanding to nickel electrodes, they should be capable of extended cycling durations to deeper depths-of-discharge than are currently practiced.
  - Understanding the signatures of the different possible selections can permit optimum recharge protocols to be selected
  - Excessive amounts of overcharge will destroy any type of nickel electrode no matter what that KOH concentration or cobalt level is used.

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Mars Mission Surface Operation Simulation Testing of Lithium-Ion Batteries

M. C. Smart, R.Bugga, L. D. Whitcanack, K. B. Chin, E. D. Davies and S. Surampudi

Jet Propulsion Laboratory, Pasadena, California

Supported by the Mars 2003 Exploration Rover and NASA Code S Battery Programs

NASA Battery Workshop
Huntsville, Alabama
Nov. 20, 2002

Outline

- Introduction and Objectives
- Mission Simulation Testing of MSP01 Lander Cells
- Mission Simulation Testing of MSP01 Lander Battery
- Mission Simulation Testing of 2003 MER Cells
- Mission Simulation Testing of 2003 MER Batteries
- Mission Simulation Testing of Next Generation Cells
- Conclusions
- Acknowledgements

Test Plan for the MSP01 Lithium-Ion Cells and Battery : Program Objectives

- Assess viability of using lithium-ion technology for future NASA applications, with emphasis upon Mars landers and rovers which will operate on the planetary surface.

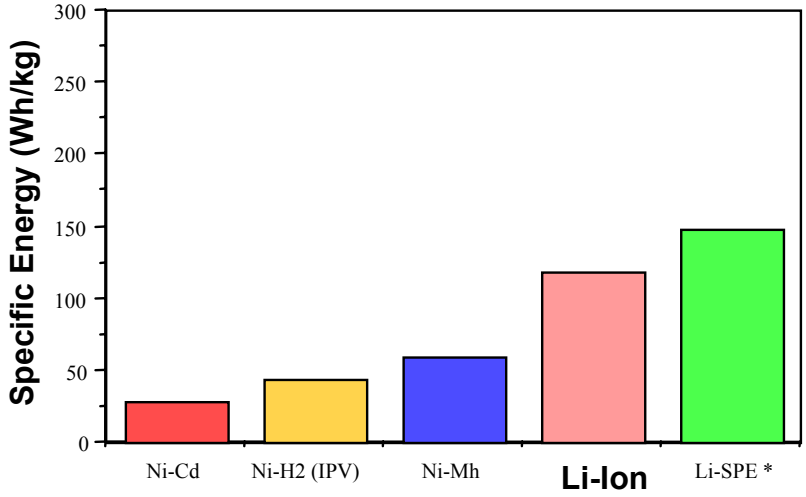
- Support the JPL 2003 Mars Exploration Rover program to assist in the delivery and testing of a 8 AHr Lithium-Ion battery (Lithion/Yardney) which will power the rover.

- Demonstrate applicability of using lithium-ion technology for future Mars applications.
    - Mars 09 Science Laboratory (Smart Lander)
    - Future Mars Surface Operations (General)

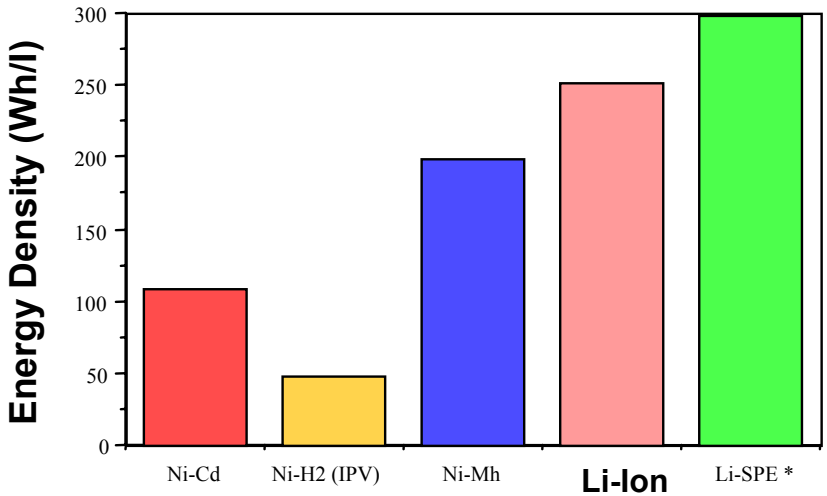
Lithium-Ion Cell/Battery Development

Potential NASA Benefits and Comparison to Conventional Technologies

Specific Energy



Energy Density



Benefit to NASA Missions

- REDUCED POWER SYSTEM MASS
- 25 % OF Ni-Cd/Ni-H_2 BATTERY MASS
  - 200-230 kg MASS SAVINGS FOR 8-10 kW GEO PAYLOADS
- REDUCED POWER SYSTEM VOLUME
  - 25 % OF Ni-Cd/Ni-H_2 BATTERY VOLUME
  - SIMPLER POWER SYSTEM INTEGRATION
- LOWER LAUNCH COSTS
  - REDUCED POWER SYSTEM WEIGHT
  - REDUCED SOLAR ARRAY SIZE
- ENHANCE SMALL SPACECRAFT MISSIONS

Technology Challenges/Drivers

MISSION	TECHNOLOGY DRIVER
LANDER/ROVER	LOW TEMP. OPERATION HIGH RATE PULSE CAPABILITY
GEO S/C	TEN-TWENTY YEAR OPERT. LIFE LARGE CAPACITY CELLS (50-200 Ah)
LEO/PLANTERARY S/C	LONG CYCLE LIFE (30,000) MED. CAPACITY CELLS (50 Ah)
AIRCRAFT	LOW TEMP OPERATION HIGH VOLTAGE BATTERIES (270 V)
UAV	LARGE CAPACITY CELLS (200 Ah) HIGH VOLTAGE BATTERIES (100V)

Lithium-Ion Cells for the Mars Surveyor 2001 Lander

EDL and Mission Simulation Tests

Requirement :

- Meet entry, descent and landing (EDL) power requirements
- Successfully cycle cells on the surface of Mars (temperature range of -20°C to 40°C)

Approach :

Store cells for > 10 months to simulate cruise period

Test cells under EDL profile at 0°C

Cycle cells under varying temperature profile

- 12 Hour charge period (-20 to 40°C)
- 12 Hour discharge period (40 to -20°C)
- Change temperature range to model seasons

Possible Evaluation Criteria:

Discharge voltage on EDL profile (>3.0V each cell)

End of discharge voltage on cycling test (>3.0V each cell)

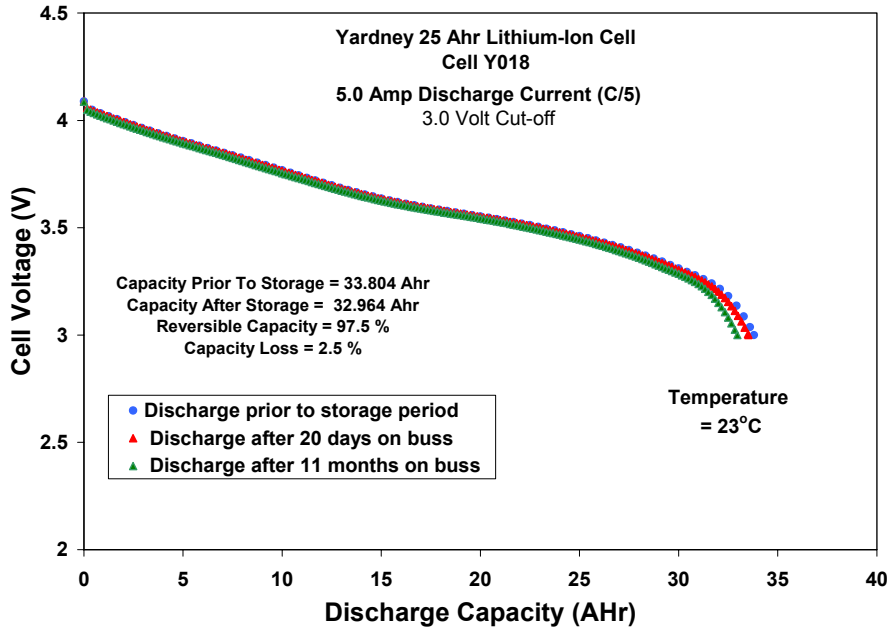
Cell variance

Capacity fade upon cycling

Yardney 25 Ah Lithium-Ion Cells for Mars Lander Applications

Storage Characteristics of MSP01 Design Cells- Results of 11 Month Storage Test

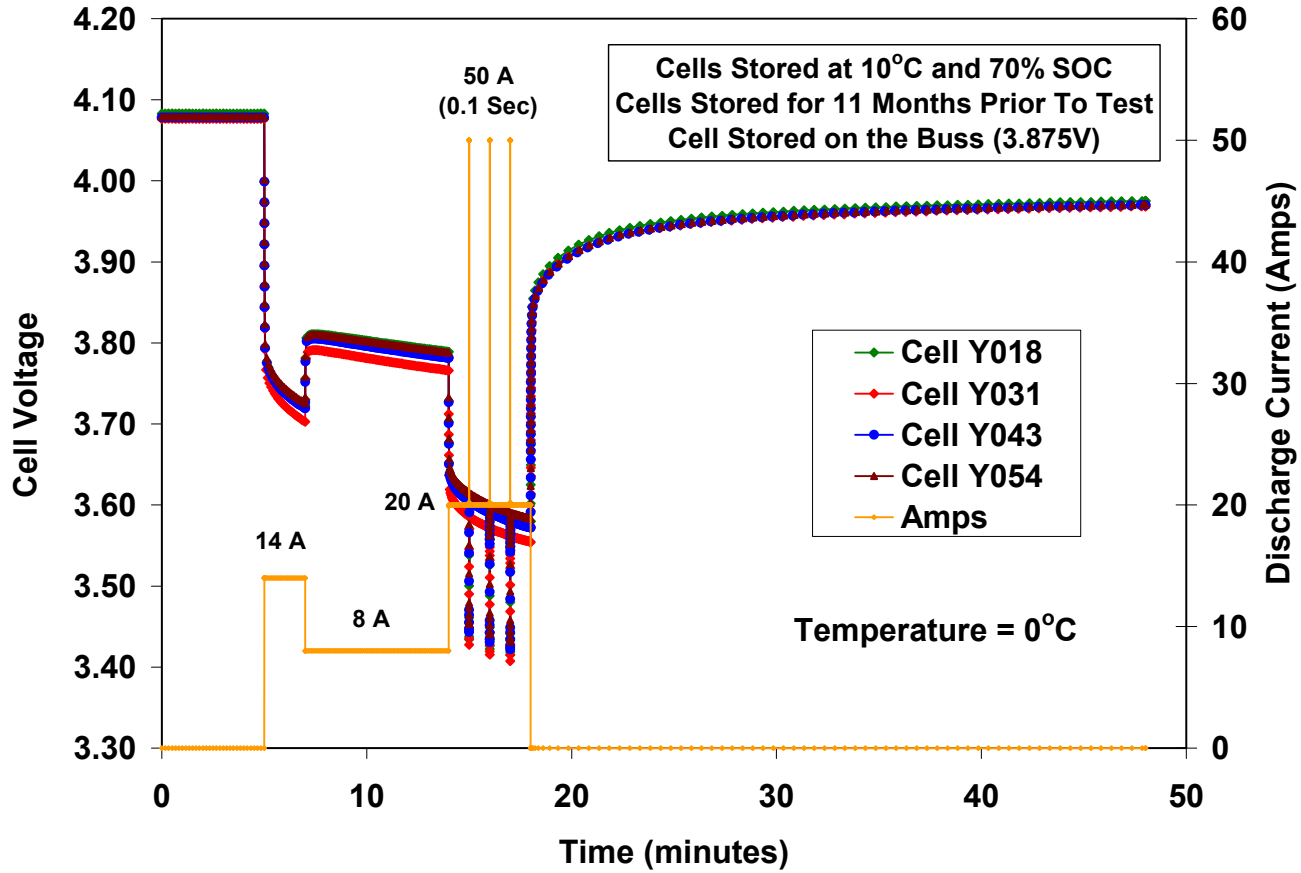
Cells Stored on the Buss at 10°C (70% SOC)



		Storage After 20 Days				Storage After 11 Months			
	Last Discharge Prior to Storage (Ahr)	1st Discharge After Storage (Ahr) 23°C	2nd Discharge After Storage (Ahr) 23°C	% of Initial Capacity (Reversible Capacity)	Permanent Capacity Loss (%)	1st Discharge After Storage (Ahr) 23°C	2nd Discharge After Storage (Ahr) 23°C	% of Initial Capacity (Reversible Capacity)	Permanent Capacity Loss (%)
Y018	33.804	26.034	33.523	99.169	0.831	25.6252	32.9636	97.515	2.485
Y031	33.962	25.959	33.534	98.738	1.262	29.059	32.266	95.006	4.994
Y043	34.153	25.445	32.788	96.005	3.995	25.639	32.999	96.622	3.378
Y054	33.727	25.922	33.460	99.210	0.790	25.478	32.917	97.599	2.401

Yardney 25 Ah Lithium-Ion Cells for Mars Lander Applications

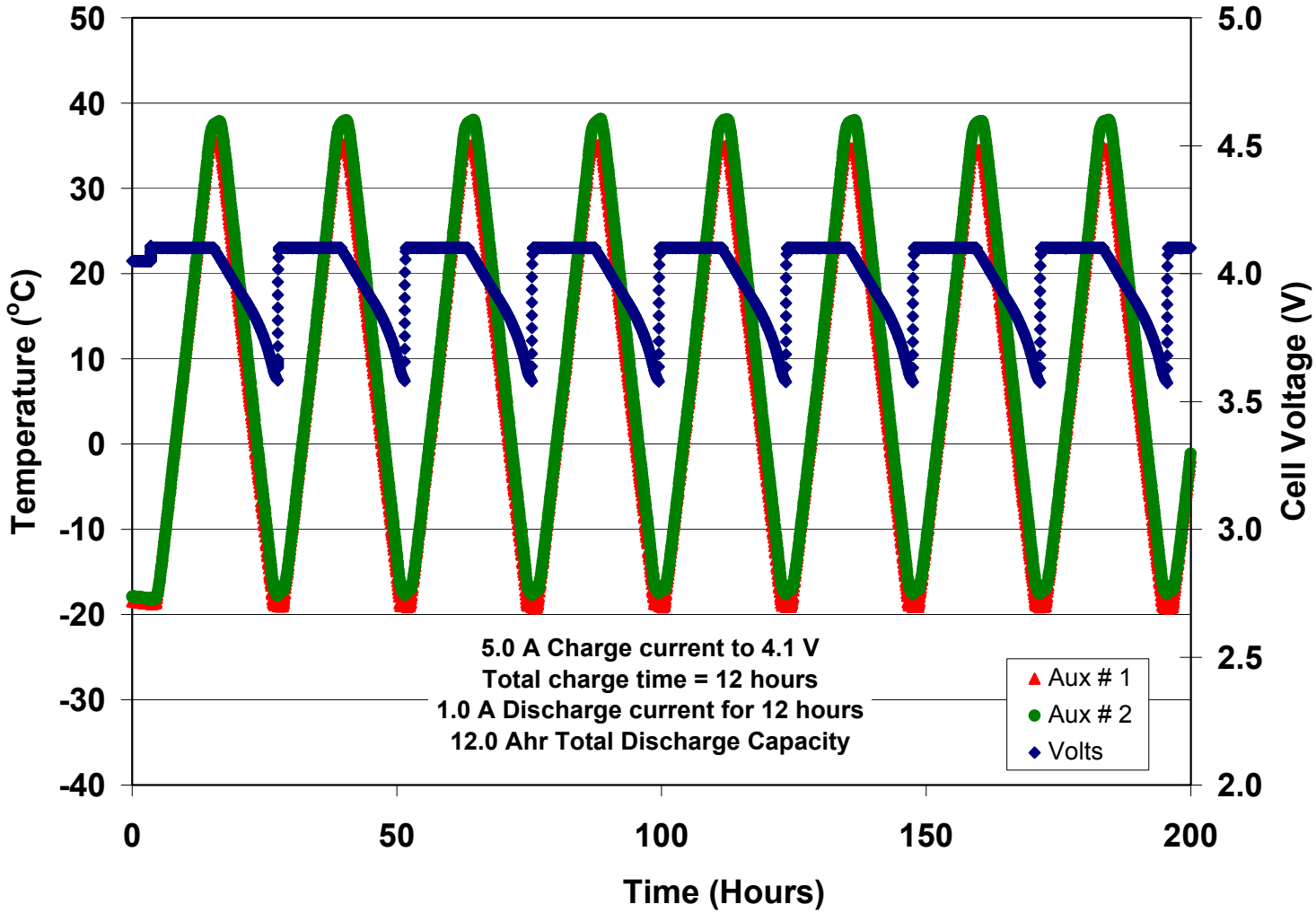
EDL Discharge Profile Simulation of MSP01 Design Cells



- Cells capable of supporting EDL load profile – Including 50 A (2C) pulses
  - Cells also display good uniformity after prolonged storage period

Lithium-Ion Cells for Mars Lander Applications

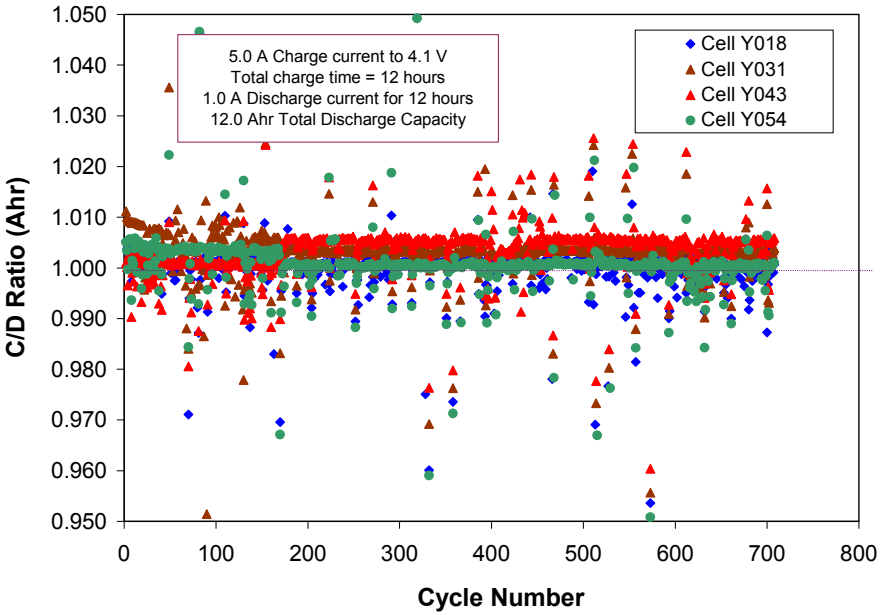
Mission Simulation Cycling (Temperature Range = - 20 to +40°C)



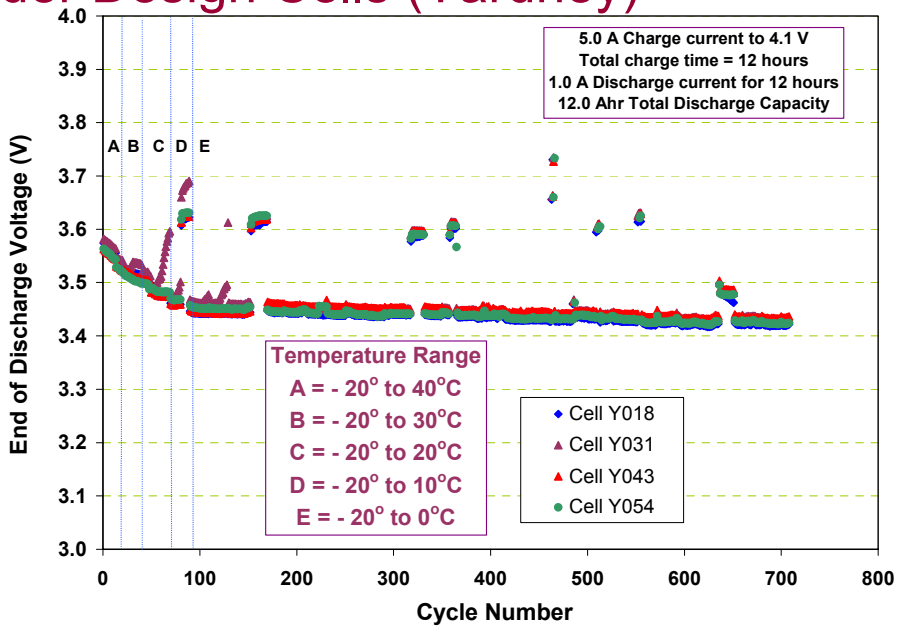
Lithium Ion Technology Demonstration for Future Smart Lander Missions

Lander Surface Operation Mission Simulation Performance Test

2001 MSP01 Surveyor Lander Design Cells (Yardney)



Charge-Discharge Ratio (AHr)



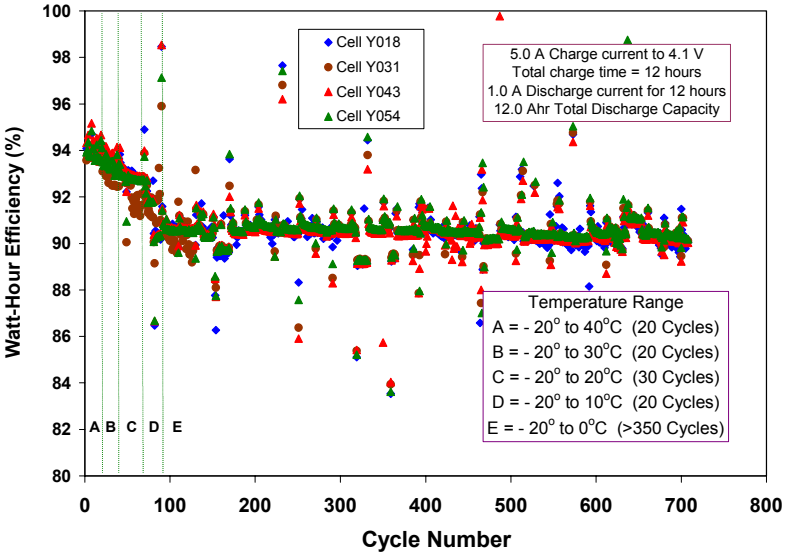
End of Discharge Voltage (EODV)

- **Minimal performance degradation observed with cells to-date.**
- **Stable performance observed (constant C/D ratio)**
- **Excellent reproducibility of cell performance observed:**
  Only 15 mV spread among 4 cells observed for the end of discharge voltage EODV
- **The coldest temperature range (-20° to 0°C) appears to be the least detrimental to cell health (< 25 mV decline in EODV observed over last 500 cycles)**
- **Cells projected to be capable of providing > 1000 cycles (EODV > 3.0V/cell)**

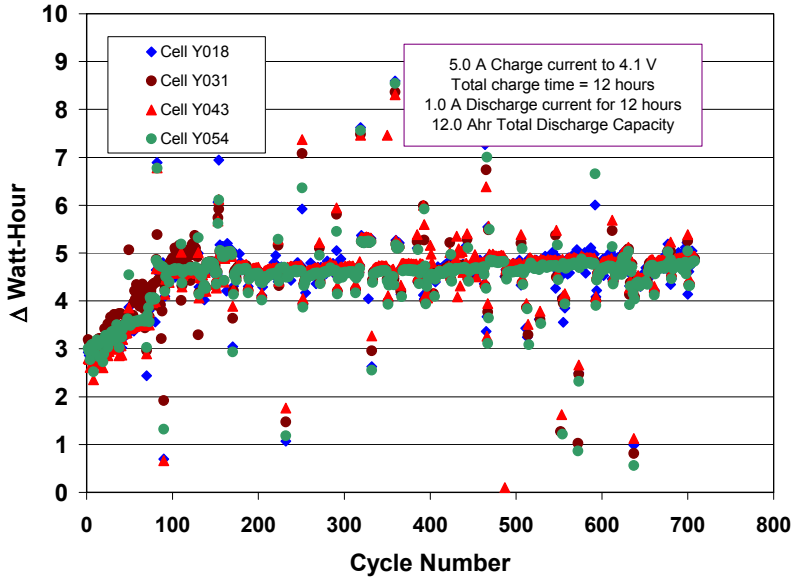
Lithium Ion Technology Demonstration for Future Smart Lander Missions

Lander Surface Operation Mission Simulation Performance Test

2001 MSP01 Surveyor Lander Design Cells (Yardney)



Watt-Hour Efficiency



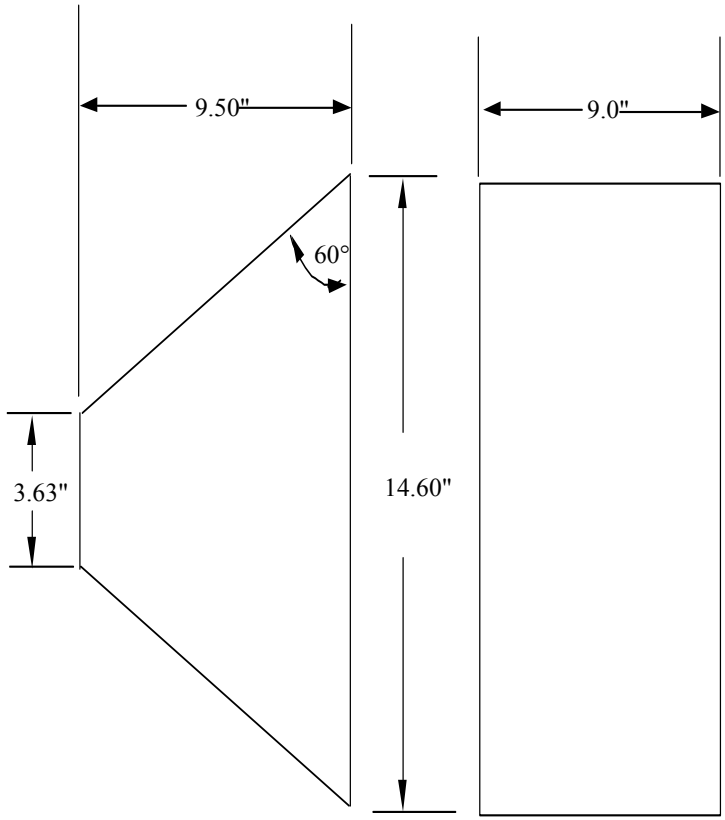
Δ Watt-Hour

- **Impedance growth appears to be minimized at the colder temperature range (-20° to 0°C)**
- **Cycling in the coldest temperature range (-20° to 0°C) results in minimal change to energy efficiency observed**
- **Long life (> 1000 cycles (EODV > 3.0V/cell)) under these conditions seems probable, providing minimal high temperature excursions.**

MSP 2001 Lander Battery

- Two 25 Ah, 8-Cell Li Ion Batteries (N+1)
- Individual Cell Monitoring and control via Cell Bypass Unit (CBU) to prevent overcharge
- Individual Charge Control Unit (CCU).
- Constant Voltage Charging at - 32.8 Vdc.
- 16 Selectable V/T curves.
- Amp Hour Integration.

Battery Envelope



Test Plan for the MSP01 Lithium-Ion Battery :

Testing Methodology

- Test Setup
  - Ensure Electrical Isolation (Cell/battery/chamber)
  - 25 Ahr 8-cell battery (24-34.4 V)

- Charge Control
  - 25 Ahr 8-cell battery (24-34.4 V)
  - Battery voltage controlled charging
  - Constant current and constant potential charging
  - Individual cell monitoring
  - Battery protection limits
    - Individual cell voltage exceeded (> 4.2 V)
    - Individual cell voltage exceeded (< 2.5 V)
    - Temperature limits exceeded (> 50°C for any input)
    - Charge/discharge capacity limit (>35 Ahr)
    - Step time (> 10 hours)
  - Battery cell balancing methodology
    (i.e., resistively discharging cells to 2.5V)

Test Plan for the MSP01 Lithium-Ion Battery :

2009 Lander Mission Simulation Testing Plan

1.0 Receiving and Inspection

- Measure battery voltage and inividual cell voltages and Impedance.
- Ensure electrical isolation (Case)

2.0 Initial Electrical Performance Characterization

- Implement cell balancing protocol : Resistively discharge each cell to 3.0 V (1 Ohm)
- 3 cycles at 20°C
  - C/5 charge rate (5 amps) to 32.8 V (8 x 4.1 = 32.8)
  - Constant potential charge to current taper cut-off (0.50 A)
  - C/5 discharge rate to 24 V (or first cell to reach 3.0V)
  - One cycle battery will be charged to 32.0 V (4.0V / cell)
- 3 cycles at 0°C (repeat testing as above)
- 3 cycles at - 20°C (C/10 charge rate (0.10 A taper cut-off)

3.0 Cruise Storage Test (10-12 Months)

- Store battery on bus with a clamp voltage of 30.40 V
  (3.8 V x 8 = 30.40 V) (~ 70 % SOC)
- Store battery at 10°C
- Record individual cell voltages

Test Plan for the MSP01 Lithium-Ion Battery :

2009 Lander Mission Simulation Testing Plan

4.0 EDL Pulse Capability Test

- Discharge battery using C/5 discharge rate to 24 V
- Cycle battery 3 times at 20°C (determination of storage impact)
- Charge battery using C/5 discharge rate to 32.8 V
- Soak battery for 24 hours at 0°C
- Initiate EDL pulse profile
  - 14 Amps (2 minutes)
  - 8 Amps (7 minutes)
  - 20 Amps (4 minutes)
  - 50 Amps (30 over baseline 20) (100 mSec)
- Discharge battery using C/5 discharge rate to 24 V

5.0 Electrical Performance Characterization

- Same as section 2.0

6.0 Mission Simulation Cycling (In Progress)

- Discharge battery using C/5 discharge rate to 24 V (optional cell balancing)
- Charge battery using C/5 discharge rate to 32.8 V (4.1V per cell)
- Program chamber to run variable temperature profile (see charts)
- Charge battery using C/5 discharge rate (5 A) to 32.4 V (4.05 V per cell)
- Total charge time 12 hours (extended taper)
- Discharge battery using C/25 rate (1A) for 12 hours

7.0 Electrical Performance Characterization

- Same as section 2.0

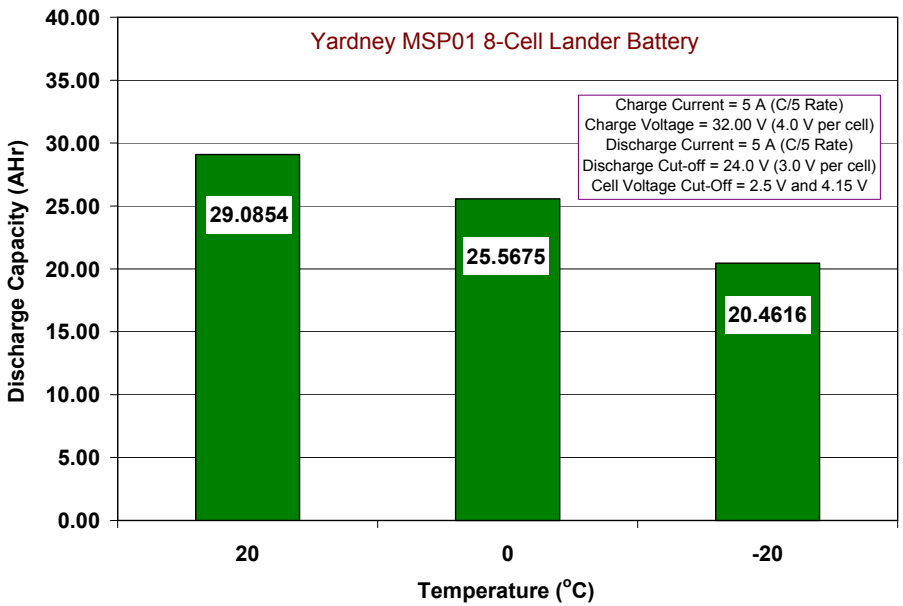
8.0 Post Mission Characterization

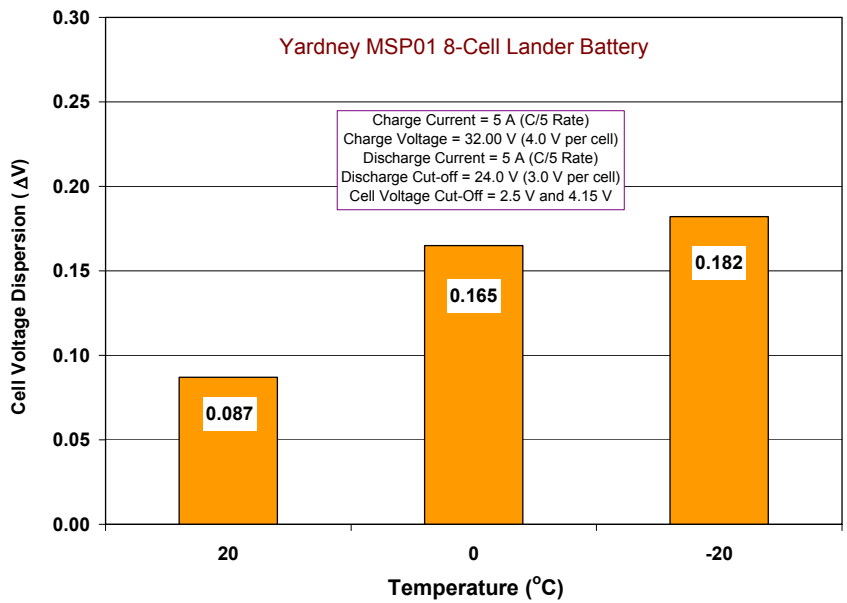
- More detailed pulse characterization
- More detailed rate characterization as a function of temperature

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Initial Characterization/Conditioning at Different Temperatures

32.0 V Charge - Discharge Capacity (AHr) at Various Temperatures





Discharge Capacity (AHr)

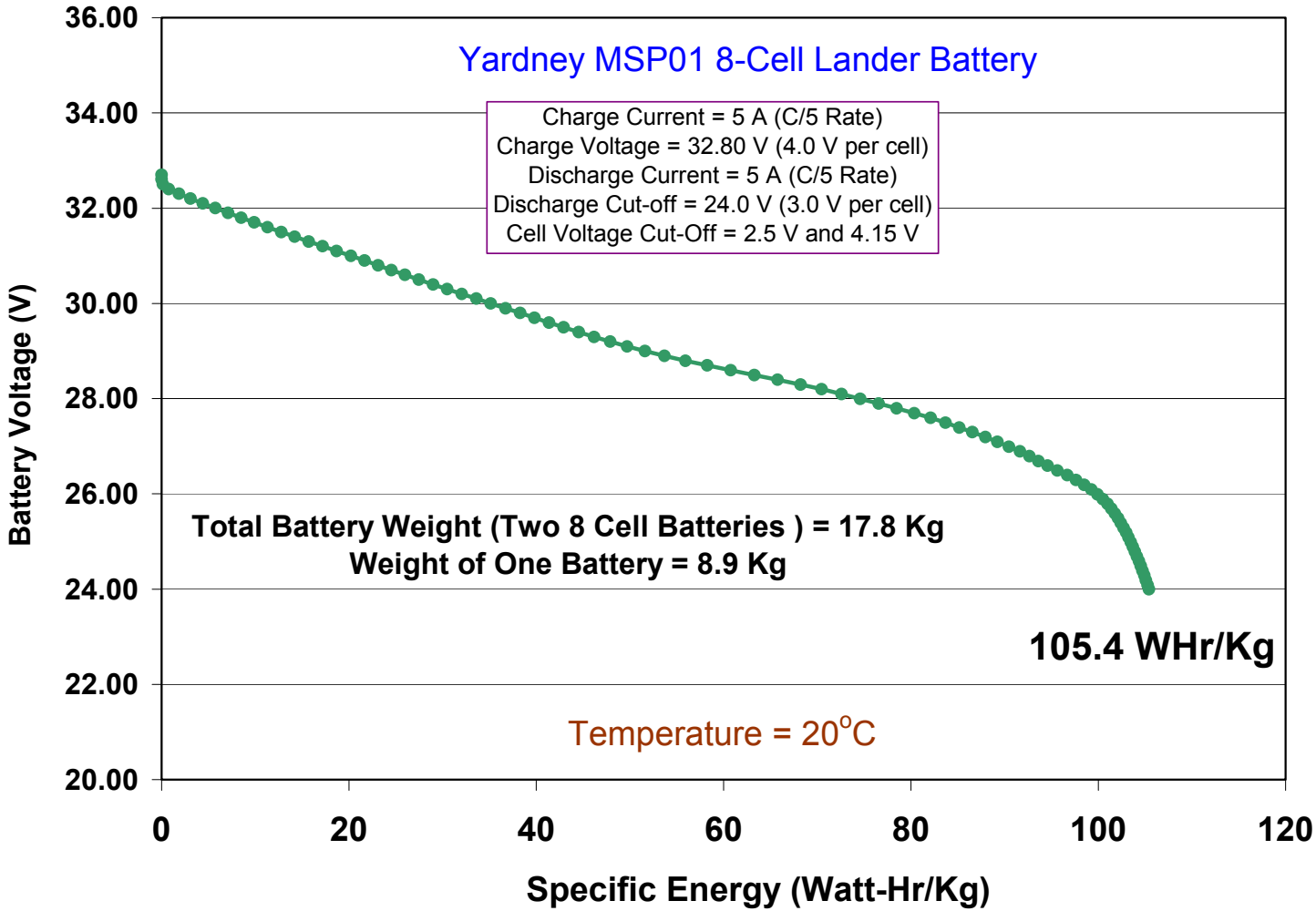
Cell Voltage Dispersion (ΔV)

- Battery capacity at different temperatures determined
- Capacity determined after cell balancing
- Greater cell voltage dispersion observed at lower temperature

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Initial Characterization/Conditioning at 20°C

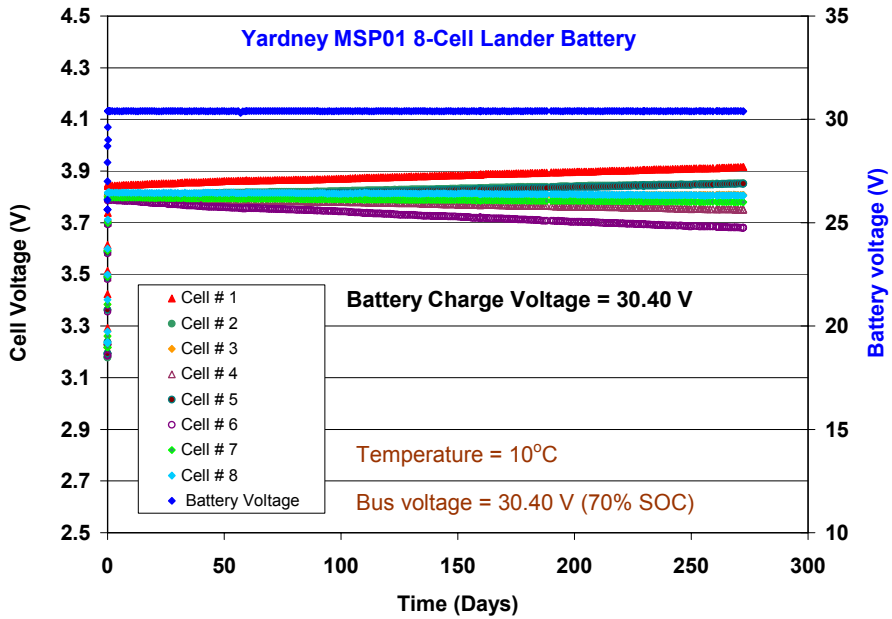
After Cell Balancing – 32.8 V Charge

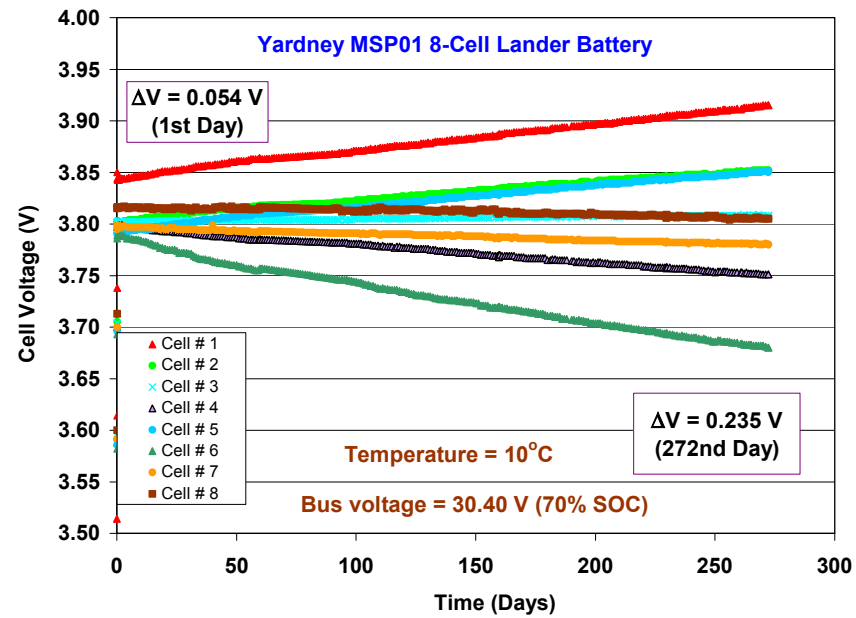


Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Cruise Storage Simulation (Bus Voltage = 30.40 V at 10°C)

Battery and Cell Voltages During Storage (~ 9 months)



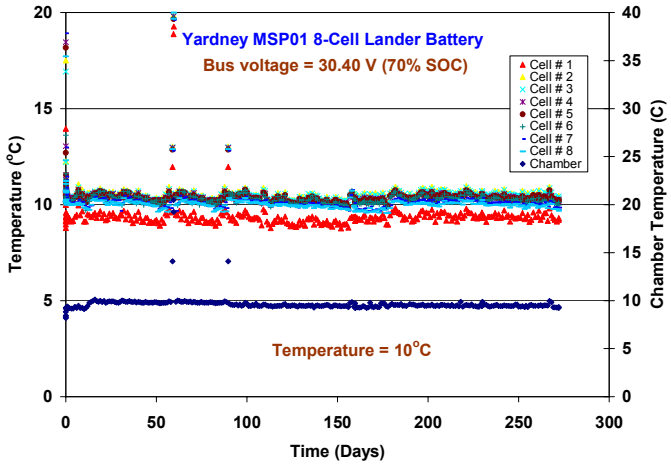


- Cells balanced prior to storage test
- Cell dispersion potential issue depending upon charge methodology

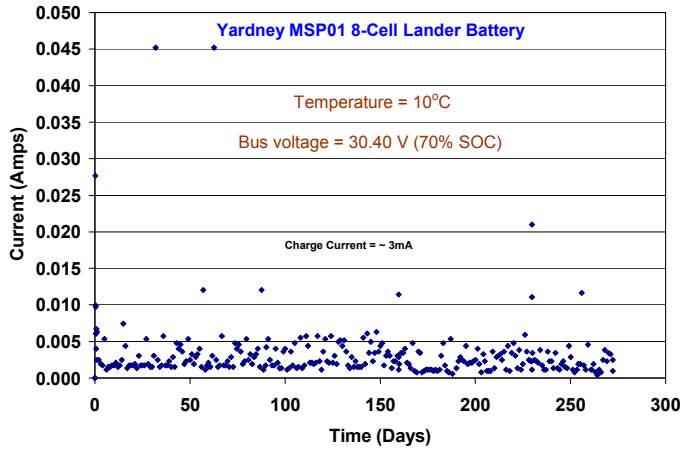
Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Cruise Storage Simulation (Bus Voltage = 30.40 V at 10°C)

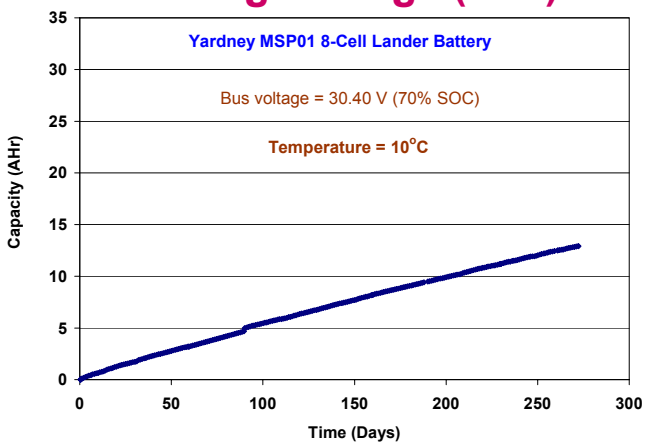
Cell and Chamber Temperatures (°C)



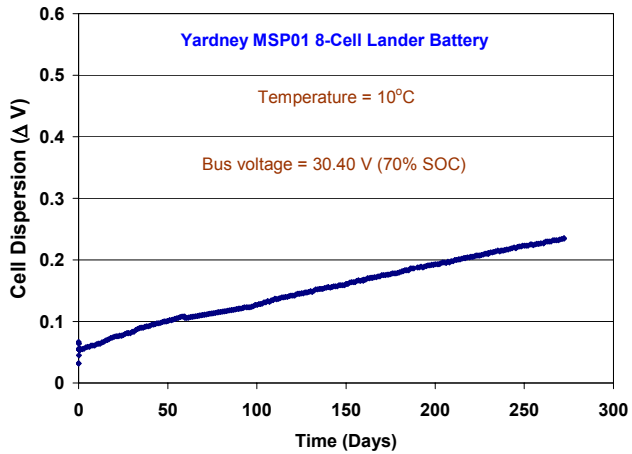
Charge current (A)



Cumulative Charge Capacity During Storage (AHr)



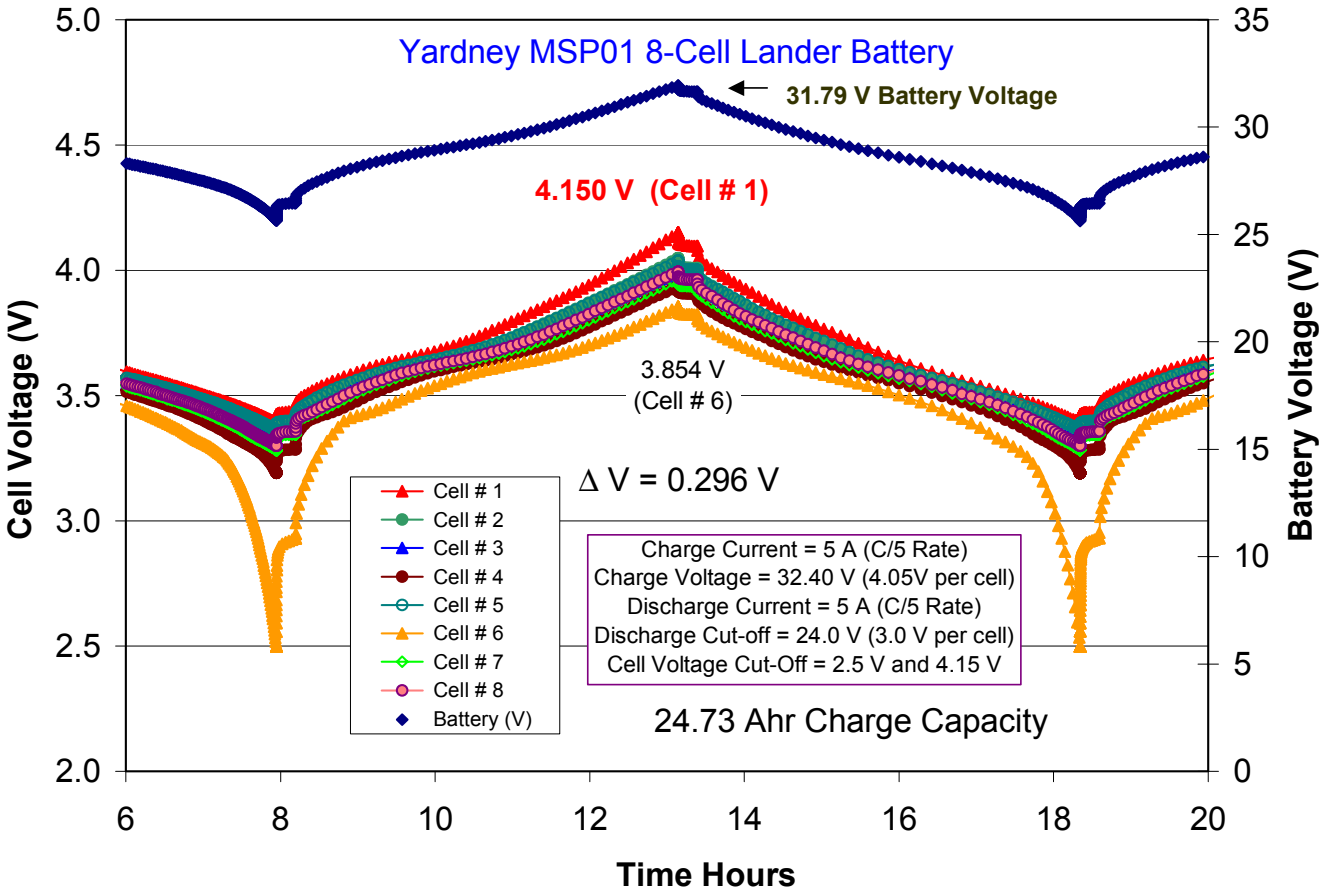
Cell Dispersion During Storage (ΔV)



Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Performance Characterization After Cruise (32.00 V at 20°C)

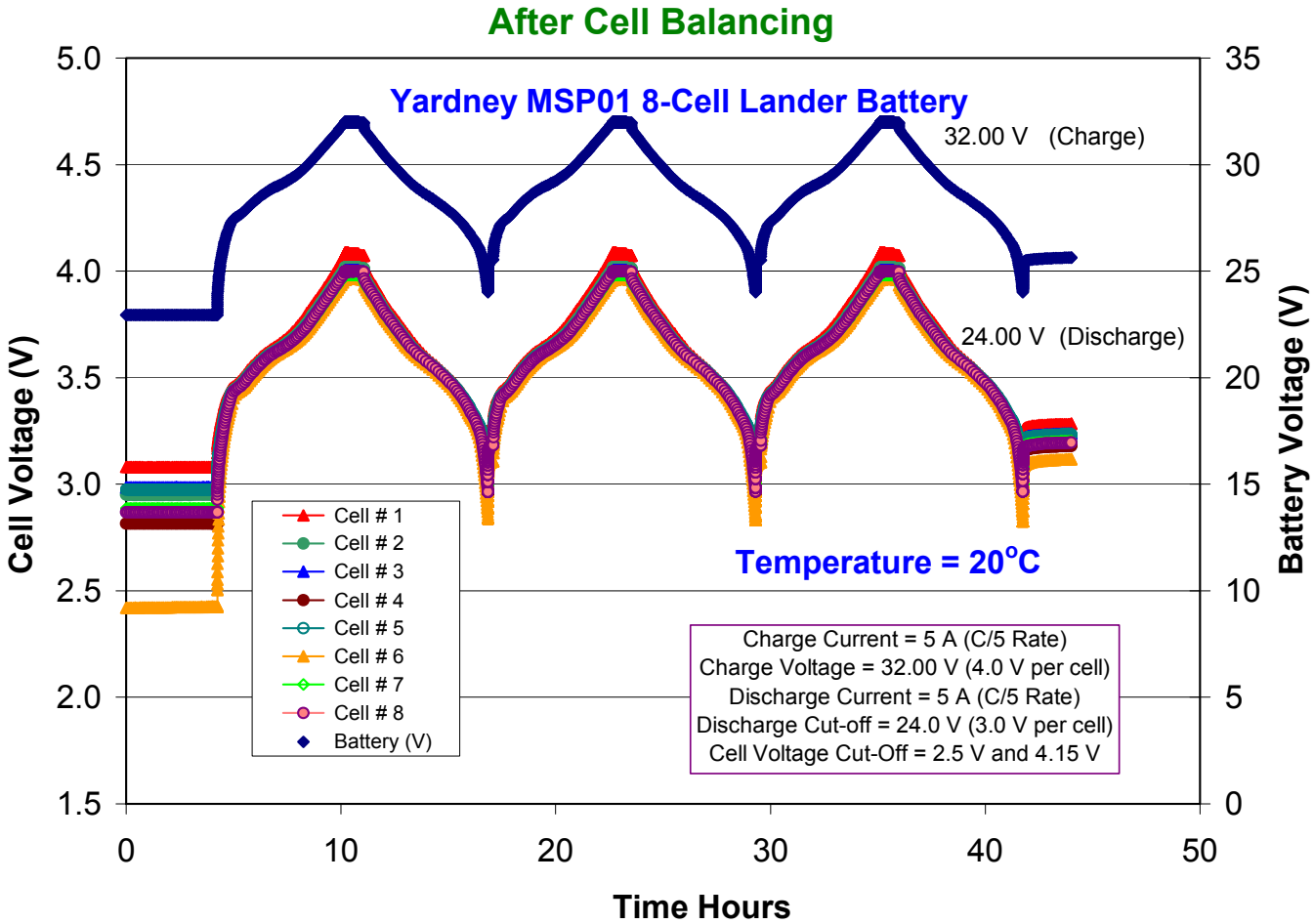
Cycling Characteristics After Storage (Temperature 20°C) – No Cell Balancing After Cruise



- Due to cell imbalance, battery was not fully charged after storage (24.73 AHr)
- Cell #1 terminated charge prior to reaching 32.40 V battery charge voltage

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Performance Characterization After Cruise (32.00 V at 20°C)

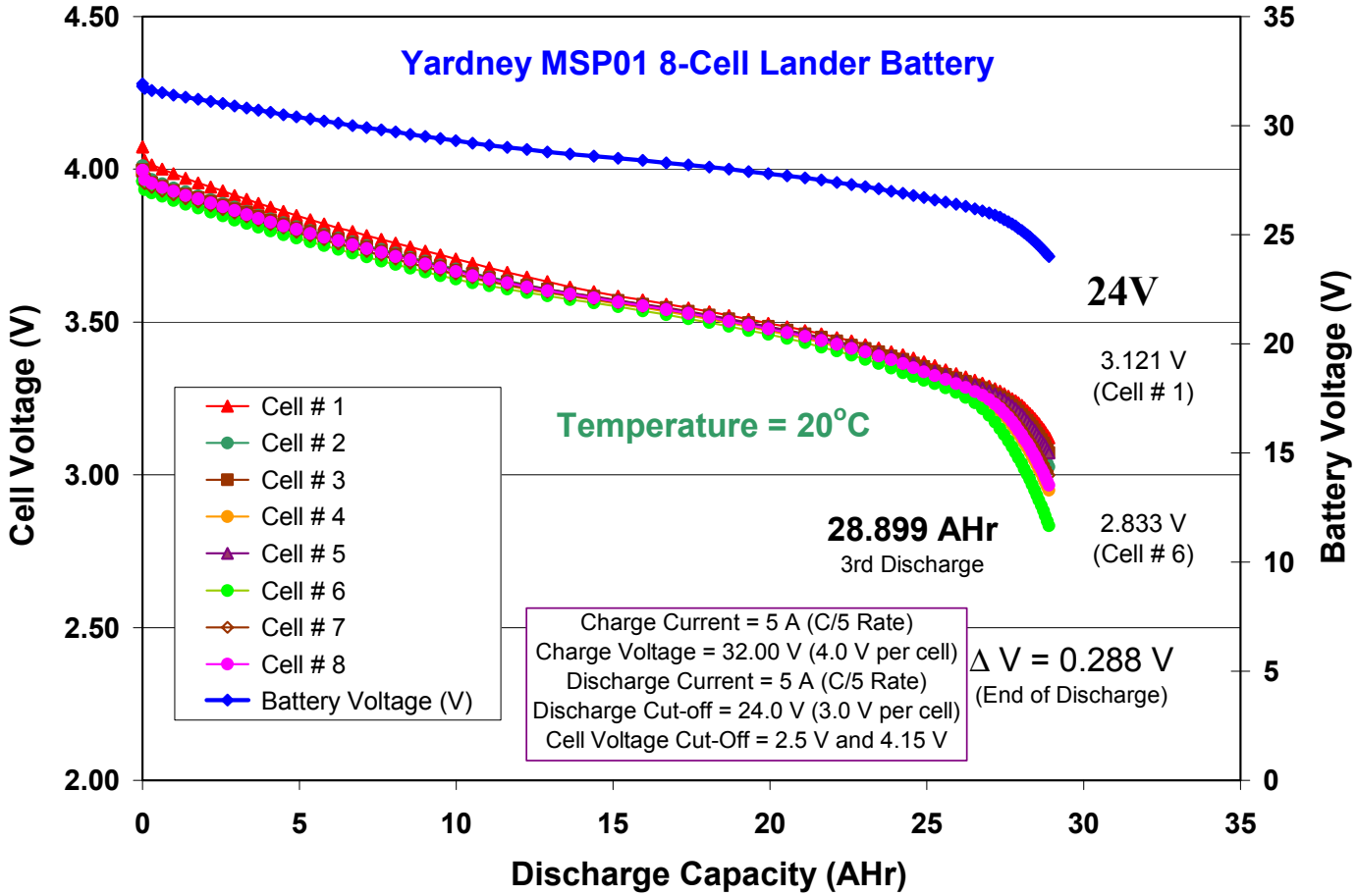


- After cell balancing cell dispersion characteristics were improved.

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Performance Characterization After Cruise (32.00 V at 20°C)

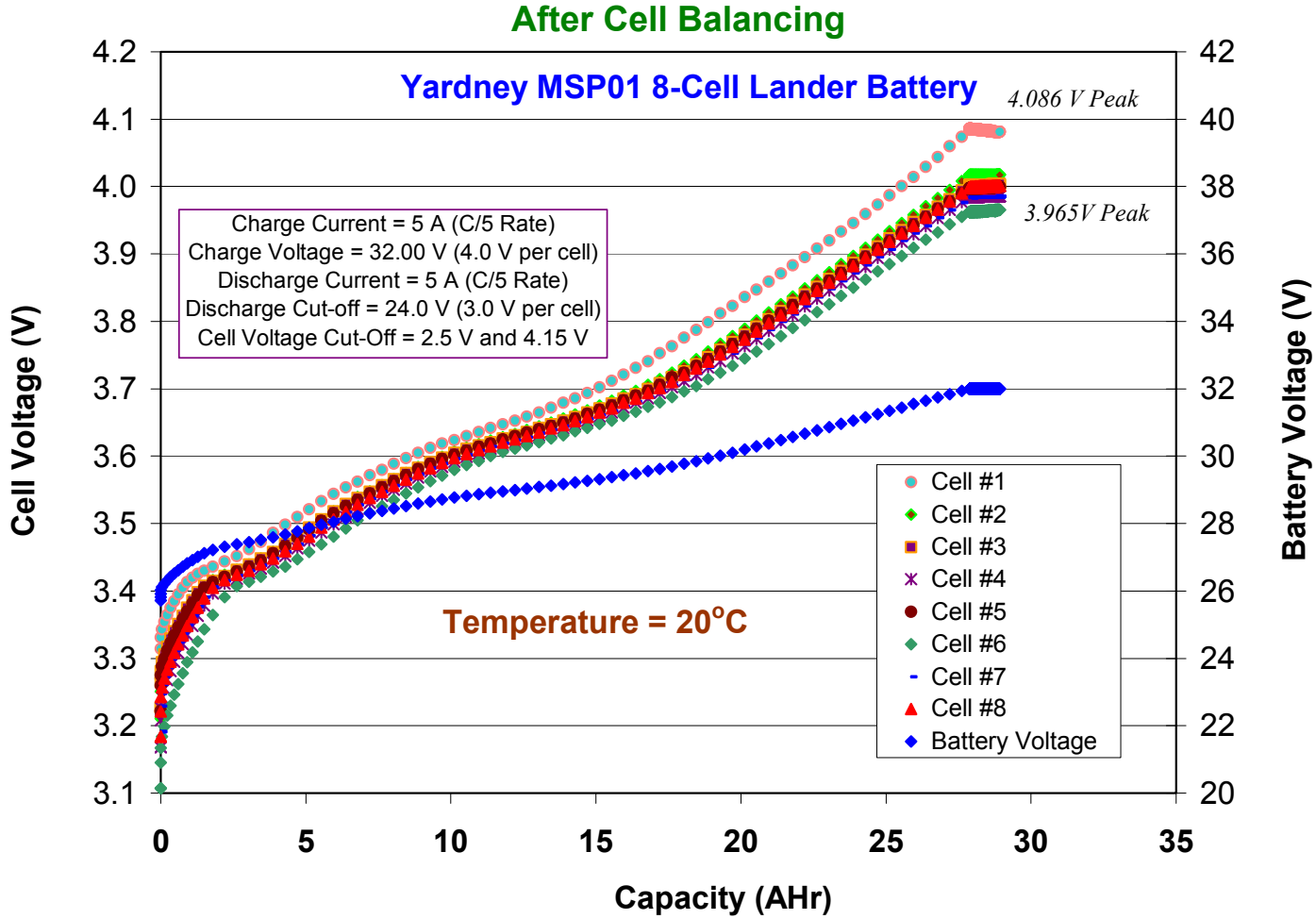
After Cell Balancing



- After cell balancing, battery was able to be cycled effectively between prescribed voltage limits (24V – 32V)
- 28.90 Ahr delivered at 20°C (32.0 V Charge or 4.00V/cell)

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Performance Characterization After Cruise (32.00 V at 20°C)

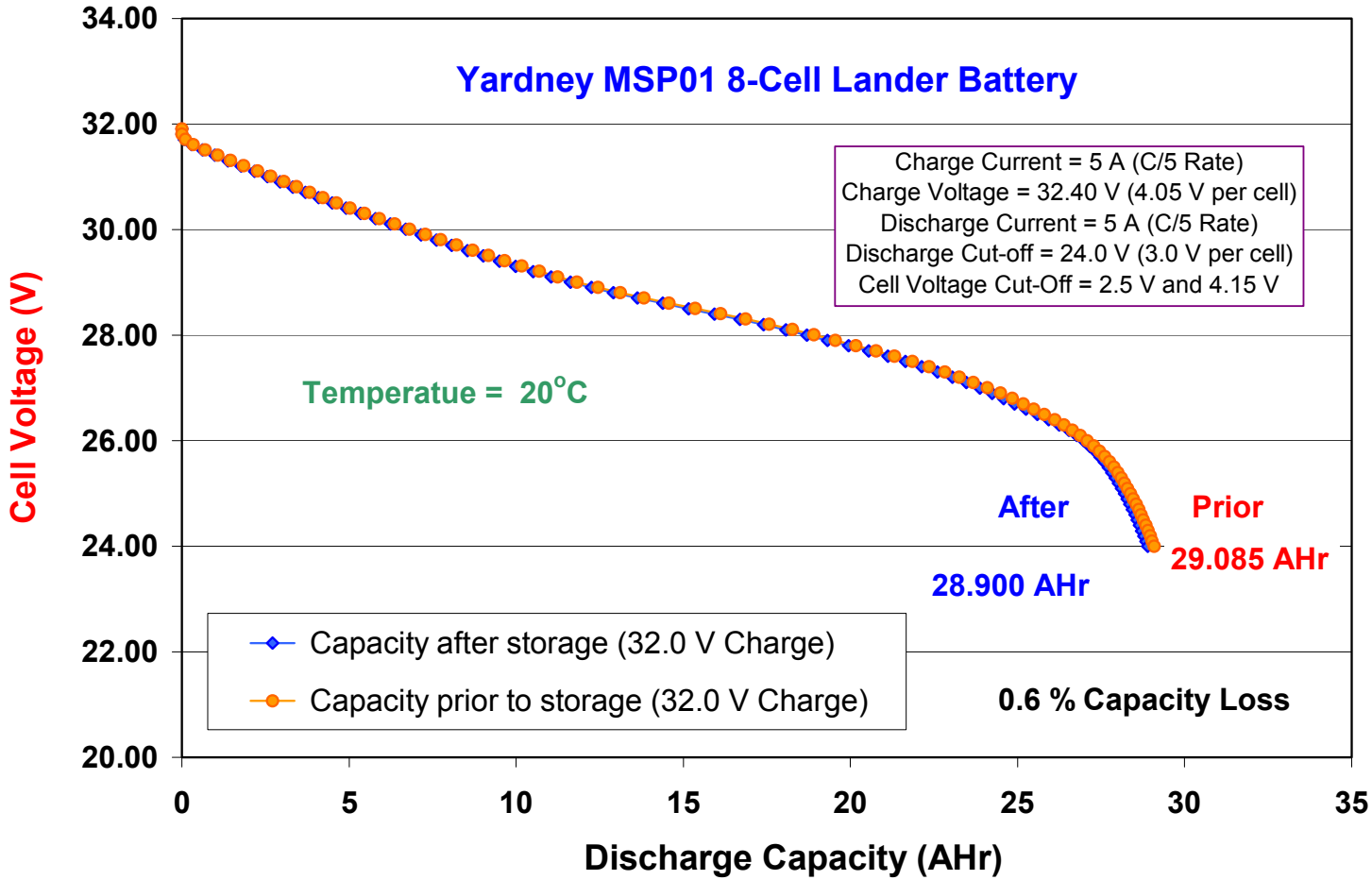


- Tighter cell dispersion after balancing cells (cell #1 and cell #6 still somewhat divergent)
  - 28.99 Ahr charged at 20°C (32.0 V Charge or 4.00V/cell)

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Performance Characterization After Cruise (32.00 V Charge)

After Cell Balancing

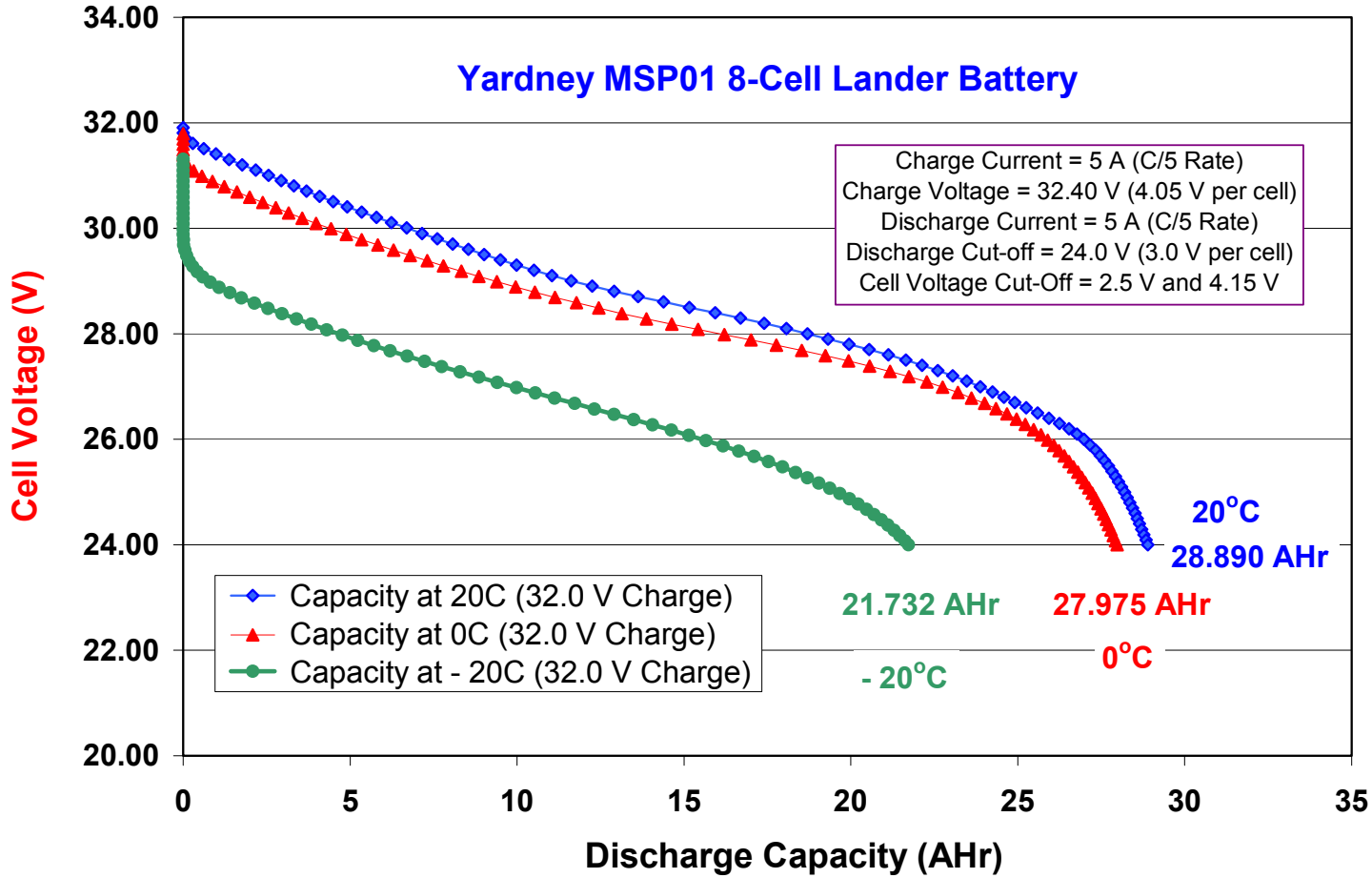


- Very little capacity loss observed due to the cruise storage period

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Performance Characterization After Cruise (32.00 V Charge)

After Cell Balancing

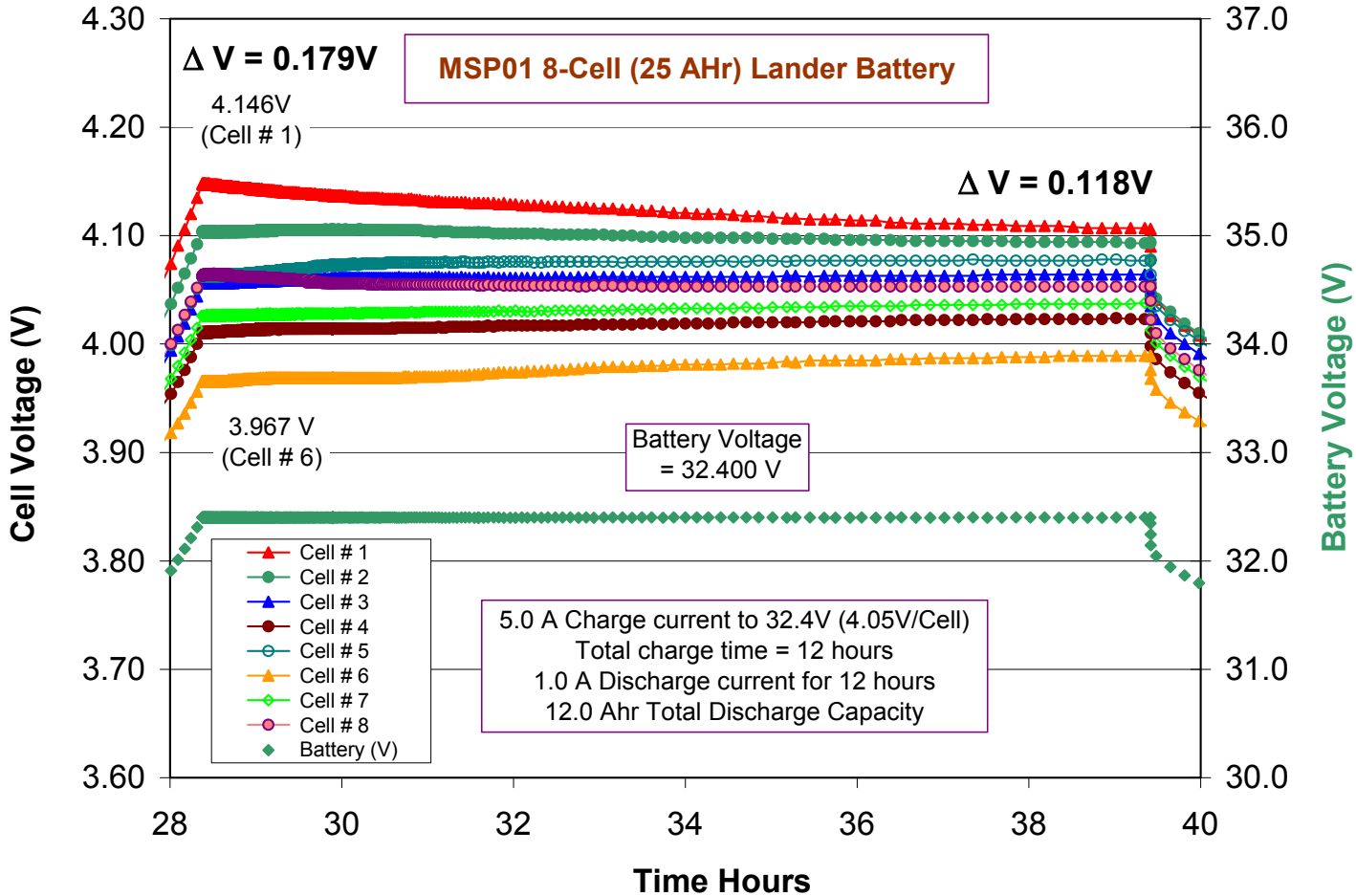


- Much higher capacities observed after cell balancing.

Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Mars Surface Operation Mission Simulation Test (MSP01 Profile)

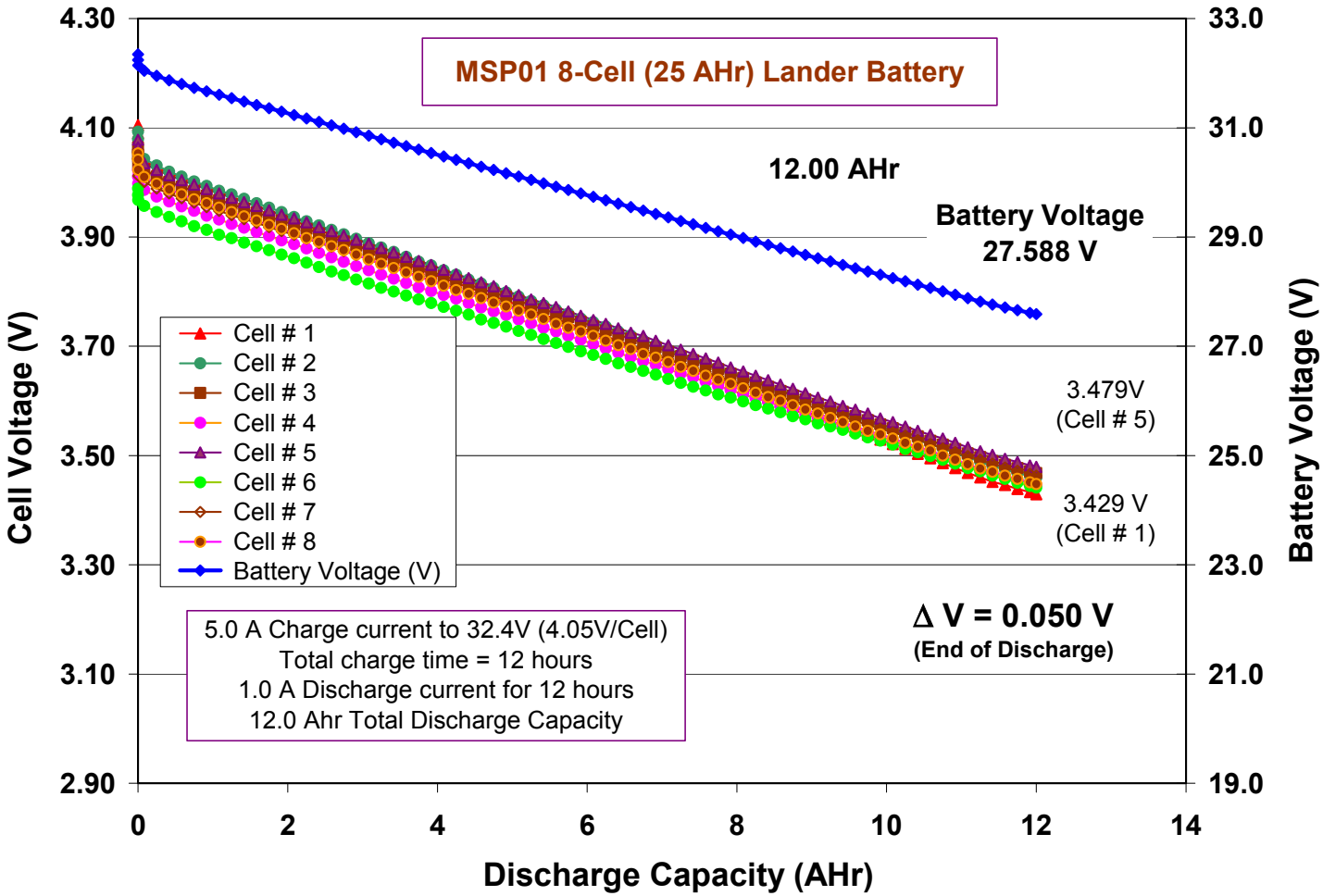
1st Full Charge (32.4 V Charge) – Cell Dispersion Characteristics



Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Mars Surface Operation Mission Simulation Test (MSP01 Profile)

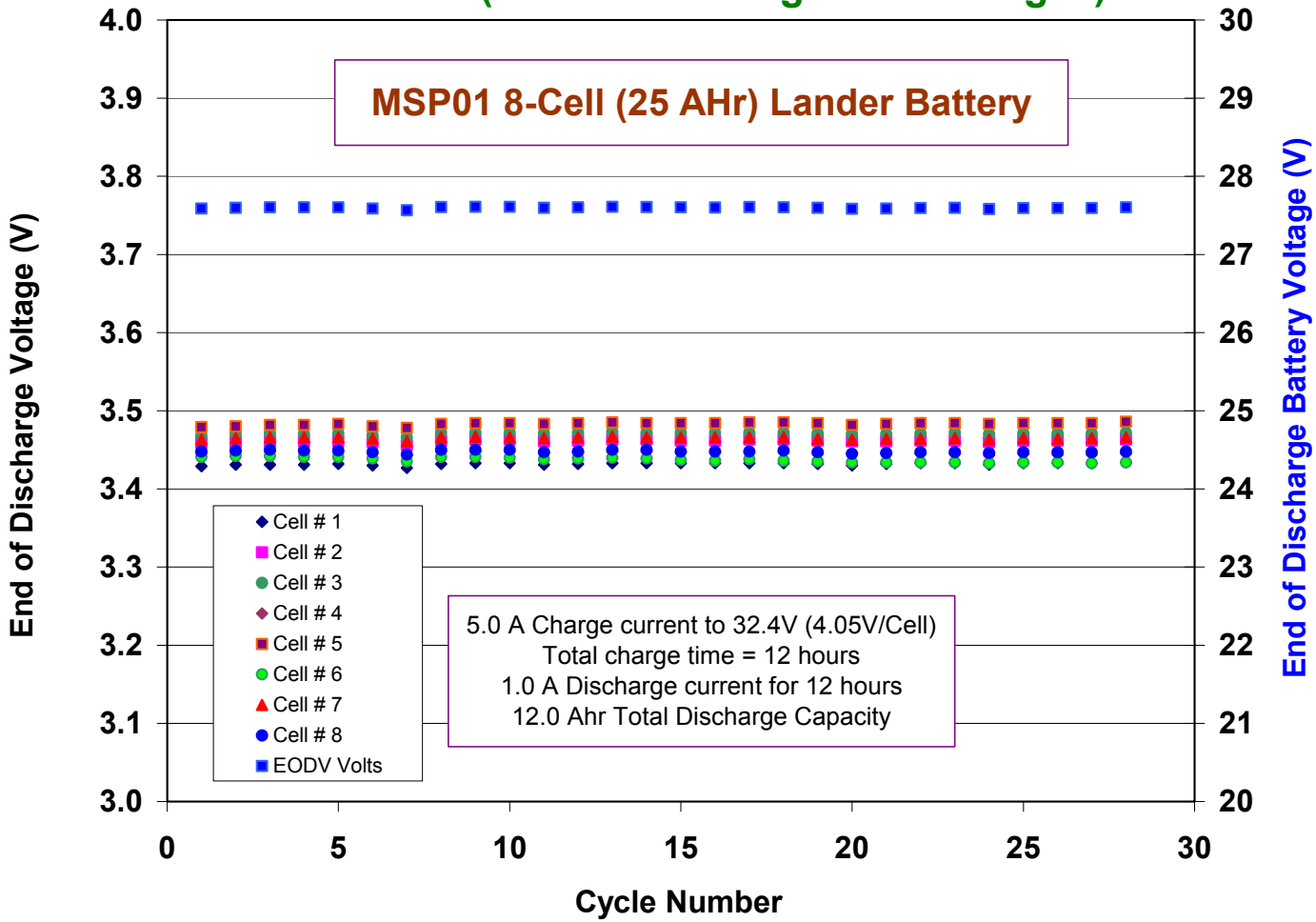
Typical Discharge (12 AHr – C/25 Rate)



Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Initial Characterization/Conditioning at Different Temperatures

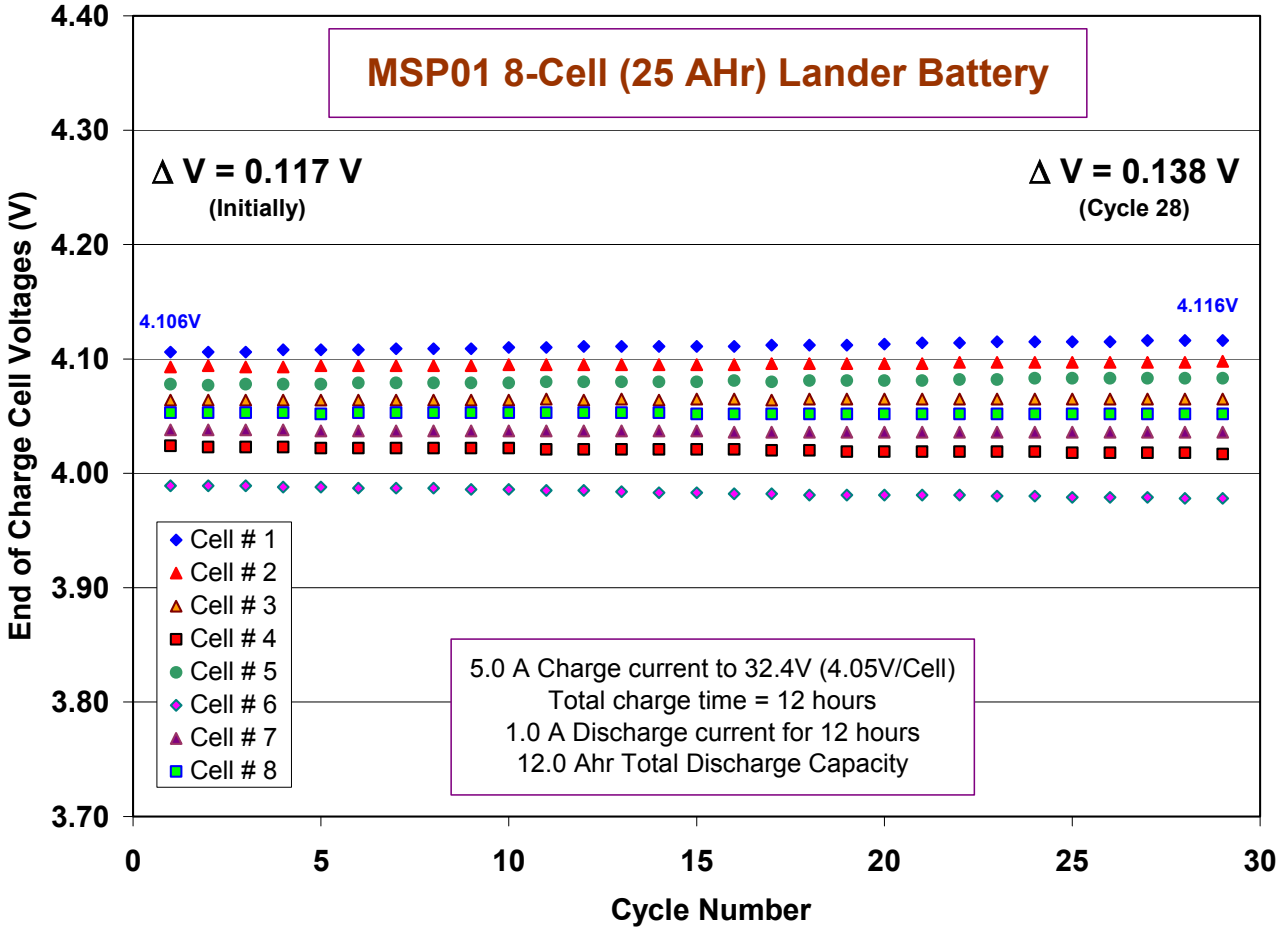
First 28 Sols (End of Discharge Cell Voltages)



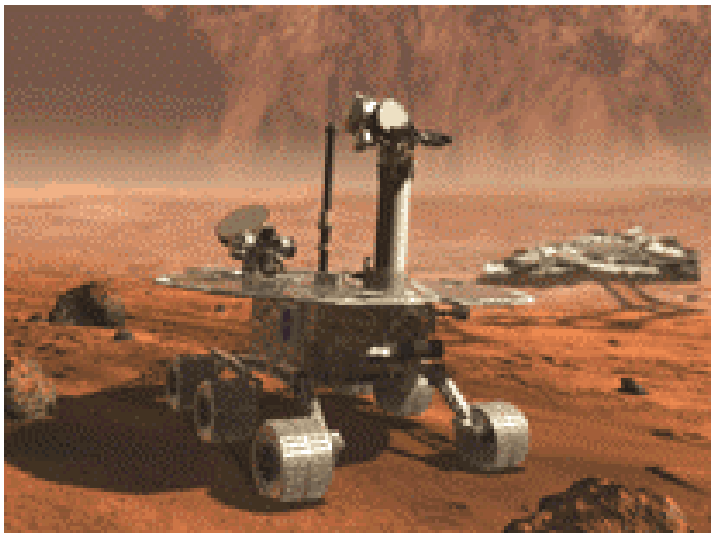
Yardney MSP01 25 Ah Lithium-Ion Battery for Mars Lander Applications

Initial Characterization/Conditioning at Different Temperatures

First 28 Sols (End of Charge Cell Voltages)



2003 MARS Exploration Rover Secondary Battery



• Rover Battery intended to support launch, cruise anomalies, and Mars surface operations

Battery Description

- Rechargeable system: Lithium-ion
- Good low temperature performance
- Demonstrated storage capability
- High specific energy > 100 Wh/kg
- Configuration: Prismatic
- Excellent performance data base
- Two parallel strings each with 8 cells
- Vendor : Yardney Tech. Prod., Inc.

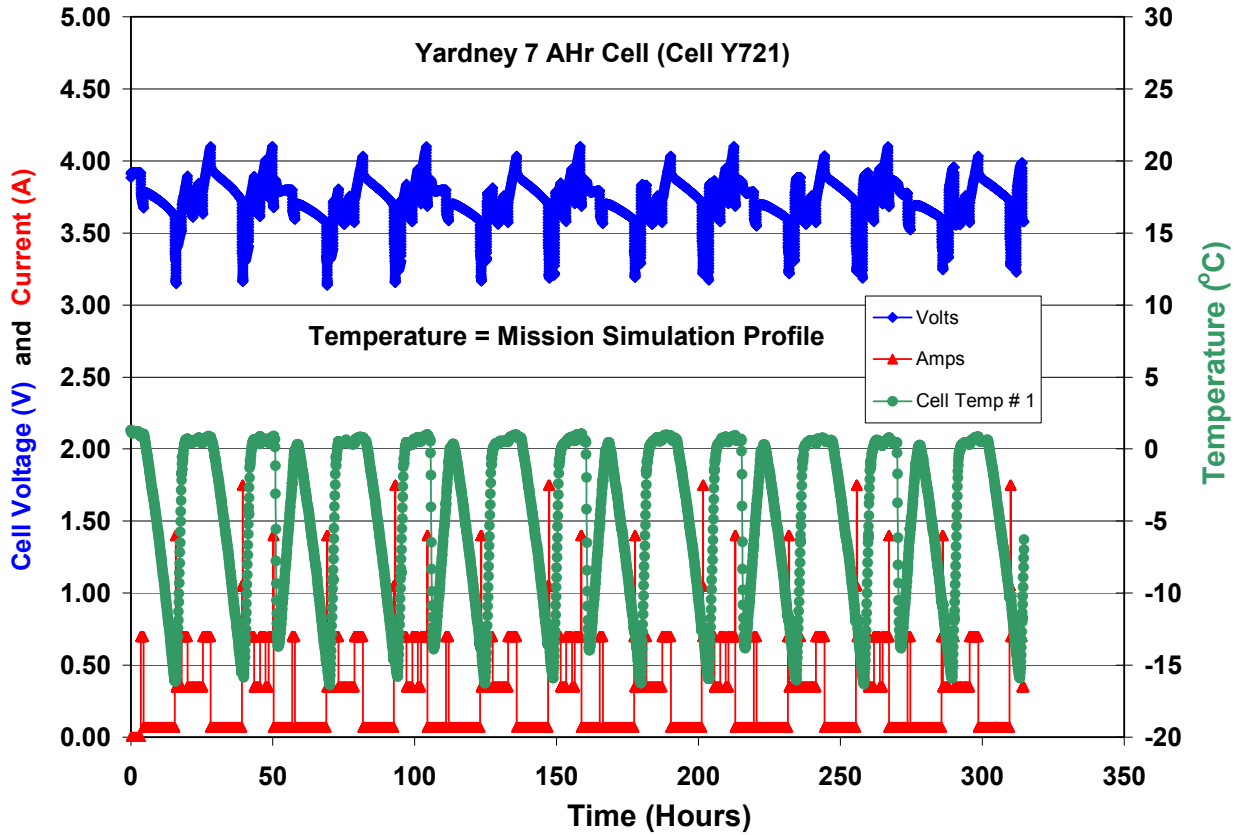
Mission Requirements

- Voltage : 32-24 V
- Capacity: 16 Ah (BOL) at RT and 10 Ah at –20°C (BOL)
- Load : C/2 max at RT; Typical C/5
- Temperature : Charge at 0-25°C and discharge >-20°C
- Light weight and compact
- Long cycle life of over 300 cycles
- Long storage life of over 2 years

Yardney Lithium-Ion Cells for Mars Rover Applications

Mission Simulation of Mars Surface Operations

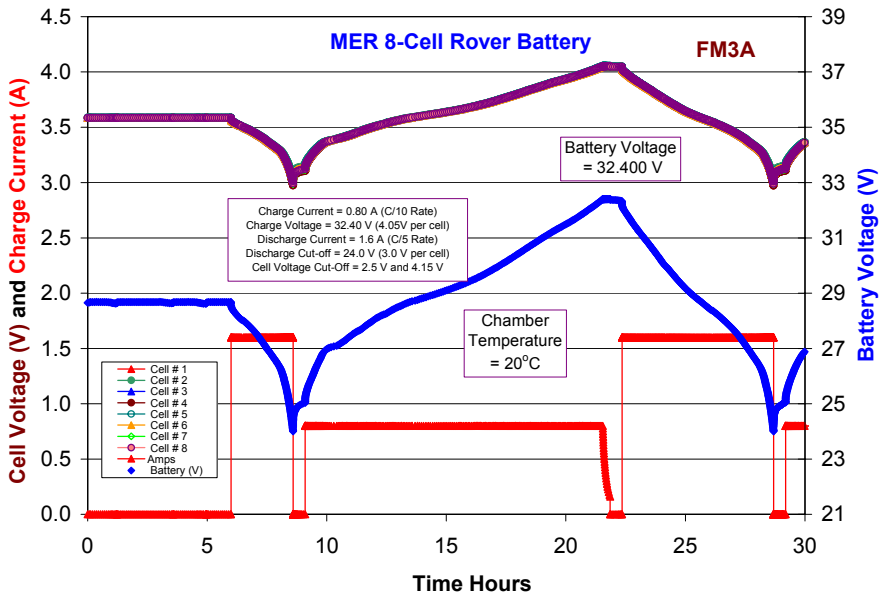
Mission Simulation Temperature Profile



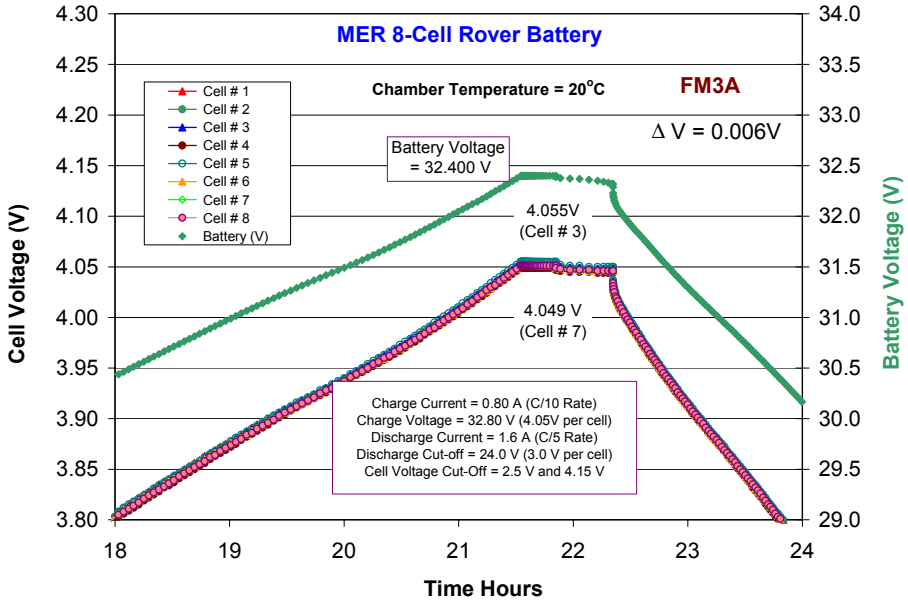
- Environmental temperature range = 0 to –20°C
- Battery will be charged by solar array during the daytime (~ 0°C charge)
- Data represents first 8 sols of operation on the surface of Mars

MER 10 Ah Rover Lithium-Ion Battery (FM3A)
Initial Characterization/Conditioning at 20°C

Battery/Cell Voltage and Current



Cell Dispersion During Charge

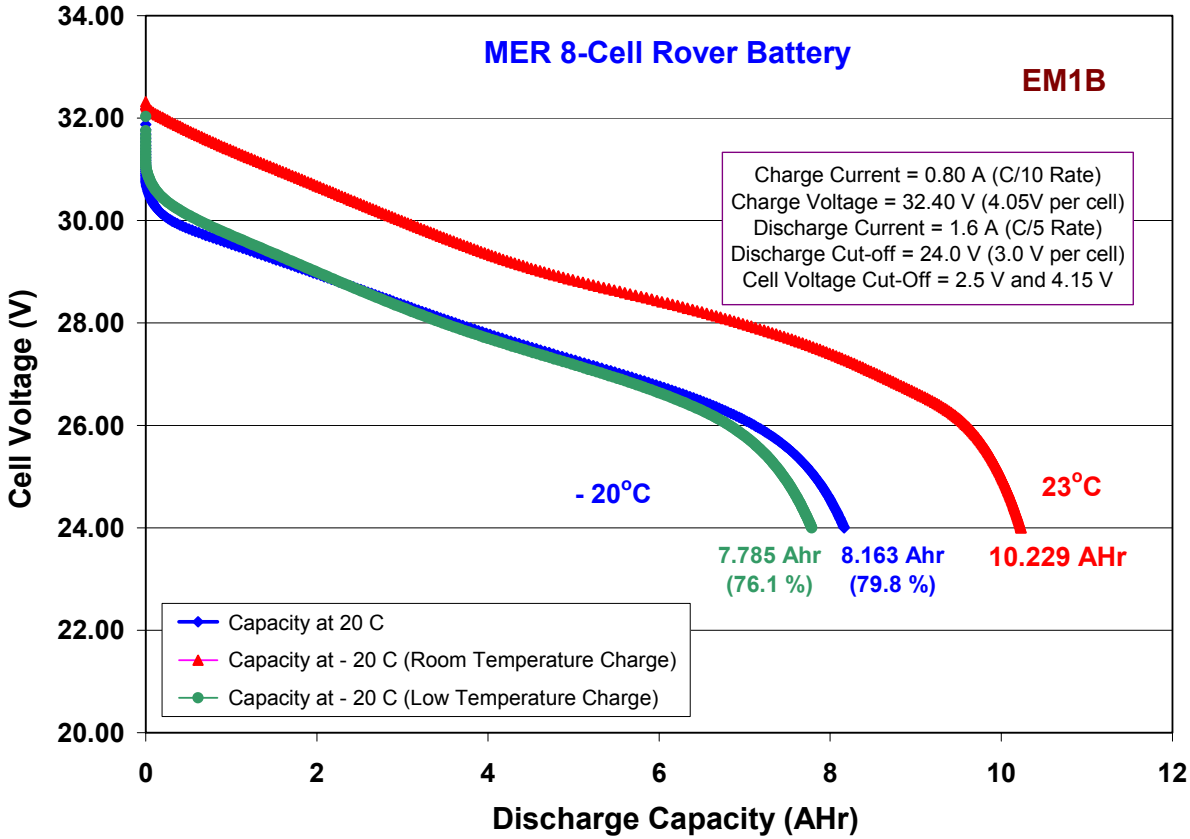


- **Conditioning cycles performed at various temperatures (20, 0, and –20°C) (C/10 charge-C/5 discharge)**
- **Minimal cell dispersion observed at the battery level (< 25 mV)**

MER 8 Ah Rover Lithium-Ion Battery (EM1B)

Initial Characterization/Conditioning Tests

Discharge Capacity at Different Temperatures

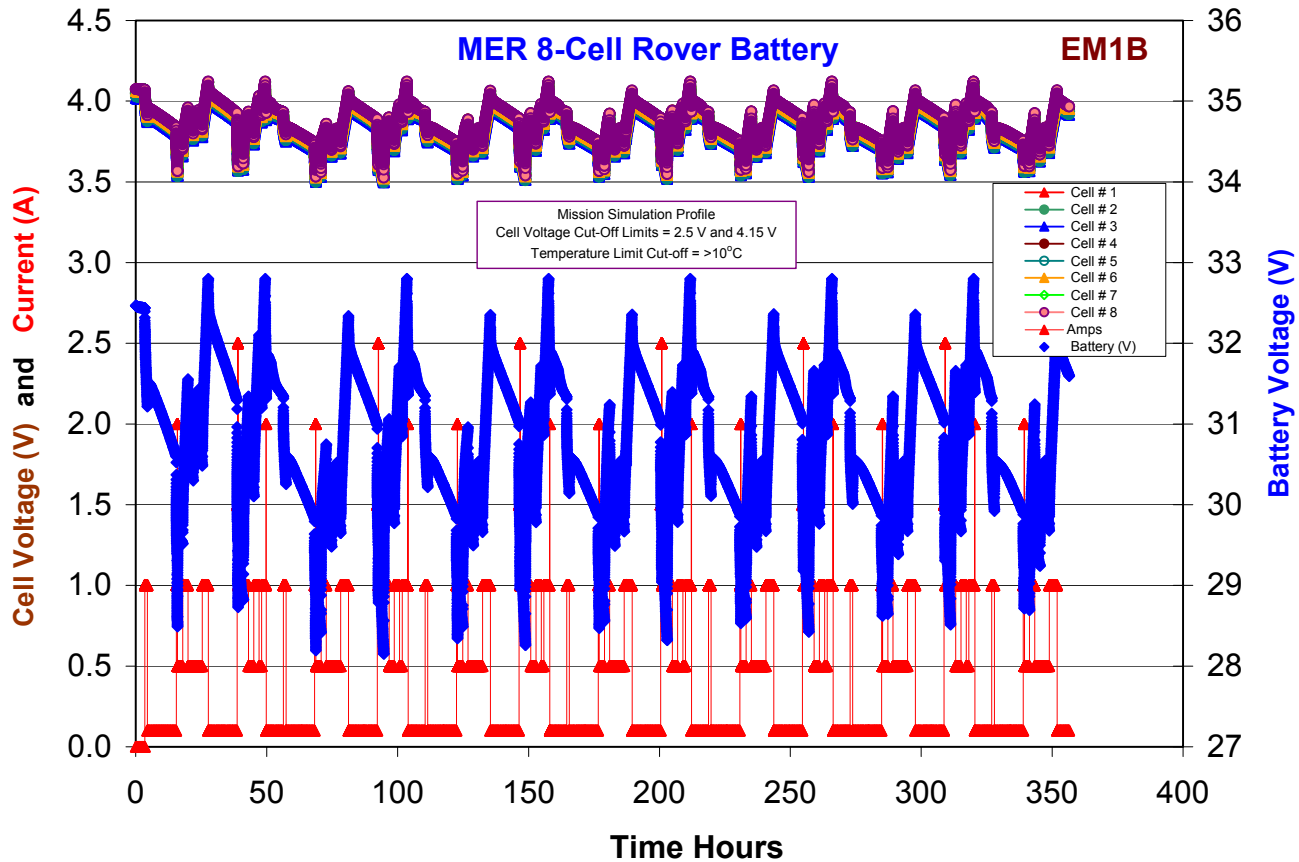


- Good low temperature performance observed at the battery level
- Over 75% of the room temperature capacity delivered at –20°C (C/5 rate)

MER 8 Ah Rover Lithium-Ion Battery (EM1B)

Mission Simulation Testing

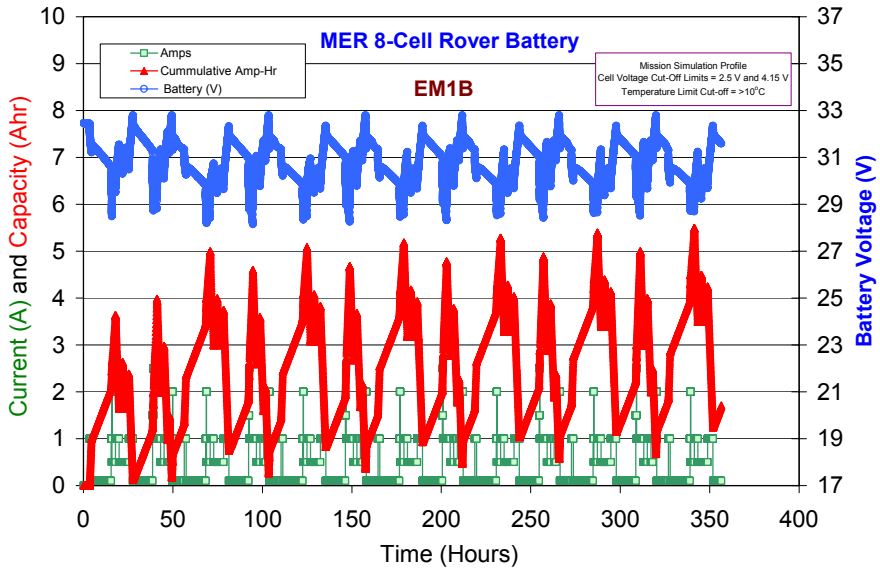
SOLS 1- 10



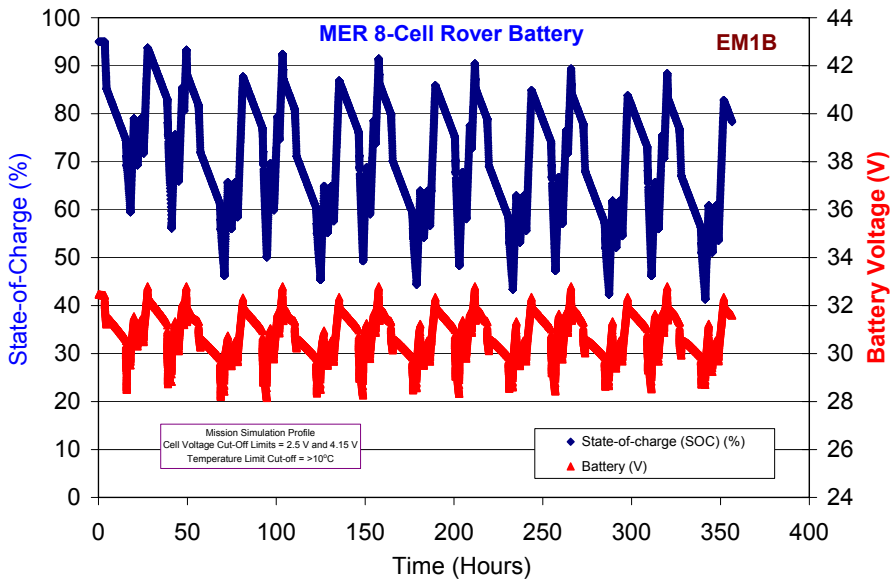
- Mission simulation performed without the benefit of battery charge control electronics
- Performance superior to that obtained at cell-level (due to fresher cells and thermal effects)

MER 8 Ah Rover Lithium-Ion Battery (EM1B)
Mission Simulation Testing
SOL 1-12 (Capacity)

SOL 1-12 (Capacity)

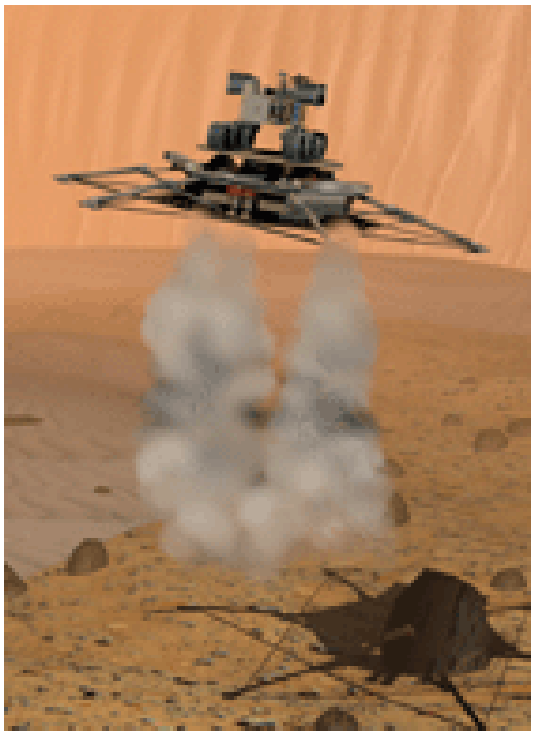


Battery State-of-Charge (SOC) (%)



- Cycling on the surface of Mars is projected to correspond to ~ 50 % DOD
  - SOC marginally decreasing with cycling (incomplete charge)
    - Trend will be off-set by integration of charge electronics

Future Missions: 2009 Smart Lander Secondary Battery



• Lander battery should be capable of supporting launch, cruise, and Mars surface operations over range of temperature (-40 to +40°C).

Battery Description *

- Rechargeable system: Lithium-ion
- High specific energy > 100 Wh/kg
- Configuration: TBD
- Capacity: 30-60 AHr
- Vendor : TBD

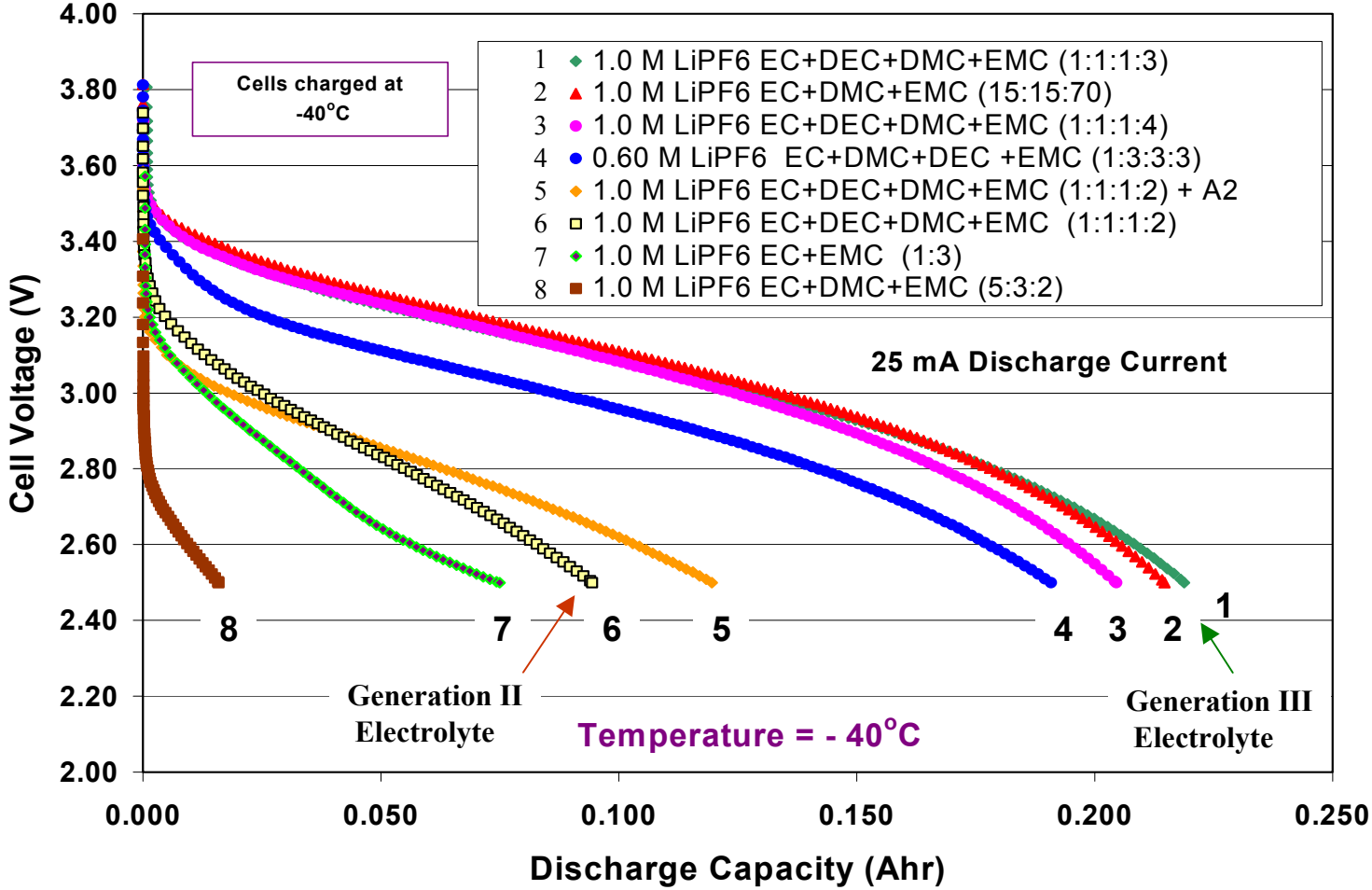
Mission Requirements *

- Voltage : 32-24 V
- Capacity: 30-60 AHr
- Load : TBD
- Temperature : Charge at –20 to -25°C and discharge >- 40°C
- Light weight and compact
- Long cycle life of over 1000 cycles
- Long storage life of over 2 years

* Mission currently being re-planned and requirements likely to change.

Future Missions: 2007 Smart Lander Secondary Battery

Low Temperature Electrolyte Development at JPL

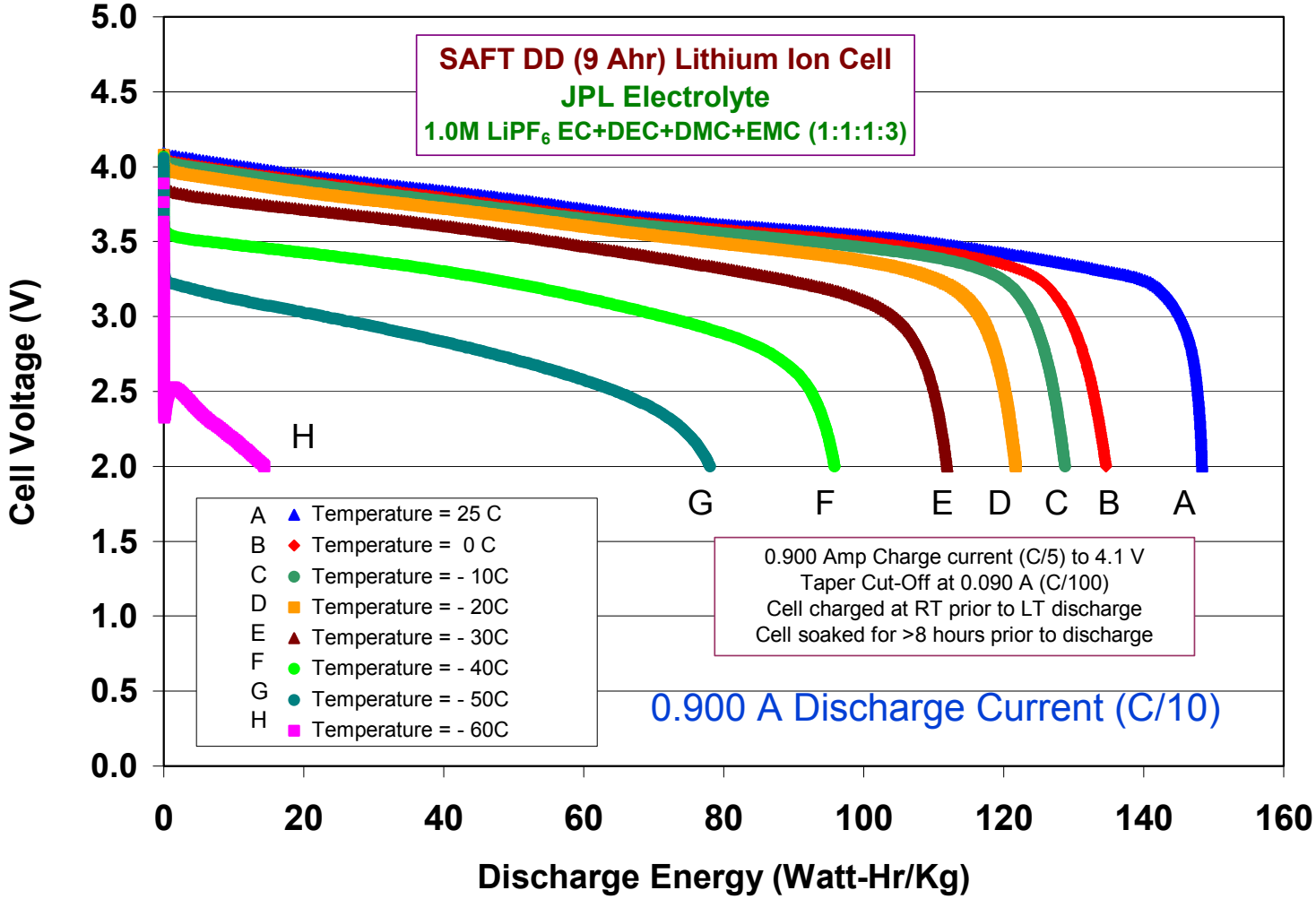


- Identified a number of improved low temperature electrolytes enabling –40°C operation
- Smart et al., *11th International Meeting on Lithium Batteries (IMLB)*, June 28, 2002, Monterey, CA

SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Cell Performance at Low Temperatures: JPL Electrolyte

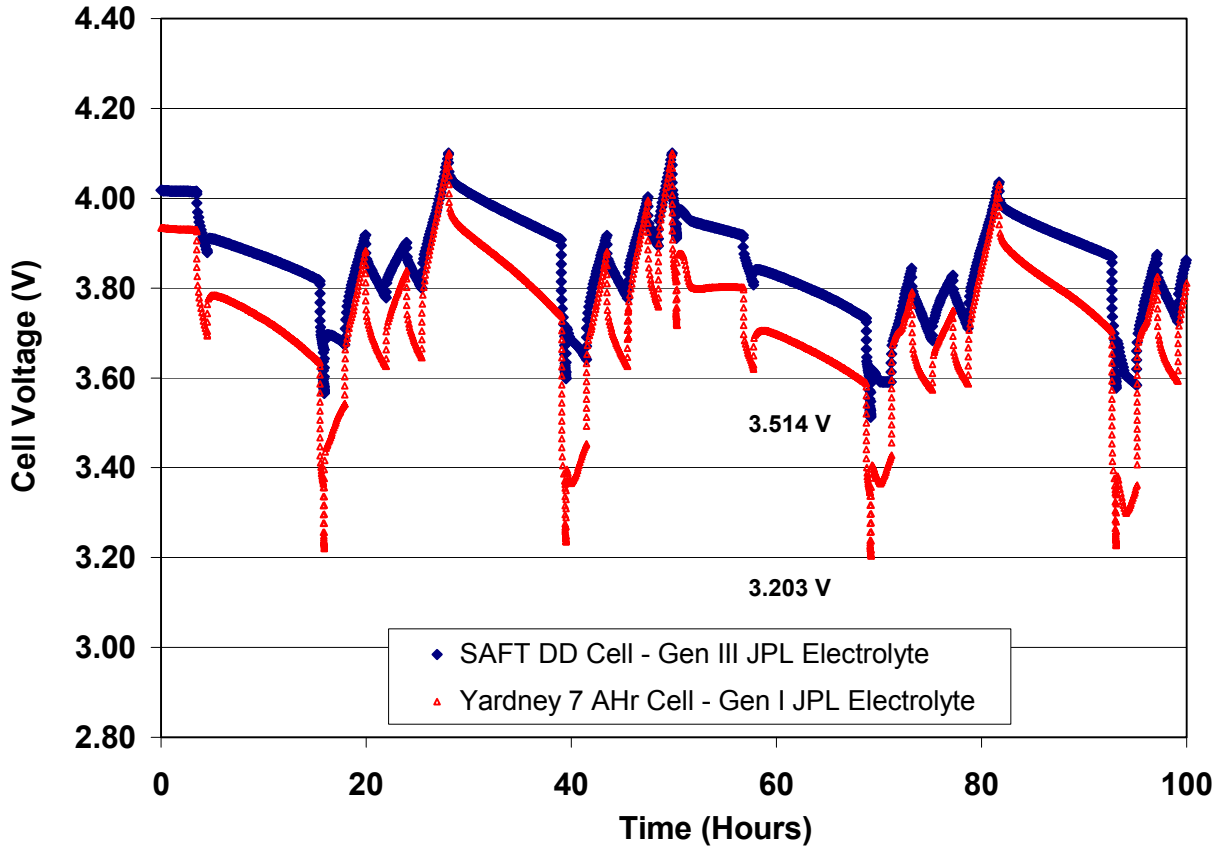
Discharge Energy (Watt-Hr/Kg) – C/10 Rate (0.90 A)



Lithium-Ion Cells for Future Mars Applications

Mission Simulation of Mars Surface Operations

2003 MER Mission Simulation Temperature Profile

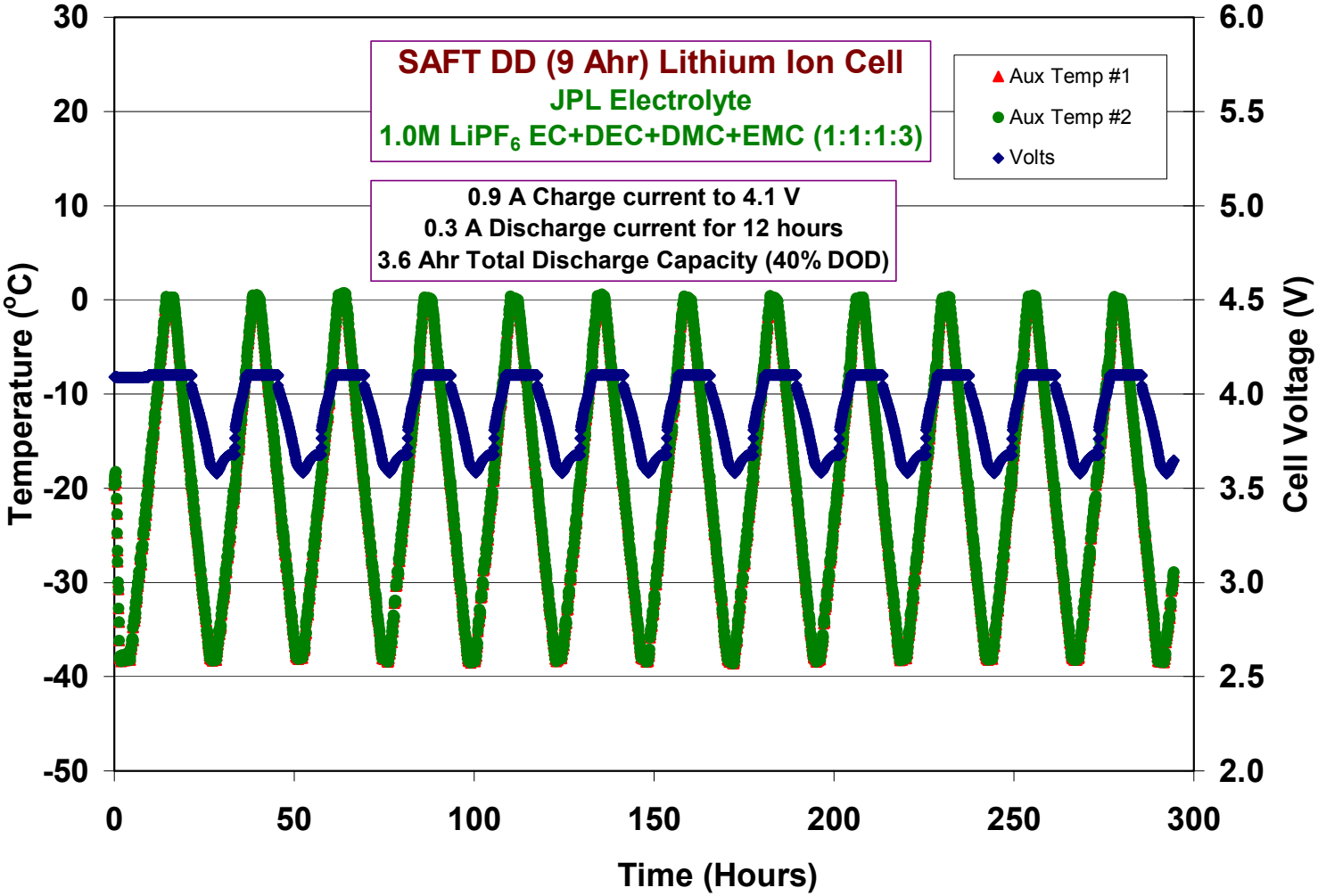


- Improved low temperature electrolytes have translated into increased mission capability.
  - Cells charged at 0°C to 4.05 V (no taper) prior to test

SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Mars Mission Surface Operation Simulation Cycling

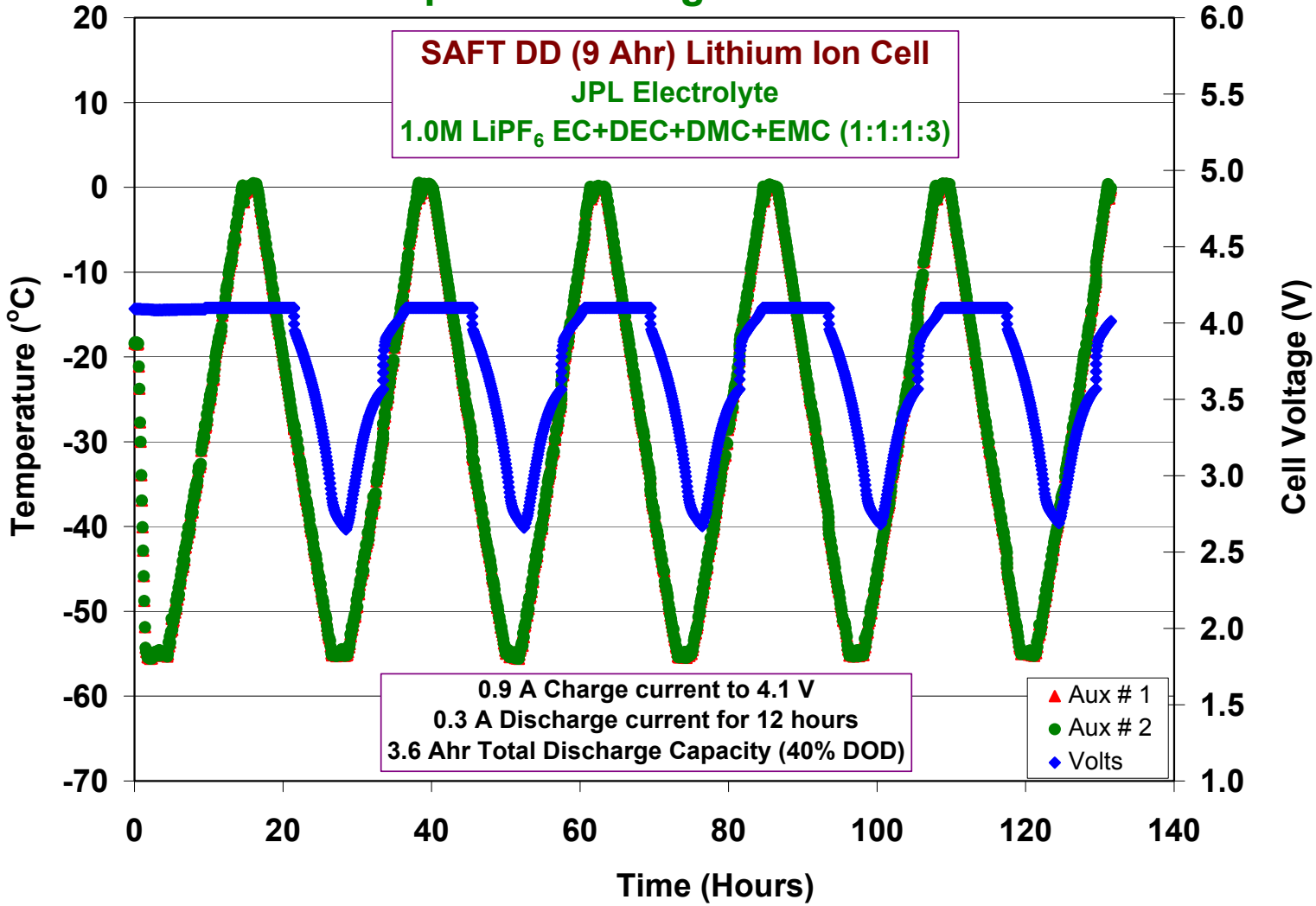
Temperature Range = - 40 to 0°C



SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Mars Mission Surface Operation Simulation Cycling

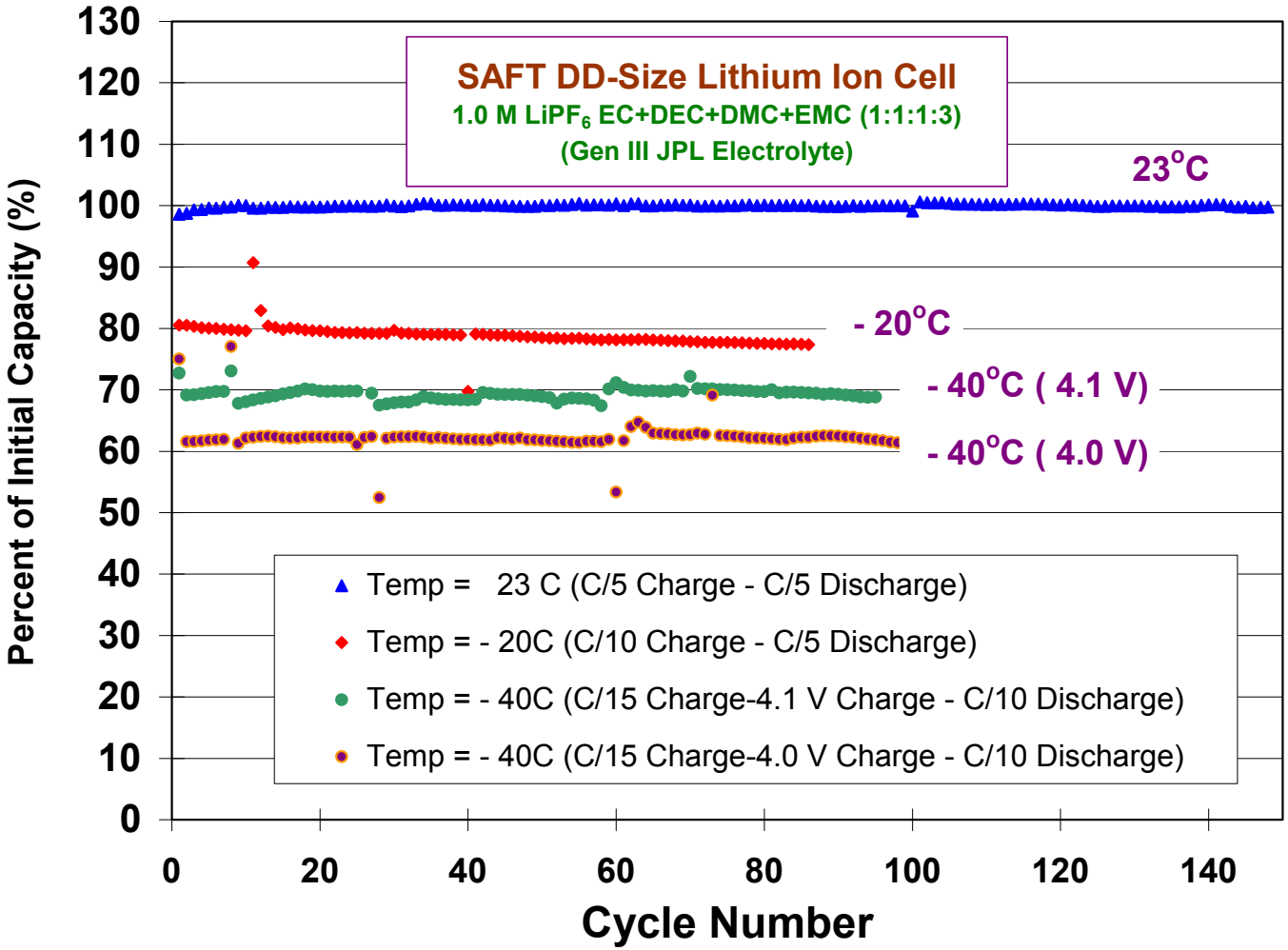
Temperature Range = - 60 to 0°C



SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Performance with Improved Anode Material and JPL Electrolyte

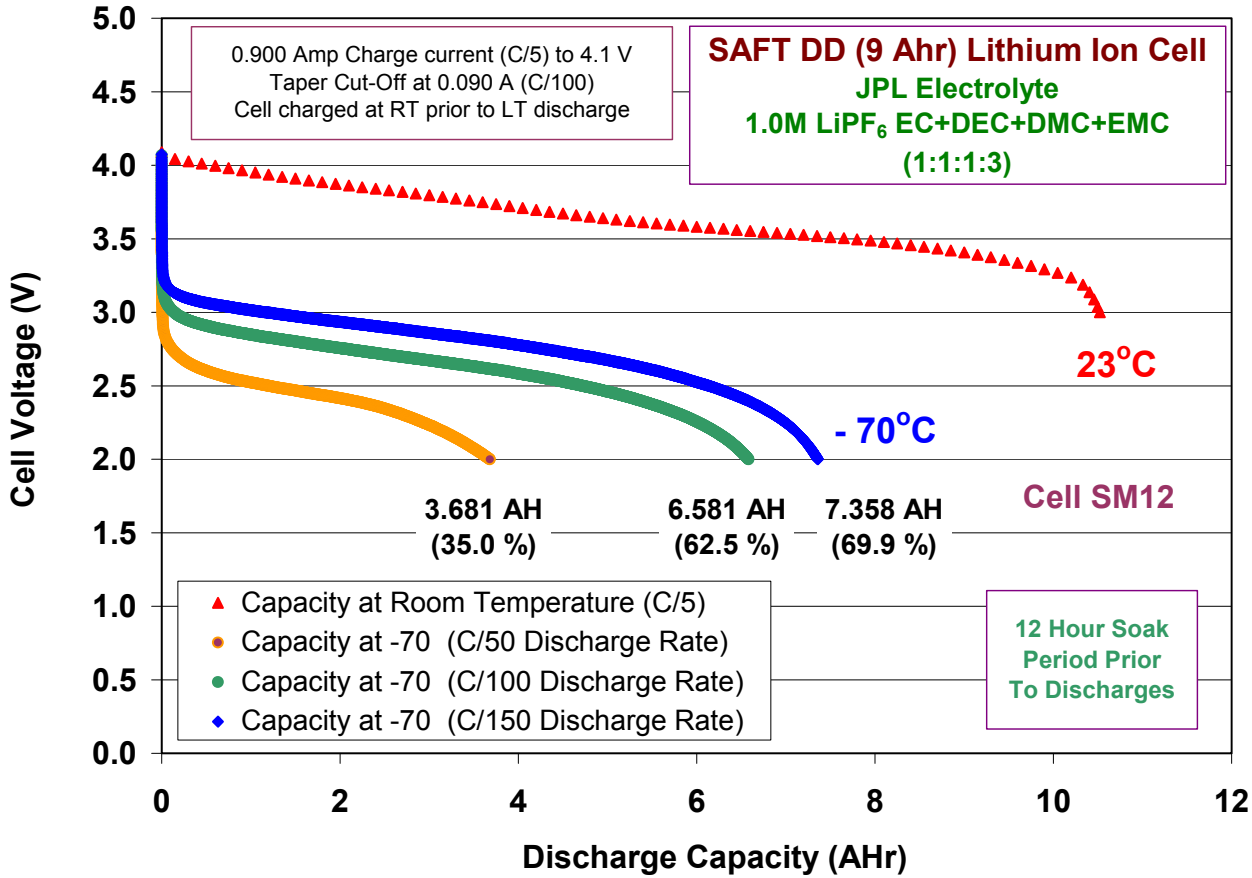
Cycle Life Performance at Different Temperatures



SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

Performance with Improved Anode Material and JPL Electrolyte

Discharge Rate Capability at –70°C



- Improved low temperature electrolytes have translated into increased mission capability.
- Introduces possibility of powering survival mode of lander or rover to very low temperatures.

SUMMARY and CONCLUSIONS

- ***Li-Ion cells/batteries for the MSP 2001 Lander mission :***
  - *Demonstrated the technology readiness of Li-Ion technology (Yardney)*
  - *Good Discharge Rate Capability (Delivers required capacity at low temp)*
  - *Good Storage Characteristics (Able to meet other requirements after cruise)*
  - *Mission Simulation Testing (Able to support > 700 sols on surface..More than 2 Years of operation)*
  - *Battery fully space qualified (Yardney/LMA/JPL) prior to mission cancellation*
  - *Lander battery was demonstrated to support efficient Mars surface operation (MSP01 profile)*
- ***Li-Ion cells/batteries for the 2003 MER mission:***
  - *Good Cycle Life Performance (Exceeds requirements at all temps)*
  - *Discharge Rate Capability (Delivers required capacity at low tem)*
  - *Mission Simulation Testing (Able to support projected surface operation load profile)*
- ***Li-Ion cells testing for future Mars Lander applications***
  - *Excellent low temperature performance demonstrated in prototype cells*
  - *Operating temperature range of – 60 to +40°C demonstrated*
  - *Improved electrolytes result in improved mission capability*
  - *Very low temperature capability may be beneficial to power survival mode*

Acknowledgments

The work described here was funded by the Code S NASA Battery Program and the Mars 2003 Exploration Rover (MER) and was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA).

GEO Li-Ion Battery for GEO Platform

Dr Y. Borthomieu, A.Sennet

Specialty Battery Group
Defense and Space Division
SAFT POITIERS

♦ AGENDA

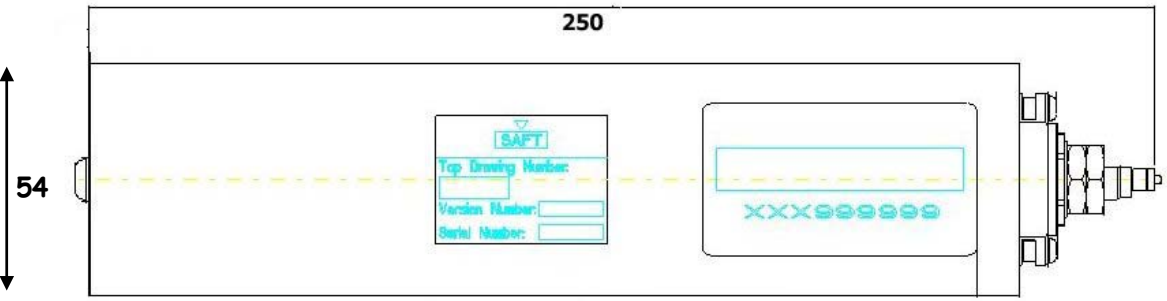
- ☐ Cell and life test up-date
- ☐ Module and battery Design
- ☐ Conclusion

Context

- Saft has started Li-Ion study for Space in 97 with Stentor :
  - As technologic satellite, Stentor purpose is to test in orbit advanced technologies such as plasmic propulsion, solar panels, batteries, deployable radiator….

- Saft has qualified cells, module and battery designs for most of the GEO plate-forms :
  - Li-Ion batteries gives tremendous advantages to the satellite power system.
  - Li-Ion batteries have been base-lined for 3 GEO satellites

VES 140 S Cell design



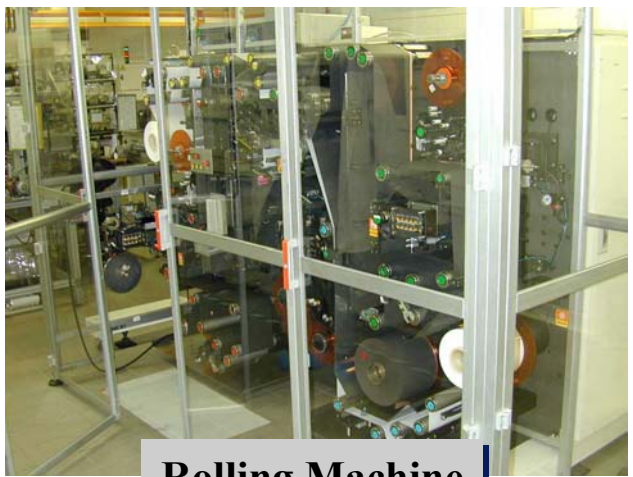
1116 +/- 25 g

- Min Guaranteed BOL Energy > 139 Wh @ 4.10 V
- Space Qualified by various customers
- VES140 S has been selected on 3 GEO programs

Industrial Product

- VES140 versus Electric Vehicle Cells :
  - Same process and tools used for the jelly roll
  - Specific covers and terminal for the VES140
- Production Line in Bordeaux :
  - Able to produce more than 32 cells/day in on shift (15 000 cells/year)
  - 6 Sigma Rules
- Status :
  - More than 1 000 VES cells and 12 000 VE cells made : reproducibility and reliability

Coating Line



Rolling Machine

The industrial production line of Bordeaux

- **The statistical graphs hereafter onto** VES 140 **cell manufacturing** demonstrate the reproducibility of the pilot line :

Cell number : 703 VES 140

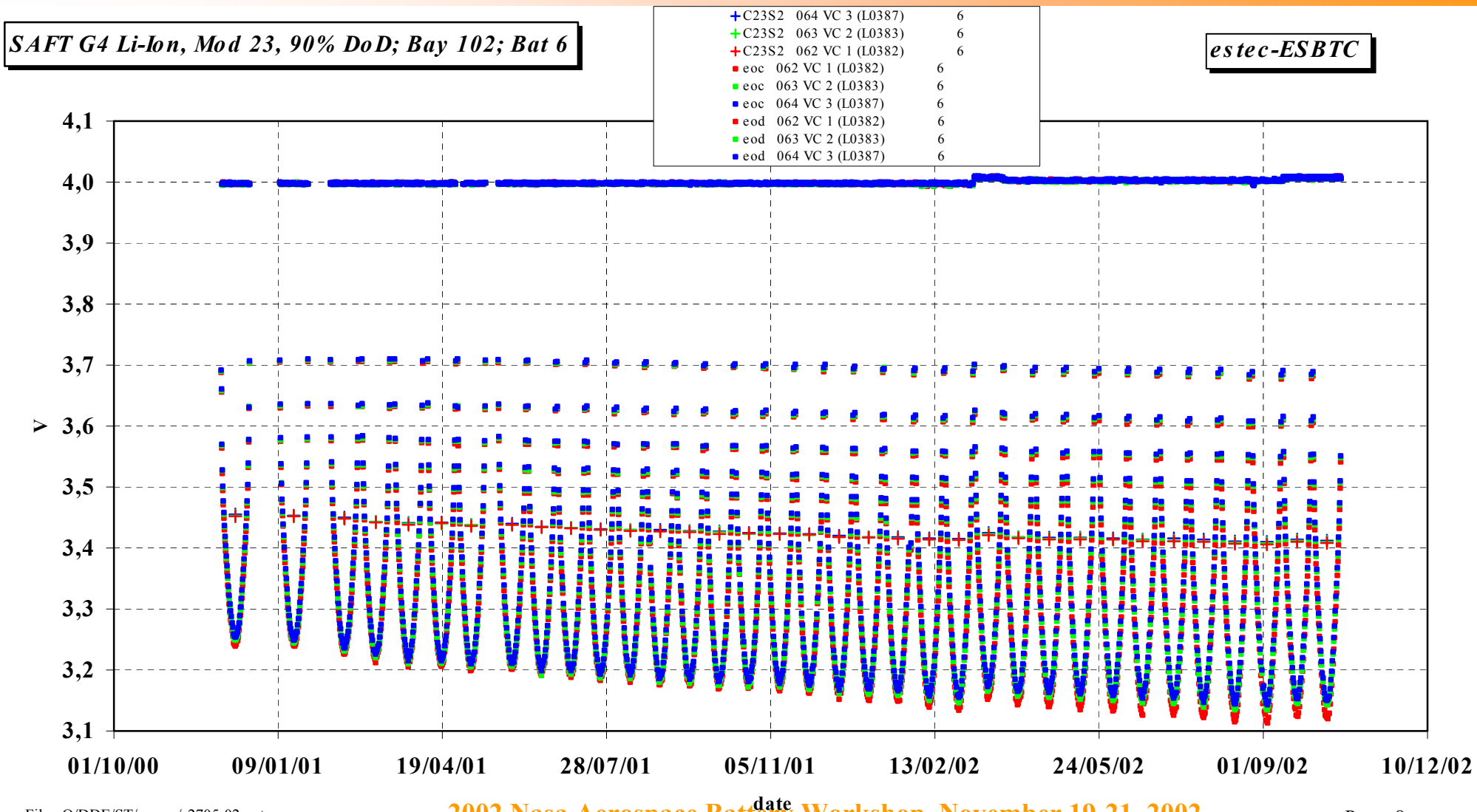
Lot number : 14 (including qualification lot)

	Energy @ 4V (Wh)	Weight (g)	Ri 20 % (mΩ)	Ri 60 % (mΩ)	Av Discharge Voltage (V)
Average	128.76	1111.0	2.520	2.624	3.539
σ	4.61	9.73	0.136	0.139	0.011

90% DOD GEO VES 140

- Module configuration (3S VES140)
- Accelerated GEO cycling 90 % DOD, 20 °C
- Charge current : 4 Amps
- EOCV = 4.0 V
- Season profile
- Test started in December 2000
- 35 seasons performed
- Energy variation : 1.2 %

GEO9 : 90% DOD GEO Accelerated Cycling



Sizing assumptions for GEO projects

- The depth of discharge : based on tests performed at 80%, 18 years

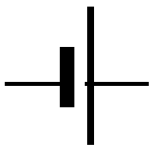
- BOL performances :
  - 139 Wh per cell at 4.1V in battery configuration.

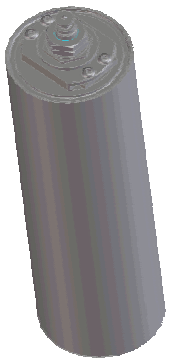
- Fading assumptions :
  - Cycling fading : loss of 3 %
  - Calendar fading : loss of 3%
  - Margin on fading : 2 %

EOL Min Guaranteed Energy : 128 Wh

Battery design for GEO Satcoms

Cell

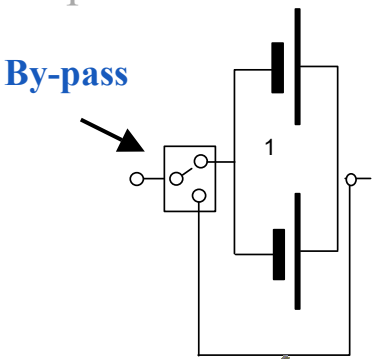


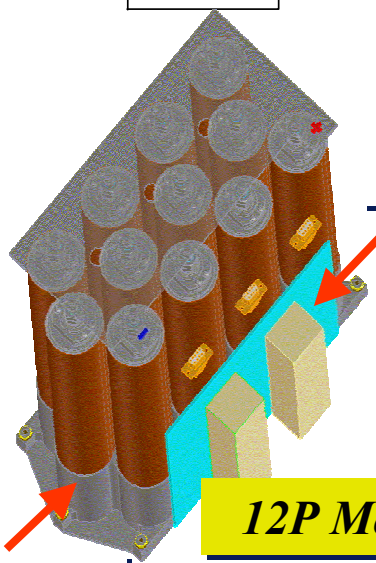


VES 140 Cell

Cell Module

paralleled cell assembly

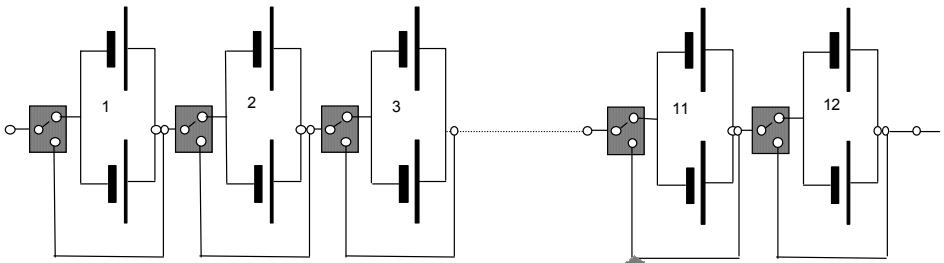


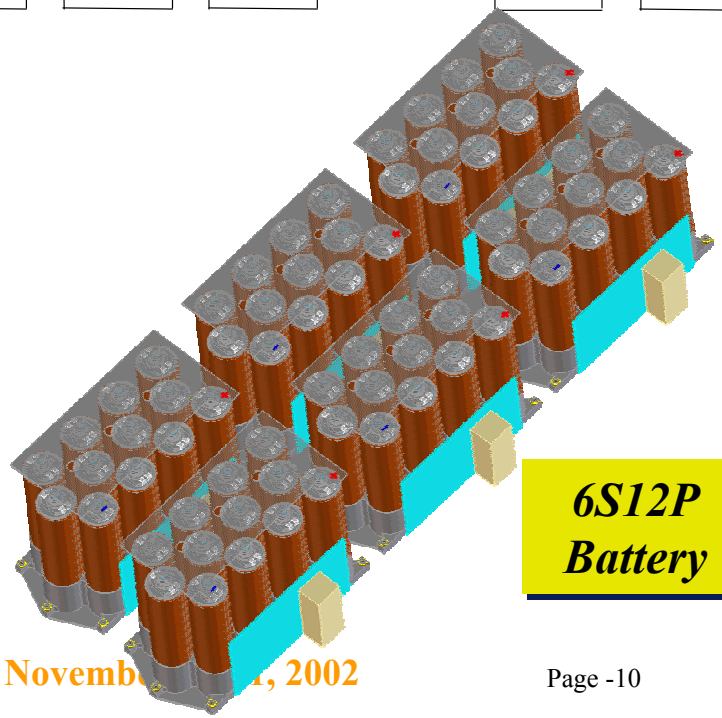


12P Module

Battery

serial module assembly

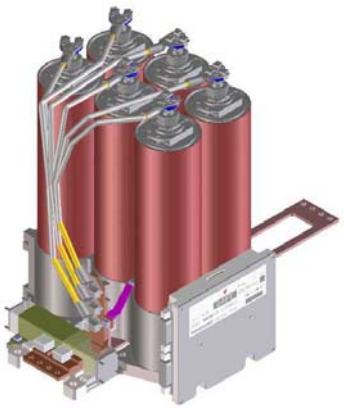


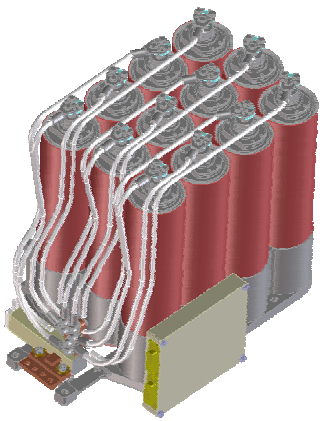


6S12P Battery

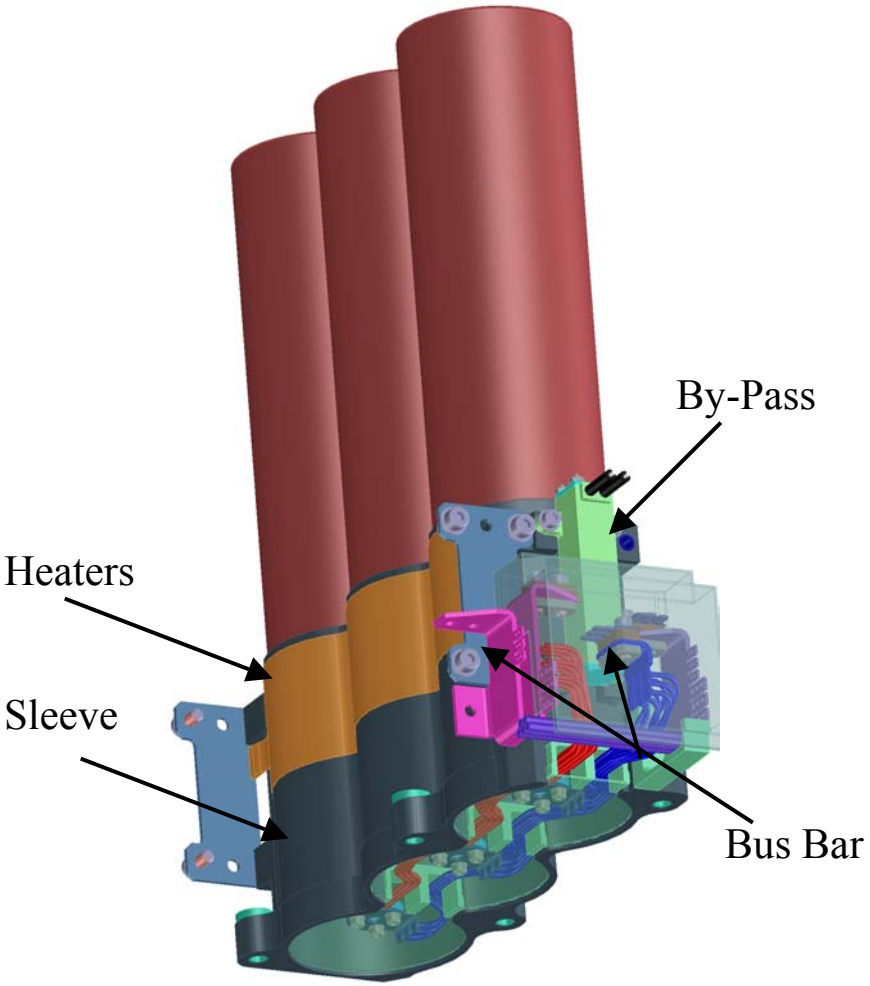
Module Types

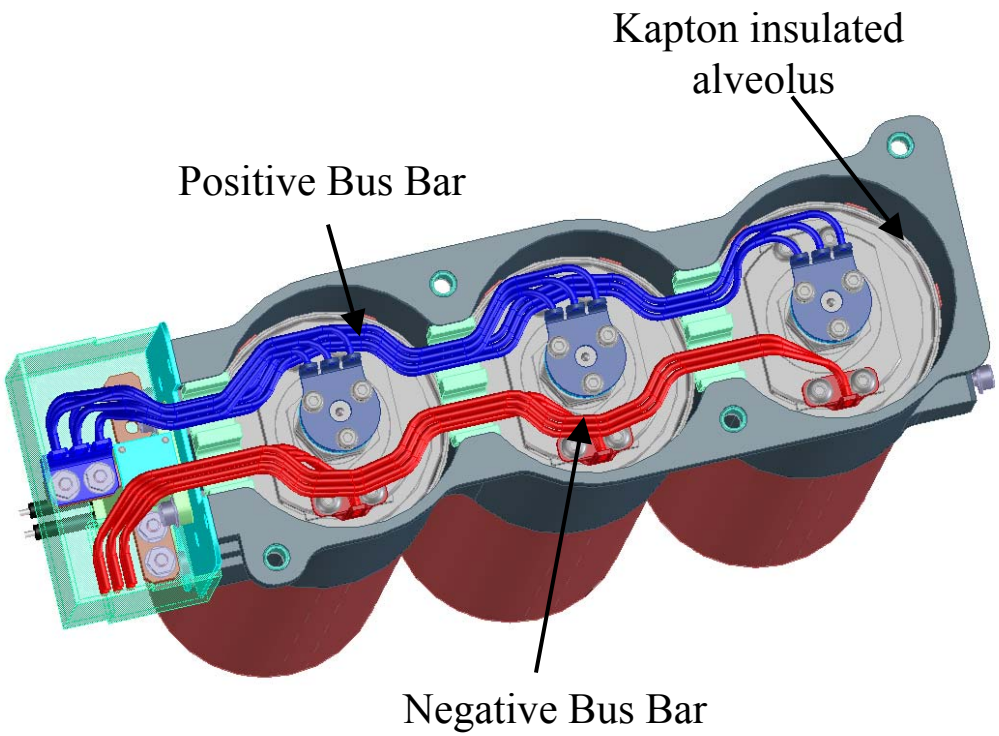
- Qualified Modules :
  - Stentor : 5 and 6 cells modules
  - Syracuse III : 3P modules
  - W3A : 6P module
  - Eurostar : 12P module





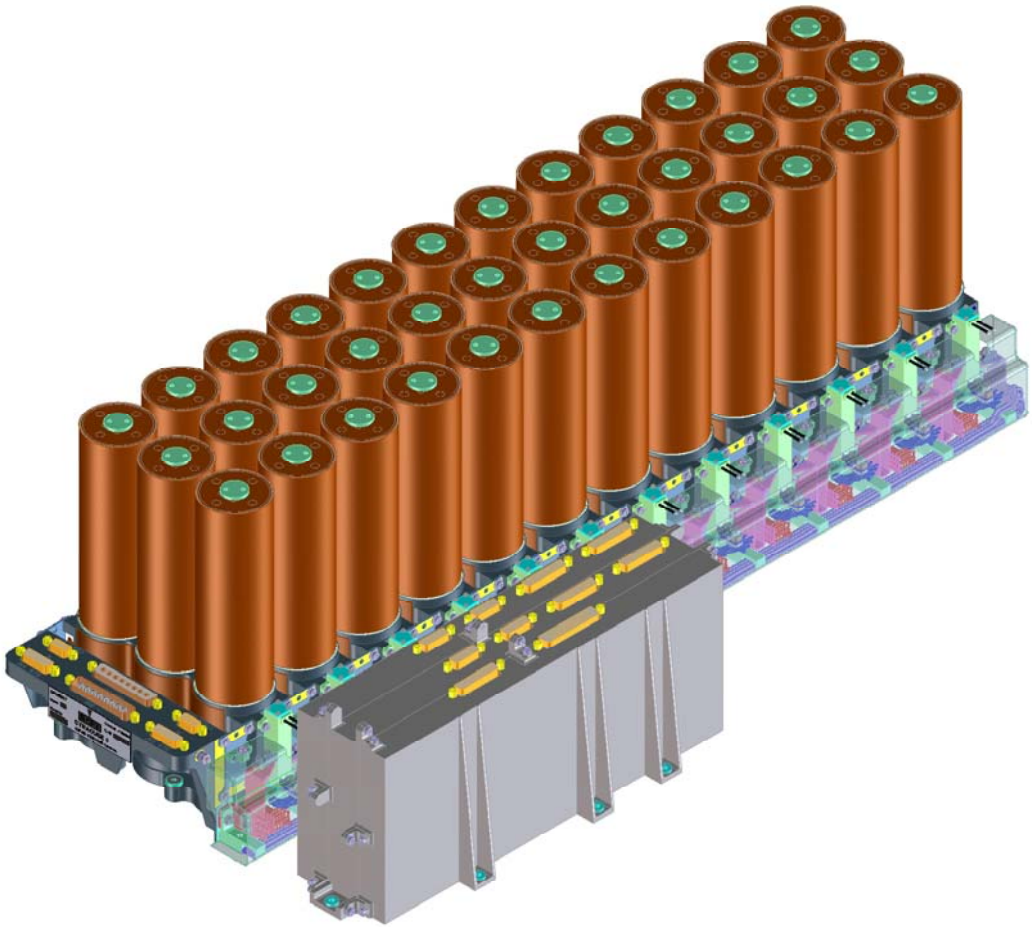
3P module


By-Pass
Heaters
Sleeve
Bus Bar

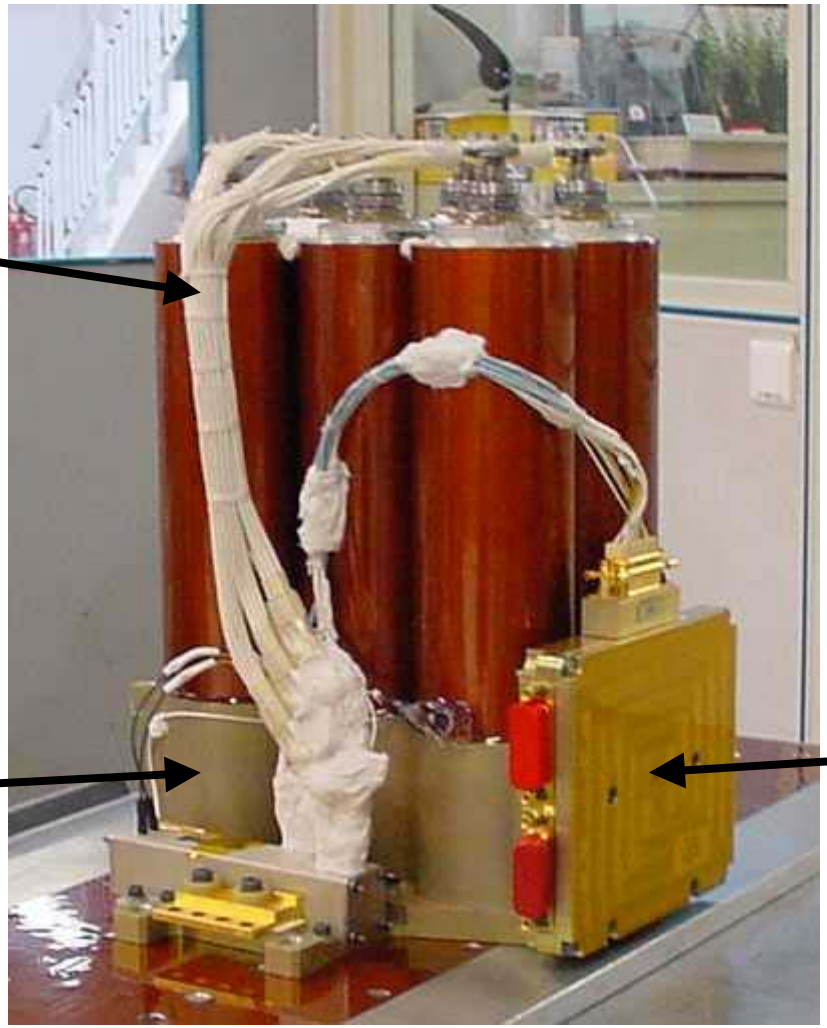

Kapton insulated alveolus
Positive Bus Bar
Negative Bus Bar

3P12S battery

- Voltage limits : from 56 to 98.4 V
- External Electronic System



6P Module



Range Table

Module Configuration (VES140)	3	4	5	6	7	8	9	10	11	12
Power (2 sets with 22 S modules)	11,5	15,3	19,1	22,9	26,8	30,6	34,4	38,2	42,0	45,9
Maximum Module Weight (Kg)	4,609	5,841	7,073	8,305	9,537	10,768	12,000	13,232	14,464	15,696
Total Battery Weight (Kg)	202,8	257,0	311,2	365,4	419,6	473,8	528,0	582,2	636,4	690,6

Module range

- Range of power for 3 to 12 P with 17 to 23 S

P / S	3	4	5	6	7	8	9	10	11	12
17	8,9	11,8	14,8	17,7	20,7	23,6	26,6	29,5	32,5	35,4
18	9,4	12,5	15,6	18,8	21,9	25,0	28,1	31,3	34,4	37,5
19	9,9	13,2	16,5	19,8	23,1	26,4	29,7	33,0	36,3	39,6
20	10,4	13,9	17,4	20,9	24,3	27,8	31,3	34,8	38,2	41,7
21	10,9	14,6	18,2	21,9	25,5	29,2	32,8	36,5	40,1	43,8
22	11,5	15,3	19,1	22,9	26,8	30,6	34,4	38,2	42,0	45,9
23	12,0	16,0	20,0	24,0	28,0	32,0	36,0	40,0	44,0	48,0

Li-Ion Battery Management :

- Li-Ion battery management can be done with existing NiH2 management system :
  - CC/CV charge management
  - voltage measurements same as per NiH2 with higher precision
  - balancing system to be done thanks an Electronic Interface Card

Battery Management : CC/CV

- Li-Ion batteries need CC/CV charge management :
  - Max End of charge Voltage : 4.1 V/cell
  - When first module voltage reaches the end of charge voltage limit : charge current is decreased by one step.
  - At least, 10 steps from C/10 to 0 amp.

- GEO specific management :
  - During eclipse :
    - BOL : 4.05 V and EOL : 4.1 V to compensate Energy loss
    - T from 15 to 30 °C
  - Solstice : 3.7 to 3.8 V, T from 10 to 20 °C

Battery Management : balancing

- All Li-Ion batteries need of balancing :
  - no overcharge to compensate cell dispersion
  - energy difference or drift in between modules due :
    - to cell current leak : versus time
    - to aging
    - External circuit leak current
- Balancing principle :
  - discharged of the highest voltage cell with a resistor shunt for a duration proportional to voltage difference
  - Criterion (TBD) : +/- 20 mV during eclipse, +/- 100 mV for solstice
  - balancing of cell can be done once per six months (solstice)

Conclusion : Projects

Li-Ion FLIGHT EXPERIENCE							
Launch Date	Satellite Country	Orbit	Mission	Battery			
				Main Customer	Battery Responsible	Battery Characteristic	Status
Planned 2002	Stentor	GEO	Telecom/ experimental	CNES	SAFT	(2) 2P 11S VES140	To be launched
Planned 2002	Smart 1	GEO	Scientific	SSC	SCC	(5) 1P 1S VES140	To be launched
Planned 2003	W3A	GEO	Telecom	ASTRIUM	ASTRIUM	(2) 6P 11S VES140	Delivered
Planned 2003	Syracuse III	GEO	Telecom	ASPI	SAFT	(2) 3P 12S VES140	Qualification
Planned 2004	Proteus	LEO	Sciences	ASPI	SAFT	3P 9S VES100	Development
Planned 2004	Amazonas	GEO	Telecom	ASTRIUM	ASTRIUM	(2) 6P 11S VES140	Recurring W3A

Testing Update on 20 and 25-Ah Lithium Ion cells

Gregg C. Bruce, Pamella Mardikian and Sherri Edwards
Eagle-Picher Energy Products Corporation

Kumar Bugga, Keith Chin, Marshall Smart and Subbarao Surampudi
JPL

NASA Aerospace Battery Workshop
19-21 November 2002

ENERGY PRODUCTS

Topics

- Introduction
- 20-Ah Cell, Design I
  - Design
  - Test Results, Cell cycling at various temperatures and storage
- 25-Ah Cell, Design II
  - Design
  - Test Results, various temperatures, cell cycling and LEO cycling
- Conclusions

Introduction

- Eagle-Picher Energy Products has worked on lithium ion batteries for approximately 8 years
- During that period EPEPC developed and delivered several cell sizes on a program funded by the USAF and Canadian DND
- Designs are wound cylindrical cells from 7 to 40-Ah
- Most cells delivered were approximately 25-Ah due to requirements of Mars missions
- Several iterations of cells were manufactured and delivered for evaluation
- The first design was 20-Ah, Design I, and the second was a 25-Ah, Design II

Introduction

- **Deliveries related to the program were:**

-	10, 20-Ah cells to JPL	05/97
-	12, 7-Ah cells to JPL	05/98
-	12, 25-Ah cells to JPL	05/98
-	10, 37.5-Ah cells to Phillips	05/98
-	10, 25-Ah cells to LMA	08/98
-	30, 25-Ah cells to JPL	09/98

Introduction

- Cells have been under test at JPL for over 5 years
- All results presented were supplied by JPL
- No events of significance to report
- The “25-Ah” cell designs evolved over time
- Increased rate capability; tabbing issues
- Increased low temperature performance; electrolyte

Design Features - Design I

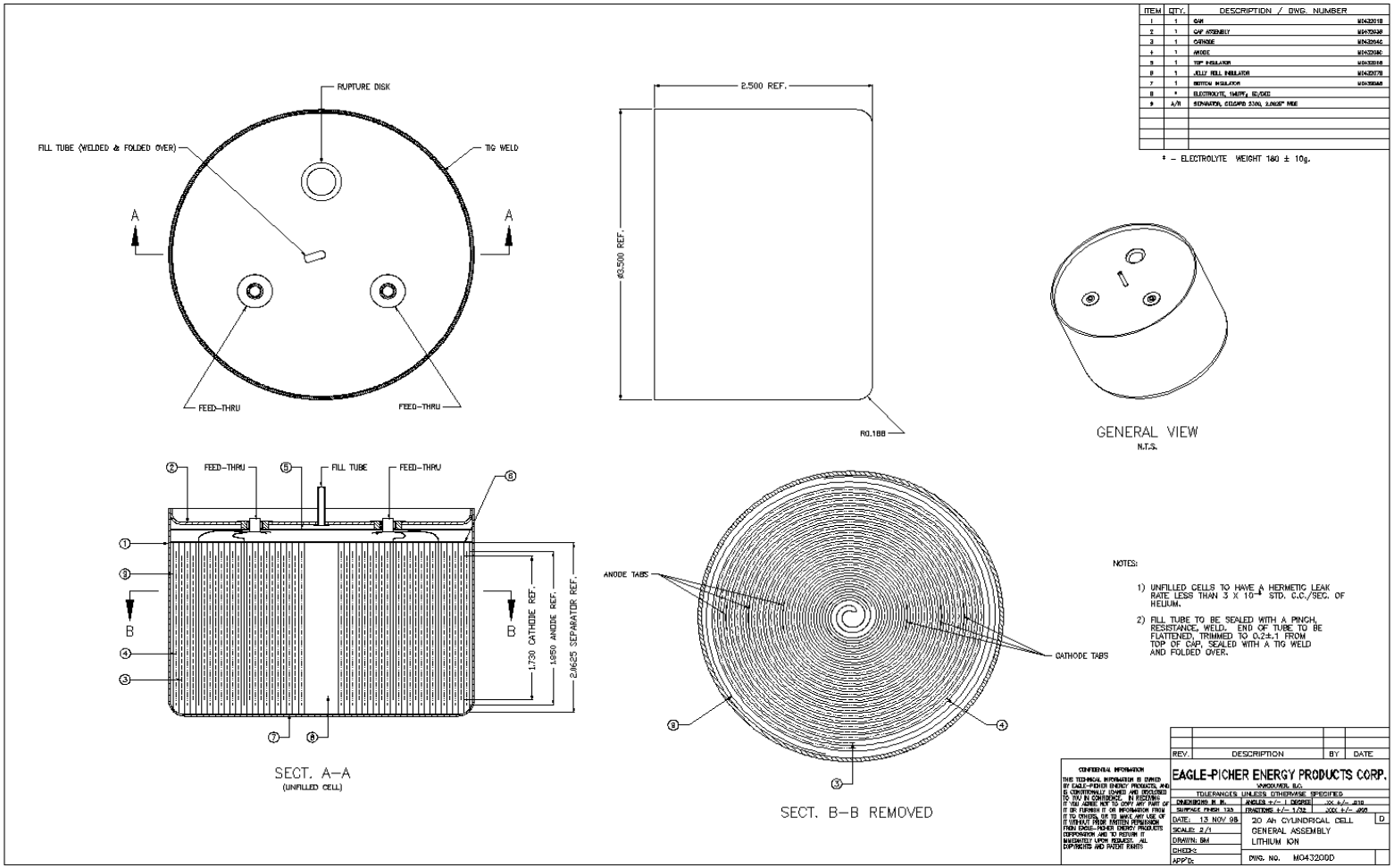
- Drawn Can - SS304

  3.50” diameter x 2.50” x 0.19”
- Standard Penetrations

  TA-23, 0.125” Mo

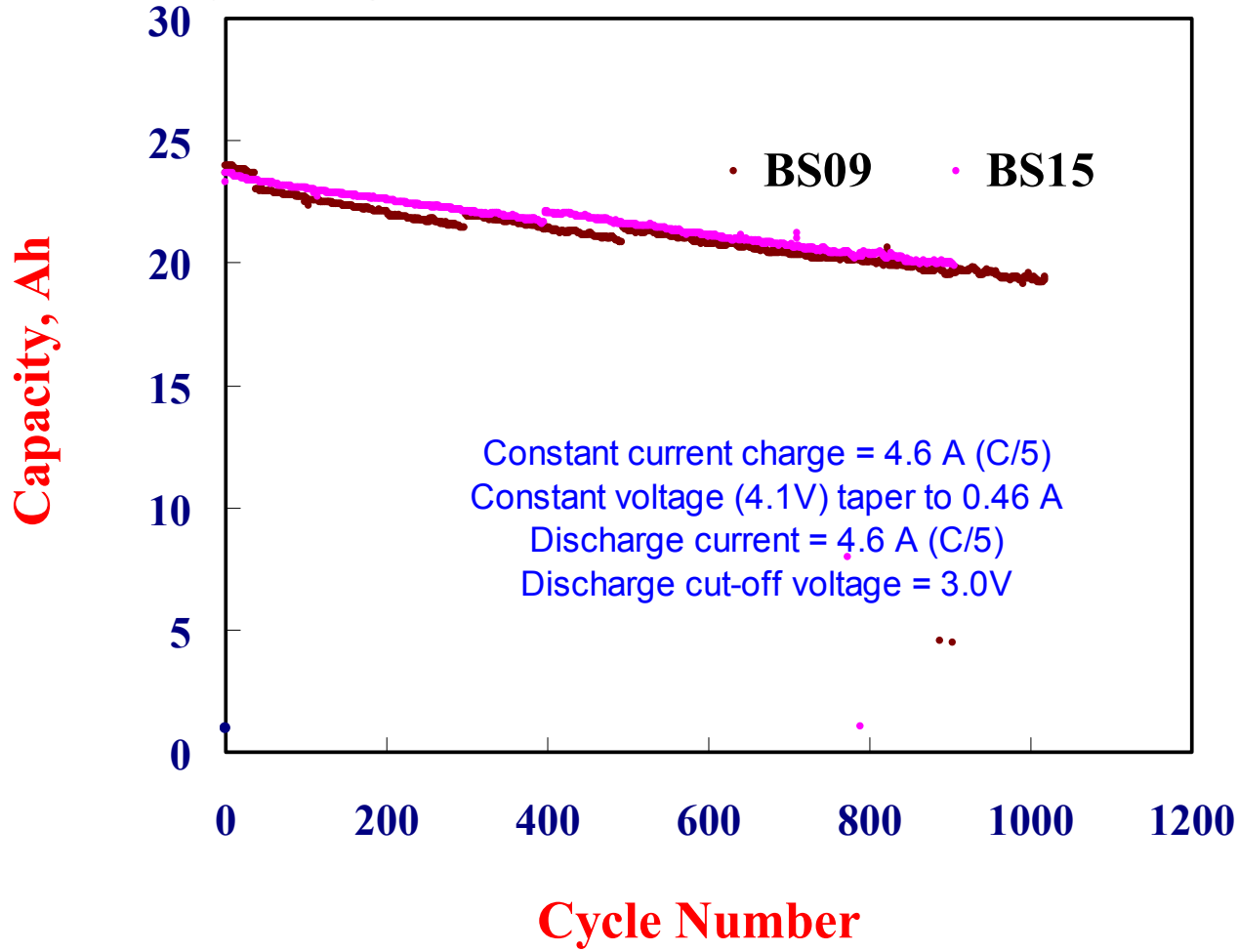
  Fill Tube, Rupture disc 235 psi
- Positive electrode, 1300 x 4.40 x 0.017 cm ($LiCoO_2$)
- Negative electrode, 1330 x 4.70 x 0.011 cm (Graphite)
- Delivered May 1997

Cell Design - Design I



20 - Ah Cylindrical Cell

Cycling at 23°C - C/5, 100% DOD

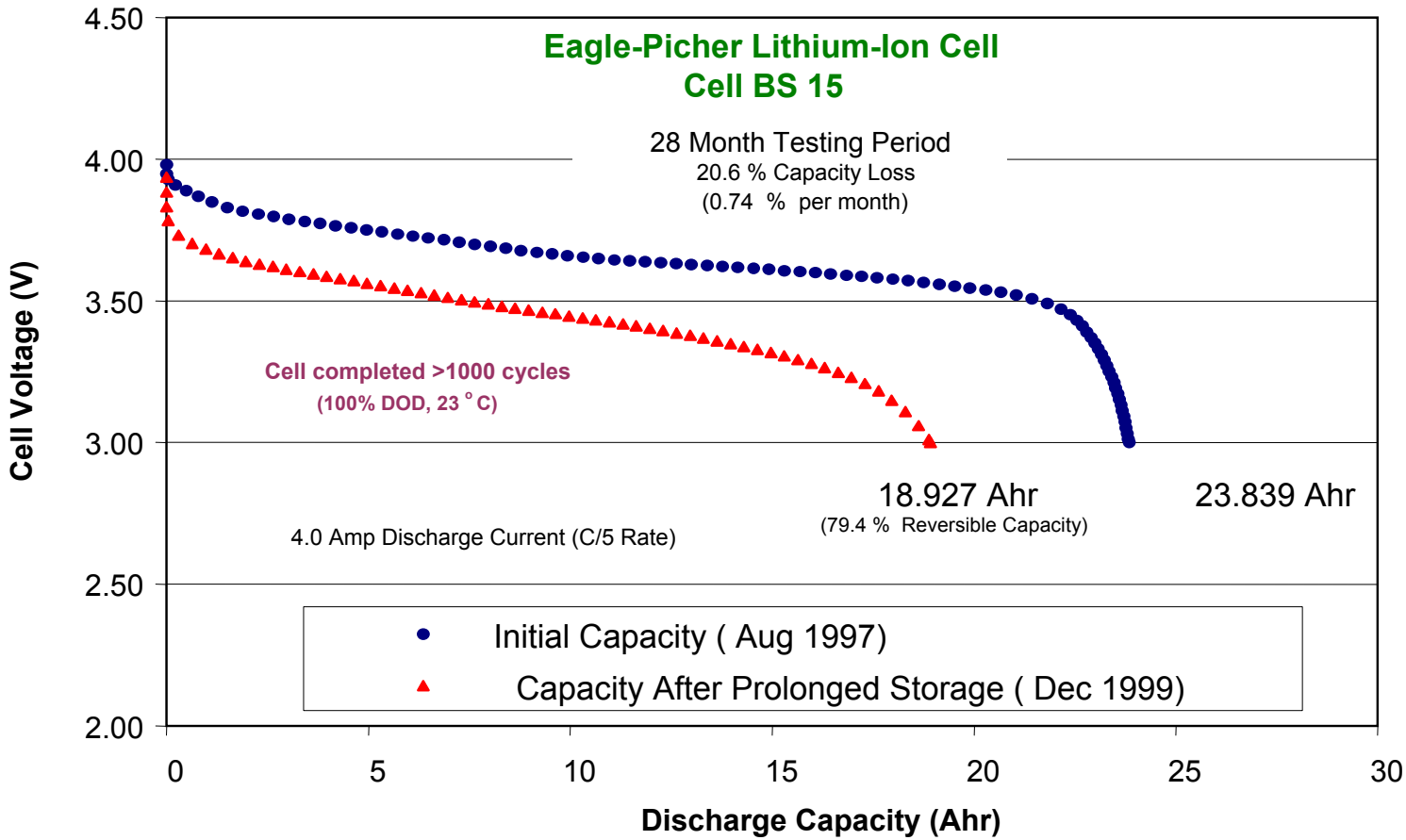


- Capacity fade rate : 0.019% per cycle.

Cell Cycling and Storage - Cycling at 100% DOD, C/5 at 23°C

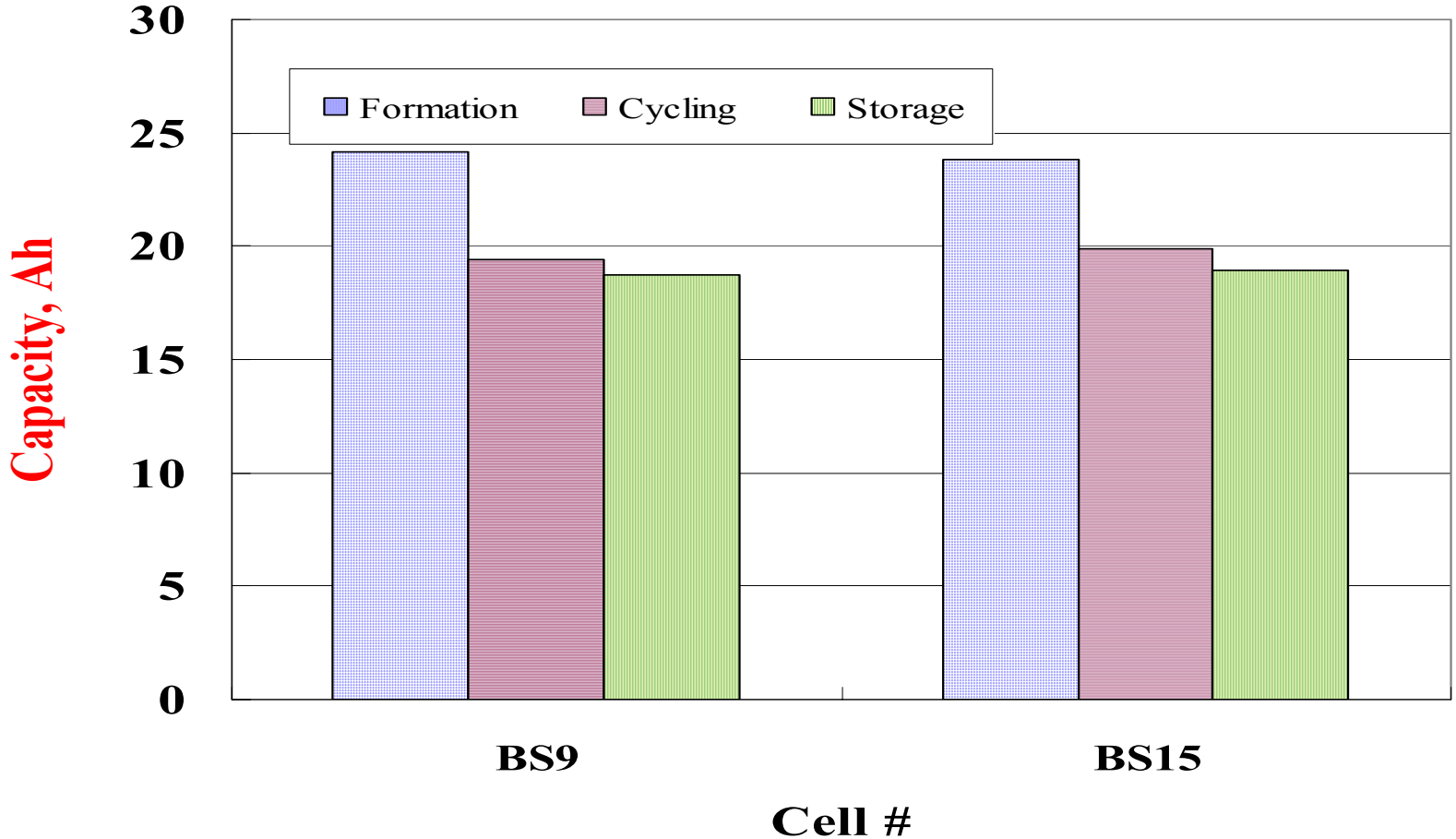
- Cells cycled for 1000 cycles at 100% DOD, at RT before storage
- Cells stored at RT, probably at 100% SOC for about 1.5 years (18 months).
- Total storage (including the cycling time) since manufacture : > 30 months.
- Cells then placed back on 100% DOD, C/5 cycling for 1500 more cycles, approximately 2 years

EPEPC cell cycled and stored at RT



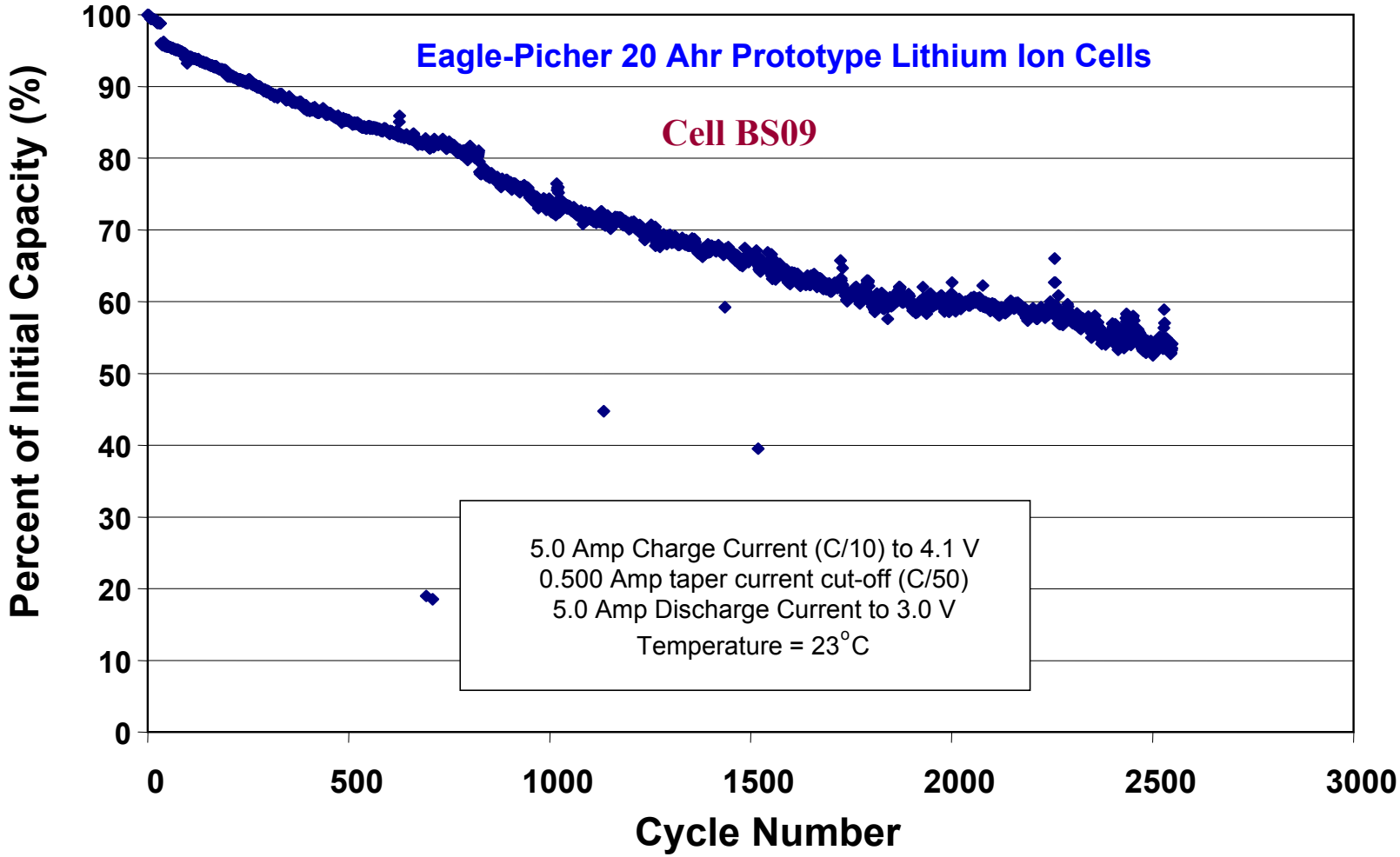
20 - Ah Cylindrical Cell

Capacity Changes upon RT Cycling (100% DOD) and storage



- 17-20 % loss during cycling (1000 cycles over 500 days) and 3-4% loss during storage (1.5 years).

Cycle Life and Storage Performance (Gen I 20 Ahr), 4.5 years Testing

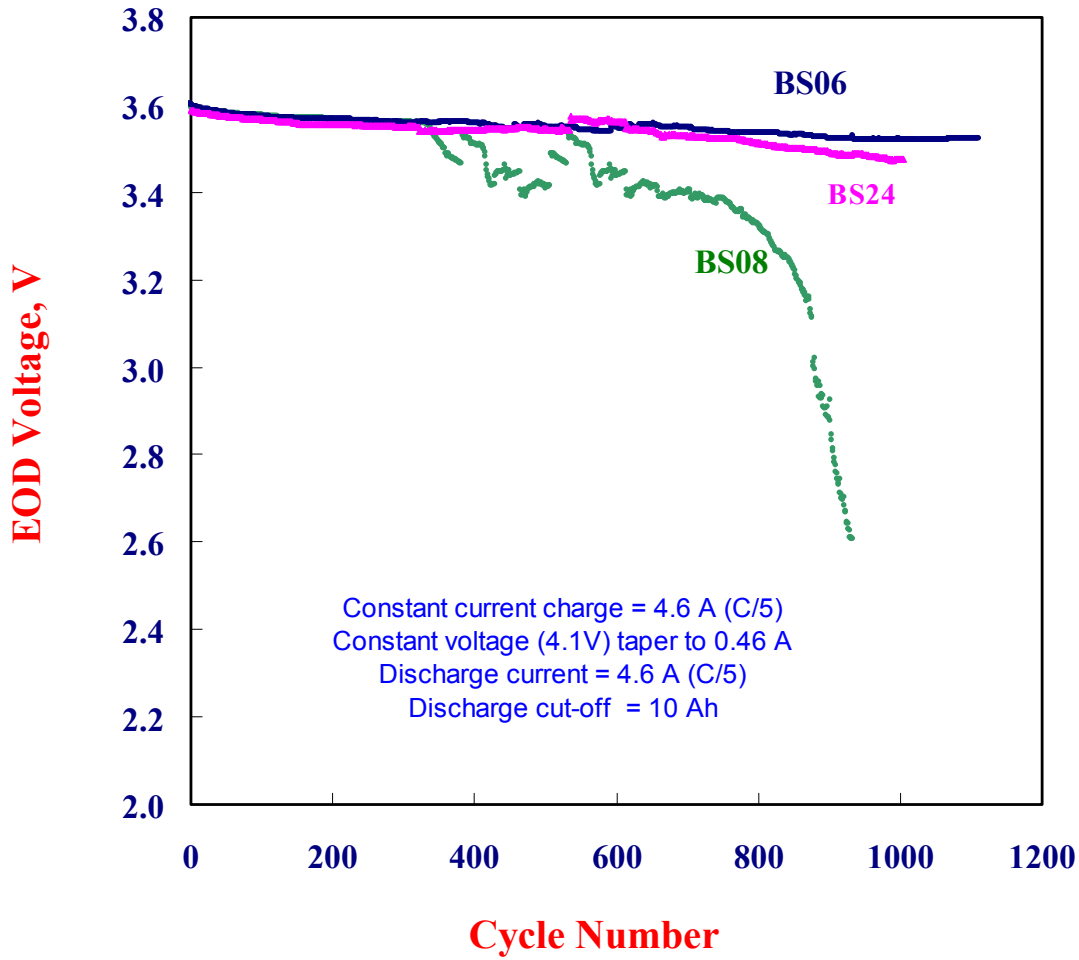


Cell Cycling and Storage - Cycling at 50% DOD at 0°C

- Cells cycled for 1000 cycles at 50% DOD and 0°C before storage
- Cells stored at 0°C, probably at 100% SOC for about 1.5 years (18 months) after cycling.
- Total storage (including the cycling time) since manufacture : > 30 months.
- Post storage tests in Jan-Feb. 00
  - Capacity check at RT
- Further storage at 0°C in progress

20 - Ah Cylindrical Cell

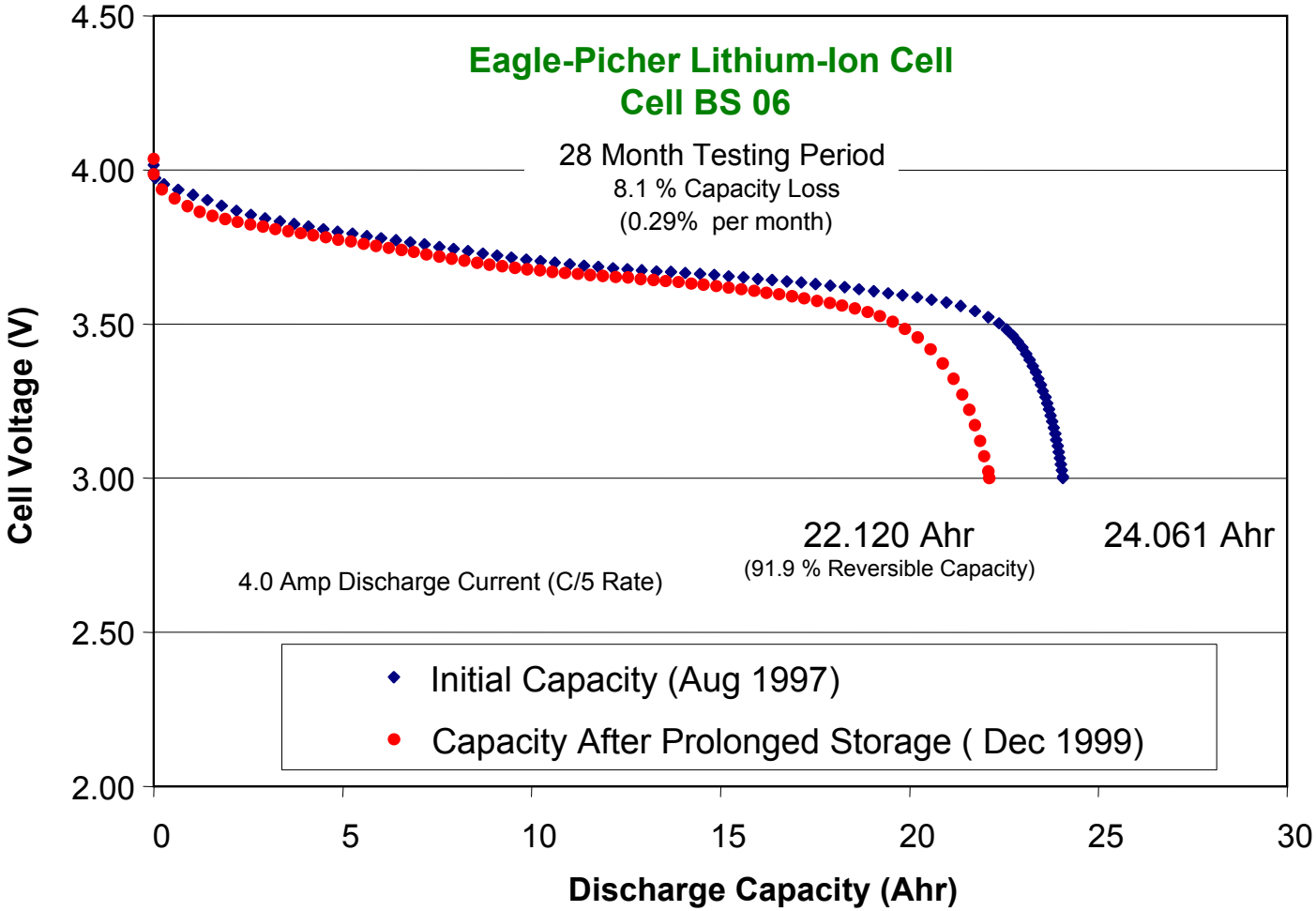
Cell Cycling and Storage - Cycling at 50% DOD at 0°C



- End of discharge voltage depression : 7-8 mV/100cycles.

20 - Ah Cylindrical Cell

Cycling at 50% DOD (1000 cycles) at 0°C then Stored at 0°C for 18 months



Conclusions - Design I

- The cycling results from the Design I cell were quite impressive with slightly greater than 50% of initial capacity after 2500 cycles at 23°C and 100% DOD, total test time approximately 4.5 years
- Storage advantage of 0°C over RT is quite evident with only a 8% loss in capacity after 1000 cycles at 0°C and 18 months storage at 100% SOC versus 20% loss with 100% DOD and storage both at 23°C

Design Features

- **Drawn Can - SS304**

  2.625” diameter x 4.50” x 0.19”

- **Standard Penetrations**

  TA-23, 0.187” Ta - 4-40 thread

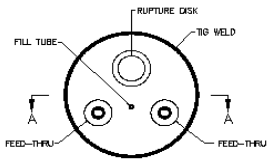
  Fill Tube, Rupture disc 150 psi

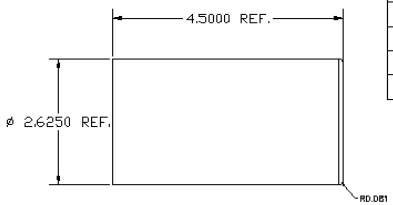
- **Positive electrode, 639 x 8.80 x 0.017 cm ($LiCoO_2$)**
- **Negative electrode, 656 x 9.10 x 0.011 cm**
- **Cells delivered September 1998**

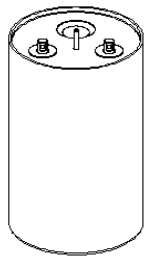
Cell Design - Design II

ITEM	QTY.	DESCRIPTION / DWG. NUMBER	
1	1	CAN	M044801
2	1	CAP ASSEMBLY	M044803
3	1	CATHODE	M044804
4	1	ANODE	M044805
5	1	TOP INSULATOR	M044806
6	1	JELLY ROLL INSULATOR	M044807
7	1	BOTTOM INSULATOR	M044808
8	*	ELECTROLYTE, 1MLIPF$_6$ EC/EMC	
9	A/R	SEPARATOR, CELGARD 2300, 4.000" WIDE	

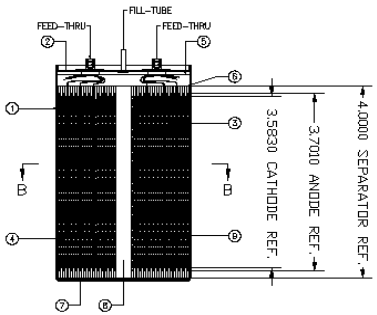
* – ELECTROLYTE WEIGHT 200 ± 10g.



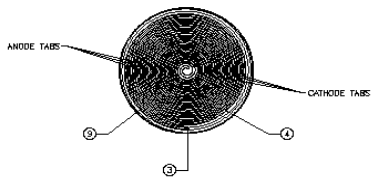




GENERAL VIEW



SECT. A–A
(UNFILLED CELL)



SECT. B–B REMOVED

NOTES:

1) UNFILLED CELLS TO HAVE A HERMETIC LEAK RATE LESS THAN 3 X 10^{-7} STD. C.C./SEC. OF HELIUM.

2) FILL TUBE TO BE SEALED WITH A PINCH, RESISTANCE, WELD. END OF TUBE TO BE FLATTENED, TRIMMED TO 0.2±.1 FROM TOP OF CAP, SEALED WITH A TIG WELD AND FOLDED OVER.

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VANCOUVER, B.C.

TOLERANCES UNLESS OTHERWISE SPECIFIED

DIMENSIONS IN IN.	ANGLES +/– 1 DEGREE	.XX +/– .010
SURFACE FINISH 125	FRACTIONS +/– 1/32	.XXX +/– .001

DATE:
SCALE:
DRAWN:
CHECK:
APPROVED:

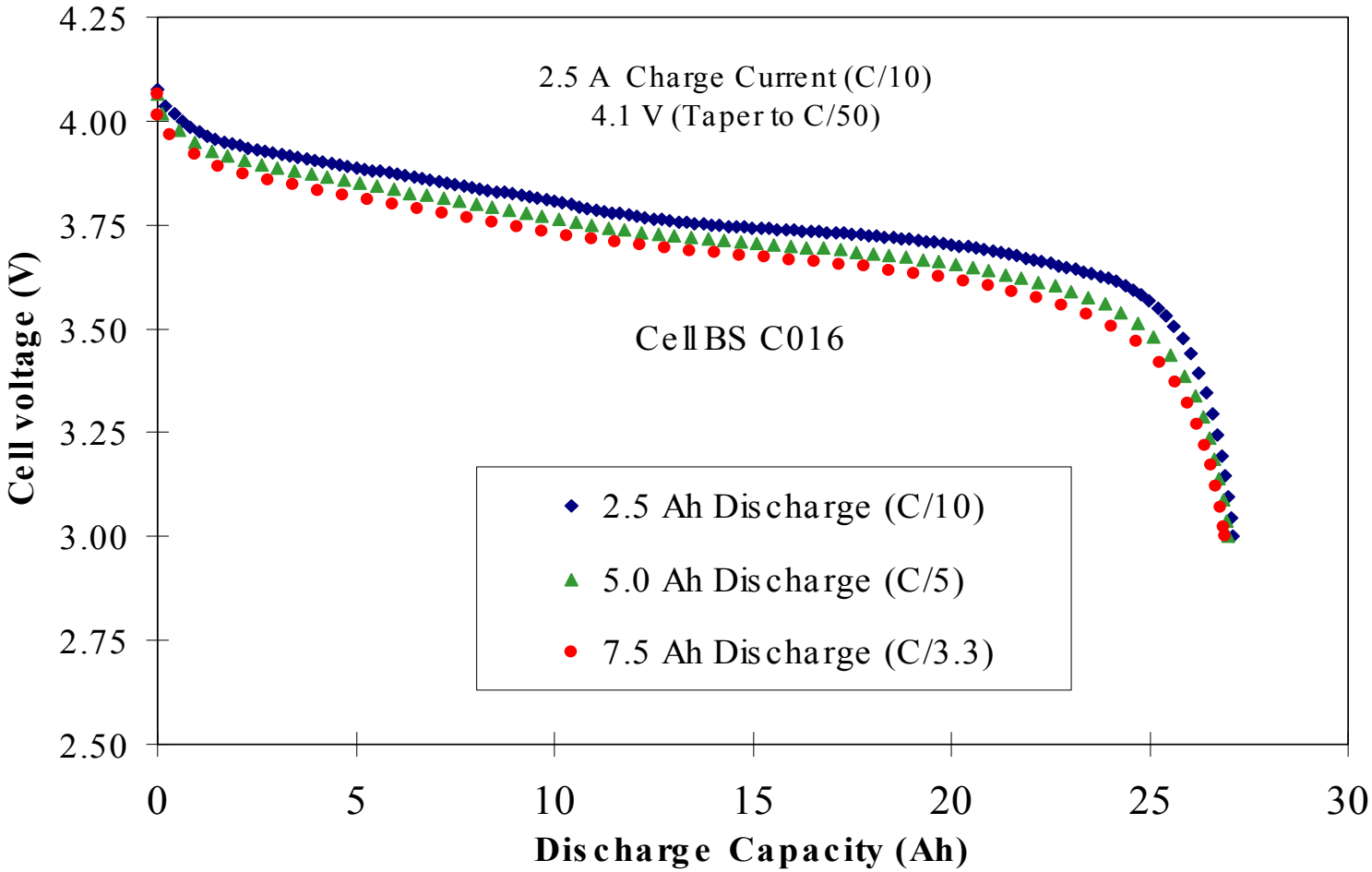
67–1143 G.A.
DESIGN II 25Ah CYLINDRICAL

DWG.#:M044800D A

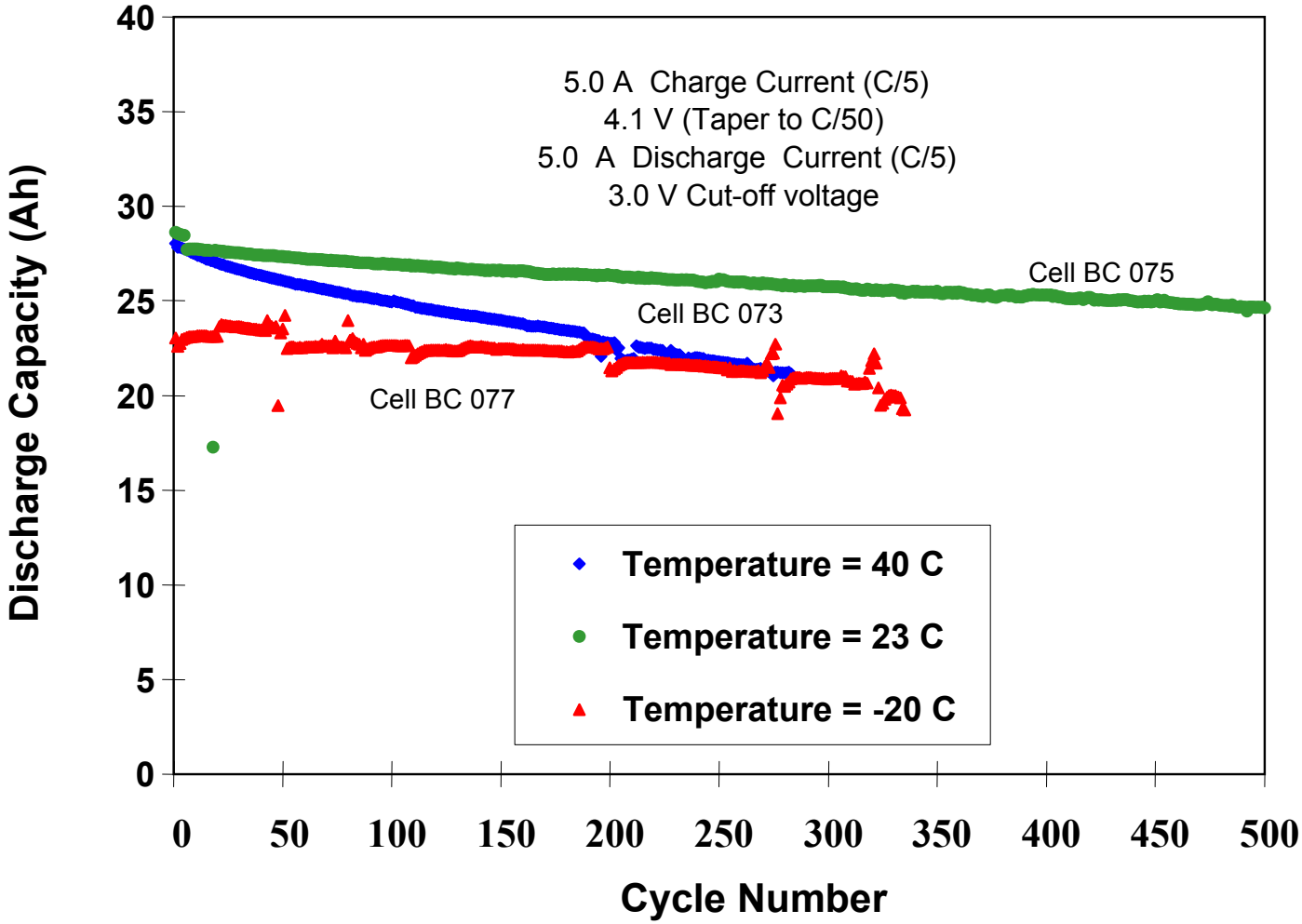
D

25 - Ah Cylindrical Cell

Eagle-Picher 25 Ah Lithium - Ion Cells for Lander Applications
Room Temperature Rate Capability

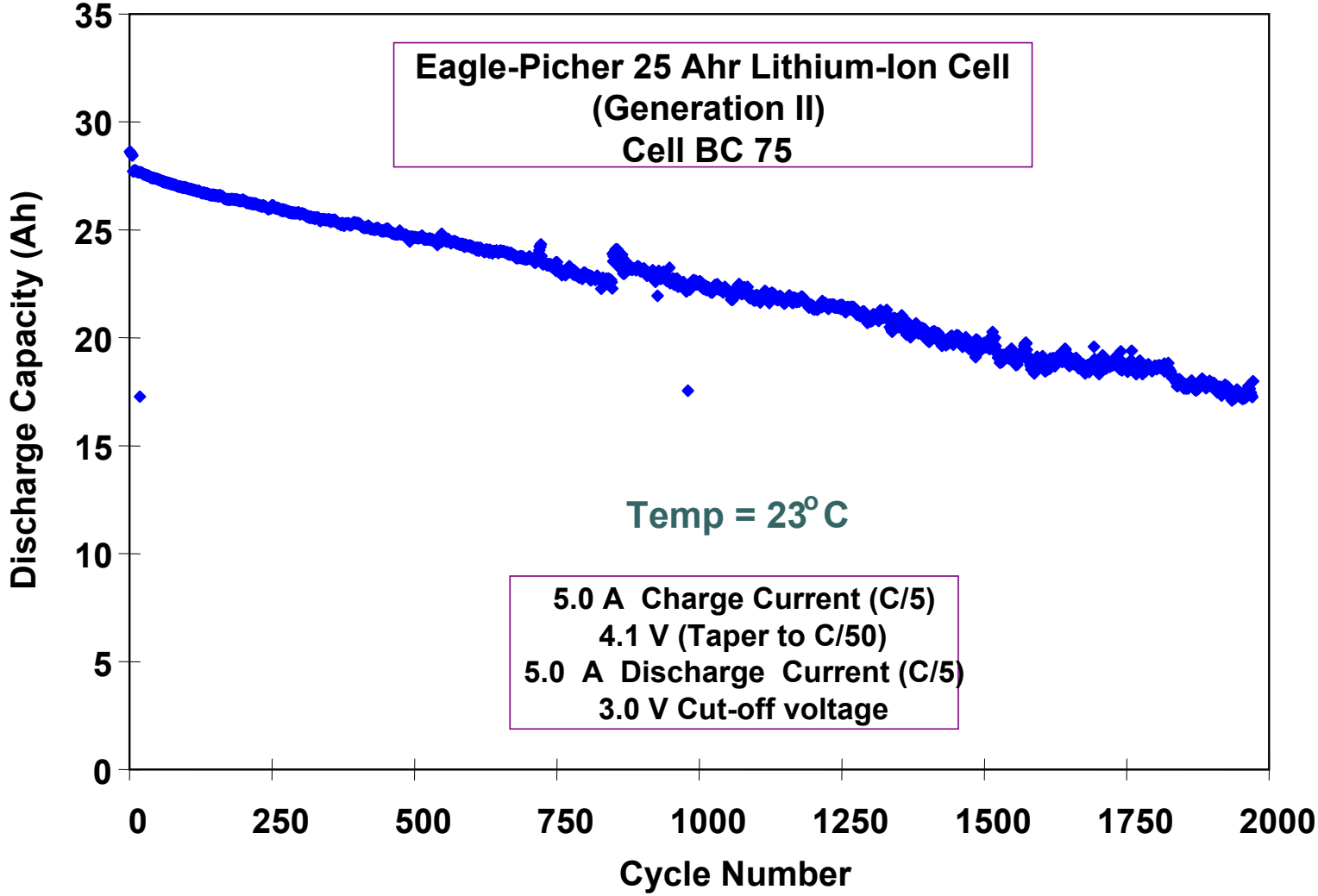


Cycle Life Characteristics at Different Temperatures (Gen II)

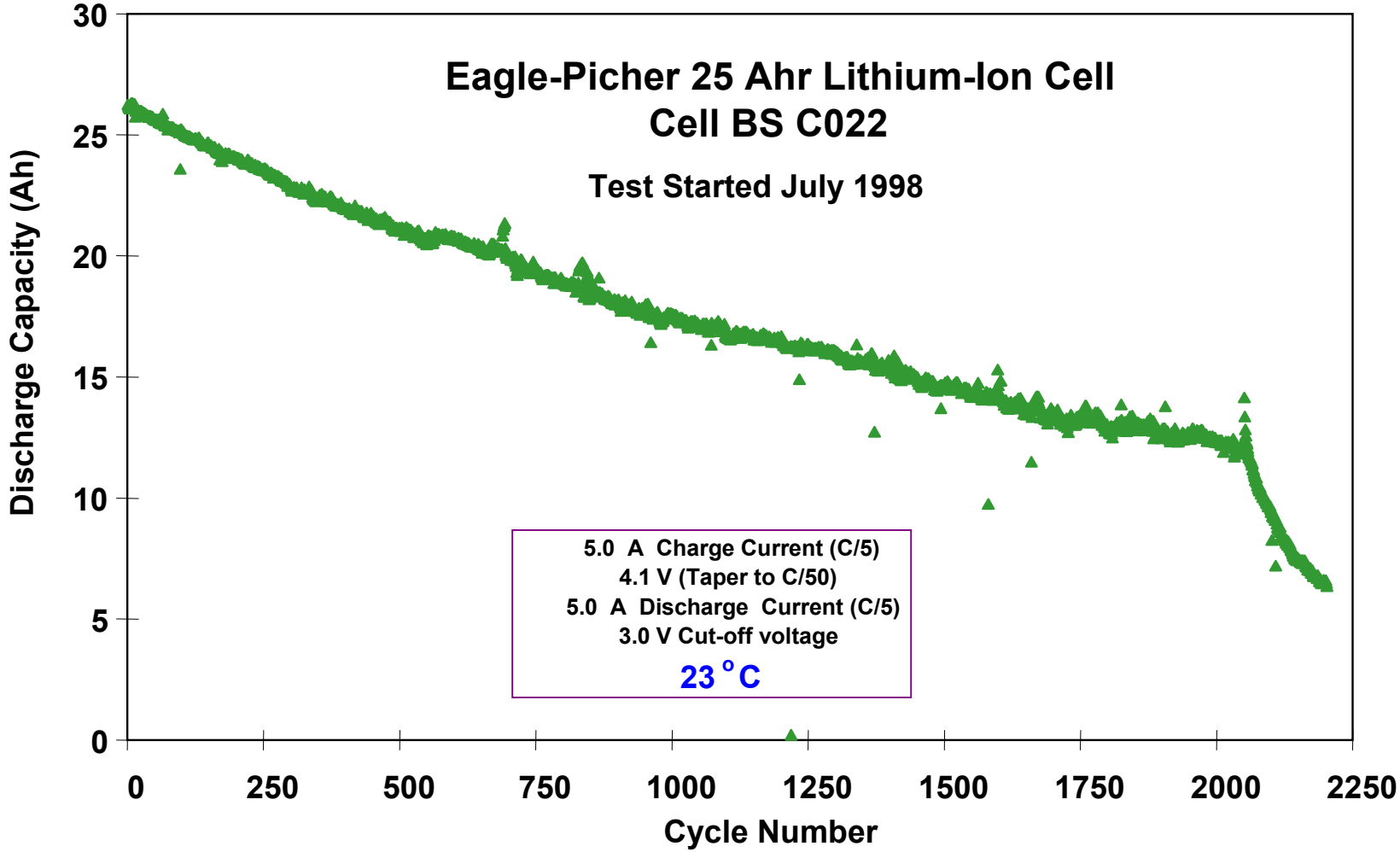


25 - Ah Cylindrical Cell

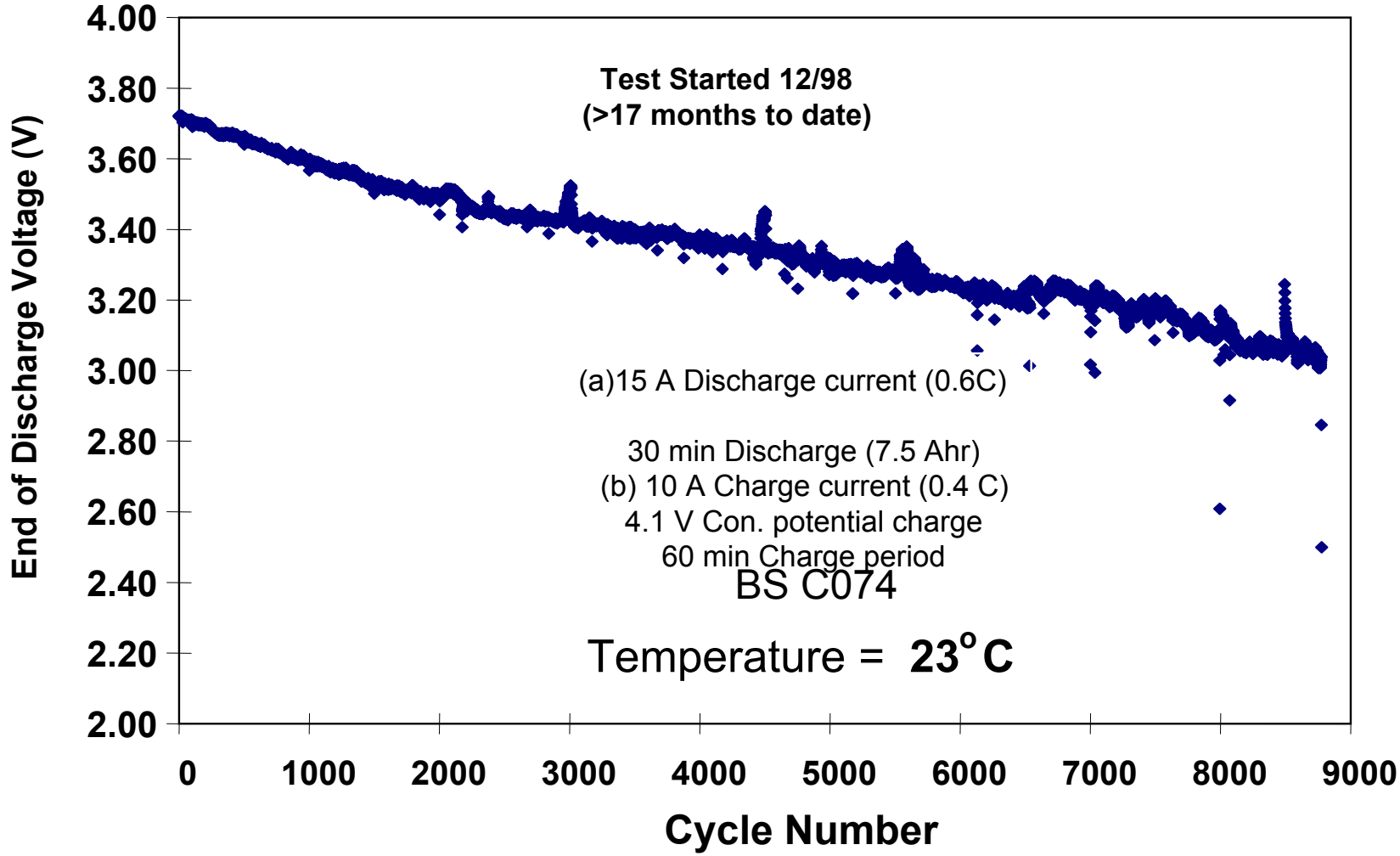
Room Temperature Cycle Life Performance (100% DOD at 23°C)



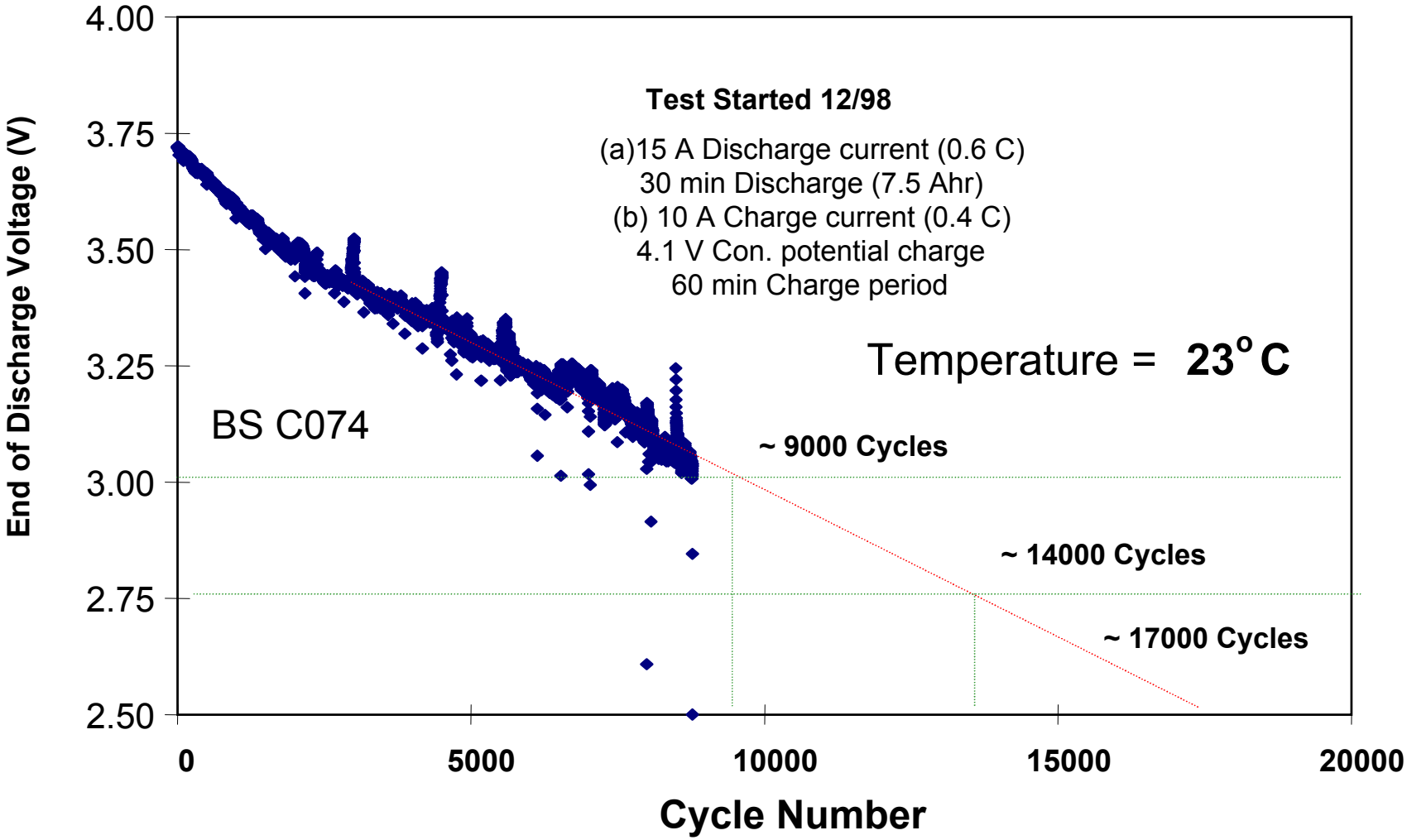
Room Temperature Cycle Life Performance (100% DOD at 23ºC)



Eagle-Picher 25-Ah Cell - JPL LEO Test Results



Eagle-Picher 25-Ah Cell - JPL LEO Test Results



Conclusions - Design II

- Design changes from Design I to II resulted in improved low temperature performance and rate capability
- Effect of temperature on capacity fade as expected
- Very good cycle life at 60% initial capacity at 2000, 100% DOD, C/5 cycles
- Simulated LEO test protocol, 30% DOD, shows 9000 cycles at 23°C. Better results would be expected at lower temperatures
- One cell vented after 2000 cycles with only a loss in capacity

Conclusions - General

- One of the first large lithium ion cells delivered for evaluation
- Showed the potential for the technology to replace existing technologies and to be mission enabling

Acknowledgements

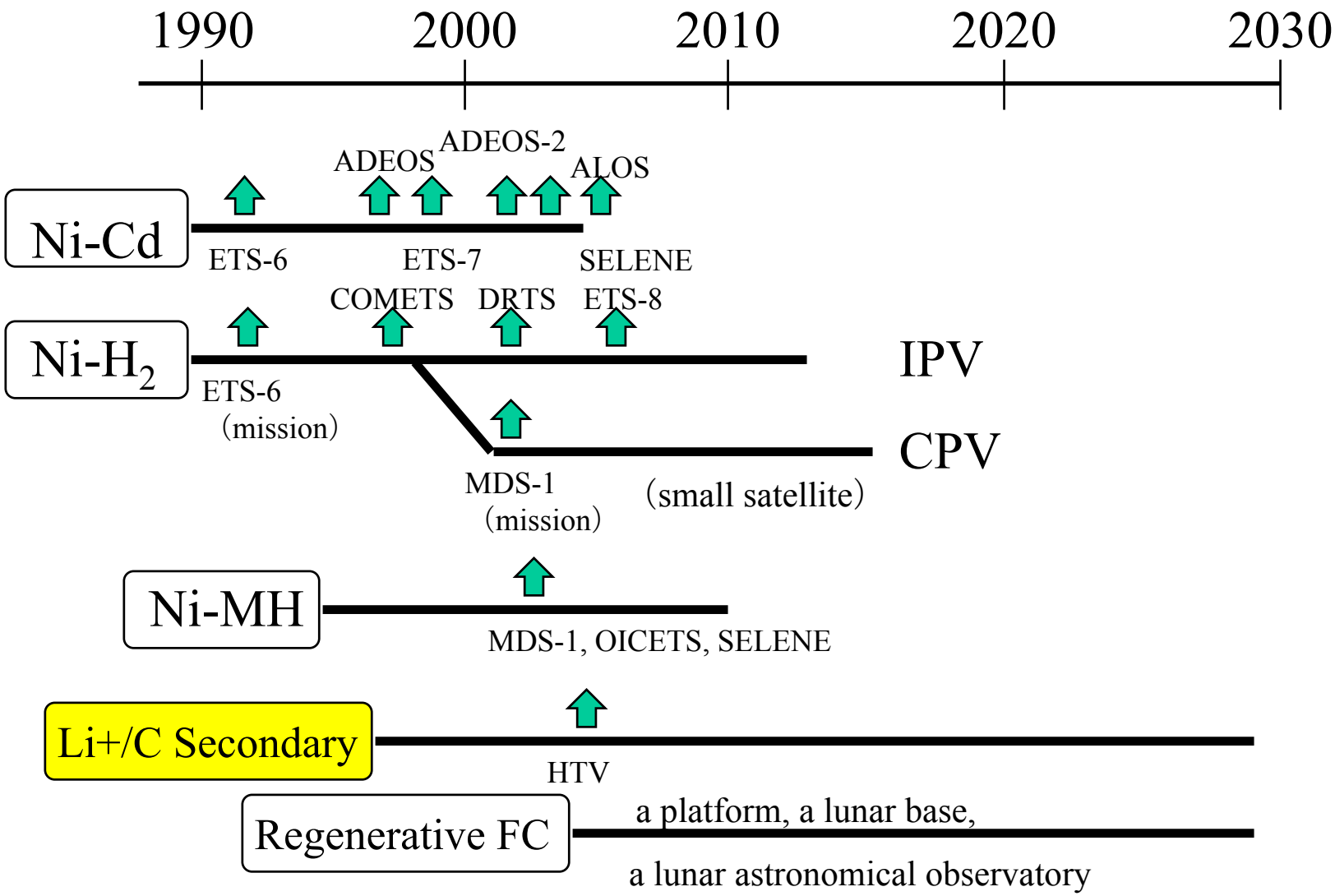
- EPEPC gratefully acknowledges the cooperation and test results provided by JPL.

Simulated LEO and GEO Cycling Tests of Lithium-Ion Cells at Tsukuba Space Center, NASDA

Y. Sone, X. Wang, H. Kusawake, and S. Kuwajima

Office of Research and Development
National Space Development Agency of Japan (NASDA)

Development of Space Batteries at NASDA



NASDA

List of Lithium Ion Secondary Cells

Data Update

Cap. /Ah	Package	Mode	Temp /℃	DOD /%	Charge (CC-CV)		Discharge	C/D Ratio	Sample Number		Date Started	Cycles	
					CC/A	CV/V (/cell)	Current /A		Initial	Present		Ended	Present
0.7	CELL	LEO	20	35.7	0.3	4.1	0.5	1.01	2	End	May-95	13,000	--
0.7	CELL	LEO	20	35.7	0.3	4.0	0.5	1.01	2	End	May-95	8,200	--
1.0	CELL	LEO	20	25	0.3	4.2	0.5	1.01	2	End	May-95	25,000	--
1.0	CELL	LEO	20	25	0.3	4.1	0.5	1.01	2	End	May-95	25,000	--
1.2	CELL	LEO	20	20.8	0.3	4.1	0.5	1.01	2	End	May-95	18,151	--
1.2	CELL	LEO	20	20.8	0.3	4.0	0.5	1.01	2	End	May-95	25,000	--
0.7	CELL	LEO	20	25	0.21	4.1	0.35	1.01	2	End	Sept-96	7,353	--
0.7	CELL	LEO	20	25	0.21	4.0	0.35	1.01	2	End	Sept-96	12,108	--
1.0	CELL	LEO	20	18	0.21	4.2	0.35	1.01	2	End	Sept-96	15,000	--
1.0	CELL	LEO	20	18	0.21	4.1	0.35	1.01	2	End	Sept-96	15,000	--
0.98	CELL	LEO	20	31	0.36	4.2	0.6	1.01	2	End	Sept-96	3,322	--
0.98	CELL	LEO	20	31	0.36	4.1	0.6	1.01	2	End	Sept-96	3,203/ 15,000	
1.0	CELL	LEO	20	30	0.36	4.2	0.6	1.01	2	End	Sept-96	15,000	--
1.0	CELL	LEO	20	30	0.36	4.1	0.6	1.01	2	End	Sept-96	3,003/ 15,000	--
1.2	CELL	LEO	20	18	0.36	4.1	0.6	1.01	2	End	Sept-96	14,143/ 15,000	--
1.2	CELL	LEO	20	18	0.36	4.0	0.6	1.01	2	End	Sept-96	15,000	--

Life Performance Test of 18650 Lithium Ion Cells

Data Update

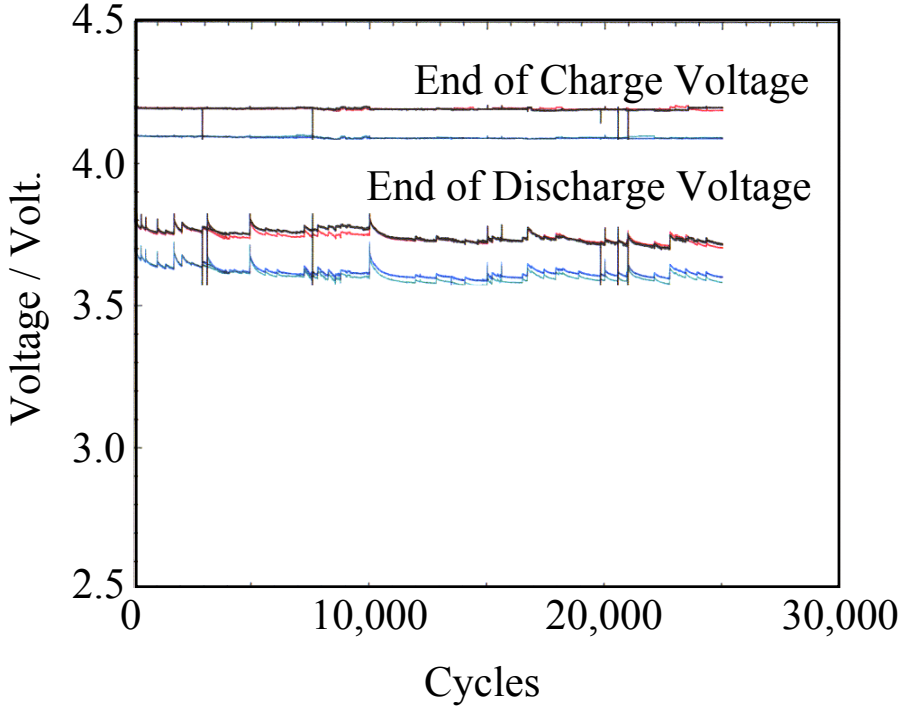


Fig. The Performance of $LiCoO_2$/Non-graphite Cells.

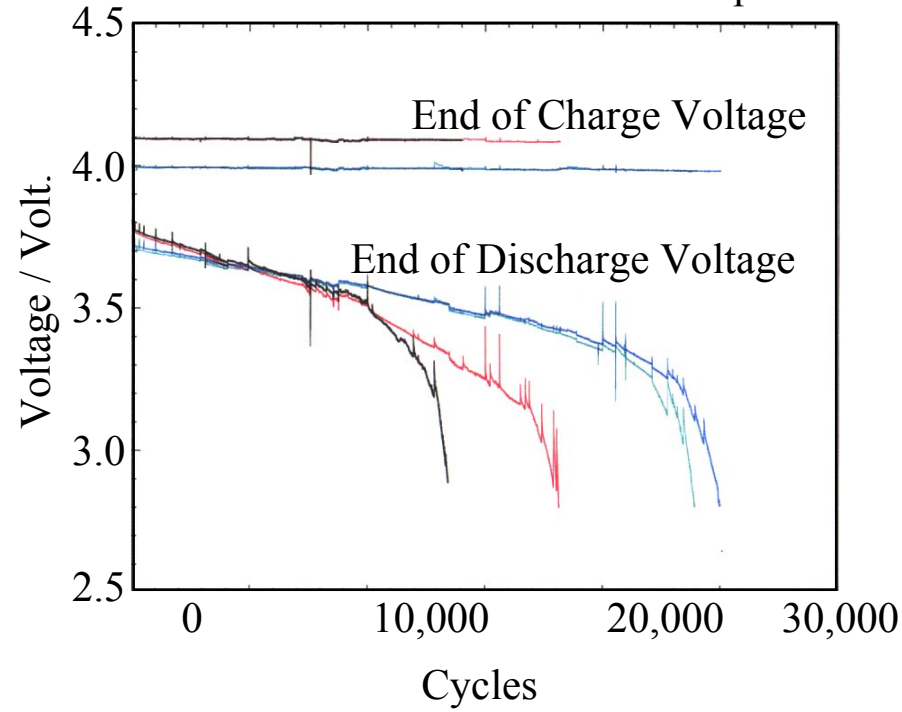


Fig. The Performance of $LiCoO_2$/Graphite Cells.

Charged up to 4.2 V

Charged up to 4.1 V

DOD=25%

Charged up to 4.1 V

Charged up to 4.0 V

DOD=25%

Commercial lithium-ion cells from several companies were tested.
Above results were the longest performance.
The LEO simulation tests using commercial cells were concluded after we observed 25,000 cycles from two different types of cells.

NASDA

List of Lithium Ion Secondary Cells

October 2002

Cap. /Ah	Package	Mode	Temp /℃	DOD /%	Charge (CC-CV)		Discharge	C/D Ratio	Sample Number		Date Started	Cycles	
					CC/A	CV/V (/cell)	Current /A		Initial	Present		Ended	Present
30	CELL	LEO	20	25	9	4.05	15	1.005	5	5	Sept-98	--	19,385
30	CELL	LEO	20	40	15	4.05	24	1.005	5	4 1)	Sept-98	10,000	--
10	CELL	LEO	20	25	3	4.05	5	1.005	2	2	June-99	--	15,998
10	CELL	LEO	20	40	5	4.05	8	1.005	3	3	June-99	--	15,965
100	CELL	LEO	15	25	25	3.95	50	1.005	5	5	May-99	--	15,340
100	CELL	LEO	15	40	50	3.95	80	1.005	5	5	July-99	--	14,935
100	CELL	GEO	15	80	10	3.95	67	1.005	5	5	Aug-99	--	919
90	CELL	LEO	10	40	45	4.2	72	1.000	5	5	June-00	--	813
90	CELL	GEO	10	80	9	4.2	60	1.000	5	5	July-00	--	651
100	BATT	GEO	15 1)	80	10	3.95	67	1.005	10	10	Jan-02	--	98
50	CELL	LEO	15	40	25	3.95	40	1.000	5	5	Sept-01	--	5,182
50	CELL	HTV	15	40	25	3.95 2)	40	1.000	5	5	Spet-01	--	2,348

1) Temperature was elevated up to 25 degrees C when sun-shine period was simulated.
2) The current rate and taper voltage for charge were changed stepwise simulating HTV operations.

Test Conditions of Lithium-Ion Secondary Cells

Orbit	LEO		GEO
DOD	25%	40%	80%
Charge Rate	0.25 – 0.33 C	0.5 C	0.1 C
Taper Voltage	3.95 – 4.20 V		
Discharge Rate	0.5 C	0.8 C	0.67 C
Ambient Temperature	10 – 20 degrees C		

10Ah $LiCoO_2$/Graphite Cells

Cell Style		Prismatic
Electrode	Positive Electrode	LiCoO2
	Negative Electrode	C (graphite) over porous Nickel
Capacity Nominal / Typical		10Ah / 12 Ah
Weight		0.43 kg
Dimensions		70 mm (W) x 23.5 mm (D) x 130 mm (H)
Energy Density	per Weight	100 Wh/kg
	per Volume	202 Wh/L
Charge Voltage		4.1 V
Discharge Voltage	Nominal Voltage	3.6 V
	Lower Limited Voltage	3.0 V

10 Ah Prismatic cells were prepared in 1999.
The company used porous Ni instead of Cu sheet current collector of the negative electrode. As is well known, Cu causes a serious damage when the cell is discharged excessively. We expected improvement of such defects in Lithium-Ion cells.

Trend Data of 10 Ah $LiCoO_2$/Graphite Cells

Data Update

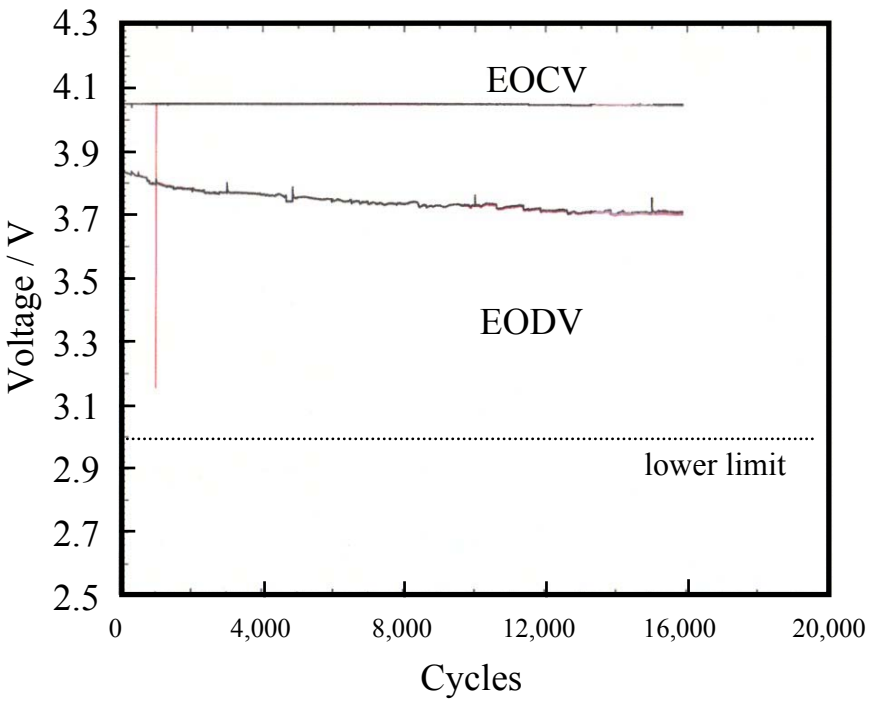


Fig. Life Cycle Trend of DOD=25% LEO Test
Two cells are connected in series.

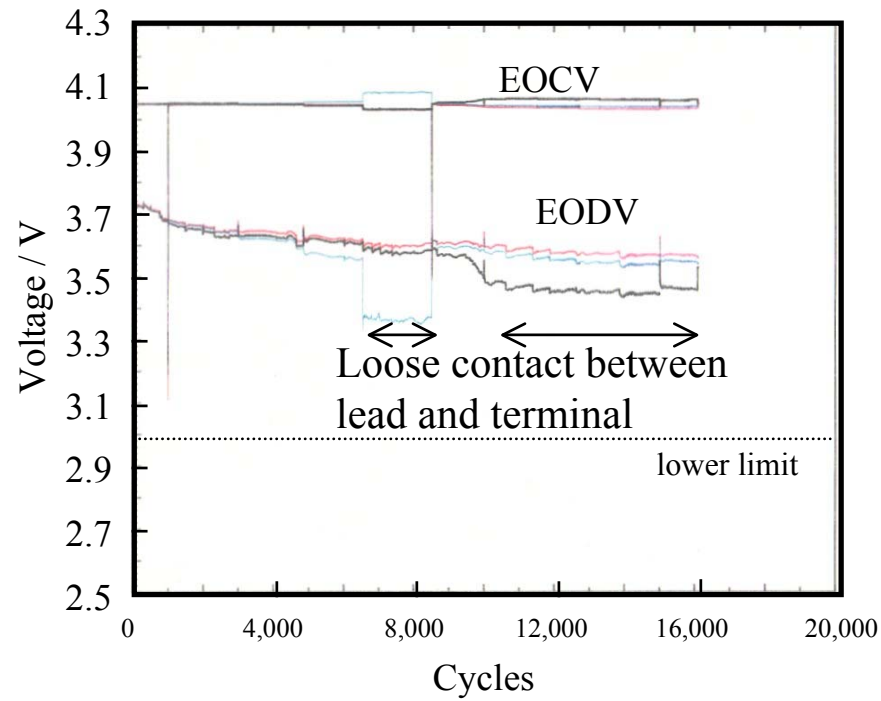


Fig. Life Cycle Trend of DOD=40% LEO Test
Three cells are connected in series.

The figures show the trends of LEO tests using 10 Ah prismatic cells. Very stable performance is still observed for DOD=25%, but for DOD=40%, one of the three cells started to show higher EOCV and lower EODV. Loose contact between terminal and lead caused these phenomena. We shall need an improvement of the terminal design.

10Ah $LiCoO_2$/Graphite Cells

Data Update

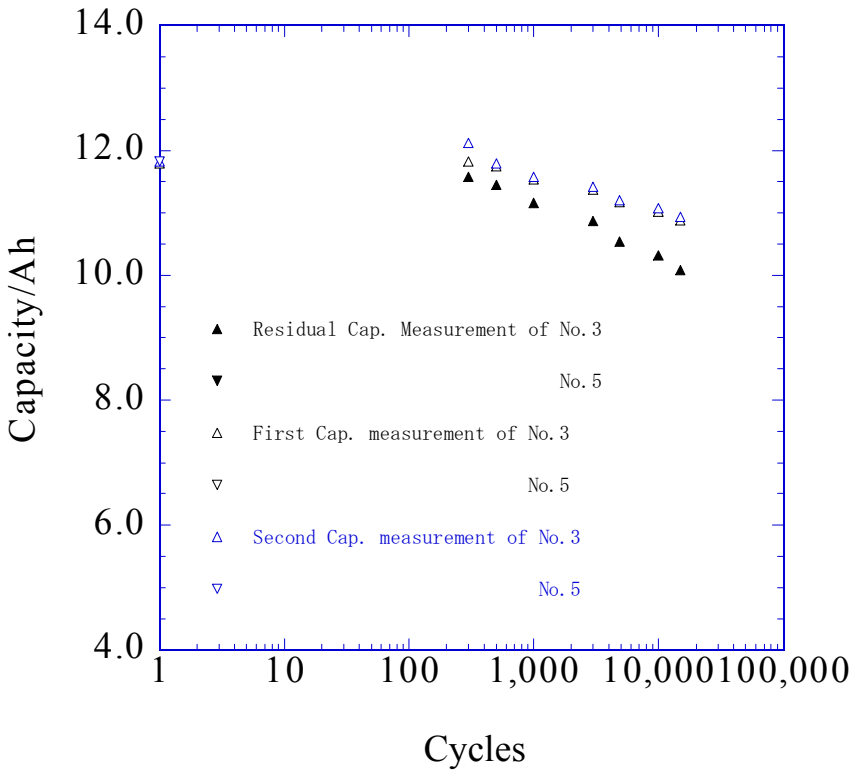


Fig. Trend of Capacity, LEO Test/DOD25%

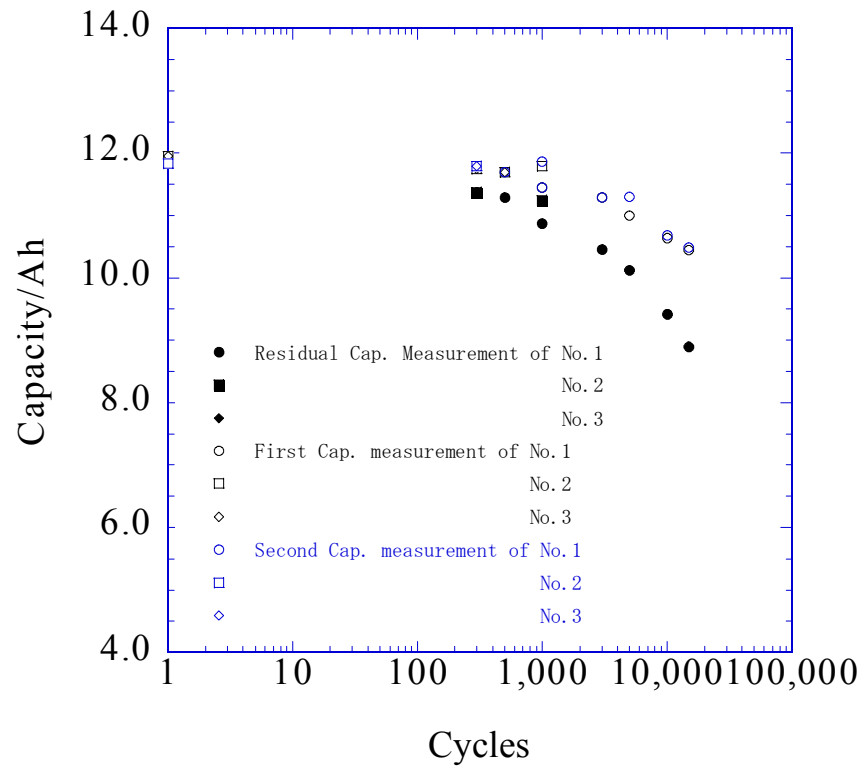


Fig. Trend of Capacity, LEO Test/DOD40%

While the performance of one of the cells was fading with respect to EOCV and EODV for DOD=40%, the capacity still exceeded over 8 Ah after 15,000 cycles.

Furthermore, we could obtain adequate capacity above the nominal when we charged cells at 0.1C for 16 hours.

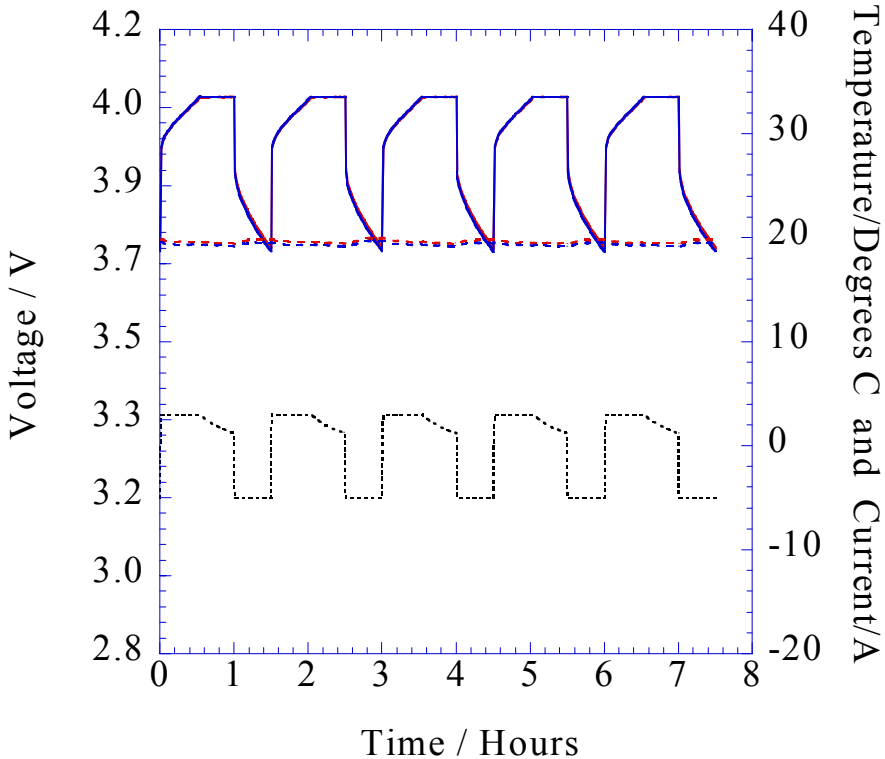


Fig. Recent Cycle Performance of DOD=25% LEO Test

Two cells are connected in series.
From 15,870th to 15,874th cycle

——— Voltage - - - - - Temperature ..... Current

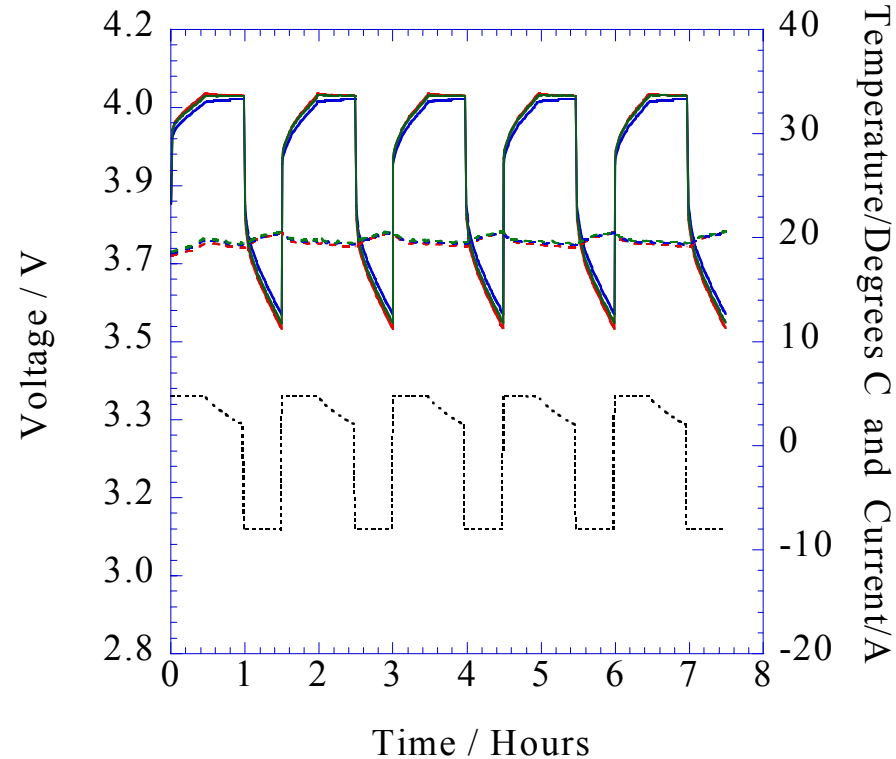


Fig. Recent Cycle Performance of DOD=40% LEO Test

Three cells are connected in series.
From 16,093rd to 16,097th cycle

——— Voltage - - - - - Temperature ..... Current

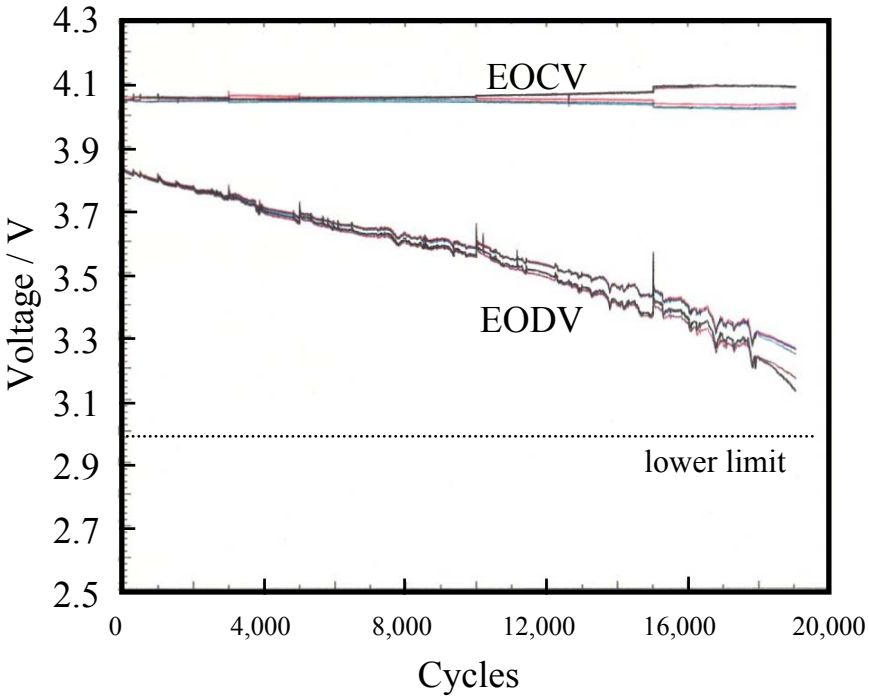
30Ah $LiCoO_2$/Graphite Cells

Cell Style		Prismatic
Electrode	Positive Electrode	LiCoO2
	Negative Electrode	C (graphite)
Capacity	Nominal / Typical	30Ah / 39 Ah
Weight		1.3 kg
Dimensions		98.5 mm (W) x 27 mm (D) x 190 mm (H)
Energy Density	per Weight	108 Wh/kg
	per Volume	278 Wh/L
Charge Voltage		4.1 V
Discharge Voltage	Nominal Voltage	3.6 V
	Lower Limited Voltage	3.0 V

The electrode design was based on normal ground applications.
The original design of the cell required 7 hours for full charging condition when the charge was started from 0% SOC.

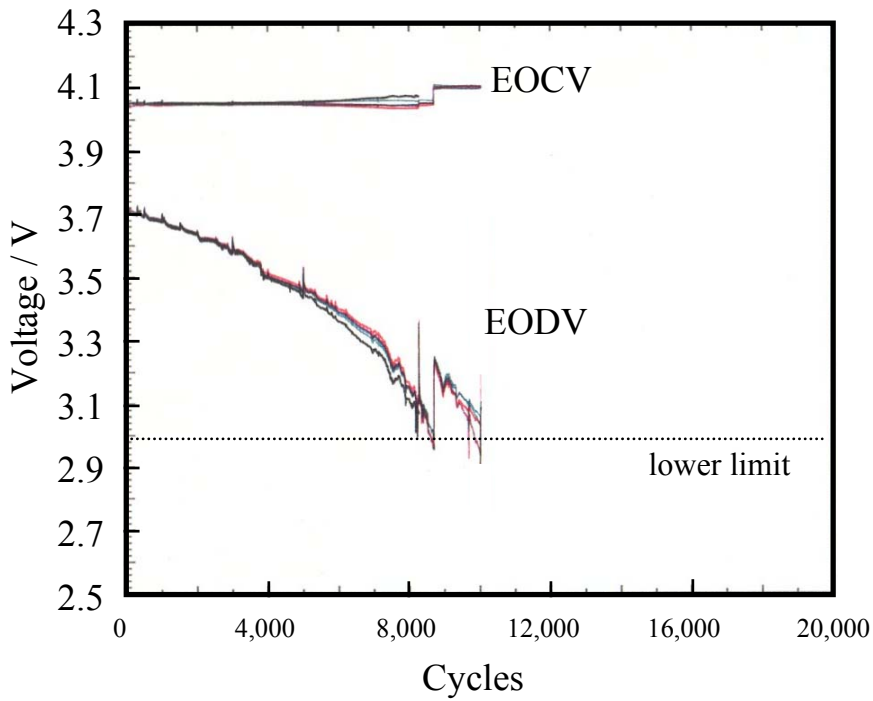
Trend Data of 30 Ah $LiCoO_2$/Graphite Cells

Data Update



Life Cycle Trend of DOD=25% LEO Test

Five cells are connected in series.



Life Cycle Trend of DOD=40% LEO Test

Five cells used to be connected in series. At 8,269 cycle, one of the cells was removed for DPA.

For DOD=25%, the performance difference among cells is increasing. For DOD=40%, a considerable decrease in EODV was observed. We analyzed the degradation by DPA and presented the results at '2000 NASA Aerospace Battery Workshop'.

The tests with DOD=40% was concluded at the 10,000th cycle.

Trend Data of 30 Ah $LiCoO_2$/Graphite Cells

Data Update

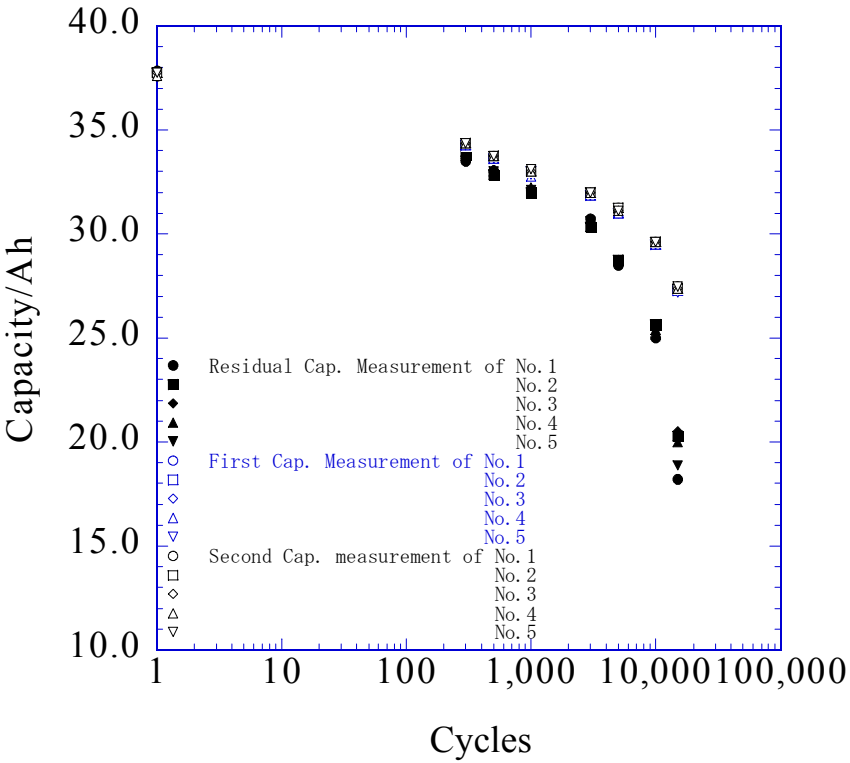


Fig. Trend of Capacity, LEO Test/DOD25%

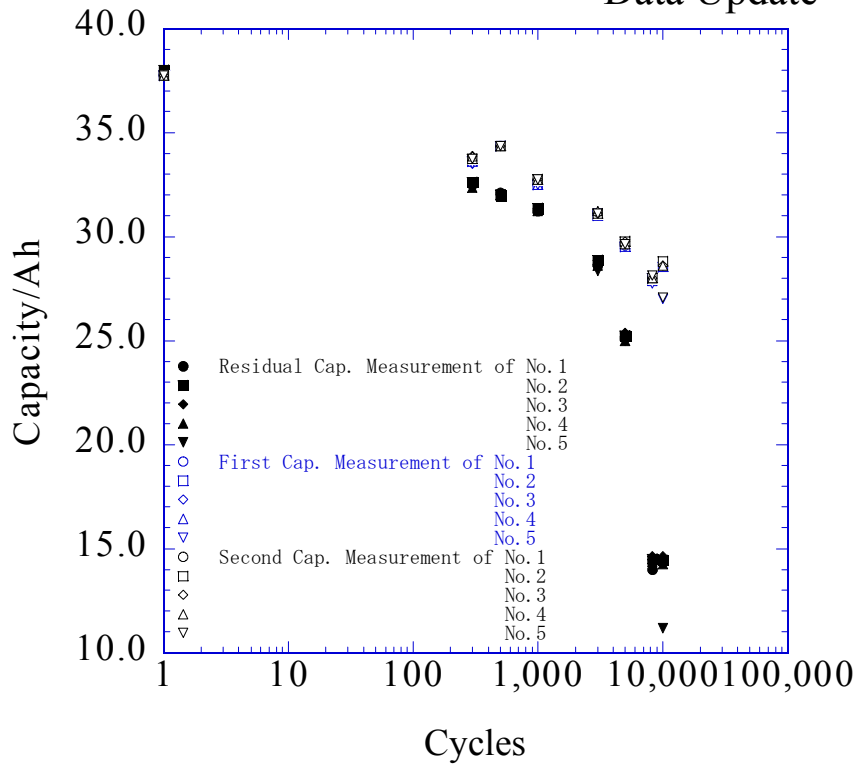


Fig. Trend of Capacity, LEO Test/DOD40%

Trend Data of 30 Ah $LiCoO_2$/Graphite Cells

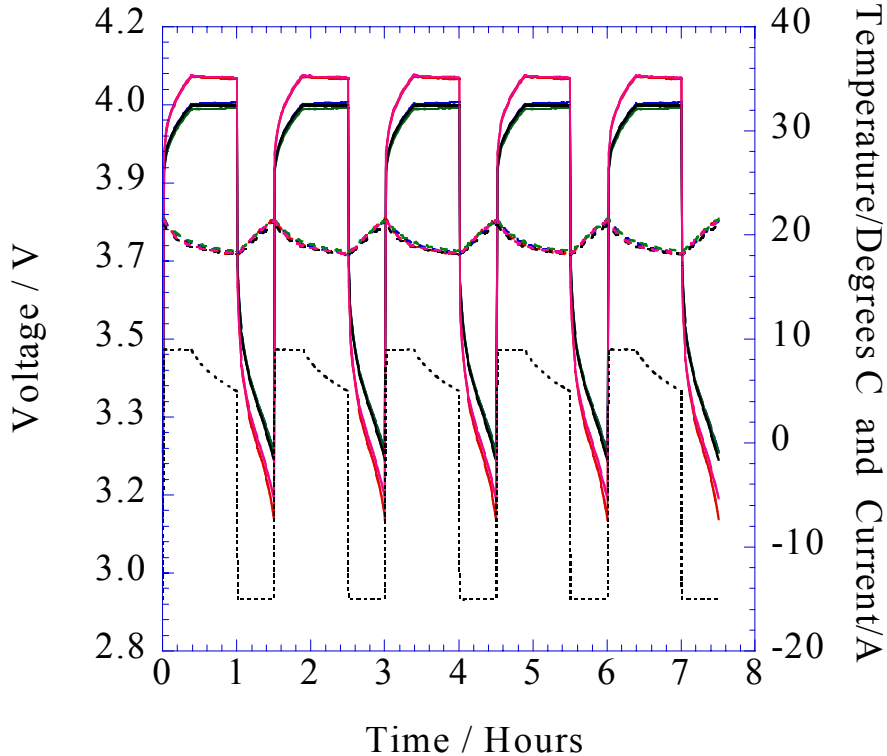


Fig. Trend data with DOD=25%, LEO Test

Five cells are connected in series.

From 19,324th to 19,328th cycle

——— Voltage - - - - - Temperature ..... Current

Data Update

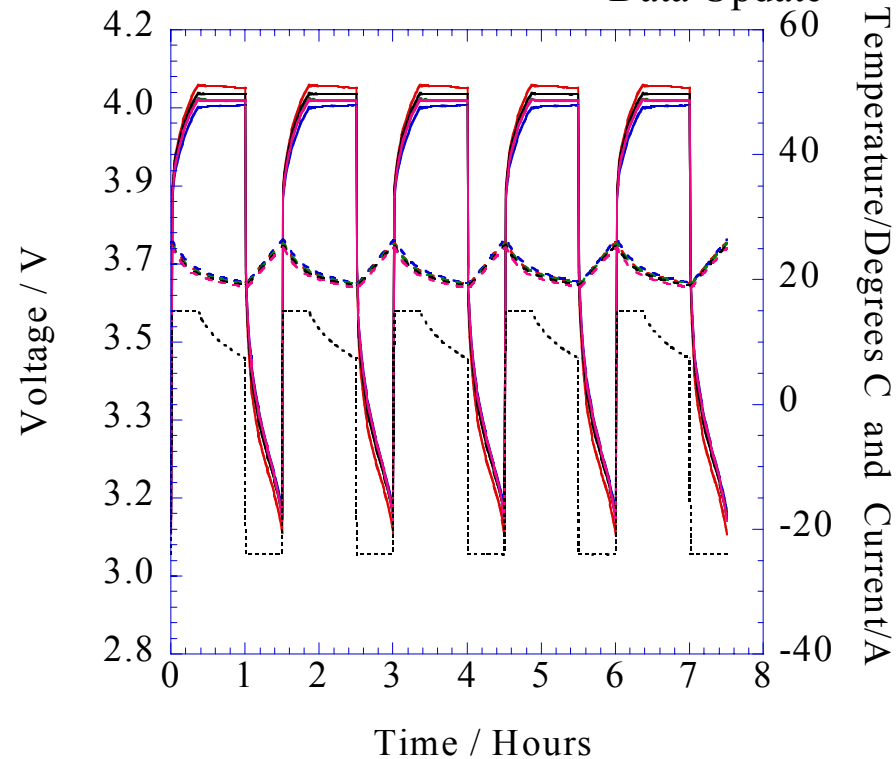


Fig. Trend data with DOD=40%, LEO Test

Four cells are connected in series.

From 8,265th to 8,269th cycle

——— Voltage - - - - - Temperature ..... Current

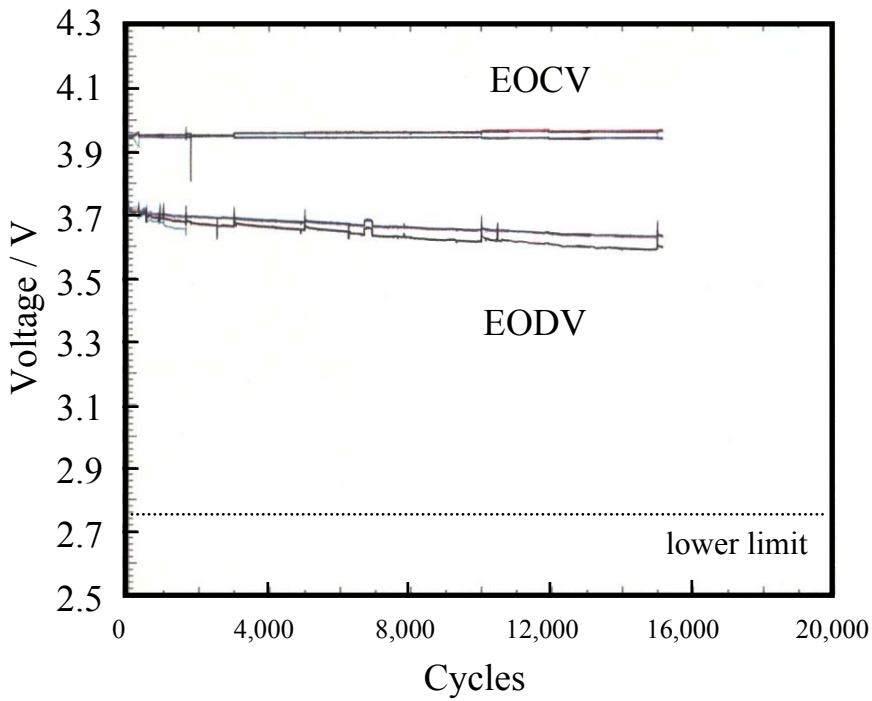
100 Ah $LiCoO_2$/Graphite Cells

Cell Style		Elliptic Cylinder
Electrode	Positive Electrode	LiCoO2
	Negative Electrode	C (graphite)
Capacity	Nominal / Typical	100Ah / 106 Ah
Weight		2.8 kg
Dimensions		130 mm (W) x 50 mm (D) x 207 mm (H)
Energy Density	per Weight	136 Wh / kg
	per Volume	309 Wh / L
Charge Voltage		3.98 V
Discharge Voltage	Nominal Voltage	3.6 V
	Lower Limited Voltage	2.75 V

Mitsubishi Electric Co., Ltd., and Japan Storage Battery Co., Ltd., are cooperating in the development of space batteries.
NASDA is evaluating the battery performance at Tsukuba Space Center.
Our target is to simulate LEO, GEO, and H-II Transfer Vehicle (HTV) operations.

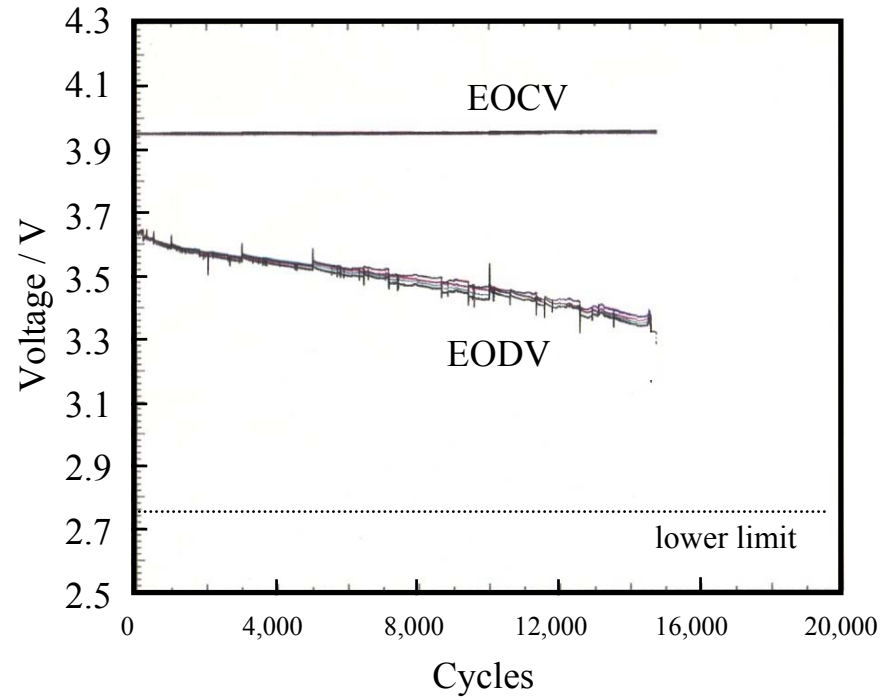
Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

Data Update



Life Cycle Trend of DOD=25% LEO Test

Five cells are connected in series.



Life Cycle Trend of DOD=40% LEO Test

Five cells are connected in series.

For DOD=25% and 40%, cell performance was very stable though EODV decreased slightly. Battery performance was very uniform and almost identical.

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

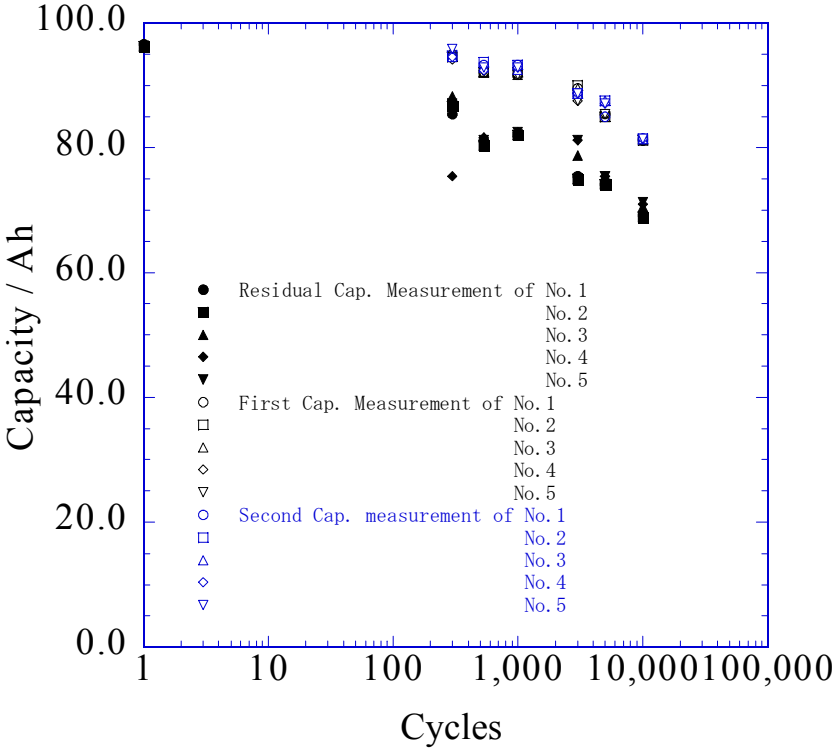


Fig. Trend of Capacity, LEO Test/DOD25%

Data Update

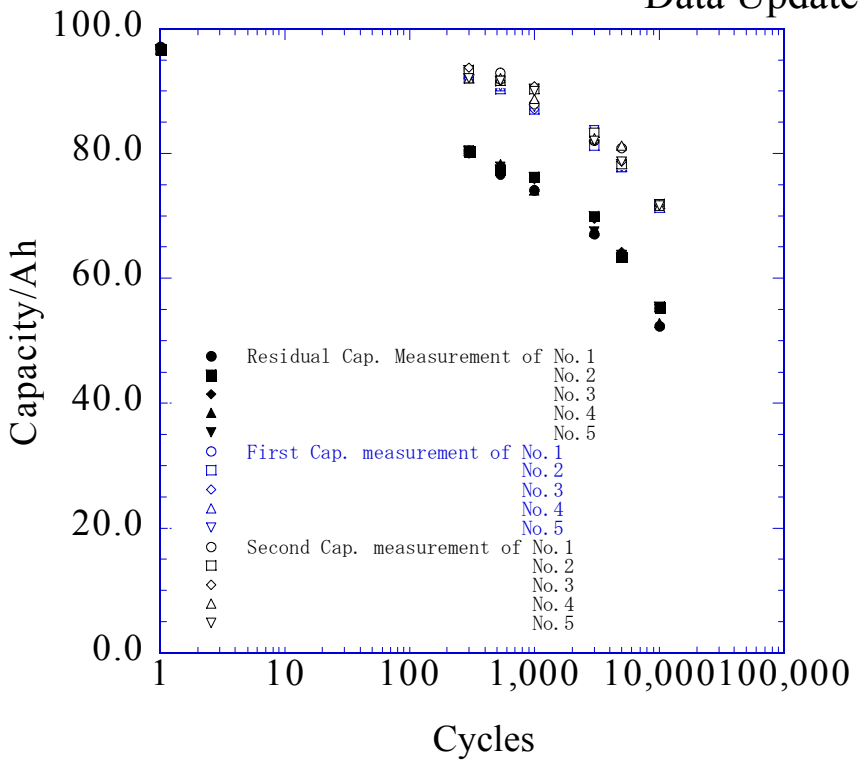


Fig. Trend of Capacity, LEO Test/DOD40%

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

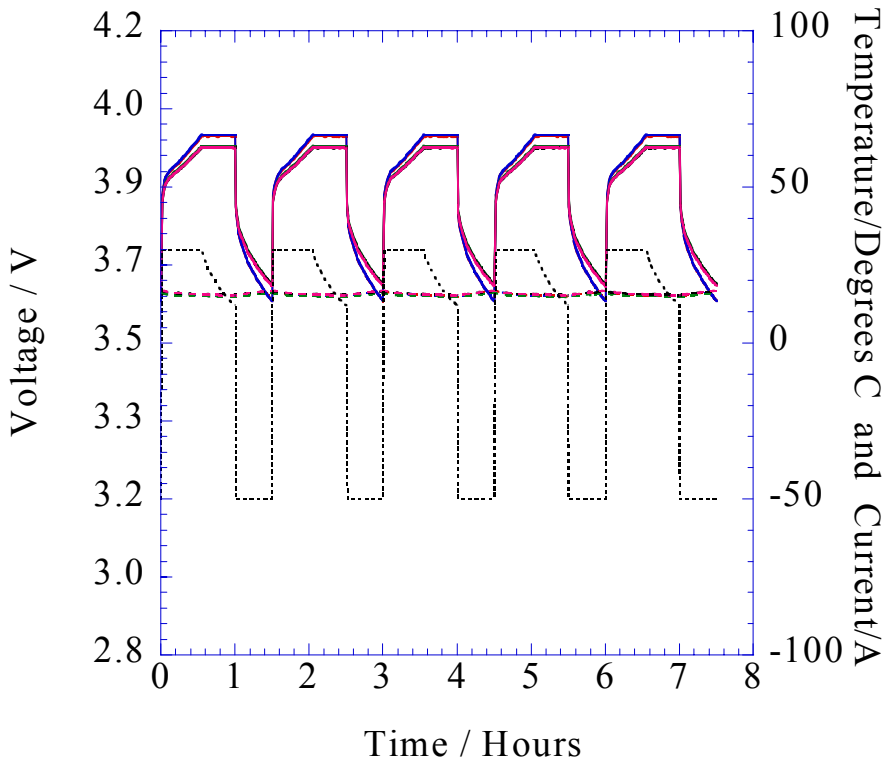


Fig. Trend data with DOD=25%, LEO Test

Five cells are connected in series.

From 15210th to 15214th cycle

——— Voltage - - - - - Temperature ..... Current

Data Update

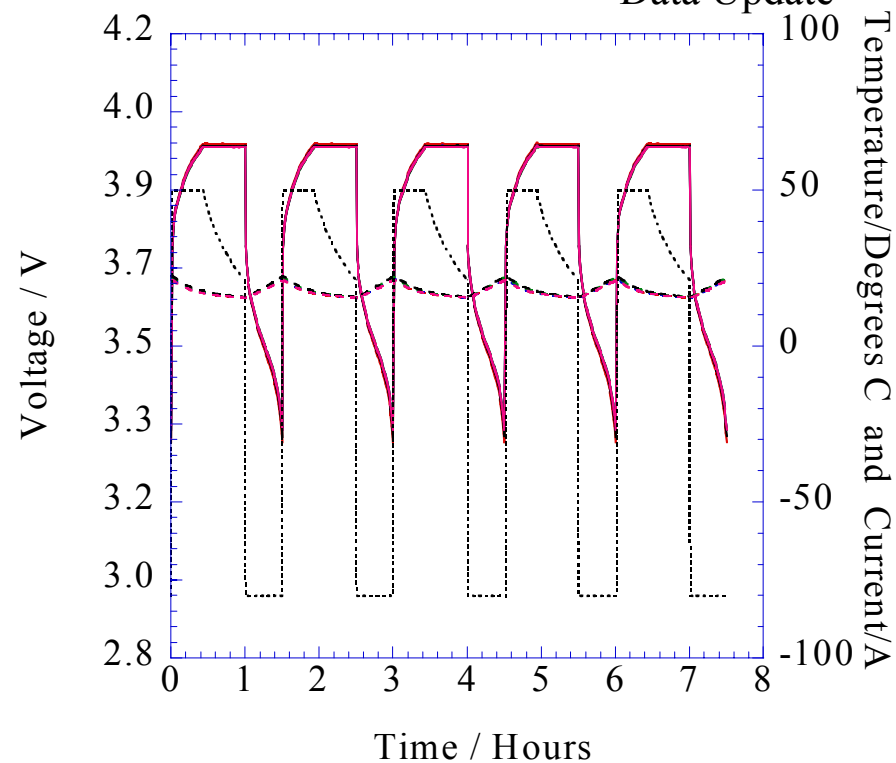


Fig. Trend data with DOD=40%, LEO Test

Five cells are connected in series.

From 14807th to 14811th cycle

——— Voltage - - - - - Temperature ..... Current

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

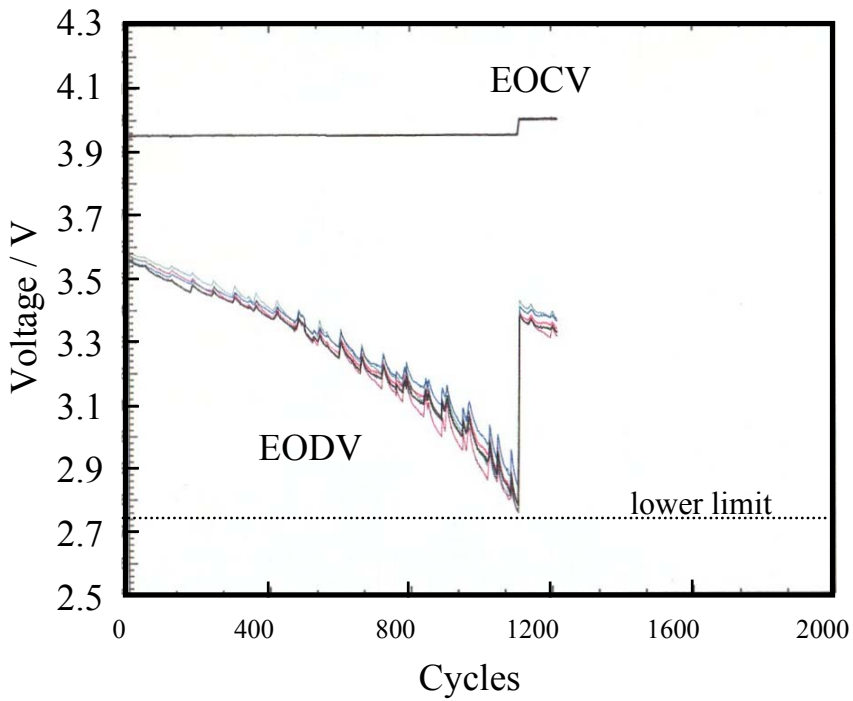


Fig. Trend data with DOD=80%, GEO Test
Five cells are connected in series.

Data Update

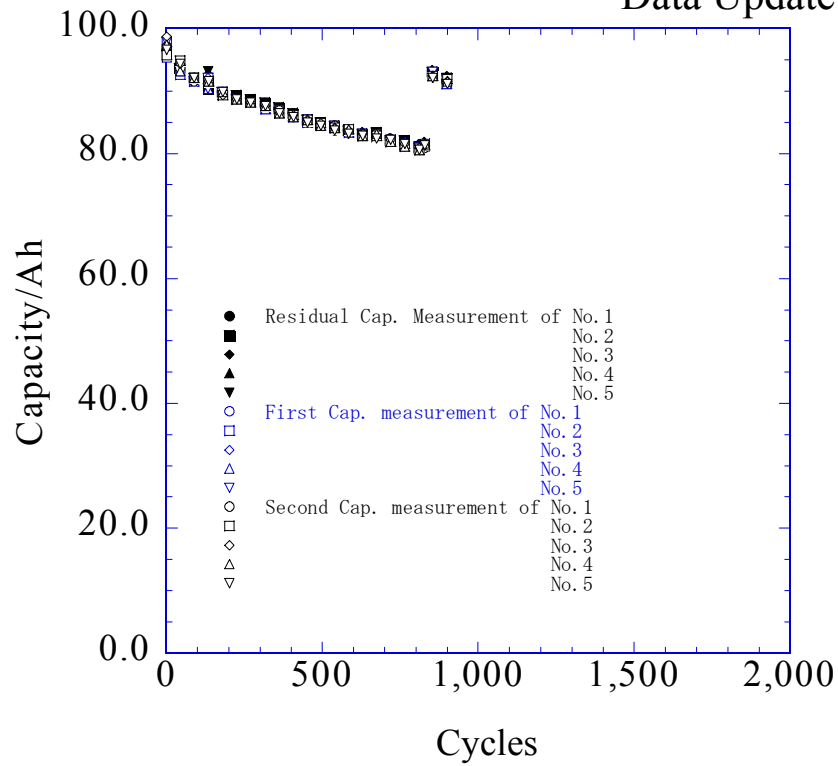


Fig. Trend of Capacity, GEO Test/DOD80%

After 1,000 cycles, the voltage decreased to 2.75 V, which is the lower voltage limit for the operation of these Lithium-Ion cells. We increased the taper voltage to 4.00V to continue our evaluation. This treatment increased EODV to 3.4 V and capacity to 95Ah, respectively.

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

Data Update

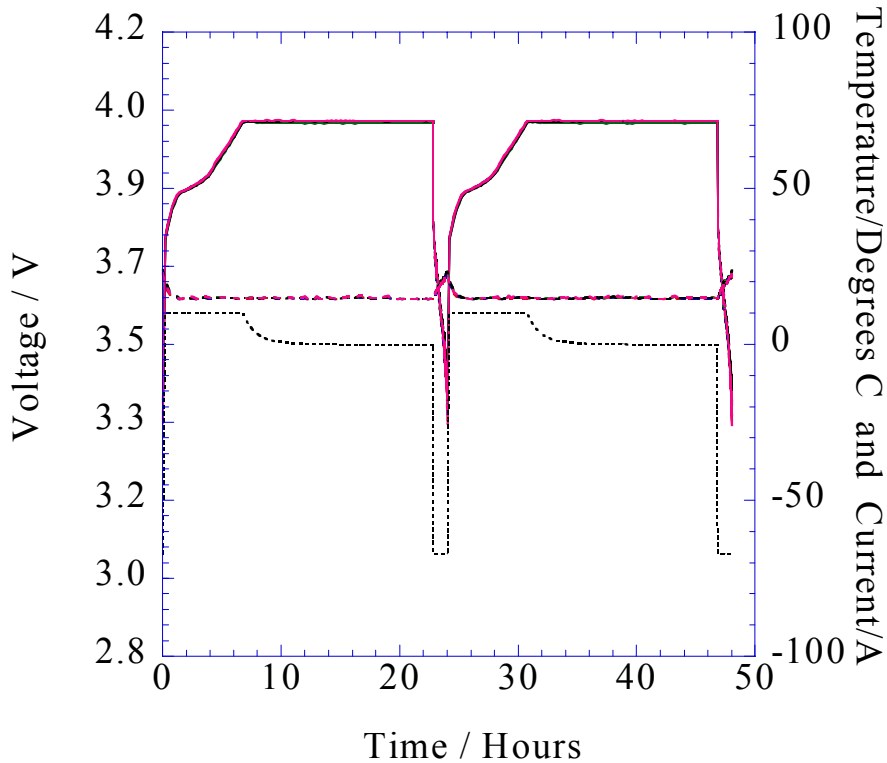


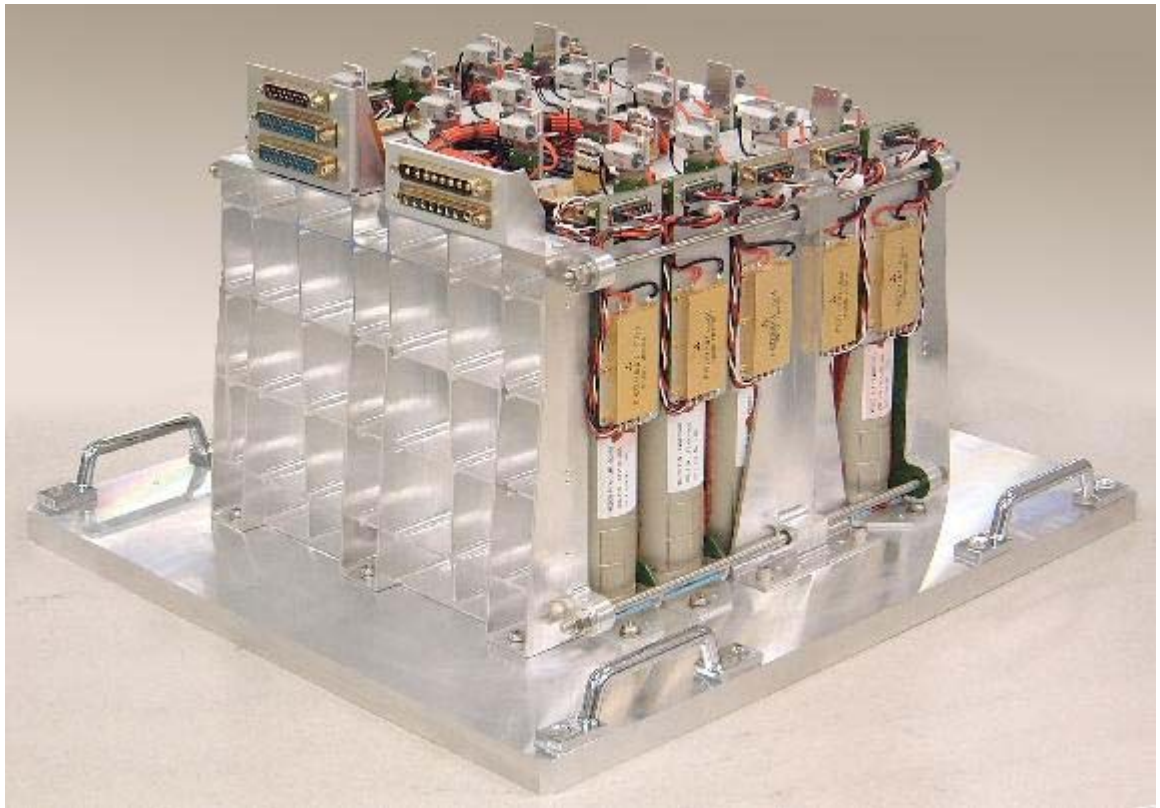
Fig. Cycle Curve with DOD=80%, GEO Test

Five cells are connected in series.

From 907th to 908th cycle

——— Voltage - - - - - Temperature ····· Current

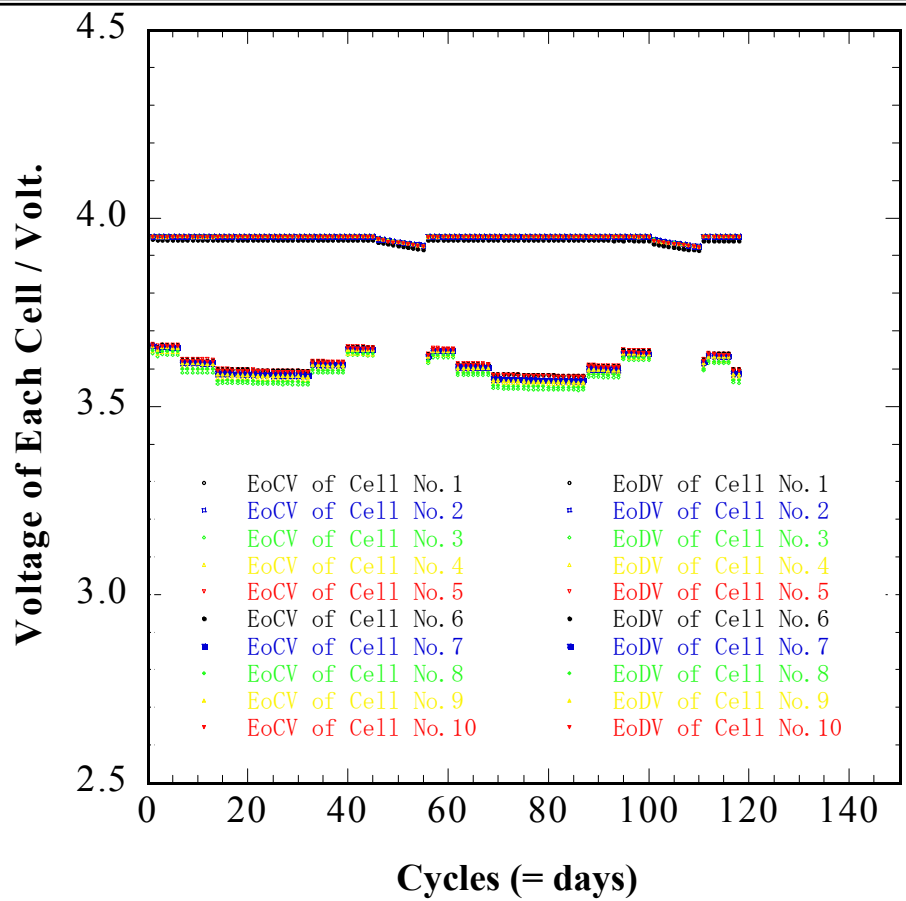
100Ah Lithium-Ion Battery



For GEO simulation, we performed cycle evaluations with constant DOD (80%). Using the above 100 Ah Lithium-Ion Battery, we combined the evaluation of cycle performance with three different DOD levels during one eclipse period with the thermally accelerated simulation of the sun-shine period in order to simulate GEO operations more precisely, .

100Ah Lithium-Ion Battery

Data Update



The maximum DOD during eclipse was 70%. The ambient temperature during the cycle test was controlled at 15 degrees C. Just before the sun-shine period, we fully charged the battery and increased the ambient temperature to 25 degrees C. The charged battery (OCV condition) was stored for 10 days at this temperature to simulate half a year storage at 0 degrees C in orbit.

Data Update

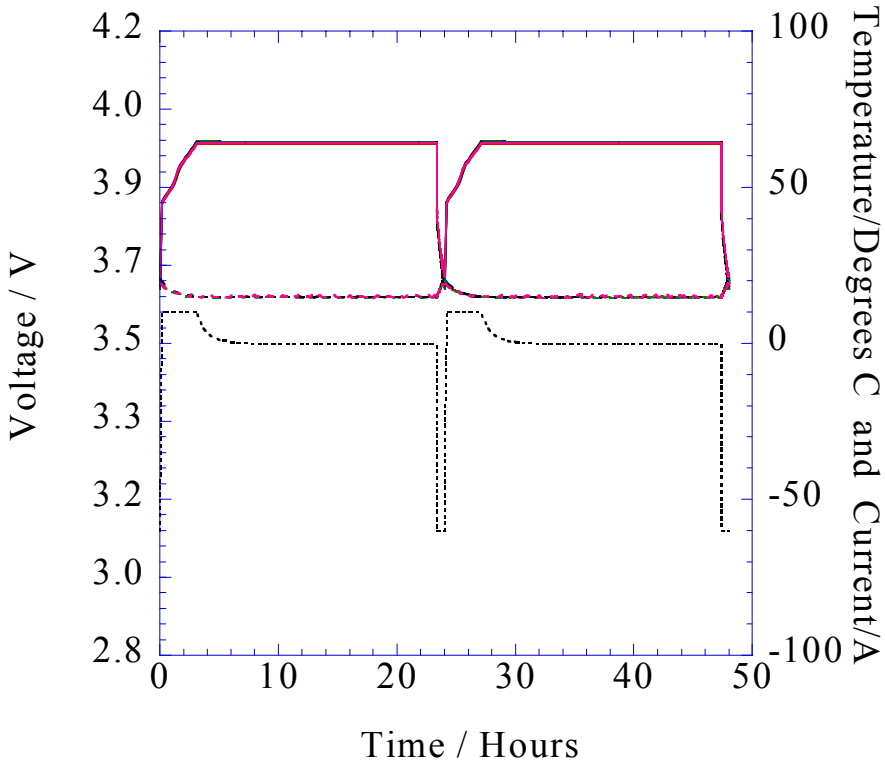


Fig. Trend data of 5 cells in Li-ion Battery

From 88th to 89th cycle

——— Voltage - - - - - Temperature ..... Current

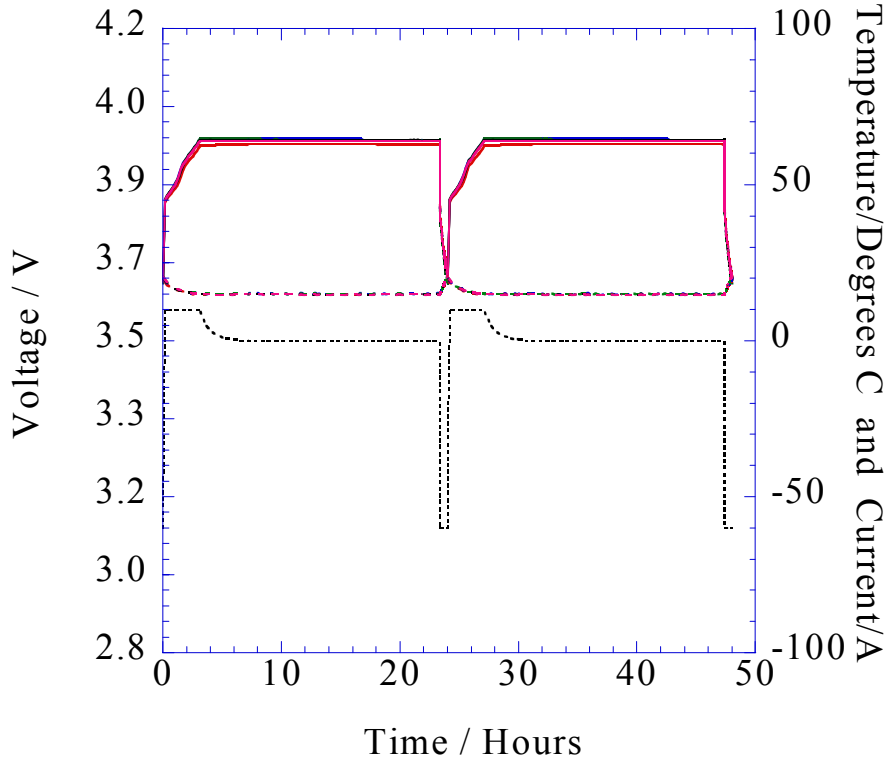


Fig. Trend data of 5 cells in Li-ion Battery

From 88th to 89th cycle

——— Voltage - - - - - Temperature ..... Current

50 Ah $LiCoO_2$/Graphite Cells

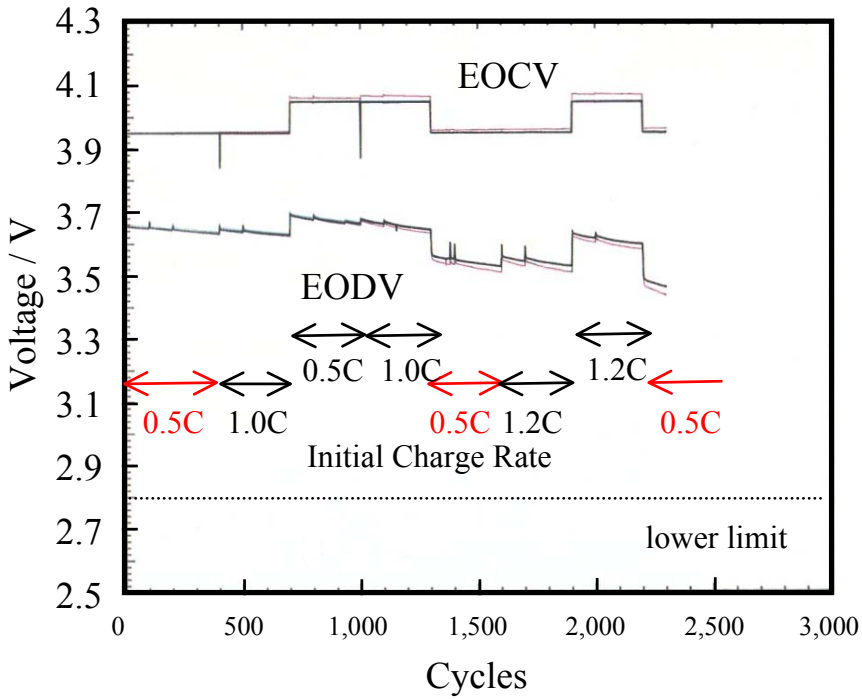
Cell Style		Elliptic Cylinder	
Electrode	Positive Electrode	LiCoO2	
	Negative Electrode	C (graphite)	
Capacity	Nominal / Typical	50 Ah / 54 Ah	40 Ah / 45 Ah
Weight		1.50 kg	1.46 kg
Dimensions		130 mm (W) x 50 mm (D) x 207 mm (H)	
Energy Density	per Weight	130 Wh / kg	111 Wh / kg
	per Volume	260 Wh / L	210 Wh / L
Charge Voltage / Higher Limited Voltage		3.98 V	
Discharge Voltage	Nominal Voltage	3.6 V	
	Lower Limited Voltage	2.75 V	

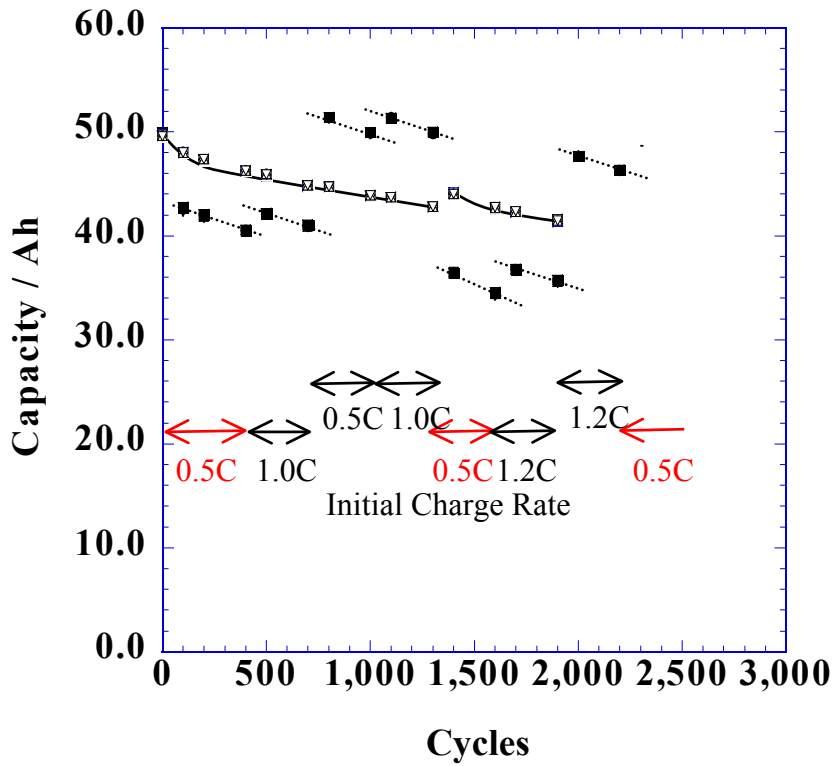
We started the test using two different designs of 50 Ah-class Lithium-Ion cells. One was the same design of electrodes and electrolyte as for the100 Ah cells. The other cell was specially designed to realize good performance in LEO mode with high DOD levels using thin electrodes.

HTV Project

Trend Data of 50 Ah $LiCoO_2$/Graphite Cells

Data Update





Life Cycle Trend of DOD=40% HTV Simulation

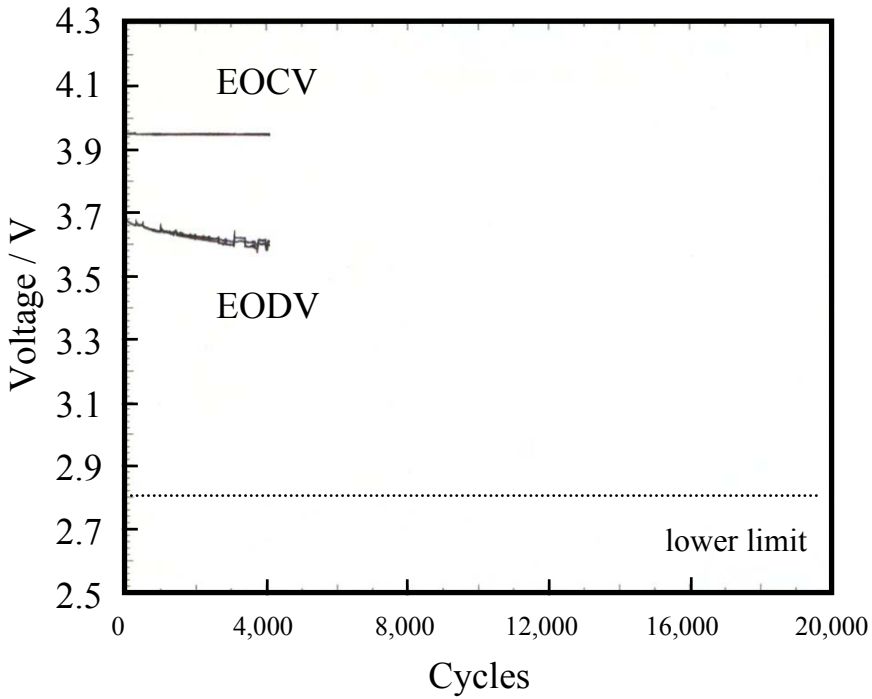
Five cells are connected in series.

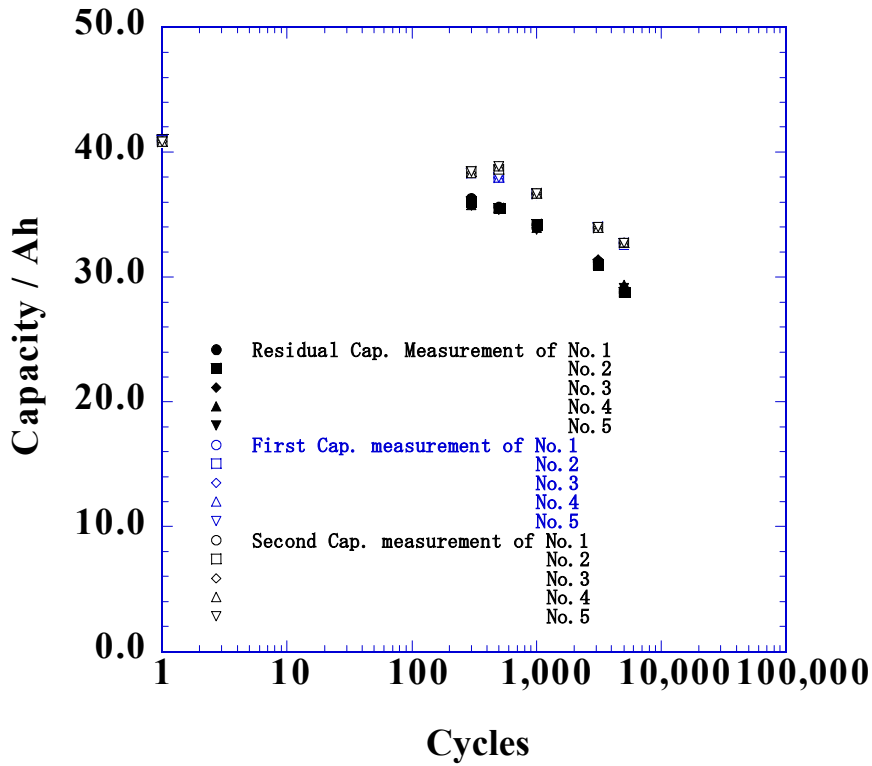
These results were obtained using the conventionally designed cells. This cell design was adopted for the H-II Transfer Vehicle (HTV) battery.

We are now checking performance limits using different levels of charge rate and taper voltage for the HTV project.

Trend Data of 50 Ah $LiCoO_2$/Graphite Cells

Data Update





Life Cycle Trend of DOD=40% LEO Test

Five cells are connected in series.

These results were obtained using the cells designed for LEO mode with high DOD levels. The initial capacity was less than 50Ah, while the trend shows higher EODV compared to the DOD=40% test of 100Ah cells.

Trend Data of 50 Ah $LiCoO_2$/Graphite Cells

Data Update

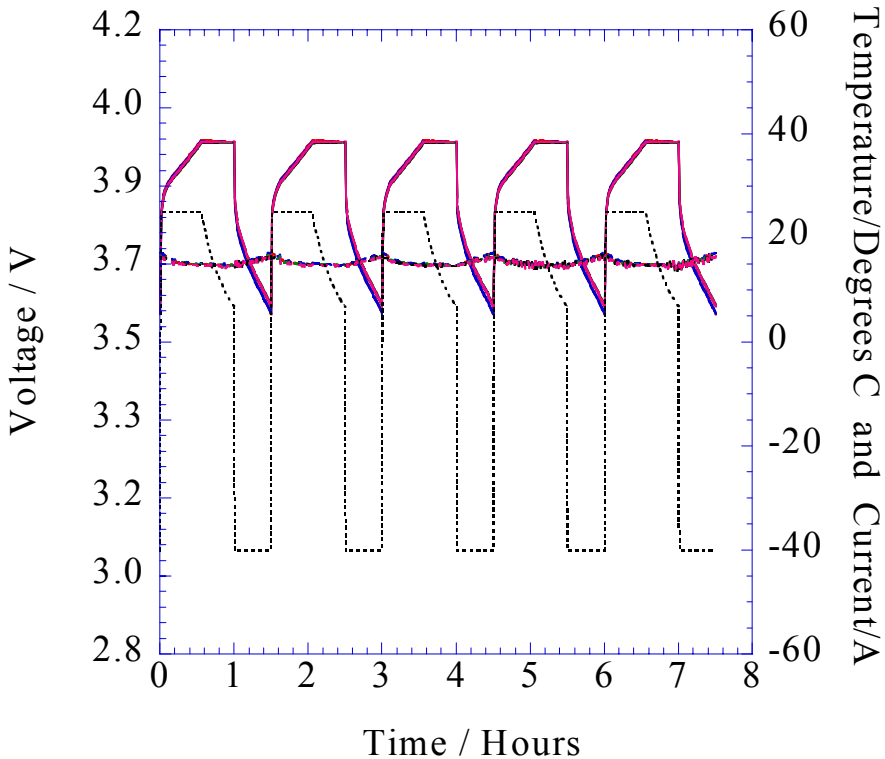


Fig. Trend data with DOD=40%, LEO Test

Five cells are connected in series.

From 5082nd to 5086th cycle

——— Voltage - - - - - Temperature ..... Current

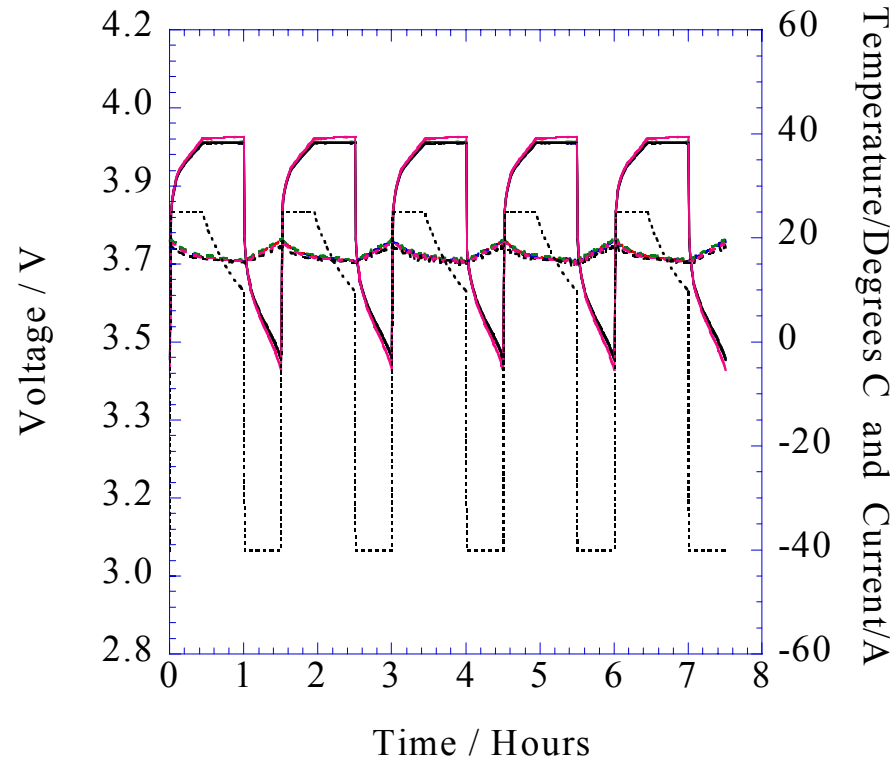


Fig. Trend data with DOD=40%, HTV Test

Five cells are connected in series.

From 2281st to 2285th cycle

——— Voltage - - - - - Temperature ..... Current

Summery

- ***10 Ah Cells***
  - In the LEO DOD=25% test, a slight decrease in EODV was observed. Two cells connected in series showed identical performance.
  - In the LEO DOD=40% test, three cells connected in series did not show identical performance, but more than 8 Ah capacity observed during the cycle test was still maintained after 15,000 cycles.
- ***30 Ah Cells***
  - In the LEO DOD=25% test, a constant decrease in EODV was observed. The differences in cell performance among five cells with series connection increased without a balance circuit.
  - In the LEO DOD=40% test, the evaluation was ended at the 10,000th cycle because discharge voltage decreased below the lower limit.
- ***100 Ah Cells***
  - In both LEO DOD=25 and 40% tests, we observed very stable performance and high EODV of cells. The difference in performance among five cells connected in series was quite small. In the GEO DOD=80% test, we observed the EODV decrease to the lower limit. We increased the charge voltage from 3.95 V/cell to 4.00 V/cell, which regained the cell performance.
- ***100Ah Battery***
  - The 100 Ah battery test was started. In order to check battery performance under GEO cycles more precisely, three different levels of DOD during one eclipse season and storage during the sun-shine period is now simulated in this test. Self-discharge of the battery was observed during sun-shine period, while the discharged level seemed very shallow.
- ***50Ah Cells***
  - We started the test of 50 Ah-class lithium-ion cells. One of them has a conventional design like that of 100 Ah cells, and is being tested to check its applicability to HTV. The other cells are designed for LEO cycles with high DOD. They have been achieving very stable performance with high EODV.

Life Test and Performance Comparisons of Lithium-ion with Traditional Battery Types

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I. Introduction

The expected transitioning of spacecraft power system batteries from the older nickel cadmium and the widely used nickel hydrogen batteries to the new lithium-ion technology introduces a number of uncertainties in the traditional performance data used to design space power systems. Some of the foremost areas of uncertainty include cycle life, degradation rates and effects, calendar life, and self-discharge.

Numerous ground tests project that for LEO cycling conditions and accelerated GEO conditions, lithium-ion batteries are capable of simply providing the number of cycles required for many space missions. However, the parametric data are not yet available that allow trades between cycle life reliability and depth-of-discharge (DOD), charge voltage levels, charge control methods, and operating temperatures to be made by system designers. These types of databases have been developed over years of testing and use for NiCd and for NiH_2 batteries. The coming years are certain to see the development of similar databases for Li-ion batteries, databases that include information on how cell degradation modes influence reliability.

The calendar life of batteries is critical in their use in space power systems, which often demand extremely long life. For example, 15 years of calendar life are commonly sought from NiH_2 batteries in GEO missions. We are not really sure of the calendar life capability of NiH_2 cells, except that it is significantly longer than the 15-20 years that has been demonstrated for properly managed NiCd batteries. At present, 20 years is typically the maximum planned for NiH_2 (5 years ground storage plus 15 years operational life). For Li-ion batteries years of real-time testing are needed to fully eliminate uncertainties regarding unexpected degradation or failure modes that may show up late in life.

The self-discharge behavior of lithium ion cells is radically different from that of NiCd or NiH_2 cells. Lithium ion cells have very low self-discharge rates, on the order of C/25,000 or less. Thus, it is possible to leave batteries open-circuited for lengthy periods of time without loss of much capacity. This is a different management approach than for NiCd or NiH_2 batteries, for which regular overcharge, trickle-charge or reconditioning was needed to maintain all cells at well-matched and high states of charge. While this is a real advantage for lithium ion, it also raises the question of how to assure that cells in lithium ion batteries are kept well matched during periods of ground or orbital inactivity, since lithium ion cells are not tolerant of overcharge.

In this report we provide some comparisons between lithium-ion battery performance and the behavior of NiCd, NiMH, and NiH_2 battery cells. These comparisons include ongoing life tests for both small and large cells, as well as accelerated and real-time tests. We also provide data on the self-discharge rates of these different types of cells as part of an effort to evaluate how to best assure that lithium ion cells remain well matched in batteries.

II. Direct Comparison of Li-ion, NiCd, and NiMH

The direct comparison of life performance for lithium ion, NiCd, and nickel metal hydride (NIMH) cells in the same environment has never before been done, largely because each or these cell types requires different charge control. We have set up a single battery that consists of 2 cells of each of these three cell types, all the cells operating in series. The issue of charge control is handled by our patented adaptive charge control system, which automatically adapts itself to the charge needed by each cell to exactly compensate for losses, using a recharge fraction (RCF) charge control approach. When each cell has been charged to the RCF required to just compensate for losses, the charge current is shunted around that cell for the remaining recharge period. All cells discharge in series in a thermal environment of 6-8 deg C as indicated in Figure 1. The six cells are all 7 to 7.5 Ah in capacity, and include two 7.5 Ah prismatic lithium ion cells, two cylindrical 7 Ah NiCd cells, and two cylindrical 7 Ah NiMH cells. The lithium ion cells were built for space applications, while the NiCd and the NiMH cells are commercial quality cells.

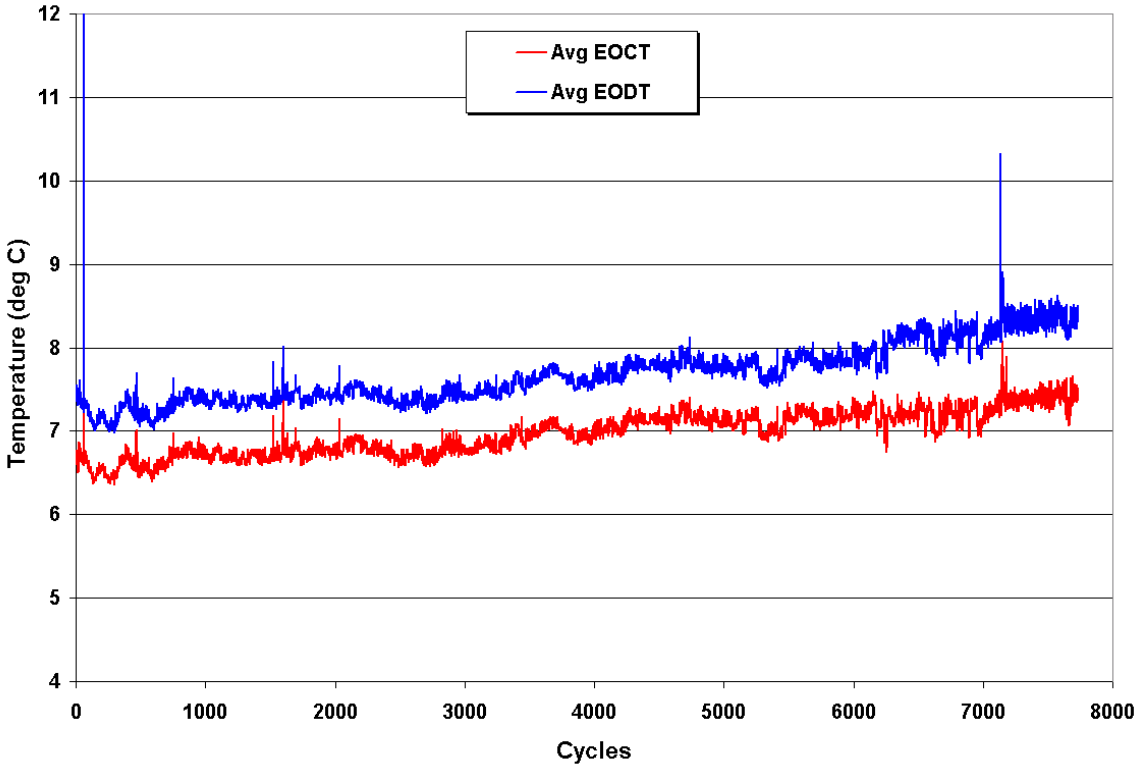

Figure 1. Average cell temperature at the end of charge and the end of discharge for 7.5 Ah cell test comparing lithium ion, NiCd, and NiMH cell performance.

This battery is operated at 20% DOD (1.5 Ah discharged each cycle) in a 90 minute cycle with 30 minutes for discharge and 60 minutes for recharge. The discharge rate is 3 amps, and the charge rate is 2.25 amps to a RCF of 0.75, then a lower charge rate computed to reach the maximum required cell RCF one minute before the end of the 60-minute recharge period. The charge control system requires several hundred cycles to adapt itself fully to the charge needs of each of the cells as shown in the voltage behavior during cycling shown in Figures 2-4. The NiCd and NiMH cells operate between 1.18 and 1.48 volts and the lithium ion cells between 3.55 and 4.0 volts.

The lithium ion cells in this test are designed to operate at low temperatures, thus the 5-10 deg C operating temperature range was selected as providing a good thermal environment to give long cycle life for all three types of cells. The charge control method used in this test basically operates by eliminating any overcharge that is not needed to keep the cells charged. Thus, for all these cells the RCF is quite low, as indicated in Figure 5. As expected, the lithium ion cells operate at essentially a 1.00 RCF after settling slightly during the first 2000 cycles (a 1.0 RCF shows up as about 0.998 in Figure 5 because of systematic measurement errors). The other cells operate between 1.004 and 1.01, depending on the cell. It is not understood why NiCd cell 3 exhibits significant variations in voltages and RCF. If it is due to soft shorts in the cell, they are not resulting in rapid cell failure with continued cycling, perhaps due to the extremely low RCF.

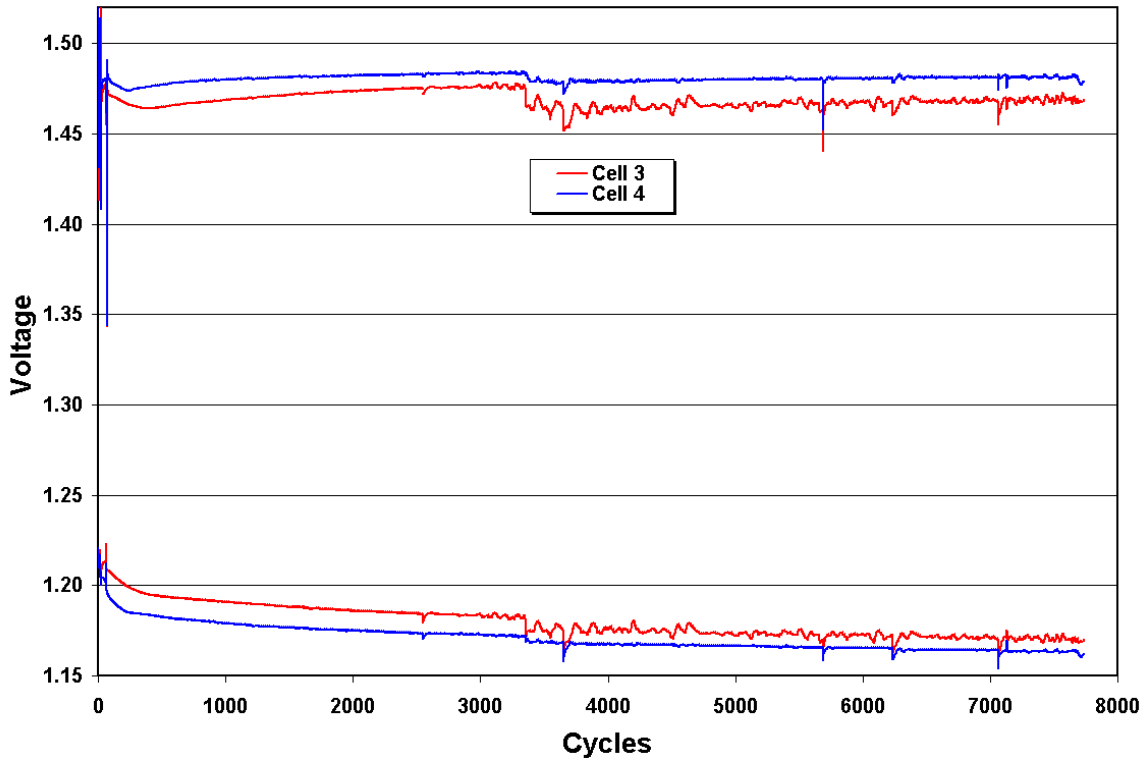

Figure 2. Cell voltages at the end of discharge and peak voltage during recharge for the two 7 Ah NiCd cells as a function of cycle number.

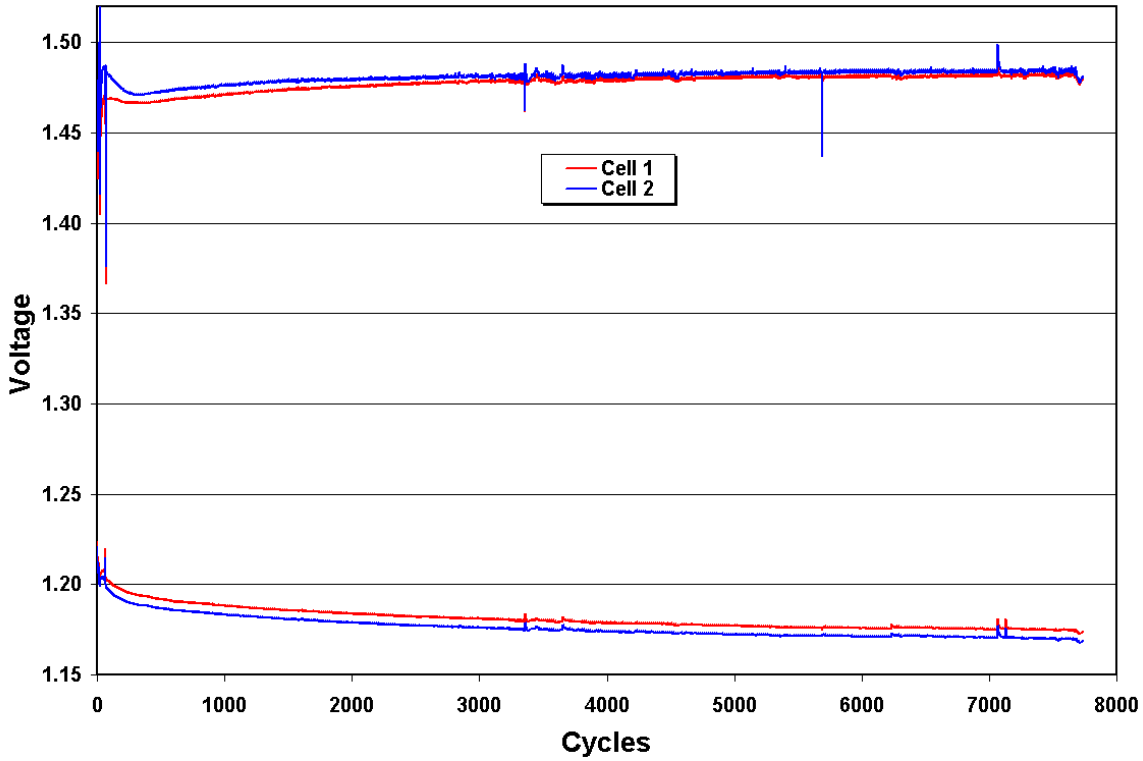

Figure 3. Cell voltages at the end of discharge and peak voltage during recharge for the two 7 Ah NiMH cells as a function of cycle number.

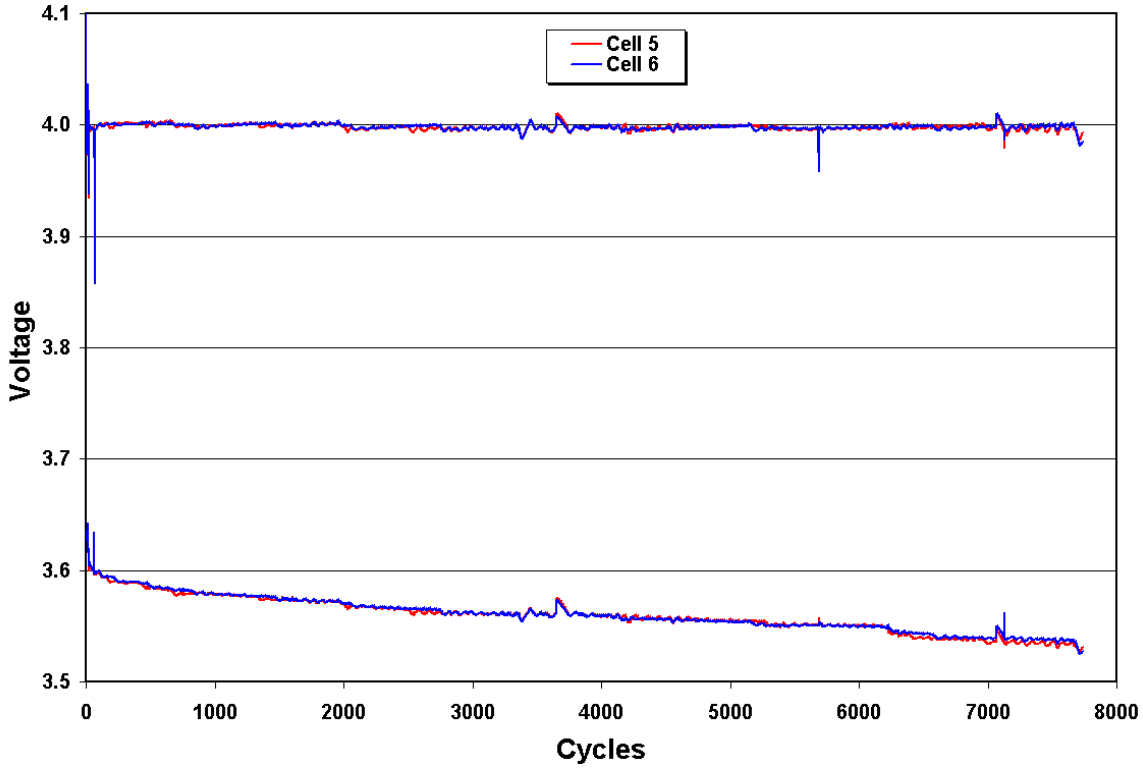

Figure 4. Cell voltages at the end of discharge and peak voltage during recharge for the two 7.5 Ah lithium-ion cells as a function of cycle number.

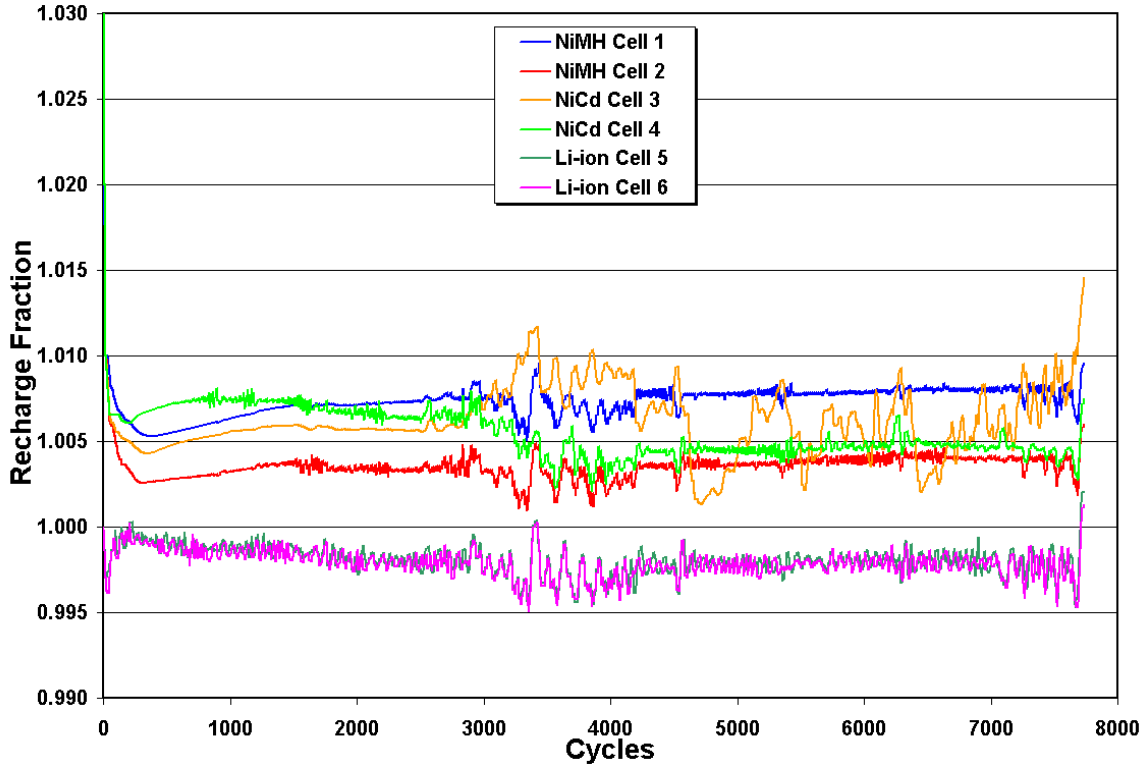

Figure 5. Recharge fraction in the 7.5 Ah cell test as a function of cycle number.

While the data in Figures 2-5 presumably represent only the early stages of cell operating life, an early comparison between the cells may be made by extrapolating the voltage differences between the peak recharge voltage and the minimum discharge voltage. This voltage difference, which is indicated in Figure 6, is a direct indication of the rate at which the cells are approaching failure. For this charge control system, the RCF and the voltages to which the cells are allowed to charge and discharge are adjusted until safe limits are reached, which define the end of life. For the NiCd, NiMH, and Li-ion cells respectively, these safe limits are 1.52, 1.54, and 4.1 volts on charge, and 1.0, 1.0, and 3.0 volts on discharge. Thus, for each cell type, a delta-V of 0.52, 0.54, and 1.10 volts corresponds to end of life. Simple linear extrapolation based on Figure 6 to these delta-V limits yields about 72,000, 56,000, and 82,000 cycles for the NiCd, NiMH, and Li-ion cells respectively. Of course, it has been reasonably well established for NiCd and NiMH cells that a linear extrapolation is not appropriate since the voltage always begins to decay more rapidly as the cells degrade over life. It is expected that the lithium-ion cells will also deviate from a linear voltage change later in life. It will be quite interesting to compare how these three cell types change voltage degradation rates later in life. Of particular interest is whether the cells eventually fail by a gradual change in operating voltage, or whether a more sudden and less predictable failure mode comes into play.

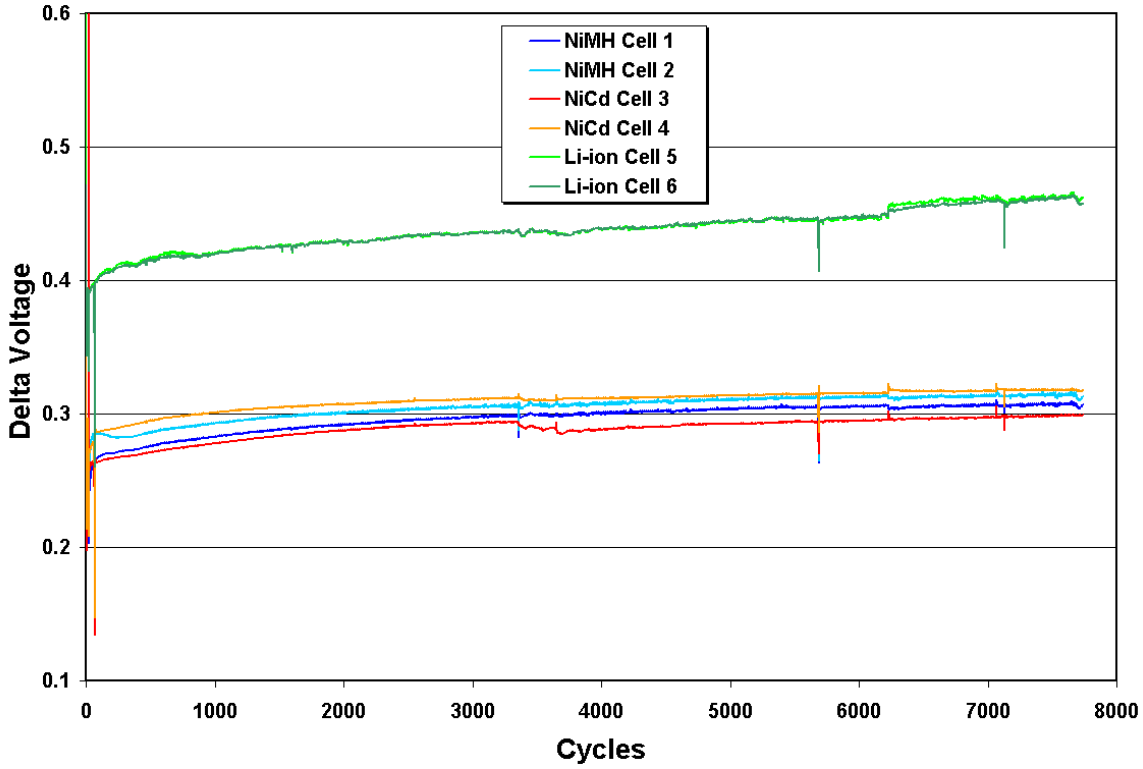

Figure 6. Delta V between peak recharge voltage and minimum discharge voltage in the 7.5 Ah cell test as a function of cycle number.

III. Cycle Life of Large Lithium Ion Cells and Nickel Hydrogen Cells

Most of today's satellite power systems operate using nickel hydrogen cells having more than 50 Ah of capacity. If these satellites transition to lithium ion batteries, it is expected that Li-ion cells of approximately 40-50 Ah size or greater will be used in many cases. Thus, comparison of nickel hydrogen technology to lithium ion should be based on test data from such larger cells. The life test database for NiH_2 cells has indicated that a lifetime on the order of 60,000 cycles or more is readily achievable at a DOD of about 30%. These tests have also demonstrated that the lifetime of a nickel hydrogen cell is significantly reduced by any overcharge above that needed to keep the cell operating. It is expected that the lifetime of lithium-ion cells is also reduced by any overcharge that is not needed to keep the cells acceptably recharged, since lithium-ion cells have no internal chemical mechanisms for reversibly accepting overcharge. For these reasons we should base comparisons of performance between these battery types on data obtained with minimal overcharge.

We have initiated a life test of lithium ion battery cells having capacities of 35 Ah (four prismatic cells) and 40 Ah (two cylindrical cells) using the adaptive charge control system described earlier. This charge control system will automatically adjust to recharge cells of differing performance characteristics and degradation rates, while

maintaining the minimum required amount of overcharge. This test is being conducted using a 90-minute cycle with 30 minutes for discharge, and using a 10 Ah discharge during each cycle. This corresponds to 25% DOD for the 40 Ah cells, and 28.6% DOD for the 35 Ah cells. The cells are being operated at a temperature of 10 deg C at the end of discharge, as indicated in Figure 7, warming up several degrees during each discharge.

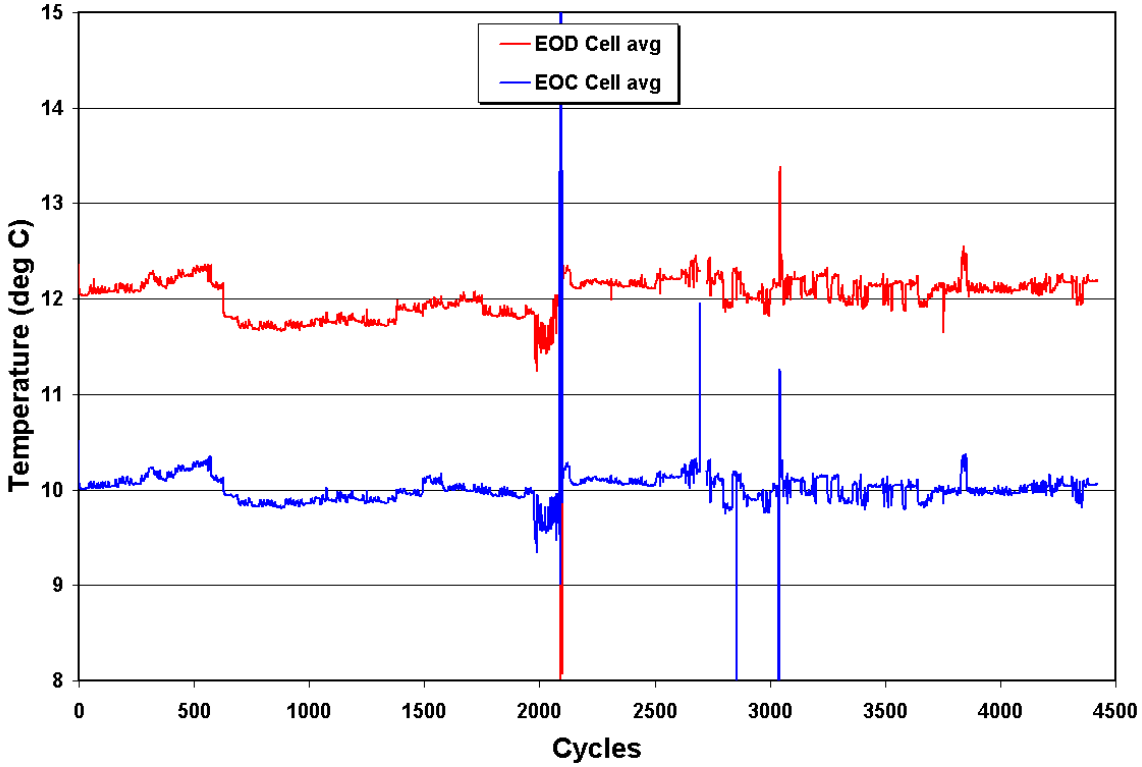

Figure 7. Test temperatures for 35 and 40 Ah lithium ion cell test as a function of cycle number.

The voltage behavior of the 35 and 40 Ah cells for the first 4500 cycles of this ongoing life test is indicated in Figures 8 and 9 respectively. These voltages show relatively stable performance during the early stages of this life test for both types of cells, although as expected, the higher capacity 40 Ah cells are maintaining a higher discharge voltage and a lower recharge voltage. The recharge ratios during the cycling are shown in Figures 10 and 11. The average RCF for both types of cells has remained essentially constant at about 0.998 throughout the test. This level actually corresponds to a RCF of 1.0 after systematic test system errors are taken into account. Within the precision and accuracy of the test equipment, we cannot yet detect an RCF that deviates from 1.0 for either of these types of cells.

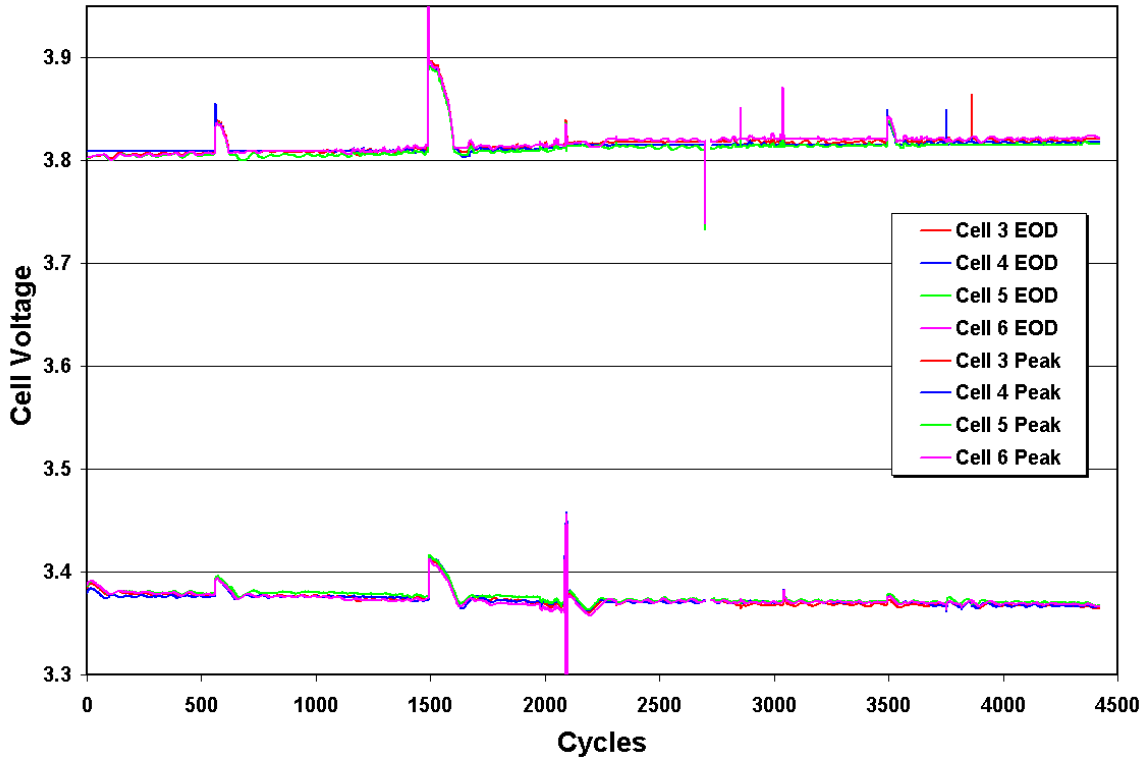

Figure 8. End of discharge and peak recharge voltages for the four 35 Ah prismatic lithium-ion cells as a function of cycle number.

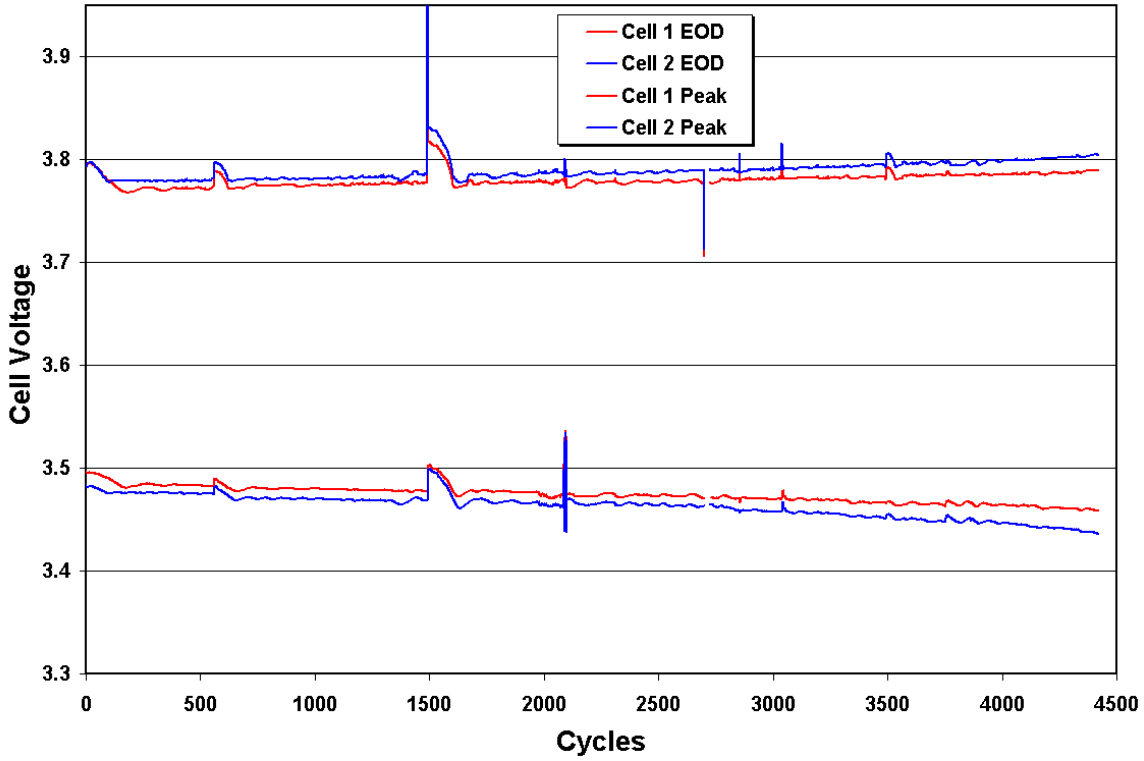

Figure 9. End of discharge and peak recharge voltages for the two 40 Ah cylindrical lithium-ion cells as a function of cycle number.

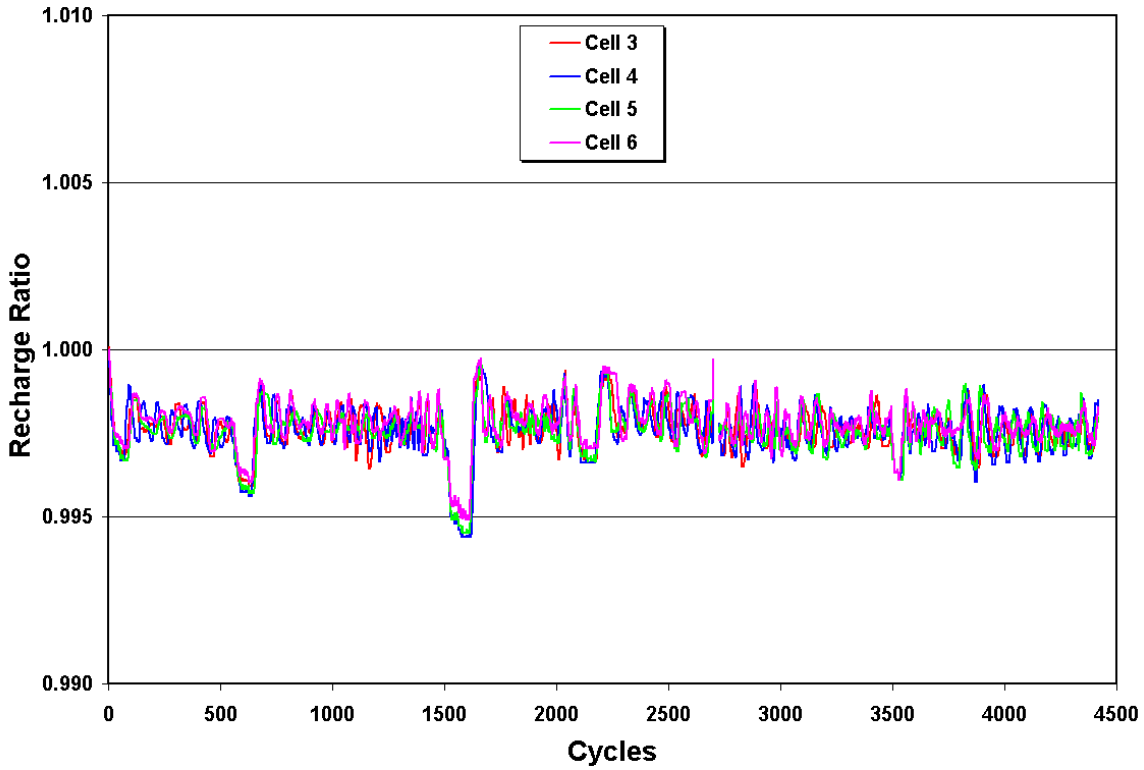

Figure 10. Recharge fractions for the four 35 Ah prismatic lithium-ion cells as a function of cycle number.

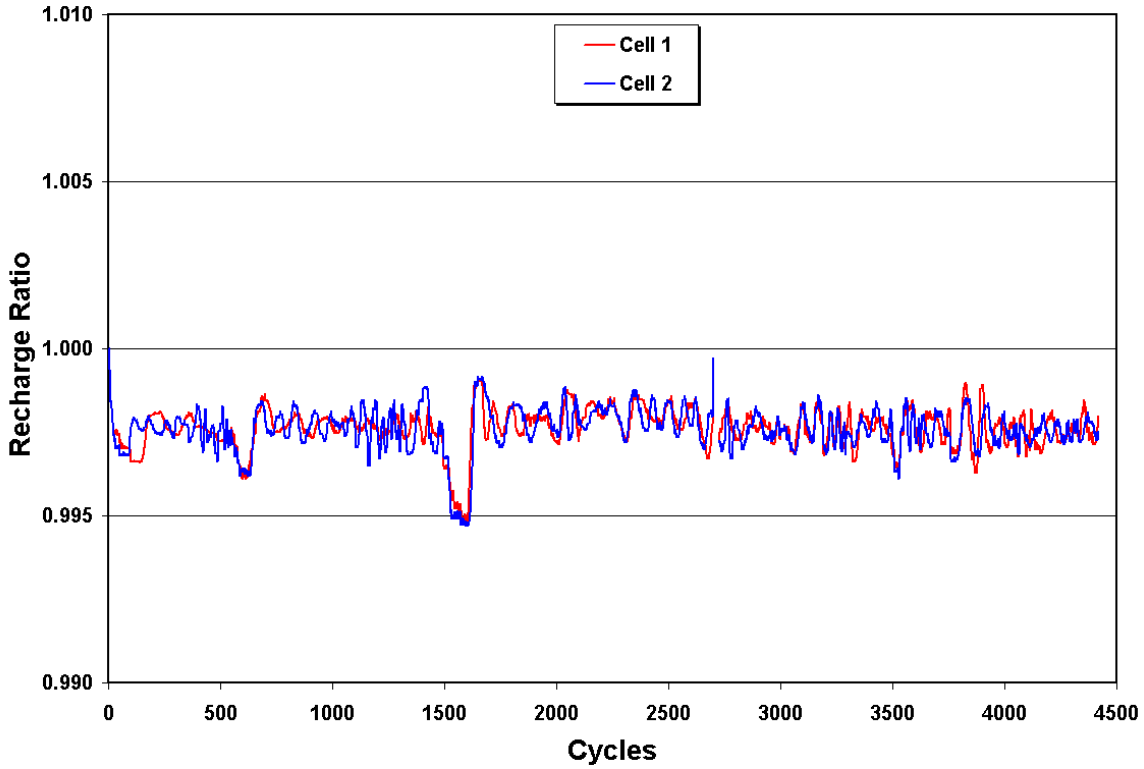

Figure 11. Recharge fractions for the two 40 Ah cylindrical lithium-ion cells as a function of cycle number.

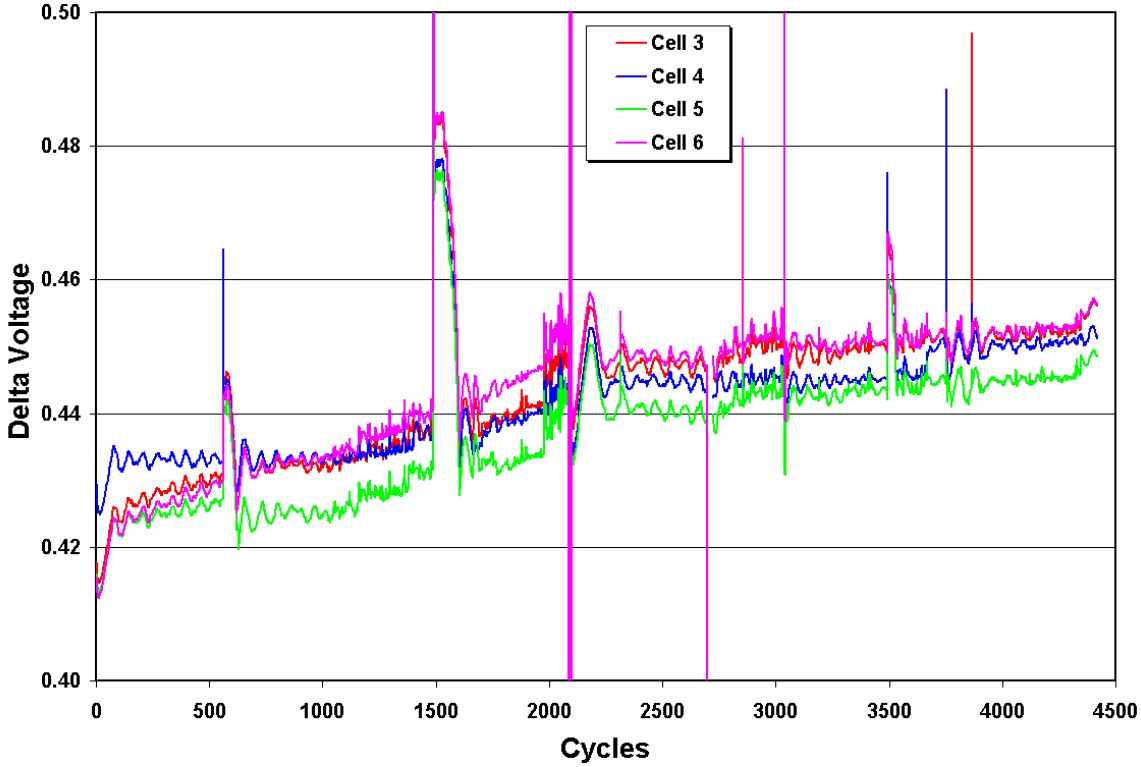

Figure 12. Delta-V between the peak recharge voltage and the minimum discharge voltage for the four 35 Ah prismatic lithium-ion cells as a function of cycle number.

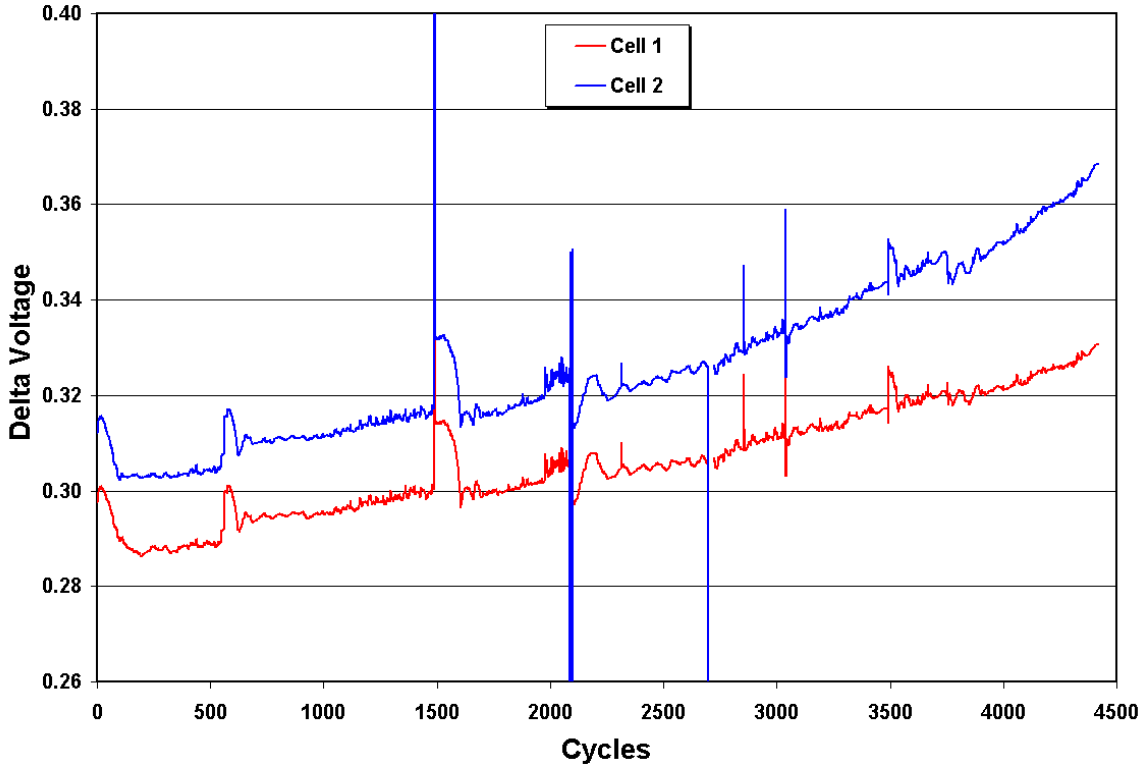

Figure 13. Delta-V between the peak recharge voltage and the minimum discharge voltage for the two 40 Ah cylindrical lithium-ion cells as a function of cycle number.

As discussed previously, cell failure occurs when the voltage swing between the peak during recharge and the minimum during discharge reaches 1.1 volts. This delta-V is plotted in Figures 12 and 13. The 40 Ah cells have a smaller delta-V, but they are not as stable during cycling as the 35 Ah cells. If we extrapolate the slopes seen in Figures 12 and 13 linearly to 1.1 volts, we get about a 60,000-cycle life for the 40 Ah cells and an 80,000-cycle life for the 35 Ah cells. It would be surprising if this linear extrapolation remains valid for such a long duration. Over ten years of calendar life would elapse for less than 60,000 cycles, thus calendar life effects as well as the effects of degradation modes that only become obvious after many more cycles could make both of these cell types depart from their present trends. Continued testing will provide data on which further comparisons between these cells and nickel hydrogen cells may be based.

However, the existing data support the notion that either of these lithium ion cell types is capable of providing quite long cycle life that may be compared with that of nickel hydrogen cells. A nickel hydrogen battery operating at the same energy density as the lithium ion cells shown in Figures 8-13 would have to operate at approximately 60% DOD. Testing of nickel hydrogen cells at 60% DOD has yielded cycle life that has varied from 10,000 cycles to over 60,000 cycles. However, in all such tests, significant overcharge in excess of the minimum required by the cell was applied, which appeared to shorten the cycle life capability of the nickel hydrogen cells.[1] In fact the tests that gave only 10,000 cycles utilized quite high temperatures (for nickel hydrogen cells) and abusive amounts of overcharge.[2] For a valid comparison with lithium ion cells, a nickel hydrogen cell test was initiated that operates the cells with minimum overcharge using our adaptive charge control system and operating the cells at a –5 deg C end of charge temperature. Figure 14 indicates the temperatures seen during the nearly 6500 cycles completed for this ongoing test. The goal for this test is 60,000 cycles at 60% DOD.

Five 60 Ah nickel hydrogen cells of the dual-anode design were obtained for this test. The dual-anode design uses a hydrogen electrode facing each surface of each nickel electrode. This feature is combined with a single layer of zircar separator to give a cell having 50% lower impedance that standard nickel hydrogen cells. These cells also contained wall wicks with recombination sites, since these have been observed to reduce the thermal stresses from overcharge. These cells were cycled in a 90 minute cycle (30 minutes for discharge) at 60% DOD, with no attempt being made to bring the cells to 100% state of charge each cycle. The adaptive charge control system was programmed to hold the end of discharge voltage at 1.1 volts by adjusting the RCF, thus cycling each cell between about 10% and 70% state of charge. Recharge was done to the prescribed RCF limit using a C-rate peak charge current, and tapering the current at a maximum voltage level that has remained between 1.51 and 1.52 volts during this test.

Figures 15 and 16 show the end of discharge voltages and the peak recharge voltages for these five cells. The initial drop in the end of discharge voltage during the first several hundred cycles of Figure 15 occurred as the adaptive charge control system allowed the cell capacity at the end of discharge to walk down to approximately 10% state of charge. Since that stabilization period, the end of discharge voltages have been essentially constant and the peak recharge voltages have increased less than 10 mv. It is noteworthy that all five cells are matched in their recharge voltage level to within 2 mv after nearly 6500 cycles.

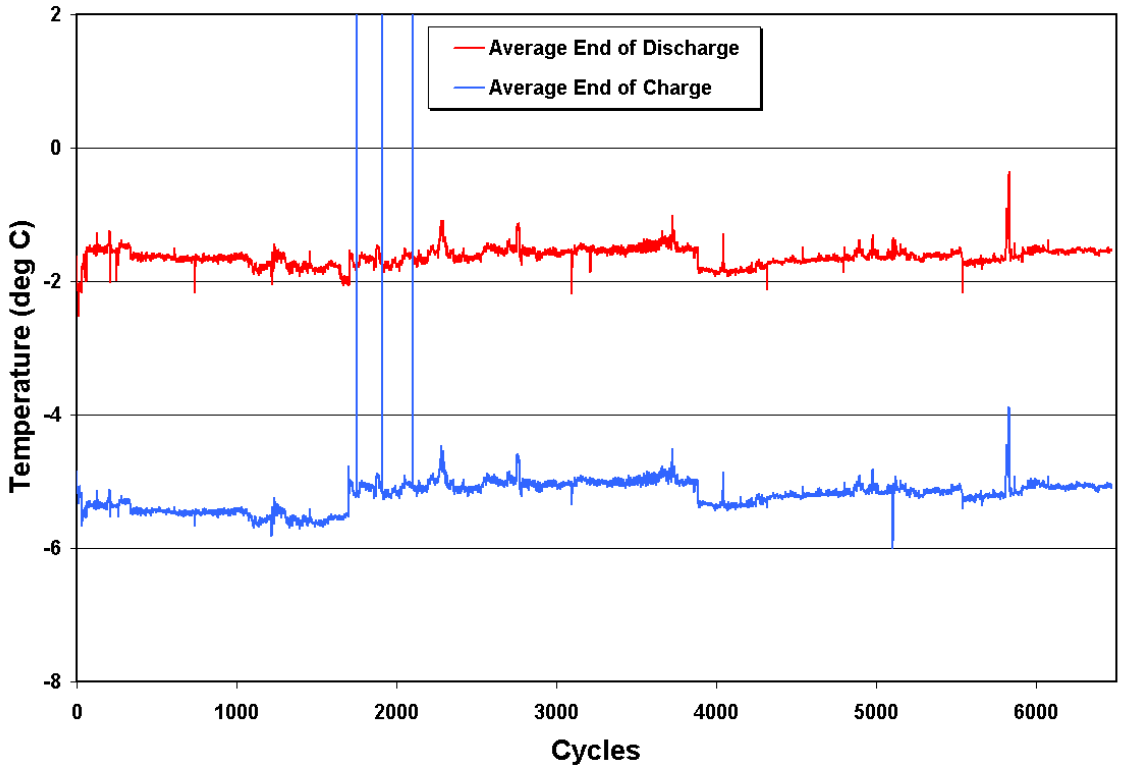

Figure 14. End of charge and end of discharge temperatures for five 60 Ah nickel hydrogen cells cycling at 60% DOD as a function of cycle number.

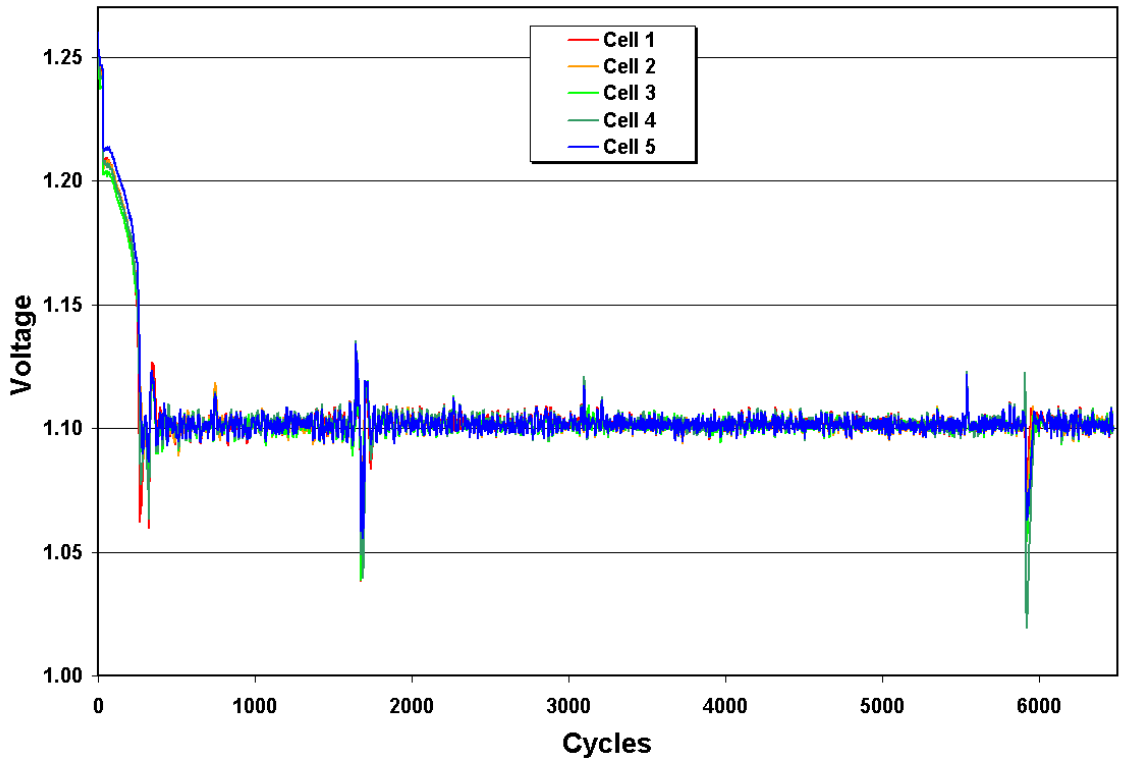

Figure 15. End of discharge voltages for five 60 Ah nickel hydrogen cells cycling at 60% DOD as a function of cycle number.

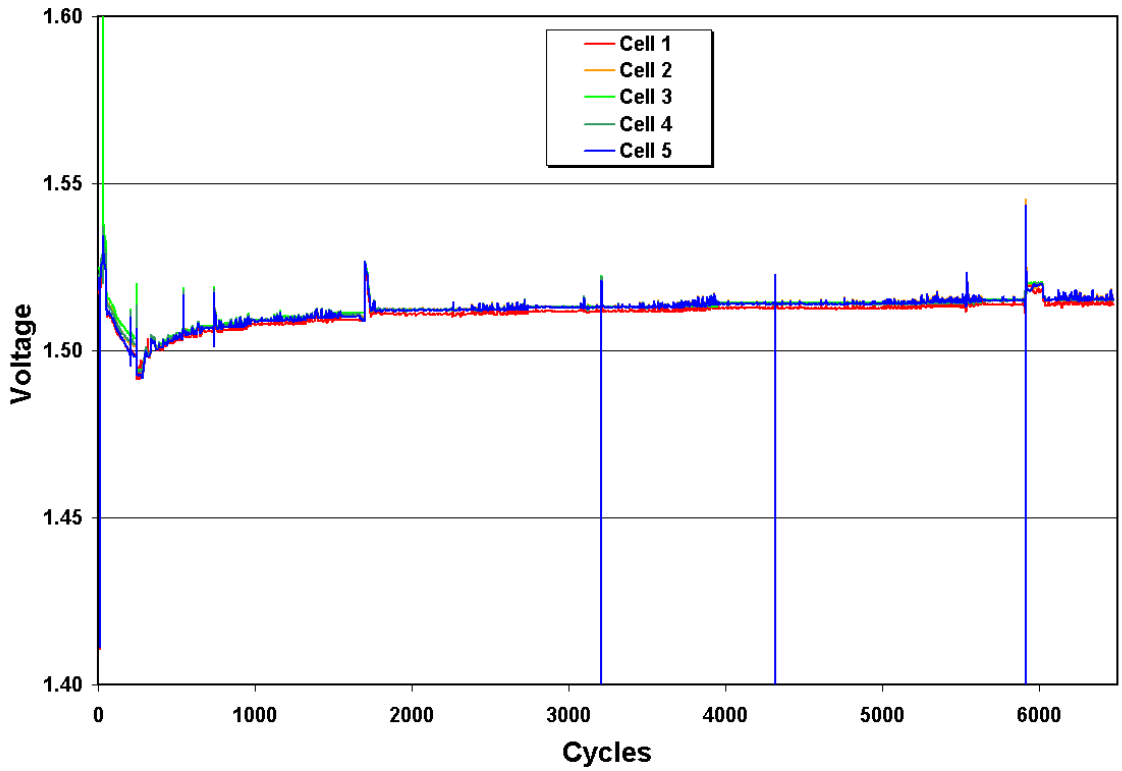

Figure 16. Peak recharge voltages for five 60 Ah nickel hydrogen cells cycling at 60% DOD as a function of cycle number.

The RCF for these five nickel hydrogen cells is shown in Figure 17. The RCF is quite low because of the low test temperature, because we are not trying to bring the cells to 100% state of charge, and because the charge control system minimizes overcharge. During nearly 6500 cycles, the RCF needed to maintain these cells has increased from about 1.004 to 1.005. This increase is presumably an indication of small decreases in charge efficiency that have taken place as nickel electrode phase changes take place or electrode degradation occurs in the cells.

The pressure in nickel hydrogen cells provides an indication of processes that change cell capacity or contribute to corrosion of the nickel electrodes over life. Each of these five cells is instrumented with a strain gauge for sensing relative pressure, giving the results in Figure 18. The noise in cell 5 pressure at about 5500 cycles is due to a loose connection in the strain gauge monitoring circuitry, and some noise has appeared in the cell 4 strain gauge at about 6000 cycles. These cells were built with a nickel precharge. The relatively flat pressures for the first several thousand cycles is likely to be due to hydrogen being generated by Ni sinter corrosion being consumed by reaction with active precharge, leading to an increase in the capacity of the cell. After the nickel precharge is completely consumed, the upward slope of the pressures is expected to reflect the rate of Ni sinter corrosion. Ultimately the amount of sinter corrosion may limit the life of these cells. Of course it is assumed in this discussion that the upward pressure drift is real, and not simply an artifact of strain gauge drift.[3] At the completion of the test strain gauge calibration will be checked and the actual level of nickel electrode corrosion will be measured.

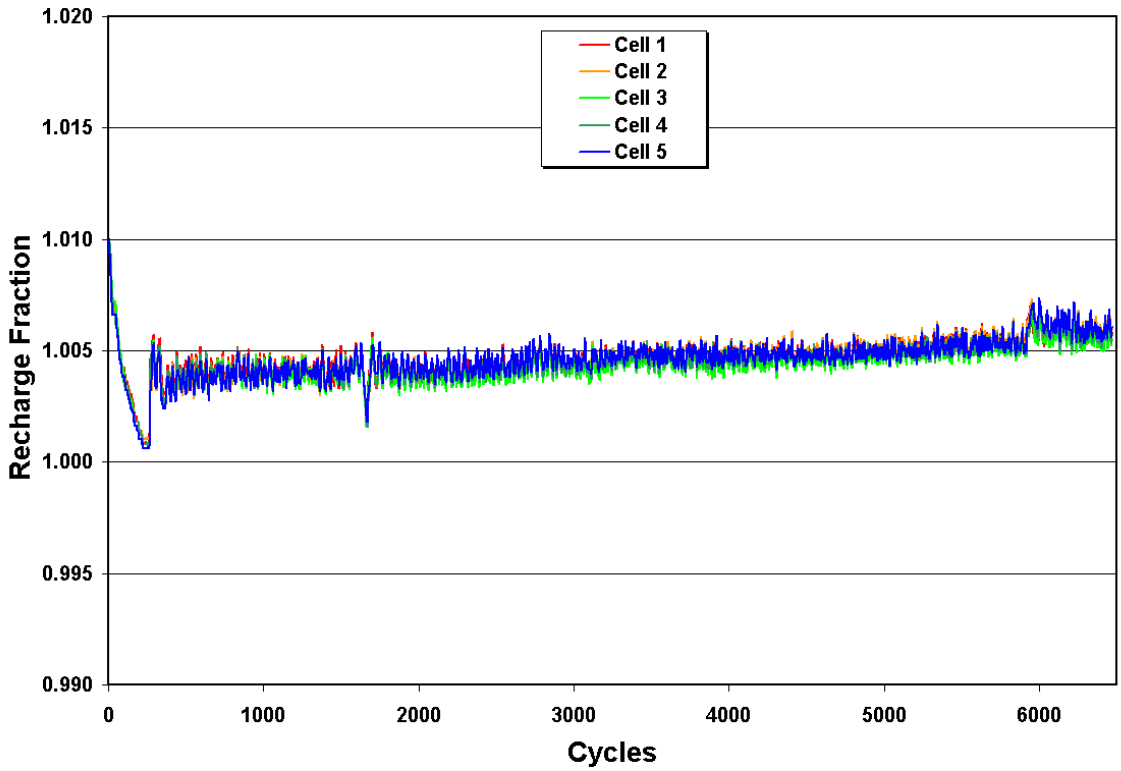

Figure 17. Recharge fractions for 60 Ah nickel hydrogen cells cycling at 60% DOD as a function of cycle number.

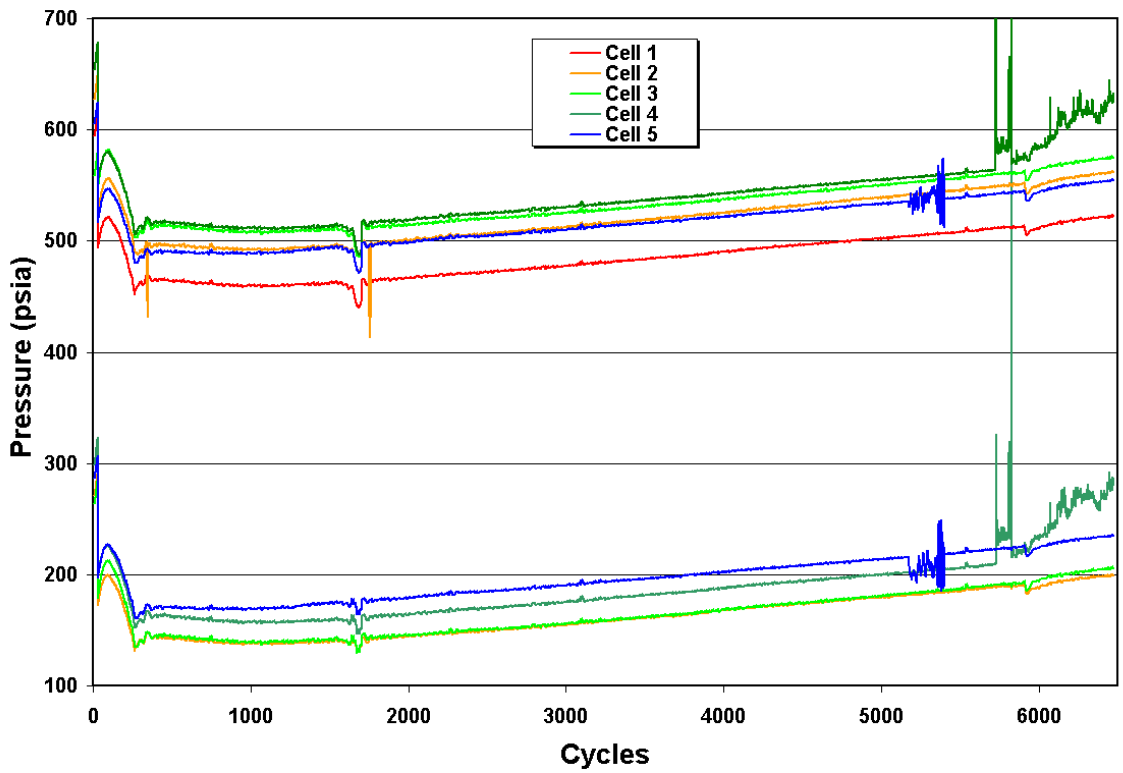

Figure 18. End of charge and end of discharge pressures for 60 Ah nickel hydrogen cells cycling at 60% DOD as a function of cycle number.

Projecting when failure of the nickel hydrogen cells may occur can be done using two methods. No trends exist in the end of discharge voltage on which extrapolation may be based, however, the voltage delta between the peak recharge voltage and the end of discharge voltage may be trended. These data are plotted in Figure 19. If we assume that failure occurs when the delta V in Figure 19 reaches 0.48 volts, which corresponds to 1.1 volts at the end of discharge and 1.58 volts at the end of recharge, a cycle life of about 70,000 cycles is obtained. This is a realistic failure criterion because previous tests of nickel hydrogen cells[4] have indicated that accelerated degradation does not begin until after peak charge voltages exceed 1.58 to 1.6 volts.

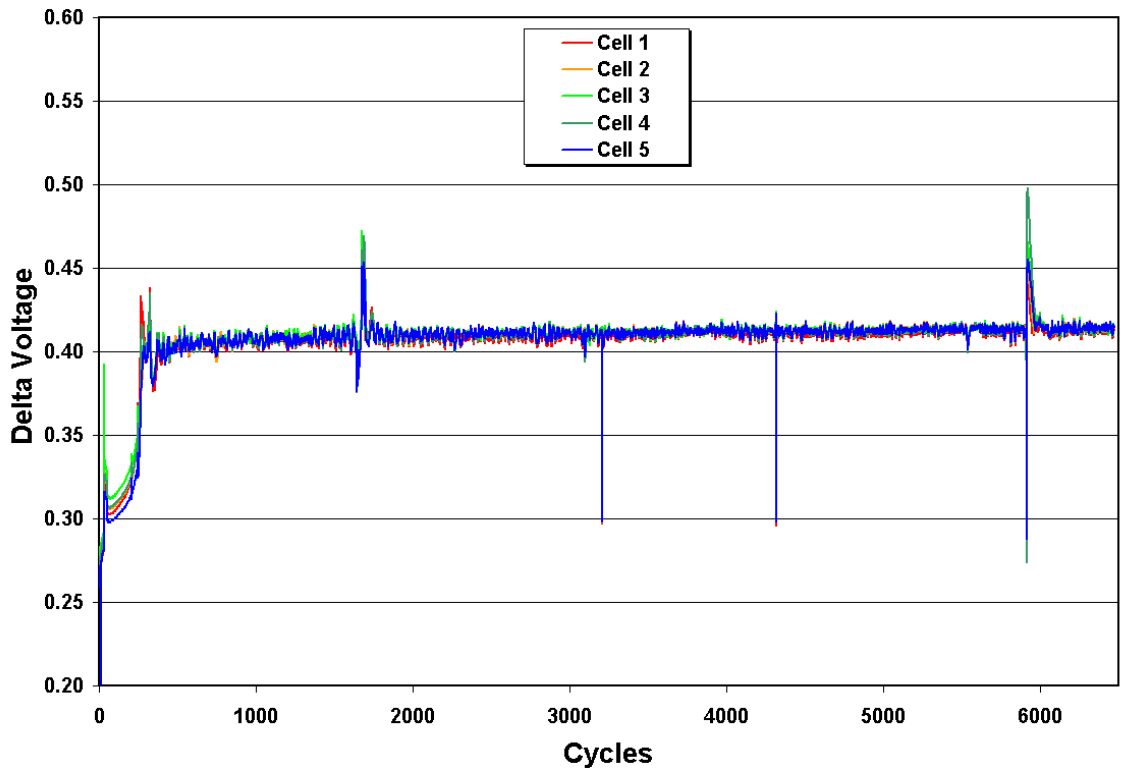

Figure 19. Difference between peak recharge voltage and end of discharge voltage for 60 Ah nickel hydrogen cells cycling at 60% DOD as a function of cycle number.

The second method for estimating life is by using the pressure increase as an indication of nickel electrode corrosion, and assuming that failure corresponds to a given level of corrosion. For example 40% corrosion of the nickel sinter has been observed to result in failure in laboratory test cells. In these cells, complete corrosion of 40% of the nickel sinter would result in approximately an 850-psi pressure increase. Using the present slope of 13.3 psi per thousand cycles, this gives an expected cell life of about 64,000 cycles. These two methods together suggest a realistic life expectation for these cells of 60,000 to 70.000 cycles at 60% DOD. This is fully consistent with our goal of 60,000 cycles, which we expect nickel hydrogen technology to be capable of at 60% DOD if operated optimally. It remains to be seen as this life test continues, whether these projections are indeed accurate.

IV. Accelerated Testing of Lithium Ion Cells

An accelerated test regime consisting of 20% DOD cycling, in a 45-minute cycle, has been used to evaluate the cycle life capabilities of a number of types of small (0.5 to 1.5 Ah) lithium ion cells.[5] This accelerated cycling regime allows cycles to be accumulated at twice the rate that can be achieved in the typical 90-minute LEO cycling regime. Reference 5 summarizes the performance of a number of cell types in this accelerated test regime. However, the question of how cycle life in the accelerated test regime relates to that from a real time LEO regime has not been established. We have obtained data that begins to address this issue for one particular type of cell, a 1.5 Ah lithium ion cell made using a porous polymer separator containing gelled electrolyte.

Four of these cells were cycled to failure in the 45-minute accelerated test regime at 20% DOD and 20 deg C, using a constant current recharge to 4.1 volts followed by a constant 4.1 volts for the remainder of the 30 minute recharge period. Failure was defined to occur when the end of discharge voltage fell below 3.0 volts. These four cells all gave consistent a cycle life of about 11,000 cycles.

In parallel with this accelerated test, a real time test was initiated using a 90 minute cycle and 20% DOD. The thermal environment followed an expected on-orbit thermal profile, increasing to about 25 deg C during recharge, and then dropping to about 14 deg C during discharge. Recharge was done at constant current to a 75% RCF (or a maximum voltage if reached before 75% RCF), then at a reduced current until the required RCF was obtained 2 minutes before the end of the recharge period. Nearly 15,000 cycles have been completed in this real time test over the past 3 years; with peak recharge voltages of about 3.9 early in the test, to 4.03-4.06 volts at present. This charge control method is clearly less aggressive than that used in the accelerated test.

The performance of the cells in these tests can be summarized by plotting the voltage difference between the peak charge voltage and the minimum discharge voltage, as has been done in Figure 20. Failure occurs when the delta-V in Figure 20 reaches 1.1 volts, which occurs at about 11,000 cycles for each of the four accelerated test cells. The two real-time test cells have completed almost 15,000 cycles, and are not yet near failure. With the presently observed slopes, the real time test cells should provide about 35,000 cycles before they fail. This is about a factor of three in cycle life acceleration, and since the cycles are accumulated twice as rapidly in the accelerated test regime, it is a factor of six acceleration in the time to failure.

In Figure 20 near 10,000 cycles in the real time test, there is a sudden shift in the voltage response of the cell. At this point the thermal controller for the test failed and went to temperature of 51 deg C for 2 days before the temperature was manually restored to ambient. The test stopped operating during this event, but the cells experienced 51 deg C temperatures while open-circuited and partially charged for about 48 hr. Following this event the cells were put back on cycling using a reduced peak charge current, which allowed them to operate at a slightly higher state of charge, and continue to cycle at about the same end of discharge voltages and peak recharge voltages. The cells appeared to exhibit an increase in impedance and a decrease in capacity following this event. It is unclear how much this event reduced the ultimate cycle life of these two cells.

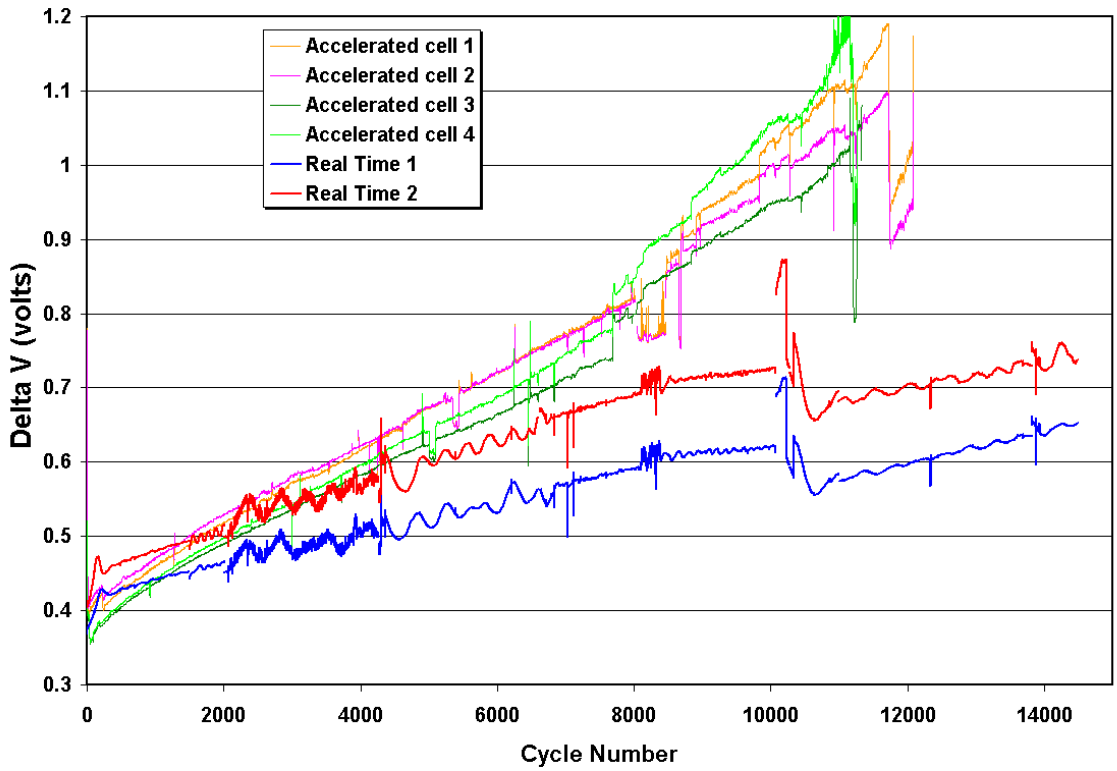

Figure 20. Difference between peak recharge voltage and minimum discharge voltage as a function of cycle number during both real-time and accelerated tests.

It remains to be seen how specific the acceleration factors seen in these tests are relative to the type of cell and the acceleration method. In these tests acceleration is achieved by the increased rates associated with the x2 reduction in cycle time, as well as by the more aggressive recharge protocol used. It is very likely that different cell types will respond differently to these different methods of accelerating degradation.

A good example of how different cell types respond differently to acceleration comes from our accelerated tests on SONY 18650 cells using an acceleration profile the same as that just described for the 1.5 Ah cells summarized in Figure 20. Two types of SONY 18650 cells were included in these tests. Older cells were acquired about 1994 and were rated at 1.2 Ah, and newer cells in 1998 having a rating of 1.5 Ah. Figure 21 shows how these two cell types (both from the same manufacturer) have responded in the same accelerated test profile. The two newer cells both failed after 32,000 to 34,000 cycles in spite of their higher ampere-hour capacity rating. The two older cells continue to cycle after 37,000 cycles with very stable performance. These 37,000 cycles represent about 3.5 calendar years of life testing on these SONY 18650 cells. It should be noted that even for the newer SONY cells, assuming a cycle life acceleration factor of 2-3 and ignoring any possible calendar life effects on performance, a real-time LEO cycle life of over 65,000 cycles would be projected.

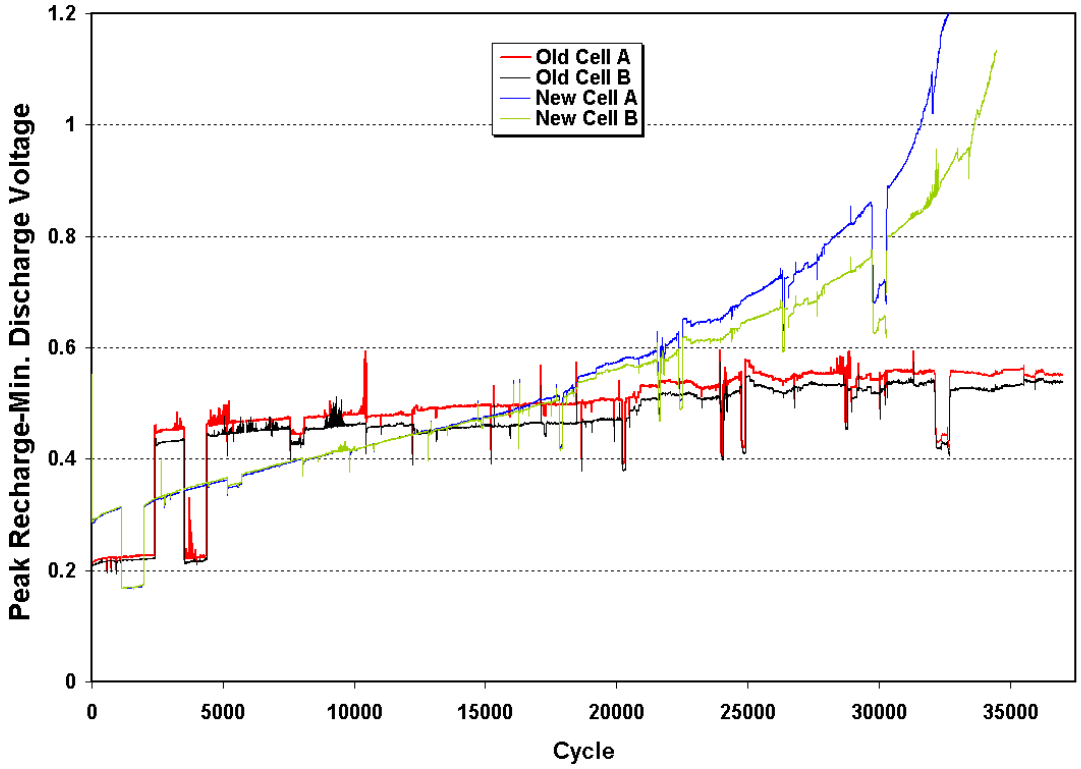

Figure 21. Difference between peak recharge voltage and minimum discharge voltage as a function of cycle number during accelerated tests on SONY 18650 cells.

V. Self-Discharge Behavior of Space Batteries

The self-discharge behavior of the traditional NiCd and NiH_2 battery cells that have been used in the past in space power systems has a very characteristic dependence on state of charge. As indicated in Figure 22, the self-discharge rate in these battery cells increases continuously as a function of state of charge, with a slope that also consistently increases as more charge is put into the cells. The shape of this self-discharge dependence on state of charge has a very important consequence in terms of battery operation. A battery contains a number of cells connected electrically in series. These cells therefore all see the same charge and discharge currents, and the only factor that can make them separate from each other in state of charge is cell-to-cell variability in self-discharge (or internal capacity loss) mechanisms. However, if the losses follow a monotonically rising state of charge dependence such as that shown in Figure 22, divergence of cell capacities will be intrinsically limited. This is because the cells having highest loss rates will settle to a reduced state of charge where the internal losses are reduced to match the cells having lower loss rates. The steeper the slope of the loss rate *vs*. state of charge curve is, the less capacity divergence will be seen between cells having differing self-discharge rates. This effect is shown schematically by the inset in Figure 22.

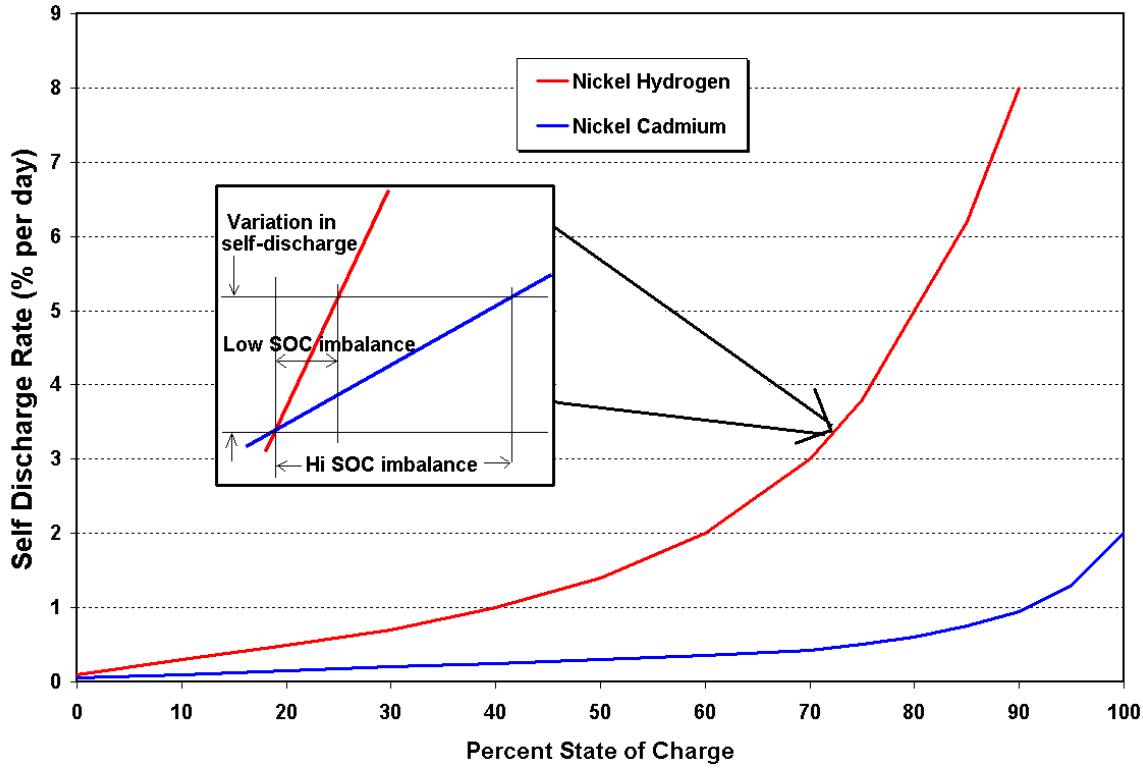

Figure 22. Self-discharge rates of nickel cadmium and nickel hydrogen cells as a function of state of charge at 10 deg C.

Degradation modes that affect internal cell losses are also important in terms of how they depend on state of charge. For NiCd cells, the formation of soft-shorts by cadmium metal dendrites is a typical degraded condition that often develops late in battery life. These soft-shorts are typically seen to form during overcharge, and thus are a phenomenon associated with increased losses at high states-of-charge. Figure 23 indicates the effect of soft shorts on the internal losses in a NiCd cell as a function of state of charge. It can be seen that at high states of charge, the soft-shorts cause rapidly increasing internal losses. This curve explains why soft shorts cause increasing cell divergence if one attempts to keep all cells fully recharged once they begin to develop. Conversely, it is possible to manage NiCd batteries with soft shorts for years of continued operation by simply avoiding the high states of charge that accelerate losses, and allowing cells to only separate sufficiently in capacity that their internal loss rates are equalized.

For lithium-ion cells the self-discharge situation is clearly quite different in that the self-discharge is very low, typically C/25,000 or less during long periods of stand, and possibly higher during electrical cycling periods. Clearly the internal losses are low enough that they cannot be easily measured with any accuracy, and their effects during cycling are difficult to detect. However, this does not mean that internal losses can be ignored in managing lithium-ion batteries. Since lithium-ion batteries are typically kept in a partially charged state during long periods of relative electrical inactivity, any differences in the low self-discharge rates between individual cells can potentially accumulate over time to result in a significant capacity divergence between the cells in

the battery. When such a battery is fully charged, the highest capacity cells can be driven to charge levels that can damage them or degrade their performance. Similarly, discharge can drive the lowest capacity cells to voltages low enough to cause possible cell degradation.

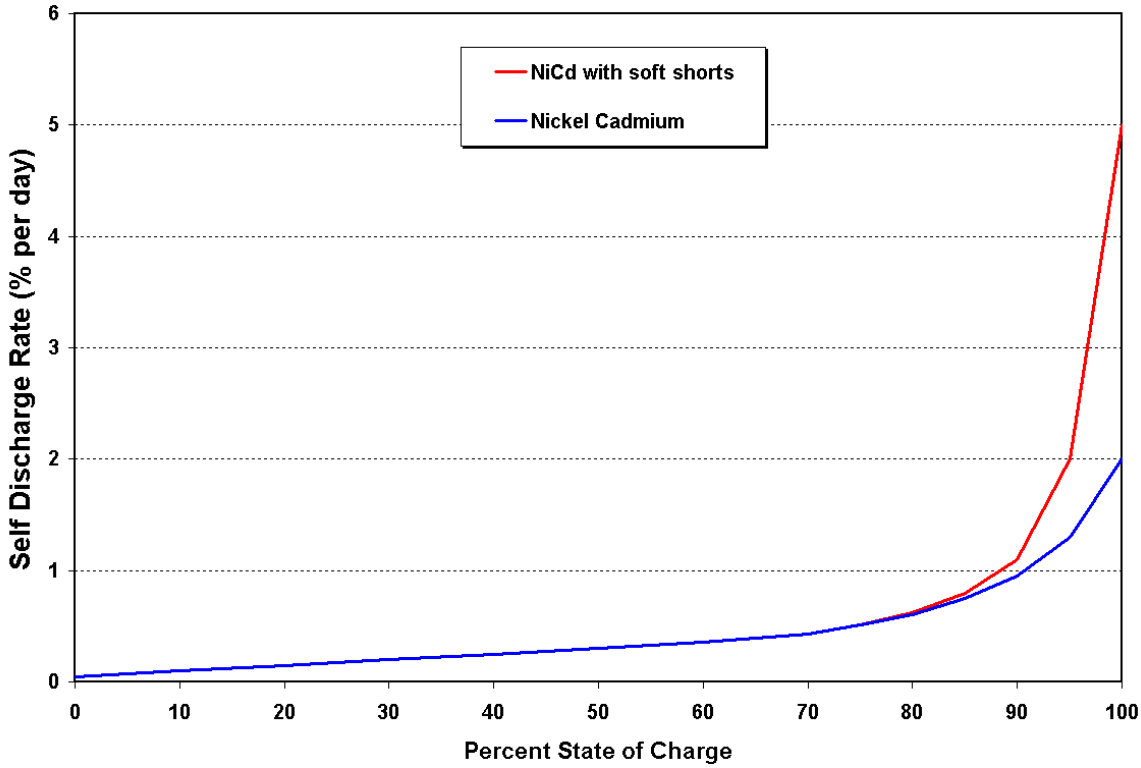

Figure 23. Effect of soft-shorts on the internal losses in NiCd cells, as a function of state of charge.

As was the case for NiCd and NiH_2 batteries, the key for avoiding this situation is to make sure that internal losses increase as cell state of charge (or voltage for Li-ion) increases. Cell divergence data during the 5-month solstice periods from real-time GEO testing has suggested that for Li/Ni-Co oxide cells the self-discharge losses are relatively constant with state of charge.[6] For Li/Co-oxide cells, models used to predict battery performance have typically assumed self-discharge rates that rise rapidly with increasing state of charge.[7] Because of the difficulty in obtaining accurate self-discharge rates from Li-ion cells, at present we really do not understand whether there are conditions where one can depend on the intrinsic chemistry within Li-ion cells to maintain cell balance during lengthy self-discharge periods.

We have recently attempted to get some data to clarify this situation by developing and applying new methods for measuring the self-discharge rates in lithium-ion cells as a function of state of charge.[8] We use three methods:

1. *Open circuit voltage decay*. The rate of voltage decay during open circuit is converted into a rate of capacity loss using a previously generated calibration relating cell open circuit voltage to state of charge.

2. *Charge return for voltage maintenance*. The charge that must be input to hold a cell at a given voltage level is measured, providing self-discharge rate assuming that this charge input just balances the self-discharge.
3. *Capacity loss during open-circuit stand*. A cell is allowed to stand at a well-defined initial state of charge for 5-6 months, after which it is fully discharged to determine the amount of self-discharge. This method is very time-consuming, requiring 5-6 months to get each point on the state of charge curve for each cell.

For all of these methods, we have found that it is critical to control temperature precisely, since cell voltage and thus the apparent state of charge often can have a significant temperature coefficient. Temperature control is particularly important since voltage decay rates of nanovolts/sec are being measured, and because voltage maintenance currents of C/10,000 or less are being applied. The measurement of self-discharge by all these methods is strongly impacted by the tendency of lithium-ion cells to remember earlier charge levels for weeks. For example, if a fully charged cell is discharged to 20% state of charge and then allowed to stand open circuited, its voltage will continue to recover for up to several weeks or more before the voltage will begin to drop slowly due to self-discharge. To make meaningful self-discharge measurements one must make sure that all other processes (such as this slow charge redistribution) in the cell are occurring at rates much less than the self-discharge rates. We require that the self-discharge rates measured by all three of the methods outlined above are consistent with each other, or that any inconsistencies are well understood, before we feel that the self-discharge rate of a lithium-ion cell has been accurately measured.

We have measured the self-discharge rate as a function of state of charge for a Li/Co-oxide cell having a graphitic anode. The results of these measurements, which took about 4 months to complete, are indicated in Figure 24. The self-discharge rate of this 5.0 Ah cell does not monotonically increase with state-of charge, but rather increases sharply near 3.6 volts (~5% SOC), then decreases gradually as the open circuit cell voltage increases to 4.15 volts (~100% SOC). A self-discharge relationship of this form will not provide any self-balancing of individual cells in a battery during long periods of stand at intermediate states-of-charge, but will actually cause cells to separate in capacity as they run down, at least until the cell voltages drop to under 3.7 volts (about 10% state of charge).

Because each lithium-ion cell type may have somewhat different self-discharge characteristics, the measurements reported in Figure 24 do not necessarily mean that other cell types will exhibit similar self-discharge behavior. However, until accurate data are obtained for a given cell type, power system designs should independently provide some assurance that differential cell losses can be compensated during long-term operation. Cell imbalance correction can be assured by the use of individual cell charge control at the system level, or by electronic cell balancing circuitry.

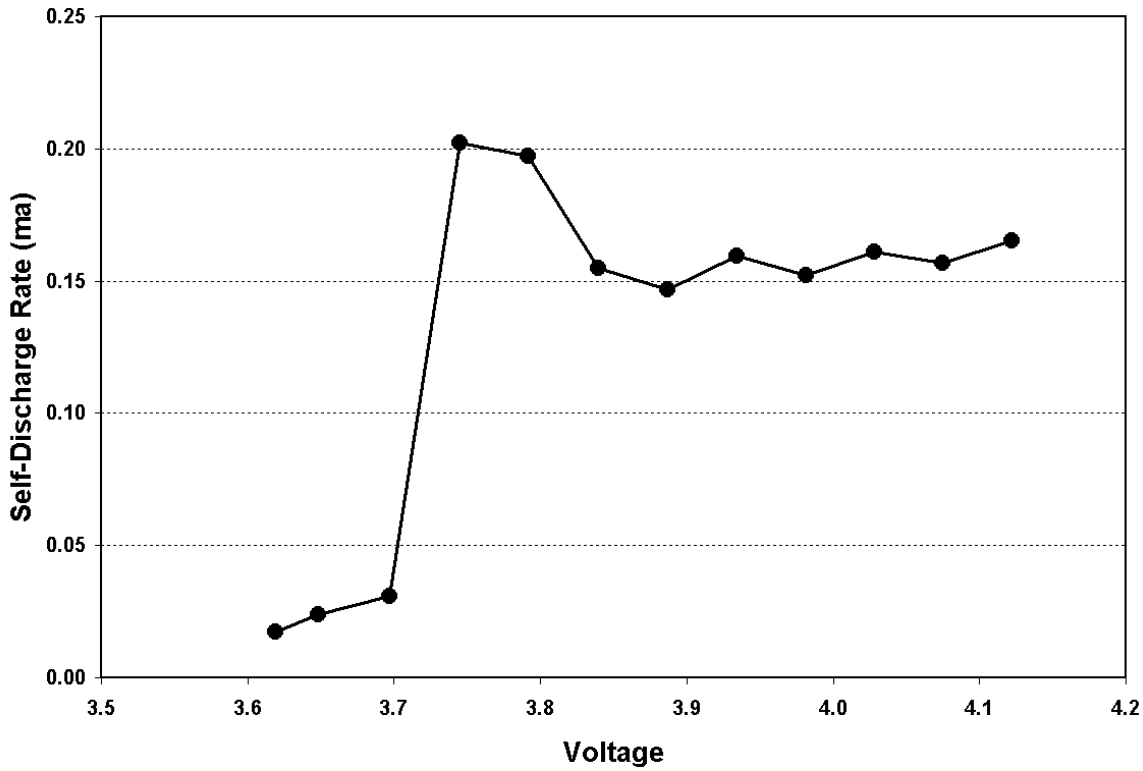

Figure 24. Self-discharge rate of an open-circuit 5.0 Ah Li-ion cell as a function of cell voltage at 20 deg C.

Conclusions

Cycle life comparisons between 7 Ah lithium ion and NiCd or NiMH cells operated in a LEO cycling regime using a charge control system that is optimized for each of these battery types, based on trending after nearly 8000 cycles, suggests that lithium-ion batteries should provide longer cycle life than these older technologies. Comparisons of larger (35 and 40 Ah) Li-ion cells to nickel hydrogen cells (again in LEO cycling) suggest that nickel hydrogen should be able to provide equivalent cycle life, but at twice the DOD. Alternatively, nickel hydrogen is capable of significantly greater cycle life at an equivalent DOD (depending on the calendar life unknowns for each technology). In terms of usable energy density in LEO applications this makes these two technologies competitive with each other. Of course in GEO-type applications, for which the DOD can be 60-70%, lithium-ion offers about a factor of two weight advantage over nickel hydrogen, and a significant volume advantage. While the calendar life capabilities of nickel hydrogen batteries has been demonstrated to be greater than 20 years, the calendar life of lithium ion (and its limitations) has not yet been established, with only 3-5 years having been demonstrated.

A relatively simple accelerated test profile has been shown to offer a 4 to 6 time acceleration factor in terms of demonstrating the cycle life of one particular lithium-ion cell. Unfortunately, there is no reason to believe that this identical acceleration factor will apply equivalently to other lithium-ion cell designs.

The maintenance of a balanced battery, in which all series connected cells have well matched capacities, depends on how internal cell loss rates depend on state of charge. Because the self-discharge rate of lithium ion cells is very low, it is only during long periods of electrical inactivity that imbalances are likely to develop. Data on internal loss rates in lithium-ion cells suggests that batteries of these cells may not always maintain balanced cells without some external cell balancing from the charge control system or cell balancing electronics.

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PROBA Lithium-ion Battery

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David Lizius, Com Dev

PROBA Mission - 1

- PROBA - Project for On Board Autonomy
- 10 MEuro€ European Space Agency mission
- Prime contractor: Verhaert, Belgium
- Goals:
  - Onboard resource management, housekeeping
  - Scheduling and execution of scientific observations
  - Scientific data collection, storage, processing & distribution
  - Data communication management
  - Performance evaluation, failure detection
  - Failure detection, reconfigurations, software exchanges

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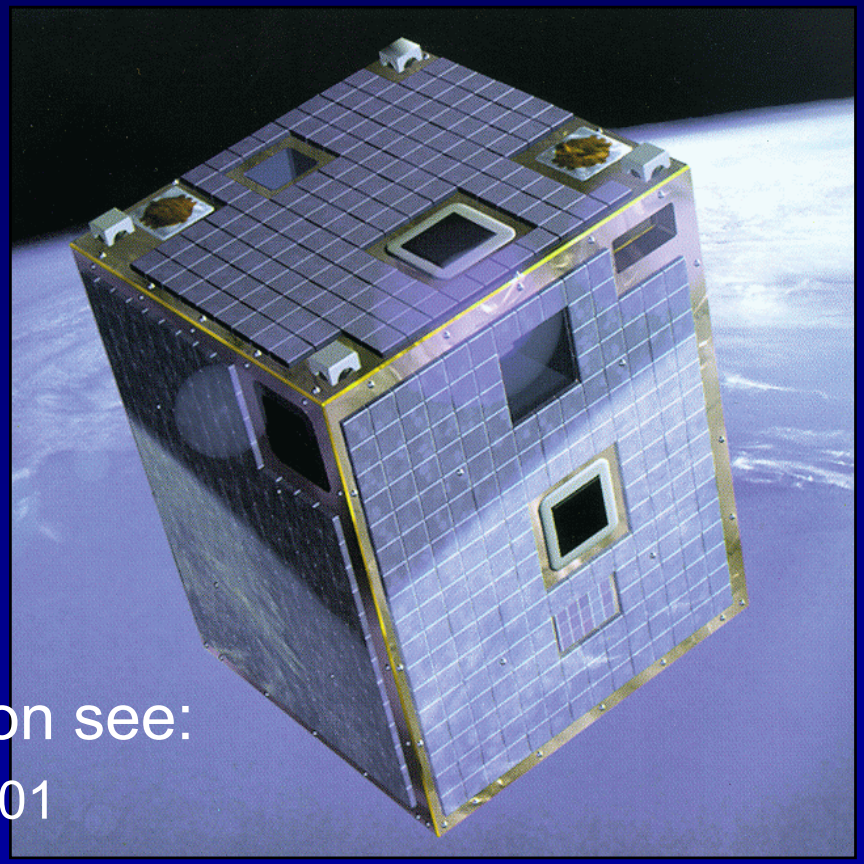
PROBA Mission - 2

- Program started Feb 1998
- FAR July 2001
- Launched Oct 22, 2001
- Nominally one-year LEO mission
- 90kg spacecraft
- Three-axis stabilized
- Body mounted arrays
- For more general PROBA information see:
  - G Dudley, NASA Battery Workshop 2001



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San Francisco, June 02

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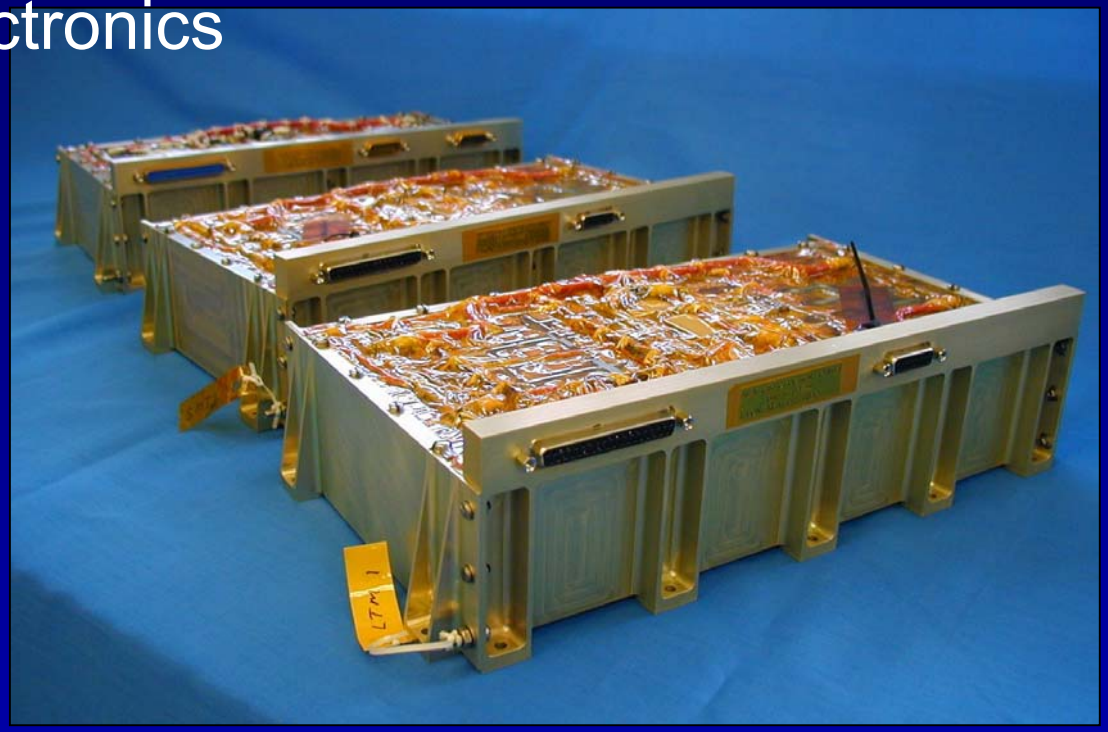
Lithium-ion Batteries - 1

- Same concept employed in contracts to supply Lithium-ion batteries to 28 spacecraft
- Batteries currently based on the Sony 18650HC cell
- No cell-level balancing electronics



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Lithium-ion Battery - 2

- First ESA Lithium-ion battery
- Late change for a NiCd solved a mass difficulty
  - NiCd 6.4 kg, Lithium-ion 1.87kg
  - Additional mass savings as counter balance not required with Lithium-ion battery
- Single module battery
- Battery topology: 6s - 6p
- Nameplate capacity: 9Ah
- Voltage range: 25.2V - 15V
- Nameplate Energy: 195 Wh
- Specific energy 104 Wh/kg

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Lithium-ion Battery - 3

- Lithium-ion battery well suited to autonomous operation
  - wide operating temperature range (passive thermal control)
  - no reconditioning required
  - no cell balancing
  - simple charge control algorithm
    - Planned to have ~CC-CV charge
    - However CV step-taper disabled prior to launch
    - No V/T relationship required
    - EOCV limit constant through mission life

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Battery EOCV - 1

- Design: EOCV=25.2V followed by step taper (4.2V/cell)
- Step taper deliberately disabled during S/C AIT
- From telemetry, charge terminated at EOCV>25.2
  - Digitisation of telemetry, sample frequency, the way step-charge was disabled
- However, $V_{telemetry}$ higher than $V_{battery}$
- Convert raw telemetry
  - Apply 0.2V calibration determined during S/C AIT
  - Correct for 250mOhm impedance between battery and voltage measurement point in harness
- Typically EOCV = 4.16V per cell

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Battery EOCV - 2

Orbit No. From 00:00 29 Sept 02	PSU800.raw (Volt)	$V_{battery}$ calibrated (Volt)	EOCV/cell (Volt)
1	25.2321	24.808	4.13
2	25.2809	24.965	4.16
3	25.3623	24.960	4.16
4	25.2874	24.989	4.16
5	25.2874	24.967	4.16
6	25.3688	24.937	4.16
7	25.3949	24.984	4.16
8	25.3916	24.984	4.16
Average	25.3257	24.949	4.16

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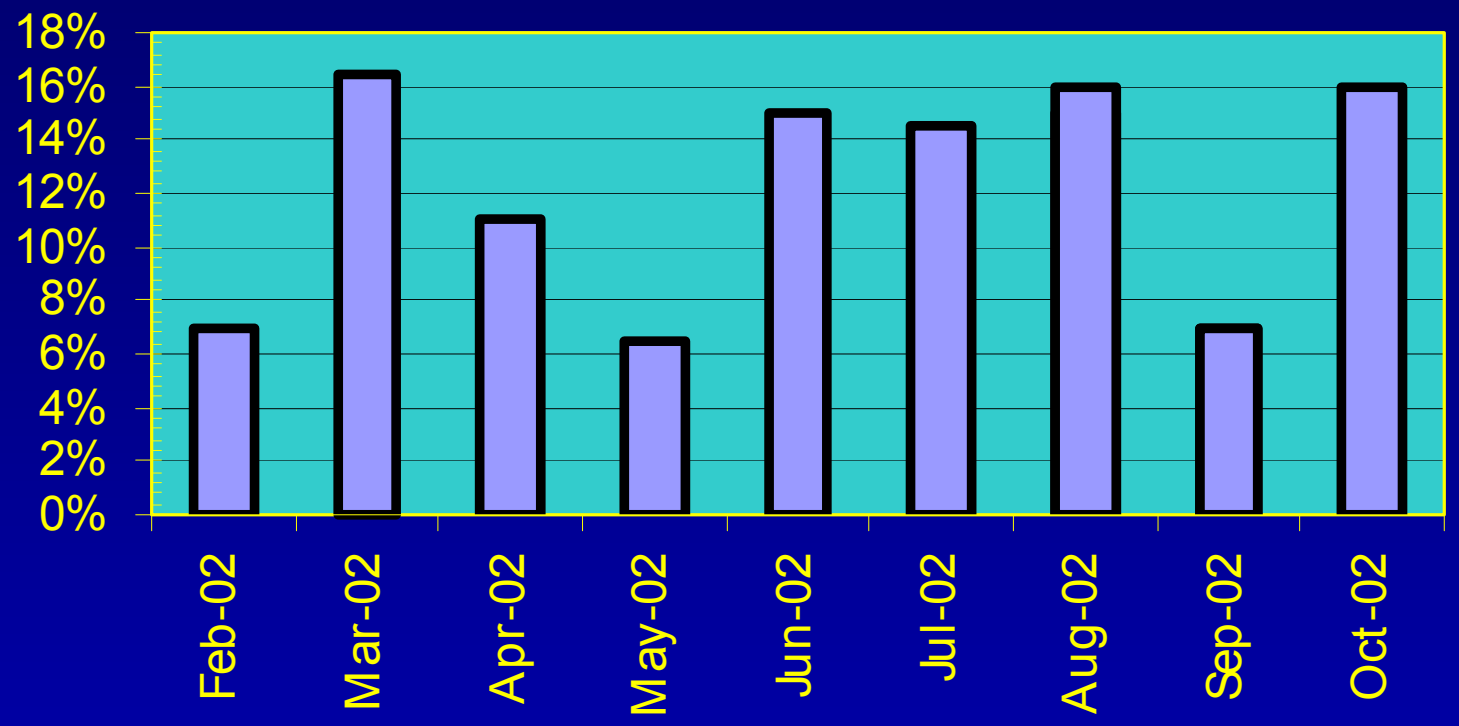
Typical In-orbit Data - 1

- In-orbit average DOD from typical day in each month
- Lower than design case of 20%



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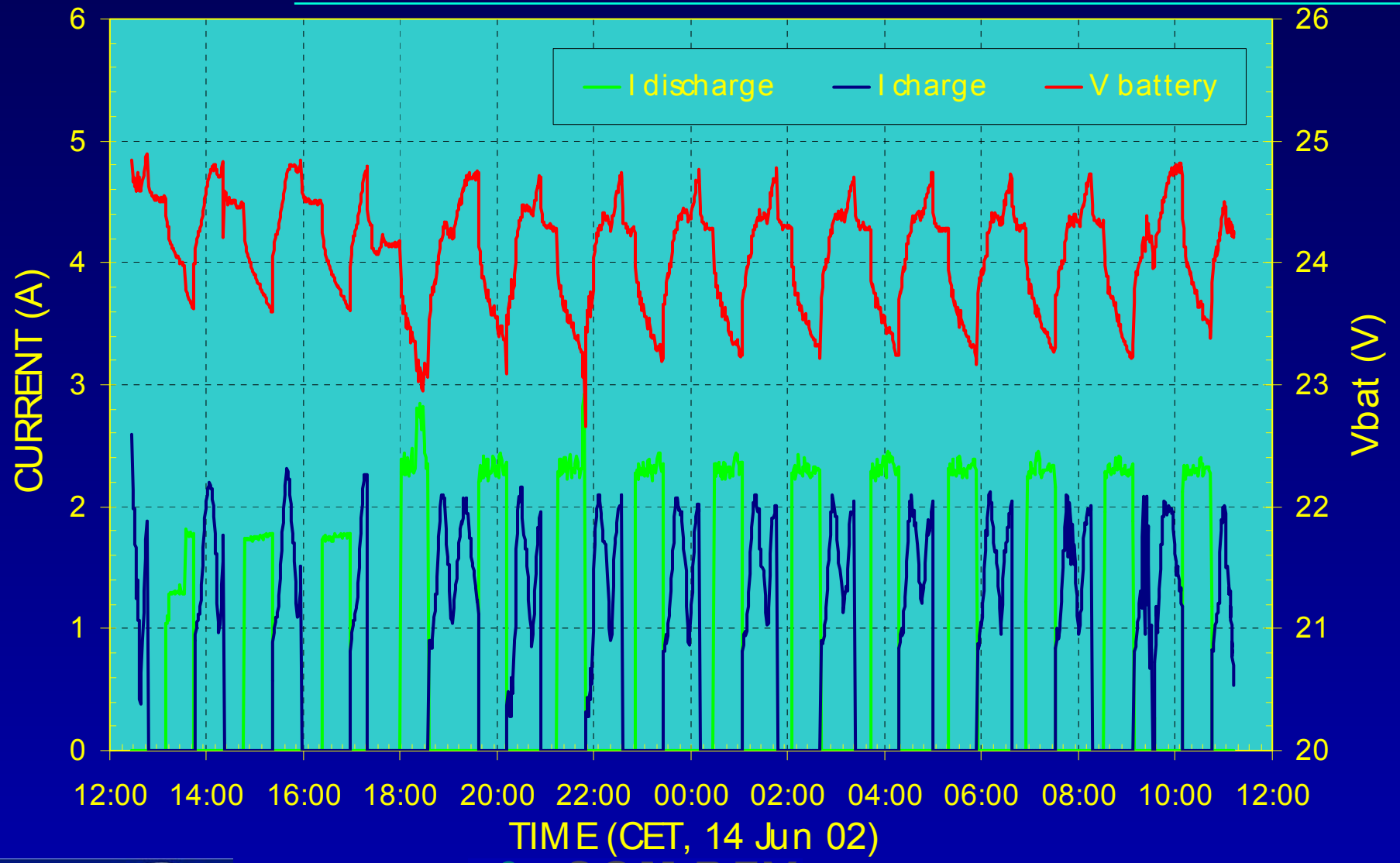
Typical In-orbit Data - 2



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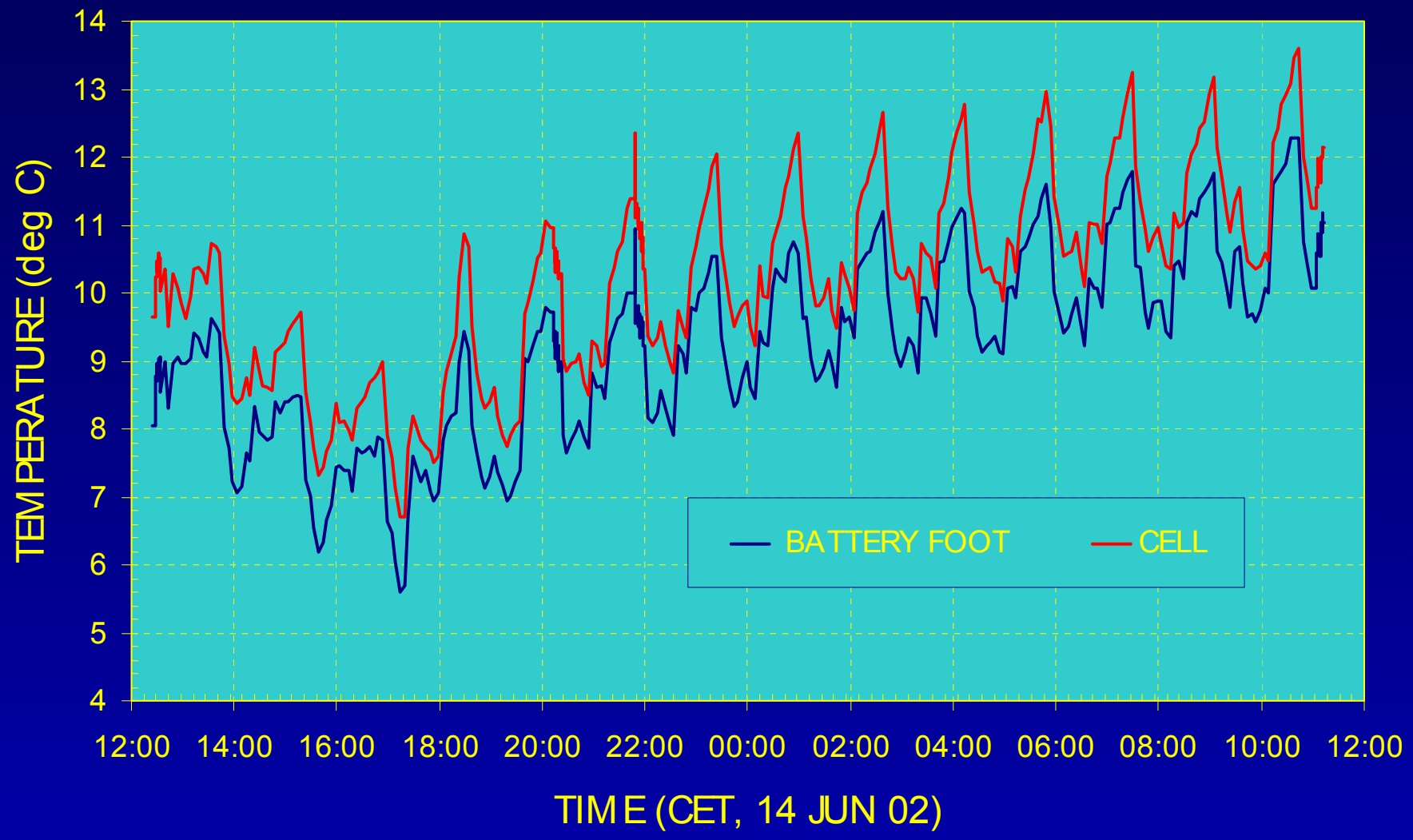
Typical In-orbit Data - 3



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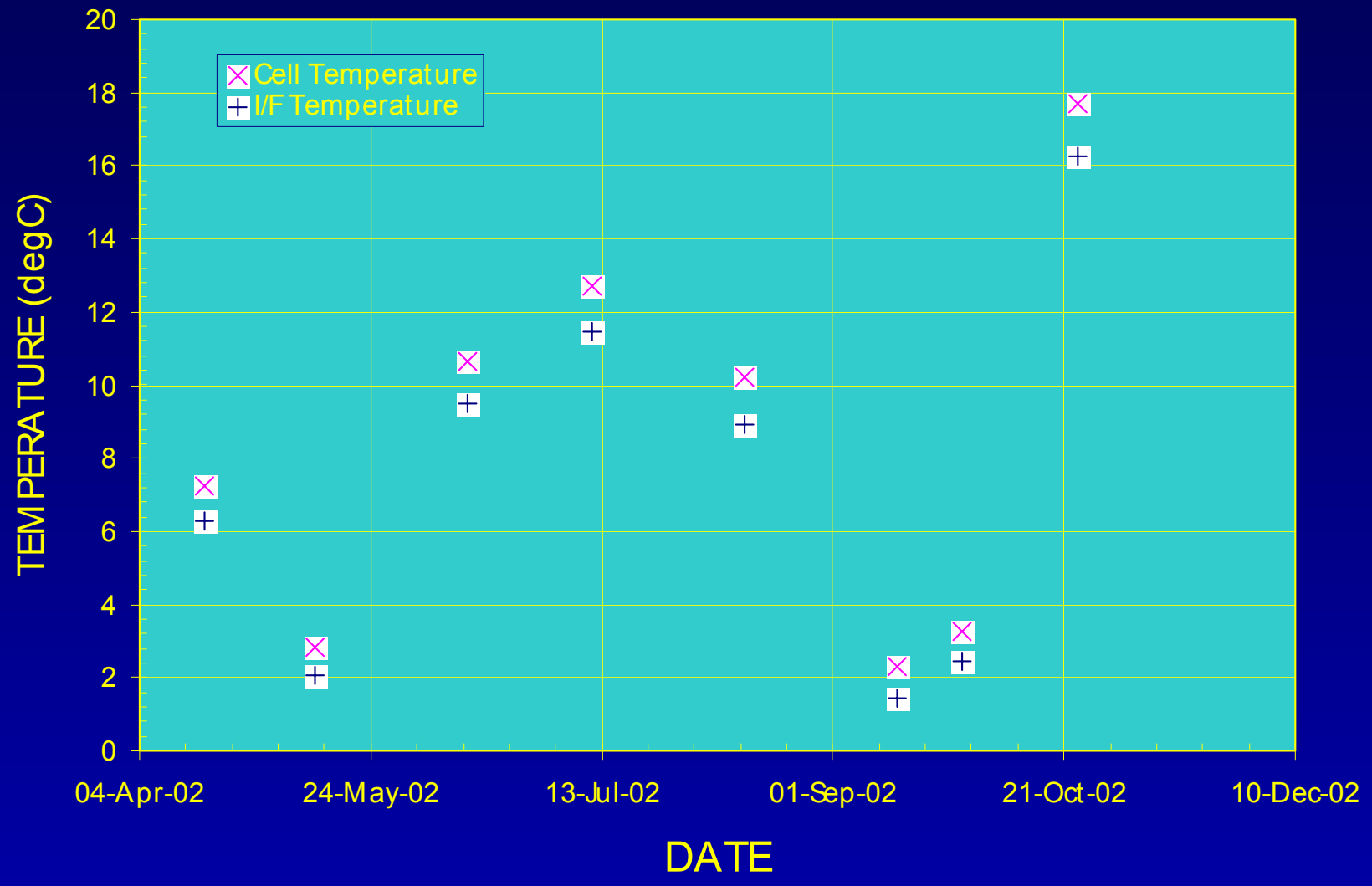
Typical In-orbit Data - 4



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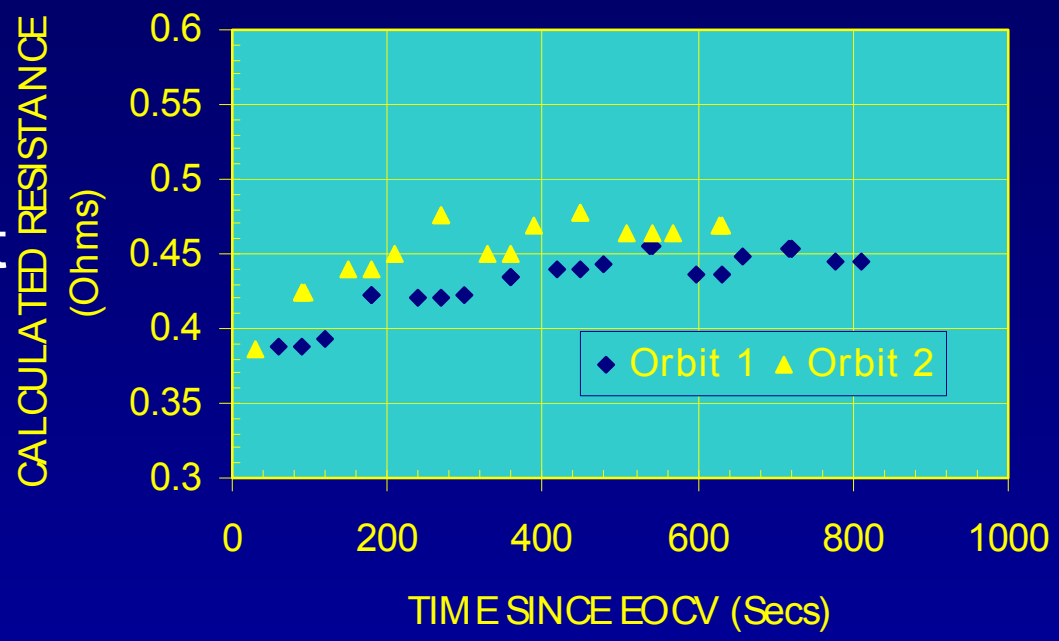
Battery Resistance - 1

- Lack of step taper enables a prediction of the battery resistance from a current interrupt technique
- V & I are measured at a point in the power harness away from the battery
- Calculated resistance is $R_{calc} = R_{battery} + R_{harness}$
- Example from 14 Jun 02



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Battery Resistance - 2

- $R_{battery} = R_{calculated} - R_{harness}$
- $R_{harness}$ = 250 mOhm, by calculation
- $R_{battery}$ varies with temperature and life
- From comparable real-time LEO life-test data, expect resistance increase 15% in the first year of operation
- Resistance = f(Temperature) and is known
- Hence we can compare expected resistance with measurements
- We conclude that battery resistance is in accordance with expectations

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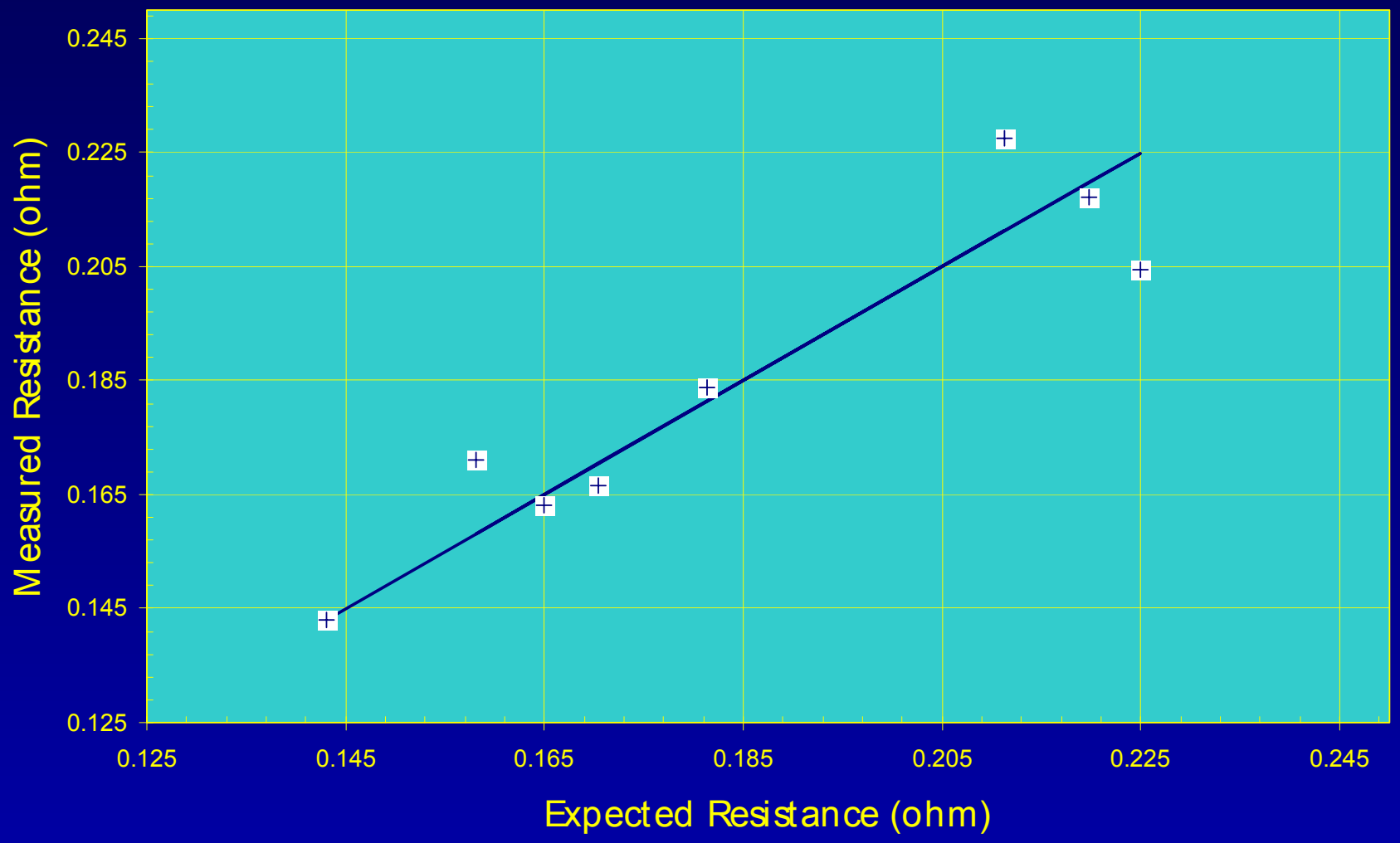
Battery Resistance - 3



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Capacity Fade - 1

- How to assess the capacity performance with limited telemetry?
- If battery were fully charged at EOC:
  - Integrate Ahr until EOD, relate OCV to SOC
- Use BEAST modelling tool
  - Predict battery voltage, SOC, temperature, thermal dissipation etc. as a function of current flows
  - Prediction requires capacity and resistance of battery
  - Resistance is measured
  - Budget for capacity derived from real-time life-tests
- Compare BEAST voltage prediction with measurements

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Capacity Fade - 2

- Example: 1st Aug 02
  - Expected R increase = 11.55%, C fade = 3.46%
  - BEAST prediction tool assumes minimum acceptance values for resistance and capacity at BOL
  - Measured PROBA battery properties at BOL better than minimum criteria
  - Hence inputs to BEAST need to be adjusted accordingly
  - Input values: R increase = 0.8%, C fade = 1.46%
- Measured EODV > expected values
- Hence battery capacity is better than budget

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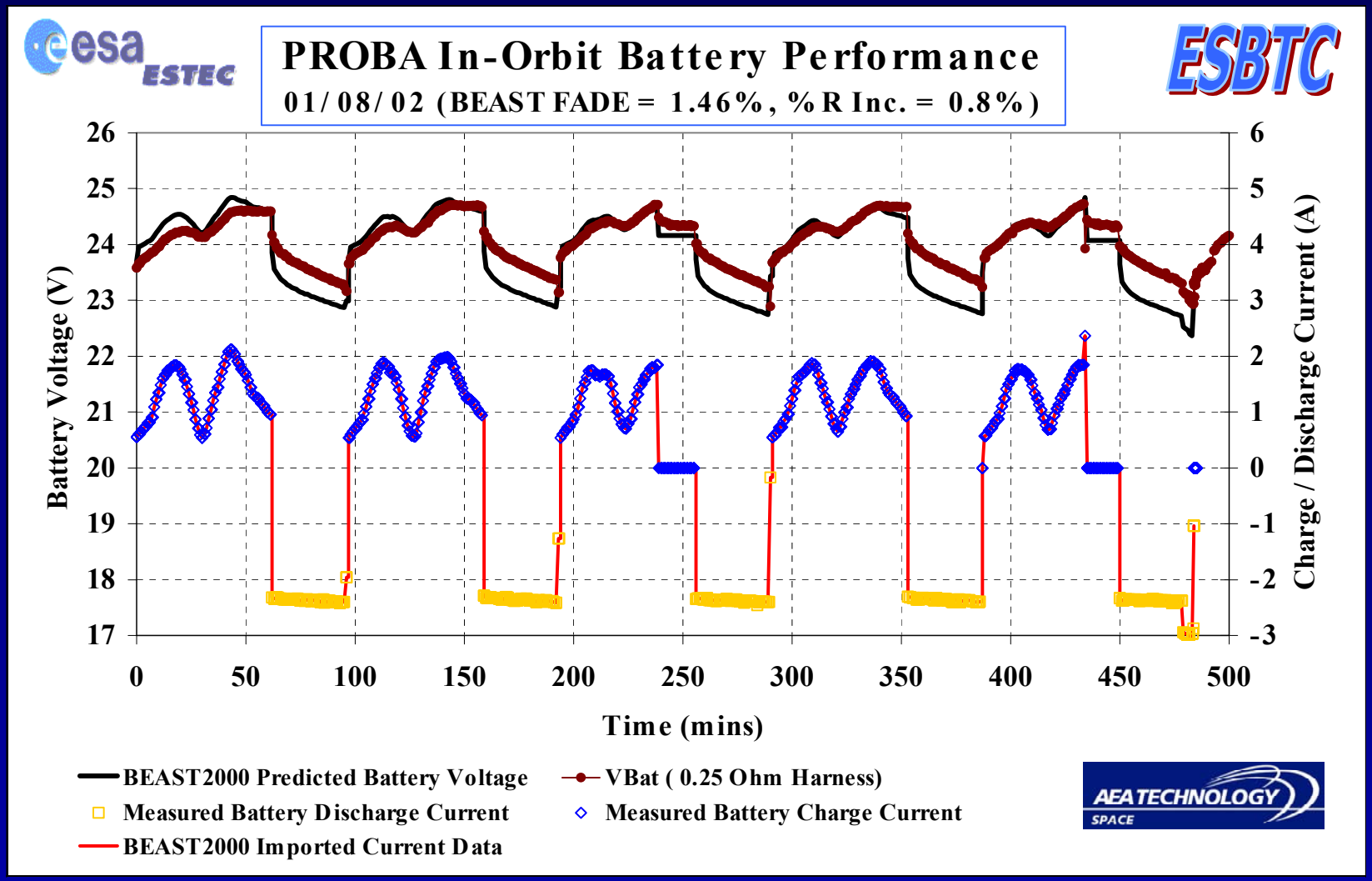
Capacity Fade - 3



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Capacity Fade - 4

- Guessed initial conditions not correct
  - need to know initial SOC or model several orbits
- After a few orbits, charge voltage is good
- Measured EODV > expected value
  - Capacity fade not as large as expected as DODs are lower than design-case
  - Resistance increase not as large and $R_{harness}$ higher than expected
- Iterating values within credible uncertainties, it is possible to get a very good fit

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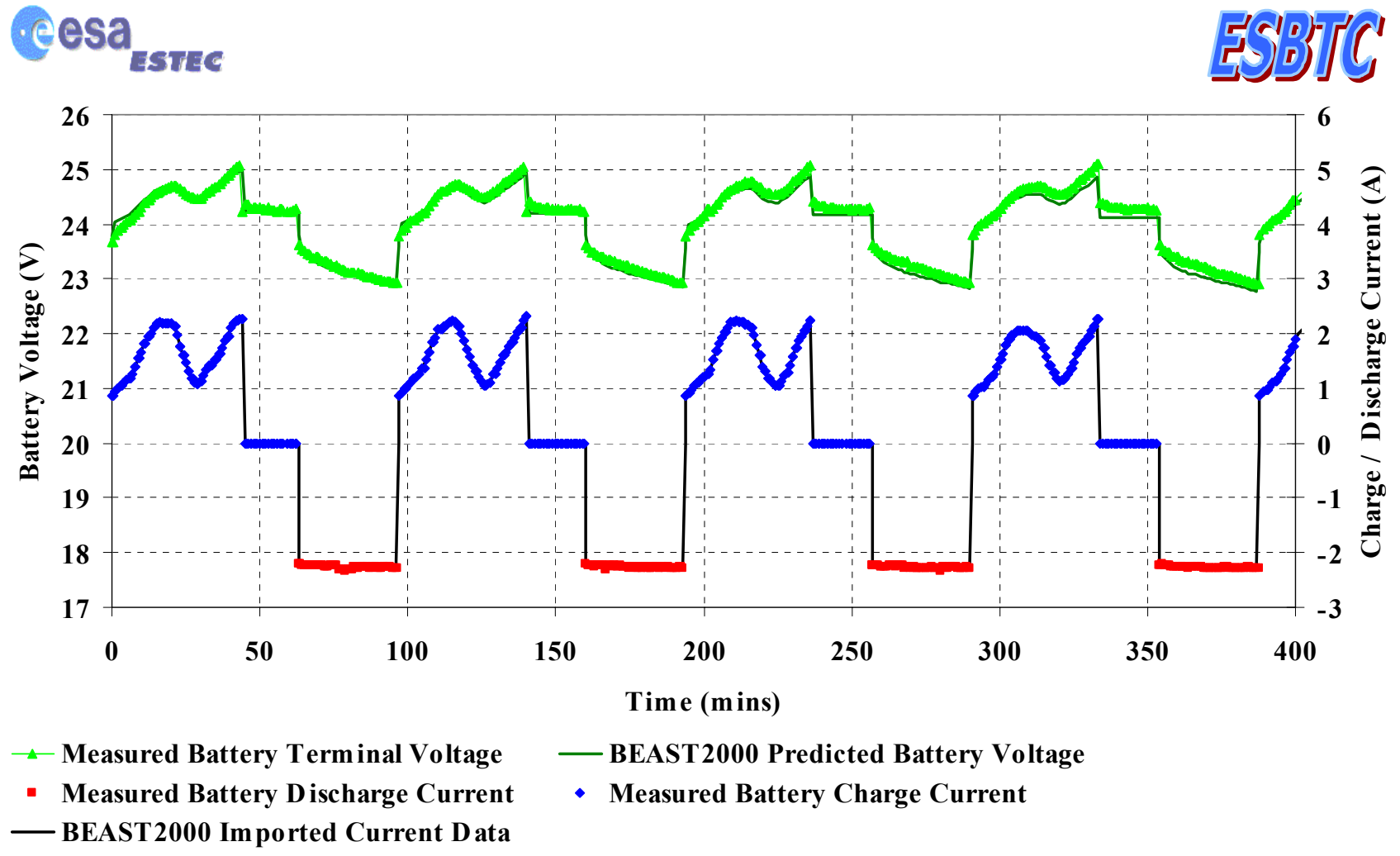
Capacity Fade - 5



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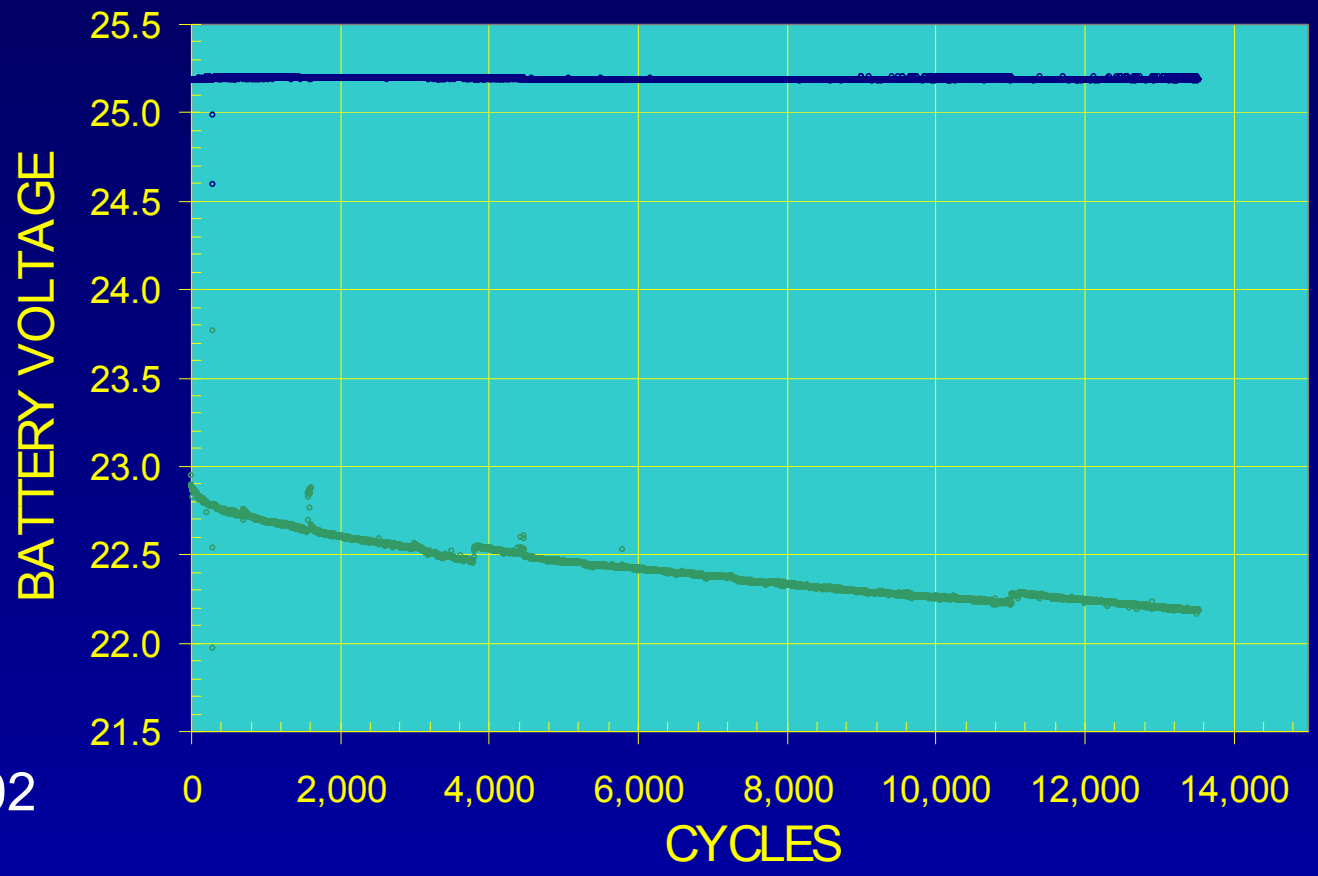
Supporting Life-test Data - 1

- ‘Real-rate’ LEO test
- 6s-12p battery
- 25.2V EOCV
- Constant 30% DOD
- Approx. real rate
  - 4,200 cycles per yr
- Average fade
  - 38mV per kcycle
- Expected life
  - >50,000 cycles
- Test at ESA BTC
- Data shown @ 5 Nov 02



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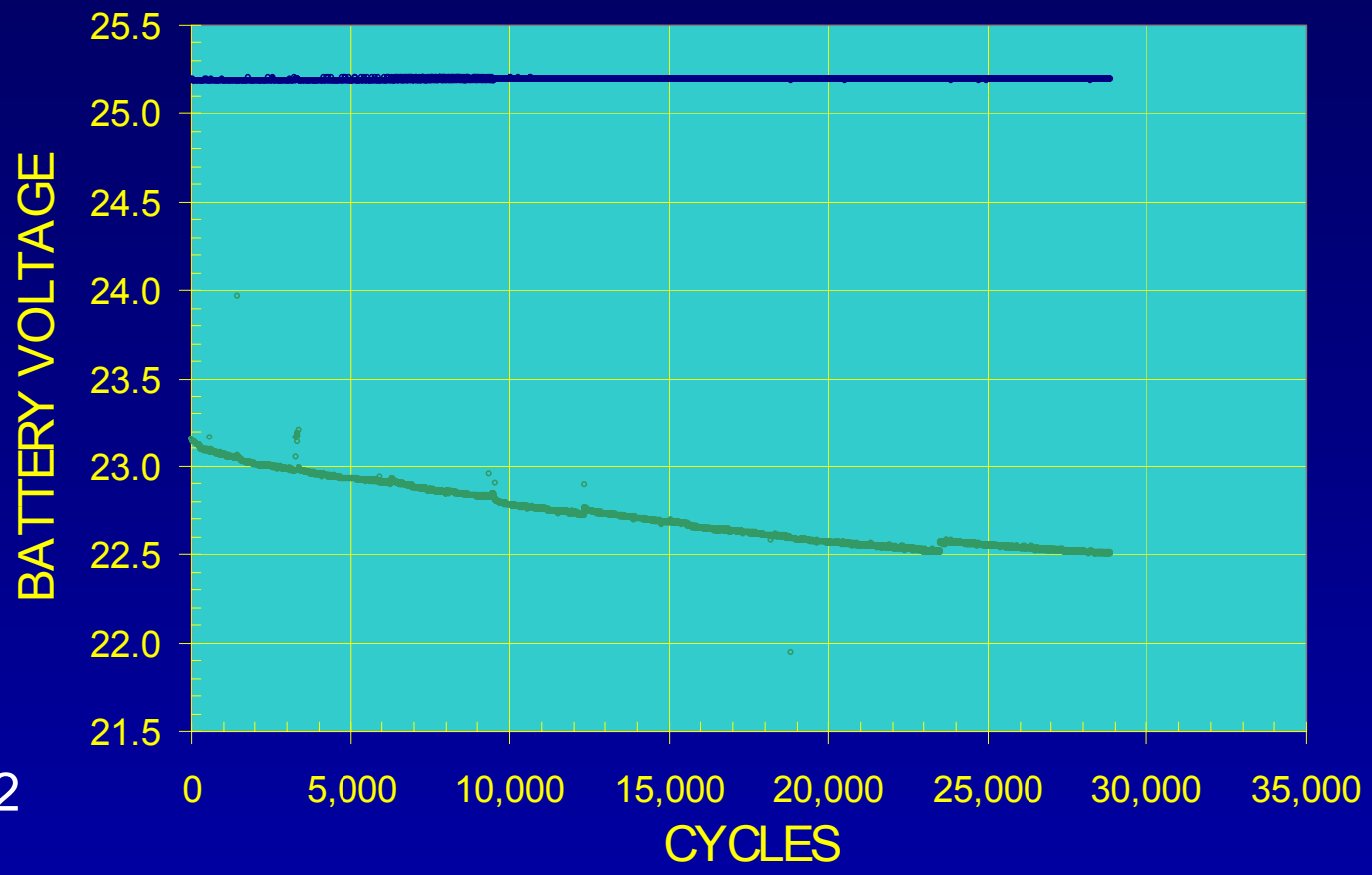
Supporting Life-test Data - 2

- ‘Accelerated’ LEO test
- 6s-12p battery
- 25.2V EOCV
- Variable DOD
  - peak 30%, av.15%
- Double rate
  - 9,400 cycles per yr
- Average fade
  - 19mV per kcycle
- Expected life
  - >50,000 cycles
- Test at ESA BTC
- Data shown @ 5 Nov 02



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Conclusions

- Demonstrated Lithium-ion battery for one year LEO
- It has been possible to derive some conclusions about battery performance from limited telemetry:
  - Resistance increase is in accordance with expectations
  - Capacity fade is less than budget, probably due to lower operating DOD
- Lithium-ion battery suits autonomous concept well
- Recently announced that the mission will be extended for another year of operation
- Life-tests show that battery life will easily exceed extended mission requirements

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Acknowledgements

- We gratefully acknowledge our customers:
  - Dirk Bernhart, Verhaert, Belgium
  - The ESA PROBA Team at ESTEC
- Geoff Dudley at the ESA Battery Test Centre
- BNSC for their support and encouragement
- ESA for the use of in-orbit

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Capacity Fade of Li-ion Cells: Experimental Studies and Mathematical Modeling

by

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Objectives

- Perform experiments to quantify capacity fade of Li-ion cells
- Develop capacity fade model to predict capacity fade of Li-ion cells

Overview

- Develop a methodology to determine the cause of capacity fade in Li-ion cells:
  - Primary Active Material (Li^+) loss
  - Secondary Active Material ($LiCoO_2$/Carbon) losses
  - Rate Capability loss
- Factors that control the capacity loss:
  - Charging protocol
  - Cycling Temperature
  - Charge and discharge rates
  - The depth of discharge (DOD)
- Quantify capacity fade using experimental data.
- Develop a capacity fade model that would predict cycle life of a Li-ion cell

Performance Studies

- Cycling Studies
- Capacity Fade Balance

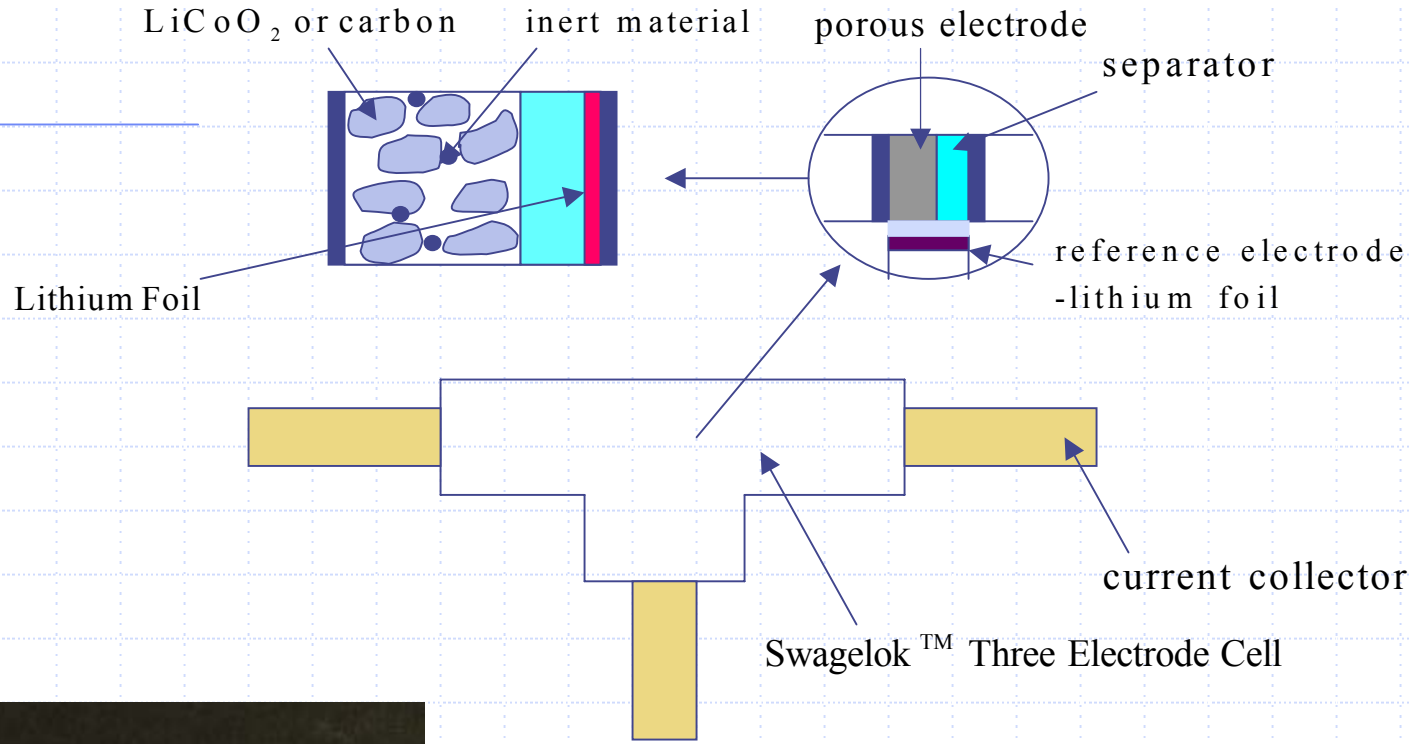
Experimental – Cycling Studies

Studies of 18650 Li-ion Cell:

- Cells cycled using Constant Current-Constant Potential (CC-CV) protocol.
  - Charged at 1A current till potential reaches 4.2 V
  - Hold potential at 4.2V till current decays to 50 mA.
- Cells were discharged at a constant current of 1 A.
- Batteries were cycled at four temperatures: RT(25°C), 45°C, 50°C and 55°C.
- Rate capability studies done after 150, 300 and 800 cycles
  - Cells charged at 1 A and discharged at different rates (C/9 to 1C).
- EIS measurements were done for fresh and cycled cells. (100 kHz ~ 1 mHz ±5 mV)

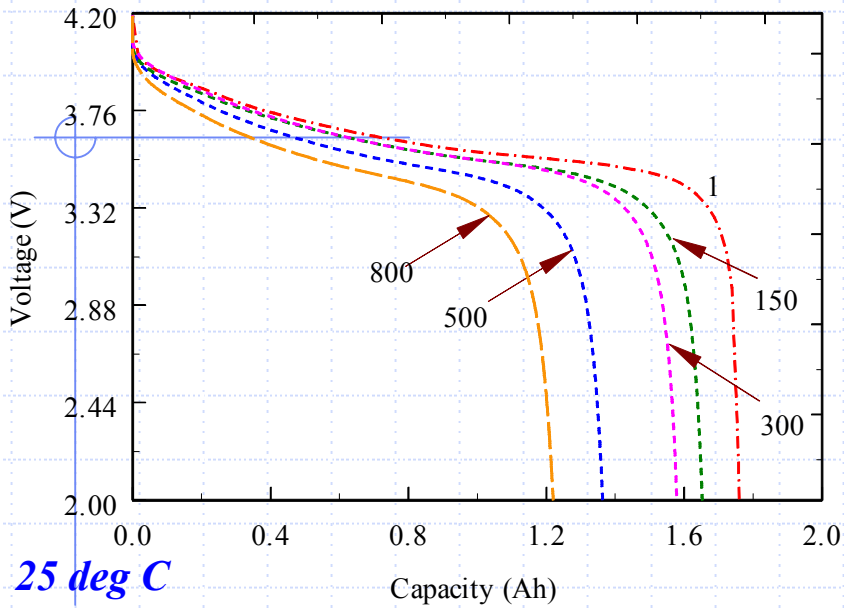
Studies of fresh and cycled electrode materials were carried out using a T-Cell assembly with Li metal being the counter and reference electrode.

Half Cell Studies: T-Cell

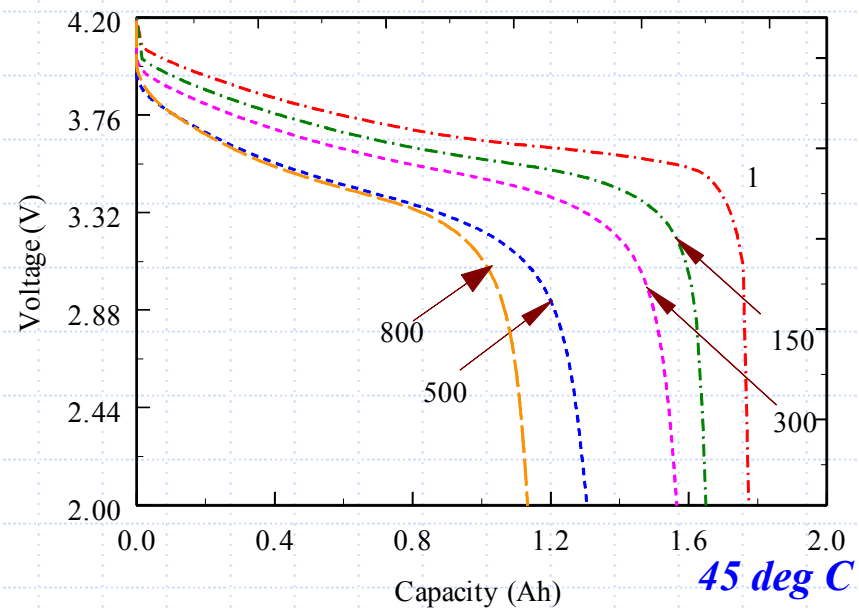


- Impedance analysis - 100 kHz ~ 1 mHz ±5 mV.
- Specific capacity measurement (~C/20 rate)
- Material characterization - XRD studies

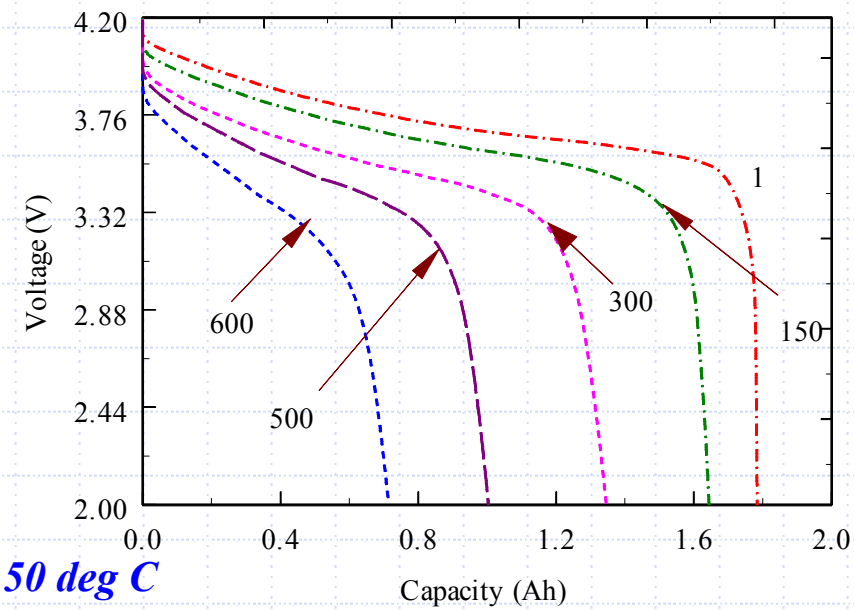
Discharge Curves at Various Cycles



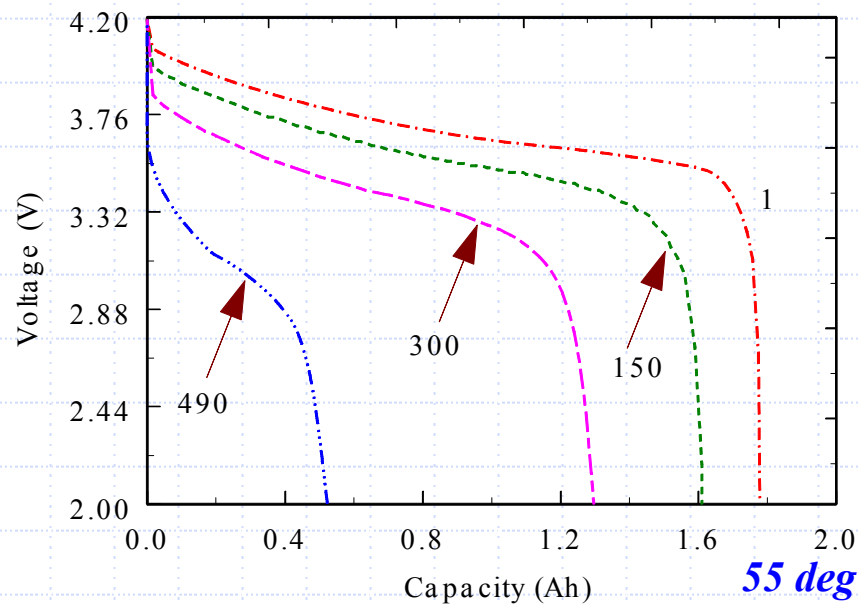
25 deg C



45 deg C

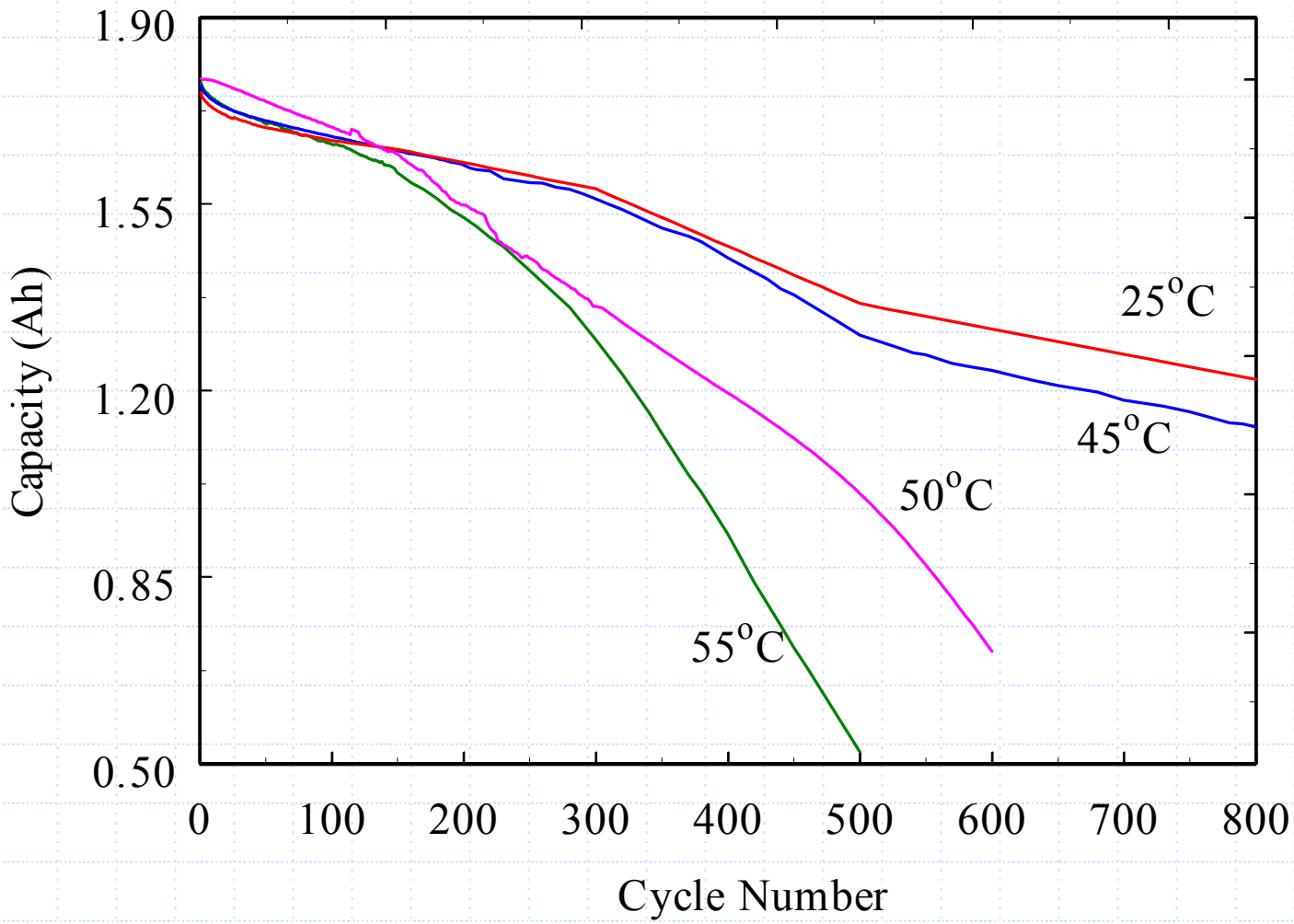


50 deg C



55 deg C

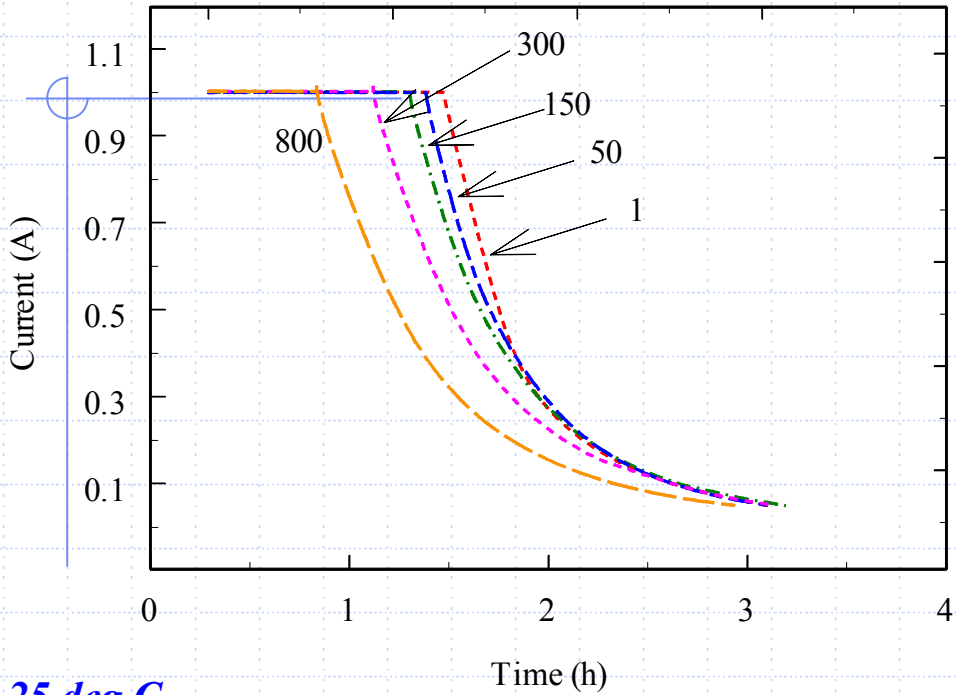
Capacity Fade as a Function of Cycle Life



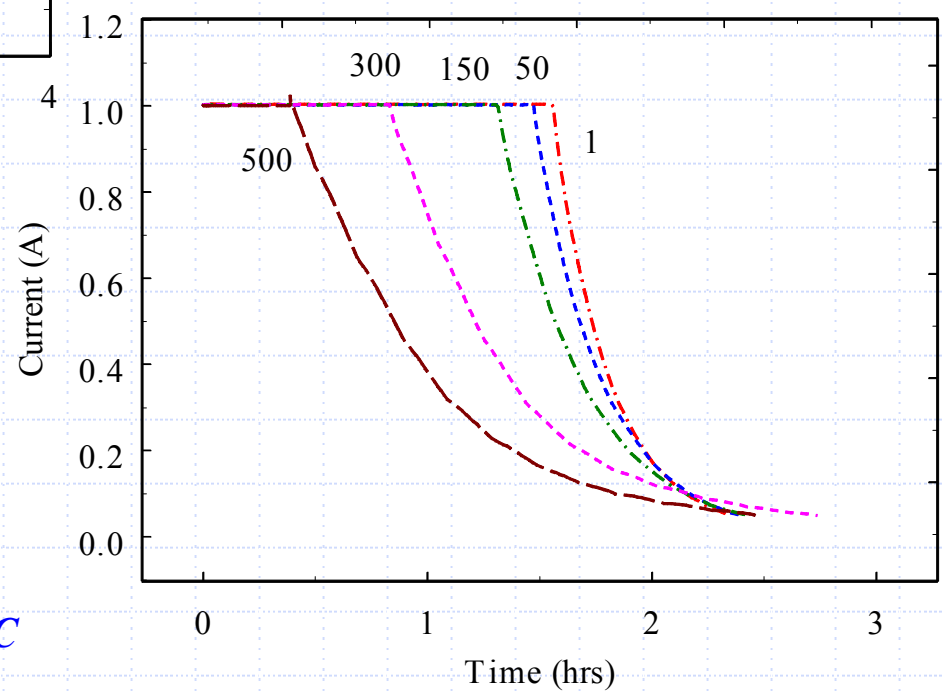
Capacity Fade as a Function of Cycle Life

Temperature	% Capacity Fade (cycle number)					
	50	100	150	300	500	800
25°C	3.8	5.11	6.06	10.29	22.5	30.63
45°C	3.8	5.46	7	11.75	26.46	36.21
50°C	2.4	5.1	7.9	23.9	43.21	-
55°C	4.3	6.4	9.4	27	70.56	-

Charge Curves at Various Cycles

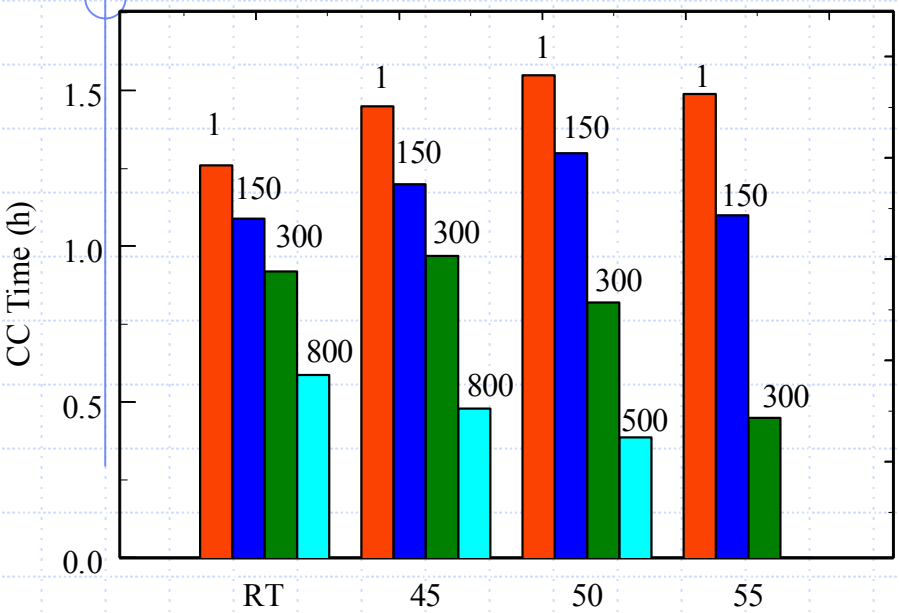


25 deg C

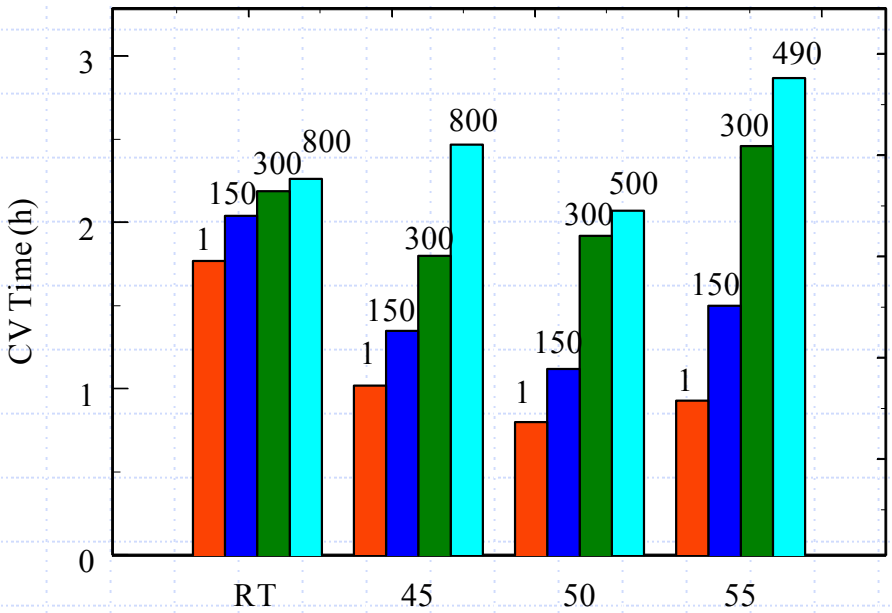


50 deg C

Change in Charging Times with Cycling

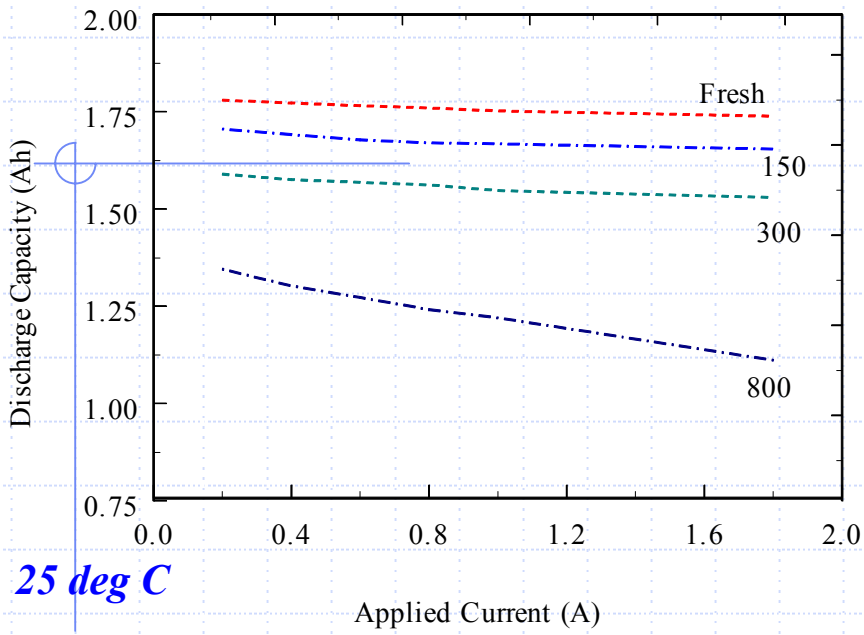


Constant Current

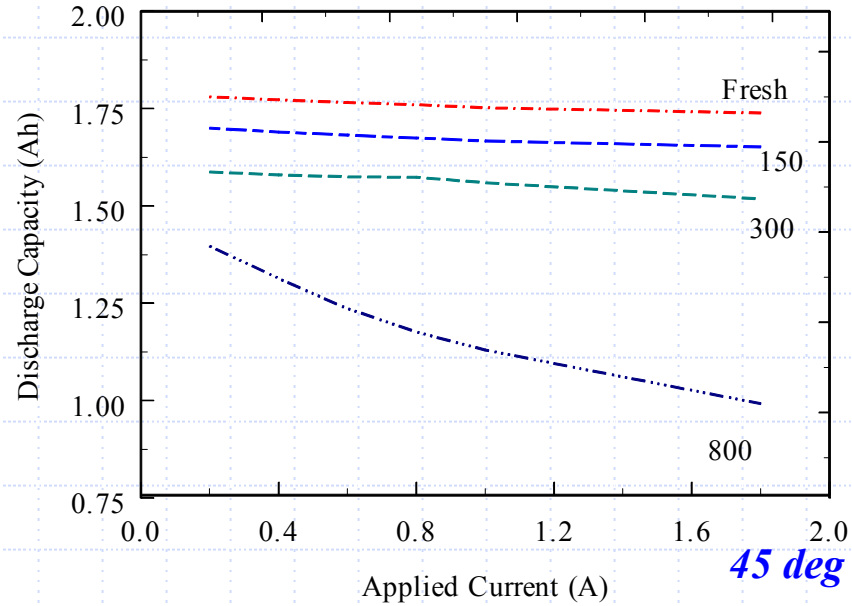


Constant Voltage

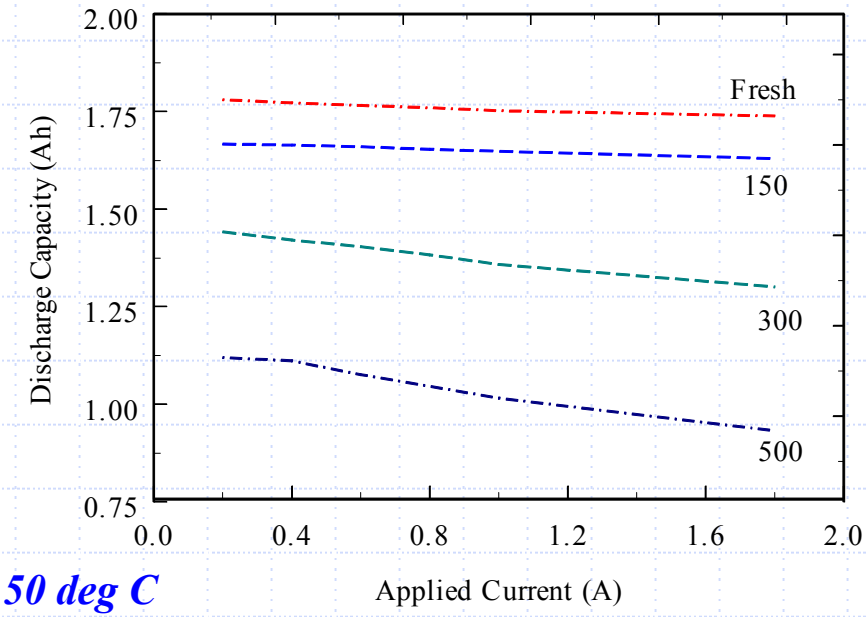
Rate Capability with Cycling



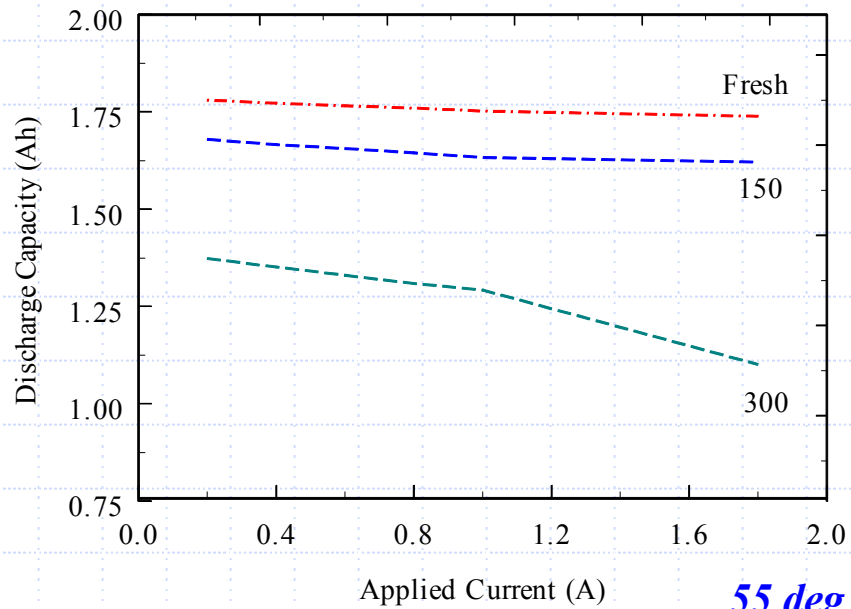
25 deg C



45 deg C

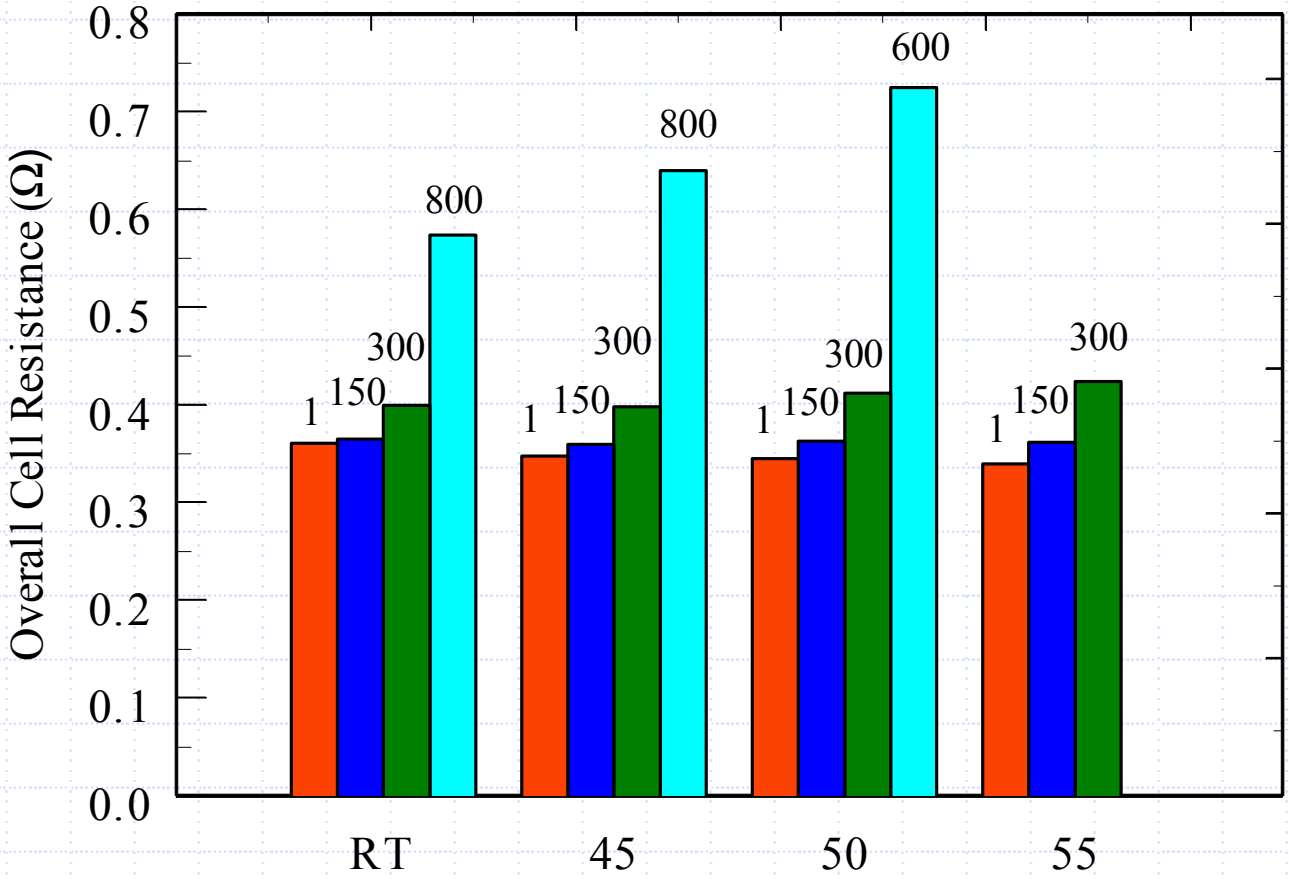


50 deg C

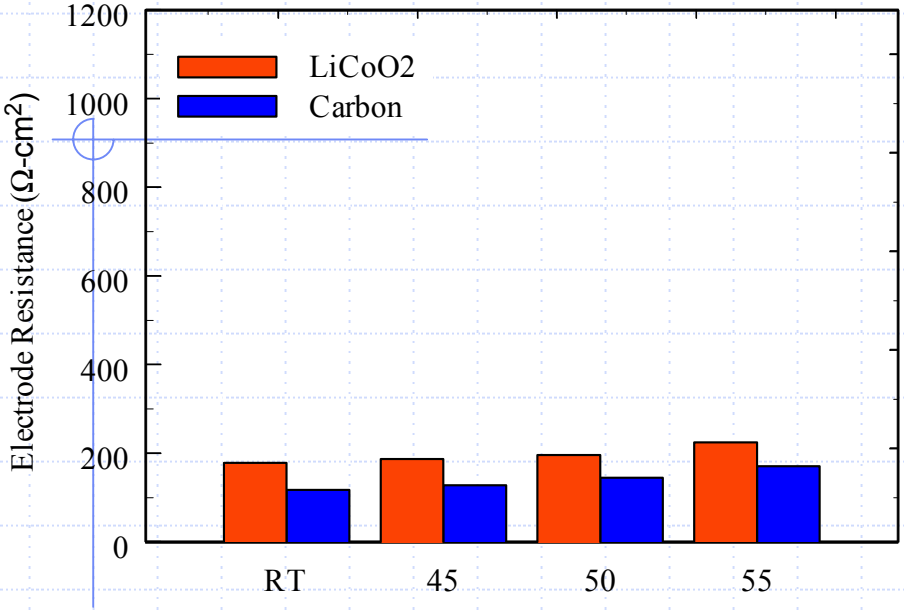


55 deg C

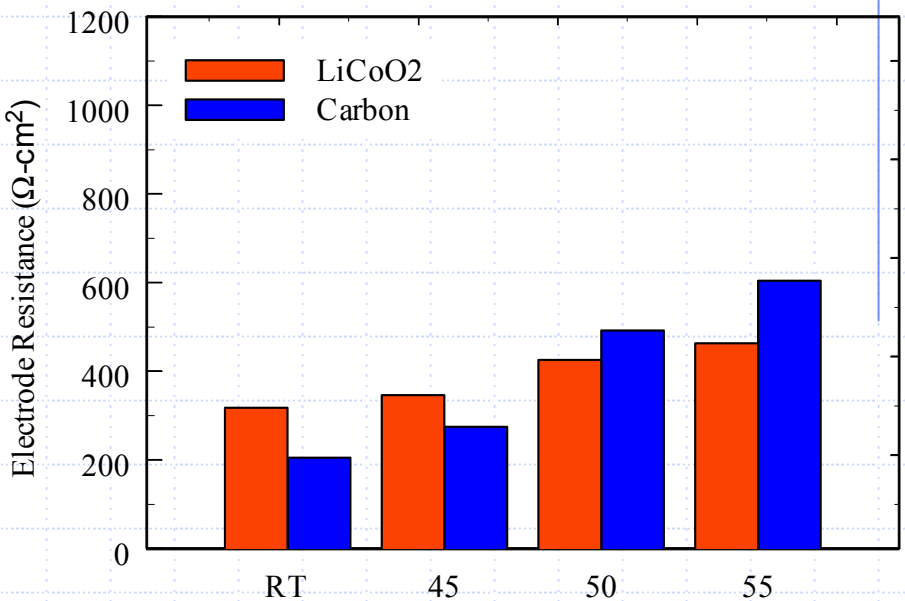
Variation of Cell Impedance with Cycling



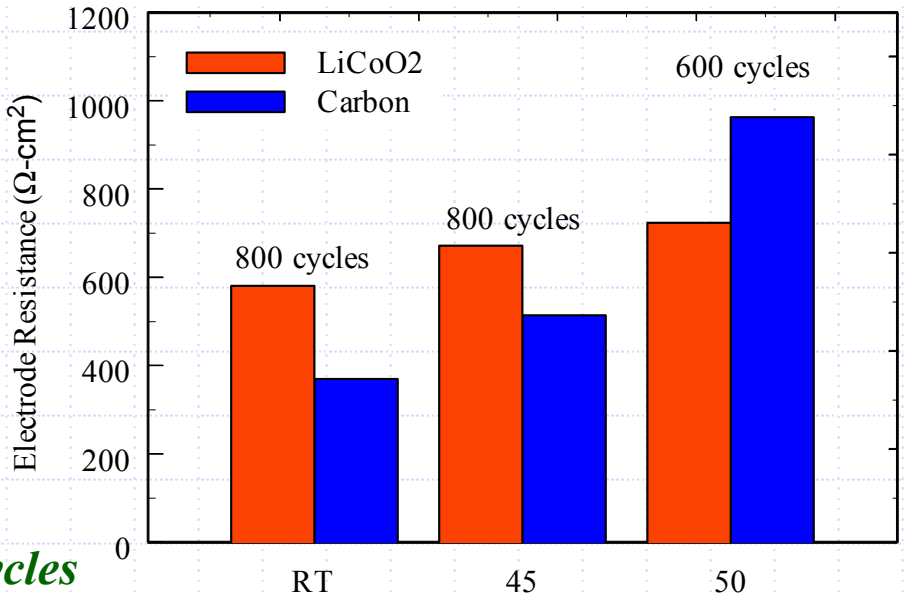
Comparison of Electrode Resistances



150 Cycles



300 Cycles



800 Cycles

Specific Capacity of Positive and Negative Electrodes at Various Cycles and Temperature

Temperature	Cycle Number	Specific Capacity (mAh/g)	
		$LiCoO_2$	Carbon
Fresh		148.132	339.896
25°C	150	145.61	334.03
	300	141.07	325.04
	800	122.14	271.10
45°C	150	143.74	332.84
	300	139.26	325.71
	800	118.43	264.56
50°C	150	143.28	331.20
	300	133.56	293.91
	600	94.05	202.53
55°C	150	142.84	328.90
	300	131.13	286.92

Possible Reasons for Rapid Capacity Fade at Elevated Temperatures

- The SEI layer formed on a graphite electrode changes in both morphology and chemical composition during cycling at elevated temperature.
- The R-OCO_2Li phase is not stable on the surface and decomposes readily when cycled at elevated temperatures that creates a more porous SEI layer and also partially exposes the graphite surface, causing loss of charge on continued cycling.
- The LiF content on electrode surface increases with increasing storage temperature mainly due to decomposition of the electrolyte salt.
- SEI and electrolyte (both solvents and salt) decomposition have a more significant influence than redox reactions on the electrochemical performance of electrode materials at elevated temperatures.

Capacity Fade Balance

$$Q = Q_1 + Q_2 + Q_3$$

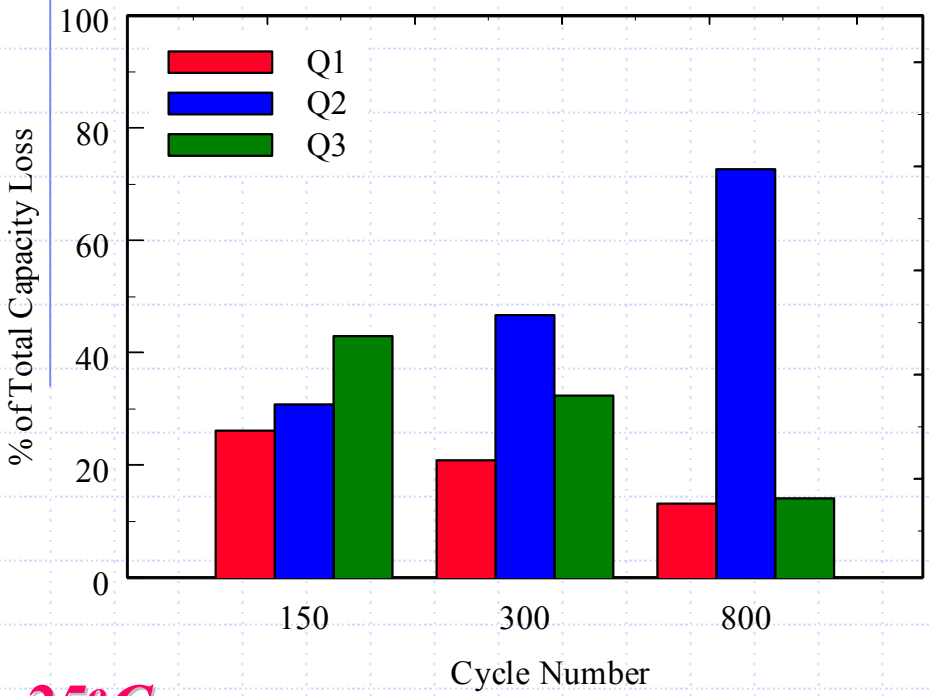
Q: Total Capacity Loss

- **Q_1:** Capacity Fade due to rate capability loss
  - Difference in capacity between C/9 and C/2 rate discharges.
- **Q_2:** Capacity Fade due to loss of secondary active material ($LiCoO_2$ and Carbon)
  - Measurement done on T-cells
- **Q_3:** Capacity Fade due to loss of primary active material (Li^+) and other losses.

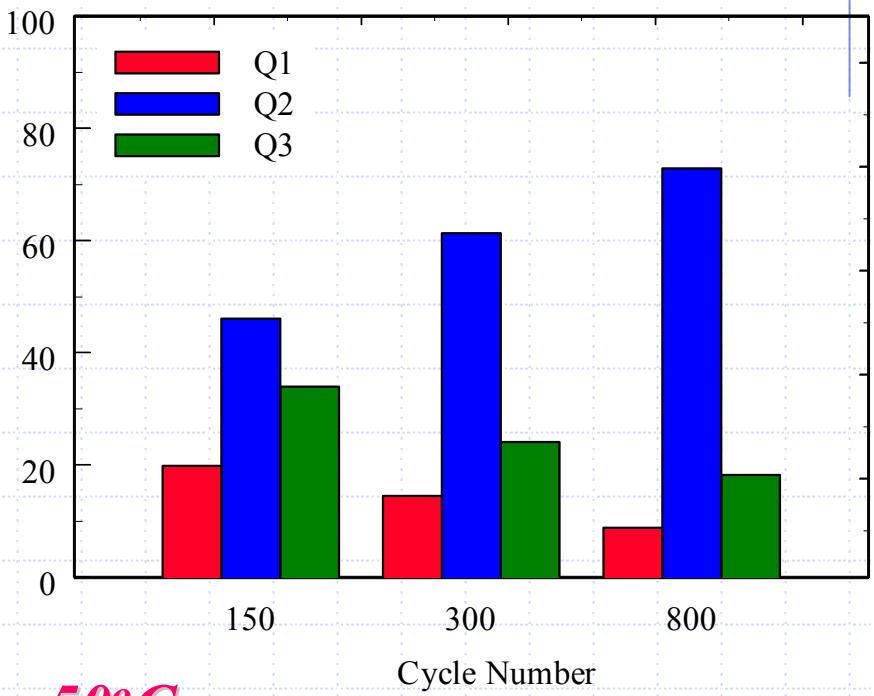
Capacity Fade - Quantified

Temperature	Cycle Number	Total Capacity Loss	Resistance Loss	Secondary Active Material Loss	Primary Active Material and Other Losses
		Q (mAh)	Q_1(mAh)	Q_2(mAh)	Q_3(mAh)
25°C	150	107	28	33	46
	300	182	38	85	59
	800	539	71	392	76
45°C	150	125	27	40	58
	300	209	33	81	95
50°C	150	141	28	65	48
	300	427	62	262	103
	600	1074	95	783	196
55°C	150	168	29	63	76
	300	481	81	302	98

Capacity Fade - Quantified



25°C



50°C

Q_1: Rate Capability Losses
Q_2: Secondary Active Material Losses
Q_3: Primary Active Material Losses

Modeling of Capacity Fade

- Diffusion Model (Empirical Approach)
- First Principles Model

Simplified Diffusion Model

- Concentration variations in the solution phase can be neglected for low to medium discharge currents.
- Solid phase potential drop is negligible as compared to kinetic and concentration over-potentials.
- Eliminating the above two results in a simple diffusion model which can be used to simulate the performance of the Li-ion Battery.
- Model considers Li^+ reaction at carbon/$LiCoO_2$ particle interface and subsequent transport in these materials.

Governing Equations: Diffusion Model

Fickian diffusion in spherical coordinates in carbon and $LiCoO_2$

$$\frac{\partial c_{Li}}{\partial t} = \frac{D_{Li}^{eff}}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c_{Li}}{\partial r} \right)$$

Initial Condition

$$t = 0,\ c_{Li} = c_{Li}^{o}$$

Boundary Conditions

$$r = 0, \quad \frac{\partial c_{Li}}{\partial r} = 0$$

$$r = R_p, \quad -D_{Li}^{eff} \frac{\partial c_{Li}}{\partial \hat{r}} = rate_{Li} = \frac{j'}{F}$$

Electrode Reaction Rates

Lithium intercalation/deintercalation reaction:

$$j'_{Li,in} = j_{o,1}\left\{e^{\frac{\alpha_{a1}F}{RT}\left[\Phi_P - U_P^{ref} - jR_f\right]} - e^{\frac{-\alpha_{c1}F}{RT}\left[\Phi_P - U_P^{ref} - jR_f\right]}\right\}$$

$$j'_{Li,de} = j_{o,2}\left\{e^{\frac{\alpha_{a2}F}{RT}\left[\Phi_N - U_N^{ref} - jR_f\right]} - e^{\frac{-\alpha_{c2}F}{RT}\left[\Phi_N - U_N^{ref} - jR_f\right]}\right\}$$

$$V = \Phi_P - \Phi_N$$

R_f refer to total resistance that includes ohmic R_Ω and polarization R_P resistances. ($R_f = R_\Omega + R_P$)

Concentration dependent exchange current density:

$$j_{o,j} = k_j\left(c_{Li,j}^{\max} - c_{Li,j}^{s}\right)^{\alpha_{a,j}}\left(c_{Li,j}^{s}\right)^{\alpha_{c,j}},\ j = 1,2$$

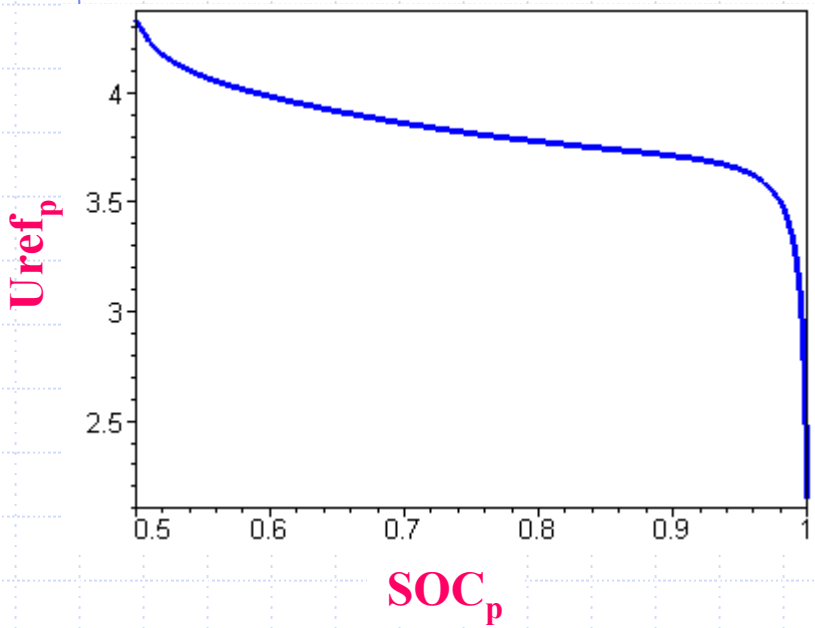
Description of Symbols & Parameters

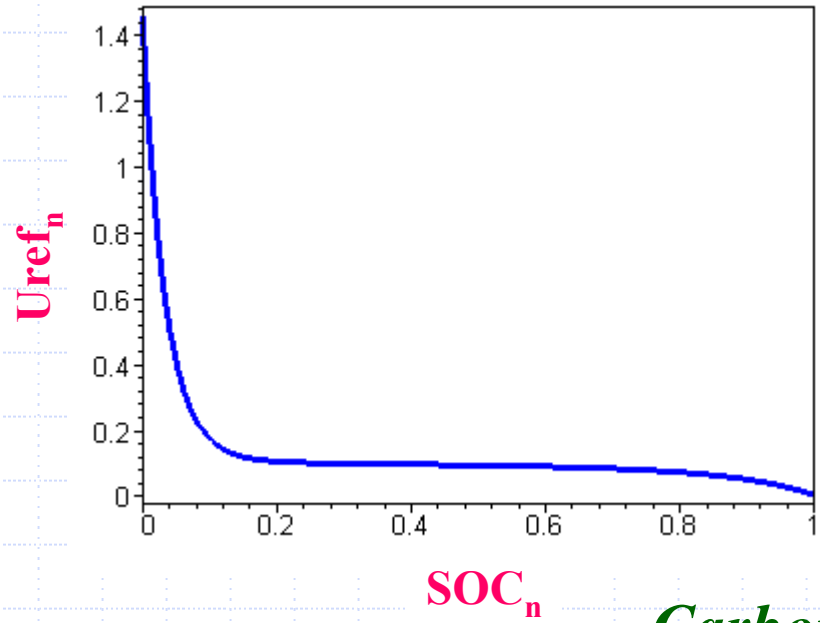
c	Lithium ion concentration, mol/m^3
D^{eff}	Effective diffusion coefficient, m^2/sec
R_p	Radius of the particle, m
$j^{`}_{Li,in}$	Local intercalation current density due to charge transfer, A/m^2
$j^{`}_{Li,de}$	Local de-intercalation current density due to charge transfer, A/m^2
$i_{o,j}$, j_{oj}	Exchange current densities, A/m^2
α_a	Anodic transfer coefficient
α_c	Cathodic transfer coefficient
ϕ	Electrode Potential (V)
U_{ref}	Reference potential of $+^{ve}$ and $-^{ve}$ electrodes (V)
R_f	Film Resistance (Ω-m^2)
i_o	Exchange current density at an interface, A/m^2
a_n	Specific surface area available for side reaction (m^{-1})
E^o	Equilibrium potential for side reaction (V)

$U_{ref} \longrightarrow$ A Function of SOC

$$U_n^{ref} = fn(SOC_n)$$

$LiCoO_2$





Carbon

$$U_p^{ref} = fn(SOC_P)$$

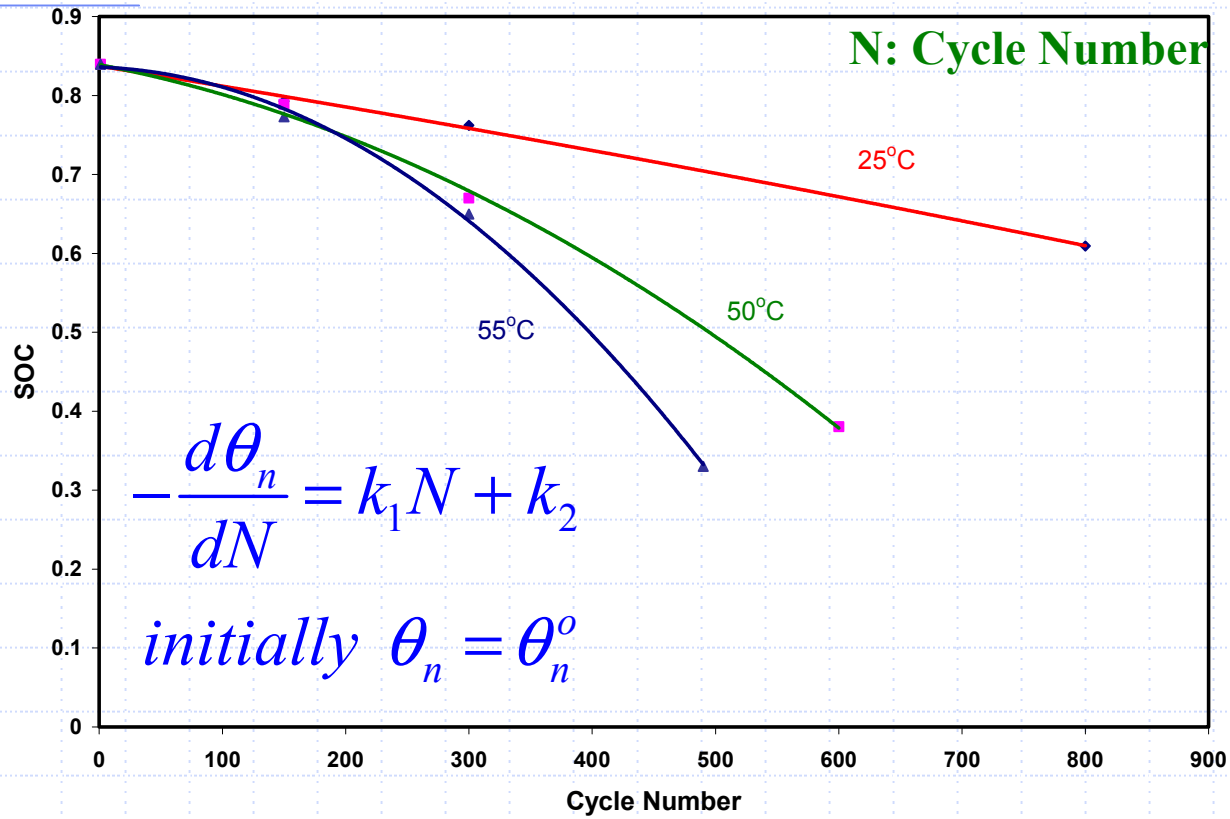
Parameters Considered for Diffusion Model

- **State of Charge of the electrode limited by capacity**
  - To account for capacity loss due to primary and secondary active materials.
- **Solid Phase Diffusion Coefficient**
  - To account for capacity loss due to rate capability.
- **Film Resistance**
  - To account for the drop in cell voltage due to increase in ohmic resistance and polarization losses.

Incorporation of Q_2 and Q_3 in Diffusion Model

- Calculate SOC of the negative electrode based on the capacity loss ($Q_2 + Q_3$).
- Develop a correlation for variation of SOC of negative electrode with cycle number.
- Using this capacity fade due to active material losses could be incorporated in the diffusion model.

Variation of SOC with Cycling



$$-\frac{d\theta_n}{dN} = k_1 N + k_2$$

$$initially \;\; \theta_n = \theta_n^o$$

k_1 accounts for capacity losses that increase rapidly under adverse cycling conditions such as high temperature.

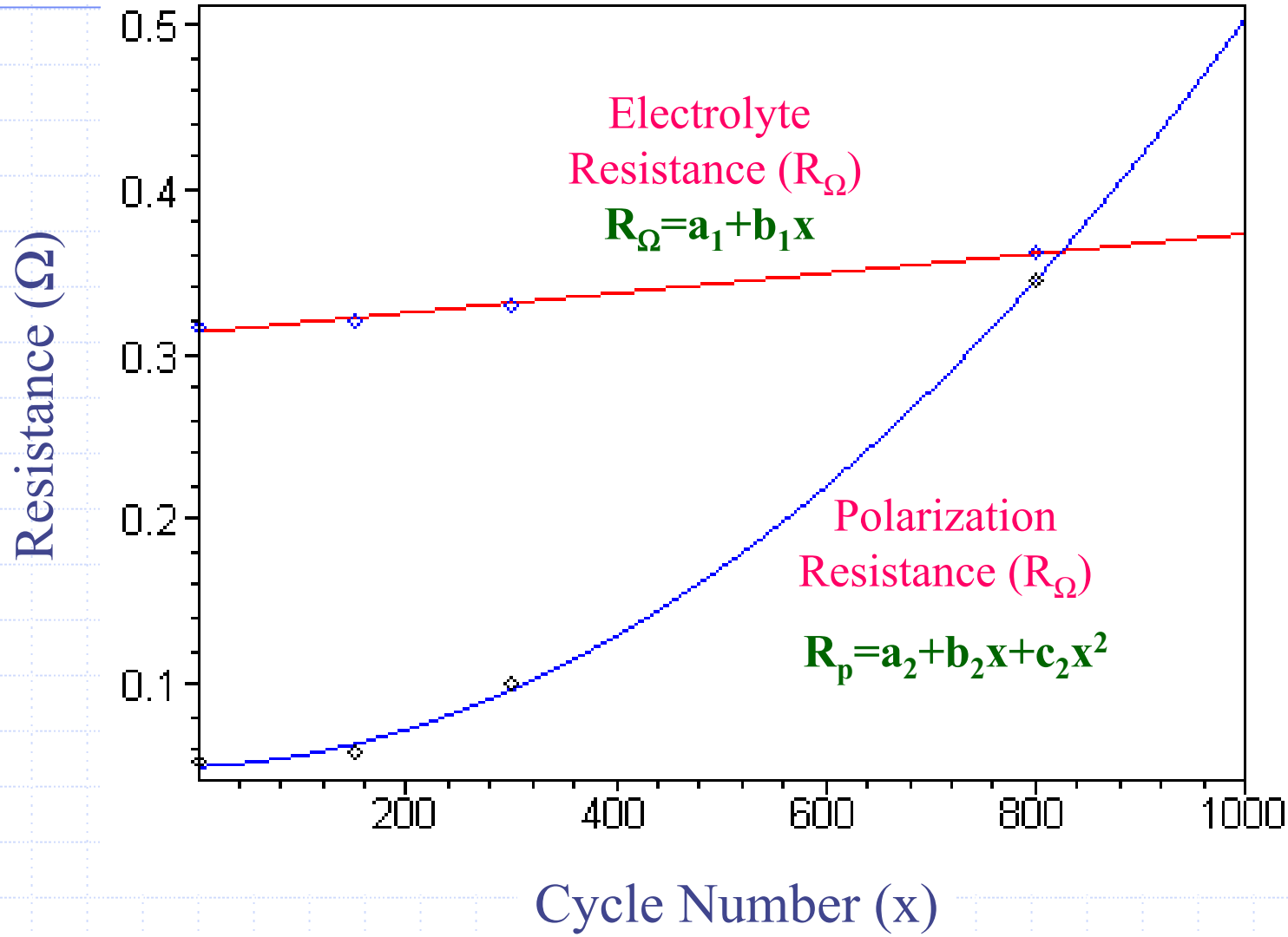
k_2 is a factor to account for capacity loss under usual conditions of charge and discharge.

Variation of k_1 and k_2 with Temperature

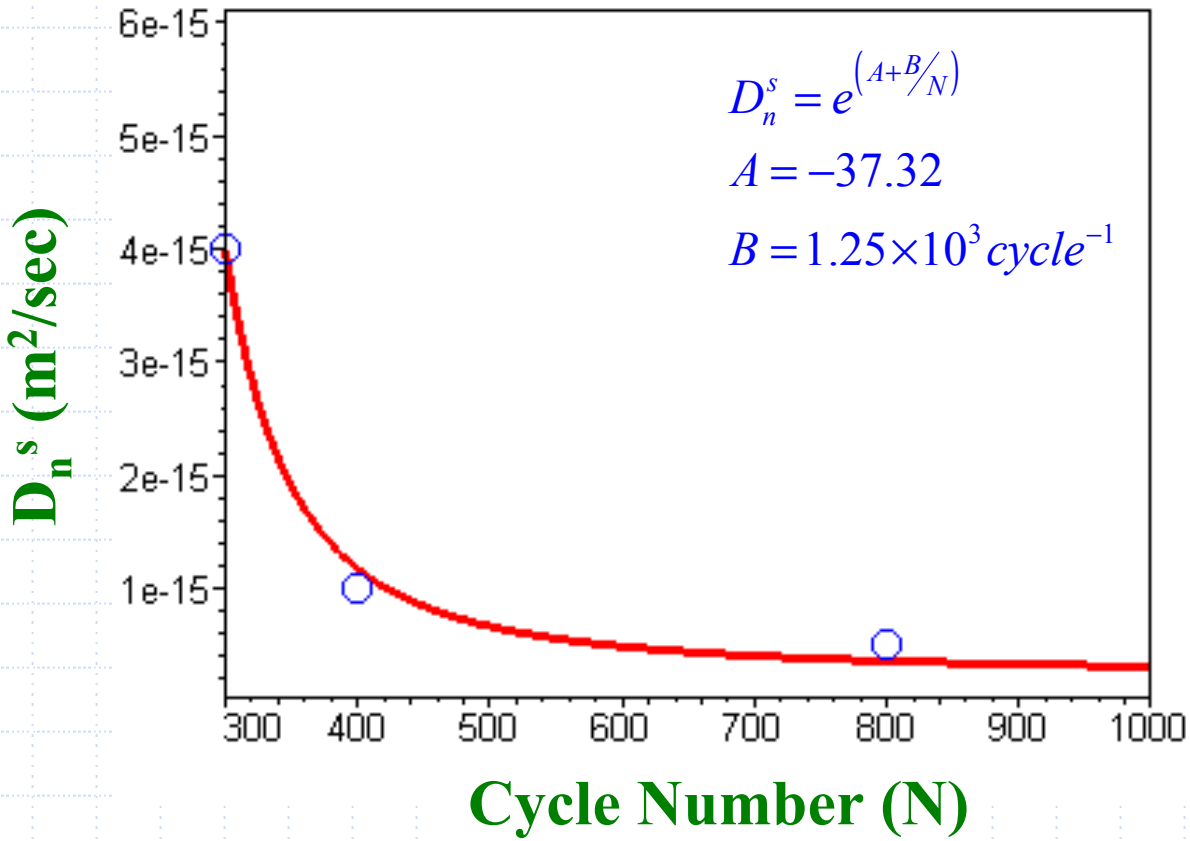
Cycling Temperature	k_1 $(Cycle)^{-2}$	k_2 $(Cycle)^{-1}$
25°C	8.5×10^{-8}	2.5×10^{-4}
50°C	1.6×10^{-6}	2.9×10^{-4}
55°C	0.4×10^{-5}	2.1×10^{-4}

Change of R_Ω and R_p with Cycling

(from Impedance Measurement)



Variation of D_n^s with Cycling (at RT)

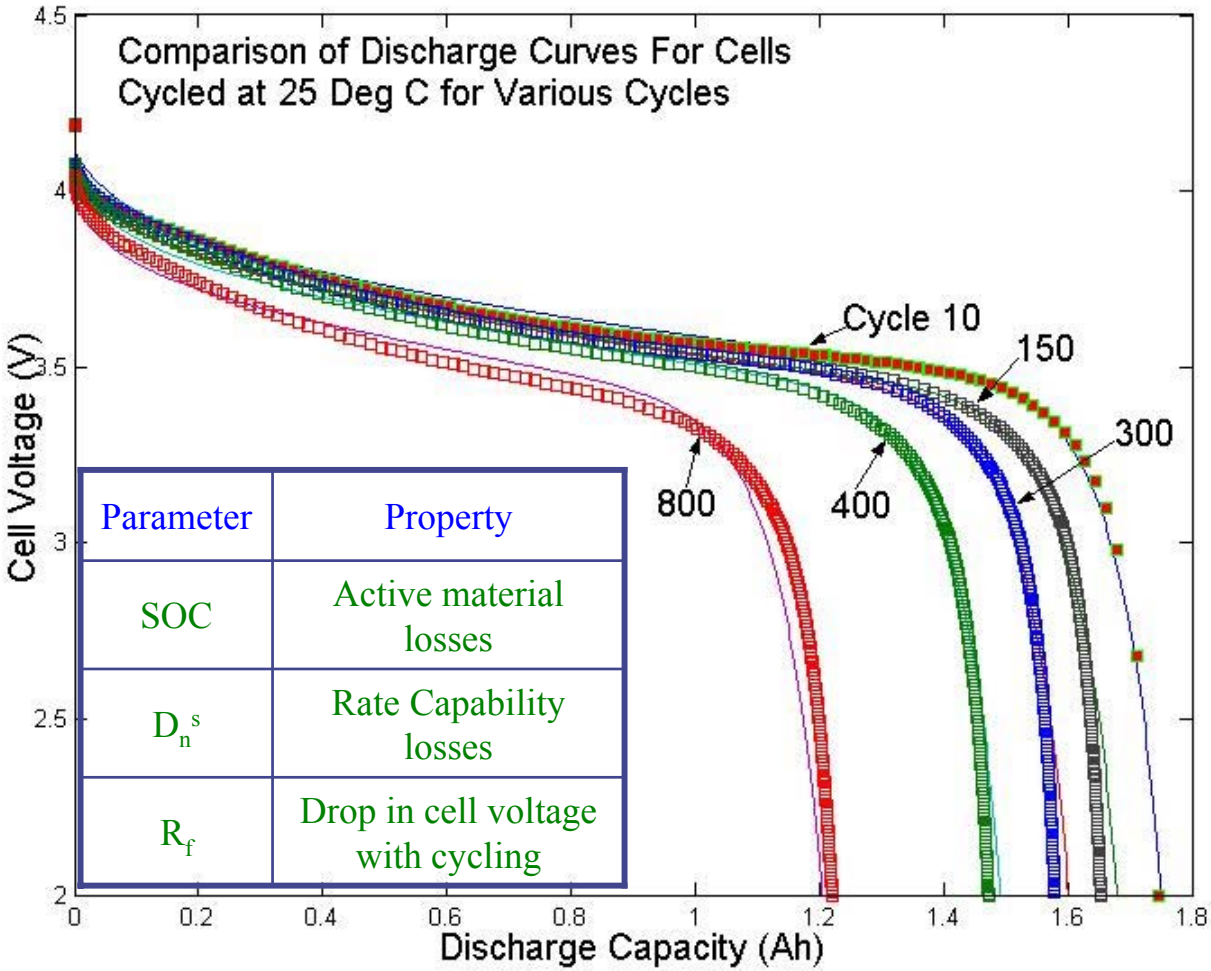


A and B are constants that depend on temperature.

How Model Works?

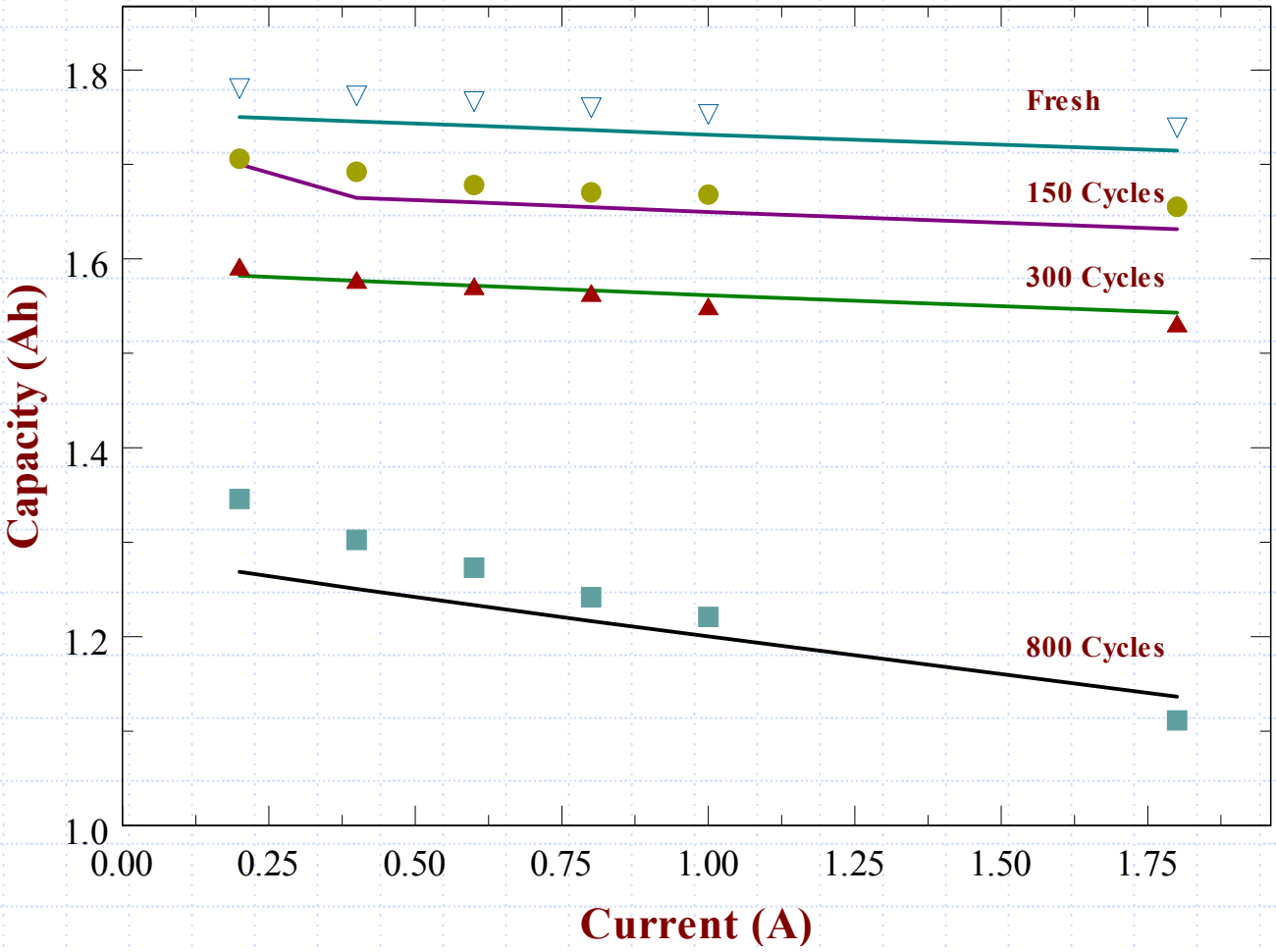
- Diffusion Model (Empirical Approach)
  - The model will need the cycle number for simulation.
  - The model first considers appropriate corrections for capacity fade parameters namely, SOC, diffusion coefficient and film resistance.
  - The model will then solve for solid phase lithium concentrations in both electrodes based on the spherical diffusion equation.
  - The model will then solve for potentials of positive and negative electrodes to get the cell voltage and hence the discharge curve for the required cycle number.

Comparison of Diffusion Model and RT Experimental Data



Parameter	Property
SOC	Active material losses
D_n^s	Rate Capability losses
R_f	Drop in cell voltage with cycling

Comparison of Diffusion Model and RT Experimental Data for Utilization (Rate Capability)



Capacity Fade Analysis

(First Principle Approach)

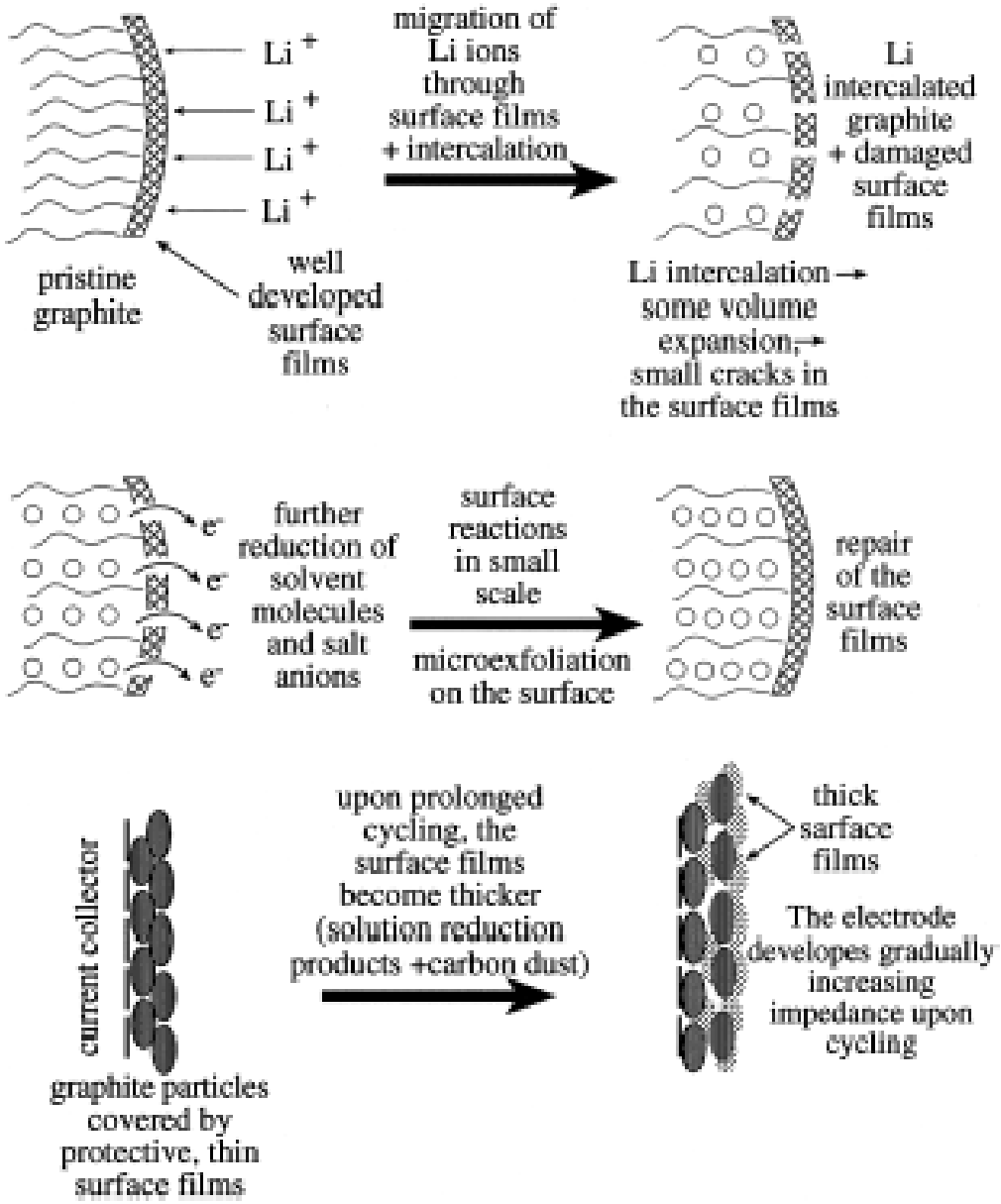
- Consideration of the electrode material limited by capacity (Negative Electrode).
- Capacity Fade factors for 18650 cells.
  - SOC of electrode material (Active Material Losses)
  - Film Resistance (Drop in the cell voltage with cycling)
  - Diffusion Coefficient (Rate Capability Losses)
- Model for active material losses.
  - Assumption of a suitable solvent reduction reaction to model the active material loss during charging.
  - Inclusion of the proposed side reaction in the diffusion model to account for the capacity loss due to active material.

Continuous Film Formation

(The Side Reaction for Capacity fade Model)

- During charging Li-ions will be intercalated into graphite.
- When Li-ion is inserted into the graphite particles, their volume increases (due to an increase in the space between the graphene planes).
- Hence the surface films on the edge planes, through which Li-ions are inserted into the graphite, are stretched.
- Since the surface films are usually comprised of Li salts, their flexibility is limited.
- Thus, they may be damaged during Li-ion insertion (due to the increase in the particle's volume), and thus the passivation is limited.
- This allows continuous small-scale reactions between the lithiated carbon and solution species, i.e., the breakdown and repair of the surface films that increase their thickness and hence the electrodes impedance upon cycling.

Fading mechanisms of graphite electrodes in any "good" solutions



Side Reaction to be assumed….

- Several possible reaction schemes available in the literature for the reactions between the lithiated carbons and solution species.
- The nature of reaction depends upon the type of solvent mixture used in the battery electrolyte and the possible contaminants in the system that includes gases like CO_2, O_2 and N_2.
- The simplest reaction scheme to be considered for modeling capacity loss is the two-electron reduction of EC or PC followed by formation of Li_2CO_3, which is the surface film over the surface of negative electrode.

Inclusion of Side Reaction in the Model

$$Li^{+} + e^{-} + \Theta_n \rightleftharpoons Li - \Theta_n$$

(Intercalation reaction)

$$(CH_2O)_2CO + 2e^{-} + 2Li^{+} \rightarrow Li_2CO_3 \downarrow + C_2H_4 \uparrow$$

(Side Reaction)

$$I = i_1 + i_2$$

I: Total applied current density for charging the cell

$$i_1 = i_{o,1}\left\{ e^{\frac{\alpha_{a1}F}{RT}\left[\Phi_N - U_N^{ref} - IR_f\right]} - e^{\frac{-\alpha_{c1}F}{RT}\left[\Phi_N - U_N^{ref} - IR_f\right]} \right\}$$

$$i_2 = i_{o,2}\left(e^{\frac{-\alpha_{c2}F}{RT}\left[\Phi_N - E^{o} - IR_f\right]} \right)$$

Tafel Kinetics for Side Reaction

SOC Correction based on extent of Side Reaction

- The number of moles of Li-ions getting lost as a result of side reaction could be estimated by:

$$C_{Li^+,2} = \frac{a_n \sum i_2 t}{F} moles/m^3$$

- The corrected SOC for any cycle number can be found out by:

$$\theta_{corr} = \theta_n^o - \theta_{lost}$$

$$\theta_{lost} = \frac{C_{Li^+,2}}{C_{\max,n}}$$

How Model Works?

- First Principles Model
  - The model will need the cycle number for simulation.
  - The model considers the side reaction occur only during charging.
  - At the end of charge step, the model solves for total current utilized for the side reaction.
  - This is followed by calculating moles of lithium lost as a result of side reaction and hence the SOC correction based on lithium lost.
  - The model will then run for second charge cycle with updated SOC and the loop continues to required cycle number.
  - Since the assumption is that side reaction takes place only during charging, it will be enough to run the model for discharge, only for the required cycle number.
  - Film resistance correction will be based on the thickness of the film formed as a result of side reaction.
  - Diffusion coefficient correction has to be done to account for rate capability losses.

Conclusions – (Performance Studies)

- Capacity fade increases with increase in temperature.
- Negative Electrode (Carbon)
  - The resistance increases with cycling due to continuous film formation.
  - With increase in temperature, anode resistance increases than that of cathode.
  - Rate of film formation of anode increases with temperature.
  - Lithiation Capacity decreases with cycling.
- Positive electrode ($LiCoO_2$)
  - Resistance increases with cycling and remains higher than negative electrode when cycled at 25°C.
  - Lithiation capacity decreases with cycling and is comparable to that of anode.

Conclusions – (Capacity Fade Model)

- A diffusion model was developed to simulate the discharge curves of Li-ion cell.
- Empirical correlations have been developed for variation of SOC of Li-ion cell with continuous cycling.
- Active material losses have been accounted through the variation of negative electrode SOC in the diffusion model.
- Rate capability losses and Polarization resistance increase have been accounted through varying the diffusion coefficient and exchange current density respectively.
- Development of a Capacity Fade model based on first principles is in progress.

Acknowledgements

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Hybrid Advanced Power Sources

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Development of the Lithium Ion Battery for Satellite

Takeshi Kiyokawa, Hiroyuki Yamazaki,
Masayoshi Goto, and Toshio Gonai,

MITSUBISHI ELECTRIC CORPORATION

Development of the Lithium Ion Battery for Satellite

- Introduction
- Developed Battery
- Electrical Design
- Thermal Design
- Mechanical Design
- Qualification Test
- Conclusion
- Battery Line-up

Introduction

- Ni-Cd or Ni-H2 battery has been used for Space.
  Recently, Lithium Ion battery(LIB) is being developed for Electric vehicle because of
  - -High energy density
  - -High discharge voltage
  - -High efficiency of charge/discharge
- We have been developing the Lithium Ion Battery for Space use to reduce the weight and to save cost.
- This LIB consists of Battery cell and Shunt circuit to protect the over-voltage and Bypass switch.

Introduction

Commercial Use for Ground → **Development Phase for Space** → **Operational Phase for Space**

for personal computer and for handy phone
0.5 - 1.0 Ah

for Electric Vehicle

To improve
-Hermetic Seal
-Light weight:>100wh/kg as battery

To improve characteristics
-Mechanical (vibration,shock)
-Electrical (large capacity >50Ah)
-Thermal (Heat generation/dissipation)
-Radiation

for GEO satellite
-15years,1320 cycles

for LEO satellite
-7years,40,000 cycles

for Space craft

Developed Battery

Battry characteristics

Battery construction:This battery are composed of 10 cells connected in series.

Battery Characteristics

Capacity	:3600（WHr）
Voltage	:32.4-40(V）
Cell Capacity	:100(AH）
Quantity of Cells	:10 cells in series

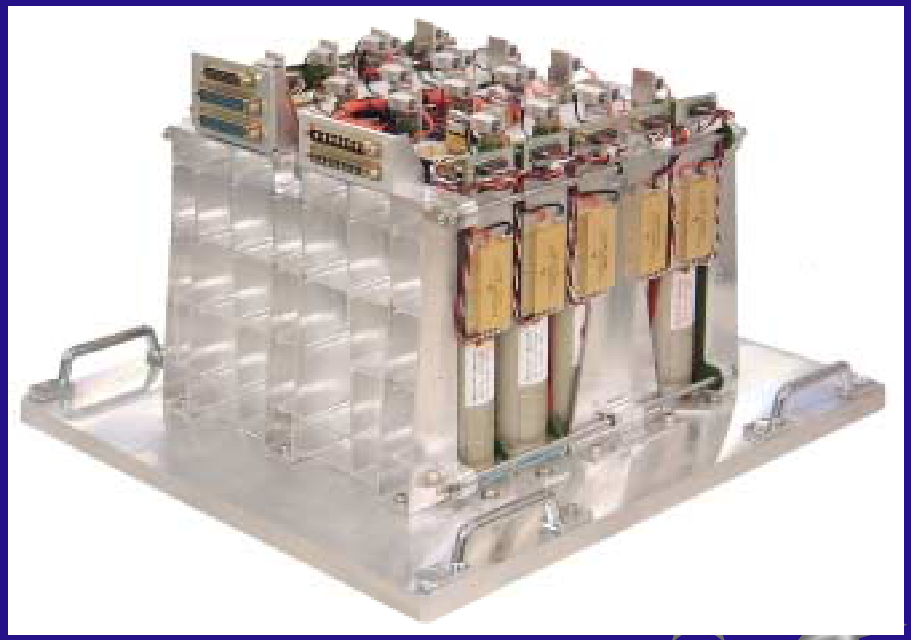
Width	:328 mm
Length	:299
Height	:352
Mass	:35 kg
Specific Energy	:103 WHr/kg

Temperature

-10deg to +35deg C for QT

0deg to +25deg C for AT

Life 15years(GEO)



LIBM100A10SS for QT

Developed Battery

Cell characteristics

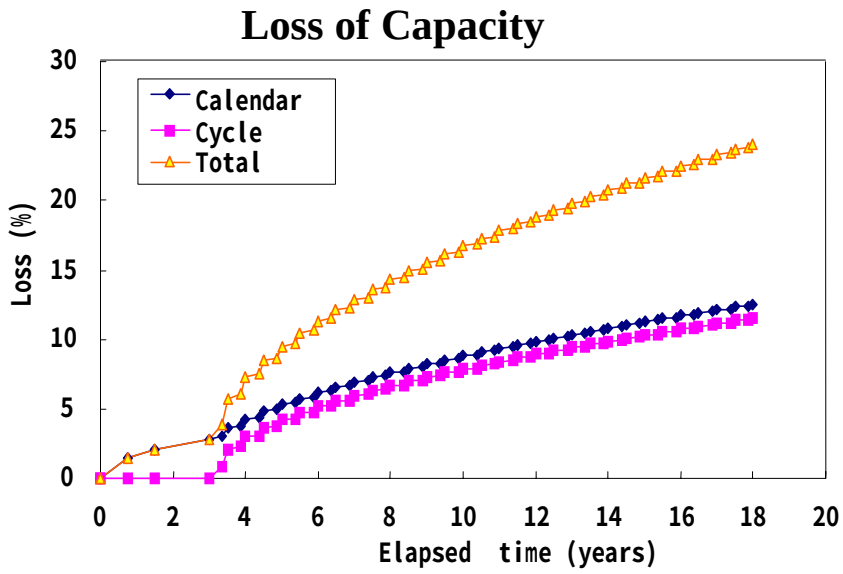
- Shape : Elliptic cylindrical
- Dimensions (mm) : H208, W130, T50
  (Include terminal: H:221.5)
- Mass : 2.8kg
- Rated capacity : 100Ah (110Ah nominal)
- Minimum discharge voltage: 2.75V
- Nominal discharge voltage: 3.6V
- Specific energy : 141Wh/kg @ nominal capacity
- Case material : Aluminum alloy
- Positive material : Lithium cobalt dioxide($LiCoO_2$)
- Negative material : Carbon materials
- Separator : Micro porous plastic film
- Electrolyte : Li salt dissolved in mixture of alkyl carbonate solvents

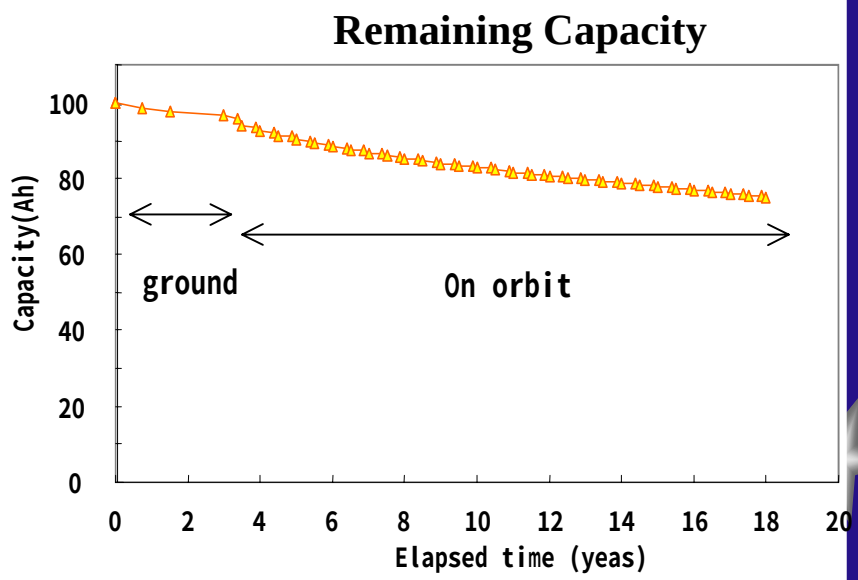
Electrical Design

Capacity

Provided Battery capacity (Cb)
Cb = (Pr x Te) / (DOD x Fl)+Margin
Pr: Power of System requirement (w)
Te: Eclipse Time (hr)
Fl: degradation Factor between EOL/BOL

Capacity degradation:22%
Temperature: 10 deg C at On orbit
Maximum DOD:70%
Average DOD: 56%
SOC: 100%
Life cycle: 15years





Electrical Design

Capacity loss

Capacity loss of a Li-ion cell

Calendar capacity loss	Cycle capacity loss
Consumption of Li-ions in a negative electrode	Increase in impedance in a positive electrode
Chemical Reaction Reaction between the Li-ions in the carbon and the electrolyte *Capacity loss* = k_f*(time)$^{1/2}$	**Mechanical Reaction** Degradation of electron paths caused by change in volume of active material particles *Capacity loss* = k_c*(cycle)$^{1/2}$

Electrical Design

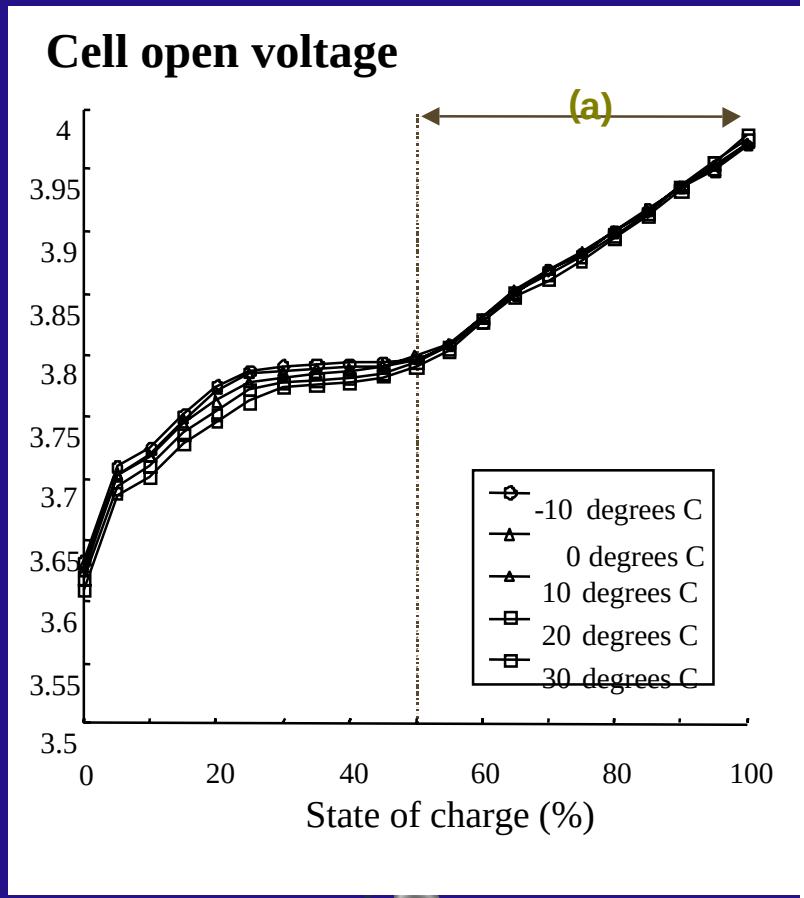
Battery Voltage

The estimated battery voltage between the output terminals of the battery module is derived from the following equation

VB = [Vcellopen - (Rcell+Rw) x I] x N

with

- Vcellopen: Cell open circuit voltage (V)
- Rcell : Cell internal DC impedance (ohm)
- Rw: BusBar, Wire, Contact resistance (ohm)
- I: Battery Current (+;charge / -;discharge)
- N: Quantity of cells



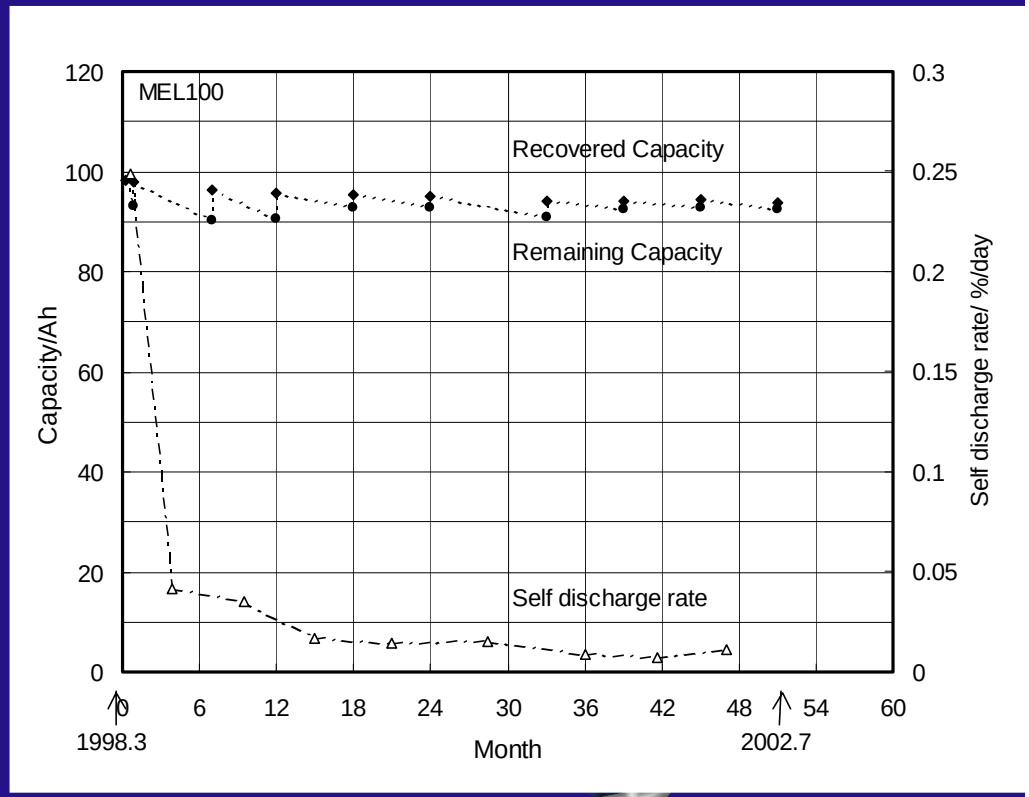
Electrical Design

Power saving

- By ratio of charge/discharge energy ratio over well 95%
  -this energy ratio depends on DC impedance

- Small self discharge current less than 0.05%/day
  -the characteristics depend on cell characteristics

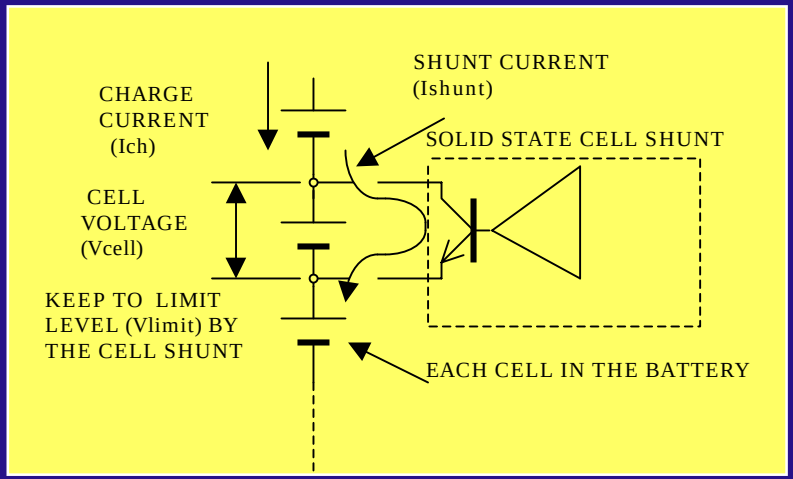
Charged storage Test

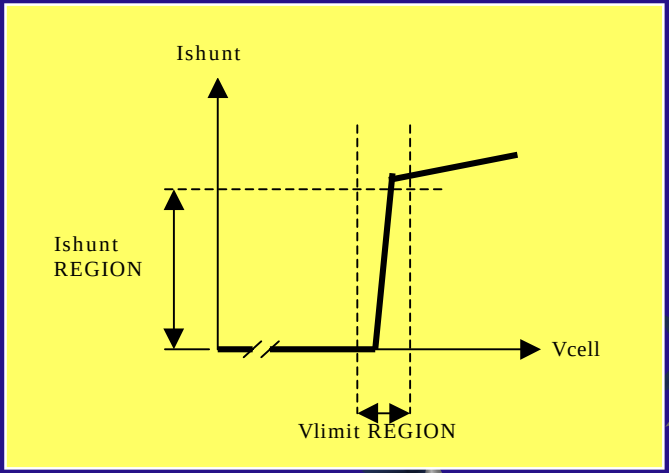


Electrical Design

Protection -over charge-

When a battery cell voltage exceeds detection level of over voltage during charging phase, the shunt circuit keeps the cell voltage to detection level by bypassing the charge current into shunt circuit. This circuit is connected to each cell in battery independently.





Electrical Design

The shunt circuit

The shunt circuit is not only to protect the over charge but also
-to equalize the each cell voltage when the each cell voltage may be drifted by leak current
-to be charging the connected battery cell to bypass the charge current when open failure on cell occurs.

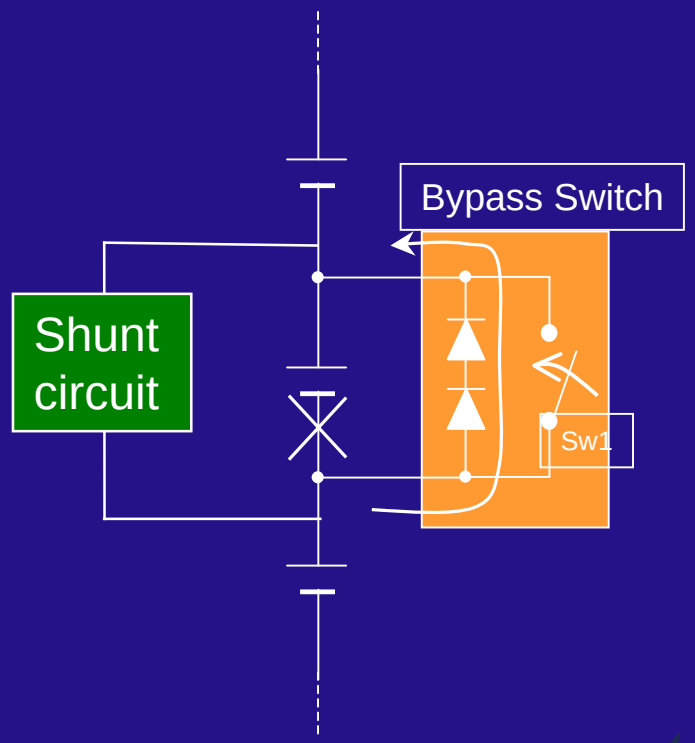
- Dimensions (Case Size) ：70×40×6.5mm
- Foot Print ：28cm²
- Mass ：40g

Electrical Design

One Cell Fail operation

When one battery cell is failed as open mode, the Bypass Switch will activate to bypass the charge/discharge current out of cell in failure.

When the Bypass Switch detects cell failure, Sw1 is closed detecting discharge current of the parallel diode.
As cell in failure is shorted by the switch, the battery keep alive.



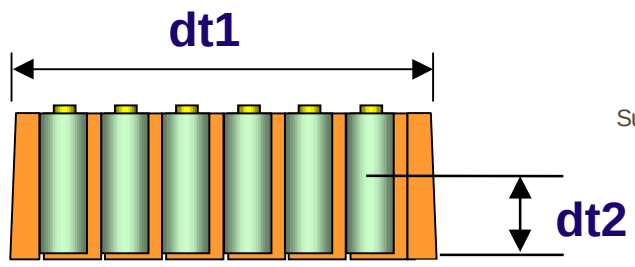
Connection of Bypass switch

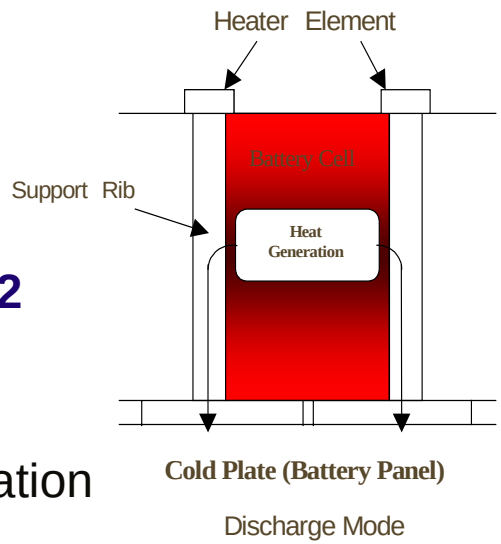
Thermal Design

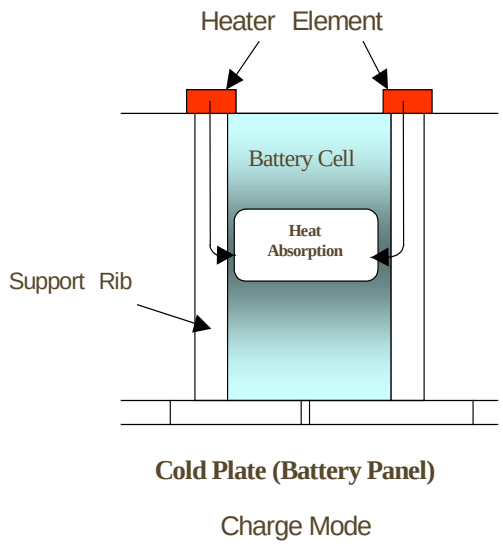
Excellent heat dissipation

and Thermal design of the battery, that the thermal gradient across the cells and across the cell and T-shape chassis shall be minimized, is performed by applying the T-shape chassis and elliptic-cylindrical cells. Because the combination realizes large connection area.

In case of GEO operation at LIBM100A10SS, The maximum thermal gradient deviation(dt1) is less than 4 degree C and temperature across (dt2)the cell and T-shape chassis plate is less than 10 degree C.







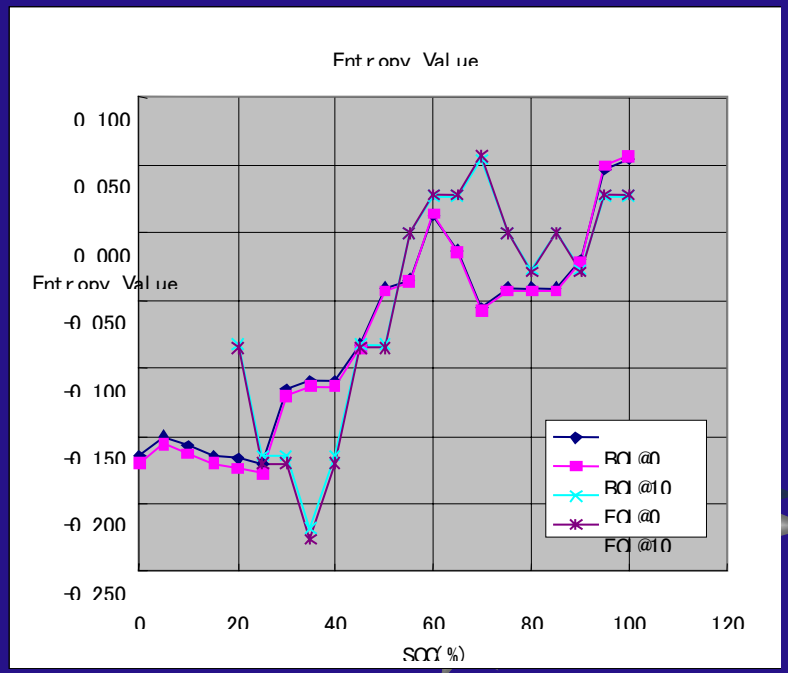
Battery heat pass and configuration

Thermal Design

Heat dissipation（P_{bat}）of battery

$$P_{bat}(w) = I^2 \cdot (\Sigma Rcell + \Sigma Rw) + I \cdot N \cdot Ke$$

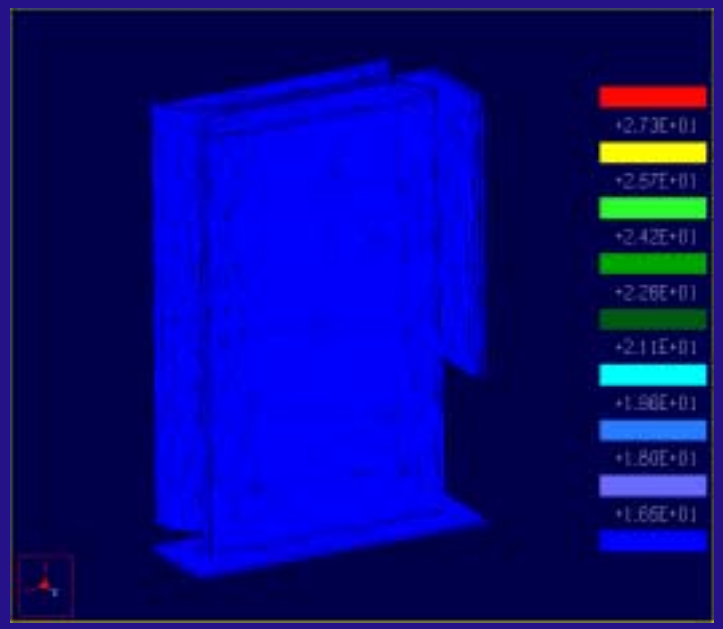
Rcell(Ω): Inherent Resistance of Cell
(1.25mΩ at BOL, 2.5mΩ at EOL in case of 100AH)
Rw (Ω) :Resistance of wire between Cells
(include lead wire)
Ke (W/I) :Entropy values
I (A) :Battery currentnt,
(+:Discharge, -:Charge current)
N :Quantity of cells

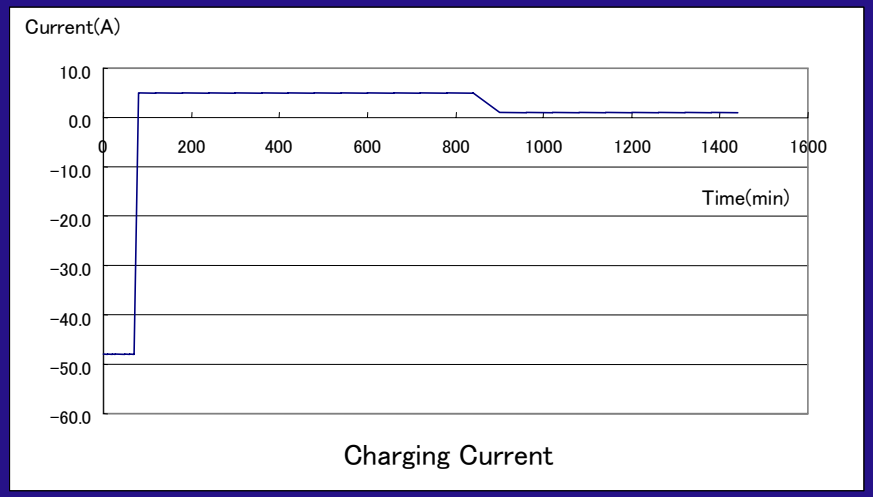


Thermal Design

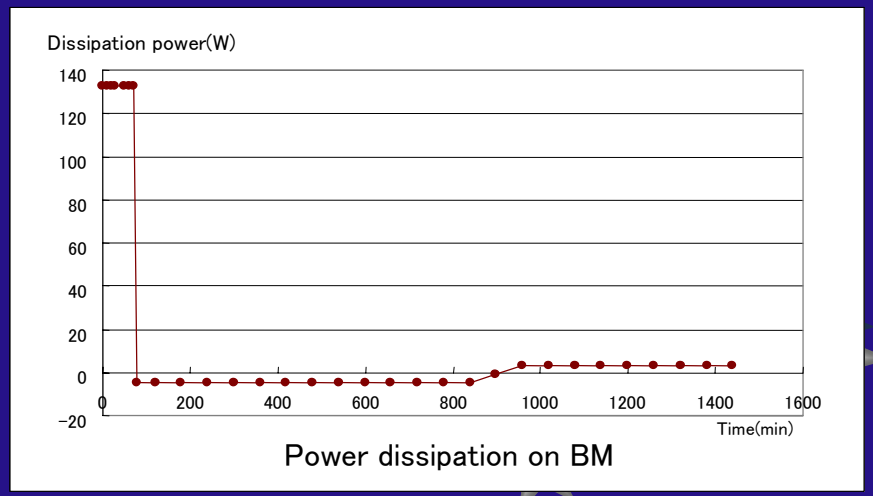
Heat generation profile on GEO

Max. temp.: 14 deg.C (dt) Cell Inside
: 4 deg.C (dt) Cell case





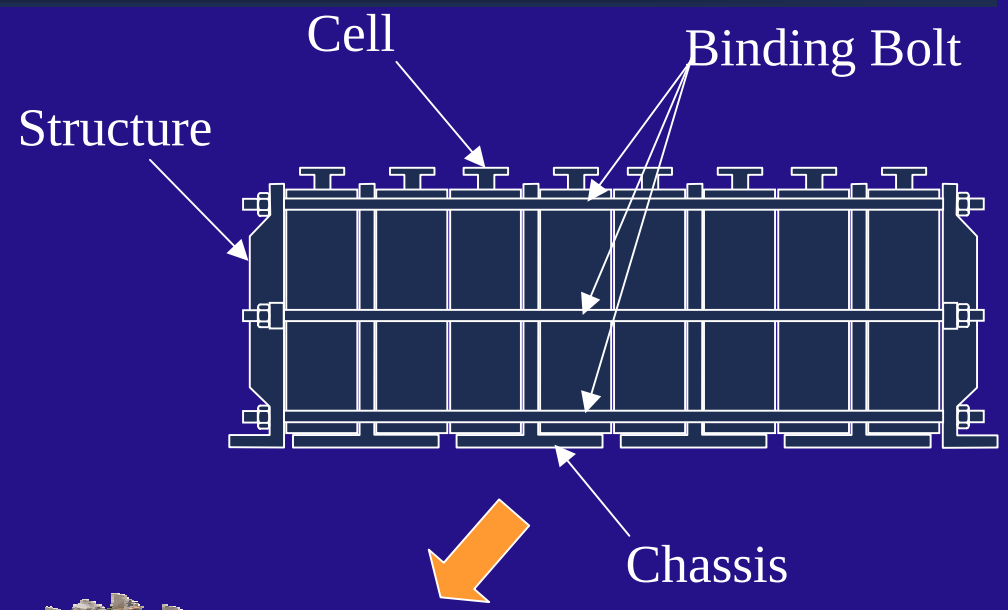
Charging Current

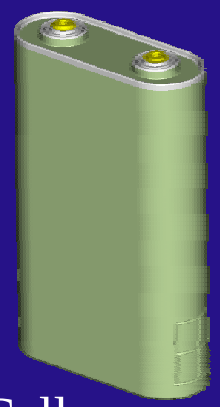


Power dissipation on BM

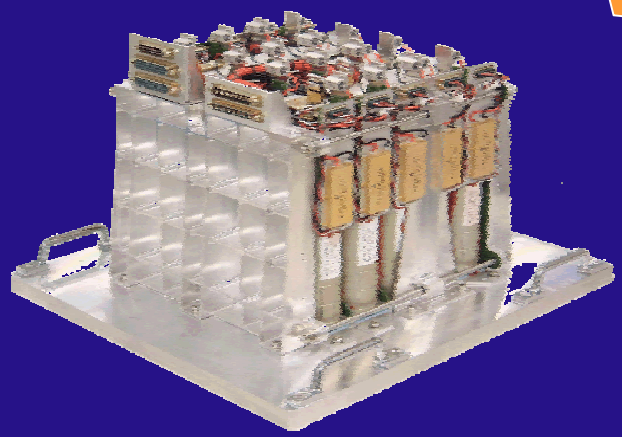
Mechanical Design

In case of LIBM100S10SS





Cell

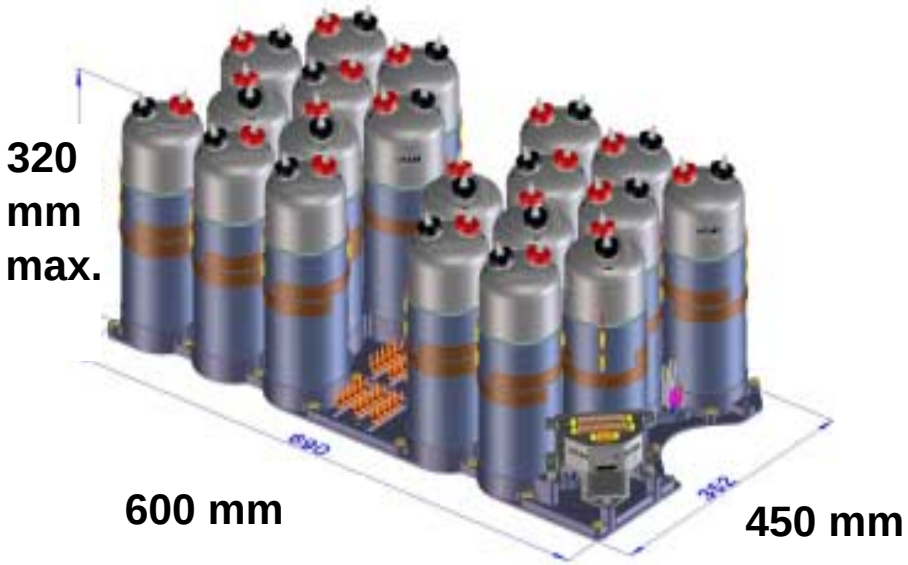


Mechanical Design

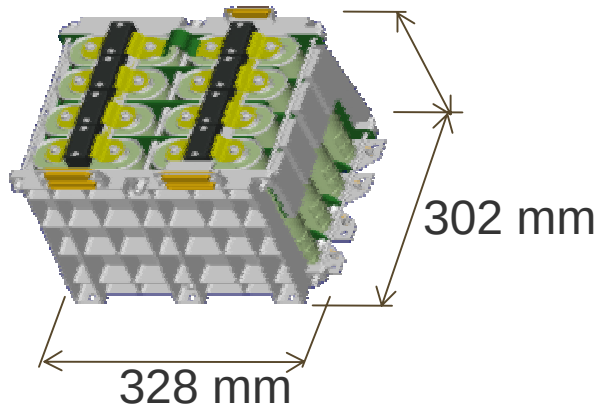
Light weight /Low cost: Apply Lithium Ion cells
-Half weight compared with NiH2
-Quarter volume compared with NiH2

Case study (3kwh case)

Constructions: { 112Ah x 20 cells } x 2 = 112Ah x 40 cells
Weight: { 59 kg } x 2 = 118 kg
Dimensions: { 450(W) x 600(L) x 320(H) mm } x 2
Foot print: 45 x 60 x 2 = 5400 cm2



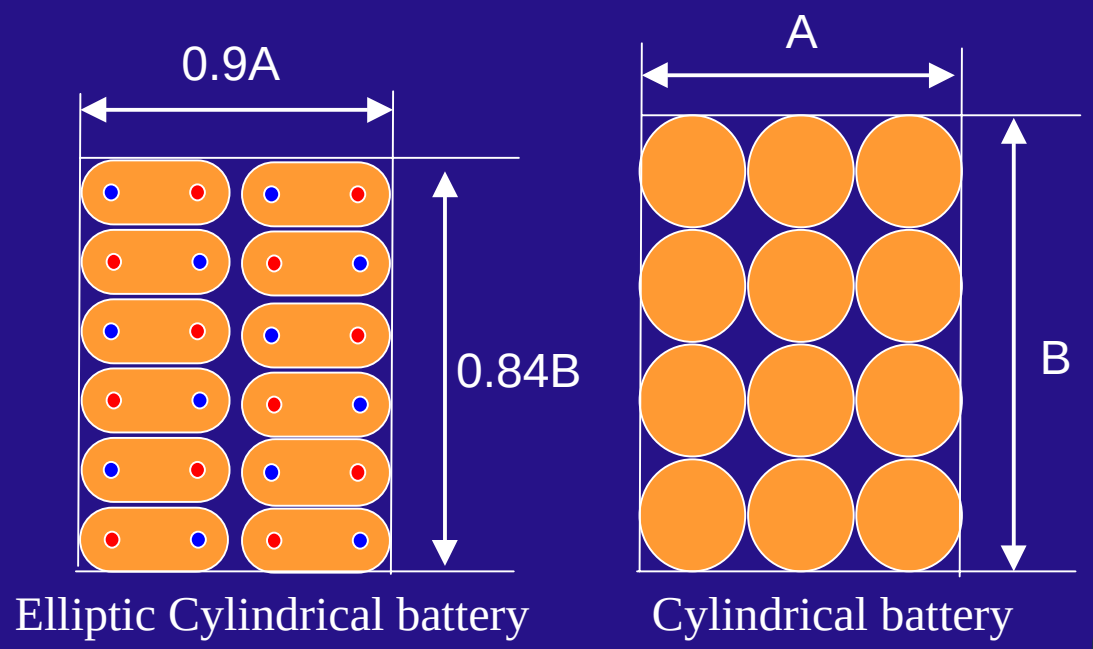
Constructions: { 100Ah x 8 cells } x 2 = 100Ah x 16 cells
Weight: { 28.3 kg } x 2 = 56.6 kg
Dimensions: { 328(W) x 302(L) x 246(H) mm } x 2
Foot print: 32.8 x 30.2 x 2 = 1982 cm2



Mechanical Design

Foot print

The foot print of elliptic cylindrical type is saved 0.75 times compared with cylindrical type



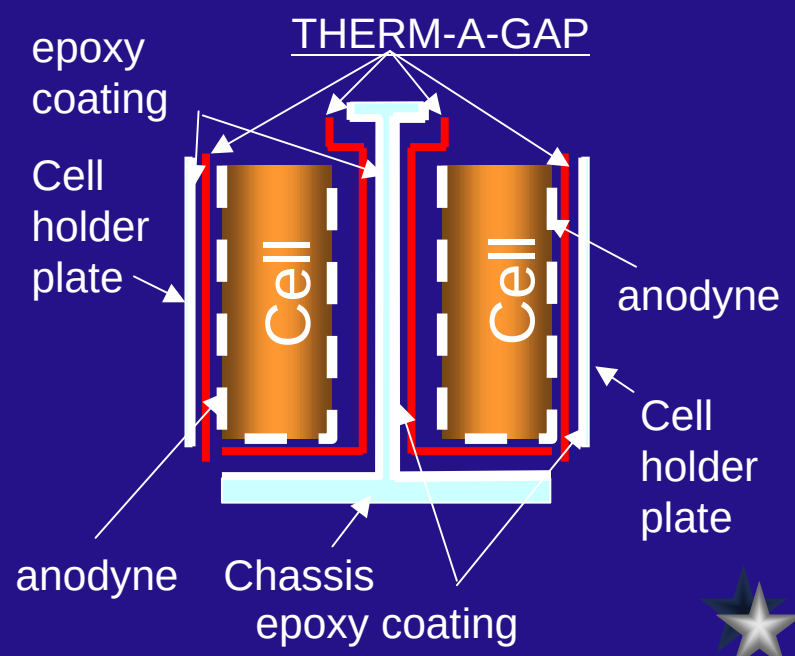
Mechanical Design

Double Insulation Method

To avoid short circuit failure between electrode/case of cells and chassis

MELCO applied the Isolation material for double insulation of cell case to battery chassis .

(1) the anodyne coating on the cell
(2) the epoxy coating on the chassis
(3) insulation filler:THERM-A-gap



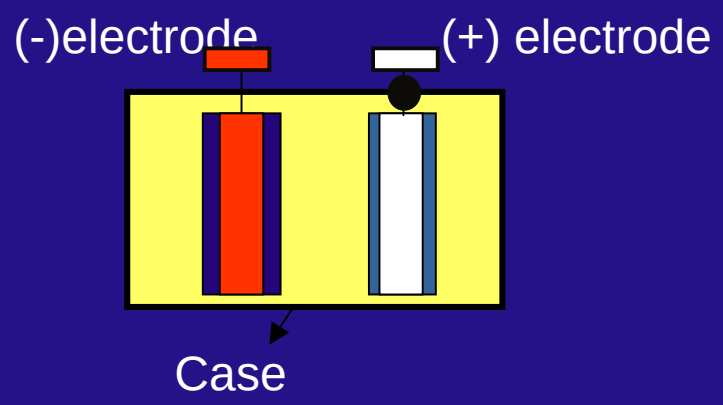
Double Insulation Method

Mechanical Design

To avoid large current failure

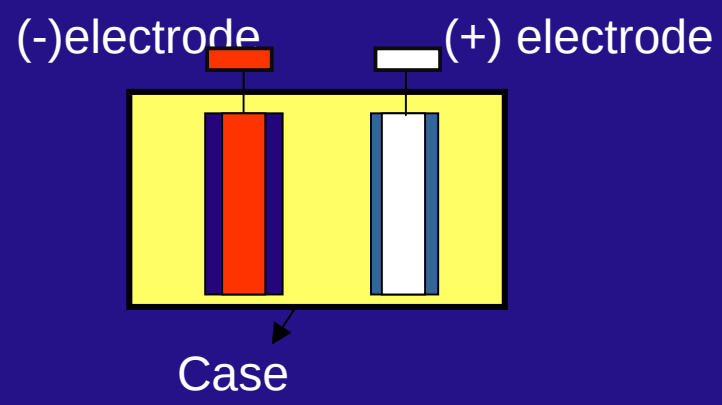
The cell case is isolated with from both of (-) / (+) electrode and case of cells.

Conventional cell case
Case is connected with Plus electrode



When the case is touched the minus electrode by tool in assembling, the failure current that is larger, is flown.

MELCO case
Case is Isolated with Plus/Mines electrode



When the case is touched the both (plus/mines) electrode by tool in assembling, the failure current is not flown.

Management

Battery Electrical Management

The monitoring circuit is composed of the current sensors, telemetry monitor and command I/F.

Telemetry

-LIB battery voltage:1ch/12bit

-Each two parallel cells voltages:10ch/12bit

-Shunt status (TBD):10ch

-LIB temperature:3ch

Command

-Cell refreshment ON/OFF command(if necessary)

-Heater on/off command

Management

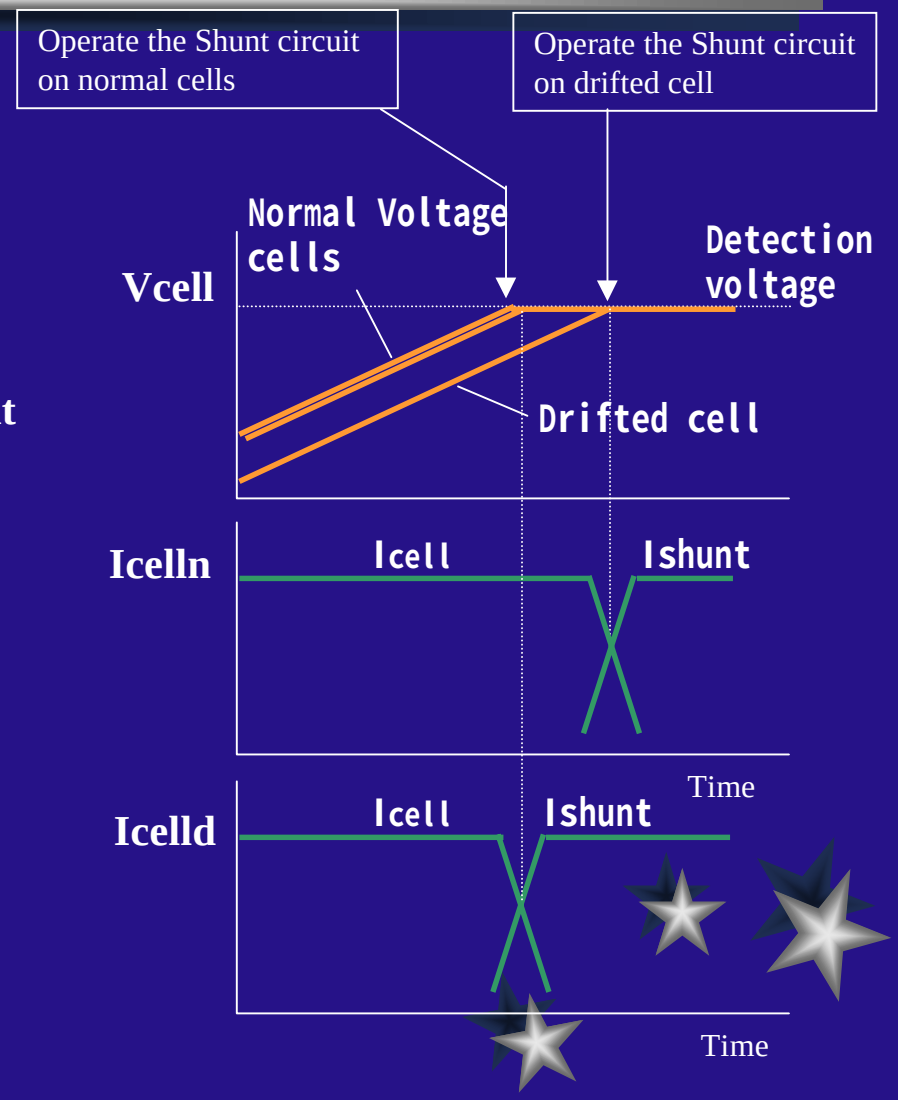
Equalizing Cells voltage

Normal voltage cells will be charged up to cell shunt level faster than drifted cell, since the leak current increased.

At this time, each normal voltage cell's shunt circuits are activated to bypass the charge current to keep setting voltage.

When the charge mode is switched to CV mode, the charge current is tapered off.

During this time, voltage of the drifted cell reaches setting voltage.

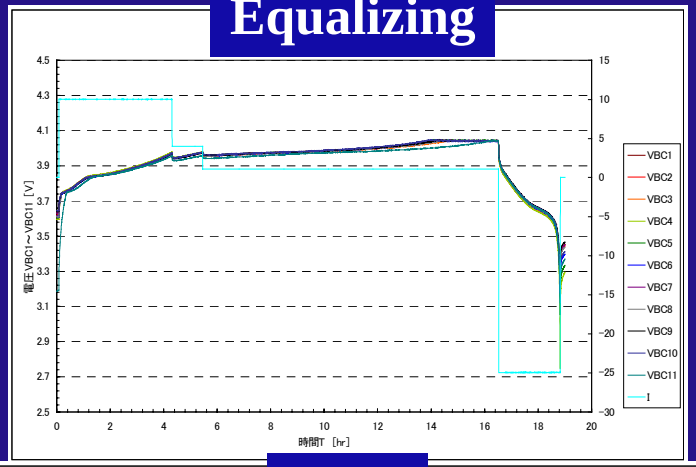


Electrical Design

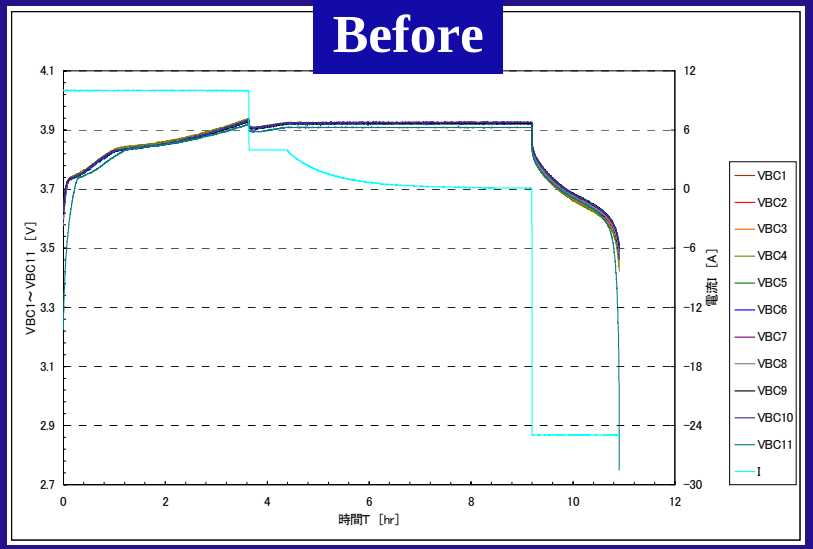
Equalizing Cells voltage

The Figures show each cell voltage in battery among before equalizing, equalizing and after equalizing. After the equalizing, the cell voltages are to be same.

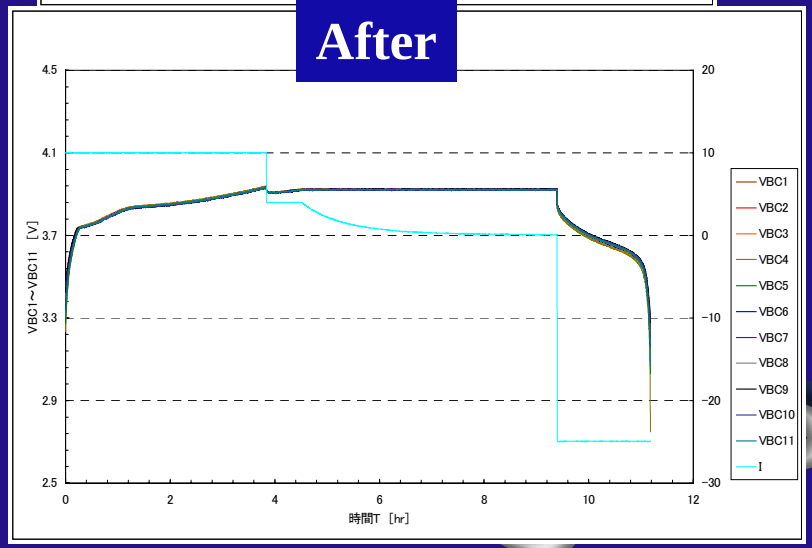
Equalizing



Before



After



Qualification Test

Qualification Model(LIBM100S10SS) Test Status

The following tests had successfully completed in the Qualification Model Battery.

(1) Electrical Performance Test

(2) Vibration Test

(3) Shock Test

(4) Thermal Vacuum Test

(5) Thermal Cycle Test

Qualification Test

Electrical Performance Test

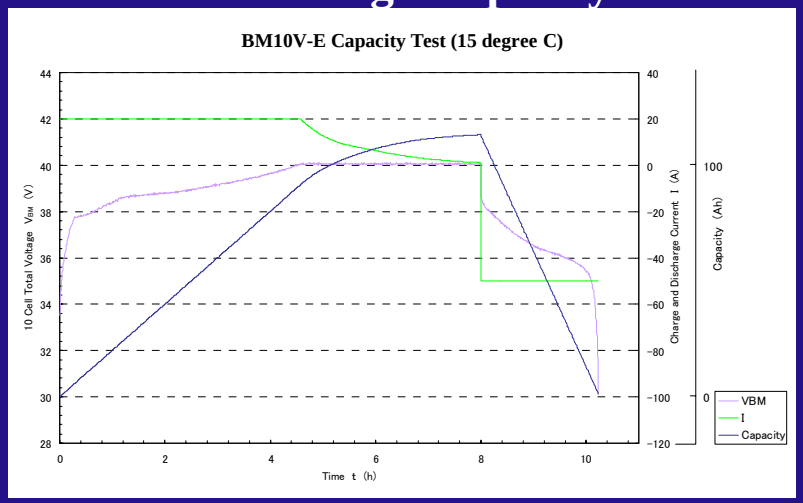
Following tests were performed as the initial functional test as a reference for trend evaluation.

1) Discharge Capacity at 15 degree C

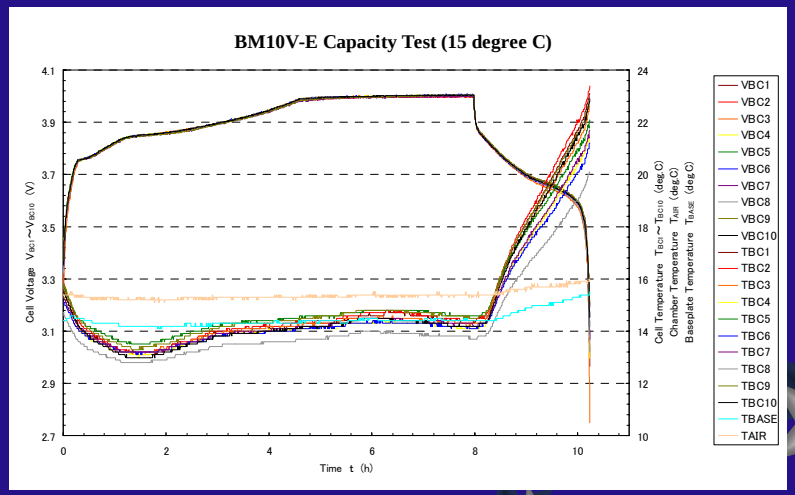
Measured Discharge Capacity : 111.9 Ah.

2) Discharge Capacity at 0 degree C

Measured Discharge Capacity : 107.4 Ah.



Battery Voltage/Capacity



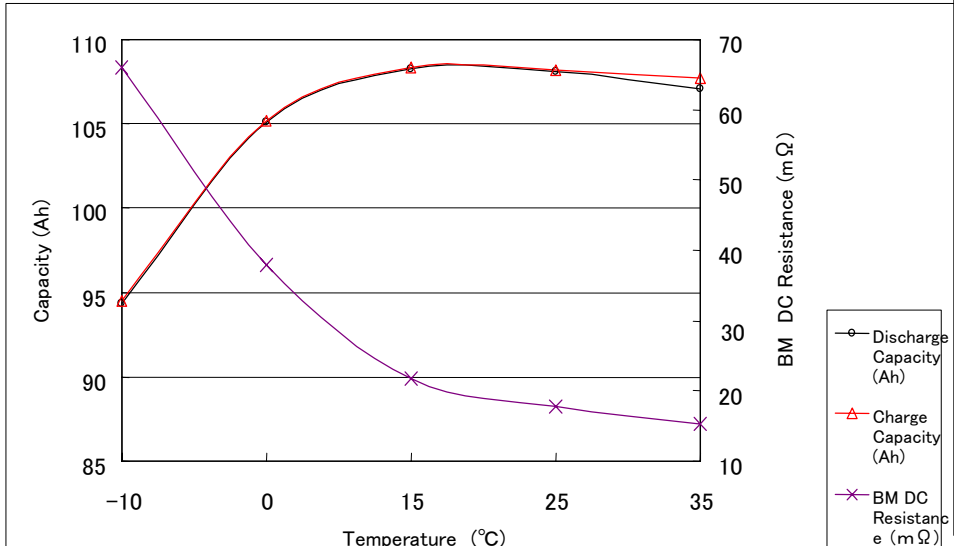
Cell Voltage/Temperature

Qualification Test

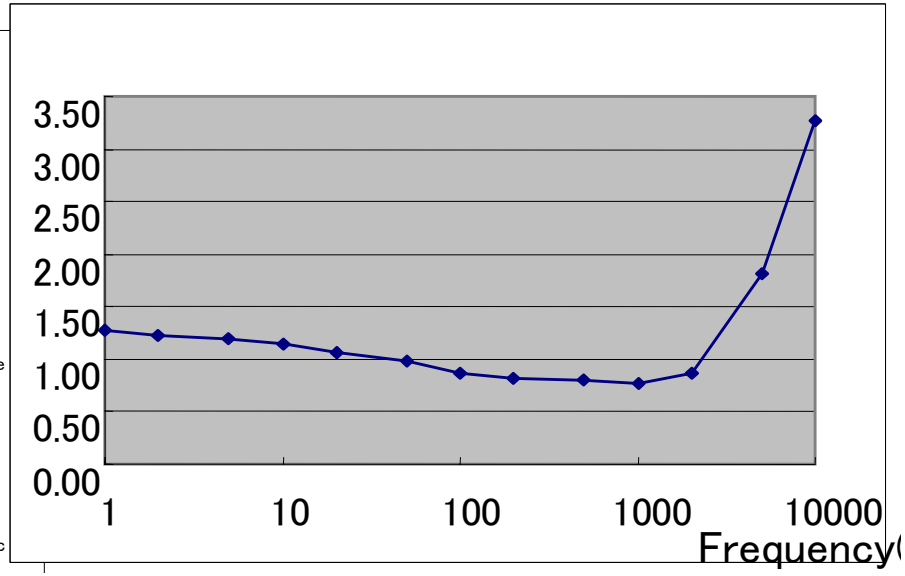
LIBPR140

Electrical Performance Test

-impedance
-Capacity.



DC Resistance, Capacity vs. Temperature



Impedance(ohm)

Qualification Test

Vibration Test

Sine and Random vibration tests were performed under the following conditions.

1) Sine Vibration

- X, Y axis

Frequency (Hz)	Level	
5 - 19.77	12.7 mm DA	2 oct/min
19.77 - 100	10G	

- Z axis

5 - 24.22	12.7 mm DA	2 oct/min
24.22 - 100	15G	

2) Random Vibration

- X, Y axis

Frequency (Hz)	PSD	Slope
20 - 70	-	6 dB/Oct
70 - 700	0.139 g2/Hz	-
700 - 2000	10G	-8 dB/Oct

Overall Level; 11.75 Grms, 180 sec

- Z axis

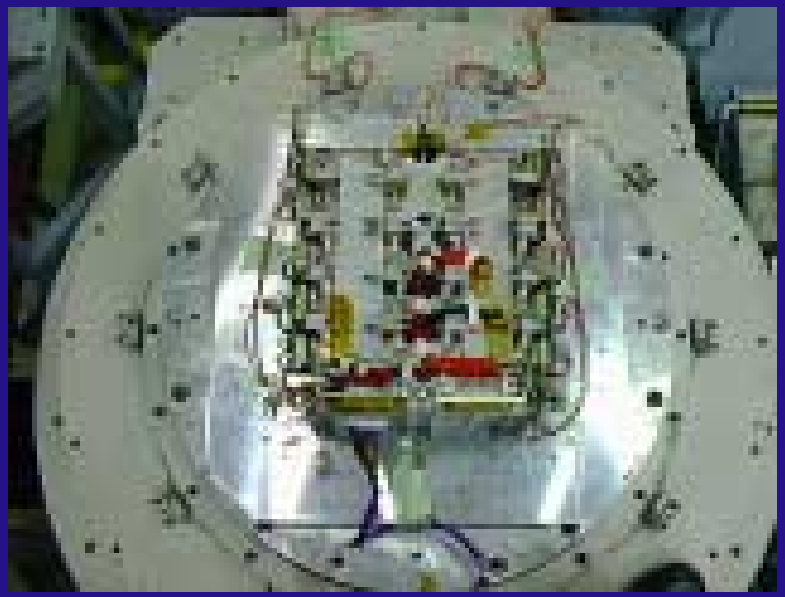
20 - 70	-	6 dB/Oct
70 - 700	0.20 g2/Hz	-
700 - 2000	10G	-8 dB/Oct

Overall Level; 14.15 Grms, 180 sec

Qualification Test

Vibration Test

Y -axis Vibration



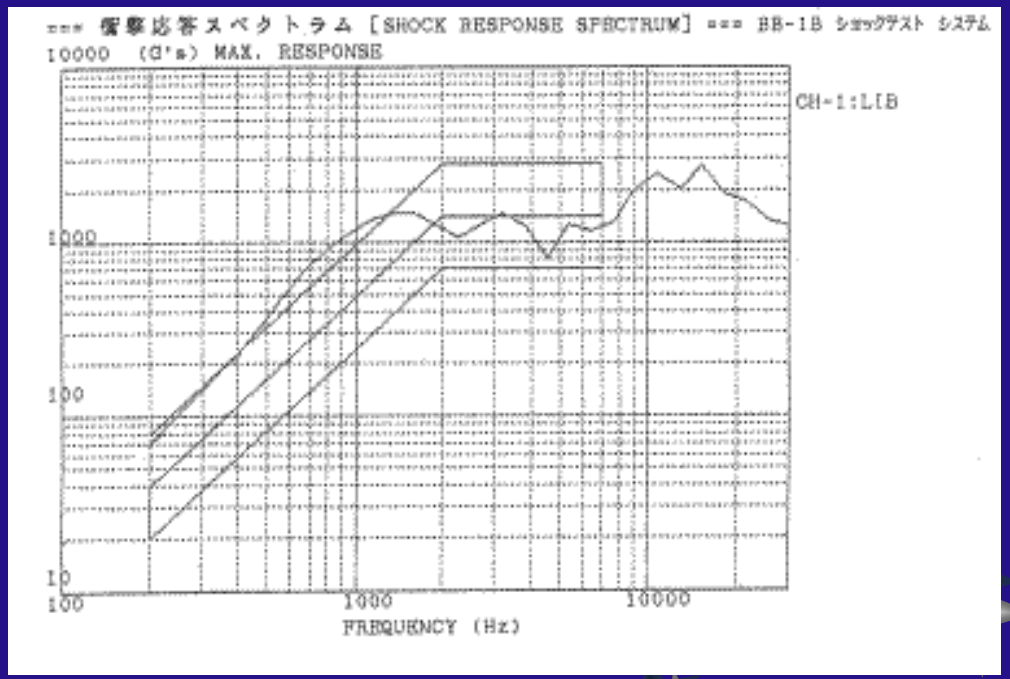
Z -axis Vibration

Qualification Test

Shock Test

Test Level	3 Times / each axis
Frequency (Hz)	Shock Response (G)
200	40
2000	1400
7000	1400

X -axis Shock Test



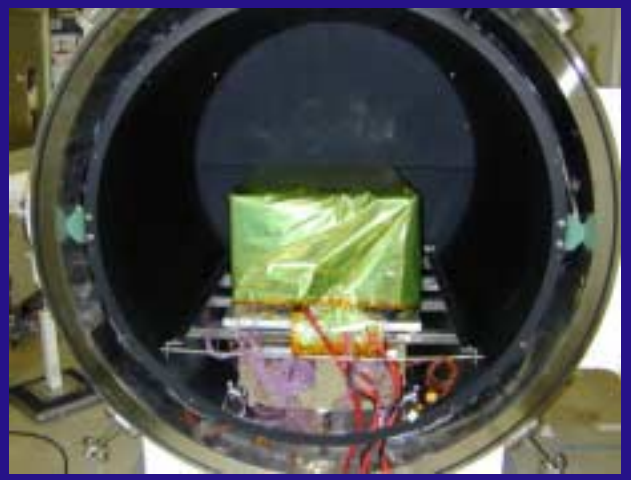
Shock Response Spectrum (First x-axis)

Qualification Test

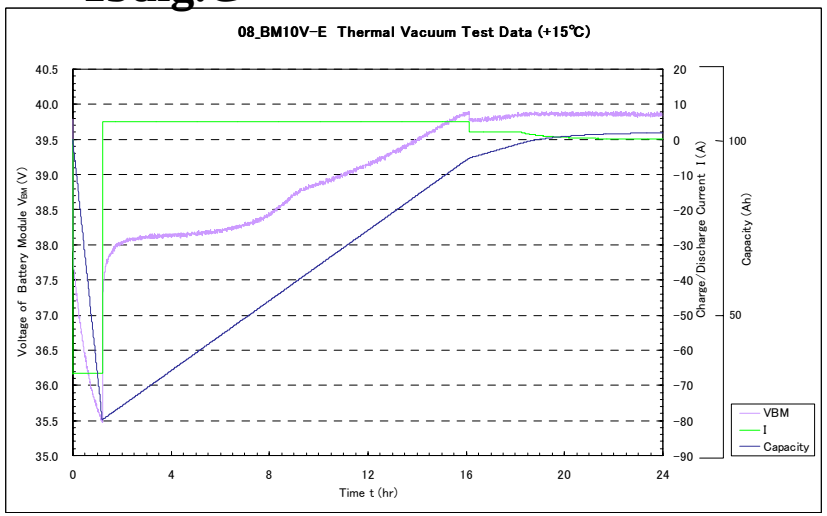
LIBPR140

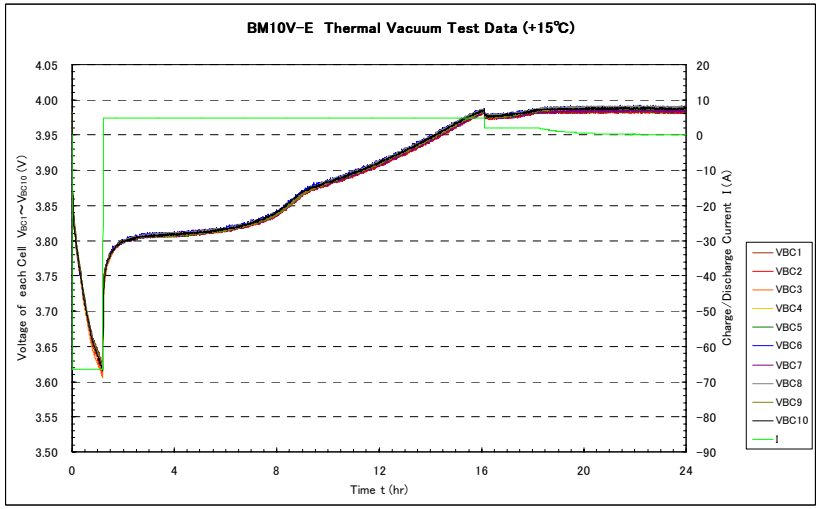
Thermal Vacuum Test

- Temperature: -10 deg.C, 0, +35 dig.C
- Vacuum rate: 1.33×10^{-3} Pa



15dig.C

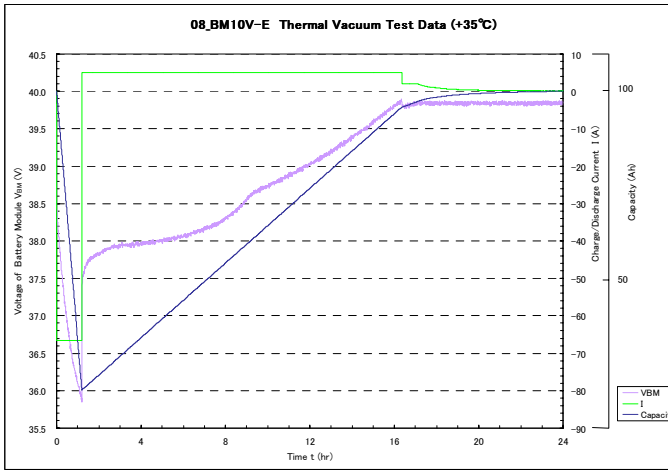


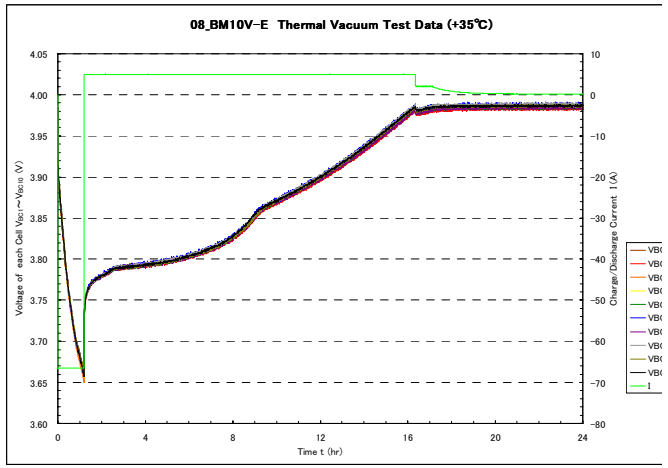


Qualification Test

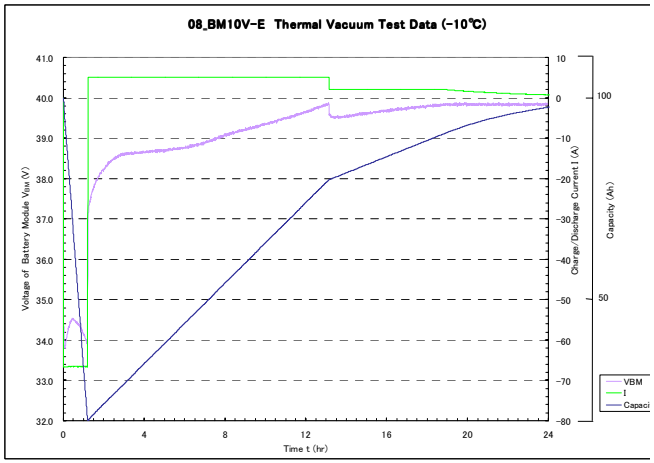
Thermal Vacuum Test

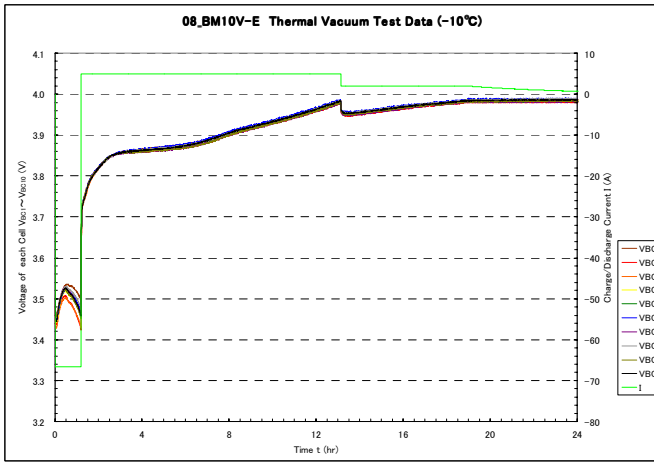
35 dig.C





-10 dig.C





Qualification Test

LIBPR140

Summary of the 100AH Cells Qualification Test

Test Type	Environment	Requirement	Results
Baseline Performance	(1)Capacity test at prescribed temperature. (2)Voltage drop at prescribed current	(1)Capacity: 100Ah (35℃,20℃ and 10℃), 90Ah (0℃), 80Ah (-10℃). (2)EoDV at high current discharge : 3.00V.	Passed
Sine Vibration	Qualification level 1 A discharge condition	No irregular phenomenon is observed.	Passed
Random Vibration	Qualification level 1 A discharge condition	No irregular phenomenon is observed.	Passed
Post-Vibration	(1)Visual inspection: measured at 25 ℃ . (2)Capacity test at 20℃	(1)No irregular phenomenon is observed. (2)The capacity: 100Ah	Passed
Shock	Qualification level	No irregular phenomenon is observed.	Passed
Pre-Thermal Vacuum	(1)Visual inspection: measured at 25 ℃ . (2)Capacity test at 20℃	The capacity: 100Ah No irregular phenomenon is observed.	Passed
Thermal Vacuum	Charge and discharge in LEO and GEO patterns at 1×10^{-5}Torr	Each cell shall be capable of operating in a pressure environment of less than 1×10^{-5}Torr for the specified period and shall meet the physical and electrical requirements of the specification.	Passed
Post-Thermal Vacuum	(1)Visual inspection: measured at 25 ℃ . (2)Capacity test at 20℃	The capacity: 100Ah No irregular phenomenon is observed.	Passed
Thermal cycles	Thermal cycle under on +35℃ to -10℃	No irregular phenomenon is observed.	
Final Performance	(1)Capacity test at prescribed temperature. (2)Voltage drop at prescribed current	(1)Capacity: 100Ah (35℃,20℃ and 10℃), 90Ah (0℃), 80Ah (-10℃). (2)EoDV at high current discharge : 3.00V.	Passed
Final Inspection	Visual inspection at 25℃	All inspection: No irregular phenomenon is observed.	Passed

Conclusion

Design summary

Melco battery has following characteristics

- Light weight /Low cost: by high energy density
  well over 100wh/kg at battery,128wh/kg at cell
- Reduction of the number of cells: High discharge voltage
  over than 3.6V/one cell
- Power saving: By ratio of charge/discharge energy ratio
  over than 95%
- Small self discharge current
  less than 0.05%/day
- No need of the reconditioning function
  By no memory effect

Conclusion

Design summary

- Superior heat dissipation
  Good combination between the T-shape chassis and elliptic cylindrical cells
- Foot print:To save the foot print by applying elliptic cylinder cells comparing with cylinder type
- Protection:
  To avoid overcharge applied shunt circuit
  To avoid extreme current when short circuit occurs between the electrode and case
- One Fail operation: Applying Unique Bypass Switch
- Long life cycle: Longer than 15 years on GEO
  Capacity degradation is smaller
  Voltage balancing : Applying Battery refresh function

Conclusion

Qualification Result

MELCO has successfully completed the development of the Lithium Ion Battery for satellite use.

-To perform the electrical characteristics

-To clear the space environment test as Qualification Level test.

After the each Qualification level test, the electrical performance such as

--Capacity

--Discharge voltage at EOD

--Impedance

have not been degraded and changed.

No irregular phenomenon has been observed mechanically.

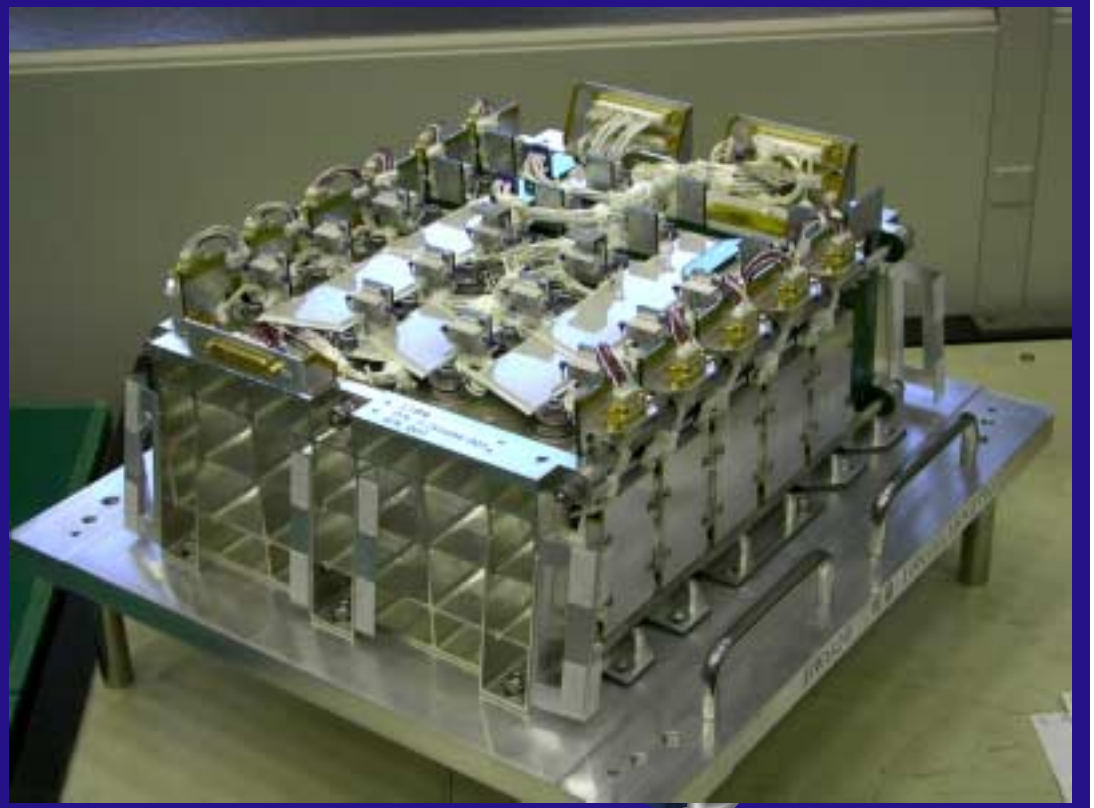
Battery Line-Up

LIBM050A11Ss--50Ah, 11 Li-Ion cells (for SERVIS-1 FM)

Battery Characteristics

Capacity	**:2035（WHr）**
Voltage	**:44-37(V）**
Cell Capacity	**:50(AH）**
Quantity of Cells	**:11 ells in series**

Width	**:328 mm**
Length	**:405**
Height	**:174.5**
Mass	**:26.4 kg**
Specific Energy	**:77 WHr/kg**



Battery Line-Up

Qualified MELCO standard battery

Battery type	Provided	Voltage		Weight	Size			Energy density
	Cap(wh)	Vmax	Vmin	Kg	W(mm)	L(mm)	H(mm)	Wh/kg
LIBM100A08S**	2880	32.0	25.6	28.5	328	299	271.5	101.0
LIBM100A10S**	3600	40.0	32.0	35.0	328	352	271.5	102.9
LIBM100A12S**	4320	48.0	38.4	41.6	328	405	271.5	103.8
LIBM050A08S**	1440	32.0	25.6	17.9	328	299	179	80.4
LIBM050A10S**	1800	40.0	32.0	21.9	328	352	179	82.1
LIBM050A12S**	2160	48.0	38.4	26.0	328	405	179	83.2

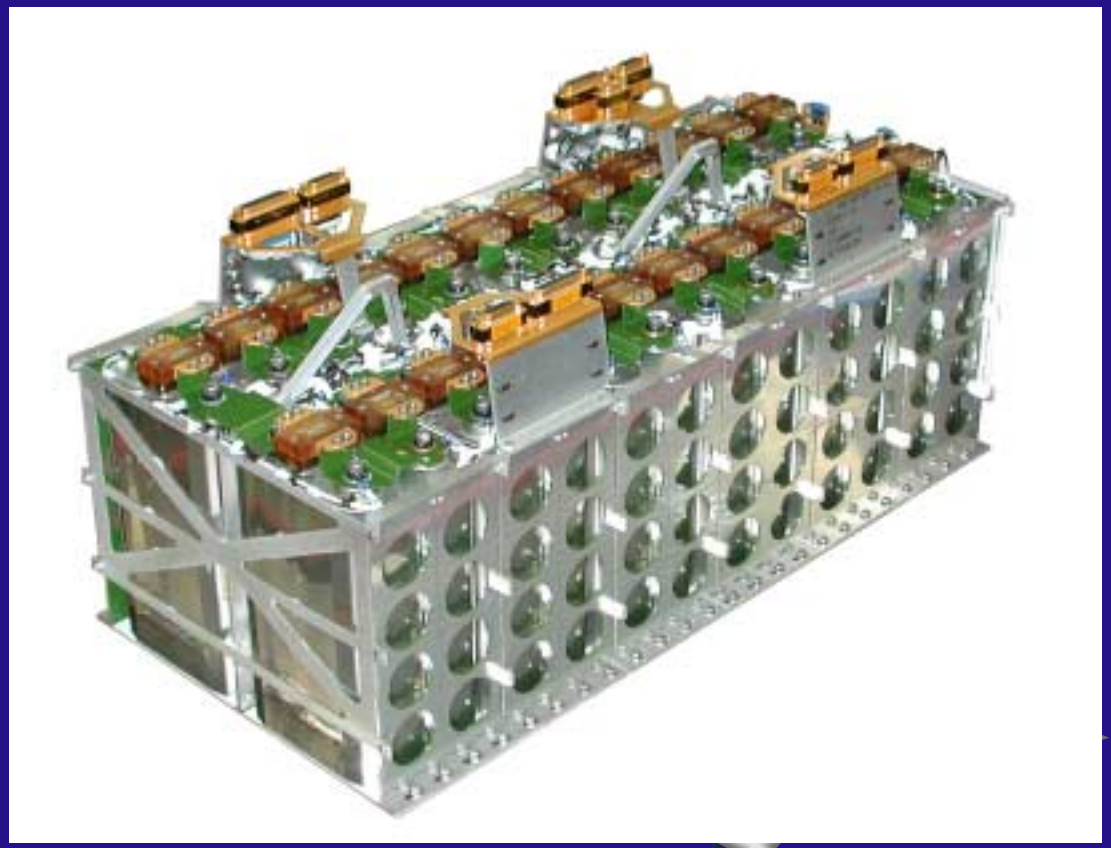
Battery Line-Up

LIBM100A24SB--100Ah, 24 Li-Ion cells Battery (for GEO)

Battery Characteristics

Capacity	:8640（WHr）
Voltage	:79.2-96(V）
Cell Capacity	:100(AH）
Quantity of Cells	:24 cells in series

Width	:315 mm
Length	:705
Height	:273
Mass	:78 kg
Specific Energy	:110 WHr/kg



Battery Line-Up

Qualified MELCO standard battery

Battery type	Provided	Voltage		Weight	Size			Energy density
	Cap(wh)	Vmax	Vmin	Kg	W(mm)	L(mm)	H(mm)	Wh/kg
LIBM100A16S**	5760	64.0	52.8	56.4	315	501	273	102.1
LIBM100A18S**	6480	72.0	59.4	60.7	315	553	273	106.8
LIBM100A20S**	7200	80.0	66.0	66.3	315	603	273	108.6
LIBM100A22S**	7920	88.0	72.6	72.4	315	655	273	109.4
LIBM100A24S**	8640	96.0	79.2	78.0	315	705	273	110.8

Development of the Lithium Ion Battery for Satellite

Thank You

Safety Performance of Small Lithium-Ion Cells in High Voltage Batteries

Philip R. Cowles: COM DEV Space

Eric C. Darcy: NASA-JSC

Frank J. Davies: HEI/Lockheed Martin

Judith A. Jeevarajan: Lockheed Martin, NASA-JSC

Robert P. Spurrett: AEA Technology

Introduction

- Small-cell EAPU work done by NASA-JSC & COM DEV
- Looking at safety features – short circuit protection - PTCs
- Early tests showed that long strings do not withstand short circuit
  - Some PTCs experience large negative voltages
  - Destructive results
- **Solution**: group cells into shorter substrings, with bypass diodes
- Work included:
  - Tests with single cells shorted
  - Tests with single cells with imposednegative voltages
  - 6s, 7s and 8s string shorts
  - Tests with protection scheme in place, on 12s and 41s x 5p

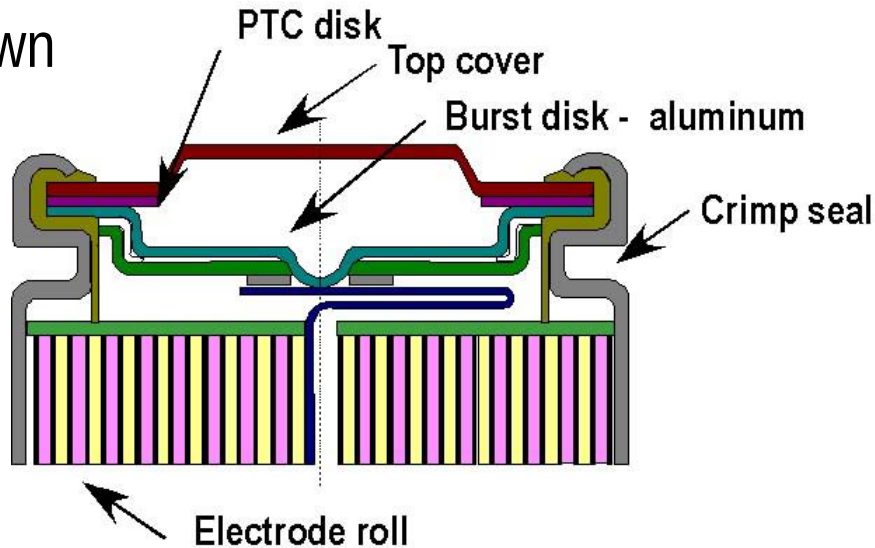
Specific Requirements

- NASA requires a '2-failure tolerance' against catastrophic failure
  - Fire, explosion, severe venting
- One failure is an external short-circuit
  The other a is failure in a cell that might propagate
- Not a usual requirement for unmanned missions
  - Most spacecraft primes have a fuse-blowing or fault clearance target
  - e.g. 2000 Amp for 20 mS

- Most obvious case is a hard short at or close to the terminals
- We also consider the case of a 'smart short'
  - defined as a low-resistance short that is
    more damaging than a hard short

The nature of a Shorted String

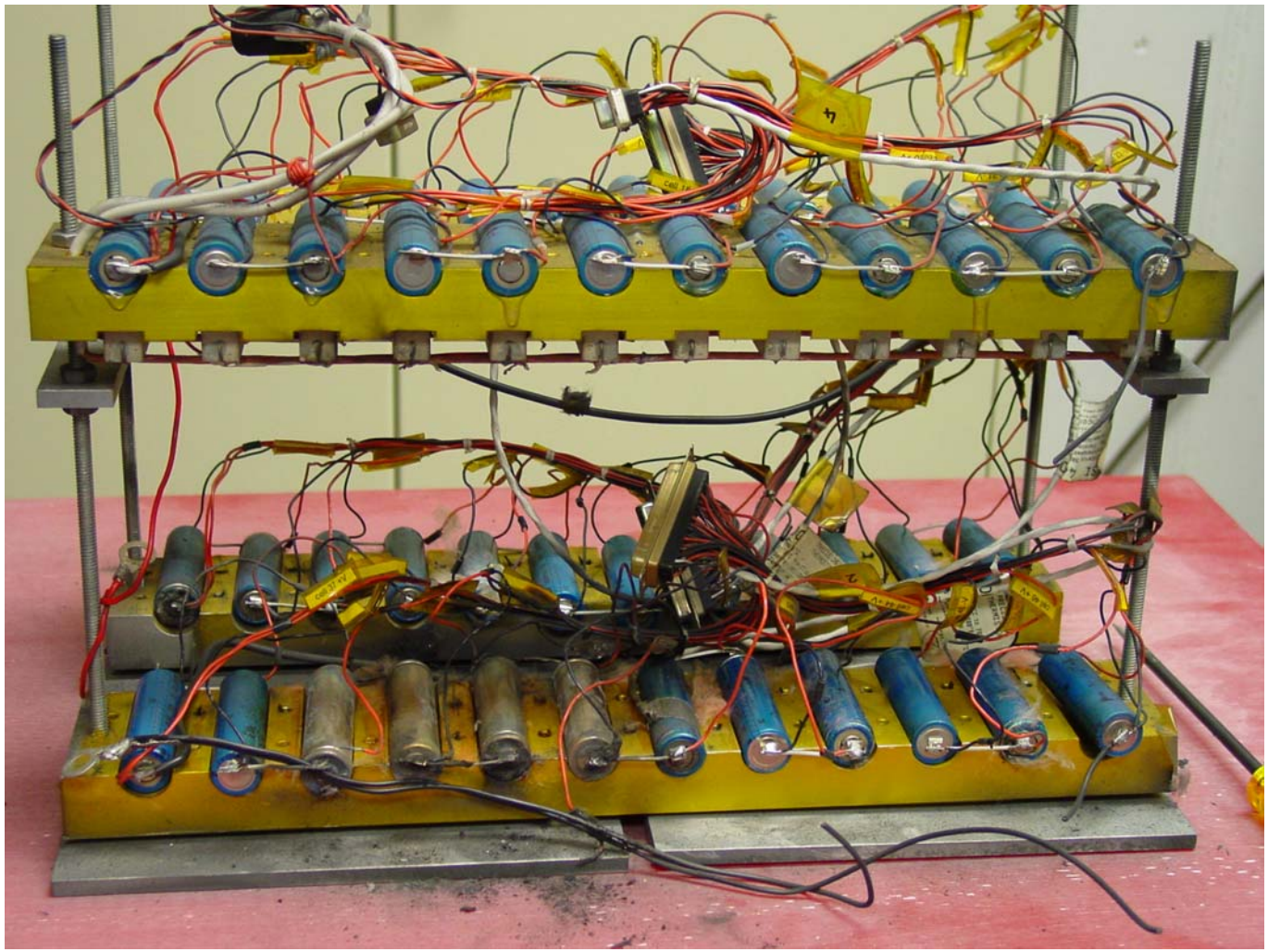
- Use fully charged cells (4.4V/cell)
- >60 amp/string inrush current
- Sony cells have a PTC device
- In a long string, all PTC's race to trip
- The winner gets a high negative voltage
- More than ~30V and it breaks down
- This implies strings of ~>7s will not be protected by the PTCs



Long String Test

- 24s x 2p test battery
  - Previously used for convergence tests
- Charge to 105.6V, 4.4V/cell
- 'Admirals' test
- Short it
- Low-rate voltage sampling on each cell + current
- Considerable damage

24s x 2p Battery - after

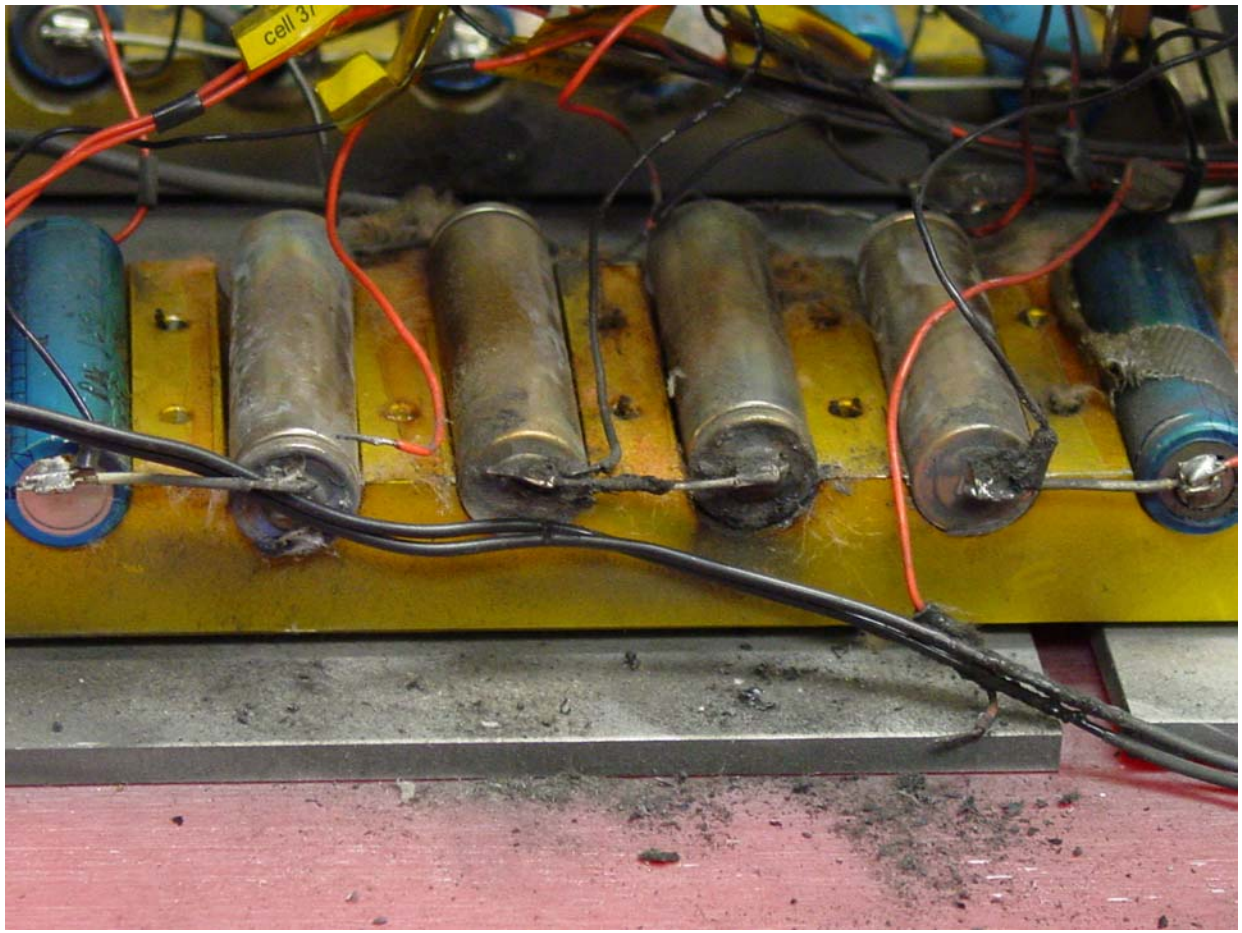


Condition of Cells after the Test

State	No. of Cells
Operating	12
No volts	27
Leaks/vents	25
Wrapper damage	23
Meltdown	4 (cells 39 – 42)

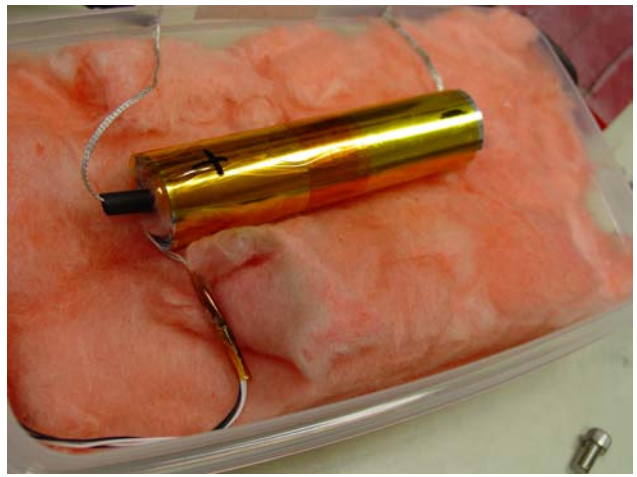
Cells 39 - 42

- Cans ~300°C
- Lost ~10g
- Aluminum internal tabs melted (>600°C)

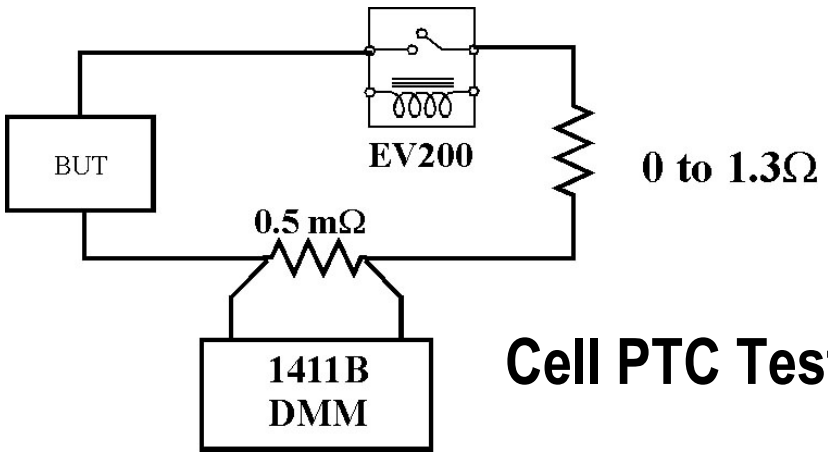


Single-Cell Tests

- Aim to understand the PTC
- Fully charged cells, 20°C
- Shorts from 0.5 mΩ to 1.3 Ω
- Cells insulated
- Measured current, voltage, time
- Estimated cell Soc, cell Rs, PTC resistance

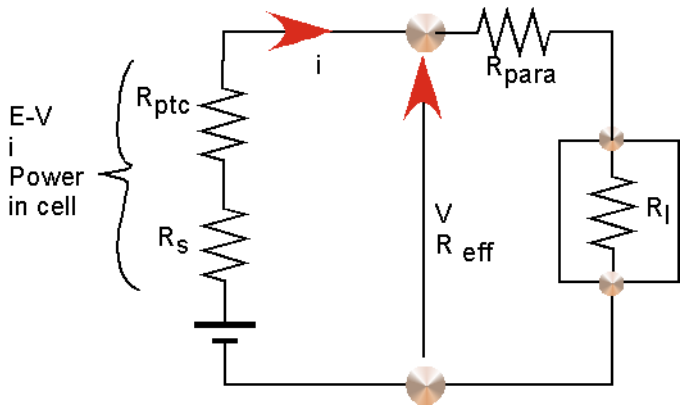


Cell partly installed

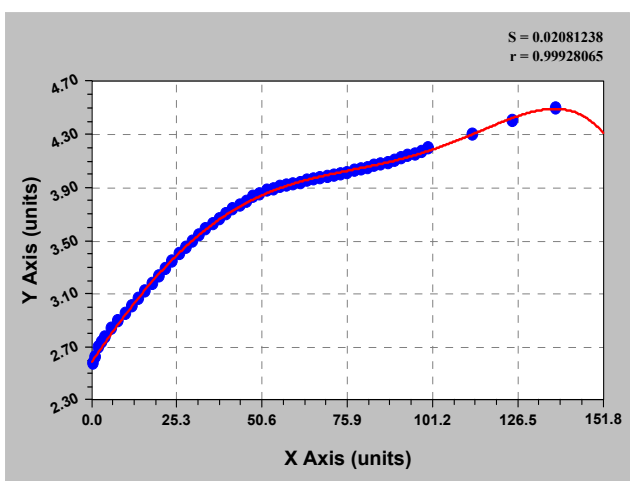


Cell PTC Test Circuit

PTC Equivalent Circuit



Cell state estimated using initial state + SoC EMF relationship



6th Degree Polynomia	
Coefficient Data:	
a =	2.586134
b =	0.037551
c =	-0.00017
d =	-2.95E-06
e =	2.02E-08
f =	1.38E-10
g =	-9.52E-13

Set Parameters

Cell initial state e.g 4.385V EMF

Load Resistance

Measured parameters are:

V, cell terminal volts (mVolts)

I, cell current (Amps)

T, cell temperature (Temp)

Derived parameters are:

Actual presented load resistance (R eff)

Ah out of cell

Wh dissipated in cell

State of charge

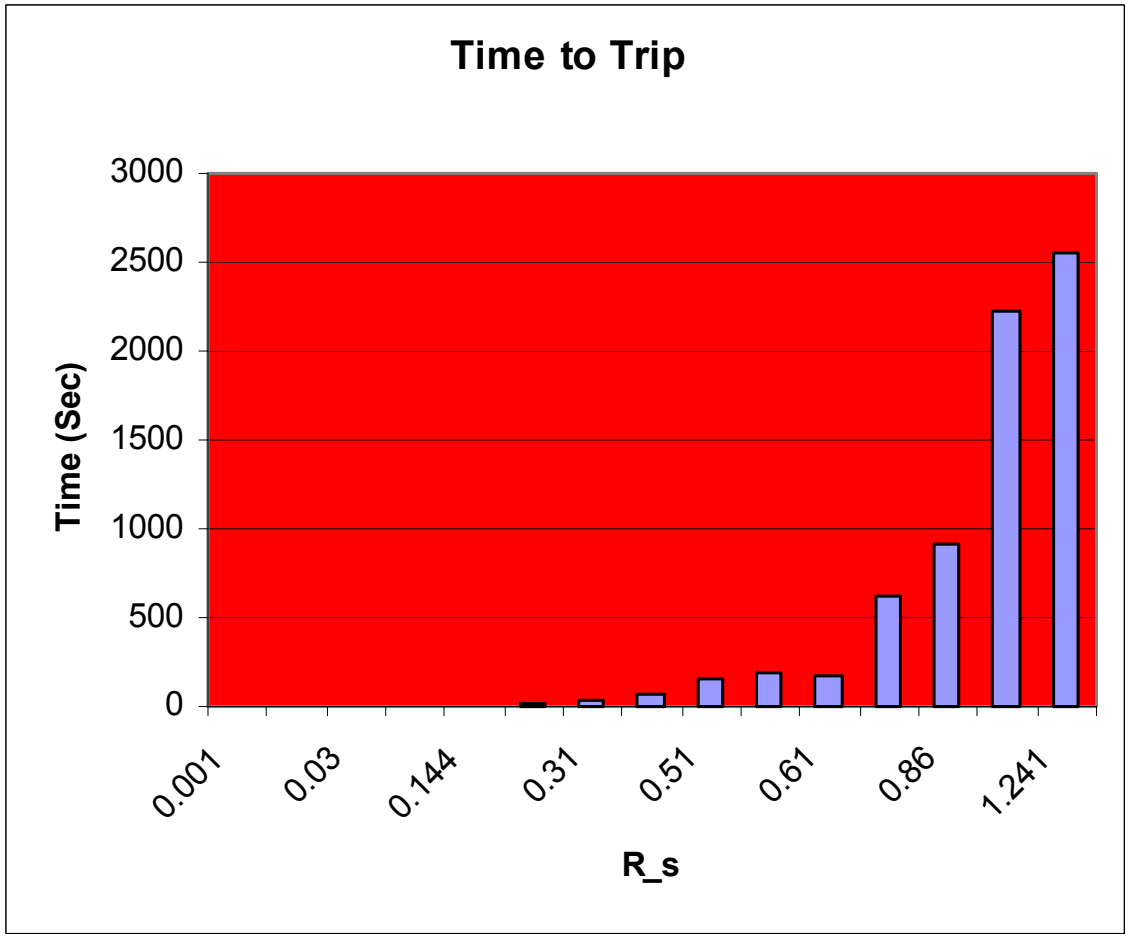
Cell EMF

Cell dissipation, PTC dissipation

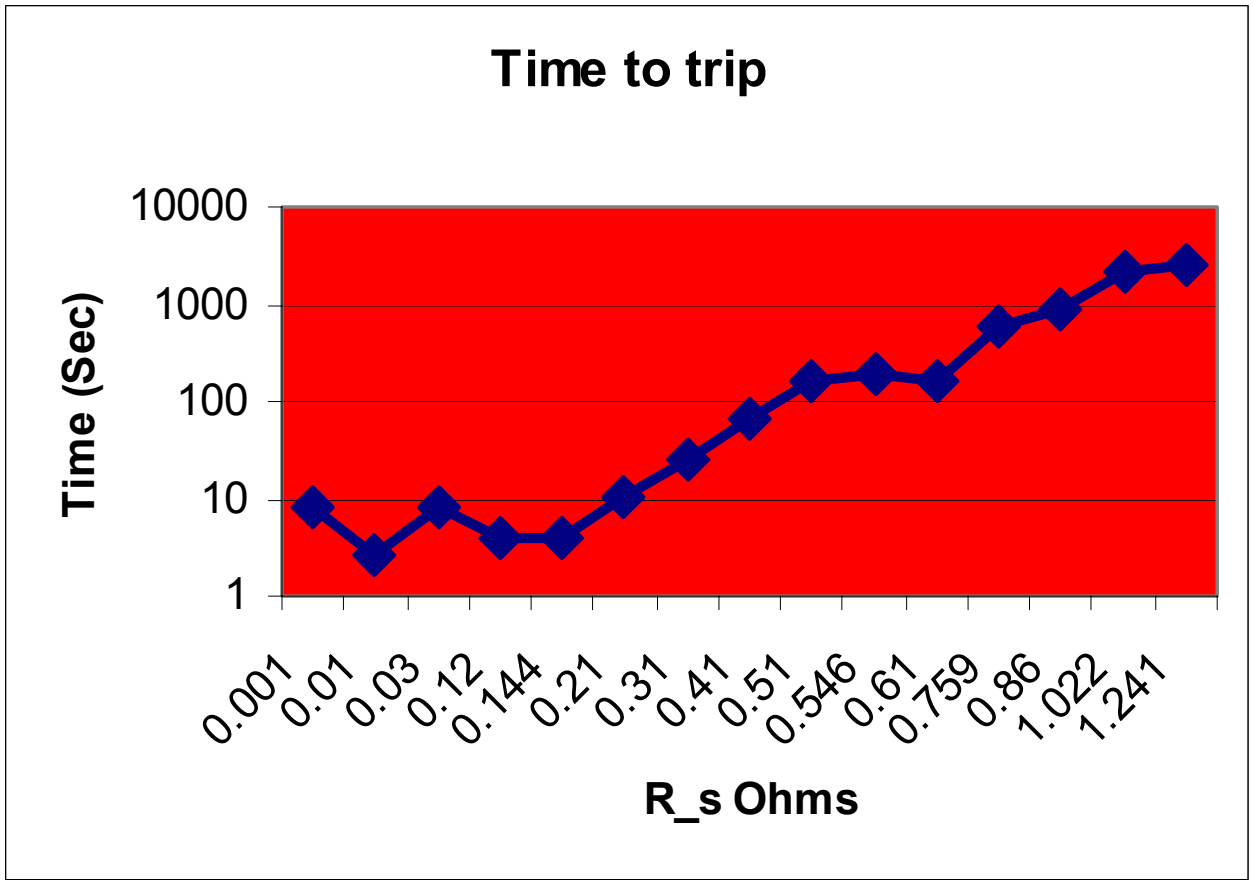
Cell dissipation energy (W-h)

Extra parasitic resistance (Rpara)

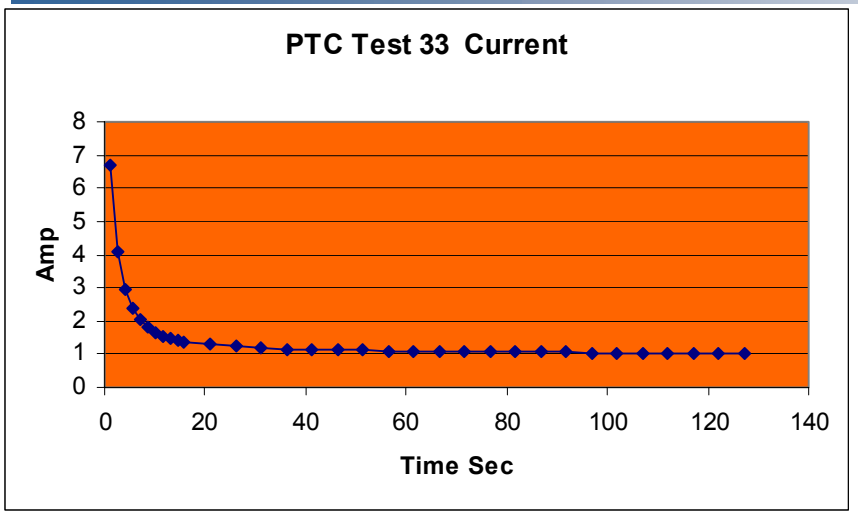
Single Cell Time-to-trip (linear)

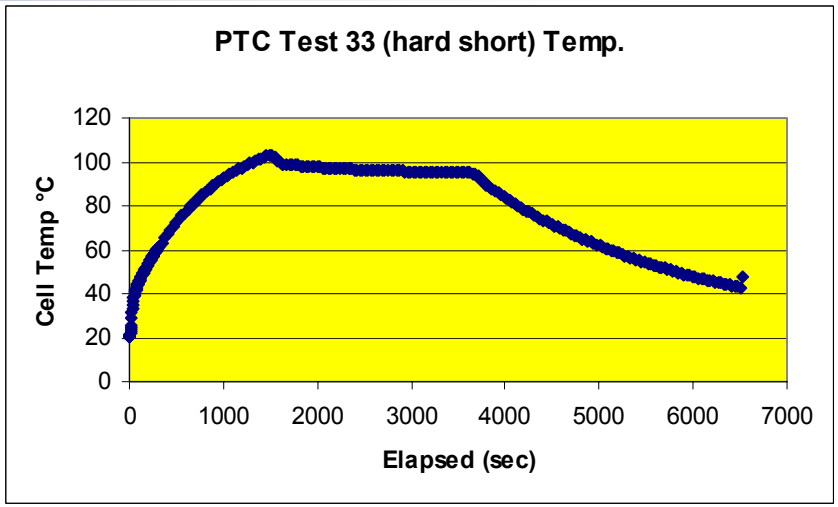


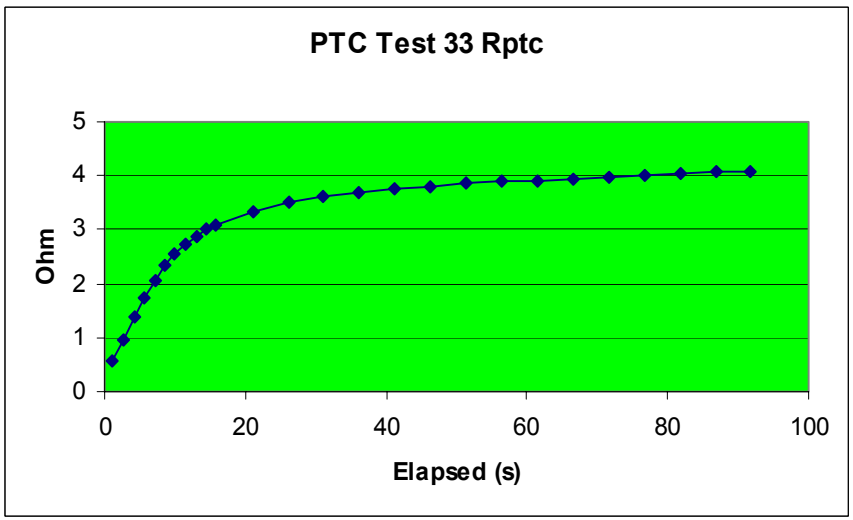
Single Cell Time-to-trip (log)

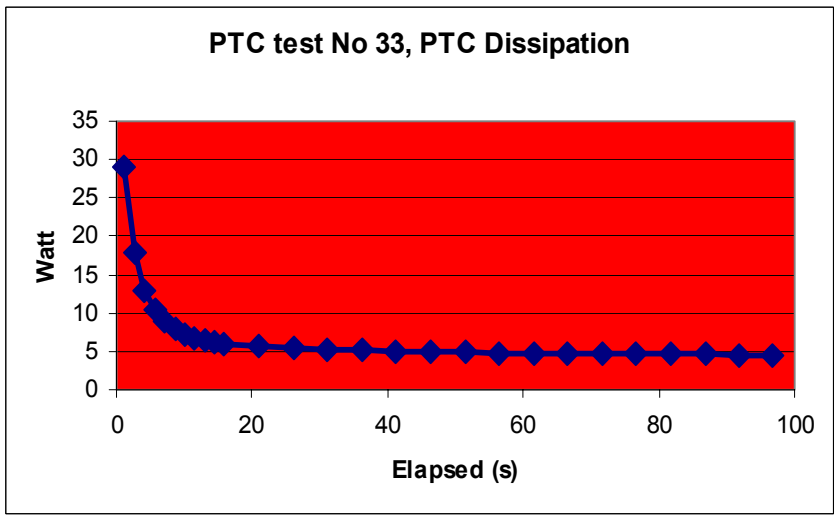


Typical Data – hard short

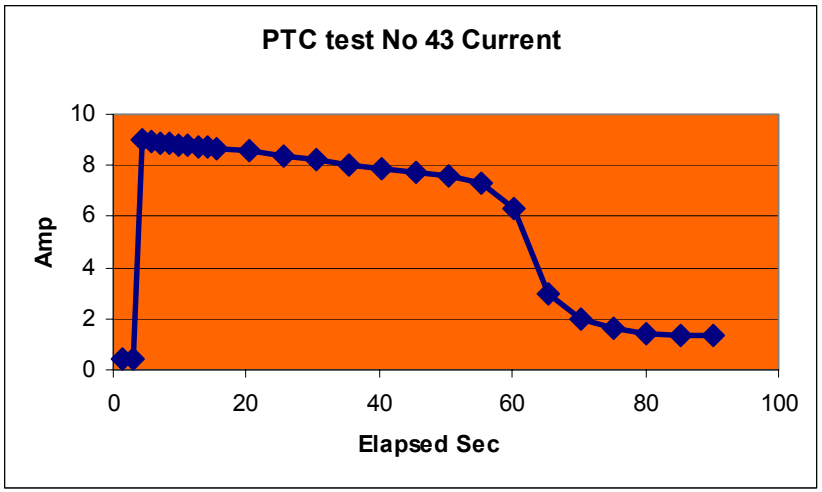


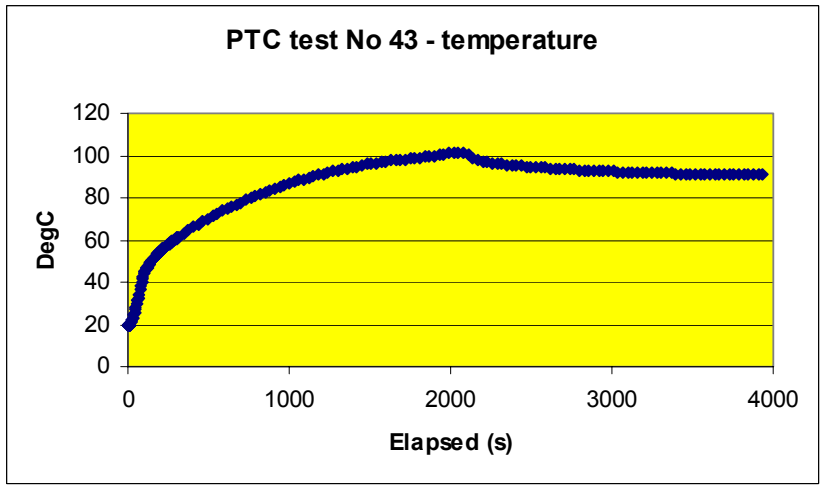


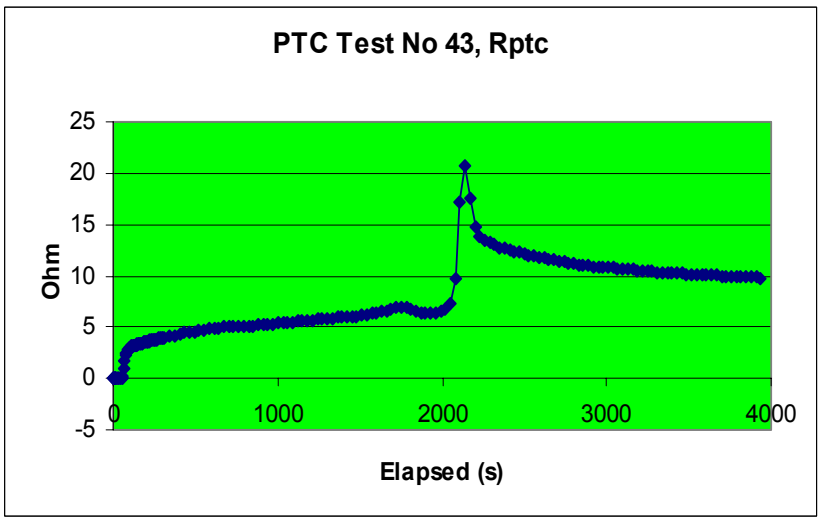


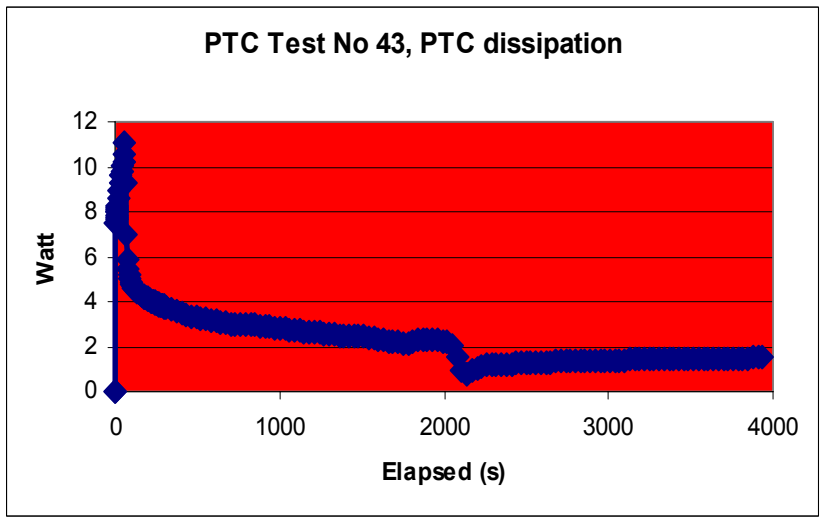


Typical Data – 0.41 Ohm



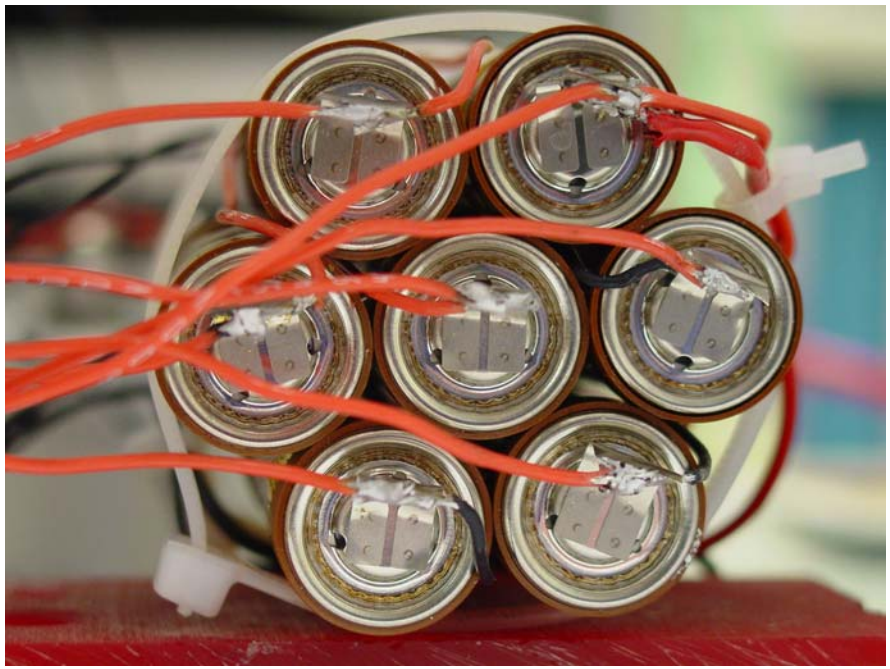






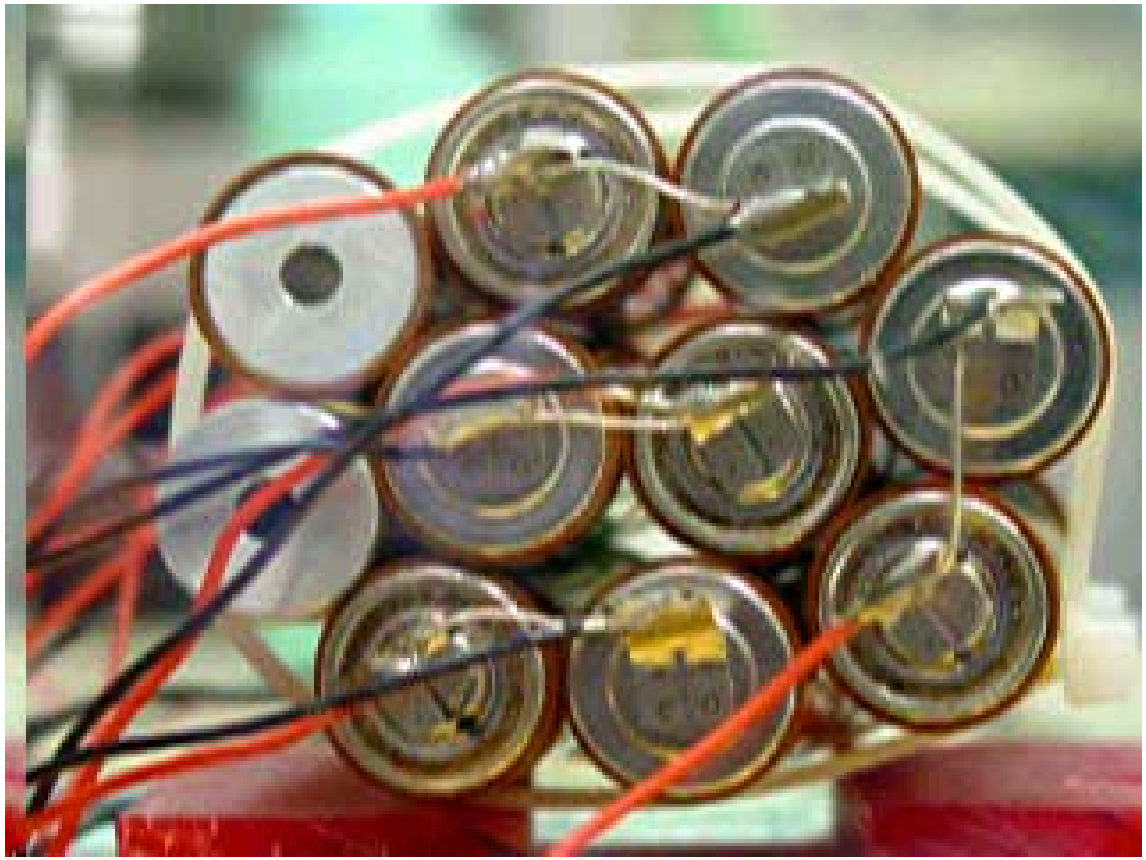
Short-String Tests

- 6, 7 and 8s strings shorted (hard shorts)
- 6s and 7s strings shut down gracefully
- With 8s, 2 out of 3 'sparked'



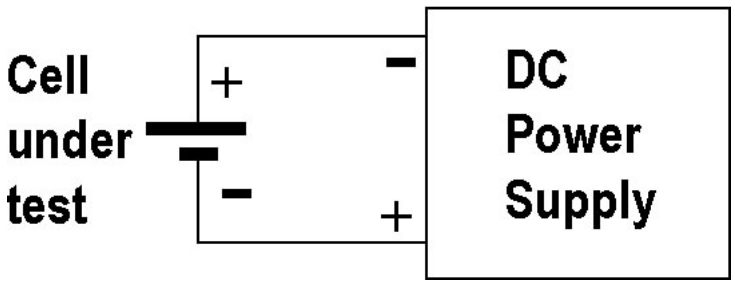
7S cell bundle ready for test

8s Test No 1



Single-cell tests with reverse voltage

- Tests conducted by NASA-JSC
- Aim to simulate the sacrificial cell by applying a negative voltage
- Use high current power supply



Single-cell results - 1

Cell No.	Temp at start	Current during trip	Time to trip (Sec)	Voltage after trip	Current after trip	Notes	DPA Notes
61	amb	18A	2.5	0.0V 1.0 cells	1.27A	No fail	
49	amb	15 A	6.056	-25.4 V 6.8 cells	0.25 A	No fail.	
60	amb	15 A	5.18	-32.36 V 8.4 cells	3.6 A	Failed after less than 1 second of -32 V then seal failure after 8 seconds	Damage to PTC and shorted seal
66	amb	15 A	4.905	-30.6 V 8.0 cells	0.23 A	Failure 43 sec after trip PTC end stayed at 70C after external supply removed	Minor damage to PTC and shorted seal

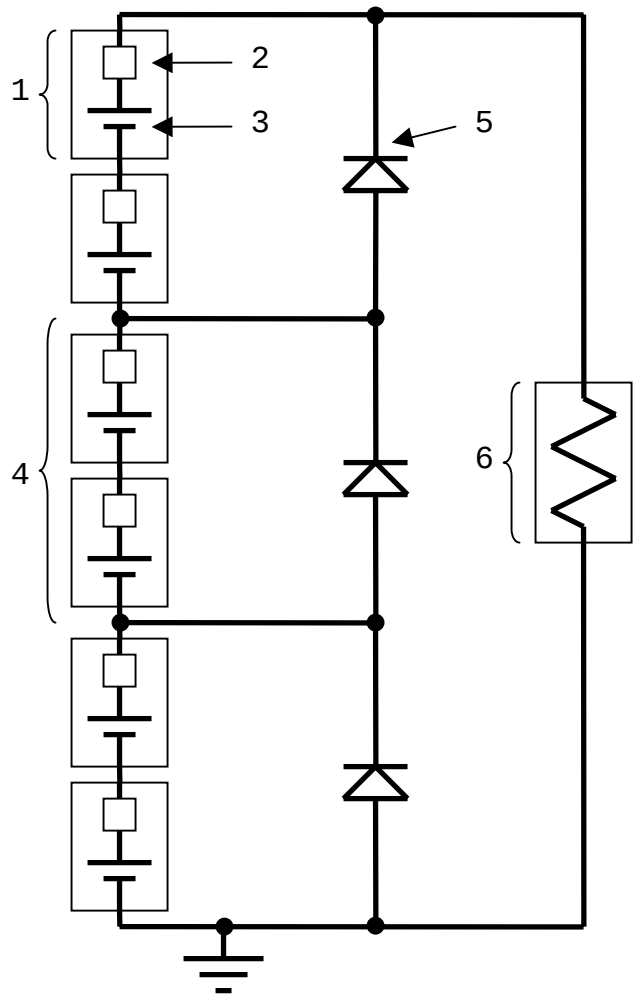
Single-cell results - 2

Cell No.	Temp at start	Current during trip	Time to trip (Sec)	Voltage after trip	Current after trip	Notes	DPA Notes
57	amb	15 A	4.383	-22.5 V 6.2 cells	0.26 A	No failure	
55	65C	13.1 A	0.9 -o 1.2	-27.3 V 7.3 cells	0.19 A	Failure after 90 sec of -27.3 V PTC end stayed at 84C after external supply removed and during purge.	No damage to PTC but seal shorted under curled over crimp edge. Thermal evidence that cell discharged itself slowly through PTC and this short.
51	65C	8.5 A	0.788	-26.8 V 7.2 cells	0.06 A	No Failure	

Single-cell tests - observations

- Temperature at PTC shoots up very quickly when PTC trips.
- Maximum temperatures on the outside of the case at the crimp go up above 200°F (95°C)
- Collateral damage caused to crimp seal
- Tests confirmed that ~7s was 'marginally safe'
- 9 Amp diodes appear to handle the ~60A inrush current

Component Parts



1. Battery cell with built-in short circuit protection.
2. Internal short circuit protection device (PTC). May be similar to Raychem Polyswitch.
3. Electrochemical part of cell (provides electromotive force)
4. Substring
5. Diode
6. Load.

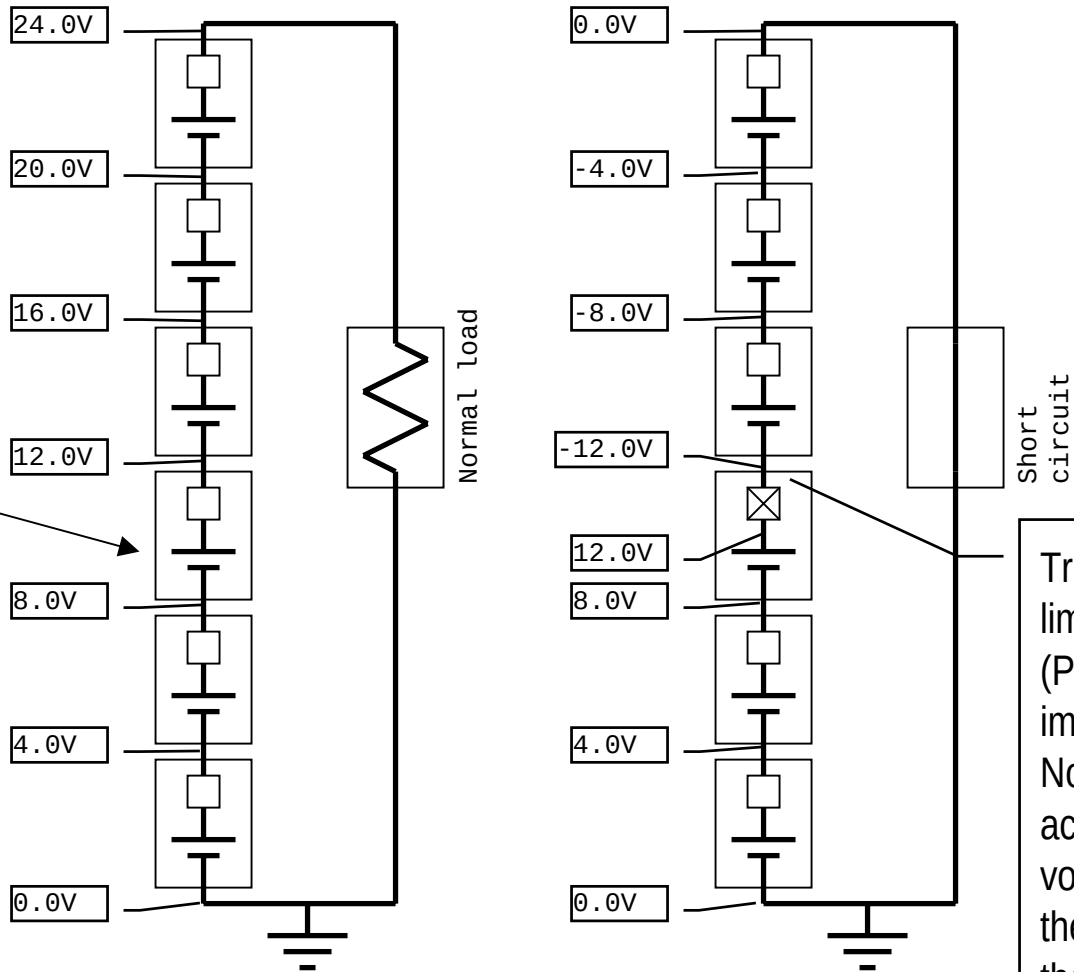
Notes:

A. More than two battery cells per substring may be used.

B. More than 3 substrings may be used.

C. The example battery system presented here is of limited size and complexity for clarity.

High voltage on PTC during Short Circuit

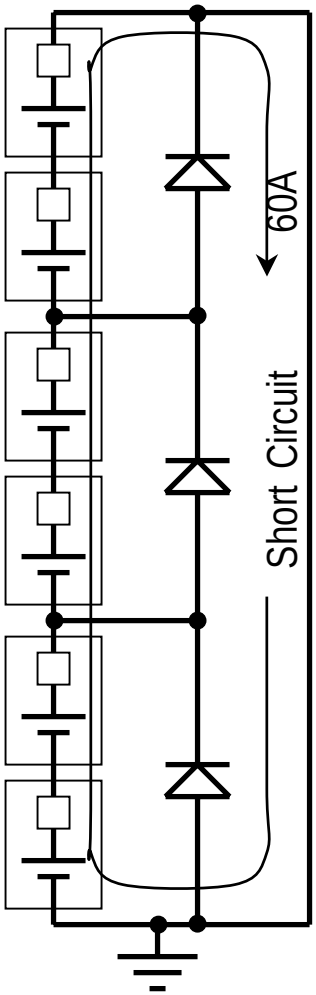


Battery Cell with built-in short circuit protection device (PTC).

Example uses Li-Ion cells charged to 4V per cell.

Tripped current limiting device (PTC) in high impedance state. Note that it has 24V across it. This voltage may exceed the voltage rating of the device.

Trip Sequence – initial stage

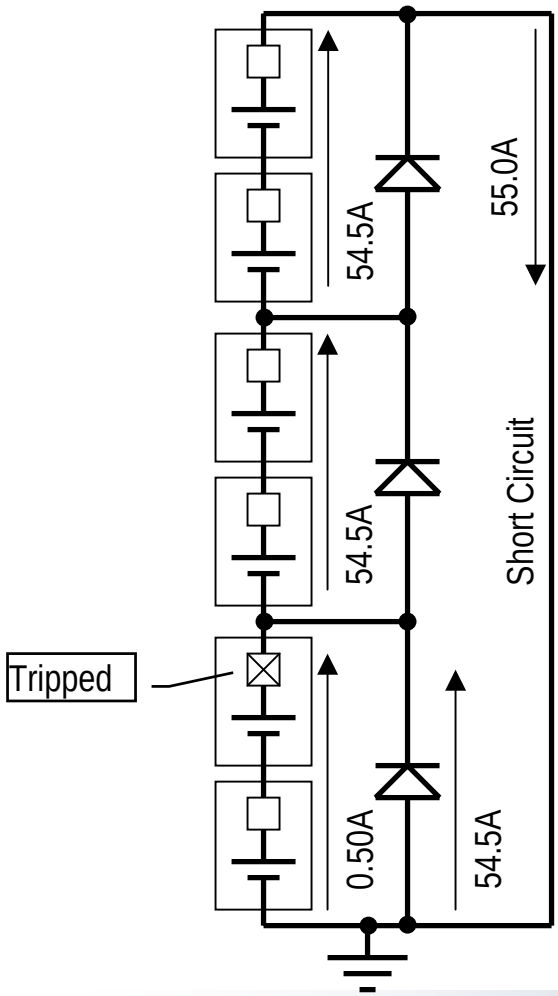


Short circuit appears. All PTC short circuit protection devices start heating up.

Notes:

1. No current through diodes yet.
2. Short circuit current is limited by cell impedances and cold PTC impedances.
3. This stage may last several seconds, depending on PTC characteristics.

Trip Sequence – later stages



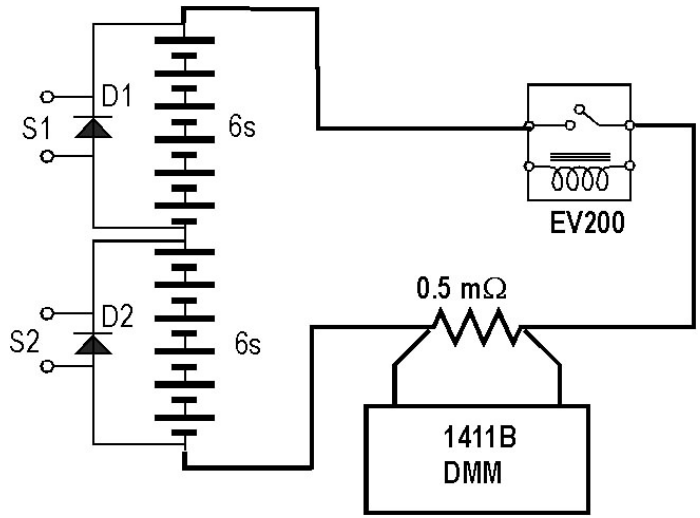
First PTC trips, shunting current through diode.

Note:

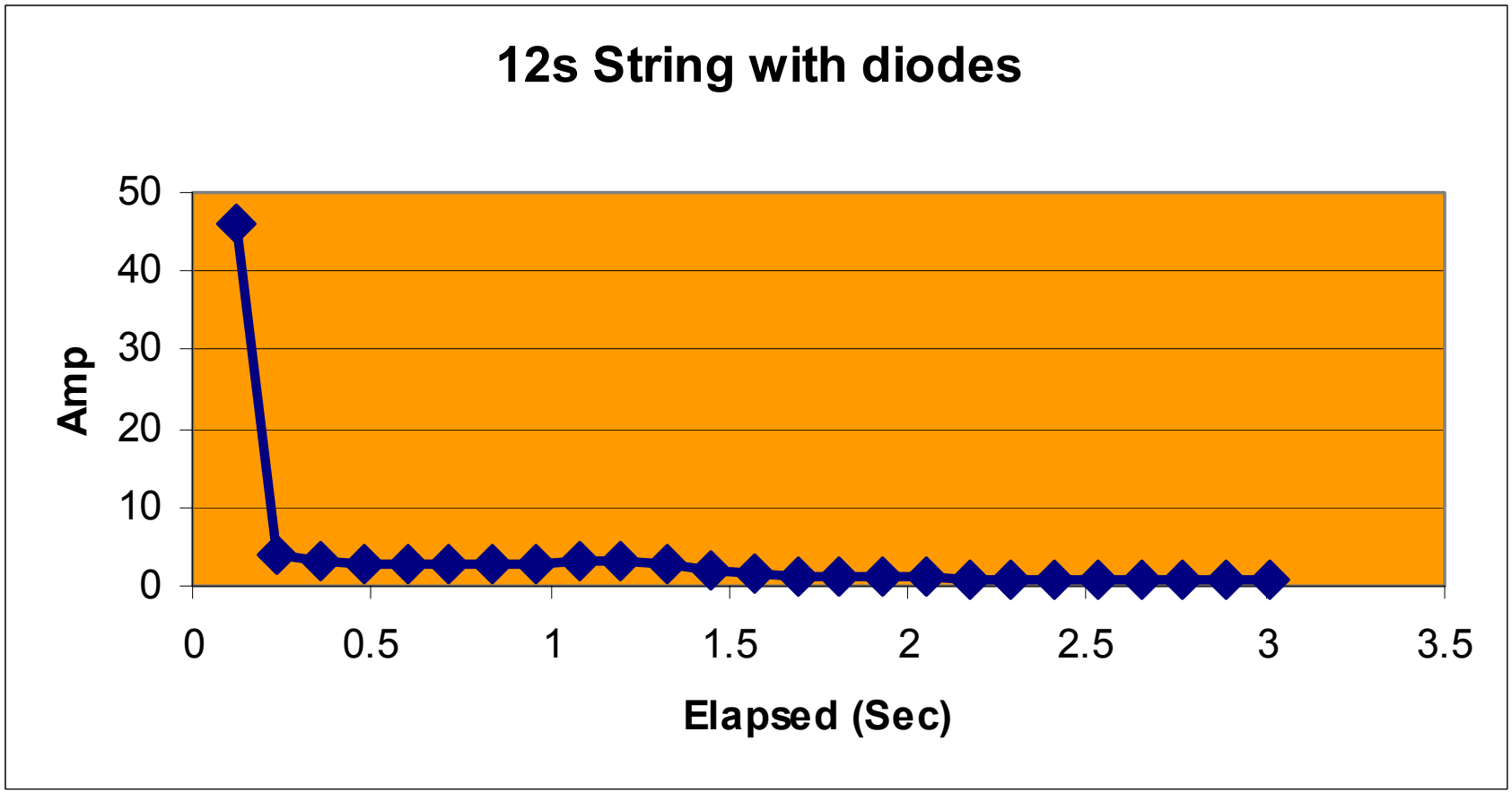
1. Small current flows through shorted substring, keeping PTC tripped.
2. Current through short is reduced, but not dramatically, since the current is still basically limited by the cell impedances. Other substrings have not tripped yet.
3. Maximum voltage across tripped PTC is two cells worth plus diode drop.
4. Diode takes almost maximum short circuit current until trip sequence is complete.
5. Which substring trips first depends on device tolerances.
6. The other substrings follow.

12s Short-Circuit Test- with diodes

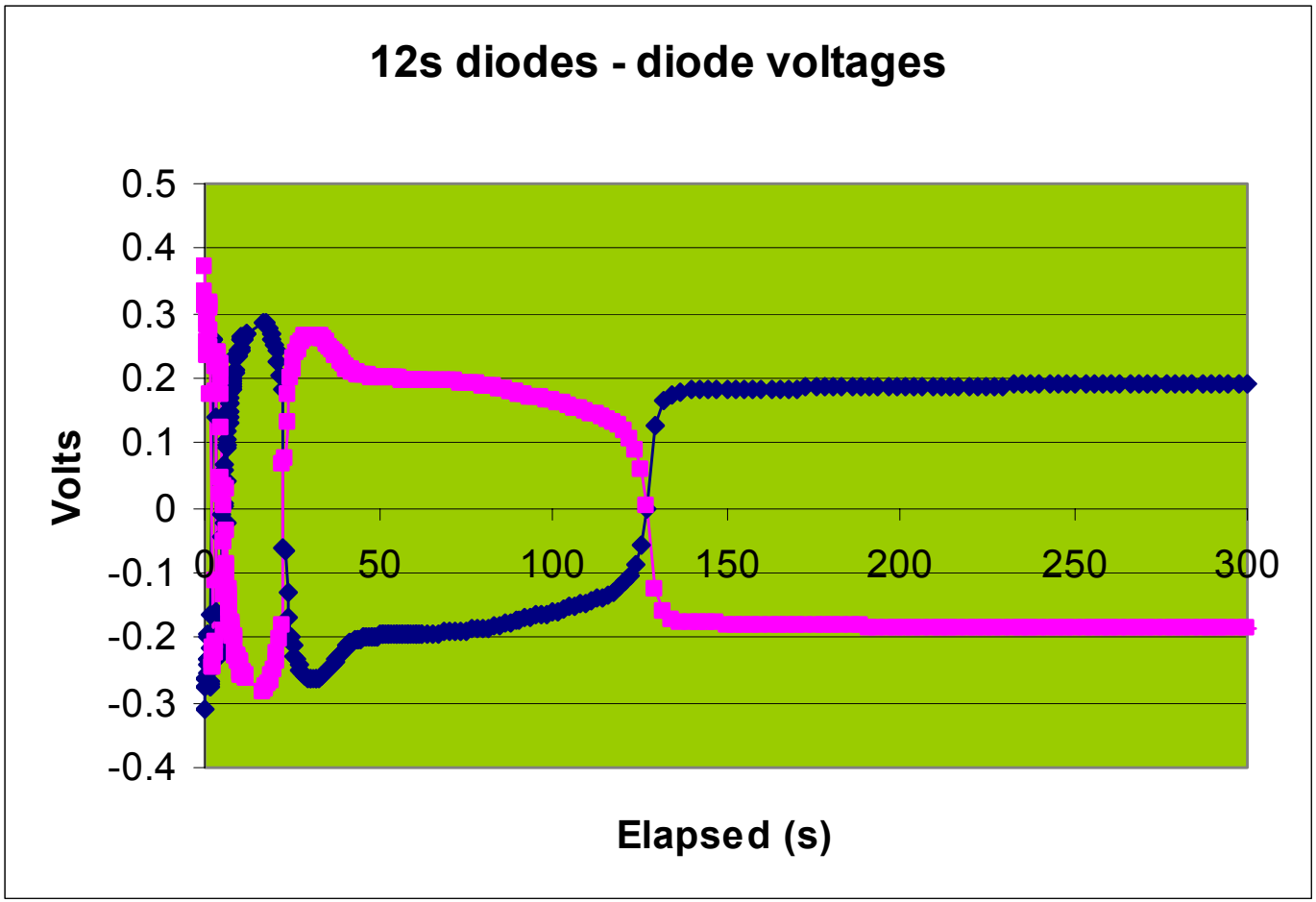
- 12s bundle configuration
- 9 Amp Schottky diodes
- Dead short
- Monitor current and diode voltages



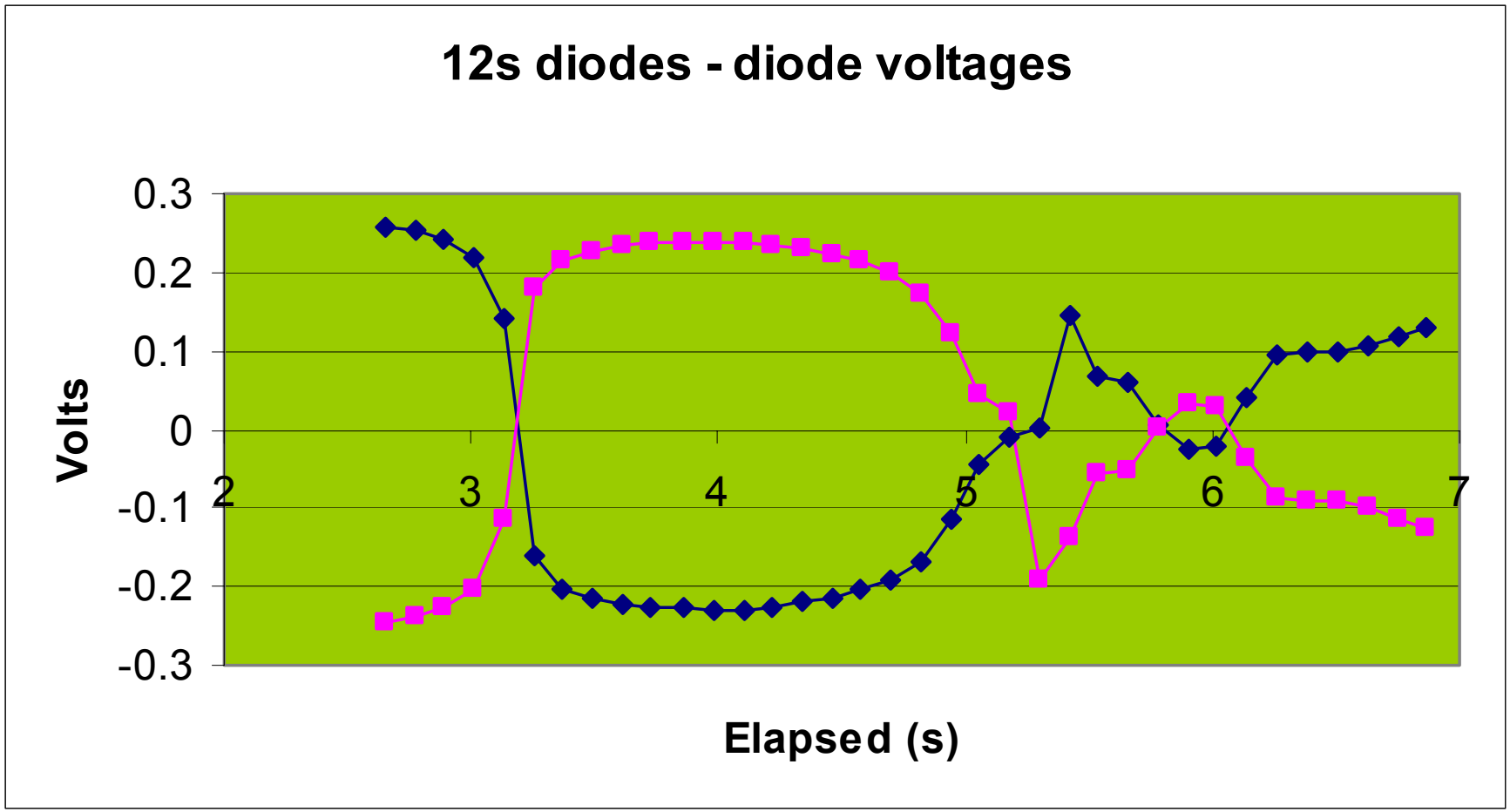
12s Short-Circuit - current



12s Test – Diode Voltage -1

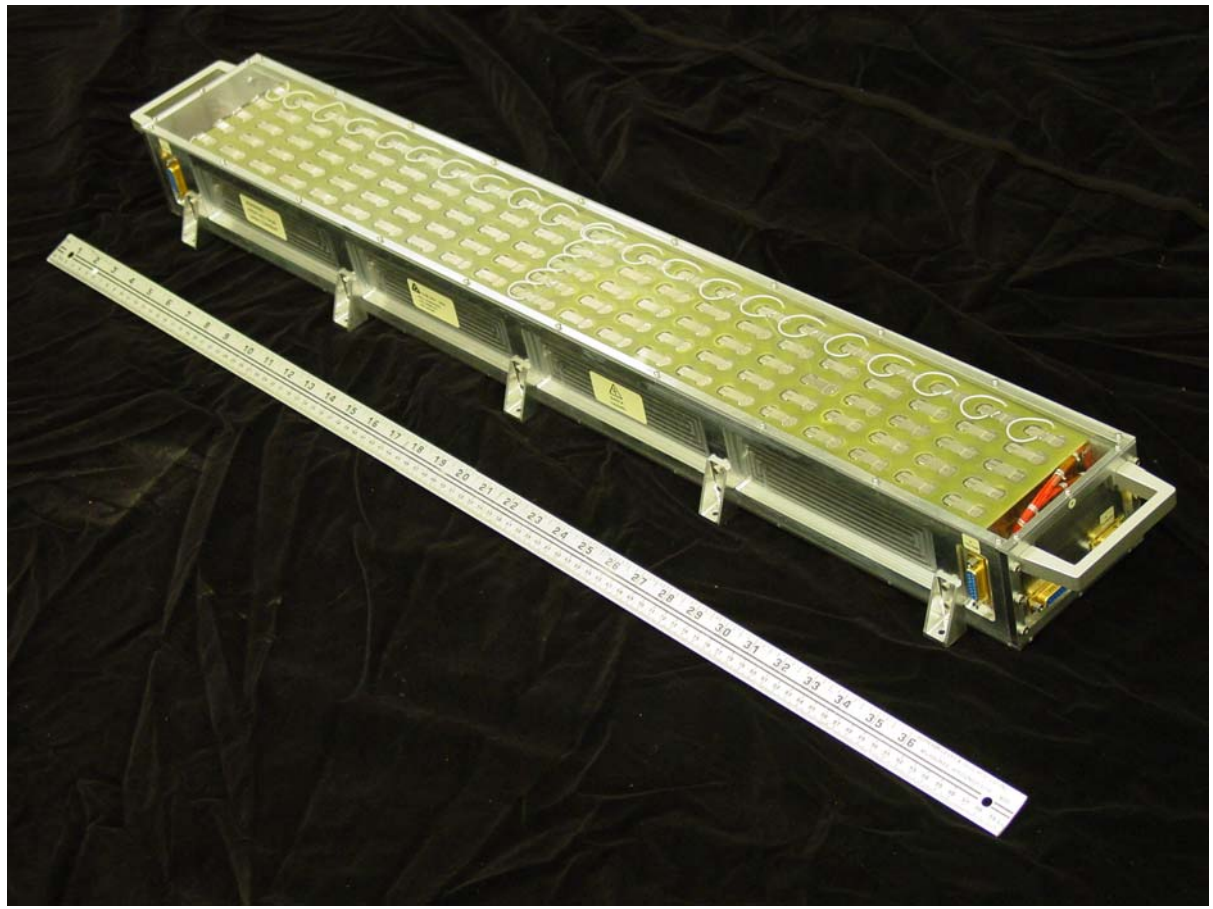


12s Test – Diode Voltage -2

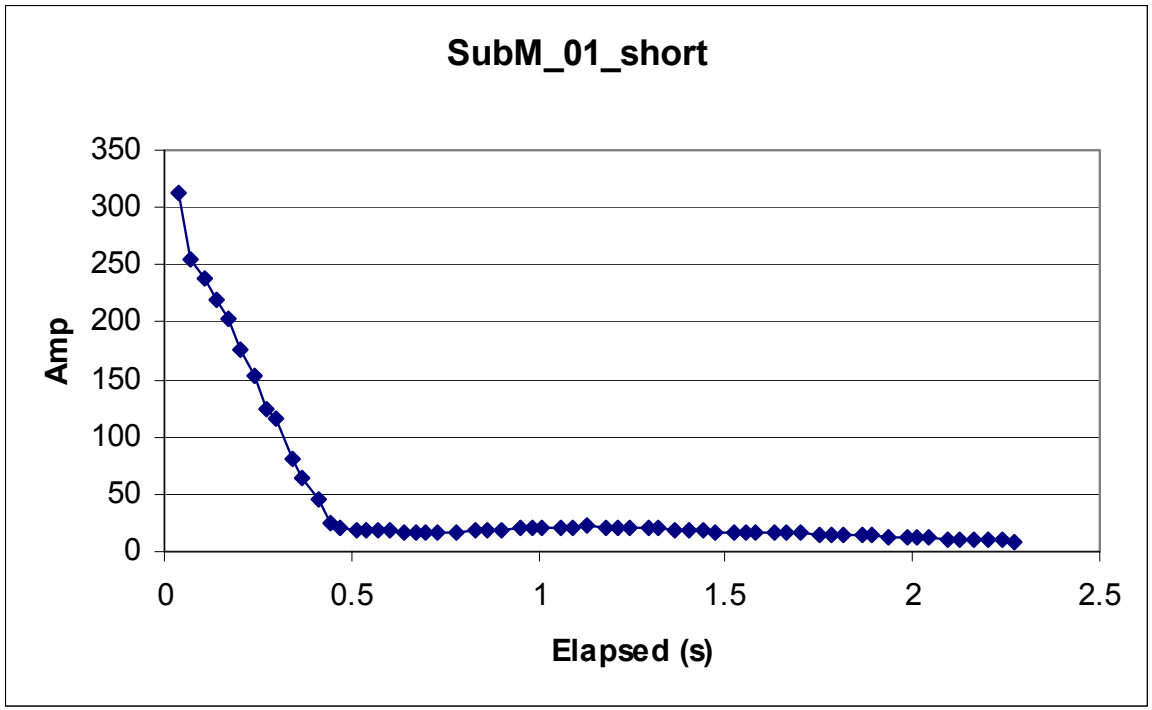


41s x 5p Short-Circuit

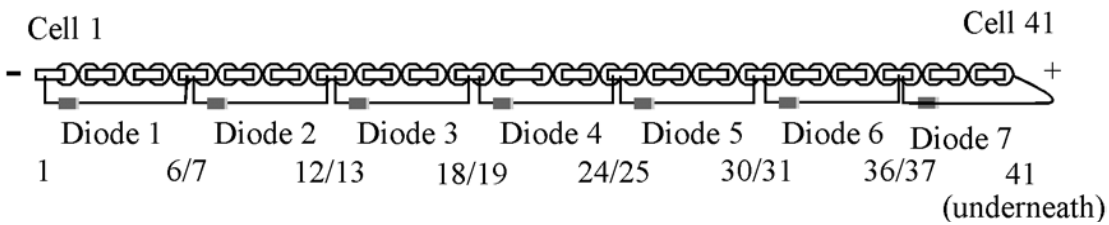
- EAPU GTM
- Charge to 180.4V
- Short
- Successful
  - no damage
  - no venting
  - still works



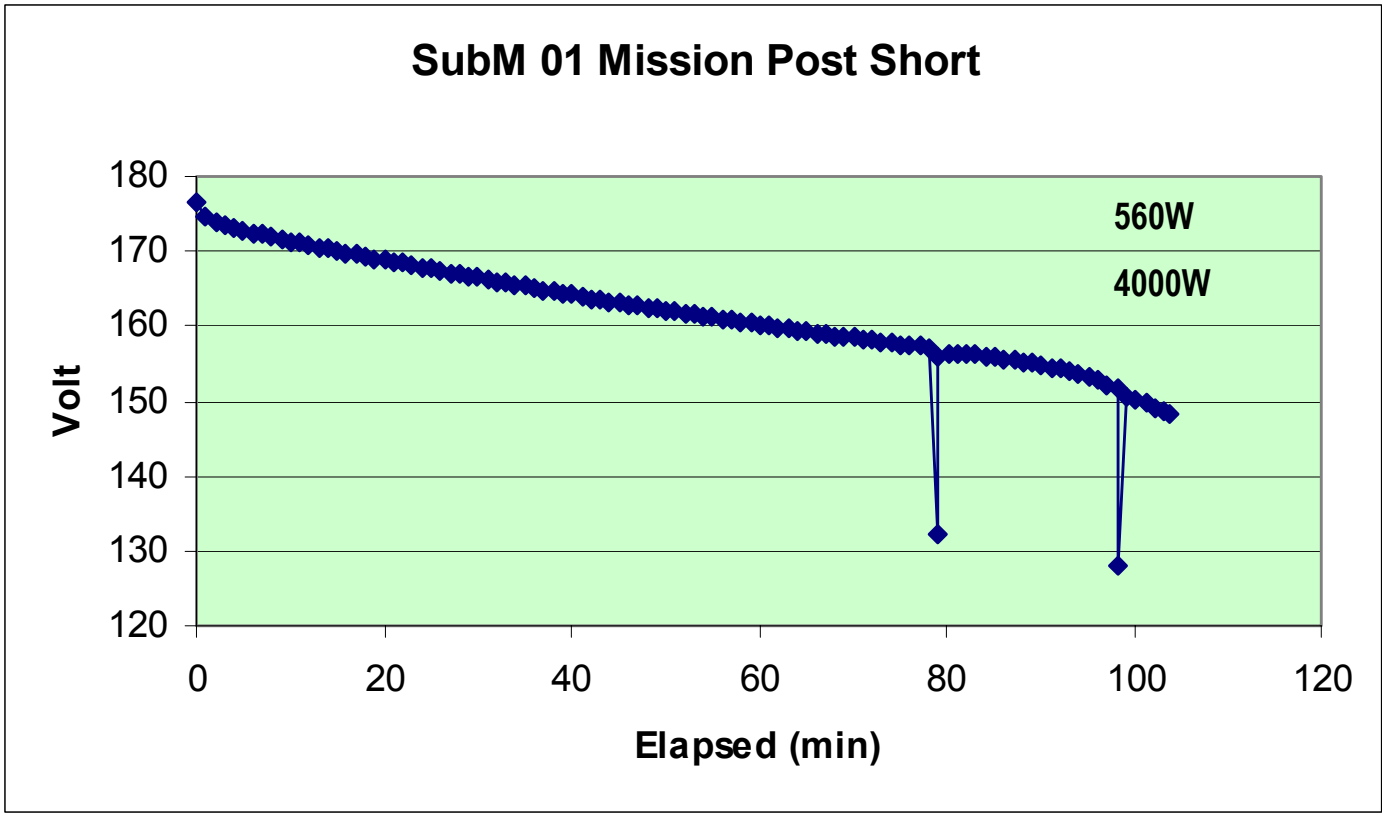
Submodule 01 Short



Short using EV200 relay, 0.5 mΩ Kelvin resistor.



Post-short EAPU Mission Cycle



Battery charged to pre-launch state, including losses

Launch and de-orbit run concatenated

Diode Protection Scheme - summary

- Advantages:
  - Increases robustness
  - Protects PTCs – allows them to operate normally
  - Allows operation of cells within voltage environment that they were designed for (short series strings, not long series strings).
  - Bypass diodes across substrings help with other high impedance cell conditions (tripped CID, shutdown separator, discharged cell) by holding down max. voltage.
- Disadvantages:
  - Added components increase size, weight and complexity.
  - Diodes sized to take maximum current are not small.
    - Testing will allow us to optimize diode sizing.

Conclusions

- We have gained considerable insight into cell PTC operation
  - Maximum voltage rating of the PTC at 65°C is 31V
  - Once tripped, PTCs are more tolerant to higher voltages
- Even without diode protection, a short with a small-cell battery is not a violent event
- The diode protection scheme works
  - Using commercial Schottky diodes
- The battery is usable afterwards
- The scheme is being implemented on current modules
- Further short-circuit tests are planned
  - To validate function in worst-case conditions
  - To better understand cell failure mechanisms

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Technologies, LLC

POWER Subsystems

C/NOFS BATTERY AND MAGNETIC PROPERTIES

William D. Cook

Dr. William Studyvin

Eagle-Picher Technologies LLC

Satellite Background

- Main mission to forecast the onset of Equatorial Ionosphiric Causing Scintilliation
- 16AH 28Volt 11 Cell Battery System utilizing CPV Technology
- Program started early 2001.
- 1 year mission with a three year goal 1700 cycles with an average DOD of 34%
- -5°C to +20°C Operational Temperatures
- Satellite weight 390Kg 6 Ft Tall 44 inches in diameter

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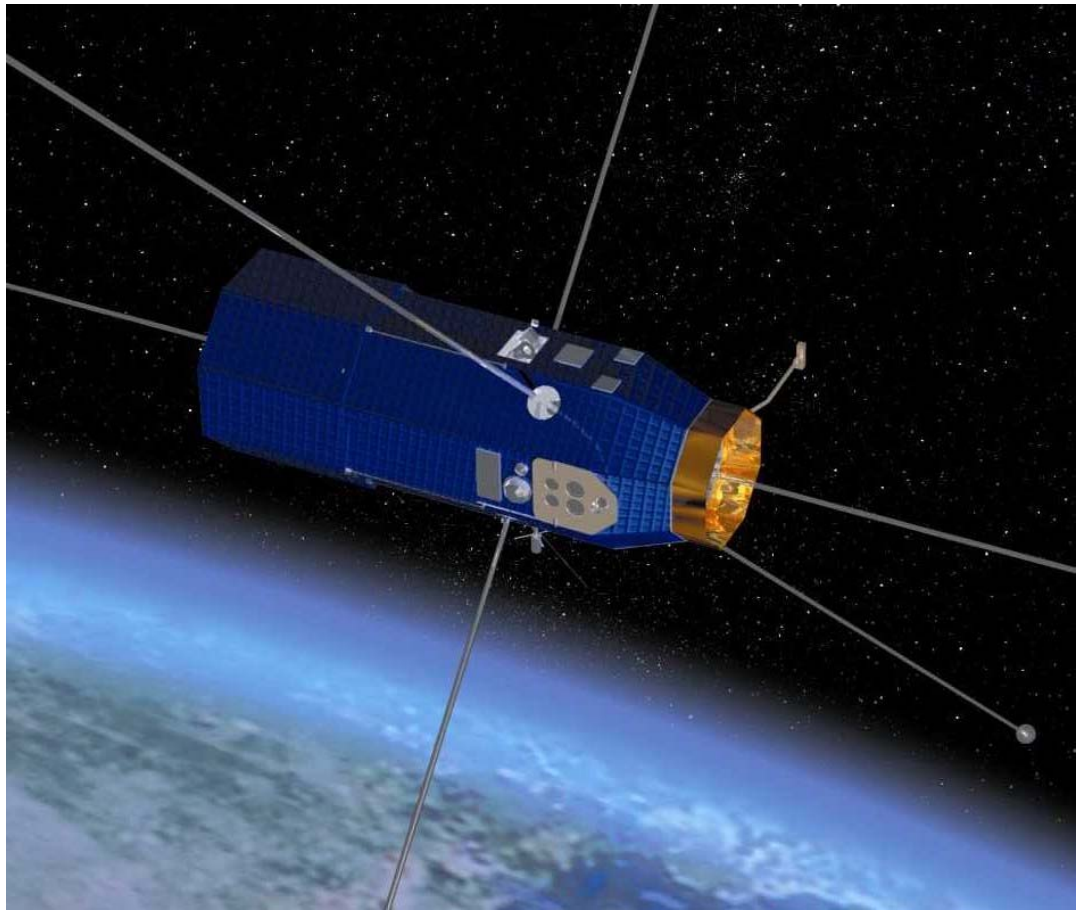
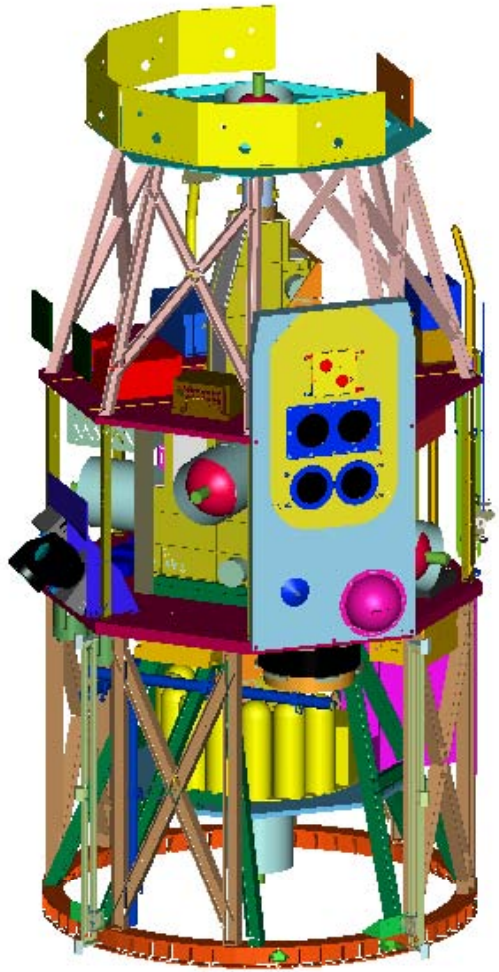
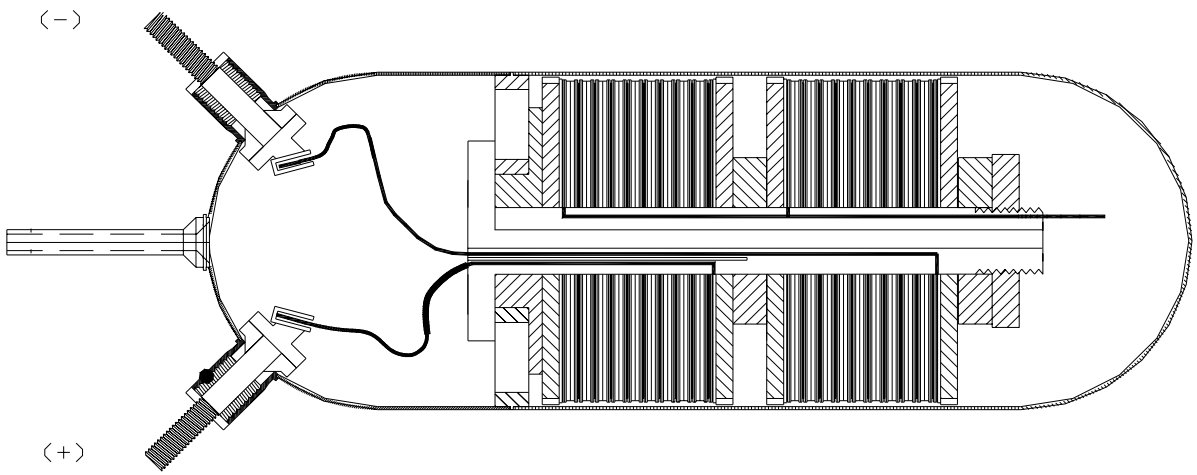
C/NOFS SATELLITE





CELL DESIGN

- Nickel-Hydrogen Electrochemistry
- Dual Stack Design
- .026 mil thich Pressure Vessel
- Two Layer Zircar
- 30 min slurry with 80% porosity
- .190 -32 Rabbit Ear Terminal Design
- MEOP of 900 PSI



CELL DESIGN SLEEVED

C/NOFS BATTERY DESIGN

- Eleven Cell CPV Design
  - Bypass Diode Modules
  - Strain Gage circuit with amplification
  - Radiator cooling during ground support
  - Unique Circular Design
  - 28 Volt 16AH System
  - One power and one telemetry connector

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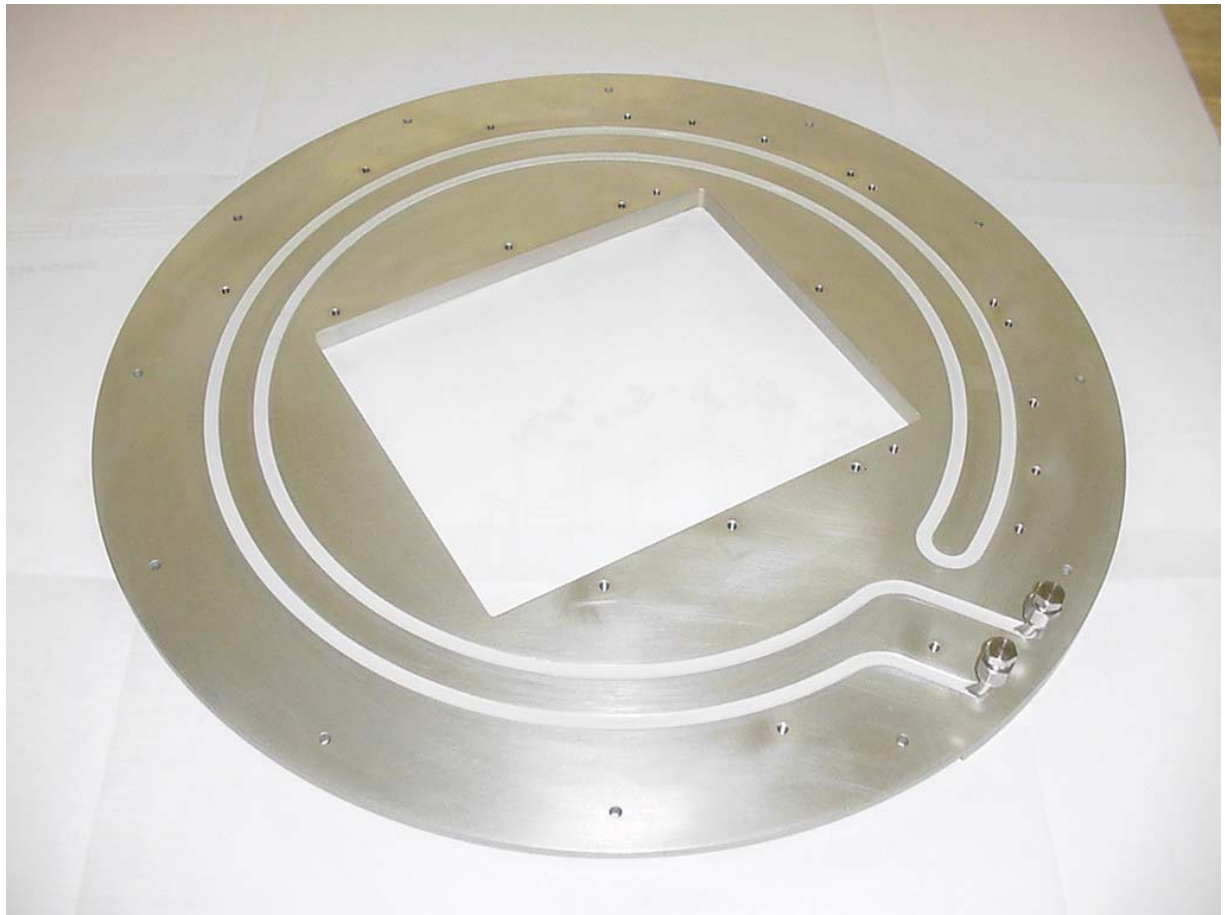
C/NOFS BATTERY DESIGN

C/NOFS RADIATOR PLATE



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BATTERY QUALIFICATION

• 10°C Capacity Test	C/2 to 22VDC
• Random Vibration	9gRMS 140 sec.
• T-vac 8 CYCLES	-10°C TO 25°C
• 10°c Charge Retention	72 Hr Open Circuit
• -5°C Capacity Test	C/2 to 22VDC
• 0°C Capacity Test	C/2 to 22VDC
• 10°C Capacity Test	C/2 to 22VDC
• 20°C Capacity Test	C/2 to 22VDC
• Overcharge protection	C/10 for 24 Hrs
• Max Discharge 2C 50ms	
• Maximum /charge 16A for 10 min.	
• Magnetic Test	
• Insulation Resistance	
• Continuity Test	

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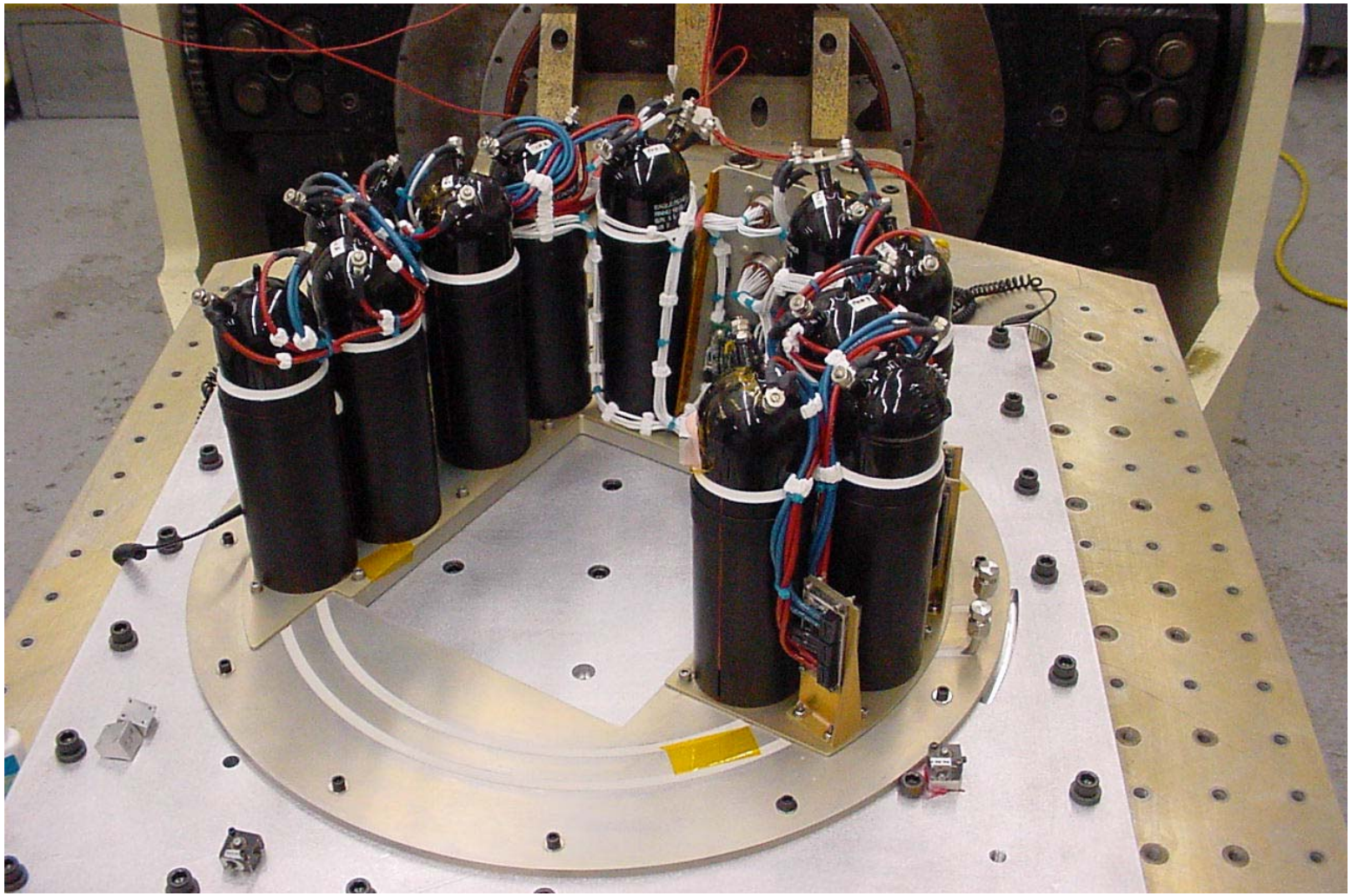
Battery Vibration Test



MAGNETIC TEST SETUP

- Testing to be performed in two modes
  - Pre Gauss (non powered 75% SOC) to establish maximum magnetic induction of the battery with zero current field
  - DC Stray AC Stray (powered 8A discharge) to establish maximum magnetic induction of the battery with the current field present
- Measurements made with Waker Scientific model FGM-402LN
- All Fixtures are non-magnetic
- All support structures are non-magnetic
- Test area must be a known magnetic environment
- The magnetic field strength was measured at a distance of one meter away when the battery was rotated 360 degrees about the three orthogonal axes

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MAGNETIC TEST SETUP

MAGNETIC TEST PROCESS

- Zero out all stray magnetic fields with battery absent to establish a baseline
- Position battery with the axis being measured in the up position in the zero rotation location
- Rotate battery 360 degrees about the orthogonal axis and record the maximum reading and angle.
- Remove the battery and re-measure the stray field.
- Subtract the average stray field from the maximum reading and then convert the Polar Coordinates to Rectangular Coordinates.
- This provides maximum rectangular reading in the three axes
- The resultant vector is then calculated by the following formula:

$$(X^2+Y^2+Z^2)^{1/2} = \text{Resultant Magnetic Impact}$$

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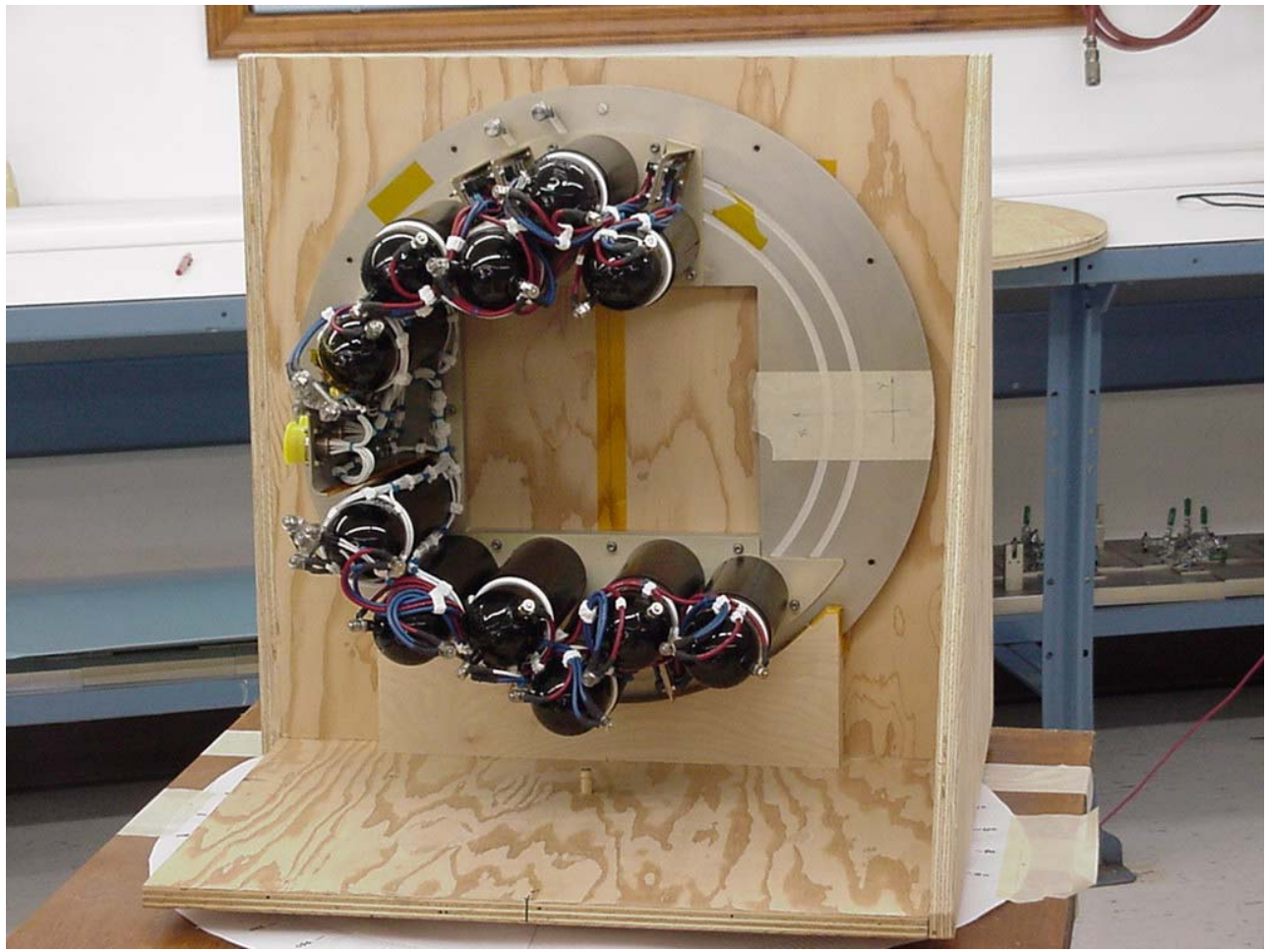
MAGNETIC TEST X AXES

MAGNETIC TEST ANOMALIES

- **Actual zeroing out effect of the earth's magnetic field was very difficult because of the magnetometer sensitivity**
- **The characterization process of the battery assembly revealed that individual cell magnetic dipoles do not resolve into a single dipole at a distance of one meter.**

MAGNETIC TEST Y AXES



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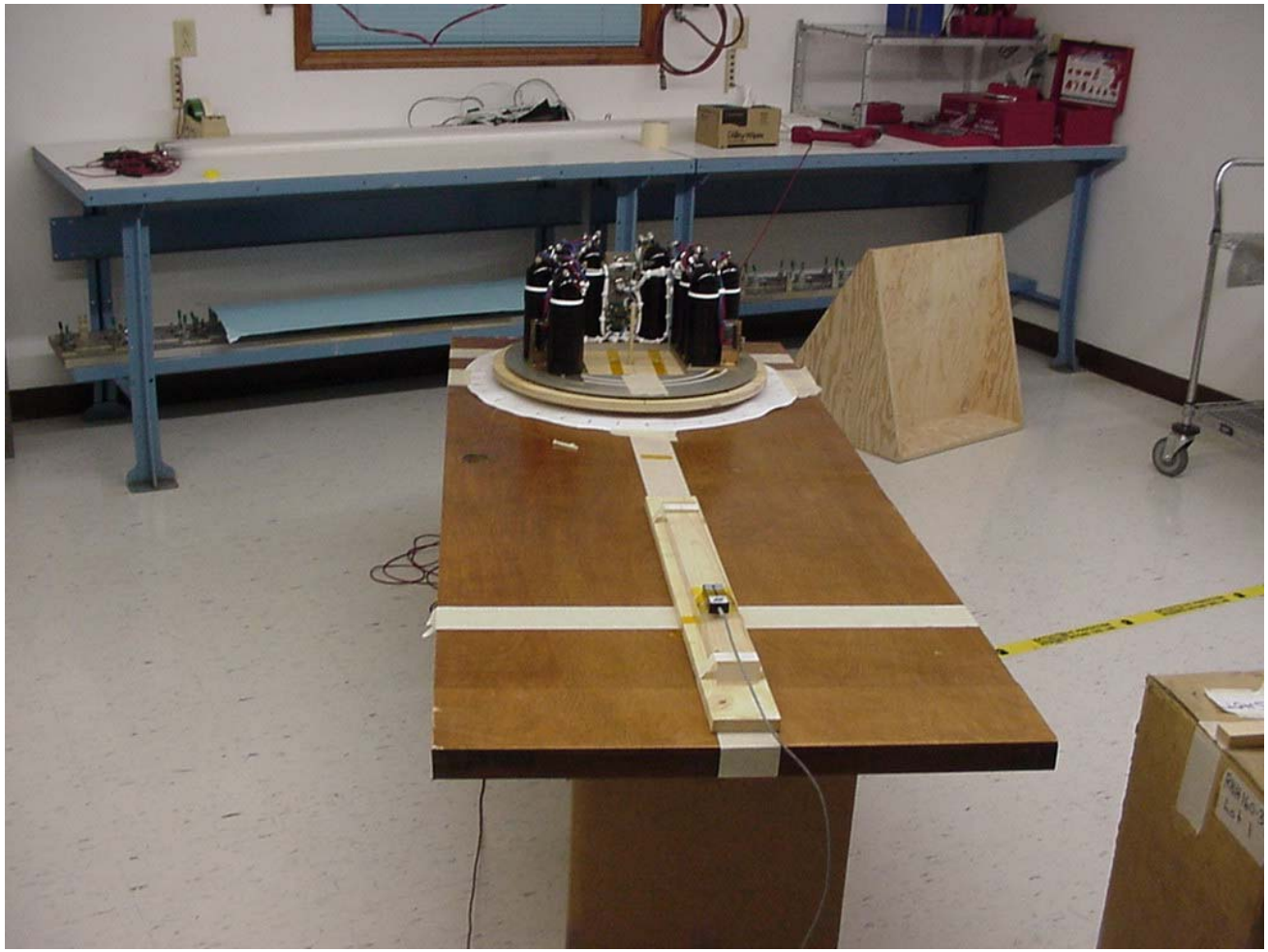
MAGNETIC TEST Z AXES



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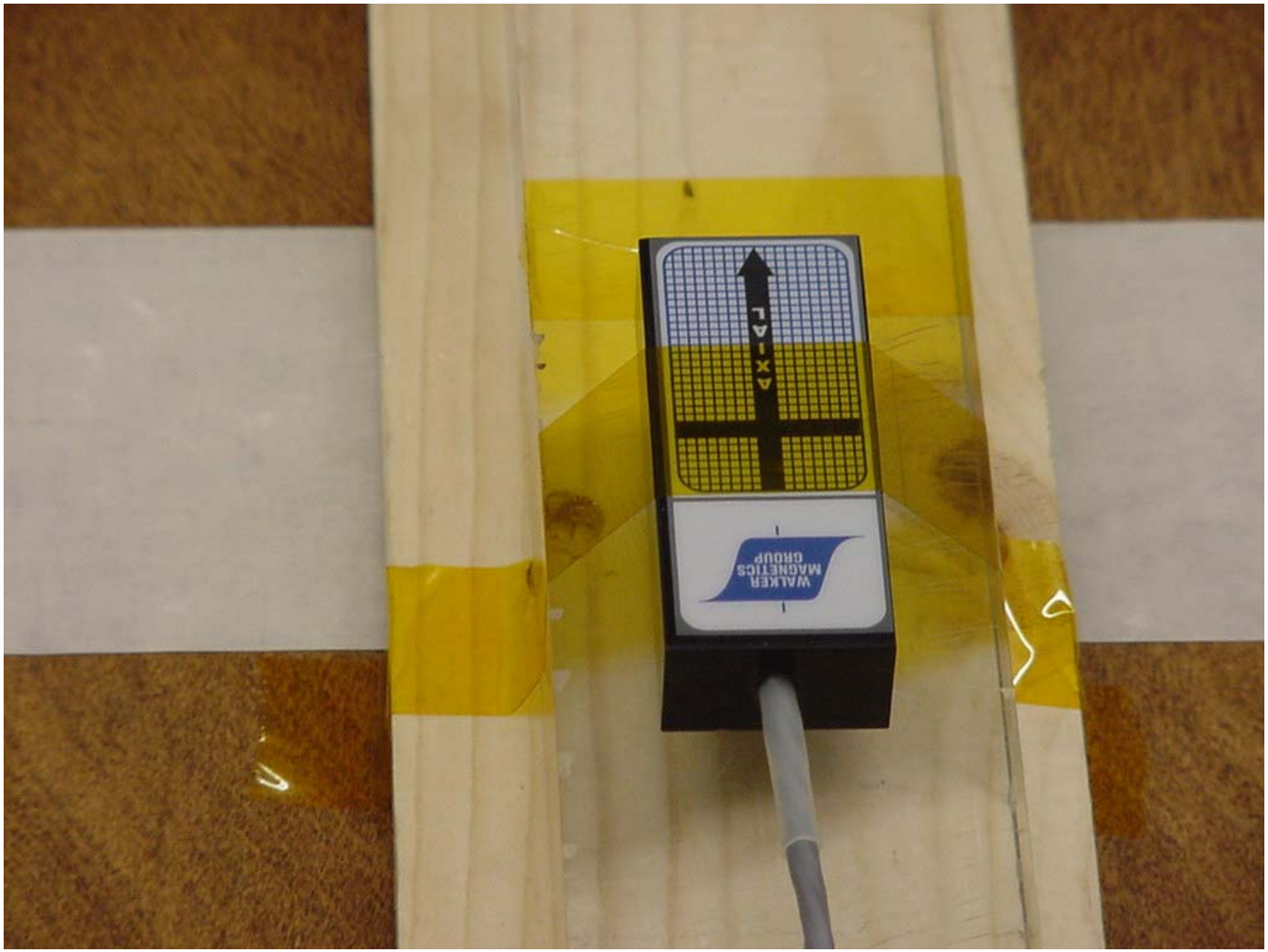
MAGNETIC TEST PROBE



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MAGNETIC PRE-GAUSS RESULTS

SAR10157 CNOFS battery 10/22/02

MAGNETIC FIELD MEASUREMENT, EUT NOT POWERED

Mode Pre Gauss

	Comment	R	Angle	Angle	Cos	Sin	X	Y	Z
		nT	Deg	Rad			nT	nT	nT
Ambient	No EUT	7							
X Axis		37							
Resulant	1 Meter	30	262	4.57	-0.1392	-0.9903	0	29.71	4.18
Ambient	No EUT	-2							
Y Axis		25							
Resulant	1 Meter	27	205	3.58	-0.9063	-0.4226	11.41	0	24.47
Ambient	No EUT	0							
Z Axis		0							
Resulant	1 Meter	0	262	4.57	-0.1392	-0.9903	0.00	0.00	0
Difference							11.41	29.71	20.30
Maximum							11.41	29.71	24.47
Squared							130	883	599
Vector		40.1							

Test performed 10/25/02

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MAGNETIC DC STRAY RESULTS

SAR10157 CNOFS battery 10/22/02

MAGNETIC FIELD MEASUREMENT, EUT NOT POWERED

Mode DC Stray

	Comment	R	Angle	Angle	Cos	Sin	X	Y	Z
		nT	Deg	Rad			nT	nT	nT
Ambient	No EUT	2							
X Axis		31							
Resulant	1 Meter	29	0	0.00	1.0000	0.0000	0	0.00	29.00
Ambient	No EUT	2							
Y Axis		34							
Resulant	1 Meter	32	340	5.93	0.9397	-0.3420	10.94	0	30.07
Ambient	No EUT	12							
Z Axis		47							
Resulant	1 Meter	35	0	0.00	1.0000	0.0000	0.00	35.00	0
Difference							10.94	35.00	1.07
Maximum							10.94	35.00	30.07
Squared							120	1225	904
Vector		47.4							

Test performed 10/25/02

MAGNETIC POSITIONAL TEST

- Determine the magnetic impact in the satellite location
- During open circuit and discharge
- Battery position fixed same as location in satellite
- Magnetometer probe was positioned to reflect the X,Y, and Z axes
- Located 1.38 m away from battery

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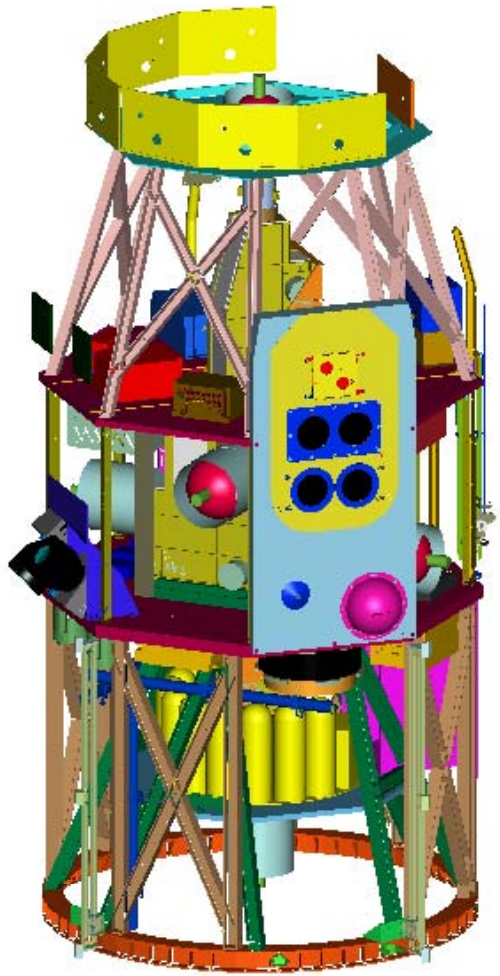
POSITION IN SATELLITE



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MAGNETIC POSITIONAL TEST

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POSITIONAL MAGNETIC RESULTS

Positional test on SAR10157 C/NOFS battery X AXIS

	Ambient	Unpowered	Powered	Composite	Perminate	DC Current
X AXIS	0	-1	4	4	1	5
Y AXIS	-4	7	11	15	10	4
Z AXIS	2	-8	-7	9	10	1
Resultant				18 nT	11.5 nT	6.5 nT

Test performed 10/25/02

Conclusion
Lessons Learned

- Difficulty with small measurement, sensitive to the environment
- Careful interpretation of the measurement
- Additional testing under different conditions to verify results

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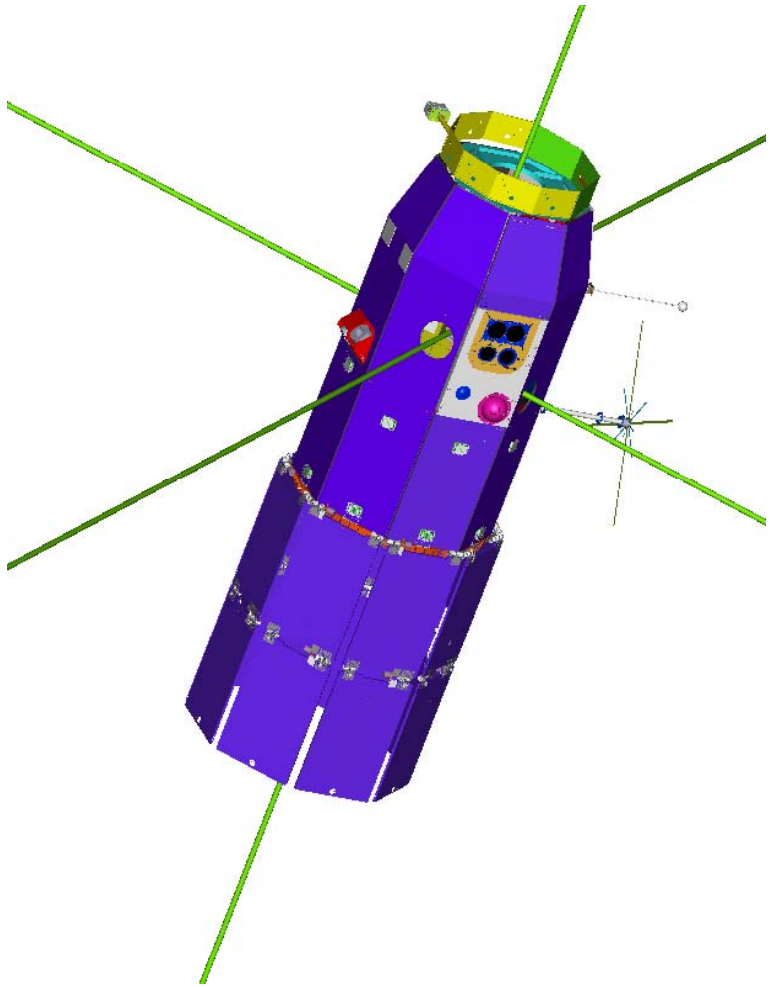
Special Thanks

SpectrumAstro



DEPLOYED CONFIGURATION

Quallion LLC: Powering Medical to Aerospace

Clay Kishiyama
Battery Engineer

NASA Space Battery Workshop
Huntsville, Alabama
November 20, 2002

QUALLION

Overview

- Company Background
- Company Organization
- Product Applications / Technologies
- Quality Systems
- 15 Ah Battery Design
- Battery Data
- Summary

Quallion's Origin

The Alfred E. Mann Entrepreneurial Spirit

POWER

- Quallion LLC 1998

MEDICAL

- Second Sight (Artificial Retina)
- MRG (Artificial Pancreas)
- Advanced Bionics (Neuro-stimulation)
- MiniMed (Insulin Pumps & Glucose Sensors)
- Pacesetter (Pacemakers)

AERO

- Spectrolab (Solar Cells)
- Heliotek

1950 1960 1970 1980 1990 2000

QUALLION

Historical Highlights

1998
- Quallion LLC Founded
- External Li-ion Batteries for Cochlear Devices

1999
- Implantable Li-ion Batteries for Neurostimulators

2000
- Manufacturing Plant Setup
- ATP $8.4M Co-Development of Injectable Li-Polymer Battery with Battery Management Circuit
- Prototyped High-Rate Capability (>10C rate) 18650 cells for DOE

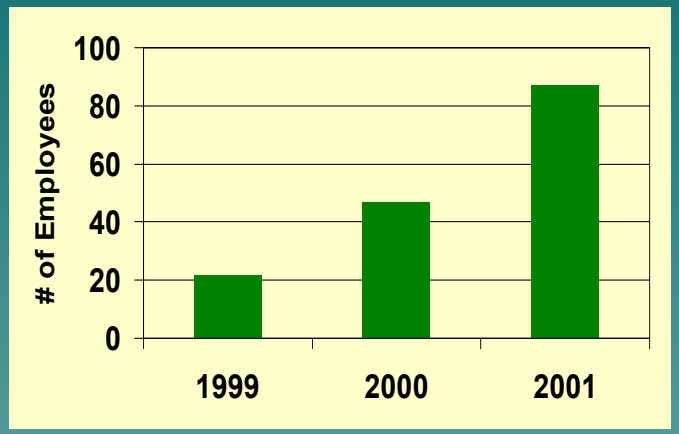
2001
- Li-ion Batteries Production for Medical Applications exceeded 30,000 units

2002
- Shipped 15Ah Satellite Cells
- New Electrolyte Systems
- Large Battery Applications
  - Aerospace
  - Combat Hybrid Vehicles
  - Robotics
  - LVAD/TAH

2003+
- Large Battery Prod
- Polymer Technology
- ISO 9001 Certification
- FDA Component Reg.

QUALLION

Quallion Organization



Facilities

HQ, R&D, Mfg:
44,000 ft² total
2,300 ft² Clean/Dry Room
(Class 10,000; -40°C d.p.)

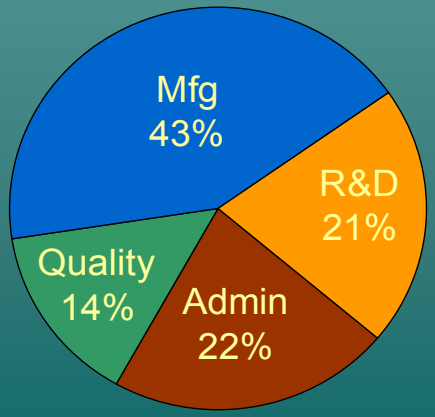
Al Mann
Chairman & CEO

Hisashi Tsukamoto
President & CTO

Director
R&D

- Advanced Material
- Advanced Battery
- Prototyping

General
Administration



Werner Hafelfinger
COO
Operations

- Business
- Product Development
- Quality Systems
- Manufacturing

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Company Strategy:

- **Vertically Integrated**
  - In-house active material & electrolyte development
  - Product Design
  - Prototyping capabilities
  - Unique battery technologies
  - Precision Manufacturing
- **Fundamental Research**
  - Collaborations with National Laboratories and Universities
  - Strategic alliances with suppliers

- **Quality**
  - High reliability design
  - Superior cell performance
  - Enhanced safety attributes
  - Secure domestic material sourcing
- **Flexibility**
  - Custom-designs
  - Custom-packaging
- **Speed to market**
  - Rapid prototyping
  - Streamlined product development
  - Flexible manufacturing
  - Application support

Customer Focus

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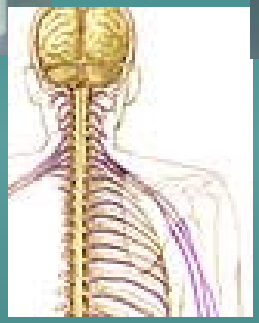
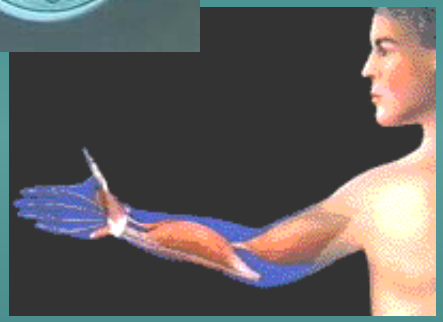
Product Applications – Implantable Devices





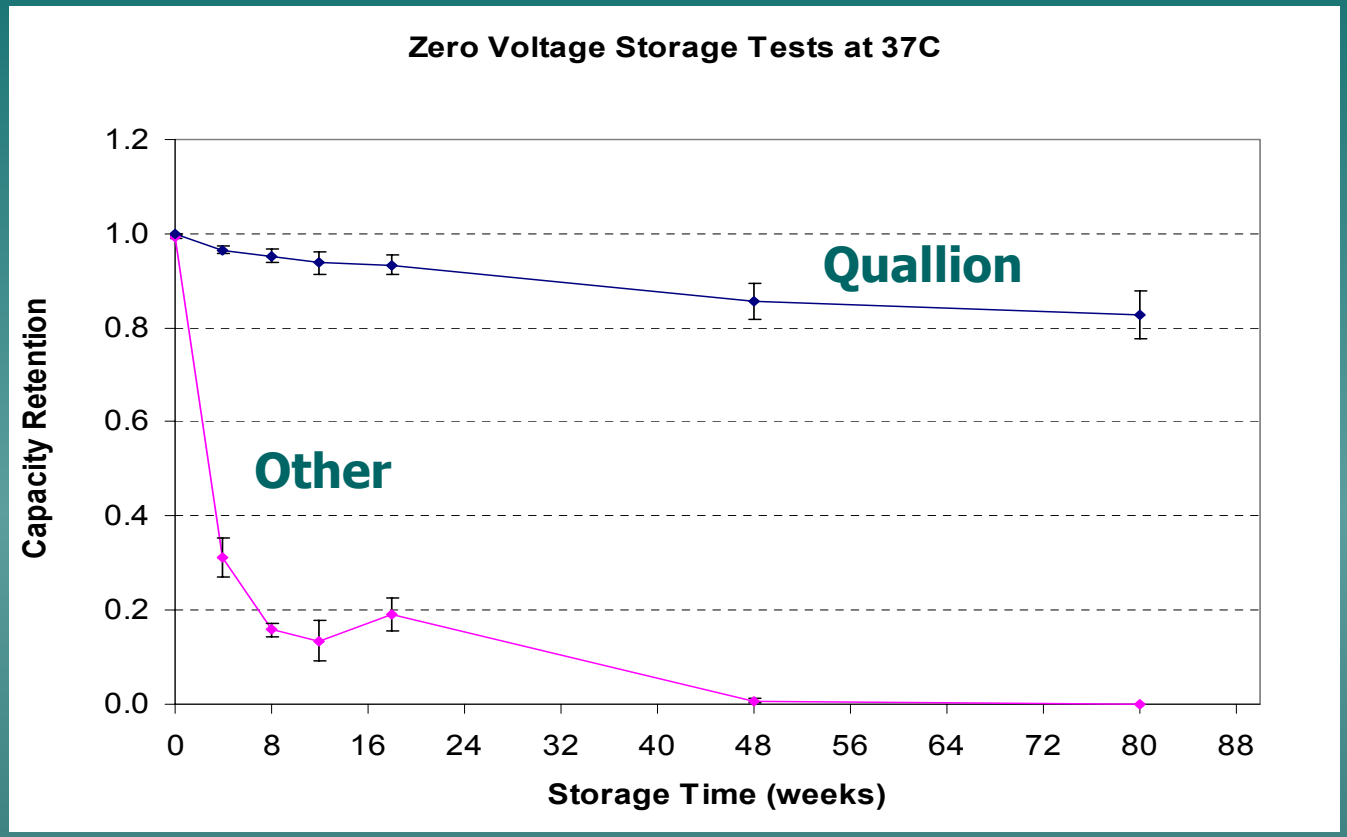
Implantables …

- Biocompatible material
- Hermetically sealed
- Long calendar life
- Long cycle life

Application oriented …

- Custom shape & size
- Remote Charging
- Protection Circuitry
- Maintenance Free

Zero-Volt™ Storage Capability



0-V storage Testing

1. Initial cycle
2. Connect 68 Ohm resistor and store at 37°C
3. Cycle after storage
4. Compare discharge capacities before and after storage

In many applications, the battery can expect long periods of unattended storage, sometimes at elevated temperature.

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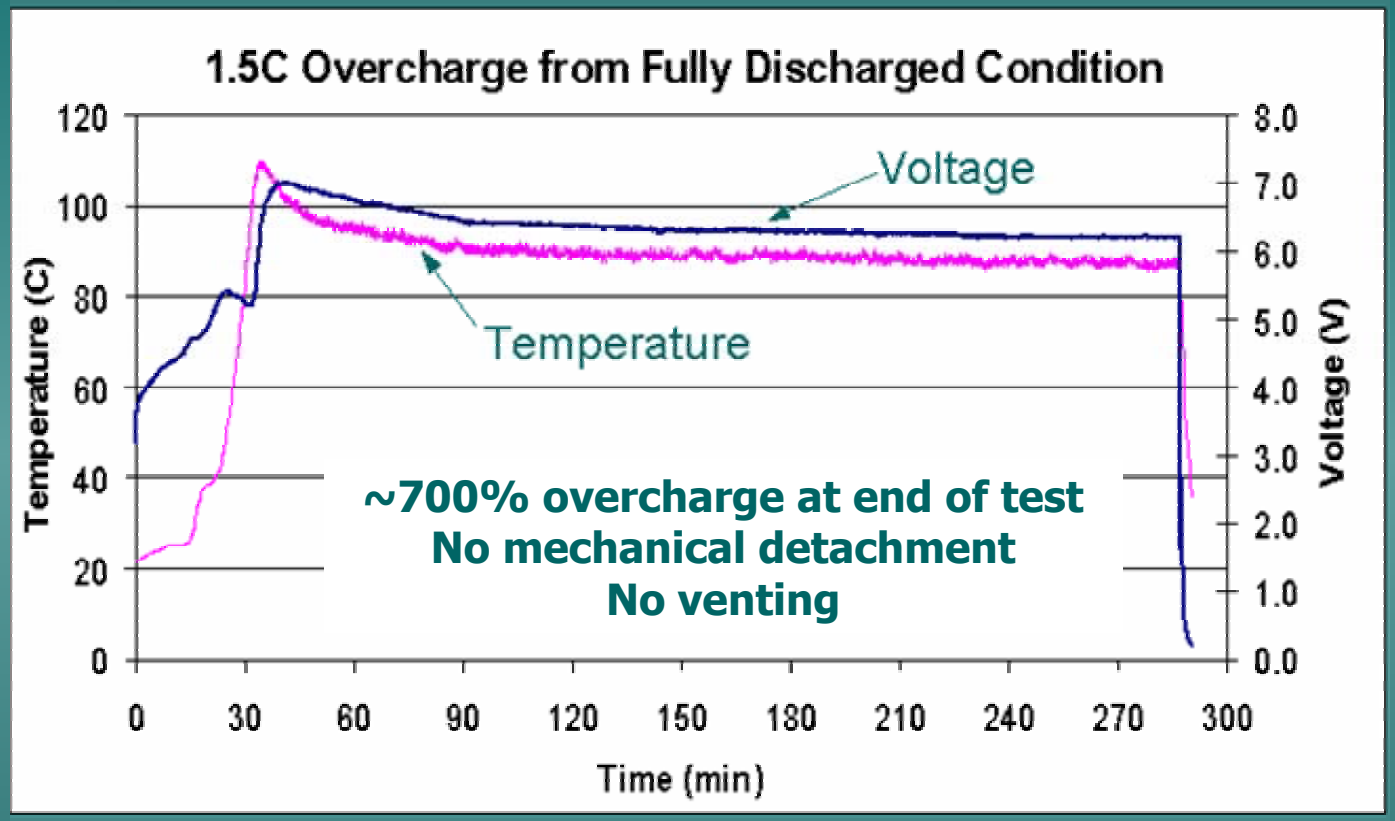
Overcharge Safety Designs



Quality Manufacturing

- **Quality Control**
  - Process & Component Traceability
  - FDA Compliant Documentation
  - Continuous Operator Training
  - Approved Supplier List
  - Retained Samples

Product Applications

– Aerospace, Military, Transportation

Aerospace …

- **Long calendar life**
- **Long cycle life**
- **High Energy Density**

Application oriented …

- **Custom Packaging**
- **Protection Circuitry**
- **Maintenance Free**

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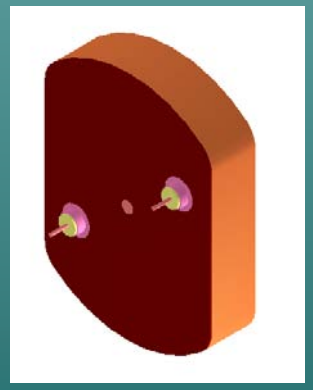
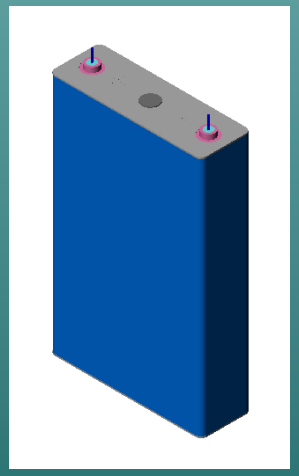
Large Battery Program

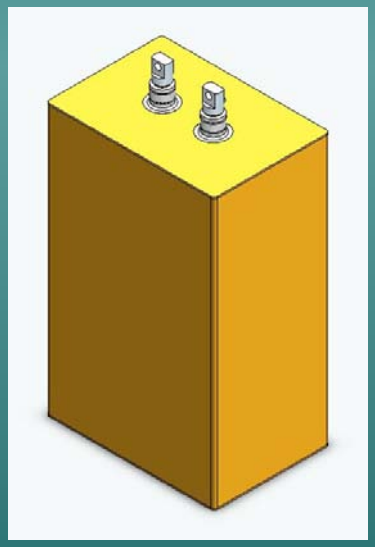
- Prismatic stack design
- Modular for scalability
- High energy density



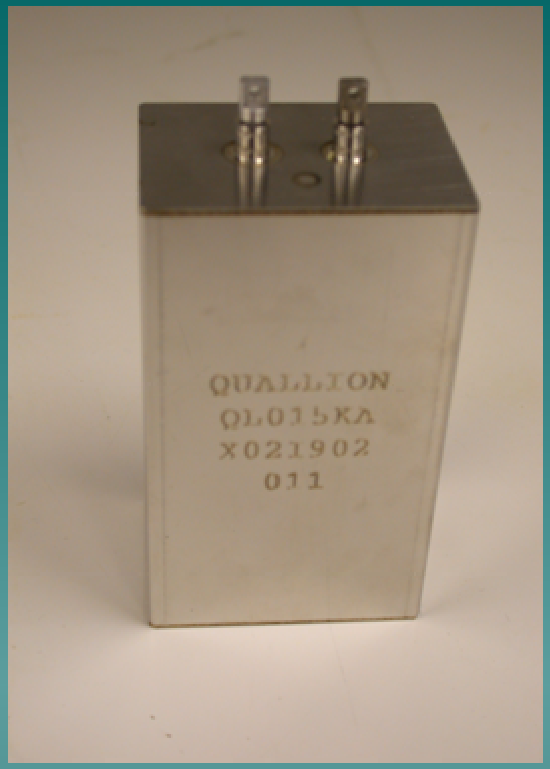
165 mAh



700 mAh



15 Ah

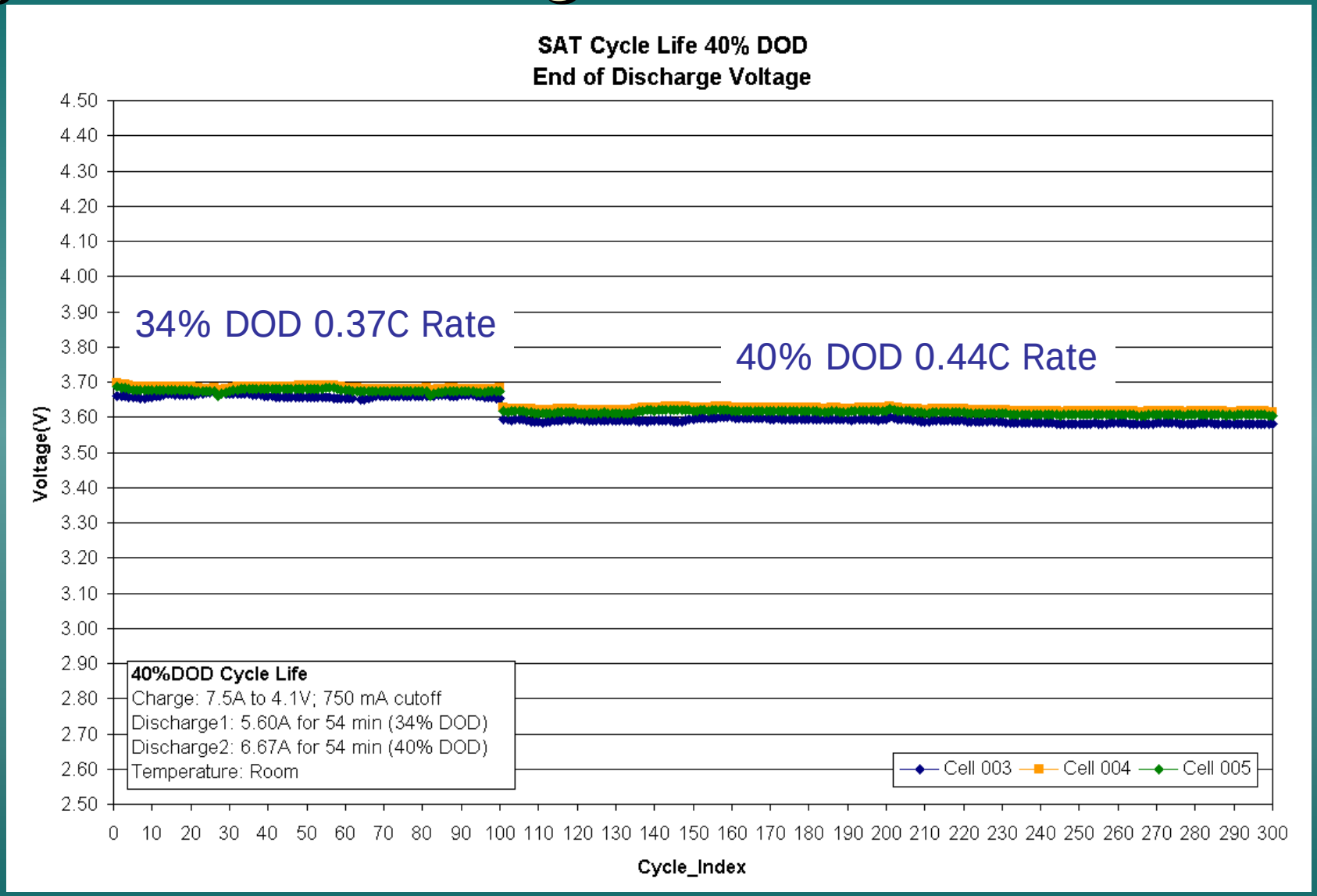


QL015KA Aerospace Cells

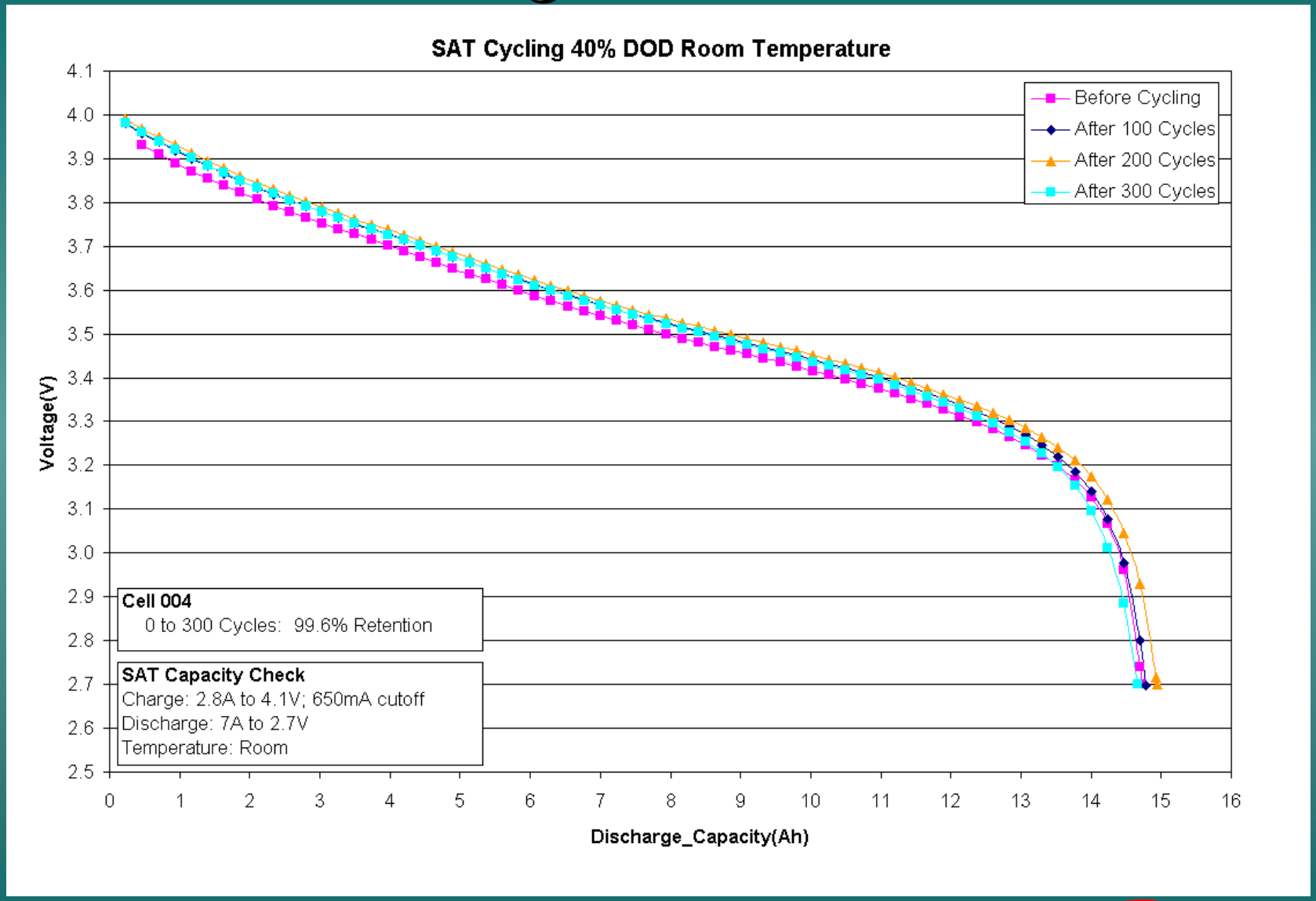
- Dimensions: 8.8 x 5.5 x 3.8 cm
- Casing: Stainless Steel
- Weight: 450 grams

- Capacity (BOL): 15 Ah
- Internal Resistance: 4 mΩ
- Weight Energy Density: 120 Wh/kg
- Volumetric Energy Density: 300 Wh/L

Cycle Life Testing



Cycle Life Testing



Long Cycle Life Chemistry

1C Rate, 40% DOD, Room Temp

Dimensions:

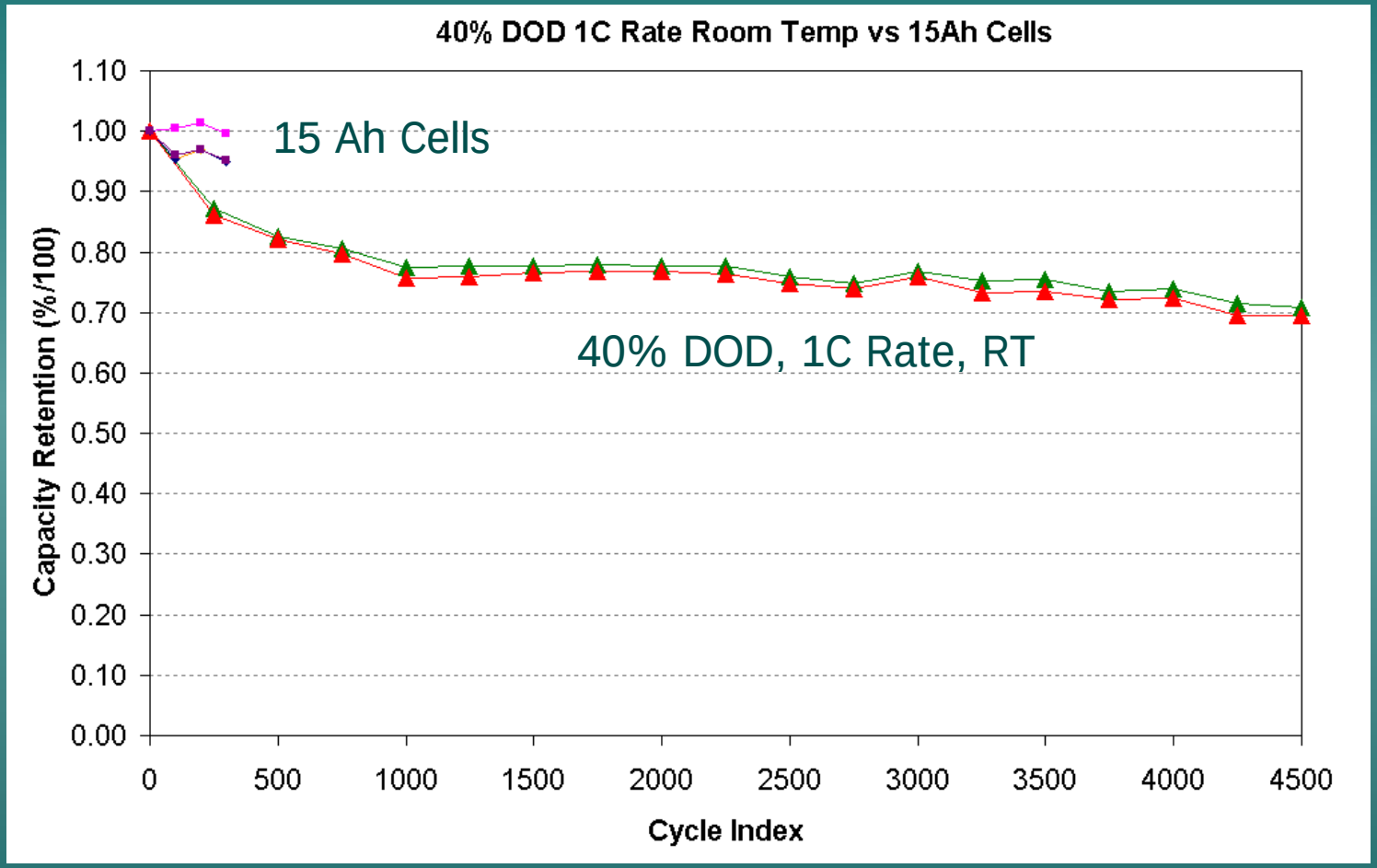
26 mm tall

17 mm wide

5.5 mm thick

130 mAh

2.5 - 4.0V



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Future Work

- **Future Plans**
  - Testing
    - Performance
    - Mechanical Stress
    - Safety
  - Modular Design Strategies
  - Battery Chemistry Platforms
    - Polymer Technology
    - Advanced Active Material

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In Summary

- **Specialty Applications**
  - Medical, Aerospace, Military
- **Vertically Integrated**
- **Fundamental Research**
- **Medical Grade Quality Systems**
- **Large Battery Development**
  - **15 Ah and larger**
  - **Polymer Technology**

QUALLION

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Verification Results of Life Estimation Method for JSB Aerospace Lithium-Ion Cell

Takefumi Inoue, Nobutaka Imamura, Hiroaki Yoshida, and Minoru Mizutani

Japan Storage Battery Co., Ltd.

Masayoshi Goto

Mitsubishi Electric Corporation

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Contents

1. About our cells for space application

2. Life calculation method

3. Verification of our calculation method

   by comparison with experimental data

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JSB's aerospace Li-ion cells

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Cell appearance

JSB has developed large-scale Li-ion Cell with MELCO.

Hermetic Seal for Space Applications

Appropriate design for Long life as Satellite application

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Specifications

Dimensions	Satellite type (Long cycle life type)			Rocket type (High specific energy type)		
	Capacity	Mass	Specific energy*	Capacity	Mass	Specific energy*
H 263mm W 165mm T 50mm	Nominal 183Ah (Rated 175Ah)	4.65kg	146 Wh/kg	Nominal 200Ah (Rated 190Ah)	4.50kg	164 Wh/kg
H 208mm W 130mm T 50mm	Nominal 110Ah (Rated 100Ah)	2.79kg	146 Wh/kg	Nominal 118Ah (Rated 110Ah)	2.72kg	162 Wh/kg
H 123mm W 130mm T 50mm	Nominal 55Ah (Rated 50Ah)	1.50kg	136 Wh/kg	Nominal 60Ah (Rated 55Ah)	1.47kg	153 Wh/kg
Charging voltage	3.98V			4.10V		

* Specific energy: Nominal value at C/2, 15 °C, BOL.

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Summary of

Life Calculation Method of JSB's

Lithium-ion Cell for Satellite Use

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Capacity retention

Capacity retention (%) =

100 – [Calendar capacity loss] - [True cycle capacity loss]

$k_f*(time)^{1/2}$

k_f : constant

$k_c*(cycle)^{1/2}$

k_c : constant

Calendar Matrix test

Temp. : 0, 15, 35 and 60 deg.C

SOC: 100, 80, 60, 30, 5, 1 and 0%

Totally 24 conditions, 36 cells

Cycling Matrix test

Temp. : 0, 15, 35 and 60 deg.C

DOD: 80, 50, 25, 10 and 3%

Totally 20 conditions, 33 cells

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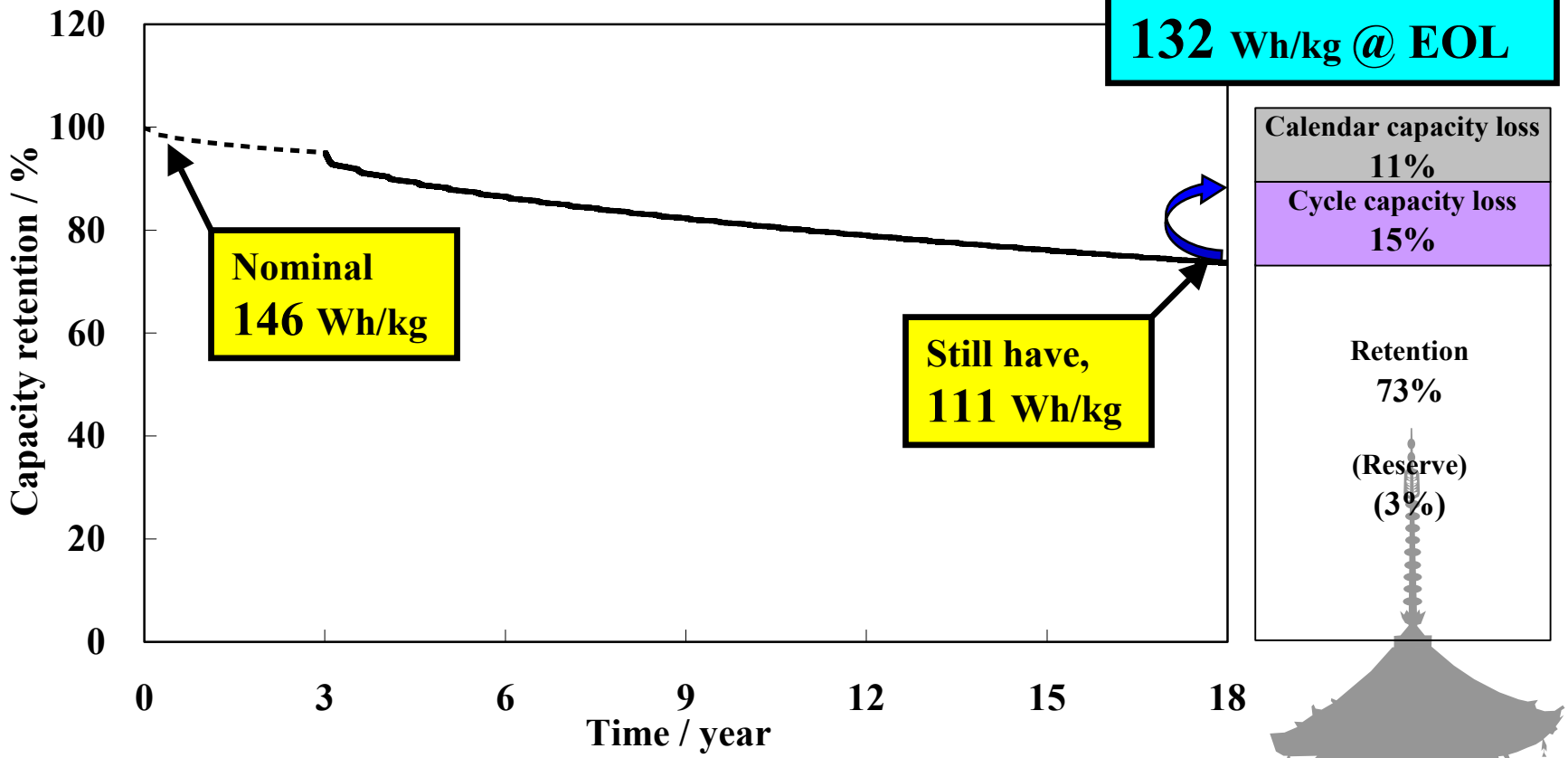
Capacity Loss Prediction during GEO Mission Life

Charging voltage
3.98V → 4.10V
Then, jump up to 90%,
132 Wh/kg @ EOL



<Ground storage>
Average storage **SOC : 10%**
Average storage temperature : **0deg.-C**
Duration : **3years** = 1095days

<Eclipse season>
Average cycle **DOD : 56% (Max.70%)**
Cycle number : **1350cycles (15years)**
Duration: 1350days
Average temperature : **10deg.-C**

<Solstice season>
Average storage **SOC : 50%**
Average storage temperature : **0deg.-C**
Duration : 275days/year x 15years = 4125days

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Verification of our calculation method by comparison with experimental data

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20%DOD cycle life (100Ah cells)

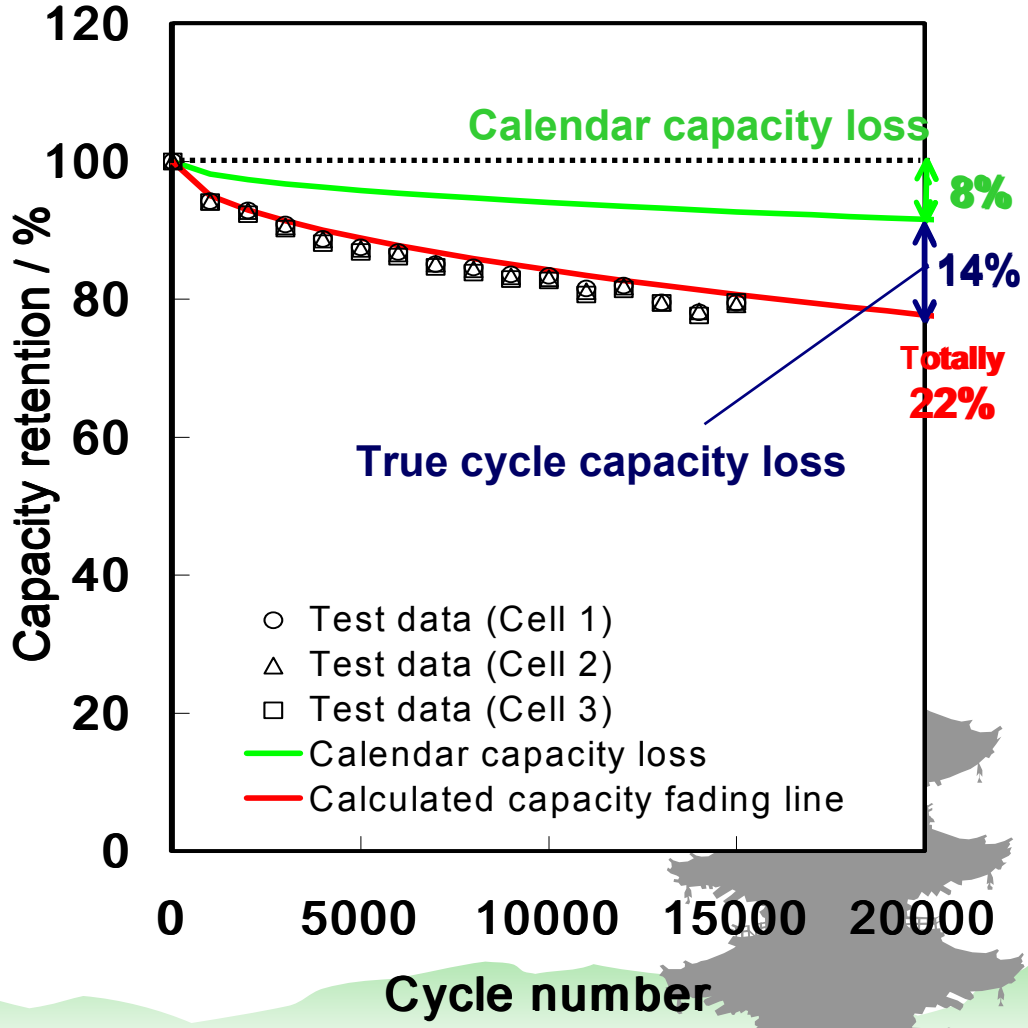
Calculated condition

20%DOD
Duration: 48 minutes / cycle
Temperature: 15 degrees C
Average SOC: 90%

Capacity retention (%) =

100 – [calendar capacity loss]

- [true cycle capacity loss]



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3+12%DOD cycle life (prototype 45Ah cells)

Calculated conditions

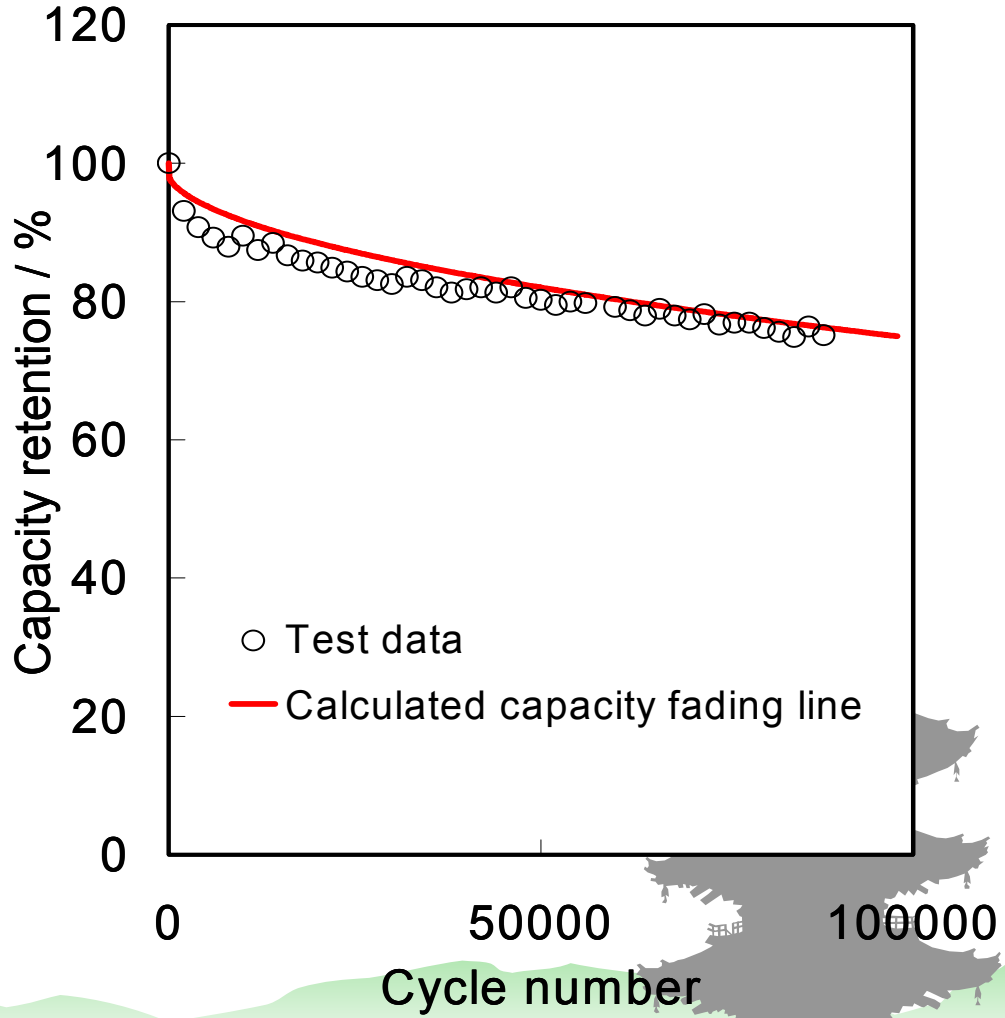
DOD: Combination of 3% and 12%

Temperature: 15 degrees C

Duration:

3%DOD: 9 minutes / cycle

12%DOD: 36 minutes / cycle



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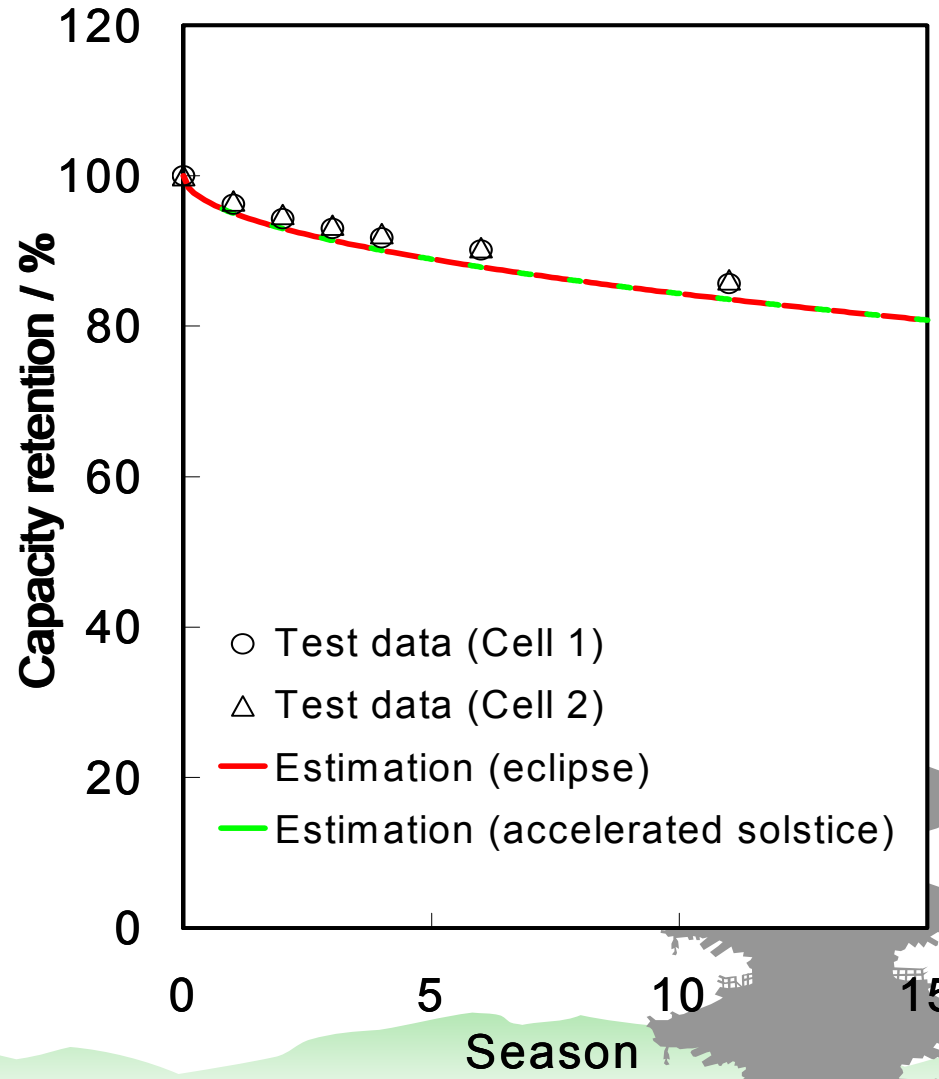
Accelerated GEO simulation (100Ah cells)

Condition (1 season)

Eclipse season
*15 degrees C for 42 days
*42 eclipse discharges (Max.70%)

Accelerated Solstice season
*At 50%SOC at 25 degrees C for 14 days

Corresponds with 140days at 50%SOC at 0 degrees C



We can calculate cell life even if on complicated conditions .

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Float charge (Storage)

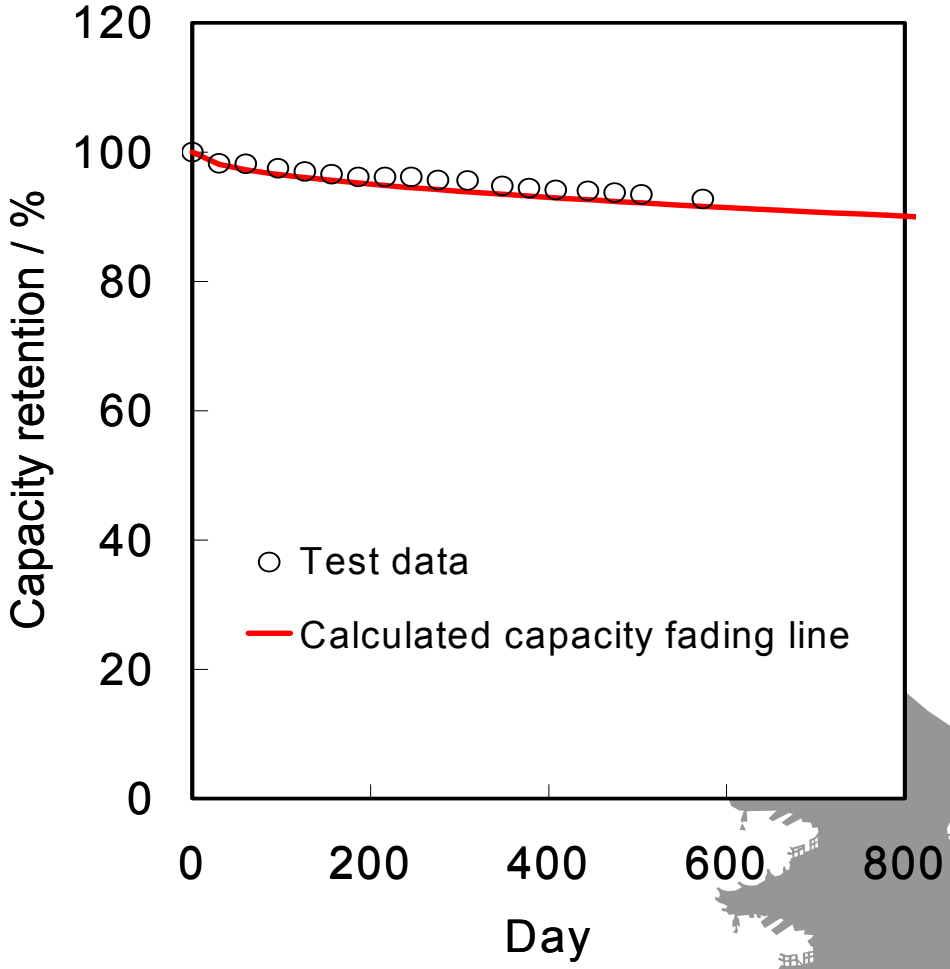
Calculated condition

SOC: 100%

Temperature: 15 degrees C

There is no cycling,

(except for capacity check)



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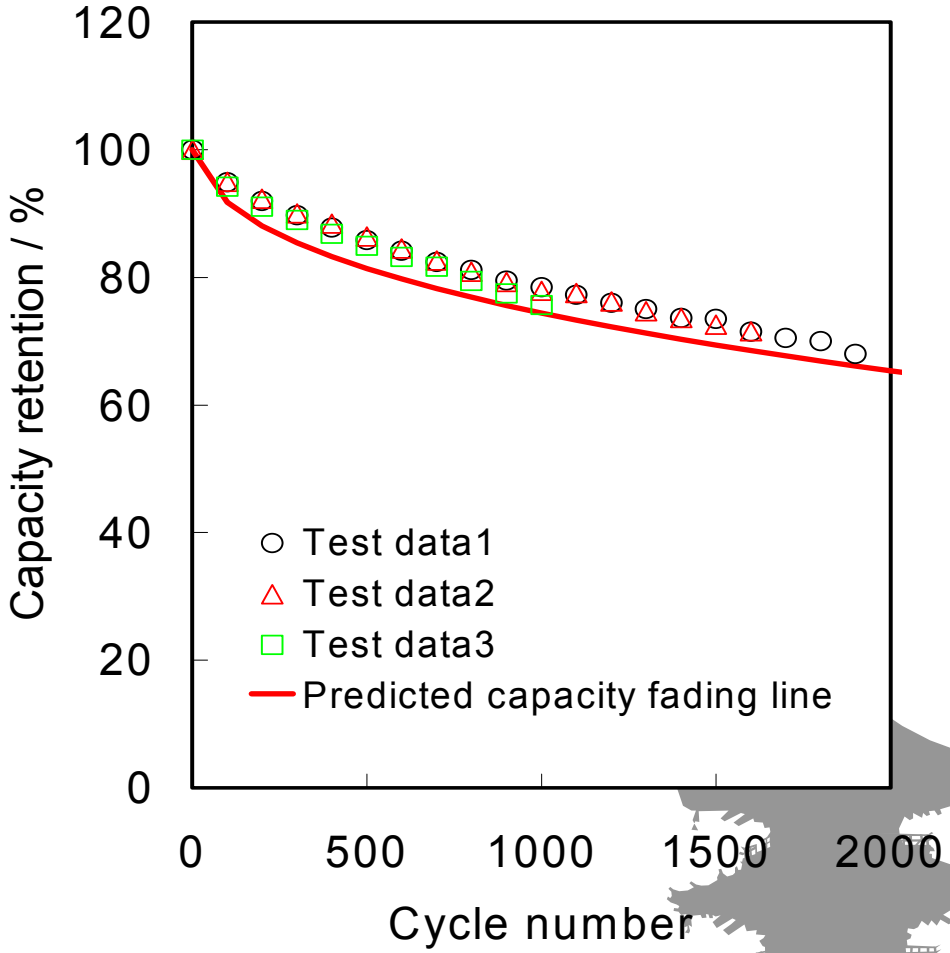
Full charge/full discharge cycle

Calculated conditions
Duration: 5 hours / cycle
Temperature: 25 degrees C
Average 80% SOC



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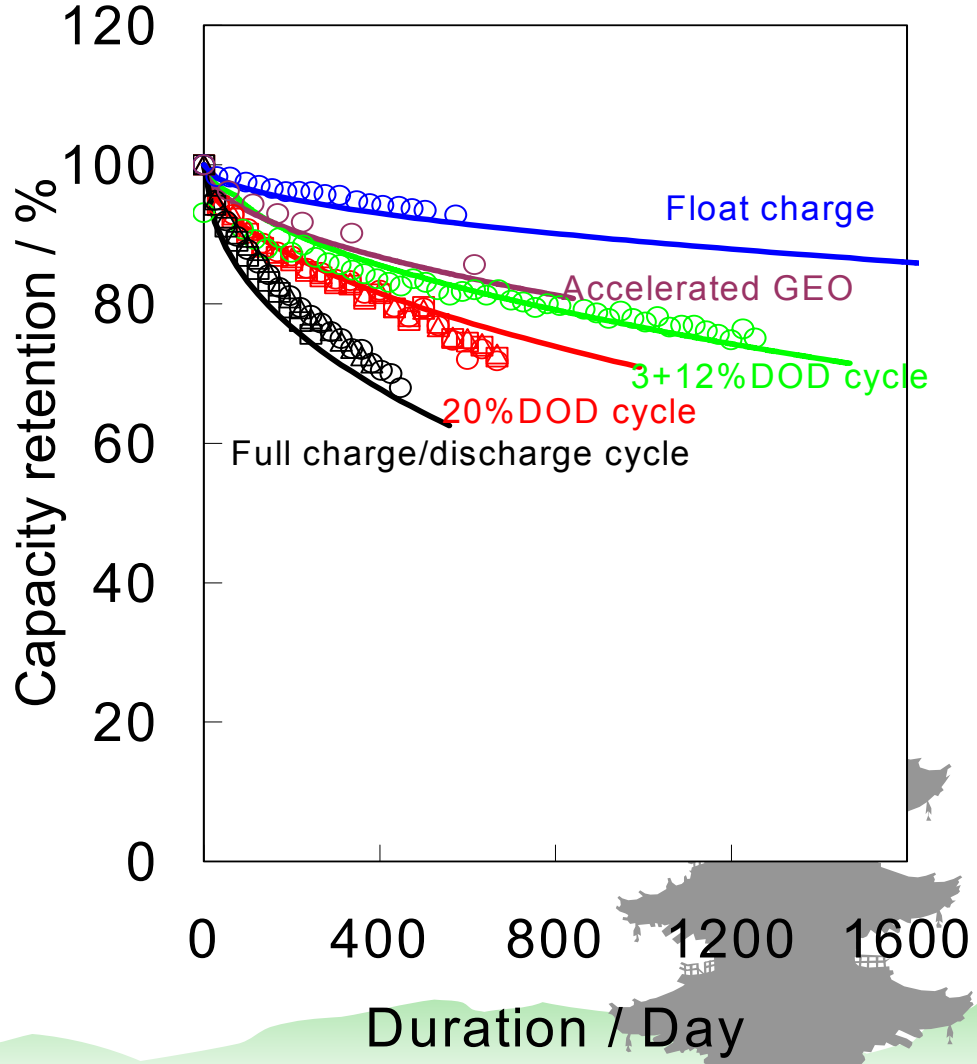
Summary of graphs

We can calculate the capacity retention both rapid and slow capacity fading conditions.

↓

We can calculate cell life at any conditions.



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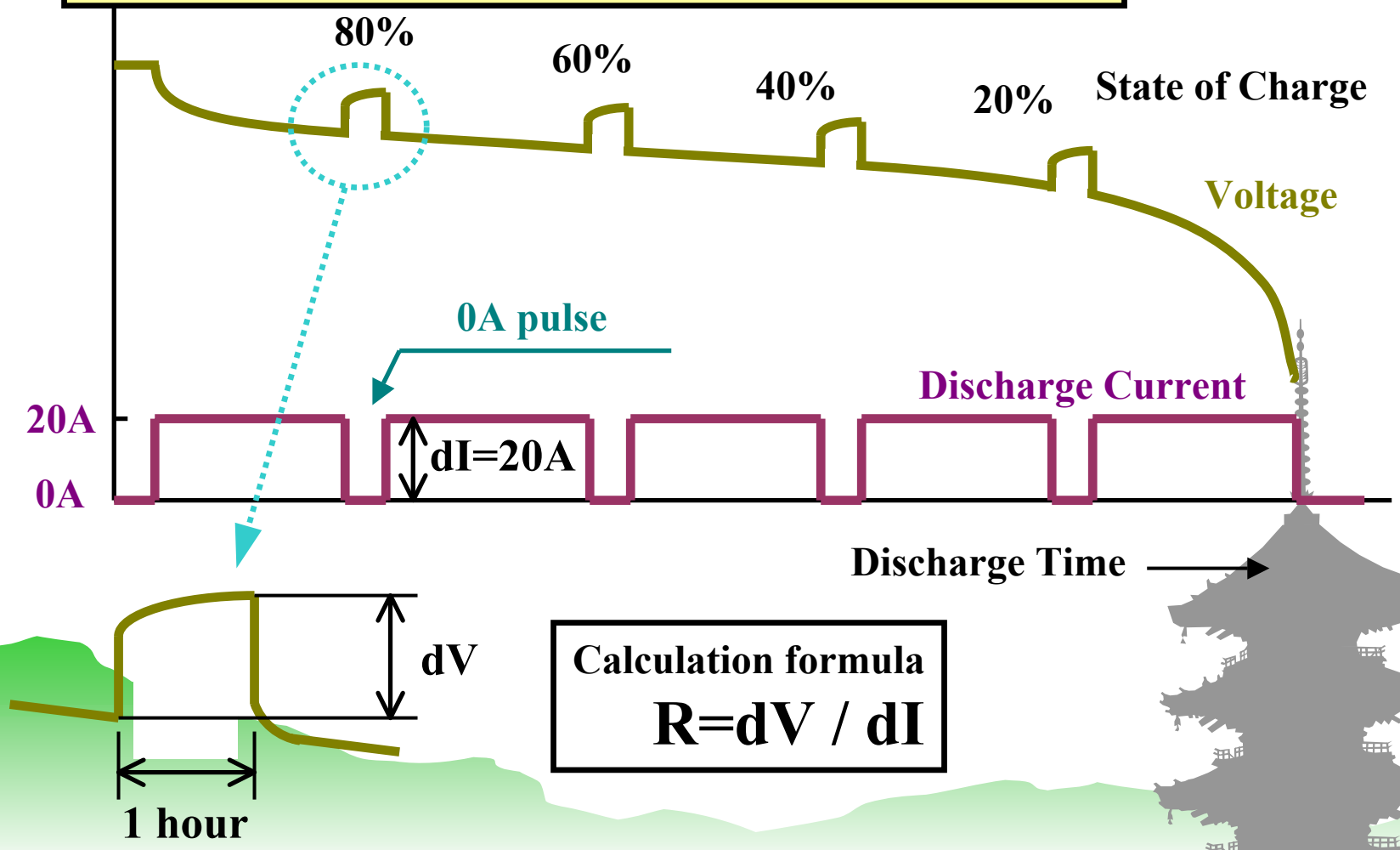
DC Impedance Measurement during the Test

All measurements are done after 15 deg.C adjustment.



Calculation formula

$$R = dV / dI$$

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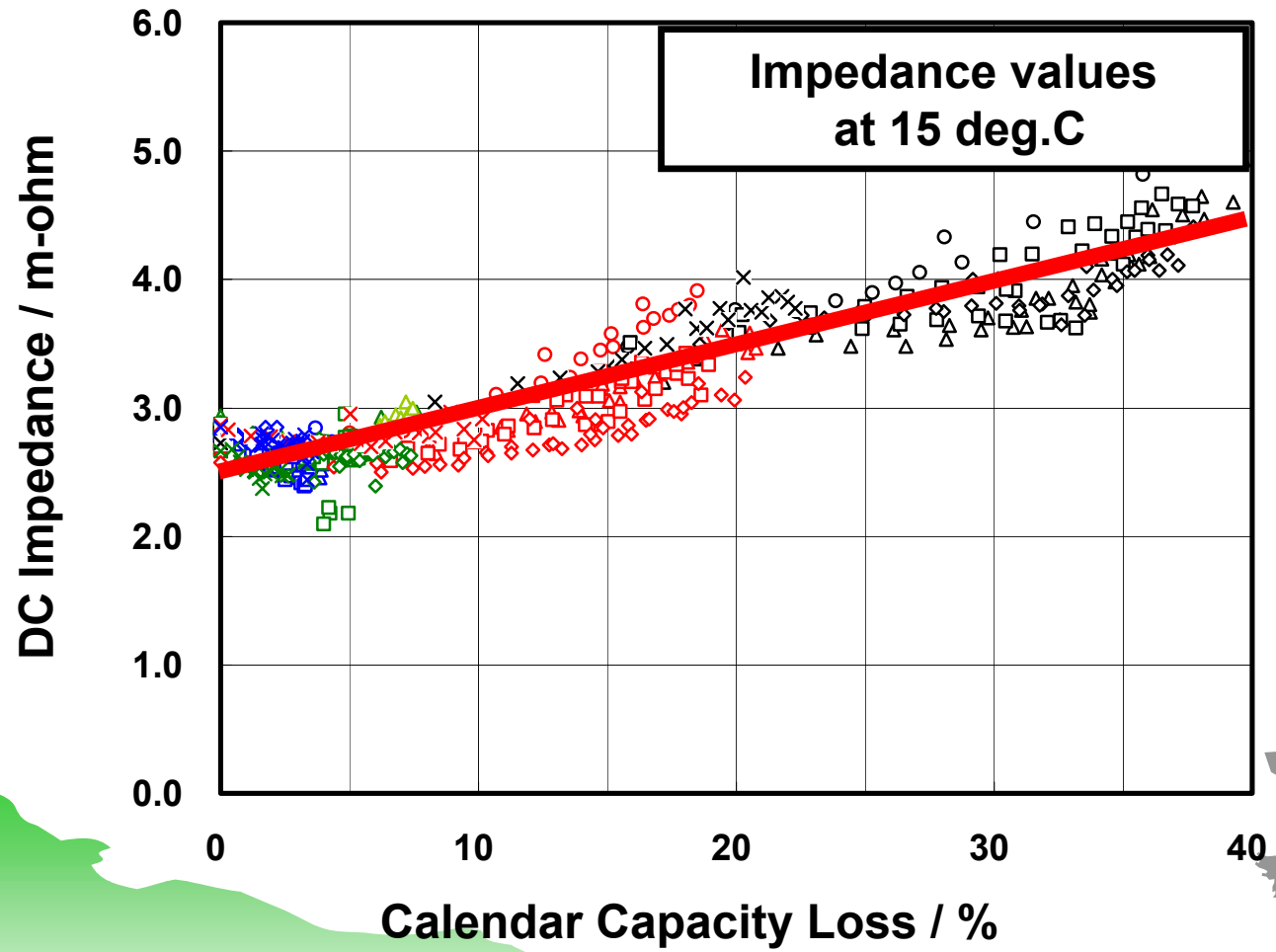
DC Impedance vs. Calendar Capacity Loss



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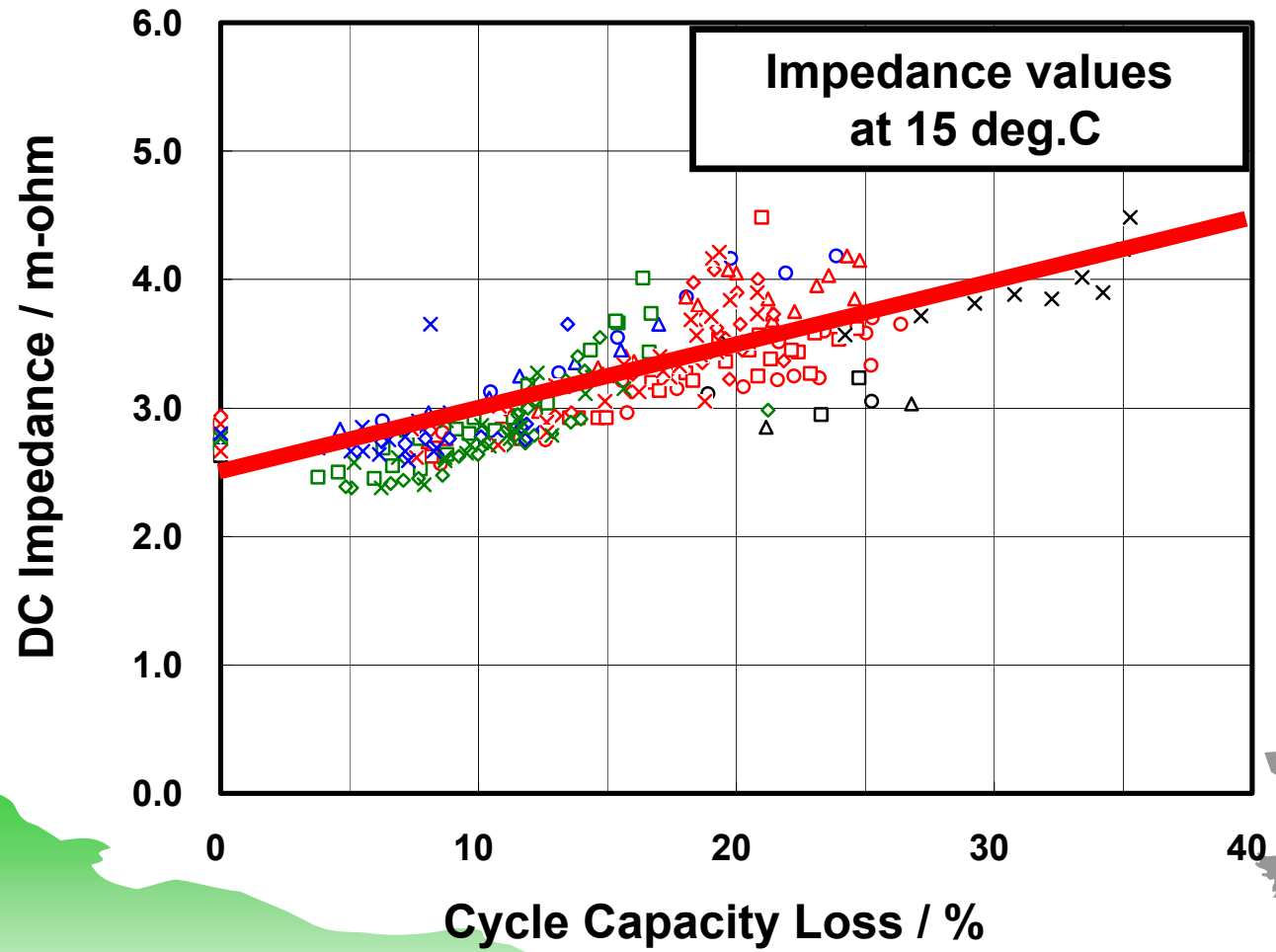
DC Impedance vs. Cycle Capacity Loss



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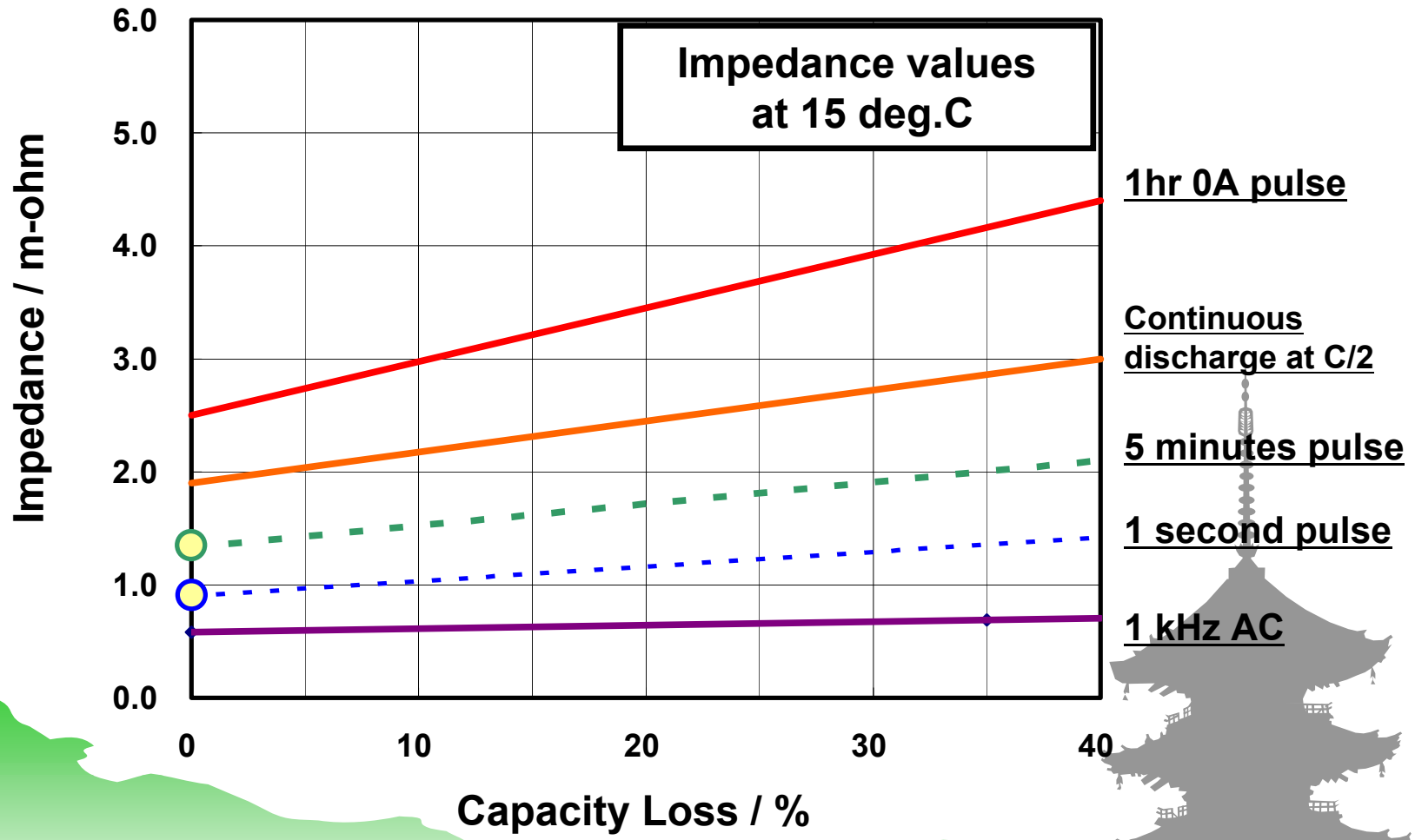
Impedance at various time range vs. Capacity Loss



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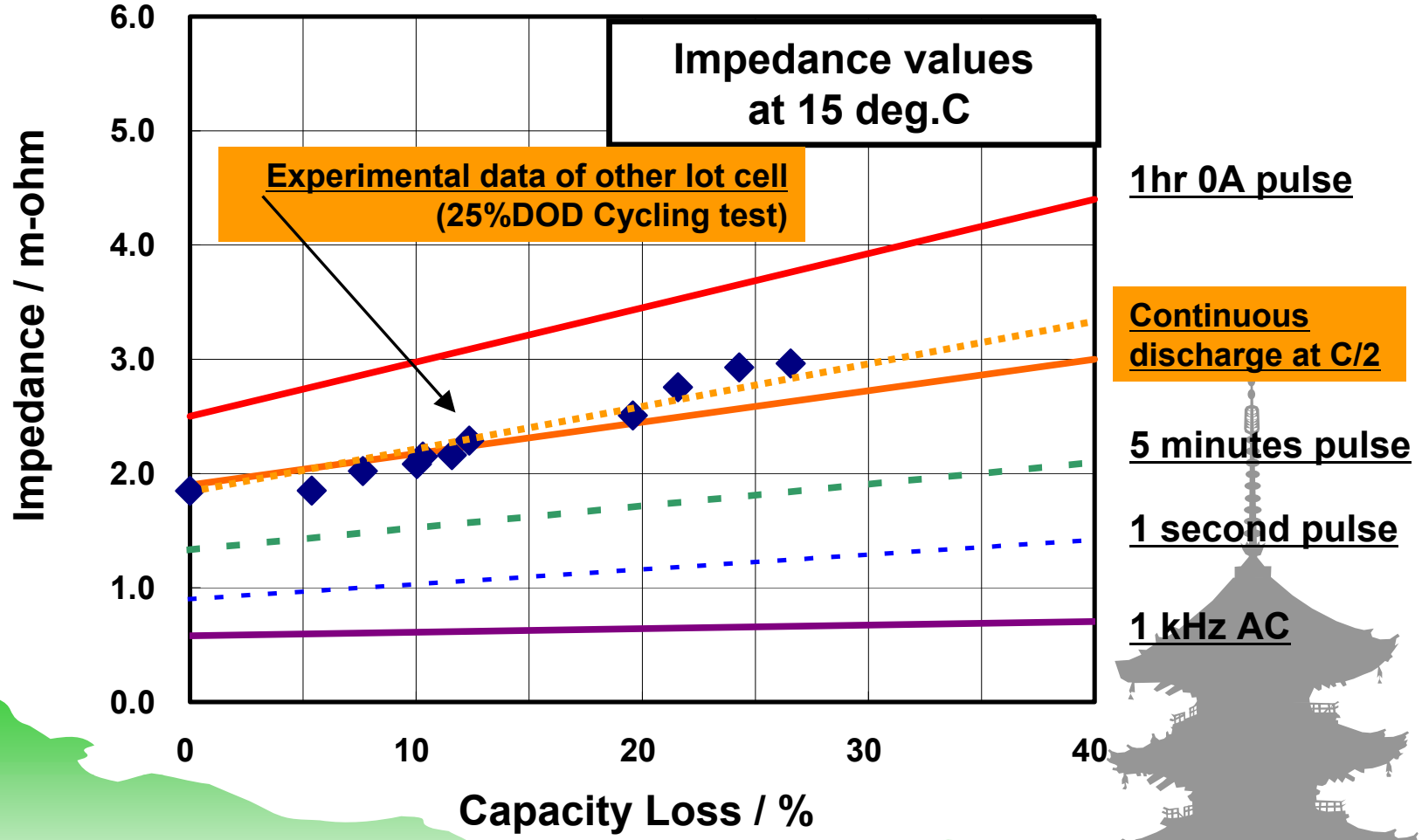
Impedance at various time range vs. Capacity Loss



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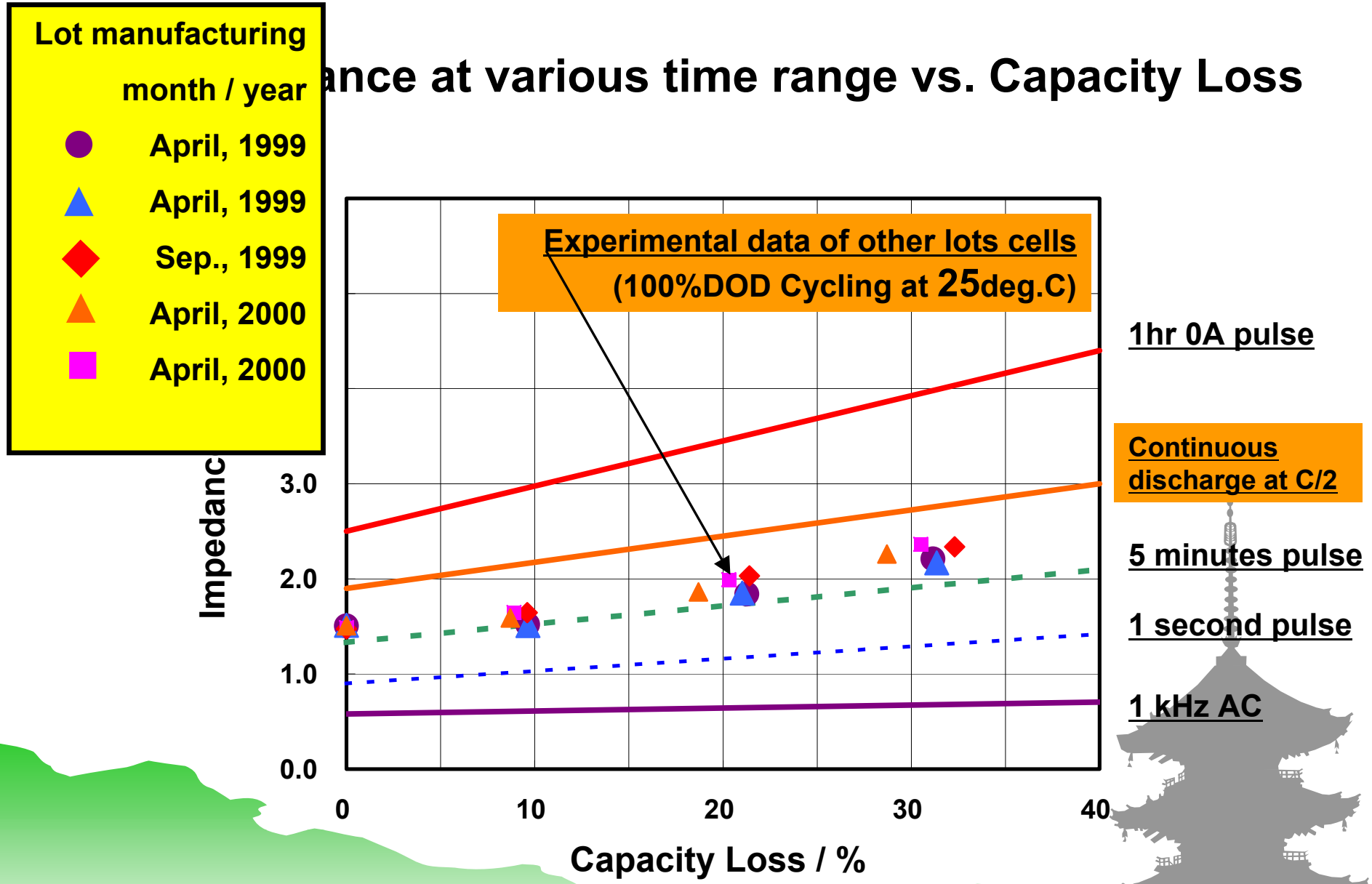
ance at various time range vs. Capacity Loss



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Conclusion

1. JSB's calculation method was verified by comparing with experimental data.

2. It has been already reported that the satellite type cells satisfy requirements for their use in LEO and GEO judging from the calculation. We have confirmed the accuracy of the calculation with the verification in this presentation.

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LITHIUM ION BATTERIES ON 2003 MARS EXPLORATION ROVER

Ratnakumar Bugga, Marshall Smart, Larry. Whitcanack, Jennifer Knight, Richard Ewell and Rao Surampudi

Jet Propulsion Laboratory, California Institute of Technology

Frank Puglia and Tim Curran

Yardney Technical Products, Pawcatuck, CT

NASA Battery Workshop, Huntsville, AL, Nov-19-21, 2002

The Mars Exploration Rover

An in situ science mission to Mars

Salient Features

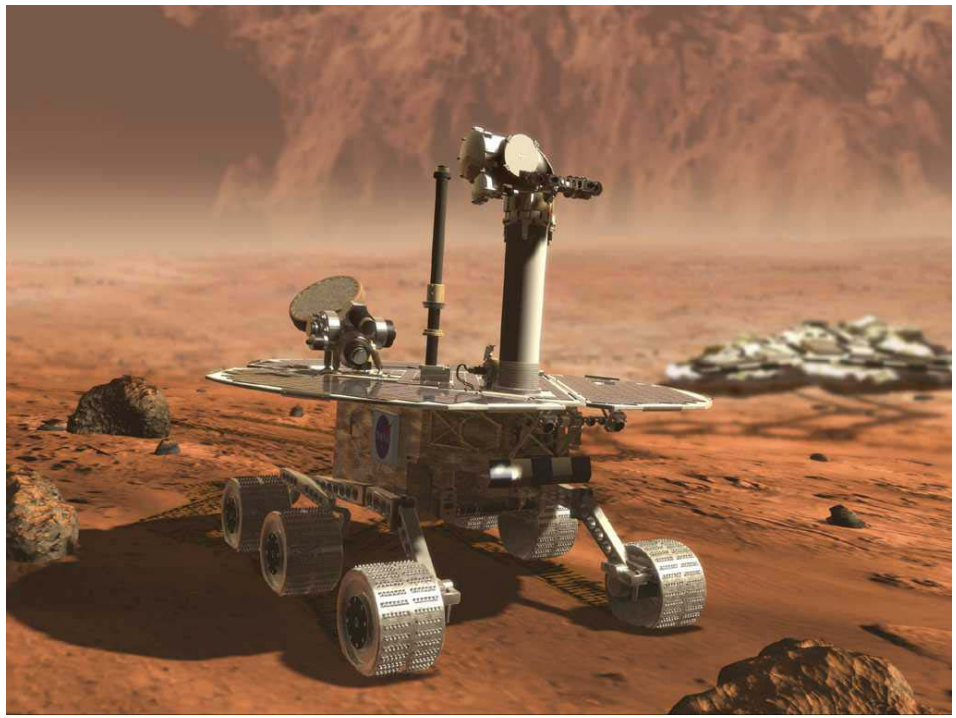
- Two identical landers launched in May-July 2003 on Delta II 7925 Launch vehicle.
- Targeted to two sites on Mars, landing January and February 2004
- Mars Pathfinder lander architecture
- Each delivers a highly capable rover carrying the Athena payload

  On a mast:
  - Camera and spectrometer

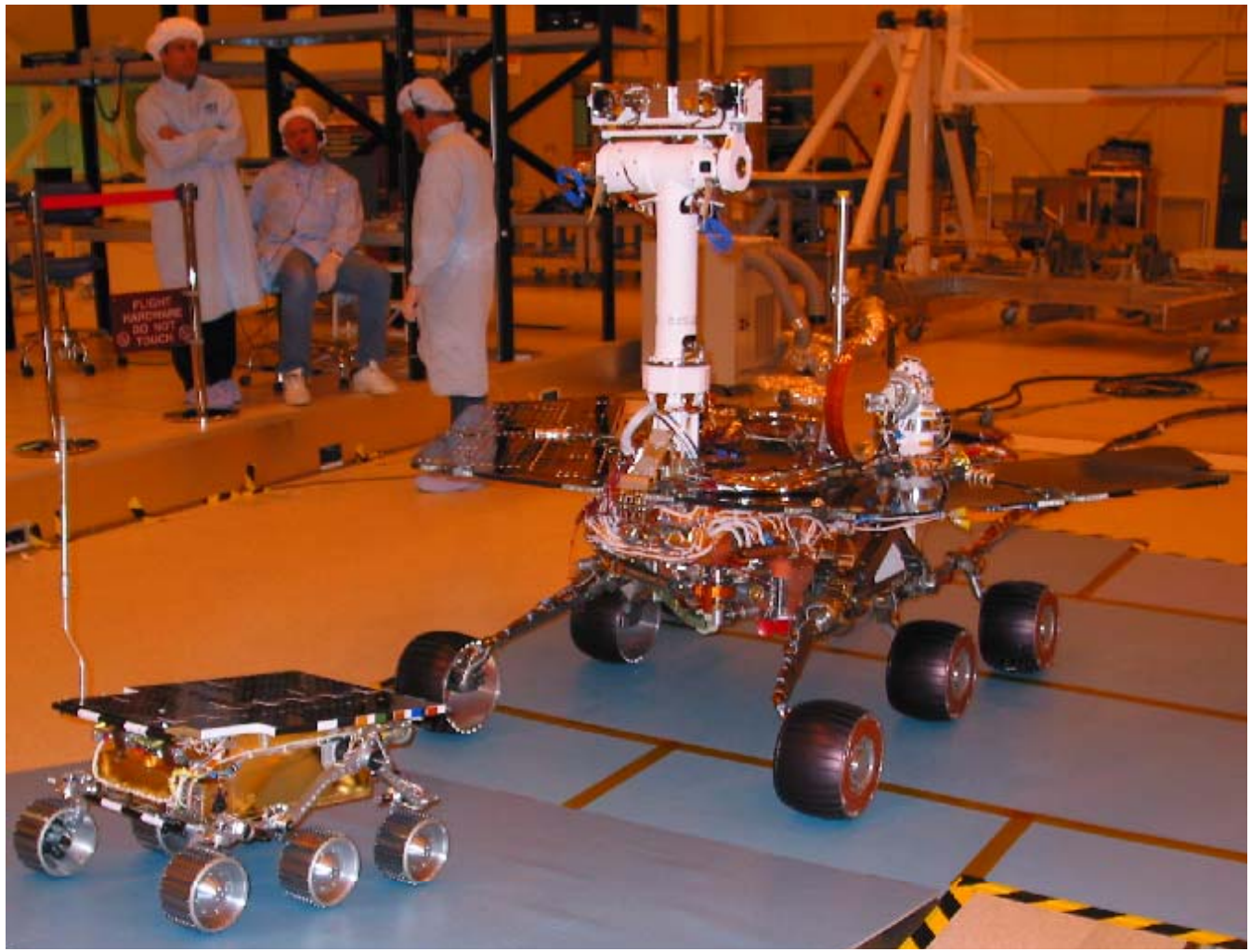
  On a 5-degree-of-freedom robotic arm:
  - Spectrometers, microscopic imager, rock abrasion tool

  On the rover:
  - Magnet array, calibration targets

- Two surface missions with an integrated traverse distance of greater than 600 meters over the 90-sol mission lifetime with a possible extended mission.



2003 MER vs. 1996 Sojourner



Mission Objectives

- **Science**
  - **Search for and characterize a diversity of rocks and soils that hold clues to past water activity**
  - **Investigate landing sites which have a high probability of containing physical and/or chemical evidence of the action of liquid water**
  - **Determine the distribution and composition of minerals, rocks, and soils**
  - **Characterize mineral assemblages and textures in the geologic context**
  - **Identify and quantify iron-bearing minerals indicating aqueous processes**
  - **Extract clues from geologic investigation related to liquid water to assess whether past environments were conducive for life**

- **Program**
  - **Demonstrate long-range traverse capabilities by mobile science platforms**
  - **Demonstrate complex science operations with two mobile laboratories**
  - **Validate the standards, protocols, and capabilities of the orbiting Mars communications infrastructure**

Science instruments (Athena Heritage)

- **Two remote sensing instruments mounted on Pancam (Panoramic Camera) Mast Assembly to select target.**
  - **Mast mounted Stereo cameras with color filters on pan/tilt gimbal.**
  - **Mini Thermal Emission Spectrometer (Mini-TES) Near and mid-IR point spectrometer for mineralogy of rocks.**

- **In-Situ Payload Elements**
  - **Mossbauer Spectrometer for mineralogy of Fe-bearing minerals in rocks.**
  - **Alpha Particle X-ray Spectrometer (APXS) for elemental chemistry.**
  - **Microscopic Imager (MI) for environmental conditions under which geologic materials formed.**
  - **Rock Abrasion Tool (RAT) to penetrate thro' rock dust and surface alteration.**

- **The front HAZCAMs provide imaging of workspace for ground planning of instrument deployments**

Rover Capabilities

Avionics

- Rad6000 Flight Computer (20Mhz, 128MB DRAM)
- 256MB Non-volatile FLASH data storage
- Analog, digital, serial IO
- Motor control for 36 brushed motors, 4 stepper motors & 4 brushless motors

Power

- Triple-Junction GaInP/GaAs/Ge cell deployable solar arrays
- (2) 8A-hr Li-Ion rechargeable batteries
- Power conversion and distribution

Navigation Sensors

- Mast mounted stereo navigation cameras - NAVCAMs - Front & Rear stereo hazard cameras - HAZCAMs - with 120deg FOV) SUNCAM (mounted on HGA gimbal)
- 6DOF IMU

Telecom

- Direct to Earth Communication (X-band) with fixed Low Gain and gimbaled High Gain Antennas
- Orbiter relay communication (UHF) with fixed monopole antenna

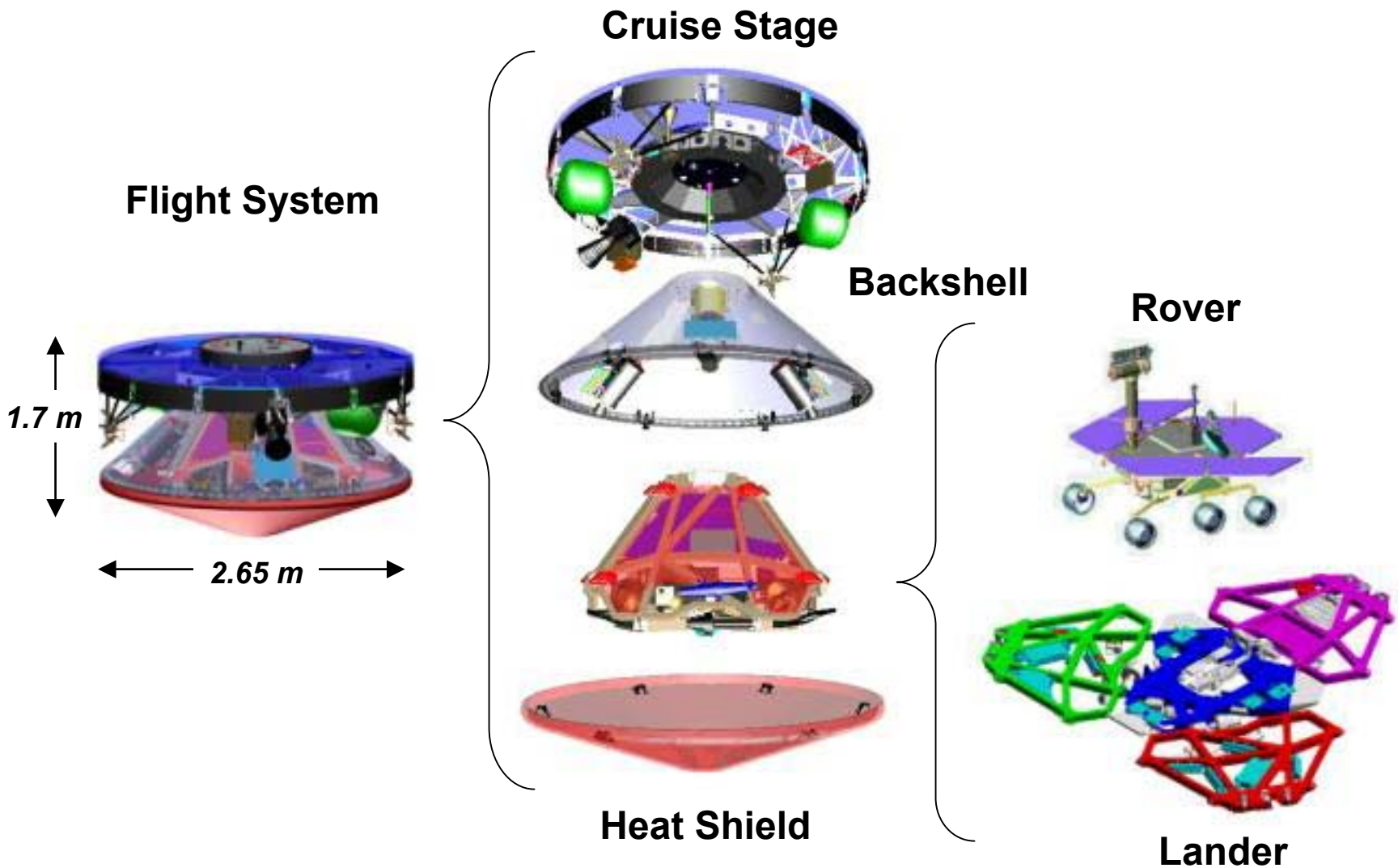
Mobility System

- 6 wheel Rocker-Bogie mechanism with 25cm diameter wheels
- 5cm/s top speed (~0.6m/minute under autonomous navigation)

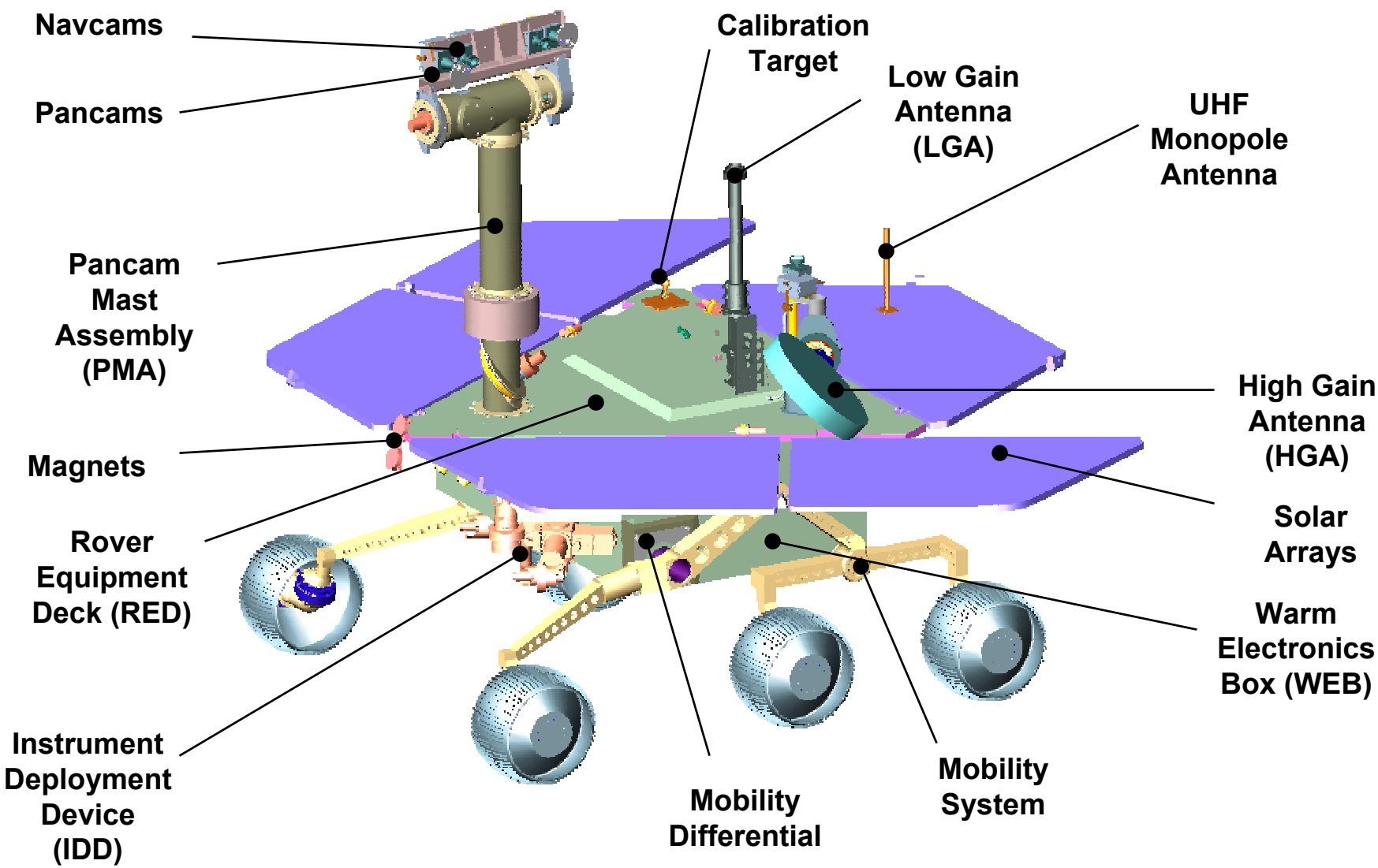
Thermal

- Aerogel insulated Warm Electronics Box
- Resistive heaters on external motors/cameras and internal components
- Radioisotope heating units (RHUs)
- Battery thermal switch heat rejection system
- SSPA Loop Heat Pipe heat rejection system

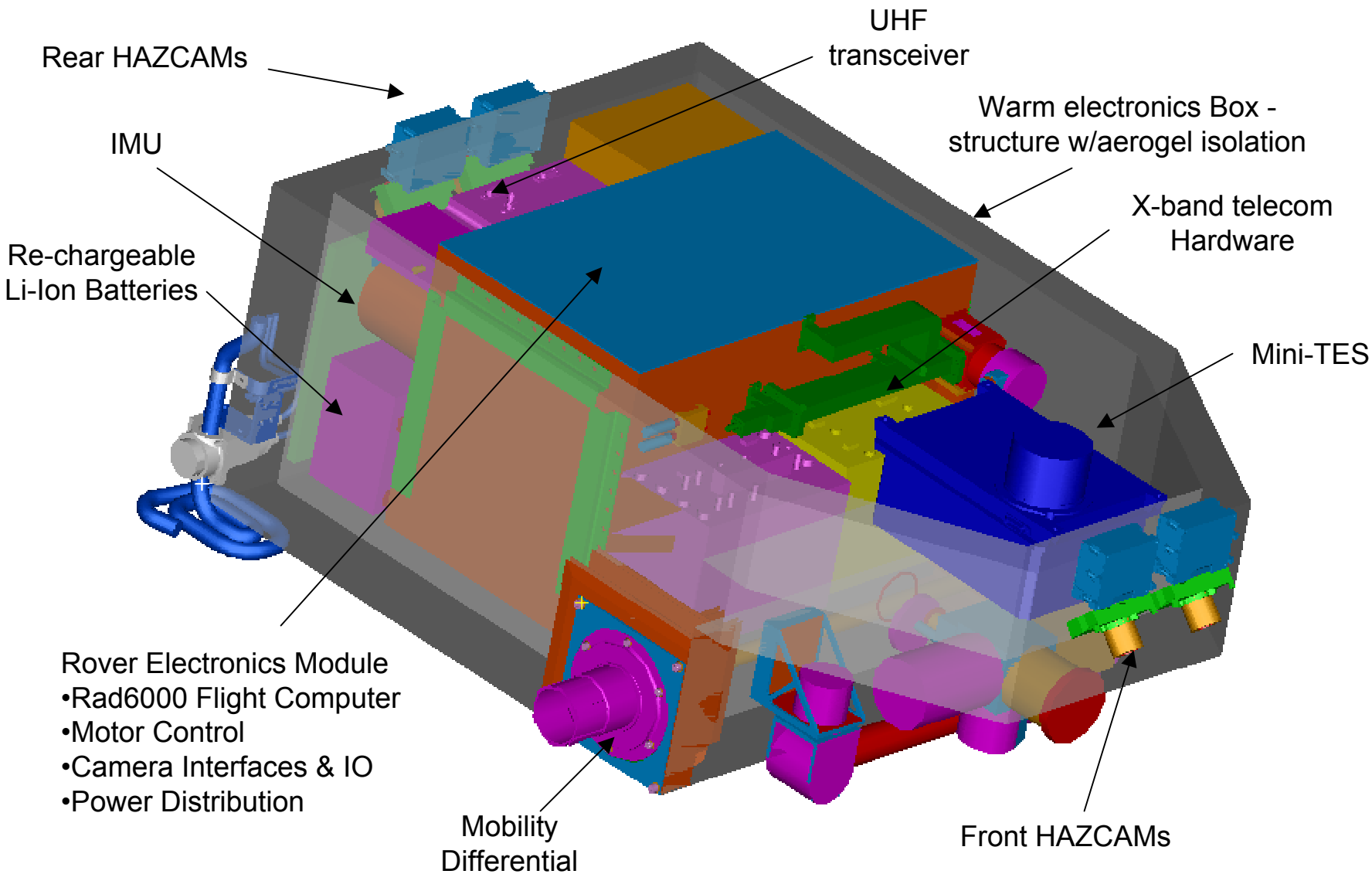
Flight System Configuration



Rover Configuration - Deployed



Rover Warm Electronics Box



Li Batteries for MER

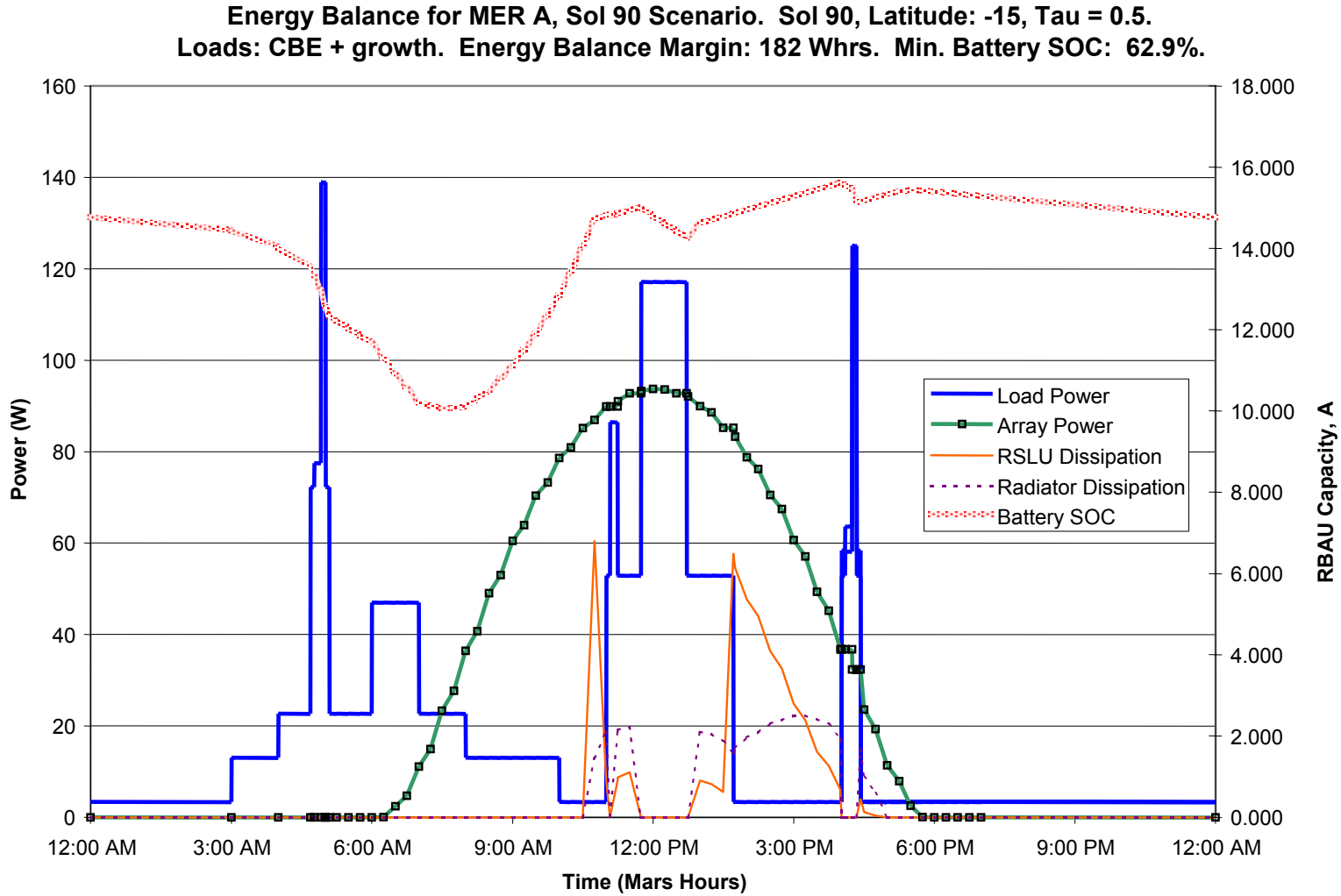
- **Primary batteries**
  - For Turn to Entry maneuvers, Entry, Descent and Landing (EDL) operations
  - Initial landing operations (Rover regress)
- **Rechargeable Li ion batteries**
  - Launch
  - Cruise anomalies
  - Pyro events
  - Surface operations through Sol 90
- **Thermal Batteries**
  - Support back shell pyros

Rover Battery Assembly Unit –Requirements

- Voltage : 24- 36 V (Cruise min. 27 V)
- Launch: The power subsystem shall be capable of supplying 200 Whrs during launch, from the switch to internal power until spacecraft separation.
  - The battery shall be capable of recycling within 30 minutes after an abort of the first opportunity.
- Cruise : Some fault cases may leave the spacecraft in a state where the solar arrays are not illuminated. Power shall be capable, at anytime, during cruise to provide 160 Whrs of energy without solar illumination (to a voltage of 27 V min).
- Surface Operations: Capable of operating on the surface of Mars for > 90 Sols.
- The Rover RBAU shall be capable of providing 283 Whrs of energy on a single charge.
- The Rover RBAU shall be capable of 270 cycles at 50 % DOD at 0° C.
- The Rover RBAU shall be capable of return to full charge over a 10 hour period
- The Power Subsystem shall assure that the loss of one secondary battery or other BCB will not impact the rest of the S/C.
- Each battery in the RBAU shall be capable of firing simultaneous three pyros (each with a load of 7 A) with an interval of at least 100 ms.

Power Profile for Surface Operations- Sol 90

Mars Exploration Rover



Criteria for Battery Selection

- **High Specific Energy and Energy Density**
  - **> 100 Wh/kg and > 200 Wh/l at cell level**
- **Good Low Temperature Performance**
  - **> 65% of RT capacity available at -20°C @ C/5 to 3.0 V/cell**
  - **> 70 % of RT capacity accepted during ≥ 0°C charge at > C/10 to 4.1 V/ cell**
- **High Discharge Rate Capability**
  - **> 85% of Low Rate Capacity available at C rate @ 25°C.**
- **Long Cycle Life**
  - **> 90 % of the initial capacity at 20°C available after 300 cycles at 50% DOD at 0°C.**
- **Good Storageability**
  - **> 85 % of the initial capacity realizable after two years of storage (at 0-10°C and 50-70% SOC)**

Rover (Rechargeable) Batteries-Trade off Studies

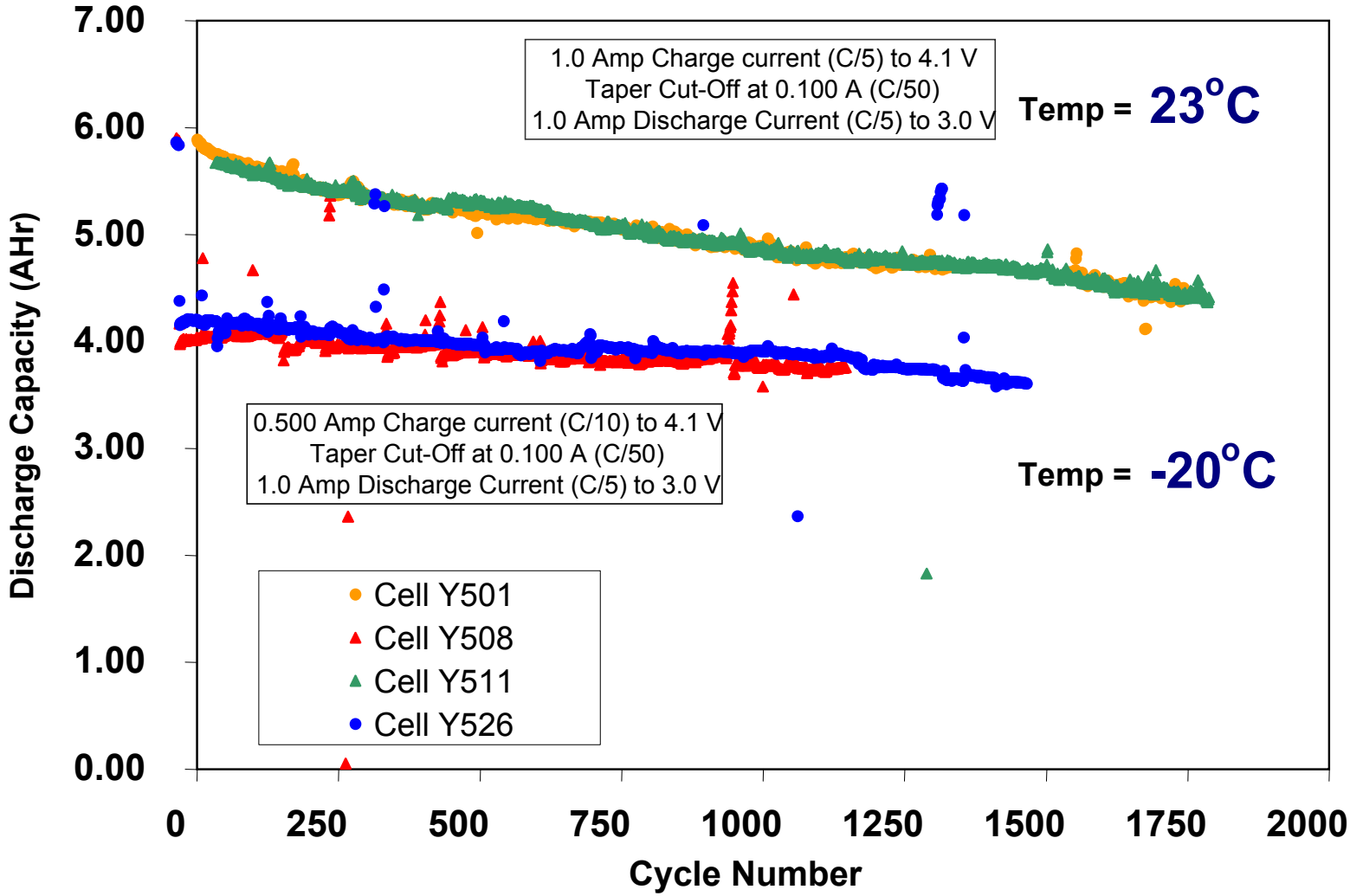
System → Characteristic ↓	Nickel-Cadmium	Nickel-Hydrogen	Silver-Zinc	Lithium-Ion
Specific Energy (Wh/kg)	25	30	~100	>100
Energy Density (Wh/lit)	100	50	~150	>250
Battery Mass for 300Wh MER (kg)	33	28	11	6
Battery Volume for 300 Wh MER (Lit)	9	17	6	2.2
Cycle Life (50% DoD)	>1000	>1000	<100	>1000
Wet life (Storageability)	Excellent	Excellent	Poor	Good
Self-Discharge (per month)	15%	30%	15-20%	<5%
Low temperature Performance (-20°C)	Moderate	Moderate	Moderate	Excellent
Temperature Range, °C	-10- 30	-10- 30	-10- 30	-20 to +40
Charge Efficiency %	80%	80%	70%	~100%

Lithium - Ion System

- **Characteristics of Lithium Ion System**
  - **High specific energy and excellent energy density**
  - **Good low temperature performance and high rate capability**
  - **High coulombic and energy efficiencies**
  - **low self discharge, good cycle life and storage life**
- **Lithium Ion system selected for MER Rover battery**
- **Proposed Battery**
  - **Voltage : 32.8 -24 V (after diode)**
  - **Capacity**
    - **16 Ah (BOL) at RT and 14 Ah at 0°C (EOL) or 8.6 Ah at -20°C (EOL)**
  - **Discharge -Charge Rates**
    - **C rate discharge (max) during at RT and < C/2 at -20°C-30°C.**
    - **Charge < C/2 at 0 to 30°C to 4.1 V/cell minimum of 11 Ah (BOL)**
  - **16 Li ion cells of 8 Ah in two parallel strings of 8 cells each.**

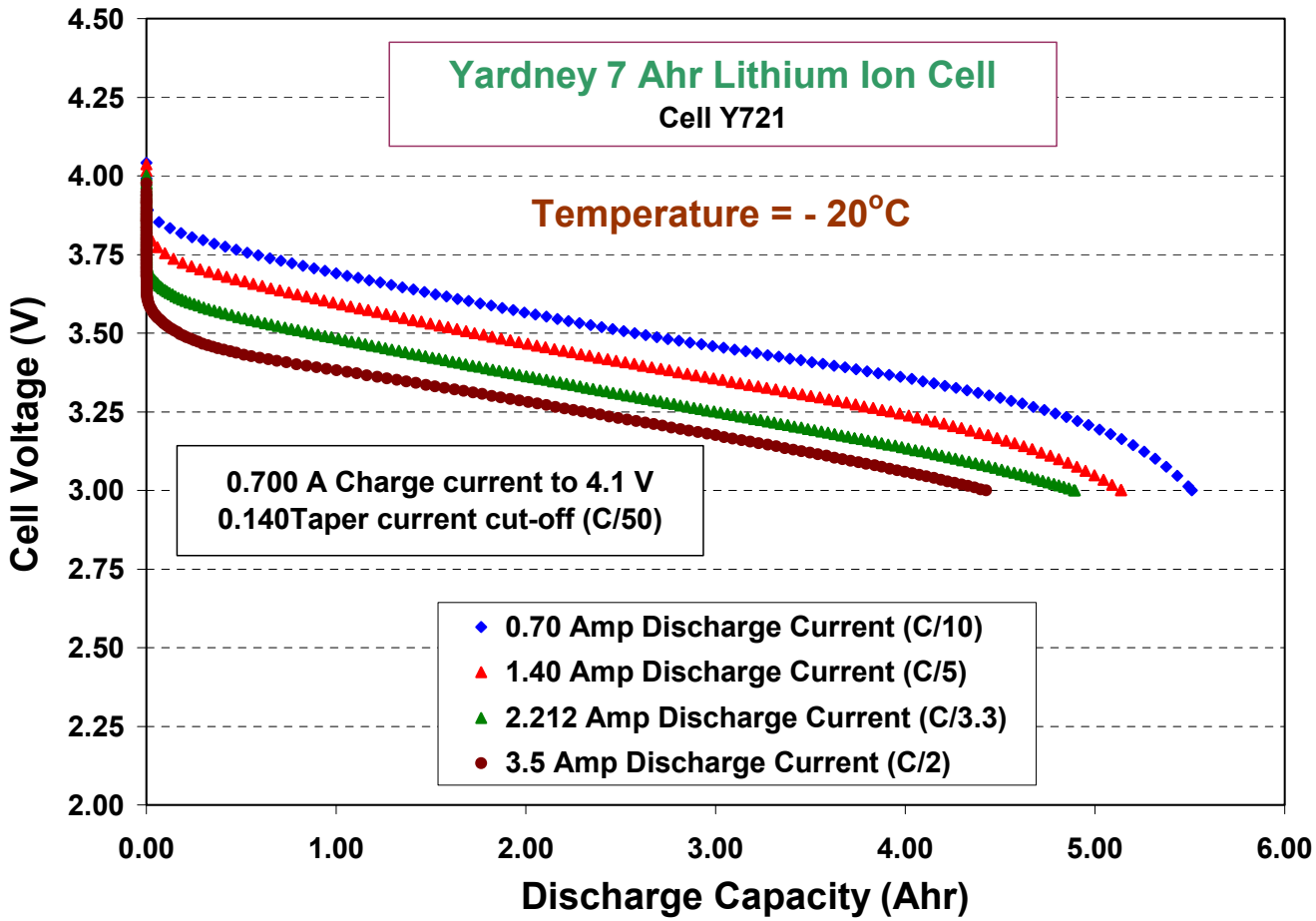
Yardney Li Ion Cells

Cycle Life at RT and LT



Yardney Li Ion Cells

Low temperature Performance



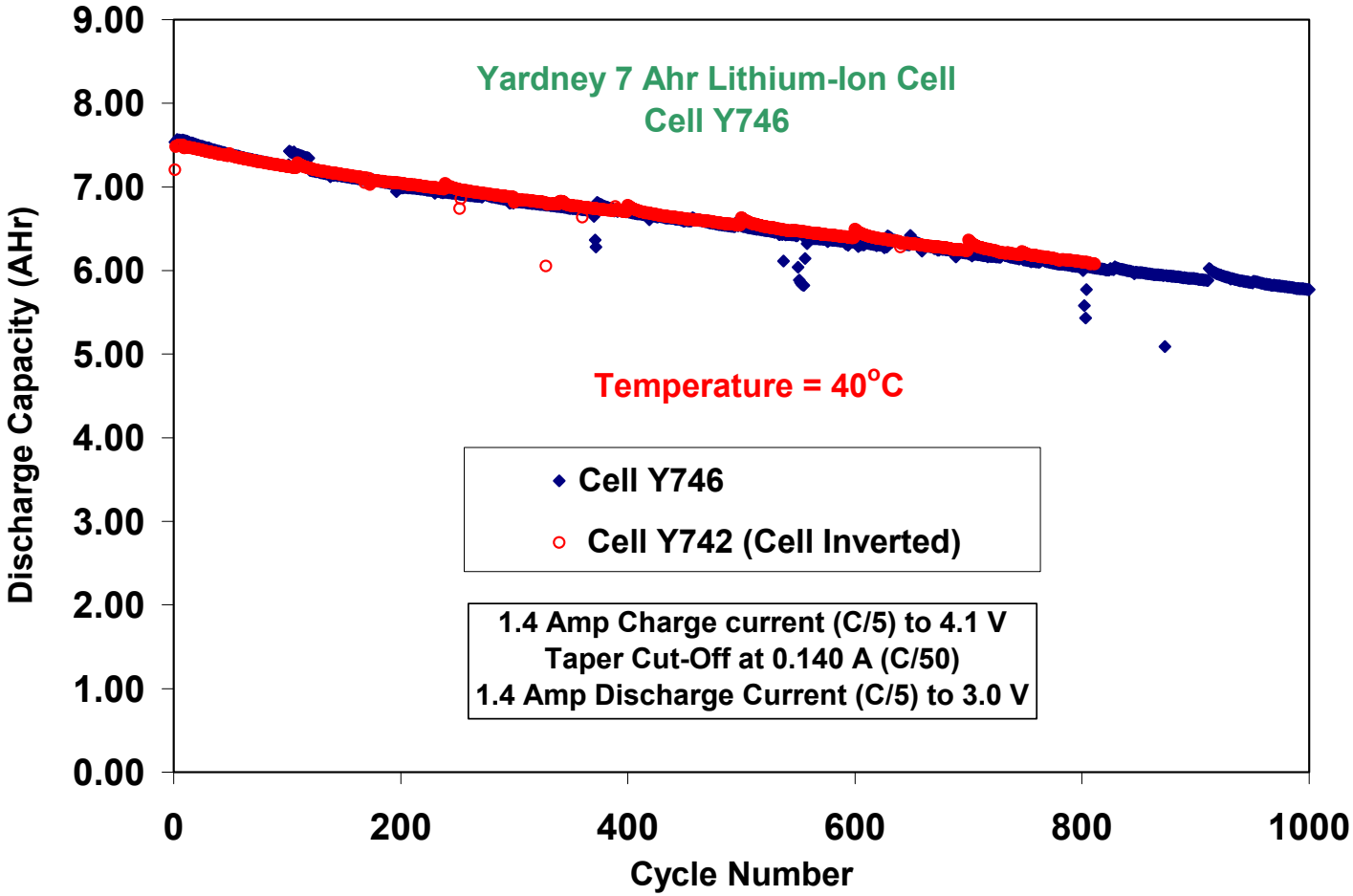
Yardney Li Ion Cells

Storage Characteristics

Cell Number	SOC on Bus	Initial Capacity 23°C (2nd Cycle)	Capacity Prior To Buss Storage at -20°C (2nd Cycle)	Capacity After 2 Years Buss Storage 23°C (6th Cycle)	% of Initial Capacity After 2 Years Buss Storage 23°C	Capacity After 2 Years Buss Storage -20°C (3rd Cycle)	% of Initial Capacity Prior to Buss Storage -20°C
Y003	**30%**	**34.0201**	21.8307	33.5936	**98.7464**	20.9120	95.79
Y004	**50%**	**33.9624**	22.4870	32.8729	**96.7922**	20.7299	92.19
Y028	**70%**	**33.4789**	----	33.5205	**100.1242**	19.2257	

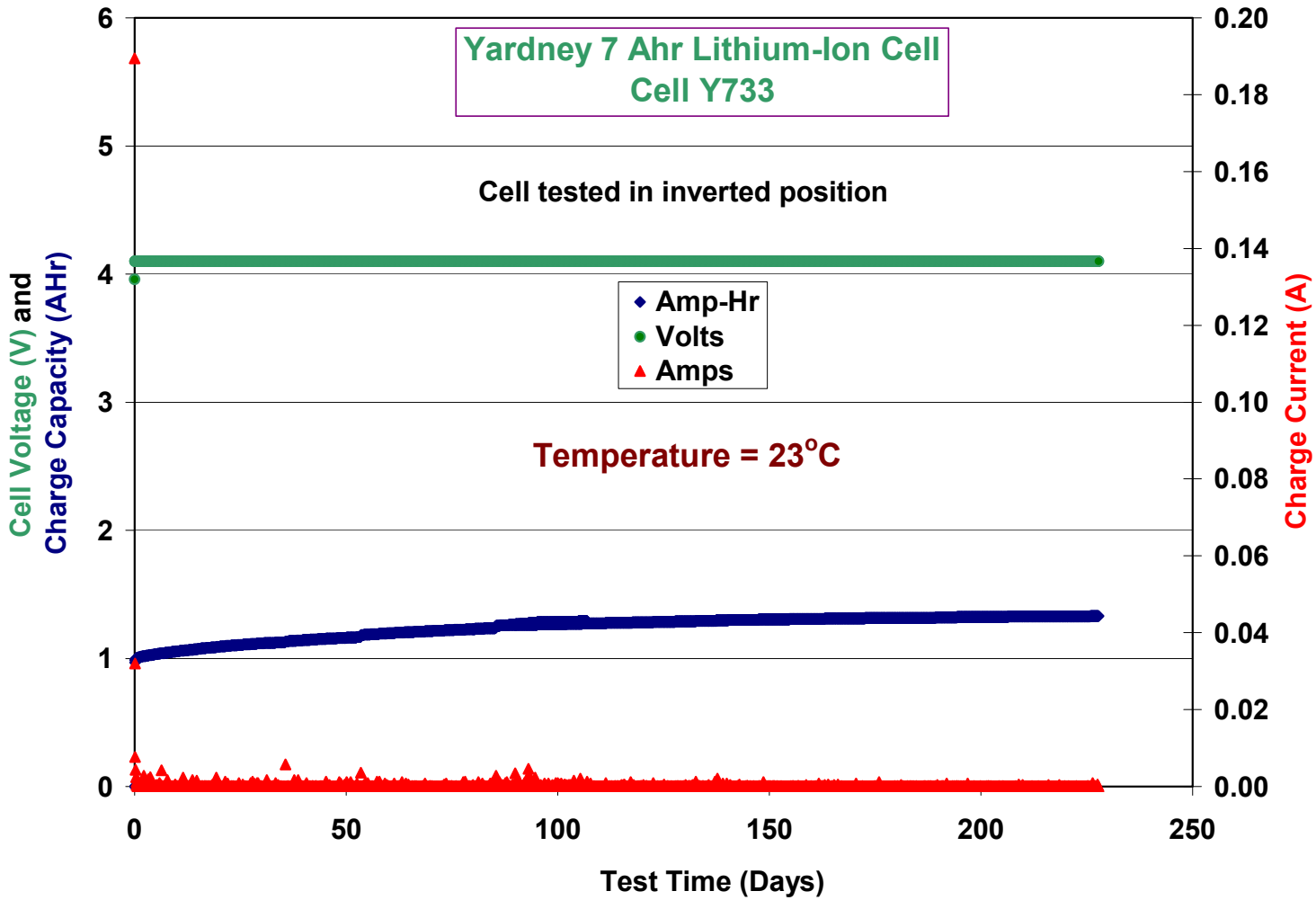
Yardney Li Ion Cells

Effect of Inverted Cell Orientation-100% DOD Cycling at 40°C



Yardney Li Ion Cells

Effect of Inverted Cell Orientation- On-buss storage at 4.1 V at 23°C



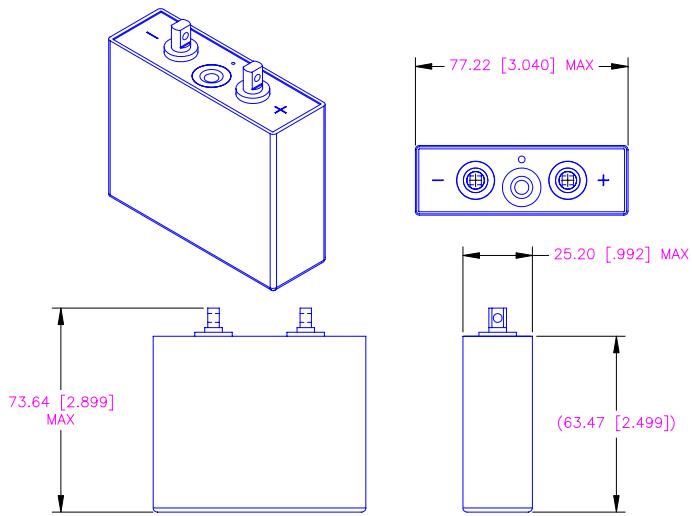
RBAU Specifications

Cell and RBAU Electrical Specs

Test Article	Temperature	Preceding charge	Discharge condition	Capacity (Ah)	Remarks
Cell Capacity (BOL)	20°C	C/5 to 4.1 (taper)	C/5 to 2.9 V	10 Ah (min)	Nominal launch
		,,	C/2 to 2.9 V	9.5 Ah	
		,,	C to 2.9 V	9 Ah	
	30°C	C/5 to 4.1 (taper)	C/5 to 2.9 V	10 Ah (min)	
	0°C	C/5 to 4.1 (taper)	C/5 to 2.9 V	8.5 Ah (min)	
	-20°C	C/10 to 4.1 (taper)	C/5 to 2.9 V	6 Ah (min)	
	-10°C	C/10 to 4.1 (taper)	C/2 to 3.0 V	18 Wh (min)	Nominal Cruise
Cycle Life Validation	EOL defined as 2 years storage and 300 cycles; shown by analyses.				
Cell Capacity (EOL)	20°C	C/5 to 4.1 (taper)	C/5 to 2.9 V	8.5 Ah (min)	Loss of 10% on storage and 12% in 300 cycles
	-20°C	C/10 to 4.1 (taper)	C/5 to 2.9 V	5 Ah (min)	For Surface Ops (280 Wh)
	0°C	C/5 to 4.1 (taper)	C/5 to 2.9 V	7.0 Ah (min)	
RBAU Capacity (BOL)	20°C	C/10 to 32.4 (taper) or 4.15 V/cell	C/5 to 24 V	9 Ah (min) on each battery	
	-20°C	C/10 to 32.4 (taper) or 4.15 V/cell	C/5 to 24 V	5 Ah (min) on each battery	
	0°C	C/10 to 32.4 (taper) or 4.15 V/cell	C/5 to 24 V	7 Ah (min) on each battery	
	30°C	C/10 to 32.4 (taper) or 4.15 V/cell	C/5 to 24 V	9 Ah (min) on each battery	
	-10°C	C/10 to 31 (taper) or 3.875V/cell	C/2 to 27 V	160 W h (min) on the RBAU	Cruise –little margin

The Cell Design

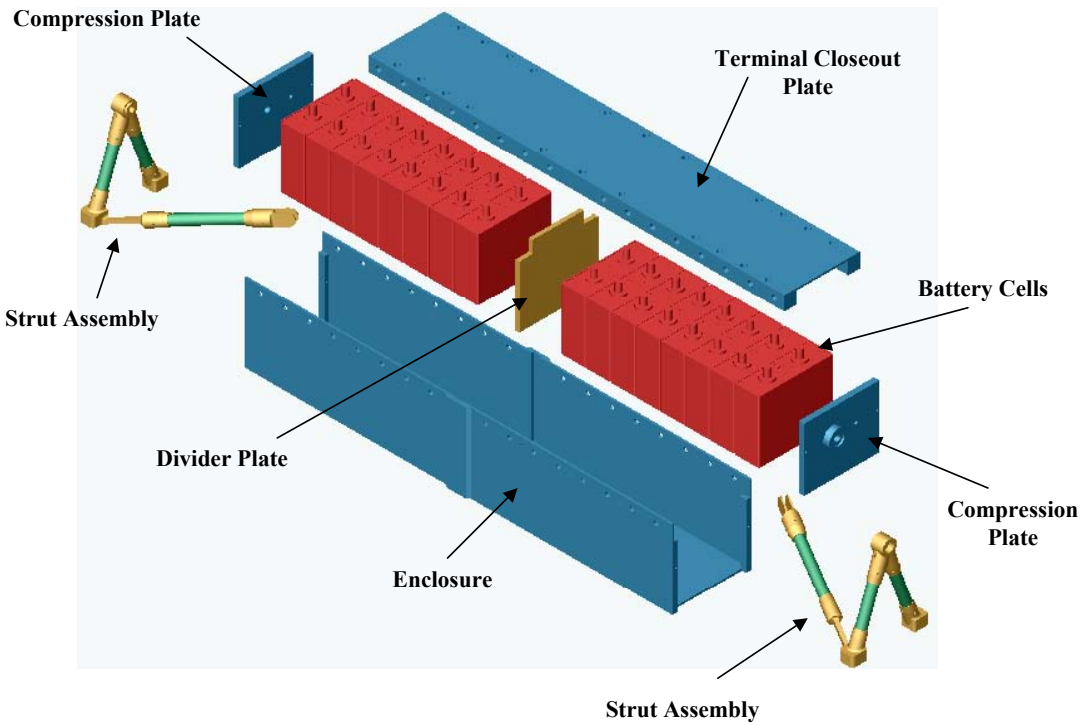
- **The cell is a true prismatic Lithium Ion cell.**
  - **Prismatic design offered improved fit into the envelope combined with superior thermal pathways.**
- **The cell used the same chemistry as was optimized for the MSP01 Lander.**
  - **This chemistry was originally developed at Yardney under the NASA/DoD Consortium.**
    - **Chemistry amenable to wide range of operating temperatures (-30 to +40oC).**
    - **Ternary electrolyte EC:DMC:DEC**
    - **Provides good storageability**
  - **Cells also utilized much of the physical cell design proven in under the MSP01 program**
    - **Time frame necessitated a low risk approach.**

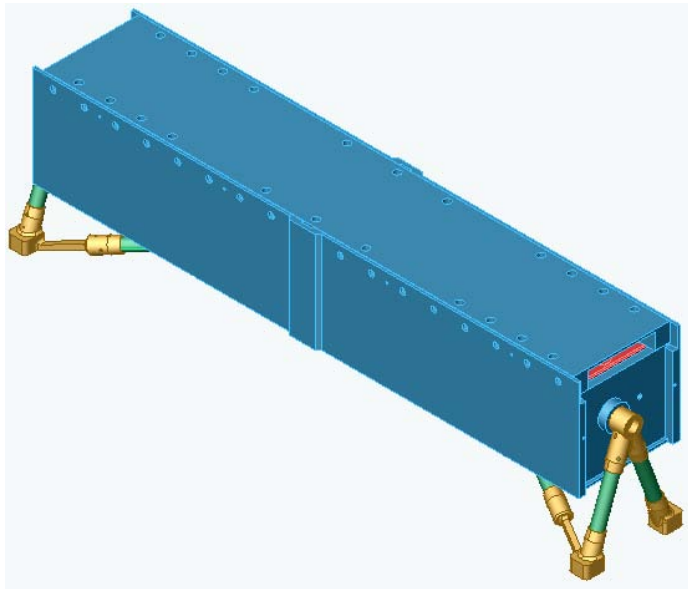


Mass: 295 grams

Volume: 123 cm^3

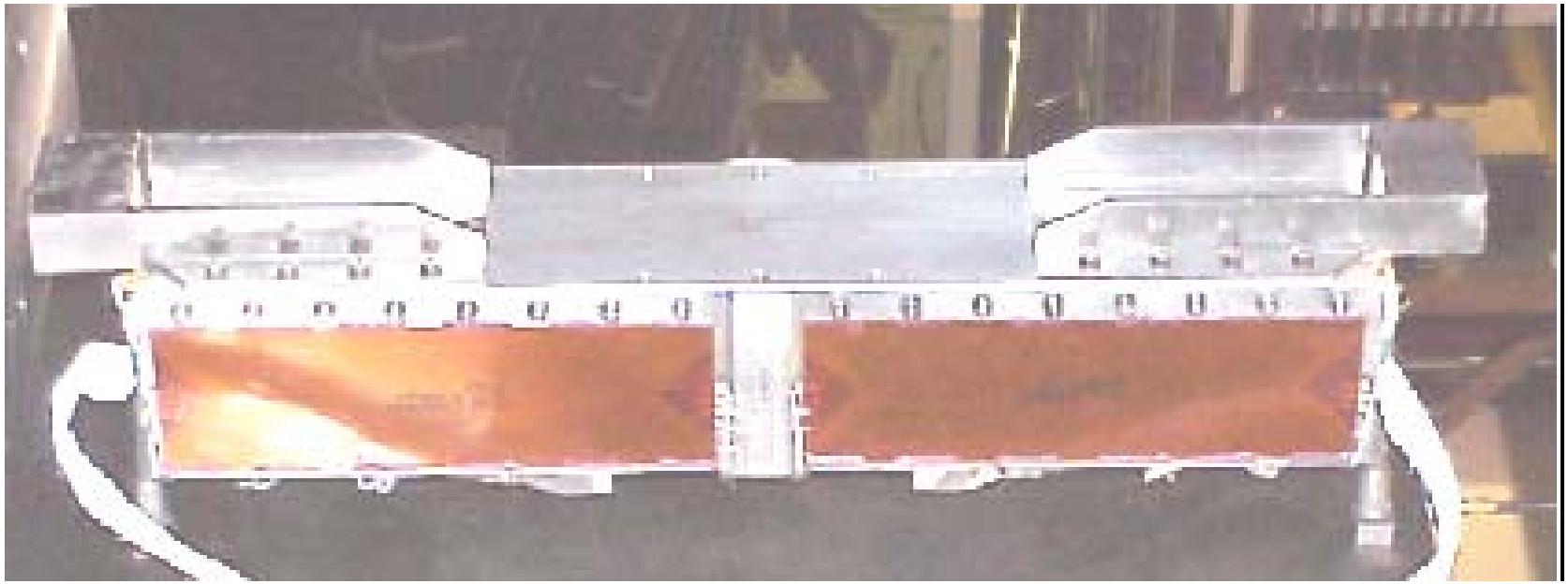
The RBAU Design





- **Two parallel batteries each with eight Li ion cells in series - 30 V, 16 Ah (480 Wh)**

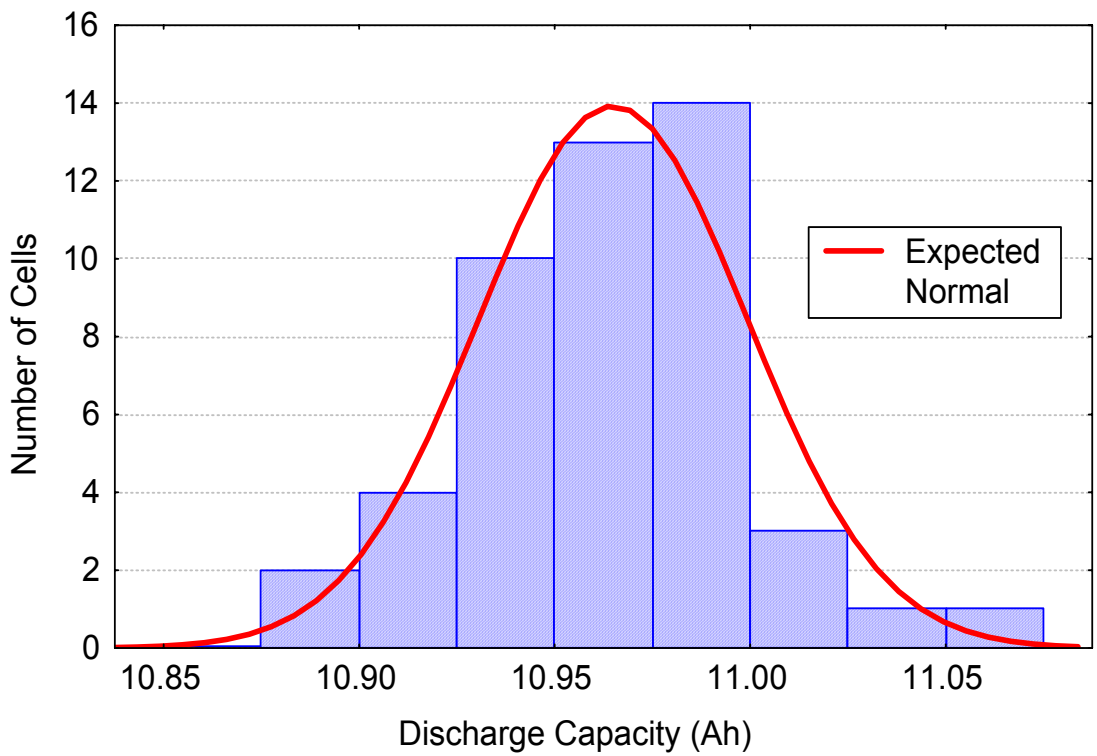
The RBAU Design



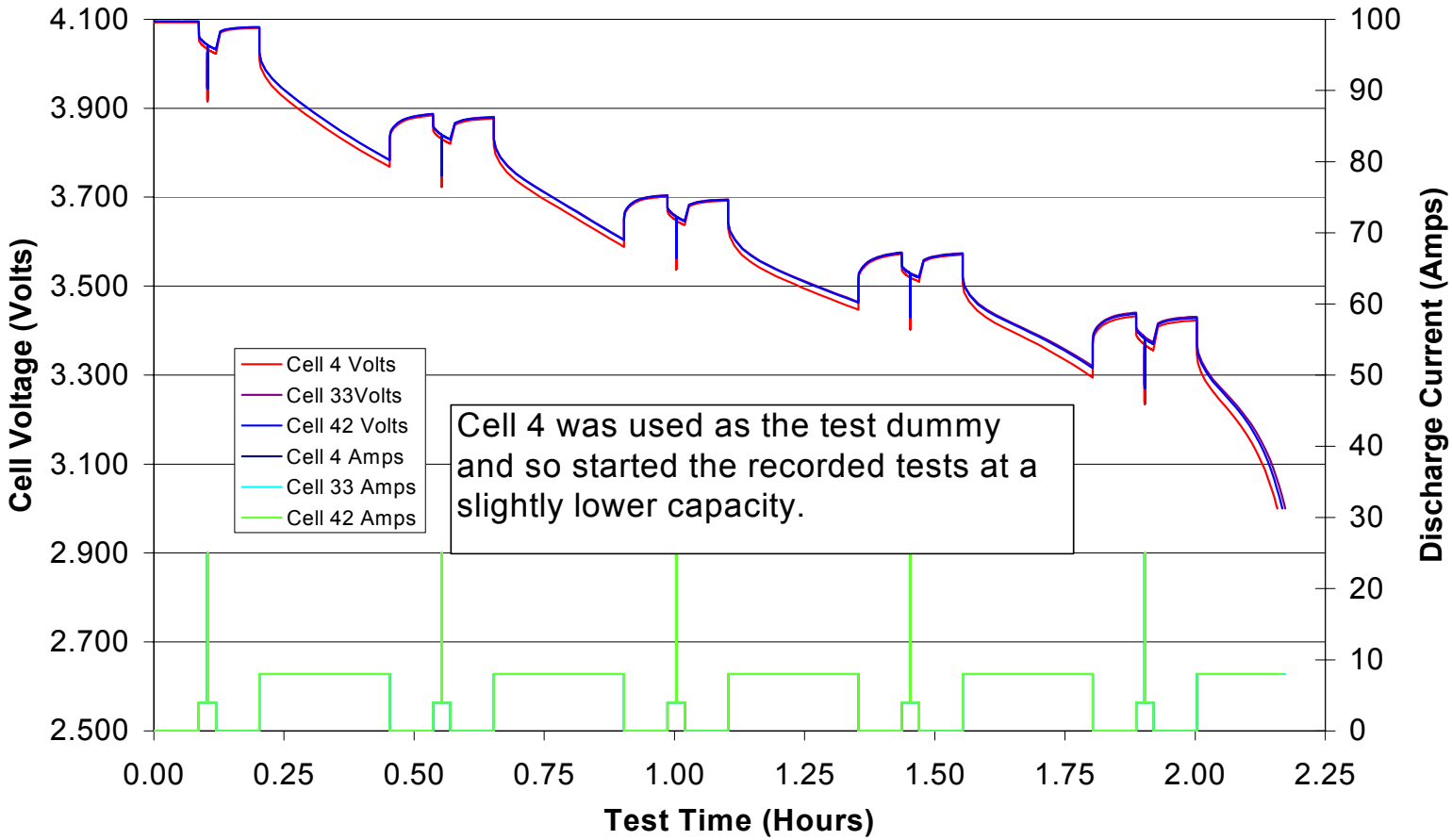
- **RBAU qualified for MER environments.**
  - **Random Vibration : 7.8 grms**
  - **Pyro Shock : 2000g**
  - **Landing load : 34 g**
  - **Thermal Vacuum : Eight cycles at 10-5 Torr at –30 to +40°C**

Cell Electrical Testing-Typical Results

- **Cells fabricated with additional QC steps (e.g., anode and cathode weights).**
- **The electrical testing of the cells showed a very tight cell to cell distribution**
  - **Entire Qualification build was less than ±1%**

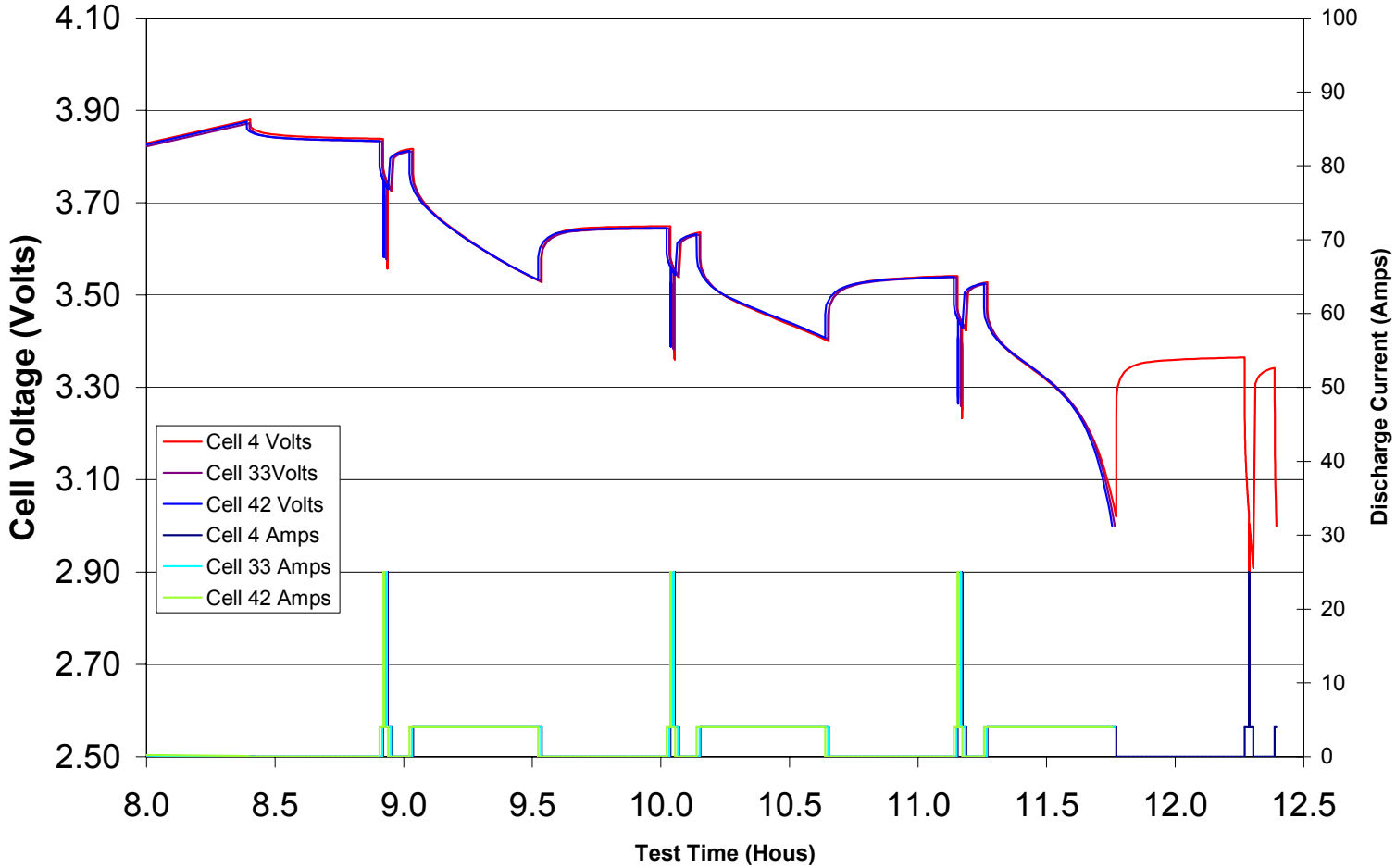


Pulse Capability of the Cells



- **20°C Requirement met at 100% of Charge and with 8Ah of capacity removed.**

Pulse Capability of the Cells



- **Cells were charged, at 0°C, at C/5, to 3.875 without a taper. Cells meet the requirement with 4 Ah removed.**
  - **This translates into a Cell OCV of 3.54 which corresponds to 35% SOC**

Electrical Testing-Cell Selection

- Cell selection consisted of two phases
  - Phase 1 was the removal of any cell that was not within ± 2.5σ on any process data or test.
  - The cells were then evaluated under an 8 criteria cell selection process.

1.) C/5 @ 20 °C (Ah)	2.) C/5 @ –20 °C (Ah)
3.) C/2 @ –10 °C (Ah)	4.) C/10 @ –20 °C (Time)
5.) C/5 @ 20 °C (Time)	6.) –20°C Rate Capability
7.) 20°C Rate Capability	8.) Self Discharge Rate

- Each of the 8 parameters underwent a weighting procedure based upon the amount that each cell varied from the mean.
  - A cell at nominal received a perfect score.
  - Variation from nominal decreased the score at the square of the amount of deviation.
- Each score was then multiplied by the weighting factor.
  - Weighting emphasis toward self discharge and charge times as ability to balance cells during mission was (is) uncertain.

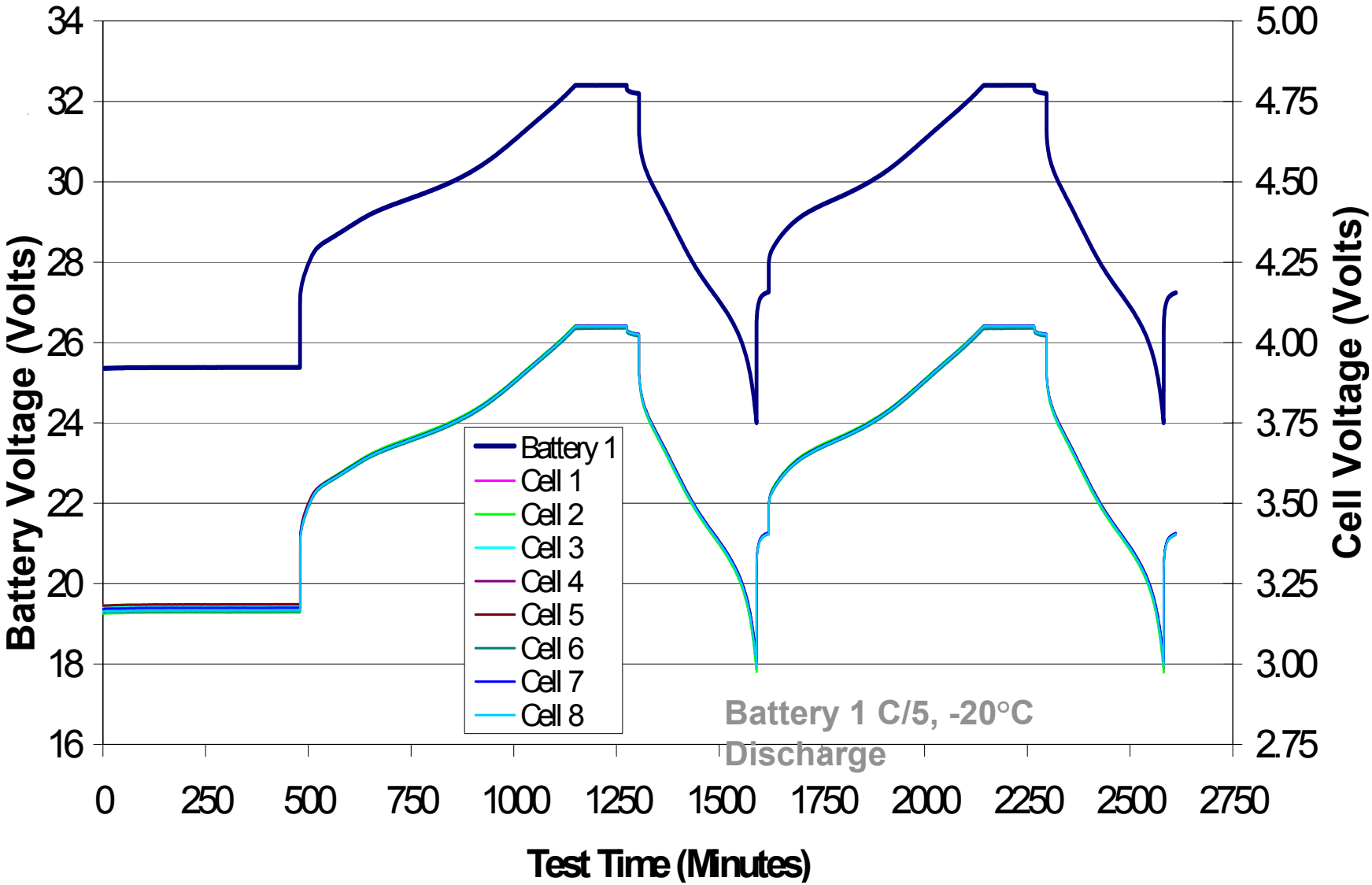
Electrical Testing-Cell Selection

- **Results: FM5 Battery 1**

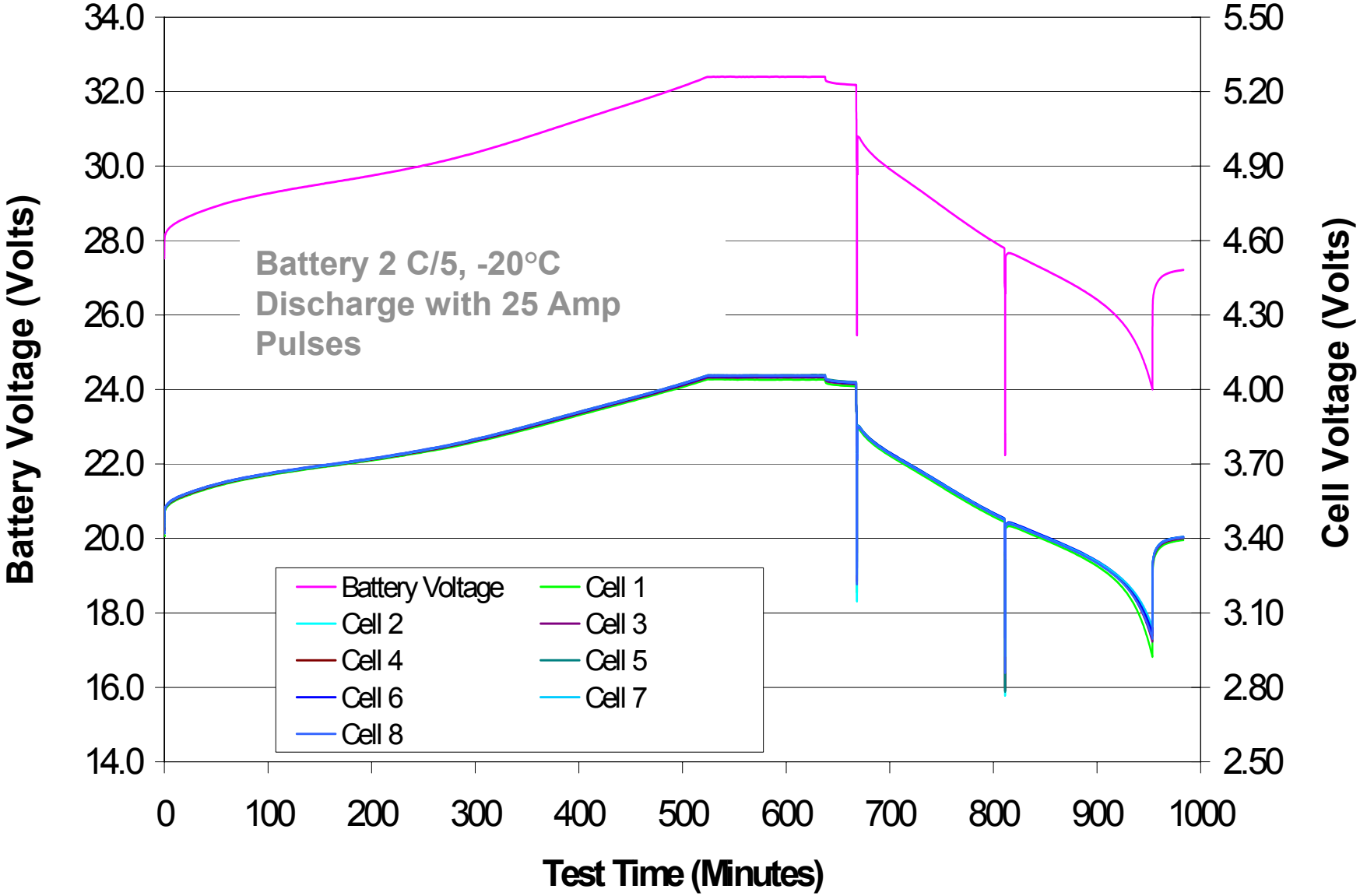
CELL ID	STAND	time_20	time_n20	C5_20A	N20_Rate	P20_rate	C2_N10A	C5_N20A
Cell 1	6.104	6.994	11.790	10.634	0.775	0.965	8.890	8.526
Cell 2	6.409	7.035	11.817	10.689	0.772	0.964	8.899	8.510
Cell 3	6.104	6.987	11.743	10.618	0.771	0.964	8.841	8.456
Cell 4	6.104	7.008	11.830	10.644	0.774	0.965	8.879	8.496
Cell 5	5.951	6.999	11.798	10.641	0.769	0.963	8.839	8.476
Cell 6	6.104	6.994	11.769	10.648	0.769	0.963	8.846	8.459
Cell 7	6.104	7.004	11.747	10.648	0.774	0.964	8.875	8.493
Cell 8	5.951	7.017	11.816	10.665	0.770	0.963	8.878	8.501
AVERAGE	**6.104**	**7.005**	**11.789**	**10.649**	**0.772**	**0.964**	**8.868**	**8.490**
STDEV	**0.141**	**0.015**	**0.033**	**0.021**	**0.003**	**0.001**	**0.023**	**0.024**
RANGE (±)	**3.85%**	**0.35%**	**0.37%**	**0.33%**	**0.45%**	**0.15%**	**0.34%**	**0.41%**

- **The 3.85% variation on the stand is multiplied by a factor of 1000 to be comparable. (Actual difference is <0.0005 V)**

Electrical Testing-RBAU Results



Electrical Testing-RBAU Results



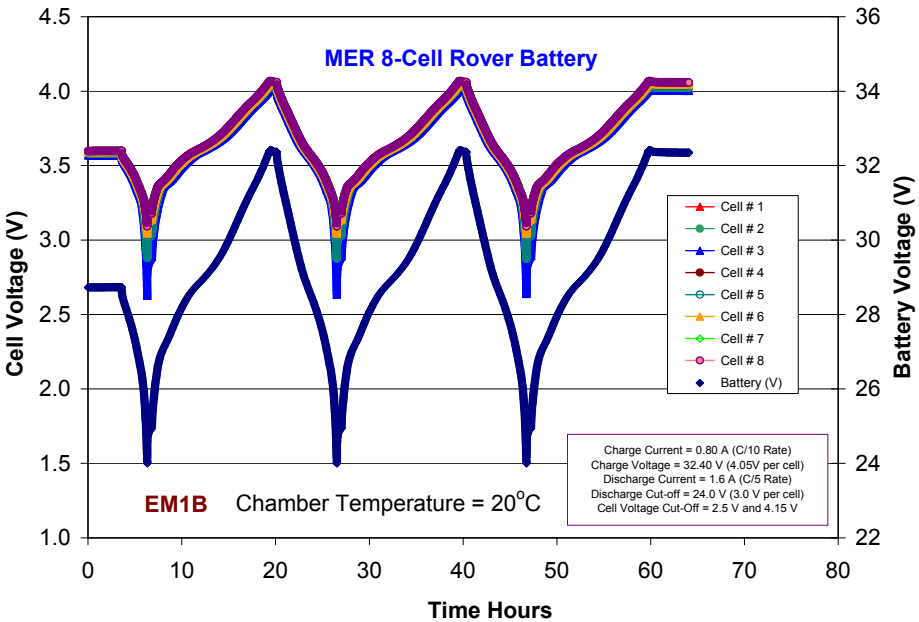
RBAU Testing (2003 MER Program)

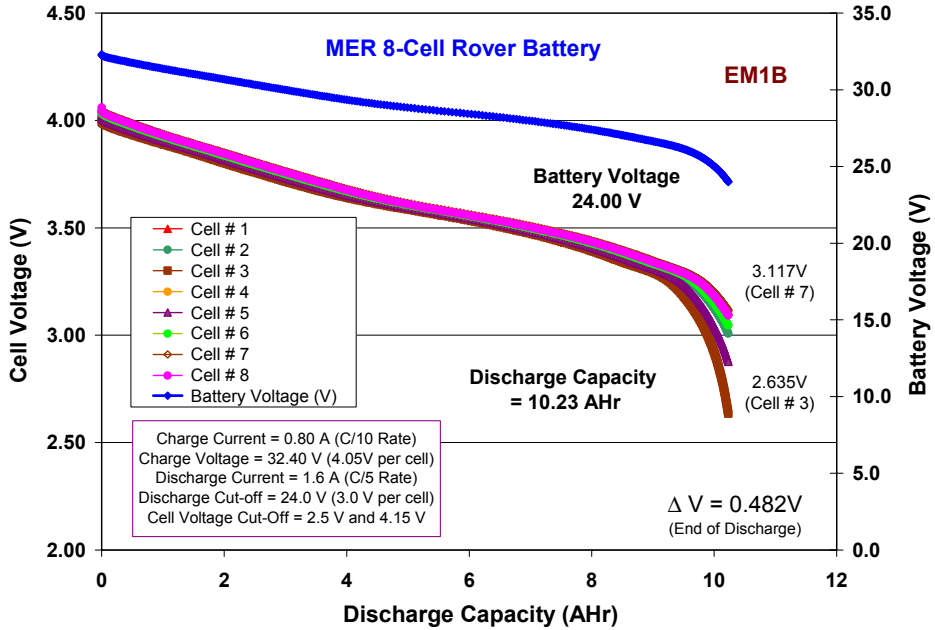
- **EM1 RBAU**
  - Acceptance Testing
  - Cruise Operation
  - EDL Operation (No pulsing)
  - Mission Surface Operation Simulation (~ 2 months of testing)
- **EM2 RBAU**
  - Acceptance Testing
- **FM1 RBAU**
  - Acceptance Testing
- **FM2 and FM 3 RBAU (ATLO)**
  - Acceptance Testing
- **Mission Simulation Battery**
  - Acceptance Testing
  - **Mission simulation**
- **Flight and flight spare RBAUs.**
  - Acceptance Testing

Acceptance Testing

- 3 Cycles at 20°C (C/5 Rate, charged to 32.4V)
- 72 Hour OCV Stand (Battery Fully Charged to 32.4V)
- 3 Cycles at - 20°C (C/5 Rate, charged to 32.4V)

Initial Characterization/Conditioning at 20°C

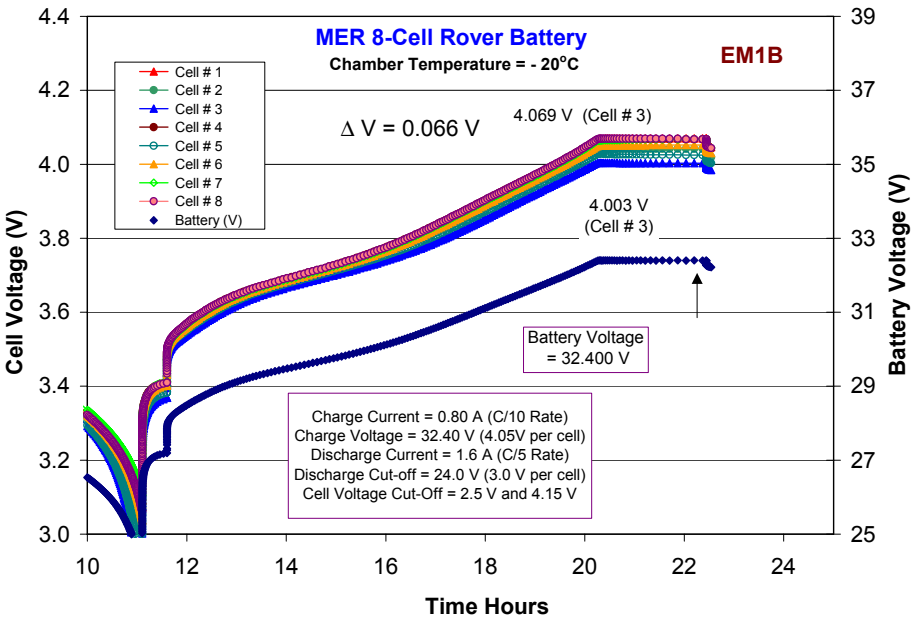


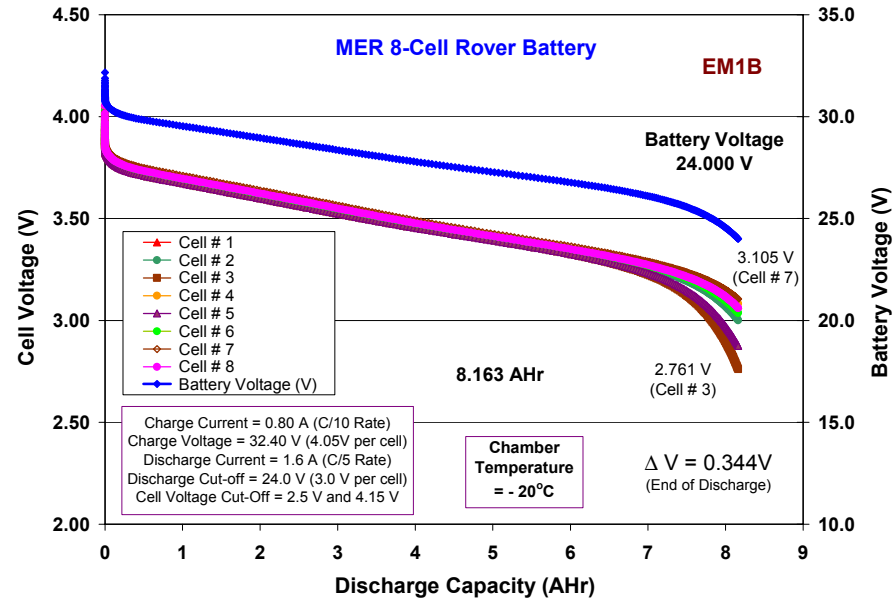


MER RBAU Engineering Module

Mars Exploration Rover

Initial Characterization/Conditioning at -20°C

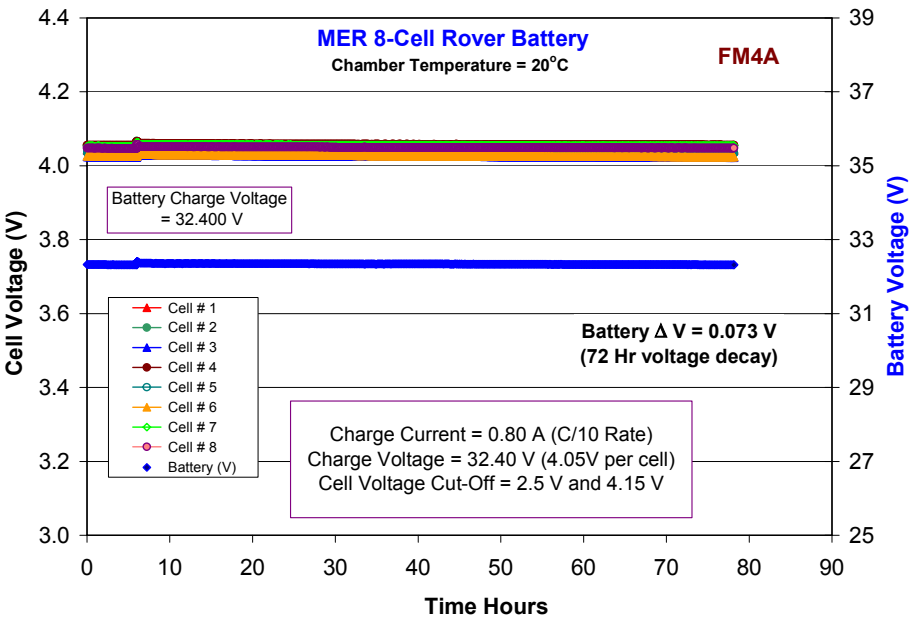


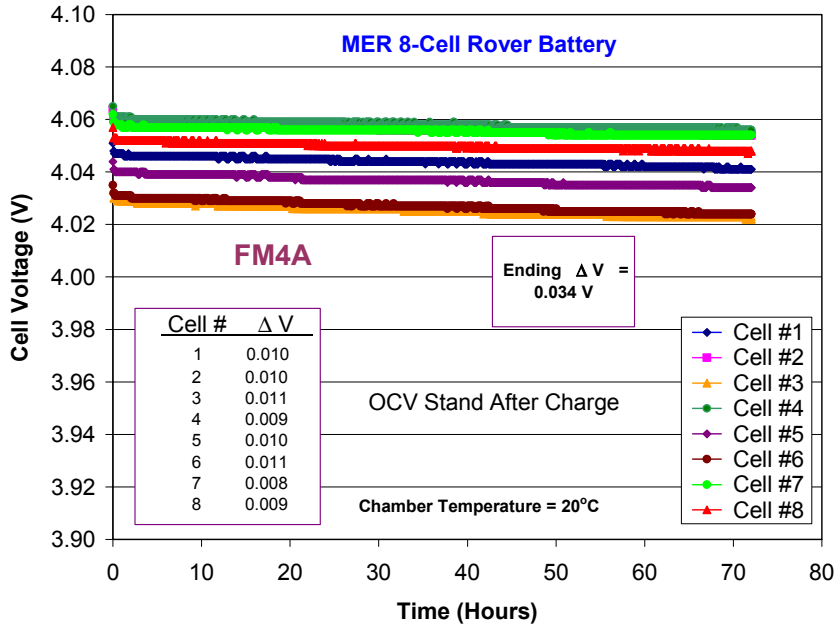


MER 8 Ah Rover Lithium-Ion Battery (FM4A)

Charge at 20°C + 72 Hr OCV Stand

Mars Exploration Rover

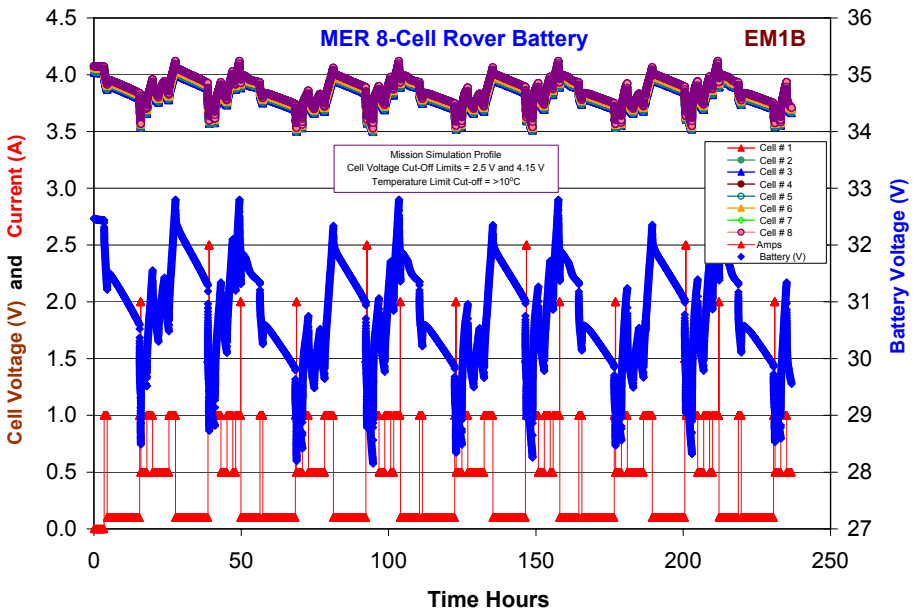


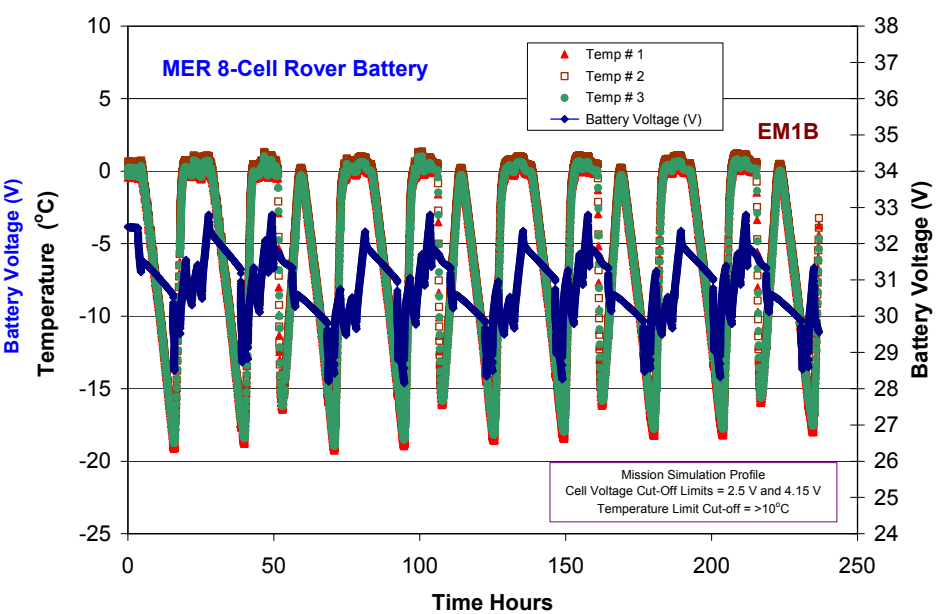


MER RBAU Engineering Module

Mars Exploration Rover

Mission Simulation Testing SOLS 1-8

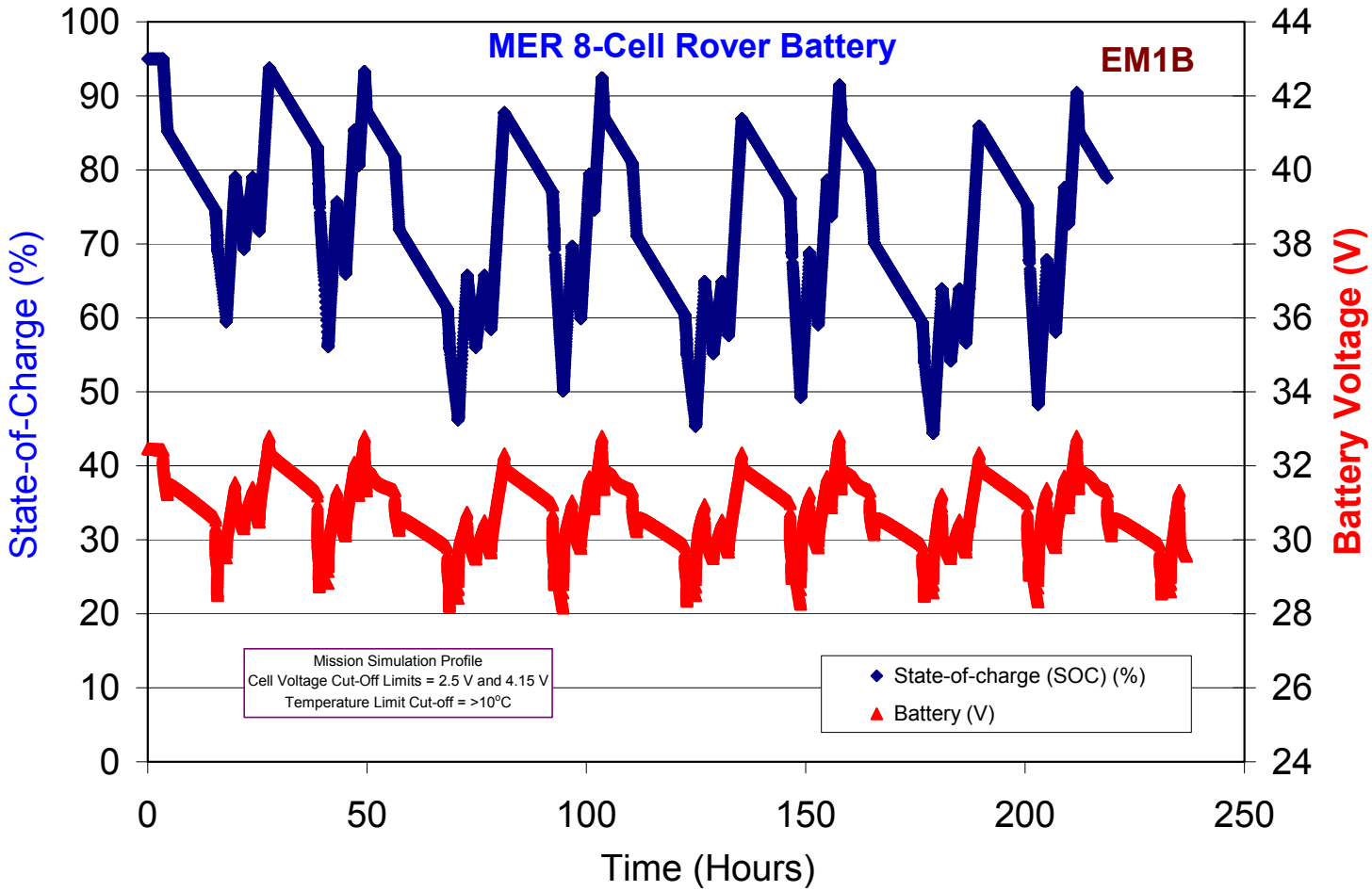




MER RBAU Engineering Module

Mars Exploration Rover

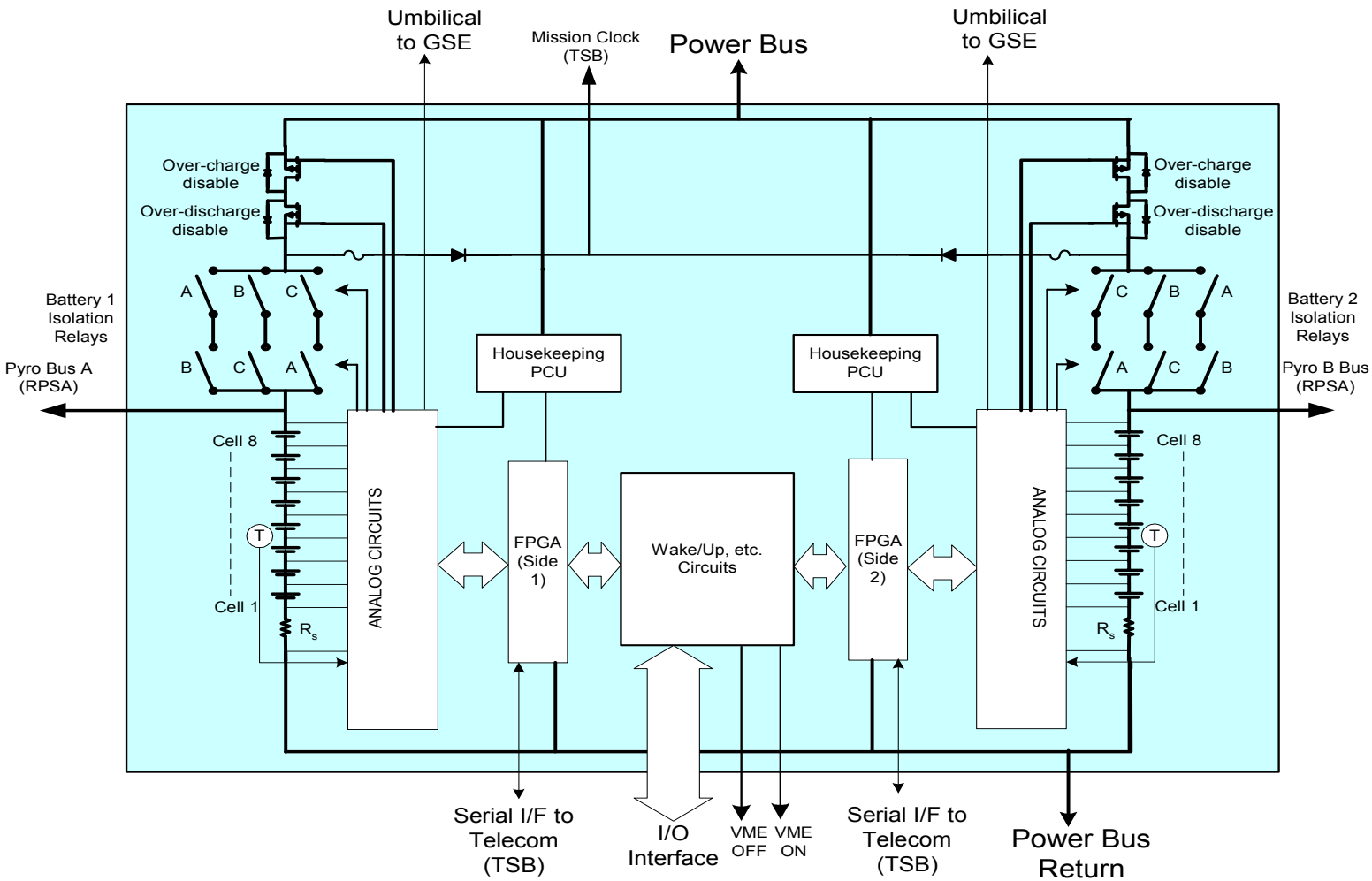
Mission Simulation Testing SOLS 1-8



Battery Control Board
Main Functional Requirements

- Monitors all of the critical power analog telemetry signals in the Rover
  - Rover solar array Voc
  - Rover solar array Isc
  - Bus voltage
  - Rover solar array current
  - Rover shunt current
  - Lander bus current (bi-directional)
  - Cruise bus current (bi-directional)
  - RPDU current
  - Rover battery voltage
  - Rover battery cell voltages (8 per battery)
  - Rover battery current (1 per battery)
  - Rover battery temperatures (5)
    - 3 internal, 1 battery case temperature, and routes 1 through umbilical
  - Measures and stores critical night time measurements
    - REM temp., SSPA LHP radiator inlet temp., Pan Cam CCD PRT

BCB: High Level Block Diagram



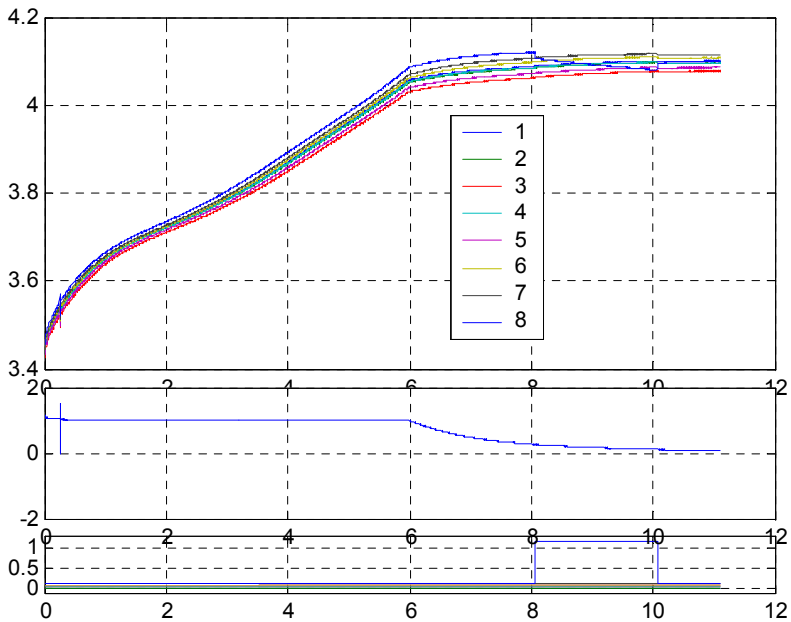
Battery Management

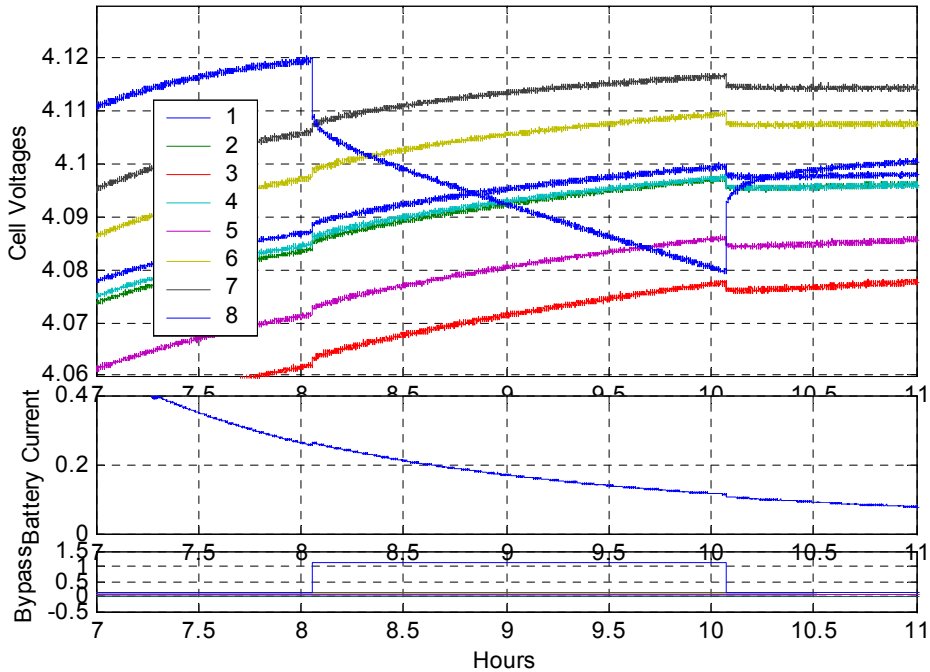
- Terminology Definitions
  - Vcmd (Vcommand)= Vsc (Vstop charge) = one of four prog levels (3.85, 3.95, 4.15, 4.20V)
  - Vbp (Vbypass) = Vcmd - 30mV
  - Vebp (Vend bypass) = Vcmd -70mV
  - Vch (Vcharge) = Vcmd - 150mV
  - Vd (Vdischarge) = 3.4V
  - Vsd (Vstop discharge) = 2.9V

Battery Management (cont.)

- Charge control
  - Stop Charge (open charge FET) if:
    - Any cell is greater than or equal to Vcmd
    - All cells are above Vbp
    - Charge rate is greater than 1C
    - Any cell is <1V and the battery is >20V.
  - Start Charge (close charge FET) if:
    - All cells are below Vch
    - After POR
  - Stop Discharge (open discharge FET) if:
    - Any cell is less than or equal to Vsd
    - Discharge rate exceeds 2C (latchoff, ground only)
  - Start Discharge (close discharge FET) if:
    - All cells are above Vd.
- Charge Balancing
  - Start cell bypassing at or above Vbp
  - Stop cell bypassing at or below Vebp

BCB/Battery Lab Results





Summary

- The 2003 Mars Exploration Rovers (MER) have Li-SO_2 primary batteries on the Lander to support the EDL operations, Li-FeS_2 thermal batteries on the back shell for firing pyros during cruise stage separation and Li ion rechargeable batteries on the Rover to assist in the launch, TCM and surface operations.
- The Rover is about ten times bigger in size, pay load and traversing capability than the previous Sojourner rover and will have a longer mission life with the rechargeable batteries.
- Lithium ion batteries fabricated by Yardney Technical Products for the MER mission show adequate performance in the operating range, in the MER environments, under steady state and pulse currents and, also in conjunction with a battery charger designed and built in-house.

Acknowledgements

The work described here was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) and was supported by NASA's 2003 Mars Exploration Rover and NASA Battery Code S Program.

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NATIONAL SPACE DEVELOPMENT AGENCY OF JAPAN

Cycling Behavior of the Commercial Lithium Ion Polymer Cells Simulating Satellite's Low-Earth-Orbit Application

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1. Introduction

Lithium Ion Polymer Batteries for Satellite Applications

Main Advantages

1) High Energy Density and Working Voltage — Weight Saving

2) Low Self Discharge — Simple Management

3) No Memory Effect — Unnecessary to Use Reconditioning

4) Flexibility in Configuration — Volume Reduce

1. Introduction

Lithium Ion Polymer Batteries for Satellite Applications

Possible Problems

1) Cycling Life Verification

2) Safety Concerns

3) Endurance to Vacuum Surroundings

1. Introduction

Lithium Ion Polymer Cells (~0.56 Ah) from Companies A, B, C, D

- 1) Cycling Life Test Simulating Low-Earth-Orbit Application
- 2) Evaluation on Effect of Operating Conditions (Charge Rate and Taper Voltage) on Cell Performances
- 3) Investigation on the Mechanism of Cell Volume Change with Cycling

2. Results and Discussion

1) Cycle Life Test at Different Charge Rates

LEO Simulation (DOD = 40%)

Charge: CC-CV, 4.1 V, 60 min, 0.5 C or 1.0 C

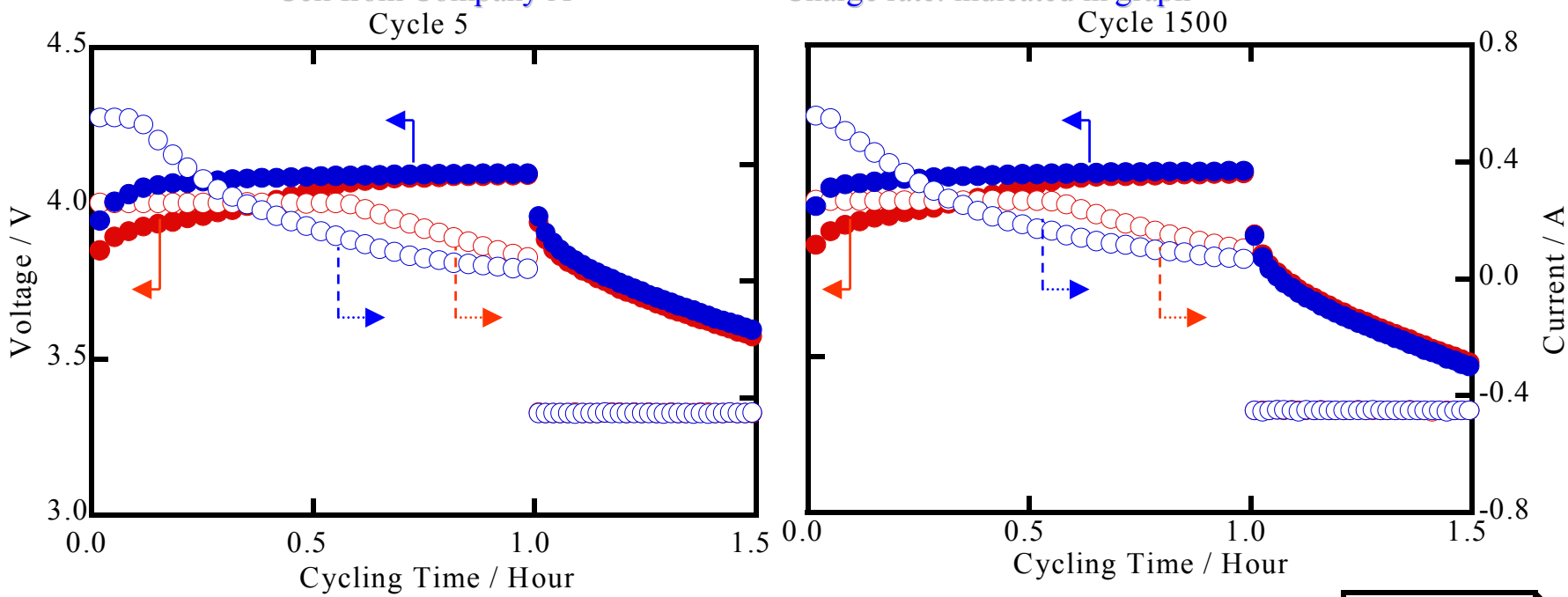
Discharge: CC, 0.8 C, 30 min

Plate Temperature: 20±2°C

2. Results and Discussion — 1) Charge Rate Effect

Cell from Company A

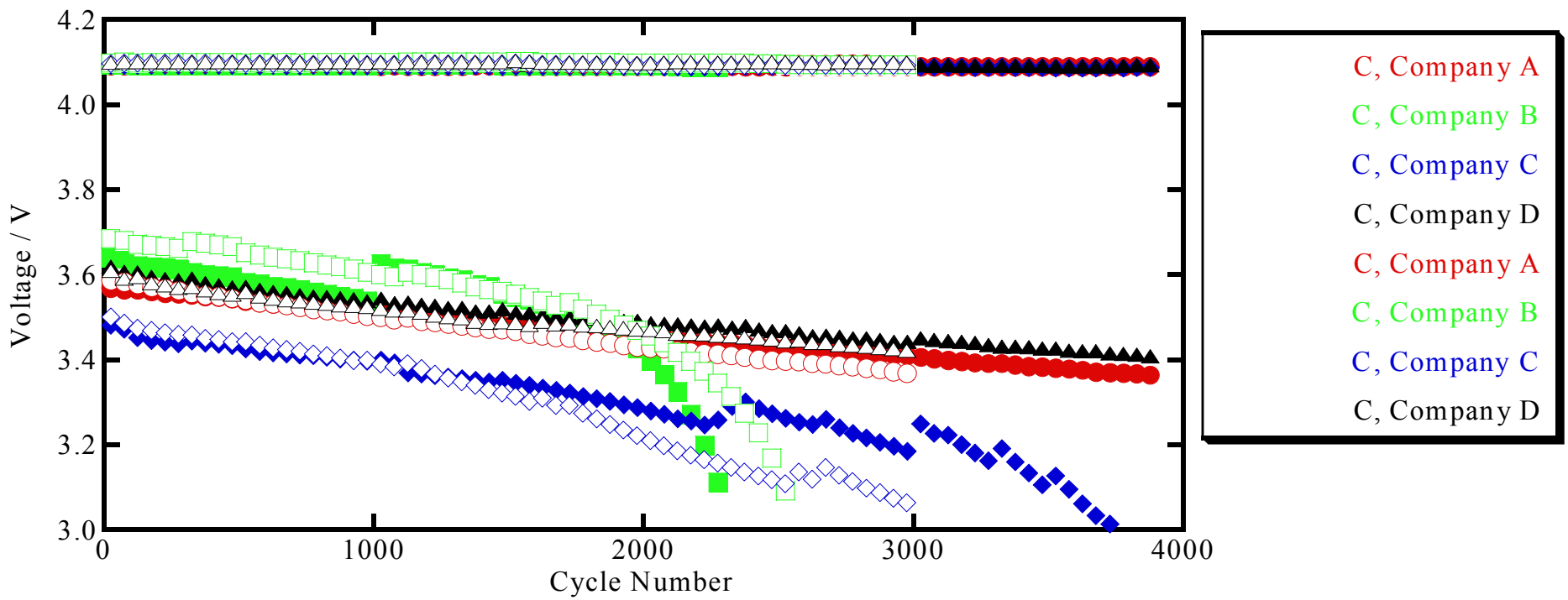
Charge rate: indicated in graph



High charge rate results in low end-of-charge current and high end-of-discharge voltage at initial cycles. But with cycling, the end-of-discharge voltage drops faster at high charge rate than that at low charge rate due to long holding time at taper voltage.

2. Results and Discussion — 1) Voltage Trend

At End of Charge/Discharge

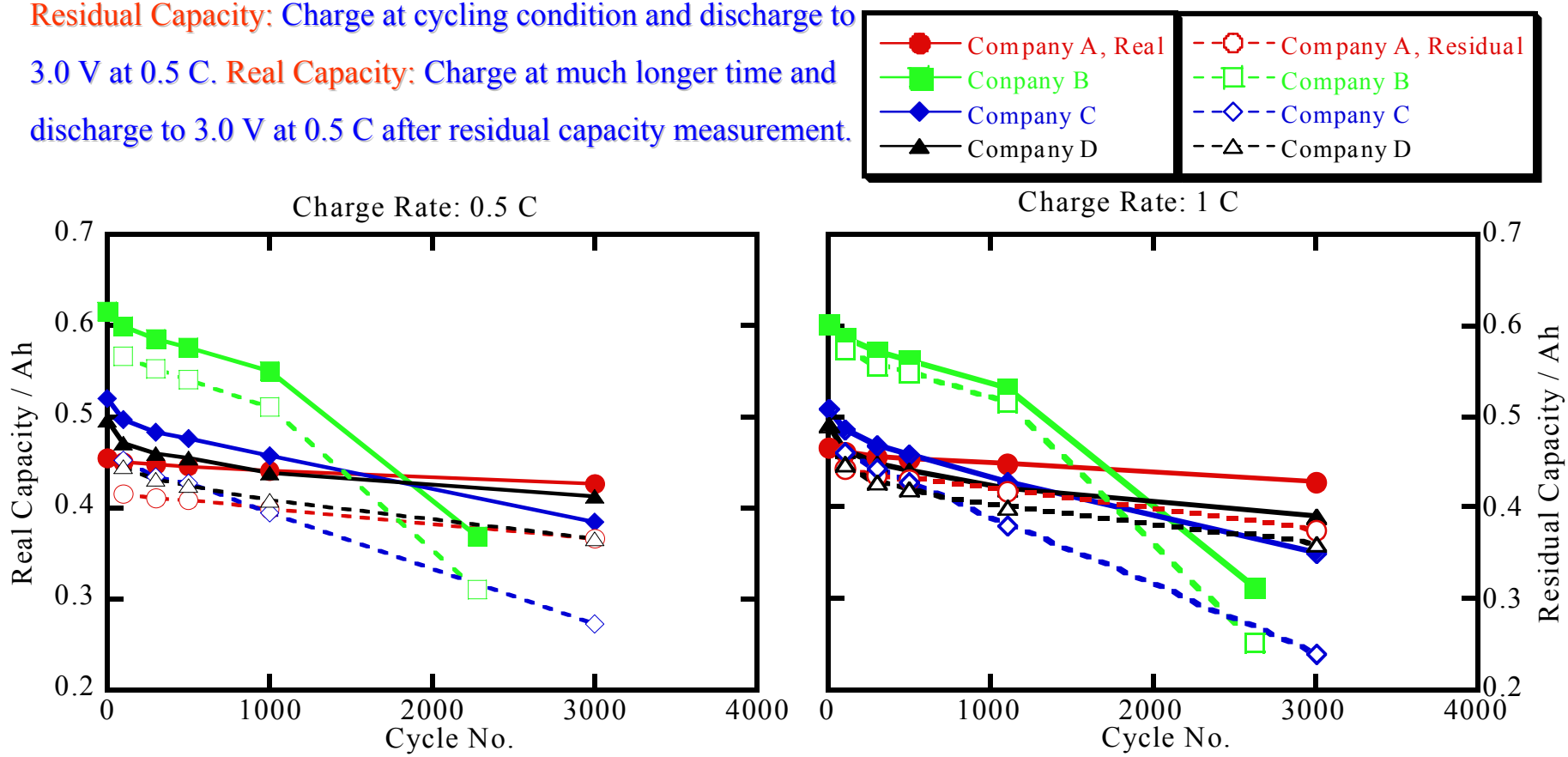


1) Cells from Companies D and A exhibit better cycling performances

2) Low charge rate is favorable to realize long cycle life

2. Results and Discussion — 1) Capacity Fading

Residual Capacity: Charge at cycling condition and discharge to 3.0 V at 0.5 C. Real Capacity: Charge at much longer time and discharge to 3.0 V at 0.5 C after residual capacity measurement.



Cells of Companies D and A exhibit slight capacity fading.

2. Results and Discussion

2) Taper Voltage Effect

LEO Simulation (DOD = 40%)

Charge: CC-CV, 0.5 C, 3.9 – 4.2 V, 60 min

Discharge: CC, 0.8 C, 30 min

Thermostat: 20±1°C

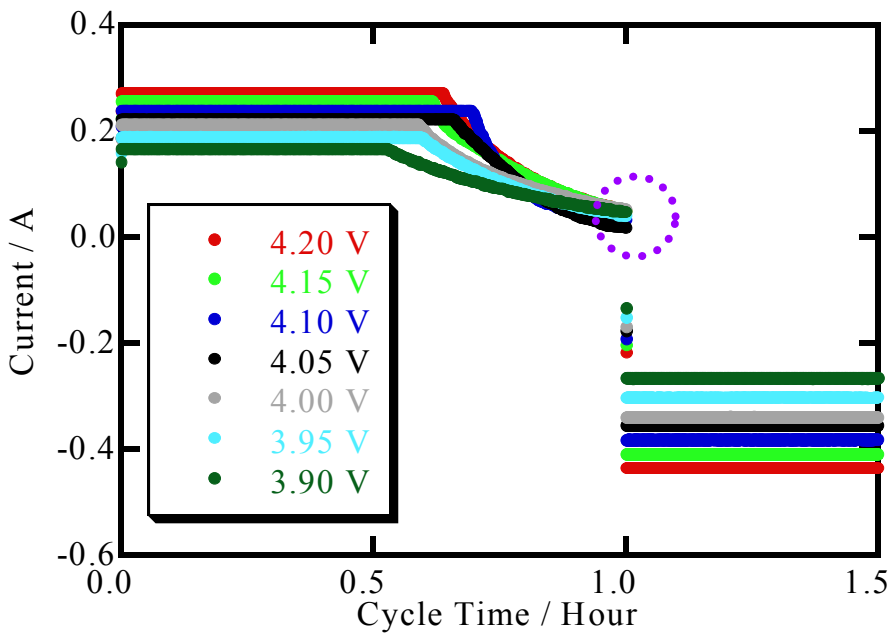
5 Cycles at Every Taper Voltage Level

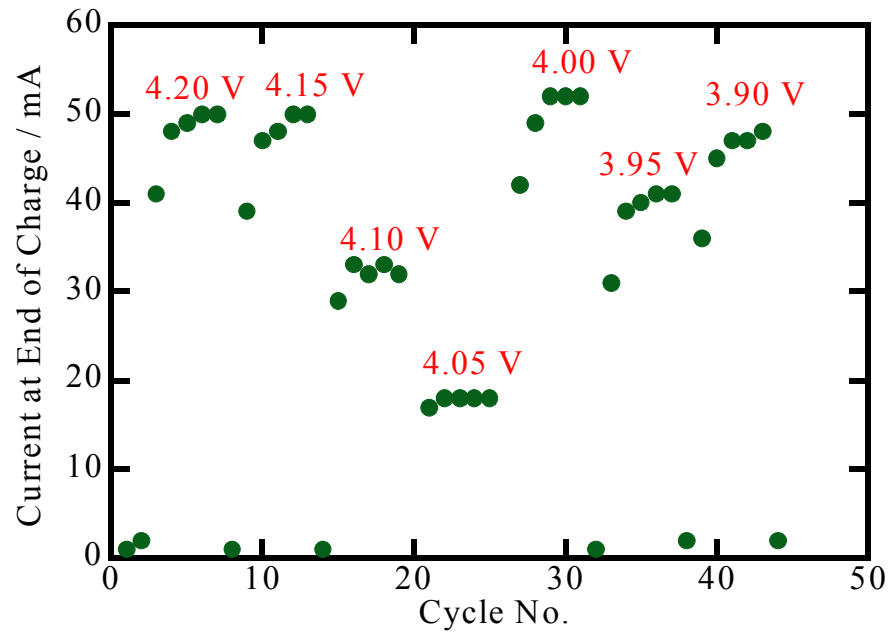
Pre-charge before Changing Taper Voltage

CC-CV, 1.0 C, 3.9 – 4.2 V, Taper Time: 2 hrs

2. Results and Discussion — 2) Current at End of Charge

Company B. Current Curve: 4th cycle at every taper voltage

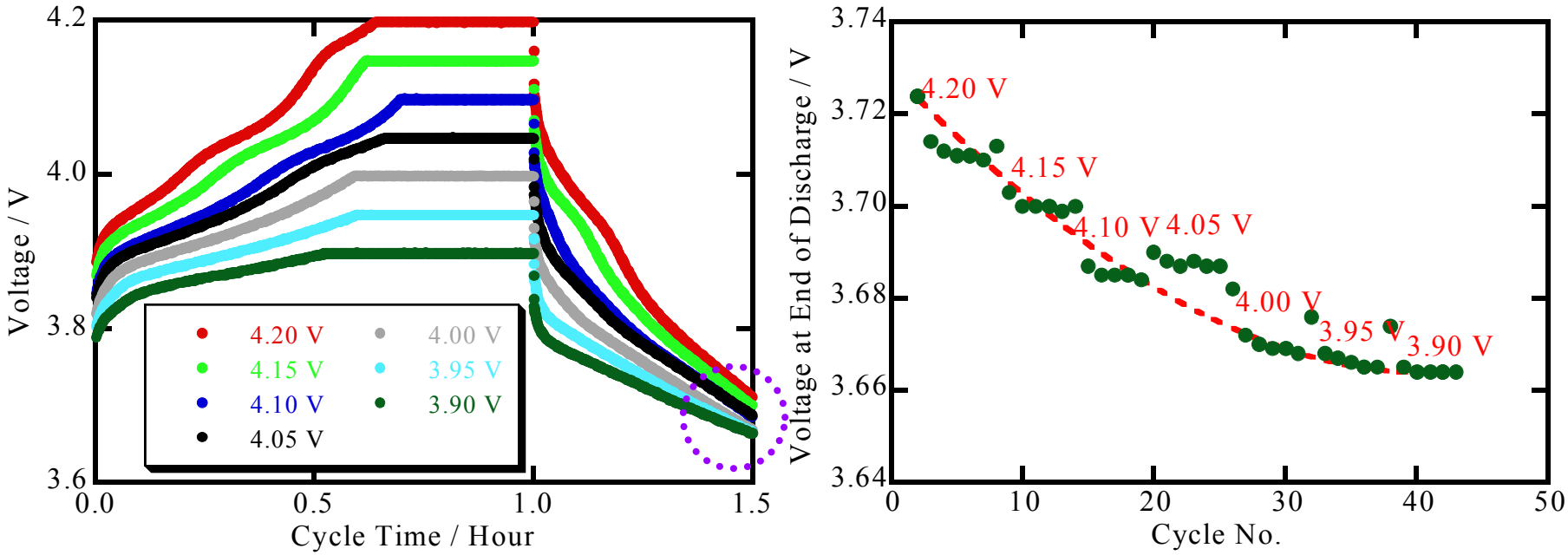




The current at end of charge is minimum at a special taper voltage of 4.05 V.

2. Results and Discussion — 2) Voltage at End of Discharge

Company B. Voltage Curve: 4th cycle at every taper voltage



The voltage at end of discharge is relatively high at this special taper voltage of 4.05 V.

2. Results and Discussion — 2) Theoretical Analysis

For a cell with charge condition of constant voltage and enough small current

$$I = I_c \exp\{-[(\Delta V/\Delta Q)/R]\,t\}$$

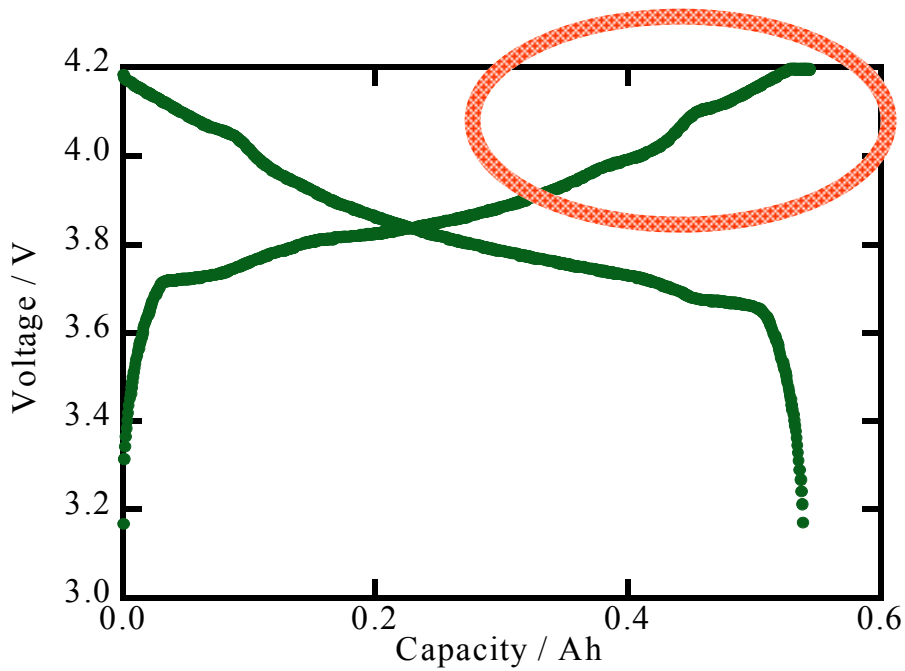
I	Current
I_C	Current after Constant-Voltage Charge
ΔV	Change of Applied Voltage
ΔQ	Change of Charge Quantity
R	Inner Cell Impedance
t	Time

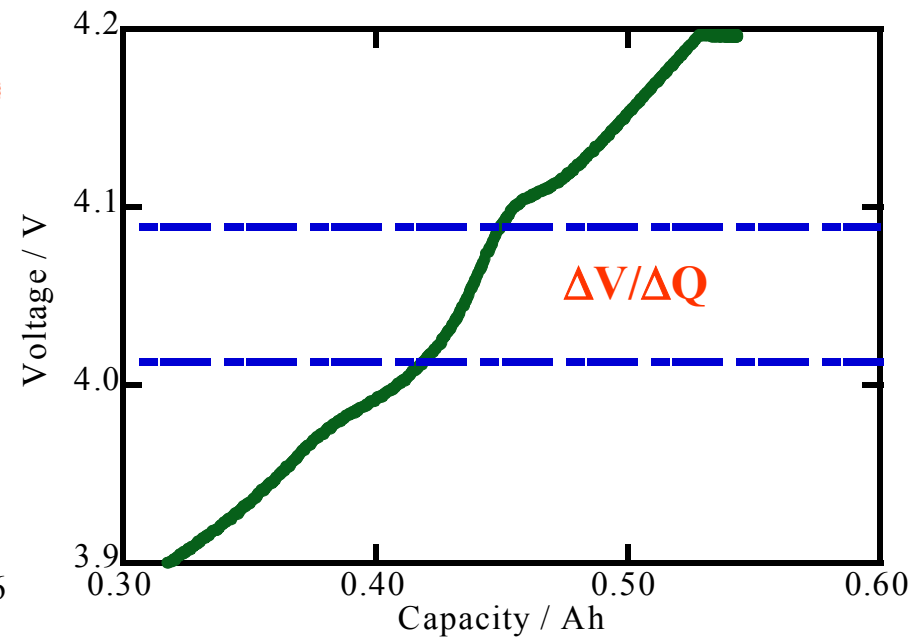
Referred to A. J. Bard, "Electrochemical Methods"

At given time, I is small if
1) $\Delta V/\Delta Q$ is large;
2) R is small

2. Results and Discussion — 2) Prediction of Optimum Voltage

Company B. Charge/discharge at Low Rate (0.1 C)





The biggest ΔV/ΔQ is found between 4.0 V and 4.1 V. So optimum taper voltage where the current at end of charge is minimum should drop in this voltage range.

2. Results and Discussion

3) In-situ Study on Cell Volume Change with Cycling

Charge: CC-CV, 1.0 C, 4.2 V, Taper Time: 2 hours

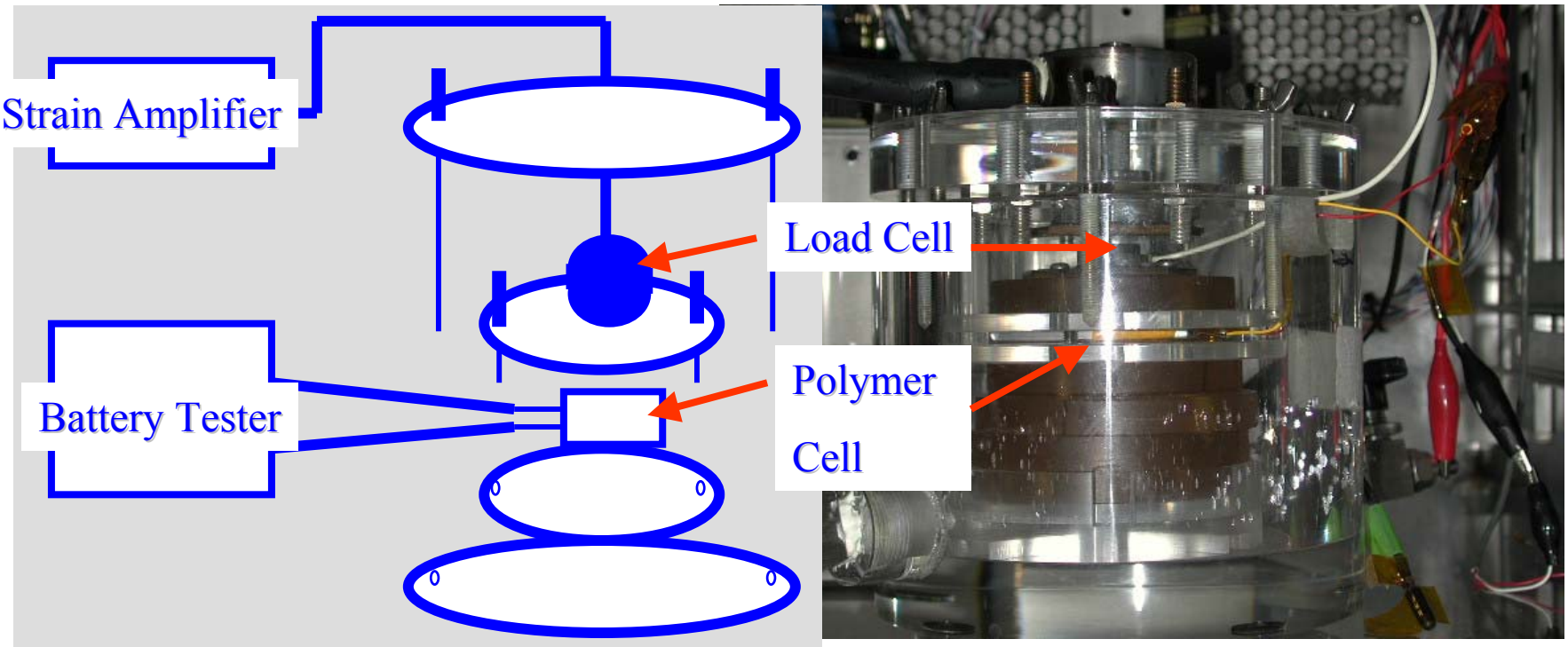
Discharge: CC, 1.0 C, 3.0 V

Load Cell Measurement: Thermostat: 20±1°C

X-ray Observation: Room Temperature: 20±3°C

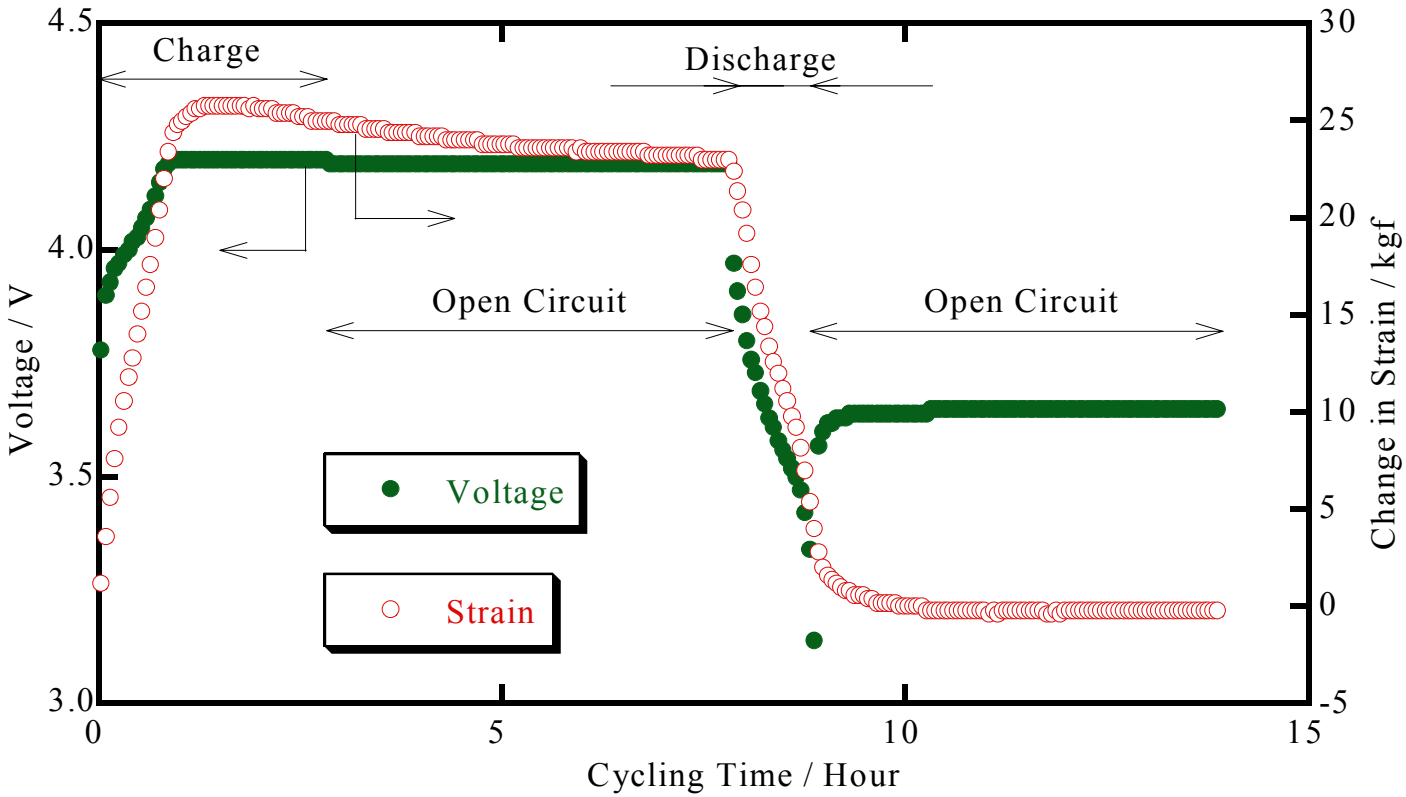
Sample: Cell form Company B

2. Results and Discussion — 3) Load Cell Measurement



The strain change reflects the cell volume change.

2. Results and Discussion — 3) Load Cell Measurement

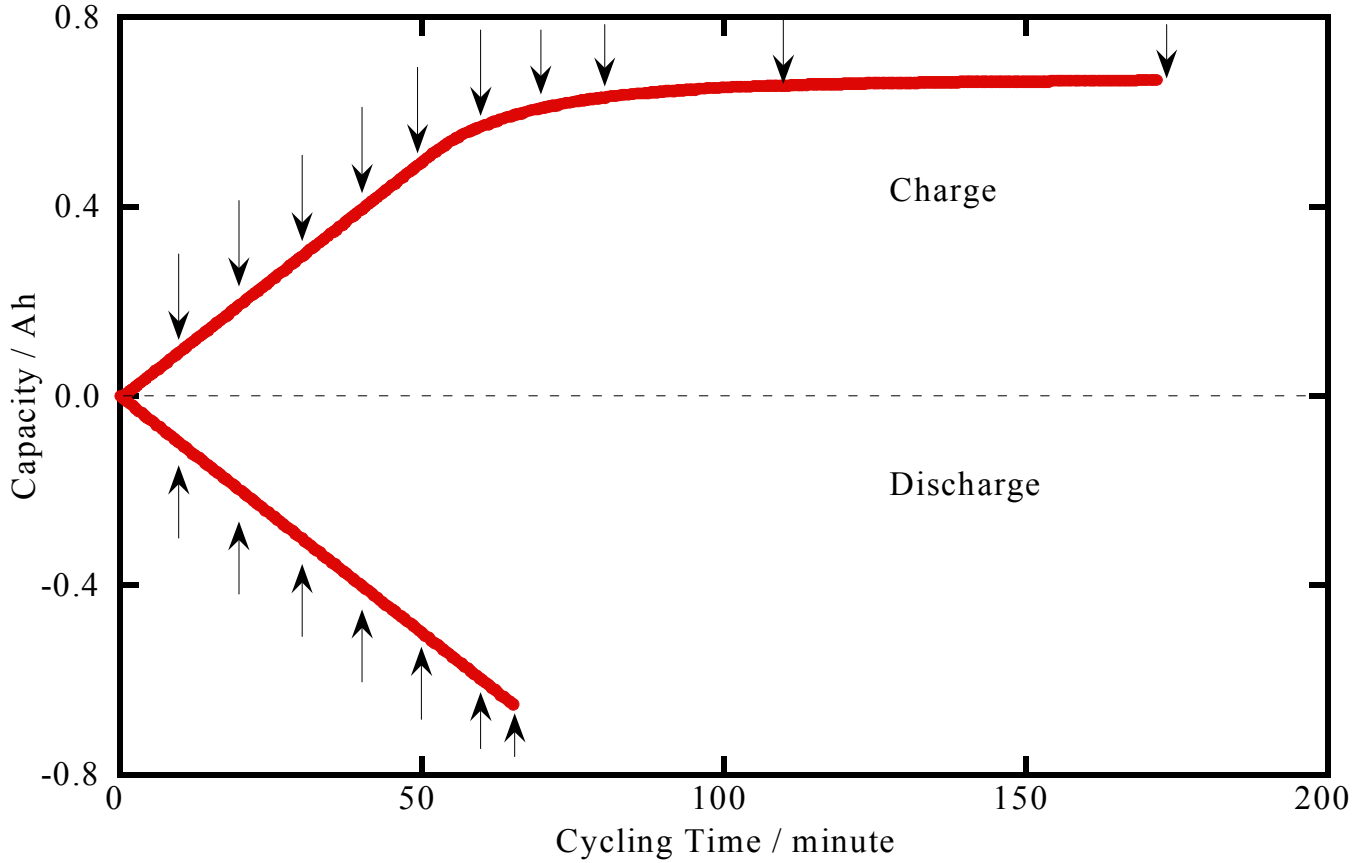


1) CHARGE: Strain first increases. The maximum strain value appears at the 38th minute after moving to CV charge phase. Then strain decreases slightly. At open circuit state, the strain decrease is observed.

2) DISCHARGE: Strain decreases. At open circuit state, strain decrease is also observed.

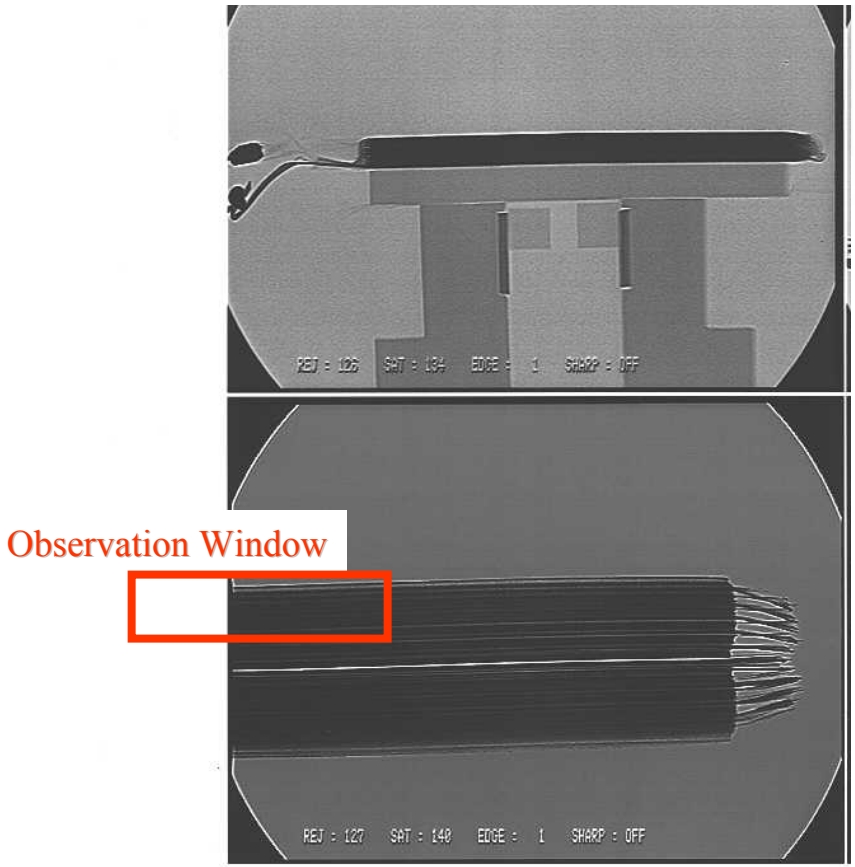
2. Results and Discussion — 3) X-Ray Observation

X-ray photo is taken at a special interval as shown in graph.

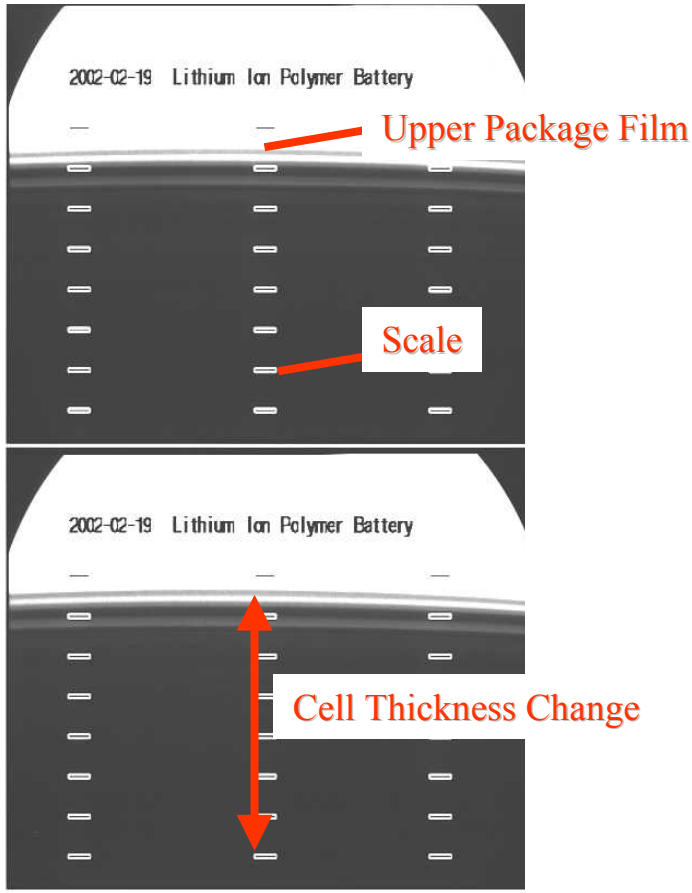


2. Results and Discussion — 3) X-Ray Observation

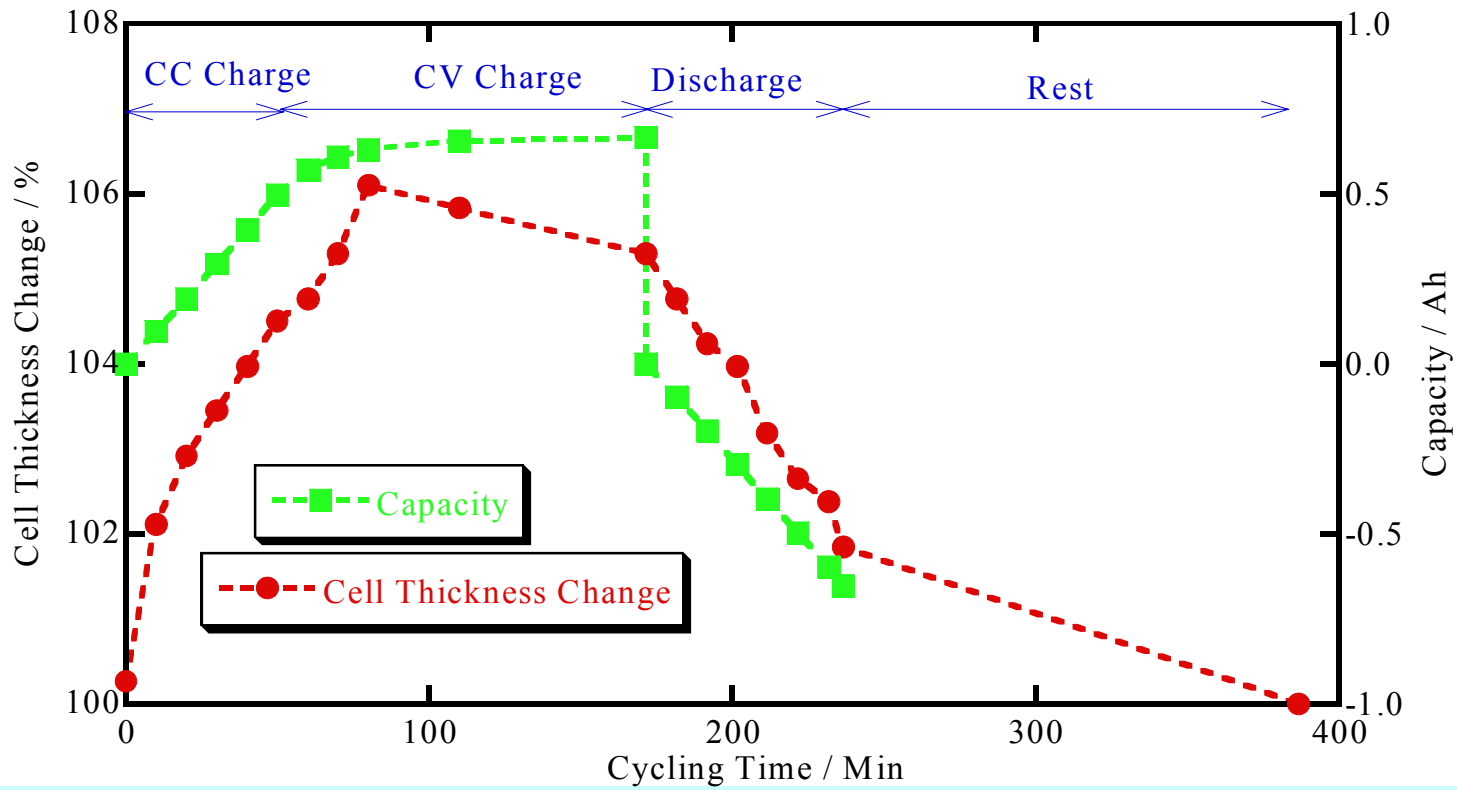
Cell Setup



Example of Experimental Result



2. Results and Discussion — 3) X-Ray Observation

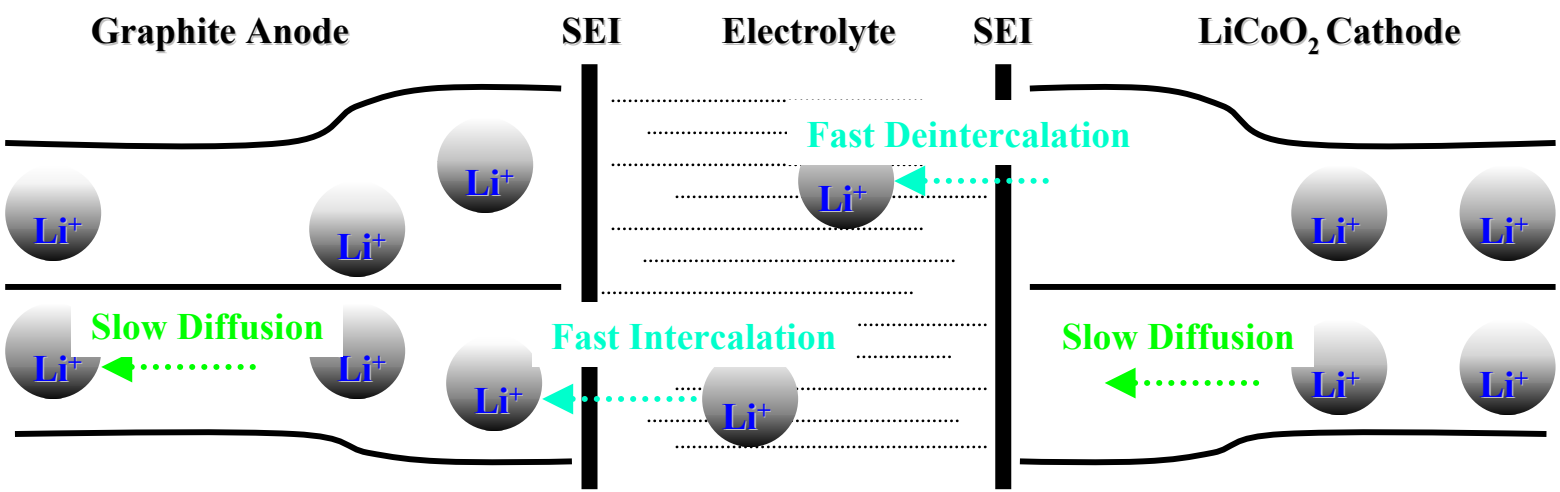


1) CHARGE: Cell thickness first increases. The maximum value appears after moving to CV charge phase. Then cell thickness decreases slightly.

2) DISCHARGE: Cell thickness decreases. At open circuit state, cell thickness decrease is observed.

2. Results and Discussion — 3) Possible Explanation

Example: Charge at High Rate



1) Fast intercalation/deintercalation of lithium ion at high rate
2) Slow diffusion of lithium ion in the electrode active materials
3) Unbalanced distribution of lithium ion near electrode/electrolyte interphase
4) Excessive volume change temporarily

Cell volume change depends on not only the state of charge but also charge/discharge rate.

3. Summary (1)

Lithium Ion Polymer Cells for Satellite Application

- 1) Cycle life test is still continued to find the cells having good cycling performances.
- 2) Though high charge rate results in good charge performance at initial cycles, the voltage at end of discharge drops faster than that at low charge rate with cycling.

3. Summary (2)

- 3) Appropriate taper voltage, where current at end of charge is minimum, may be predicted by charge curve.
- 4) The delay of cell volume change as a function of state of charge is observed by in-situ studies of load cell and X-ray observation.

LITHIUM ION DD CELLS
SPACE APPLICATION CYCLING UPDATE

HAIYAN CROFT

BOB STANIEWICZ

SAFT America Inc.

Advanced Battery Systems Division

Cockeysville, MD

The 2002 NASA Aerospace Battery Workshop

Huntsville, Alabama

November 19- 21, 2002

DD Cell

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OVERVIEW

- DD CELLS
  - CHEMISTRY
  - HOW ACCELERATED TESTING IS PERFORMED
  - LEO TESTING
  - GEO TESTING
  - 100% DOD at RT
  - 100% DOD at –20^{0}C
  - CONCLUSION

CHEMISTRY

- CHEMISTRY
  - POSITIVE MATERIAL: $LiNi_{1-x-y}Co_xM_yO_2$
  - NEGATIVE IS ADMIXTURE OF TWO GRAPHITES WITH NON-PVDF BINDER
- CAPACITY: 9.5 AH
- ENERGY DENSITY: 140 WH/KG

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HARDWARE

- STAINLESS STEEL HARDWARE
- CELL DIMENSION: CYLINDRIAL
  - CELL OD 32 MM OR 1.32 IN
  - CELL HEIGHT 122MM OR 4.8 IN
- MULTIMPLE TABS ON ELECTRODES
- CELL WEIGHT: 250 GRAMS

- LEO AND GEO CYCLING DEMONSTRATING PERFORMANCES FOR PLANETARY AND INTERPLANETARY APPLICATIONS

DEPTH OF DISCHARGE	CYCLES ACHIEVED TO DATE	EOL
30%	25,000	40K CYCLES
60%	2800	1350
100%@-20C	1000	

ACCELERATED TESTING METHODS

WE JUDGED WHAT MIGHT BE REASONABLE, ACCELERATED TRADE-OFFS OF TIME AND CURRENT TO ACCOMPLISH CYCLE DEMONSTRATION

GEO – ACCELERATION IS STRAIGHTFORWARD:

WE ADOPTED 1.2 HOURS FOR DISCHARGE

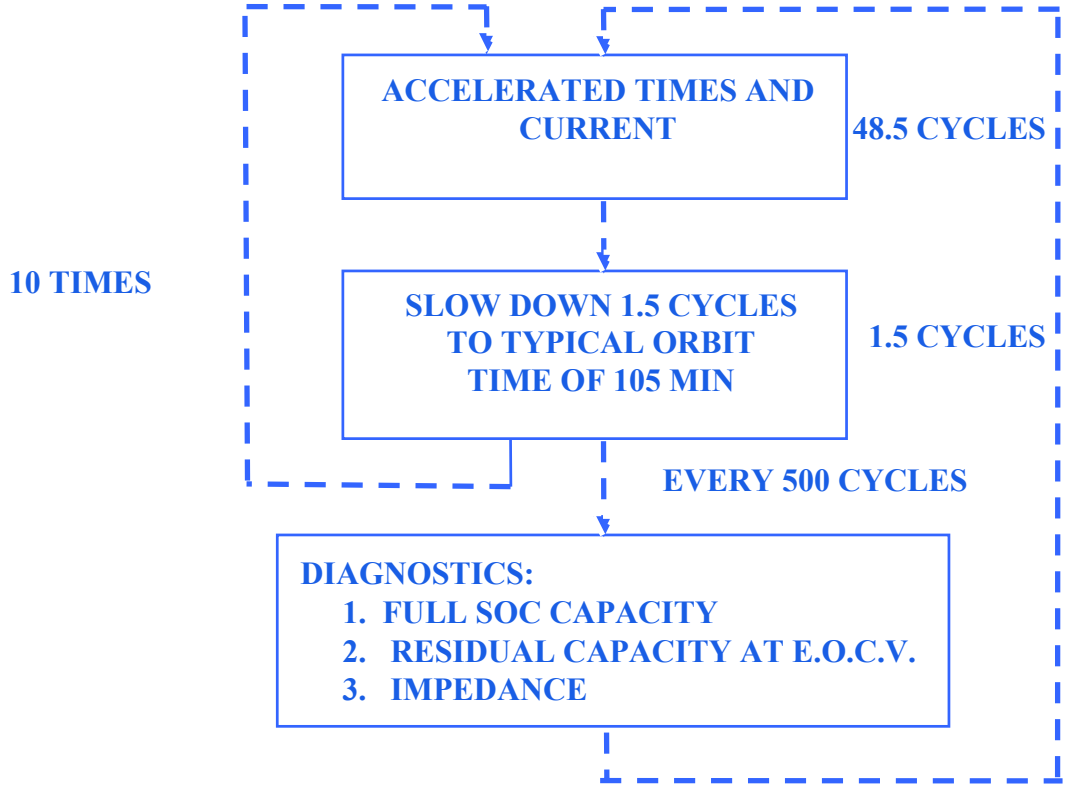
4.8 HOURS FOR CHARGE

THE DISCHARGE IS AT A CONSTANT DOD RATHER THAN A TRUE SEASON WITH THE WELL-KNOW PARABOLIC ECLIPSE DURATION

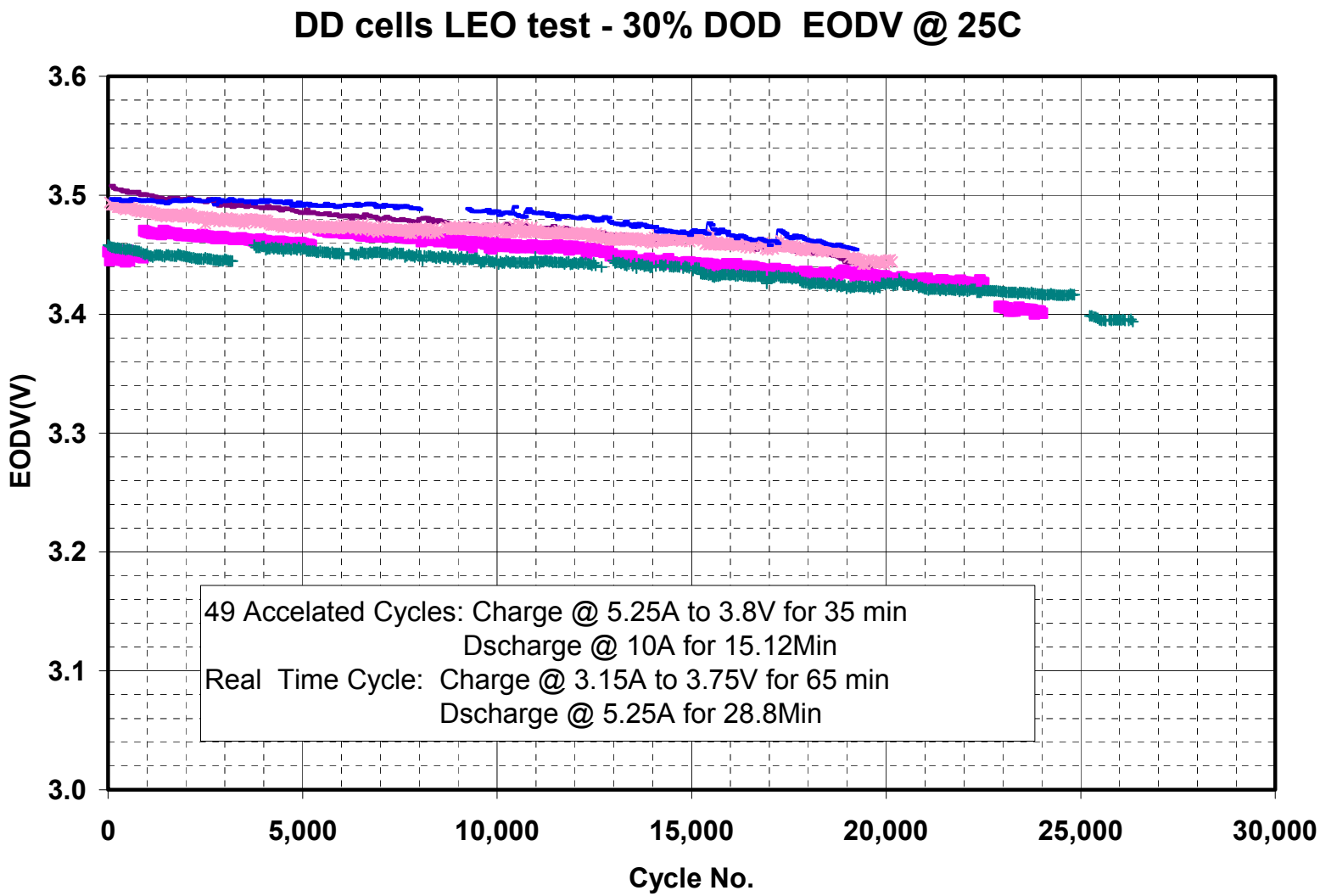
LEO – ACCELERATION REQUIRES A CAREFUL BALANCE OF SHORTEN TIME AND CURRENT INCREASE

	CYCLES/DAY	CURRENT (A)	TIME (M)
30% DOD	28.7	DIS 10	15.12
		CHG 5.25	35

LEO TESTING



SLOWING DOWN TO REAL TIME ORBIT RATES OF 105 MIN. EVERY 50 CYCLES IS ESSENTIAL SO THAT E.O.D.V. REFLECTS TRUE ORBIT CONDITIONS


DD cells LEO test - 30% DOD EODV @ 25C
3.6
3.5
3.4
3.3
3.2
3.1
3.0
EODV(V)
0
5,000
10,000
15,000
20,000
25,000
30,000
Cycle No.
49 Accelated Cycles: Charge @ 5.25A to 3.8V for 35 min
Dscharge @ 10A for 15.12Min
Real Time Cycle: Charge @ 3.15A to 3.75V for 65 min
Dscharge @ 5.25A for 28.8Min

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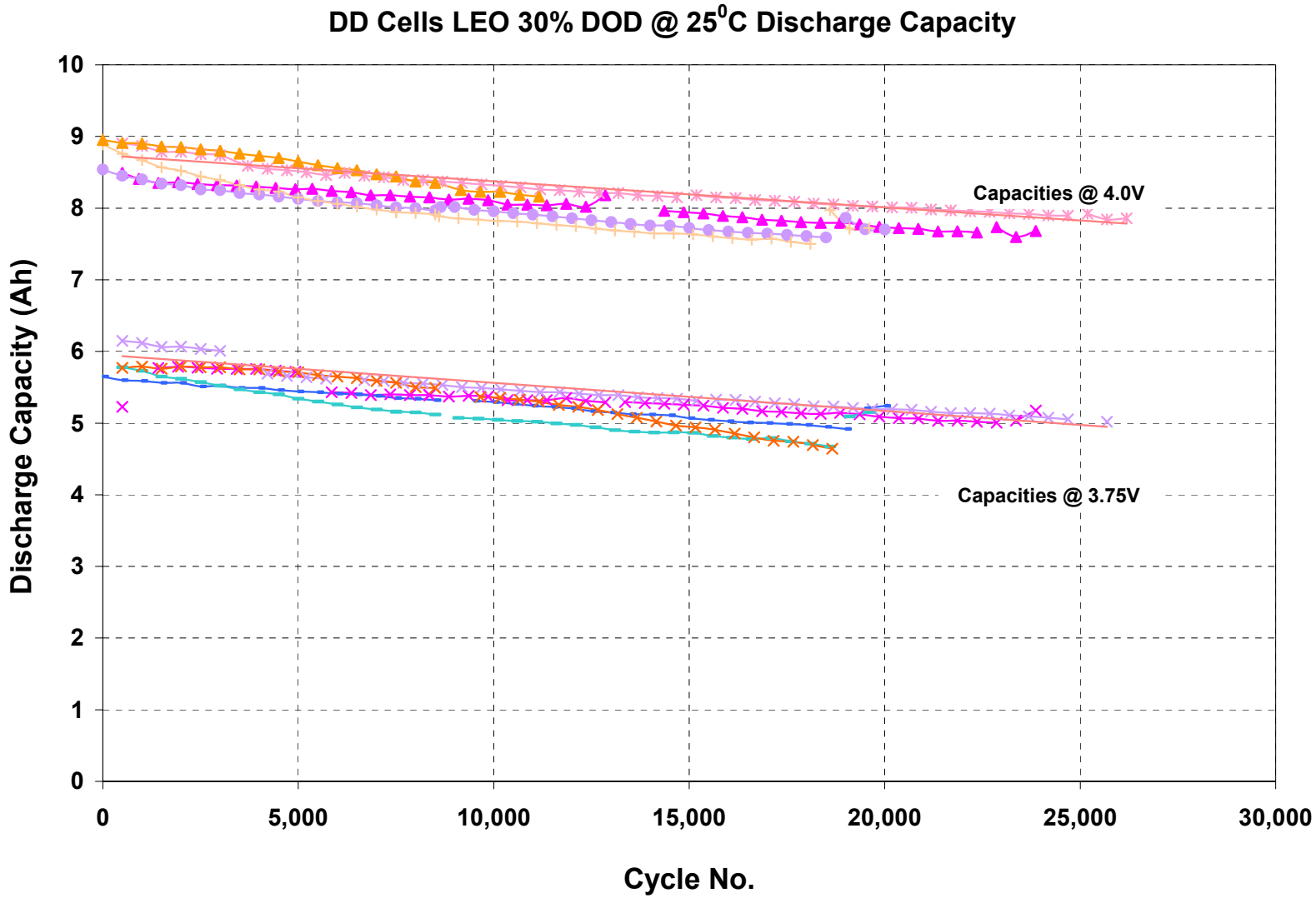
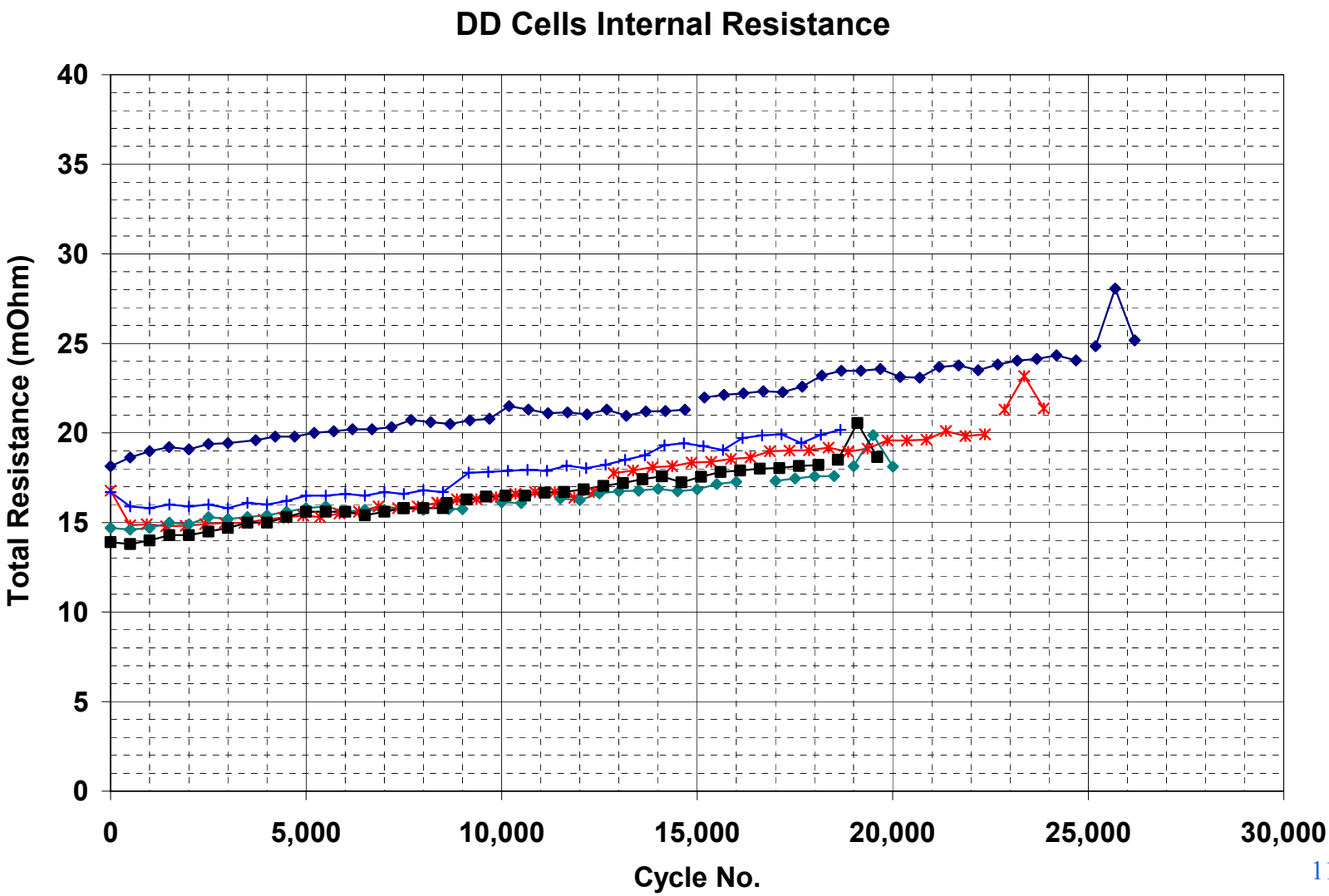
LEO TESTING




DD Cells Internal Resistance
Total Resistance (mOhm)
40
35
30
25
20
15
10
5
0
0
5,000
10,000
15,000
20,000
25,000
30,000
Cycle No.

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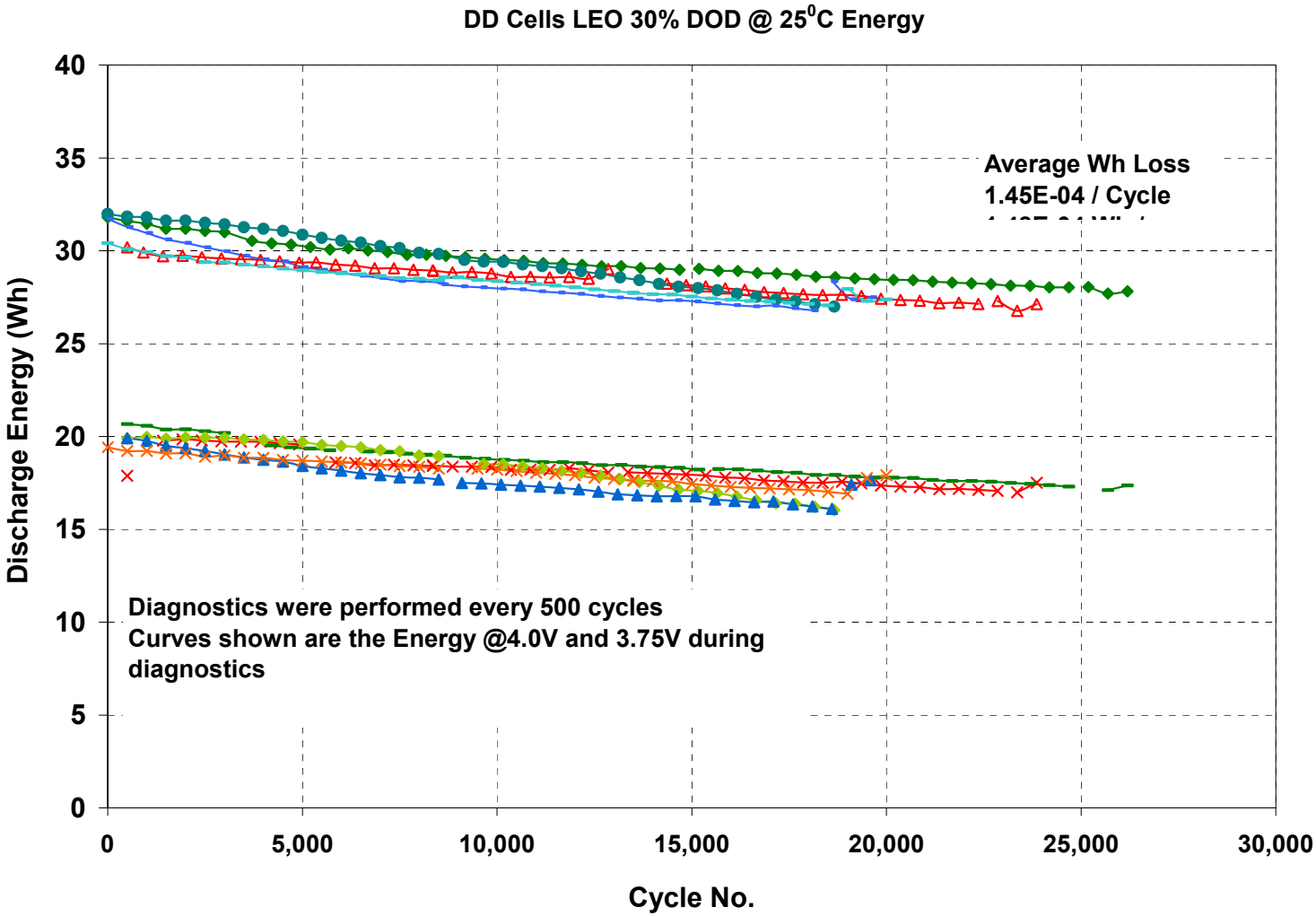
LEO TESTING

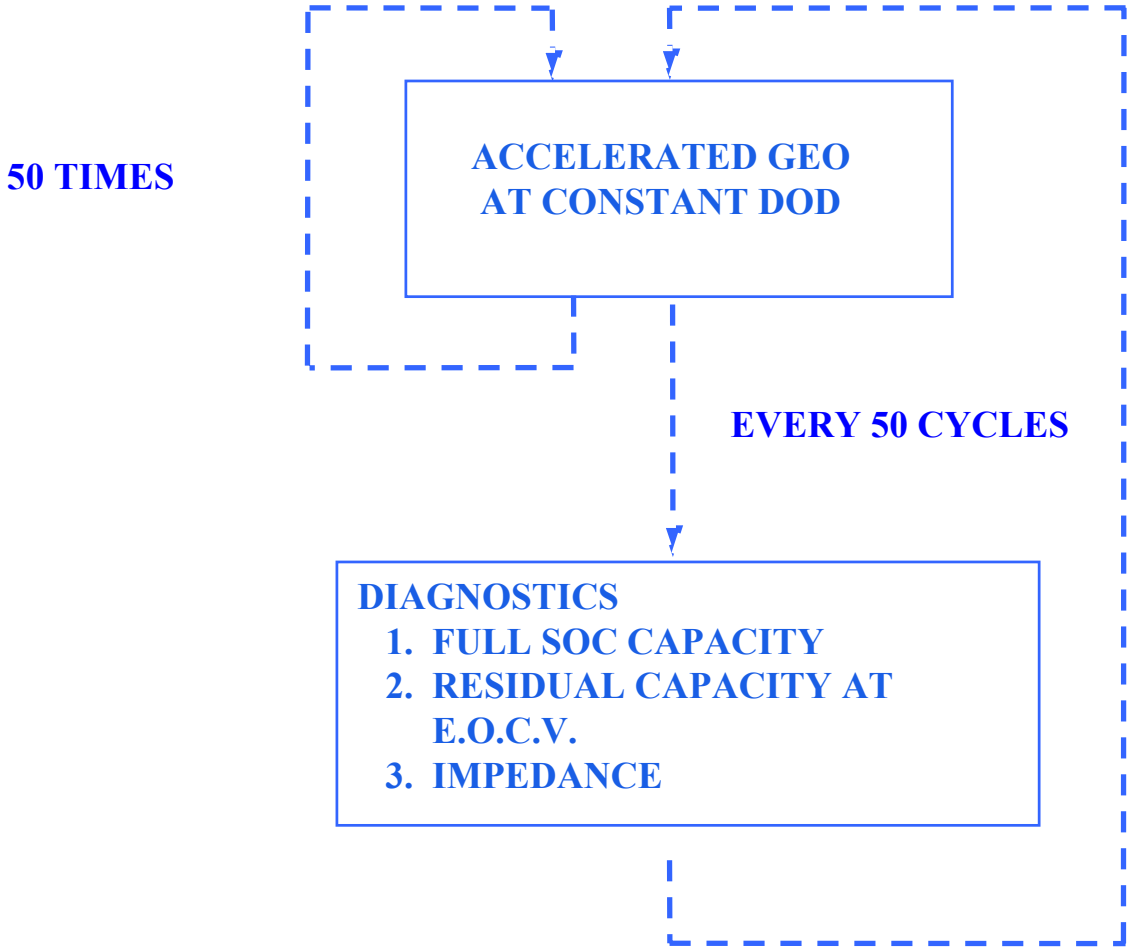


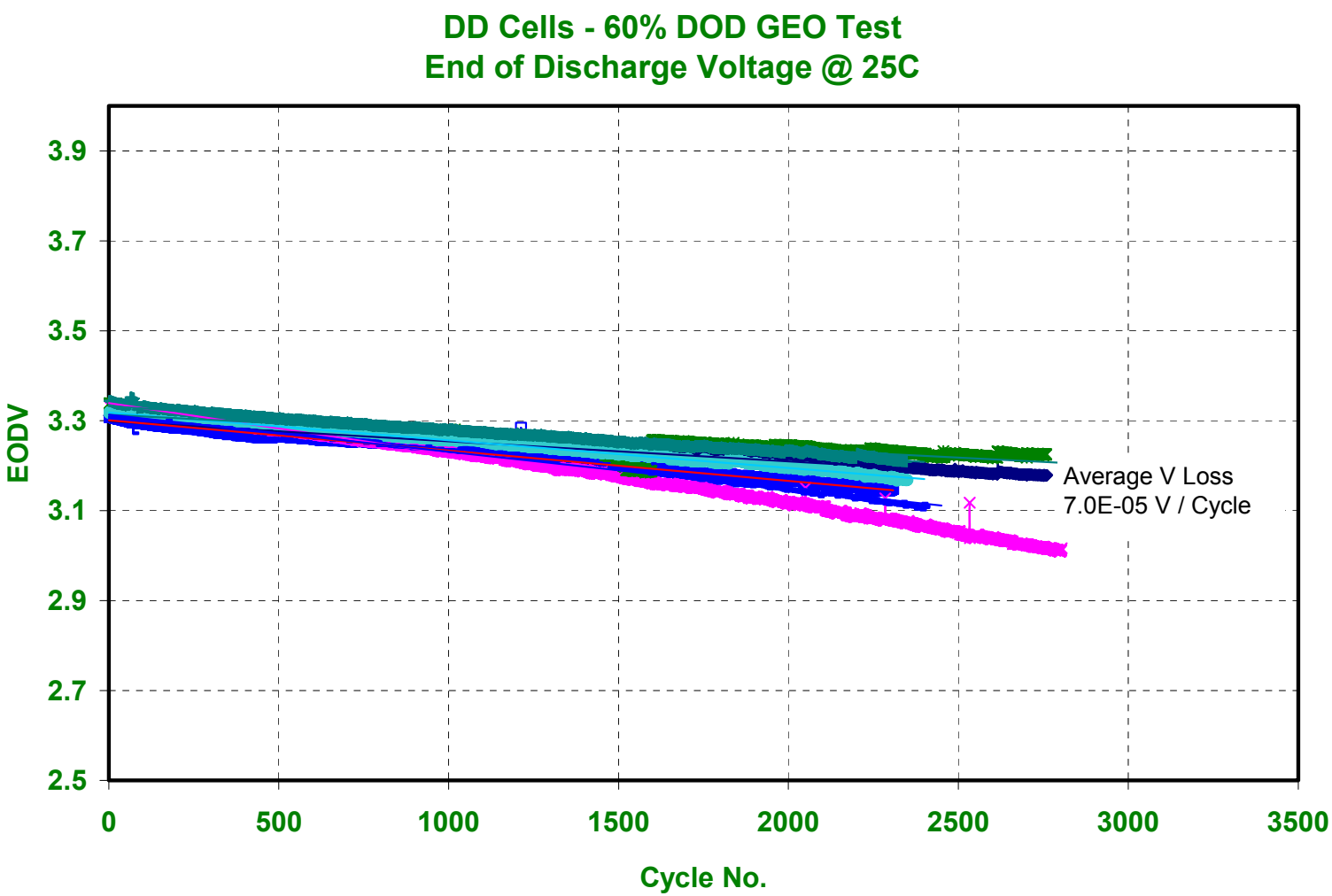
25^{0}C 30% DOD LEO Cycling, Prediction For 40,000 Cycles

	Start		EOL
➢ EODV	3.46V	DV=64 mV	EODV=3.396
➢ Capacity	8.5Ah @4.0V	DAh=1.92Ah	6.58Ah@4.0V
➢ Energy	30Wh	DWh=5.9Ah	24Wh

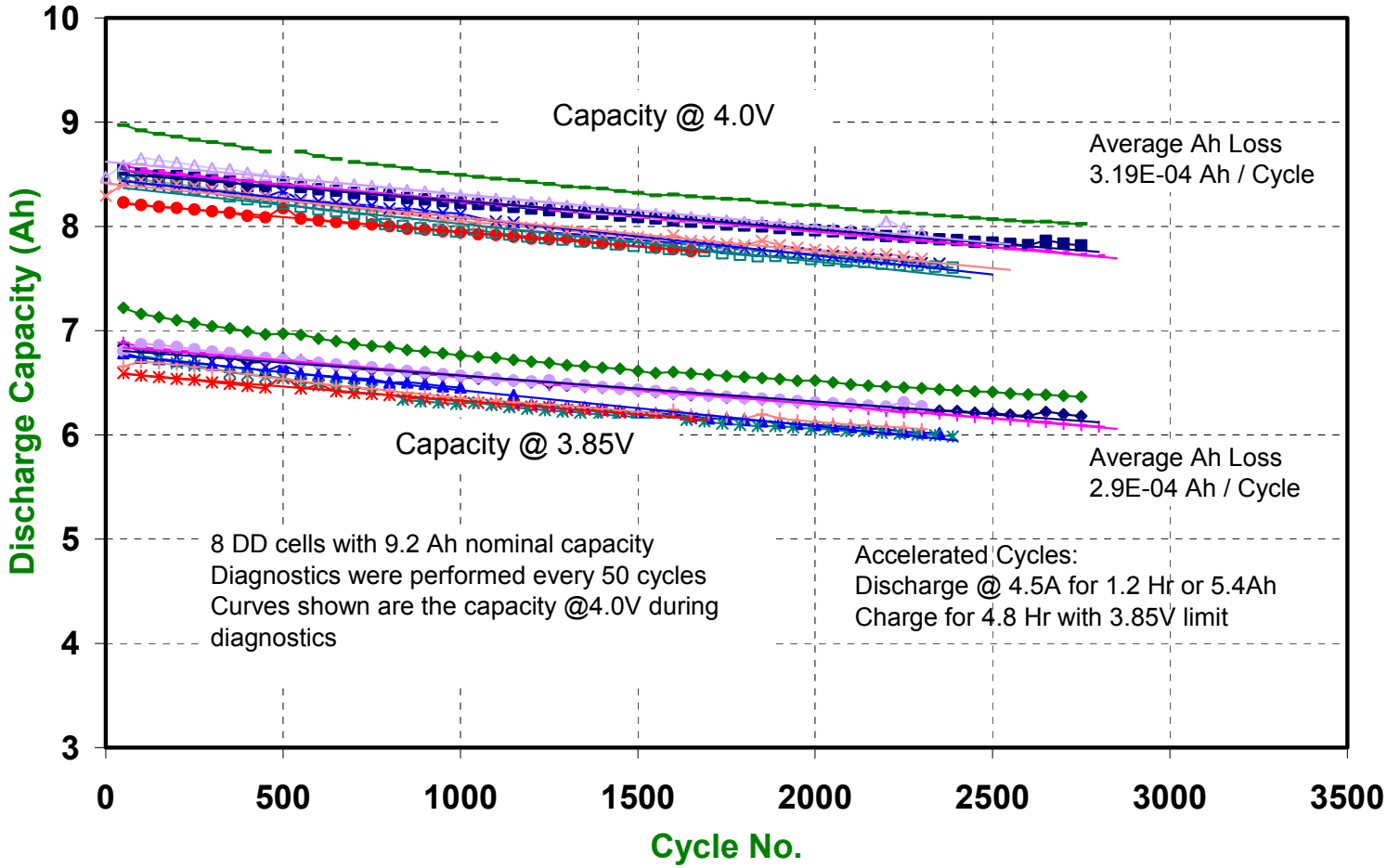
➢ EOL Conditions are 9Wh out, still a reserve of 5Wh charged or a reserve of 55% over demand

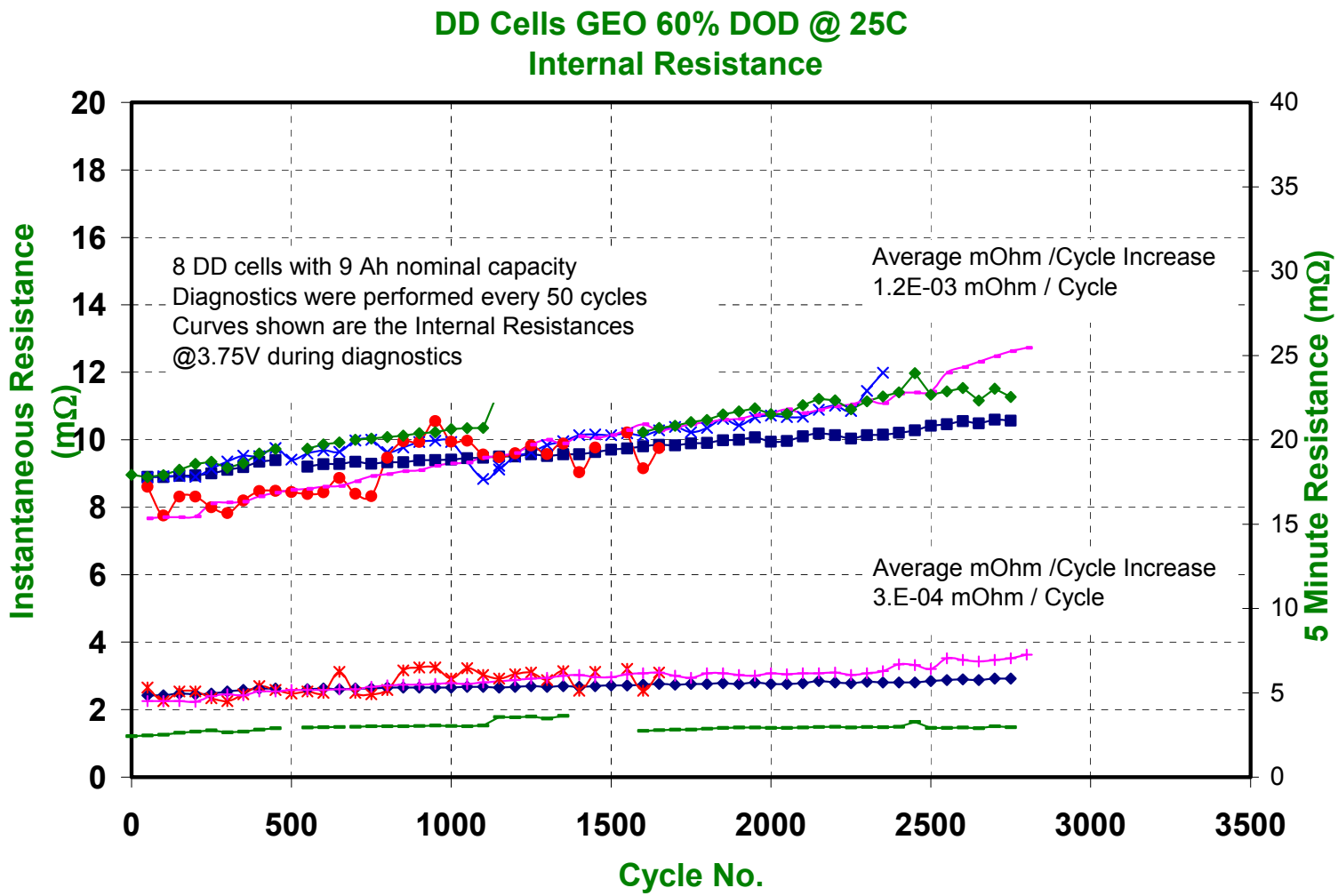
GEO TESTING

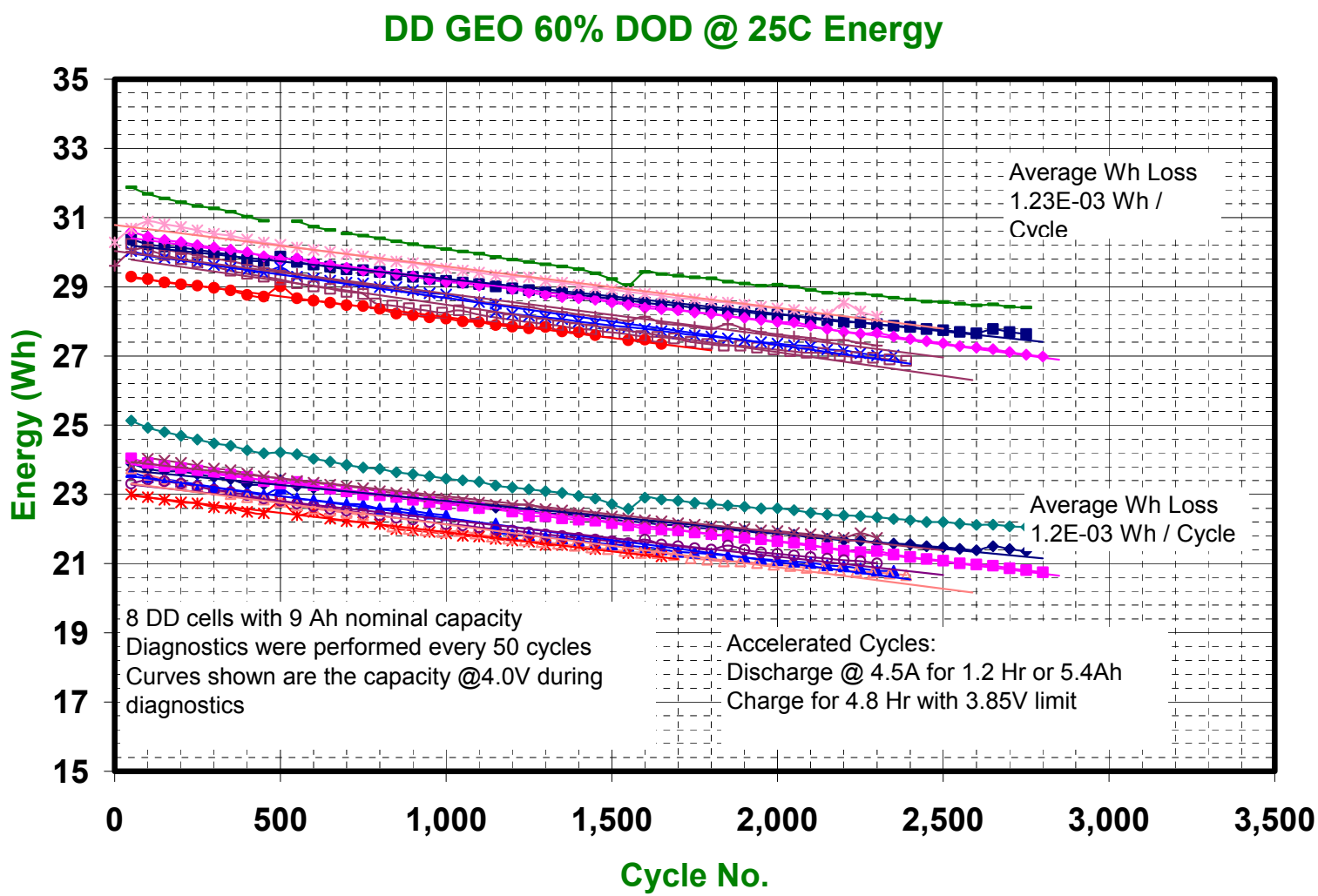

50 TIMES
ACCELERATED GEO
AT CONSTANT DOD
EVERY 50 CYCLES
DIAGNOSTICS
1. FULL SOC CAPACITY
2. RESIDUAL CAPACITY AT E.O.C.V.
3. IMPEDANCE


DD Cells - 60% DOD GEO Test
End of Discharge Voltage @ 25C
EODV
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
0
500
1000
1500
2000
2500
3000
3500
Cycle No.
Average V Loss
7.0E-05 V / Cycle

DD Cells GEO 60% DOD @ 25C Discharge Capacity




DD Cells GEO 60% DOD @ 25C
Internal Resistance
8 DD cells with 9 Ah nominal capacity
Diagnostics were performed every 50 cycles
Curves shown are the Internal Resistances
@3.75V during diagnostics
Average mOhm /Cycle Increase
1.2E-03 mOhm / Cycle
Average mOhm /Cycle Increase
3.E-04 mOhm / Cycle
Instantaneous Resistance (mΩ)
5 Minute Resistance (mΩ)
Cycle No.
0
2
4
6
8
10
12
14
16
18
20
0
5
10
15
20
25
30
35
40
0
500
1000
1500
2000
2500
3000
3500


DD GEO 60% DOD @ 25C Energy
Energy (Wh)
35
33
31
29
27
25
23
21
19
17
15
0
500
1,000
1,500
2,000
2,500
3,000
3,500
Cycle No.
Average Wh Loss
1.23E-03 Wh /
Cycle
Average Wh Loss
1.2E-03 Wh / Cycle
8 DD cells with 9 Ah nominal capacity
Diagnostics were performed every 50 cycles
Curves shown are the capacity @4.0V during
diagnostics
Accelerated Cycles:
Discharge @ 4.5A for 1.2 Hr or 5.4Ah
Charge for 4.8 Hr with 3.85V limit

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GEO RESULTS

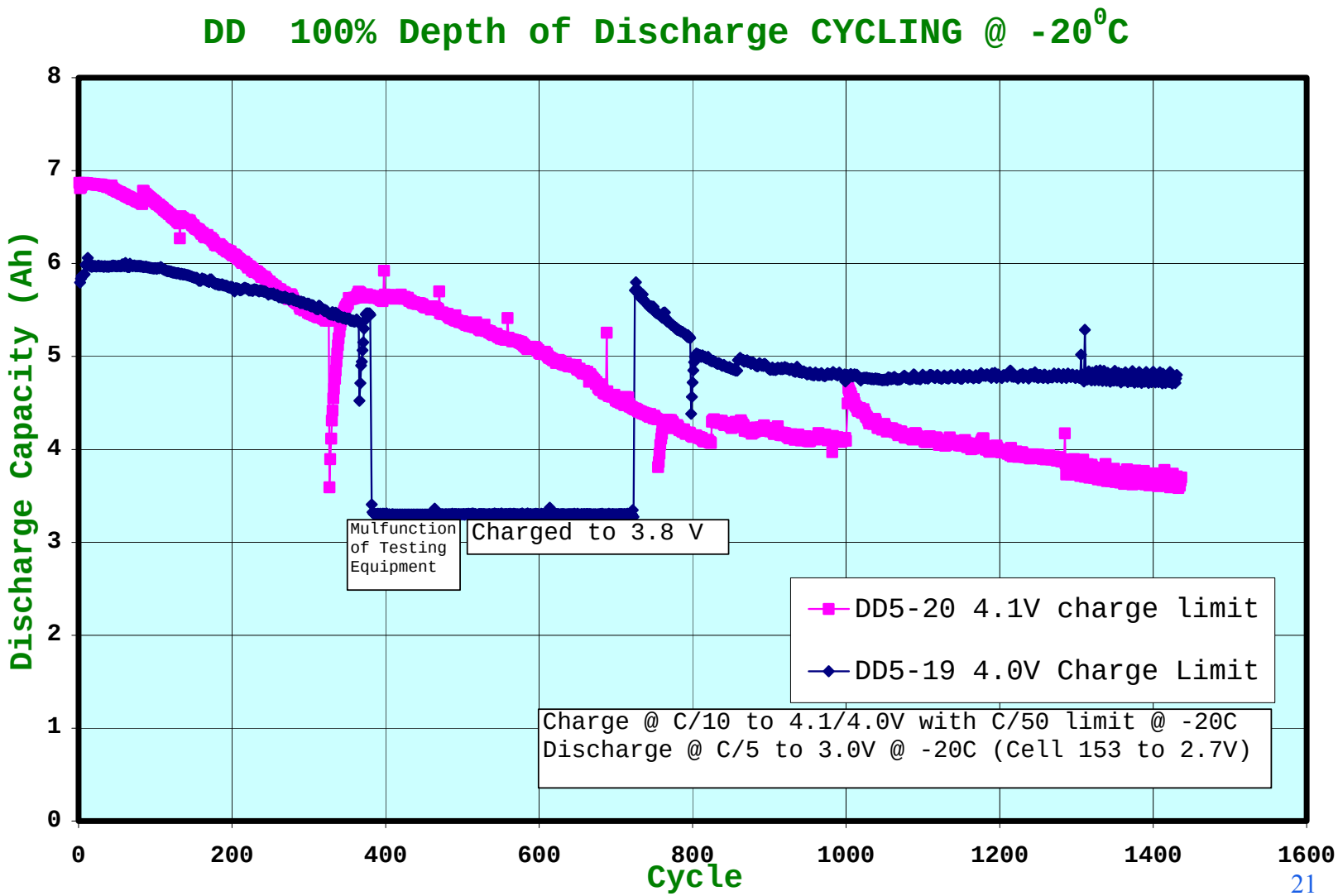
25^0C 60% DOD GEO Cycling

- By EOL 1350 cycles, 5.4% Energy Loss
- 2800 cycles, 11.5% Energy Loss

LIMITED NO. OF CELLS ON OCV TEST

- Cells stored on open circuit at 50% SOC at ambient temperature which is reasonable since a cycling cell is on average at 50% SOC
- Capacity measurement conducted at ambient temperature
- Diagnostic tests performed for impedance and capacity
- After 3.5 years storage data shows almost no capacity loss or impedance growth yet, thus we are unable to quantitatively state a loss factor on this group of cells, but it will be very low.

100% DOD @ -20^{0}C


DD 100% Depth of Discharge CYCLING @ -20^{0}C
Discharge Capacity (Ah)
Cycle
0
1
2
3
4
5
6
7
8
0
200
400
600
800
1000
1200
1400
1600
Mulfunction of Testing Equipment
Charged to 3.8 V
DD5-20 4.1V charge limit
DD5-19 4.0V Charge Limit
Charge @ C/10 to 4.1/4.0V with C/50 limit @ -20C
Discharge @ C/5 to 3.0V @ -20C (Cell 153 to 2.7V)

100% DOD

-20^{0}C 100% DOD Cycling

- @ 4.0V Charge Limit Capacity loss is less than 4.1V Charge Limit
- @4.0V Charge Limit
  17% loss at 1430 cycles

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CONCLUSION

- 30% DOD LEO Cycling,
  Predicted 19% Energy loss by 40,000 cycles

- By EOL 1350 cycles, 5.4% Energy Loss
  2800 cycles, 11.5% Energy Loss

- 100% DOD at -20^{0}C, 17% loss at 1430 cycles for 4.0V charge limit

Lithium-ion Batteries for the Mars Express Orbiter

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(rob.spurrett@aeat.co.uk)
Rod Ng, AEA Technology
Bill Moulford, AEA Technology
David Lizius, COM DEV

Mars Express Mission - 1

- European Space Agency ‘cornerstone’ mission to Mars
- New flexible mission following loss of Mars 96
- Re-use of some instrument spares
- Mars closest to Earth for 17 years next year
- Searching for life on Mars
- Polar orbit 300km by 6,800 km
- Global coverage in one year
- Deploys planetary lander: Beagle2
- Primary mission: One Martian year mission (687 Earth days)
- Extended mission: One additional Martian year

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COM DEV SPACE GROUP

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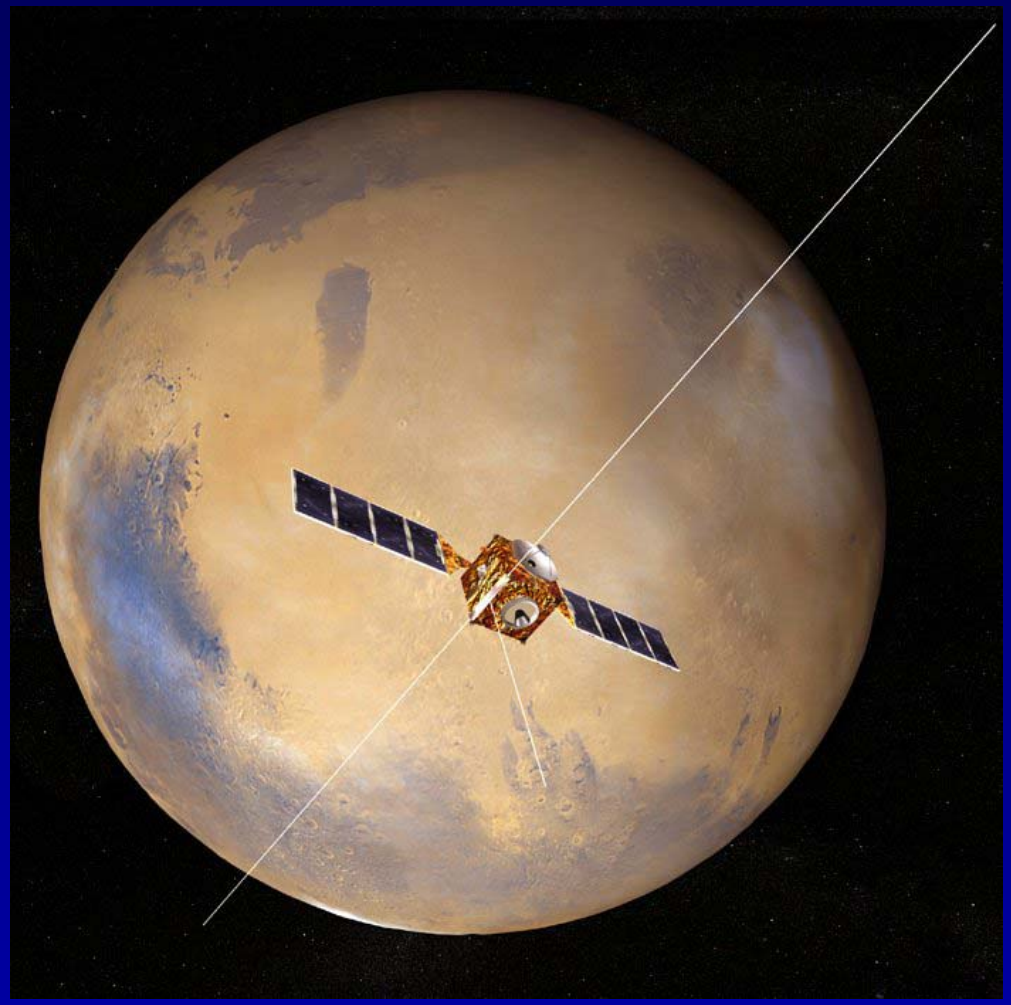
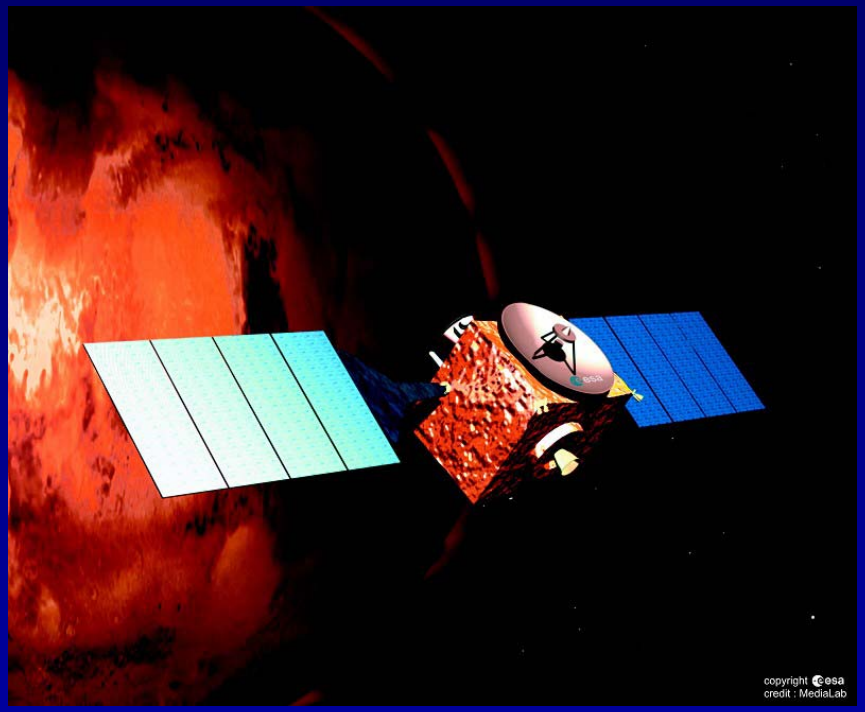
Mars Express Mission - 2





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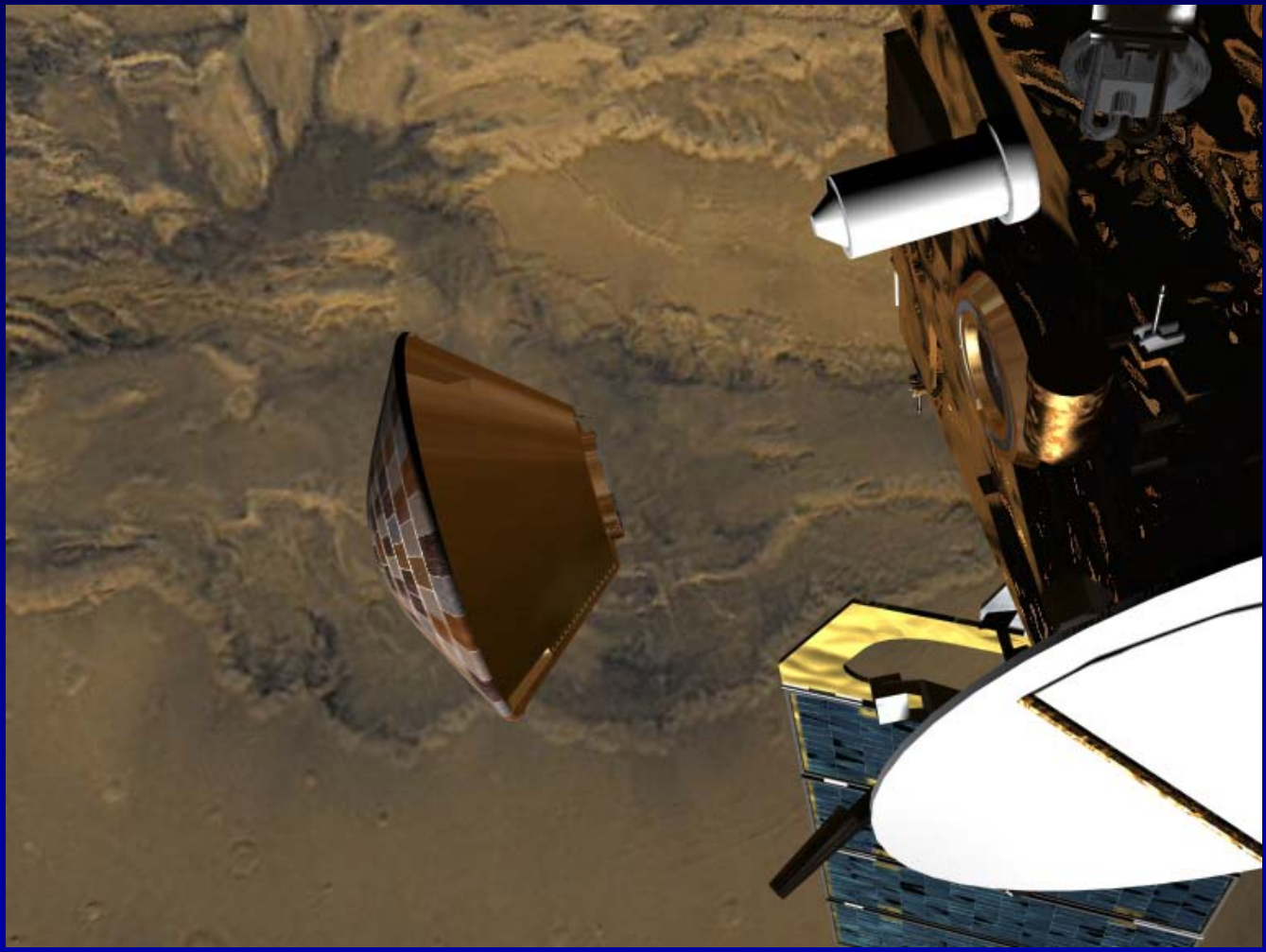
Mars Express Mission - 3



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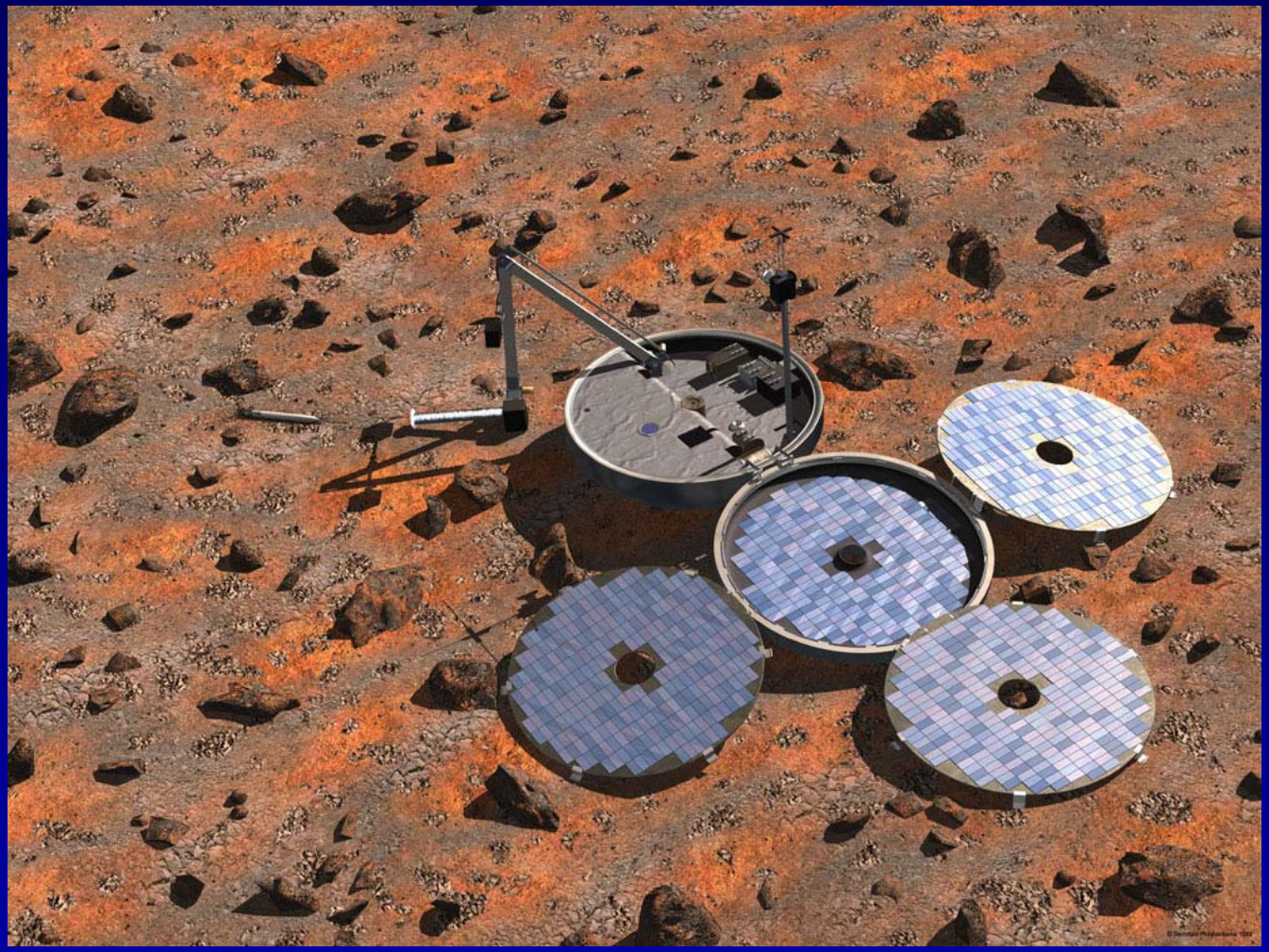
Mars Express Mission - 4



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Mars Lander Battery - 1

- Europe's first Mars Lander
- Beagle2
- Prime: Astrium - UK
- Non-standard configuration to fit Lander geometry
  - Configuration 6s-9p
  - 13.5 Ah, 25.2 V to 15 V
  - Nameplate energy 292 Wh
  - Mass 2.63 kg
  - Specific energy 111 Wh/kg
- Unit sterilization 14 Nov 2002
- Survival heater for -30degC

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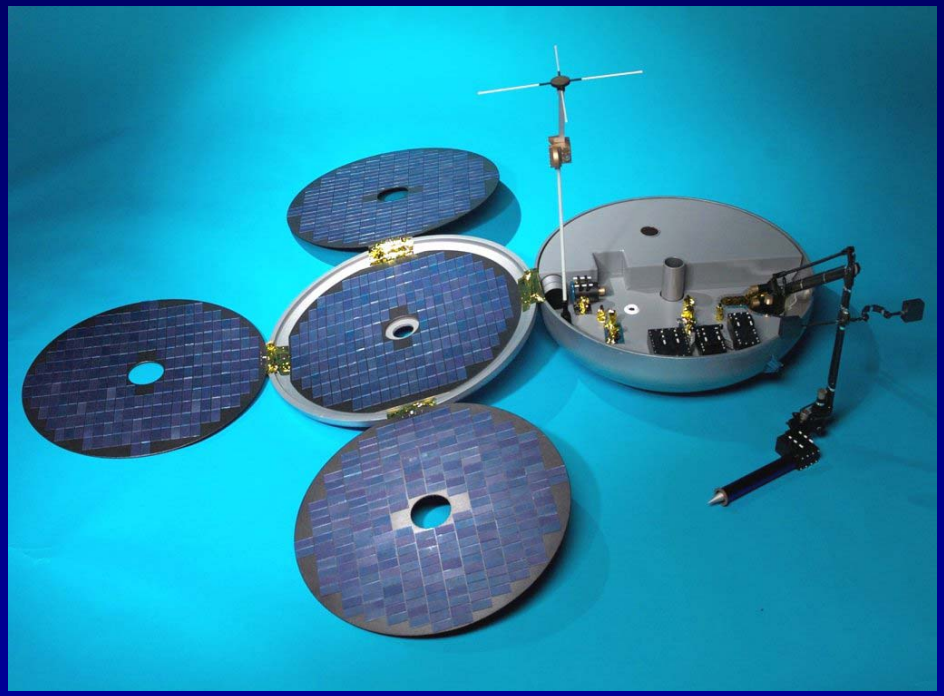
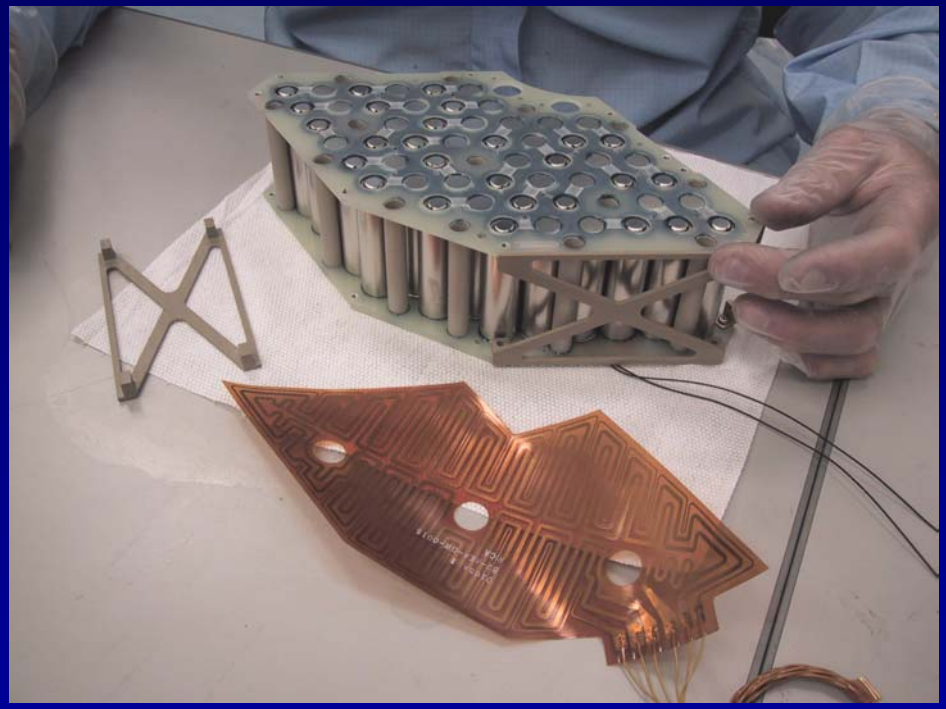
Mars Lander Battery - 2





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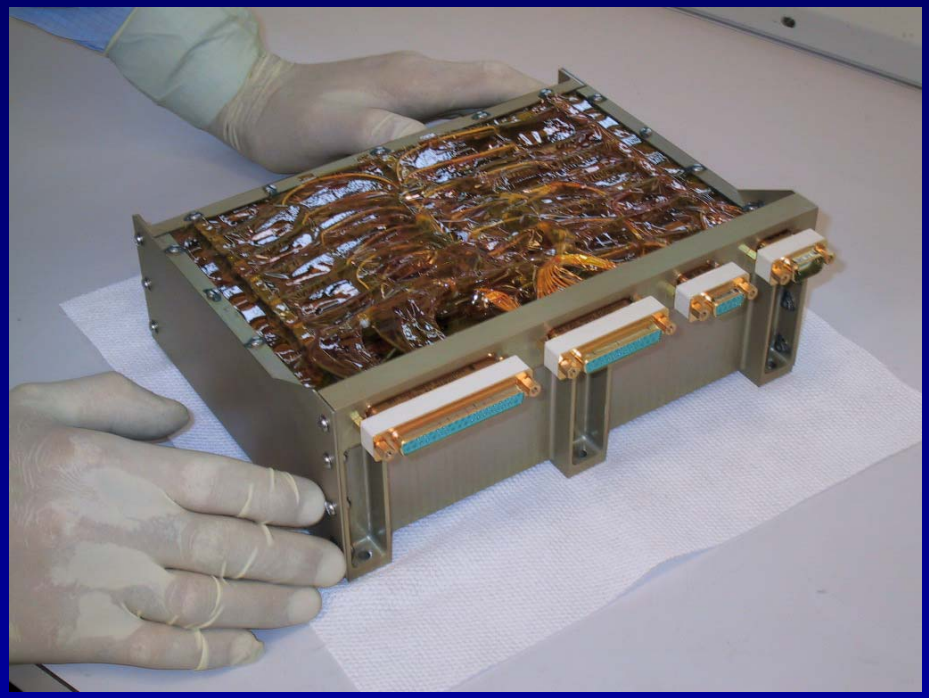
Mars Express Orbiter Battery

- Orbiter Prime: Astrium, France
- Three battery modules per S/C
  - Configuration 6s-16p
  - 24Ah, 25.2V to 15V
  - Nameplate energy 518 Wh
  - Mass 4.5kg
  - Specific energy 115 Wh/kg
- Each module has a dedicated charge/discharge controller
- Spacecraft powered by any two modules from three
  - Battery 6s-32p, 48 Ah



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Orbiter Battery Qualification

Sine vibration (qualification levels)	5 to 15.8 Hz: 15 mm peak-to-peak 15.8 Hz to 100 Hz: 15 g	
Random vibration (qualification levels)	Out of plane:	20 to 100: +3 db/octave 100 to 400: 0.5 g^2/Hz 400 to 2000: -6 dB/octave 18.3 g RMS total
	In-plane	20 to 100: +6 db/octave 100 to 400: 0.1 g^2/Hz 400 to 2000: -3 dB/octave 9.9 g RMS total
Vibration response (fn)	Out of plane: 750 to 800 Hz In-plane: 1,000 to 1,100 Hz	
Non-operating TV	5 cycles between –28 degC and +59 degC, 2 hour dwells	
Operating TV	Worst case power cycle operated at –20 degC, +10 degC and +50 degC	

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Mission Schedule

- TB/TV test completed on FM S/C on 7 Nov 200
- Launch window May 23rd to June 21st 2003
- 230 day cruise to Mars, arriving Jan 2004
- Primary mission
  - 1st Martian-year (687 days, 1.94 Earth-years)
  - 2,235 orbits of 454 minutes duration
- Extended mission
  - Additional Martian-year (687 days, 1.94 Earth-years)
  - 2,511orbits 404 minutes
- Each orbit has up to 5 battery discharges
- Two periods each Martian-year with no eclipses

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Life-Test Philosophy

- Contract awarded in June 1999
- Principle life-test is highly representative real-time simulation (RL)
- Two additional accelerated tests for early risk retirement
- Fully accelerated (FA)
  - Two Mars years orbits (52 months) in 11 months
  - Test completed in October 2000
- Partially accelerated (PA)
  - Two Mars years orbits (52 months) in 18 months
  - Test Completed in June 2001

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Real-time Test Profiles - 1

Mission Phase	Mission Days	Test details
AIT Simulation	-254 to -230	*Cycling to represent expected AIT testing on FM*
LEOP Simulation	-230 to -229	*Cycling to represent LEOP operations*
Cruise	-229 to 0	*Battery 50% SOC, 20 degC*
Orbit 30 Cycling	0 to 30	
Orbit 60 Cycling	30 to 98	
Orbit 110 Cycling	99 to 148	
Orbit 160 Cycling	149 to 229	
Battery dormant #1	230 to 302	*Battery fully charged, 20 degC*
Orbit 358 Cycling	303 to 346	
Orbit 370 Cycling	347 to 365	
Orbit 378 Cycling	366 to 368	
Orbit 399 Cycling	369 to 398	
Orbit 410 Cycling	399 to 458	
Orbit 470 Cycling	459 to 526	
Battery dormant #2	527 to 600	*Battery fully charged, 20 degC*
Orbit 640 Cycling	601 to 629	
Orbit 651 Cycling	630 to 653	
Orbit 665 Cycling	654 to 689	*Completion of Primary Mission (1 Mars Year)*

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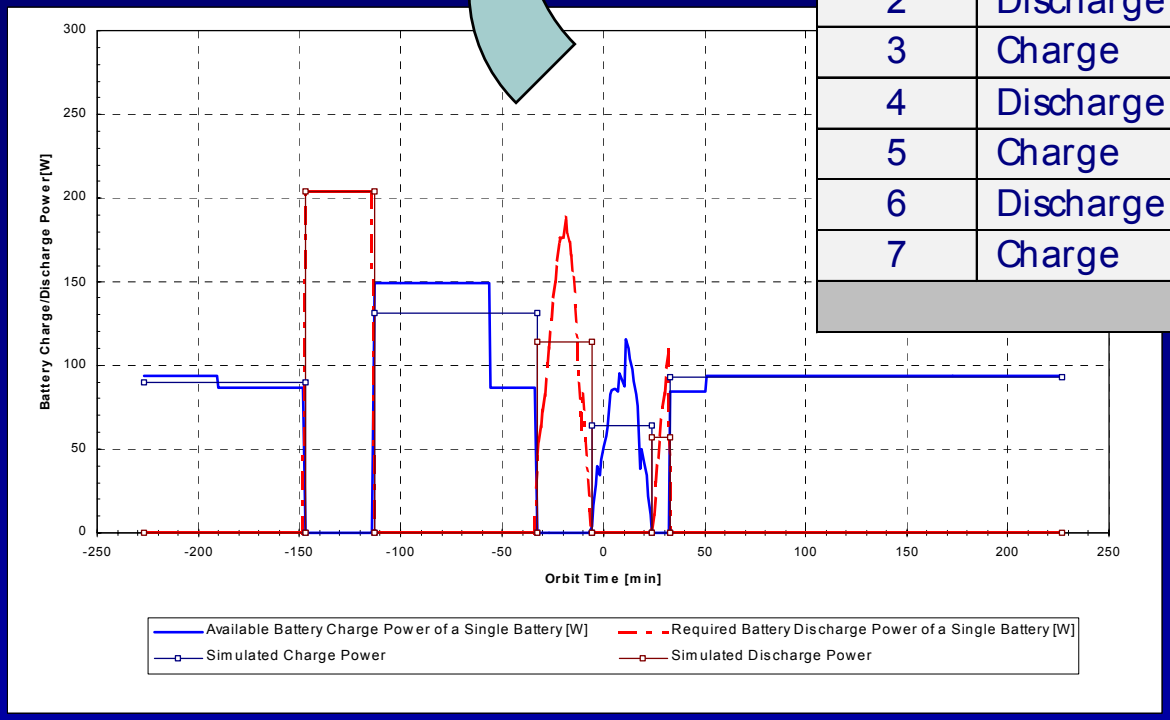
RL Test Profile - 2

Orbit Type: Mars Day 378				
Phase	Mode	Charge Power (W)	Discharge Power (W)	Duration (min)
1	Charge	44.9	0.0	80
2	Discharge	0.0	101.9	34
3	Charge	65.5	0.0	80
4	Discharge	0.0	56.9	27
5	Charge	31.8	0.0	30
6	Discharge	0.0	28.3	9
7	Charge	46.3	0.0	194
			Total	454



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RL Test Profile - Summary

Cycle Type	Battery Discharge	Peak DOD	Primary Mission Cycles (One Mars Year)	Extended Mission Cycles (Two Mars Years)
Low Cycle	0 Wh < 25 Wh	2.5%	1800	4300
Standard Cycle	25 Wh < 100 Wh	10%	1990	3130
High Cycle	100 Wh < 250 Wh	24%	1000	1340
Extreme Cycle	250 Wh < 350 Wh	34%	240	510
Total number of Cycles			5030	8980

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Accelerated Test Profiles - 1

- Accelerated by removing AIT and non-cycling parts
- Partially Accelerated (PA) test
  - Same discharge rates and powers as realistic test
  - Charge rate is increased to be same as discharge rate
  - Two Mars-year mission tested in 18 months
- Fully Accelerated (FA) test
  - Accelerated charge and discharge rates
  - Two Mars-year mission tested in 11 months
- Same number of cycles and DODs as realistic test
  - Taken in a different order to simplify the test sequence

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Accelerated Test Profiles - 2

- 50 repeating loops to simulate first Mars year

Cycle Type	Cycles per Loop	Total Cycles	PA Test Loop Duration (days)	FA Test Loop Duration (days)
Low Cycle (2.5%)	36	1800	0.75	0.375
Standard Cycle (10%)	40	2000	1.65	0.824
High Cycle (24%)	20	1000	2.57	1.285
Extreme Cycle (34%)	5	250	0.77	0.383
Total Loop Duration			5.74	2.87
Duration for 1st Mars Year (ex. capacity tests)			272 days	144 days

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Accelerated Test Profiles - 3

- 125 repeating loops to simulate second Mars year

Cycle Type	Cycles per Loop	Total Cycles	PA Test Loop Duration (days)	FA Test Loop Duration (days)
Low Cycle (2.5%)	20	2500	0.42	0.21
Standard Cycle (10%)	10	1250	0.43	0.22
High Cycle (24%)	3	375	0.39	0.19
Extreme Cycle (34%)	2	250	0.32	0.16
Total Loop Duration			1.56	0.78
Duration for 2nd Mars Year (ex. capacity tests)			195 days	97.5 days

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Real-time Test Results

Real-time Test Results

- Test started:
  - 5 Dec 1999
- First Mars-year completed:
  - 6 Nov 2002
- Test item:
  - 12Ah test module, 6s-8p
  - Same voltage, 1/4 capacity of flight battery
  - Same batch of cells as flight battery
- Test temperature:
  - 20 degC (max I/F temp)

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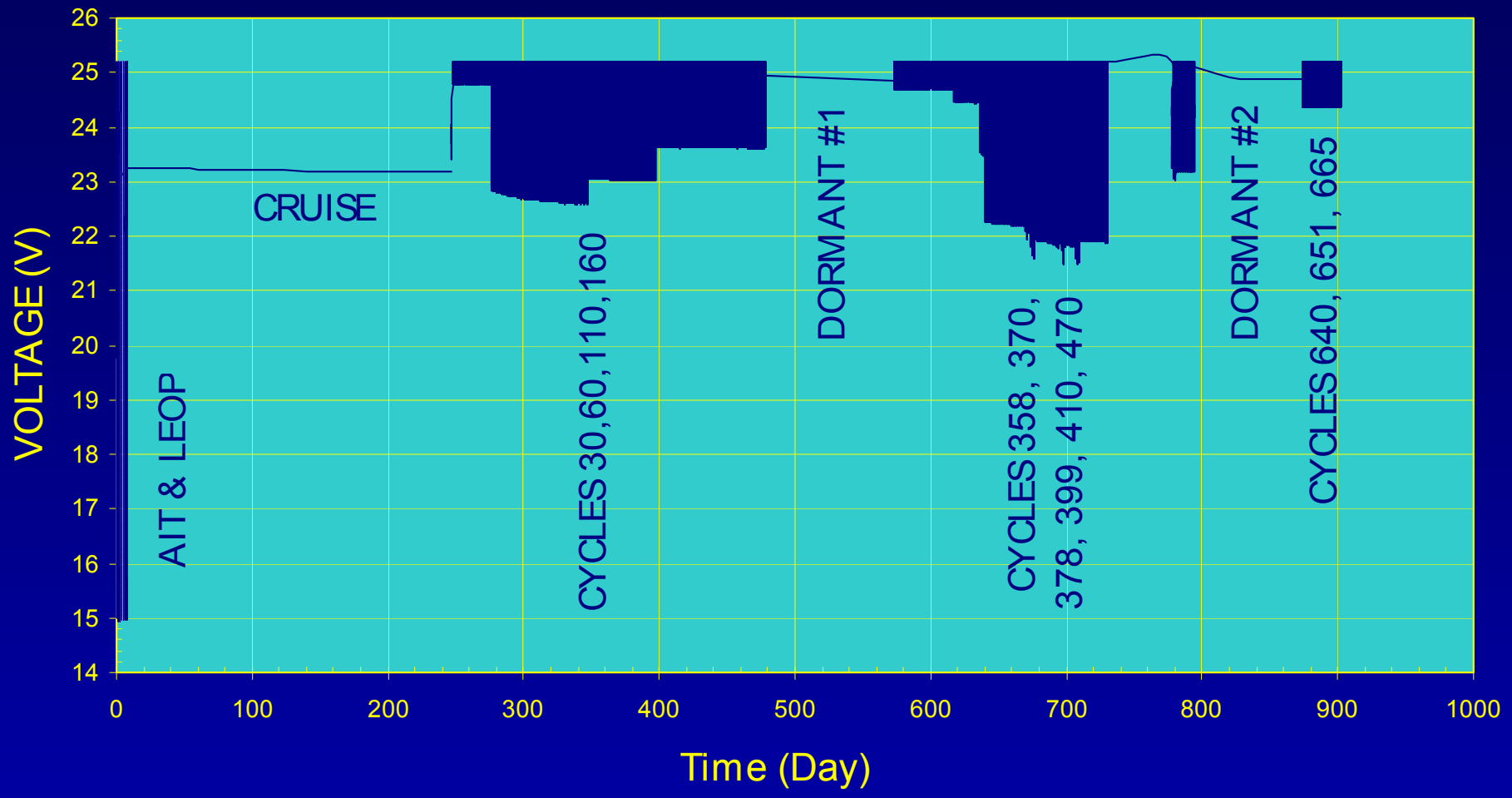
Battery Voltage



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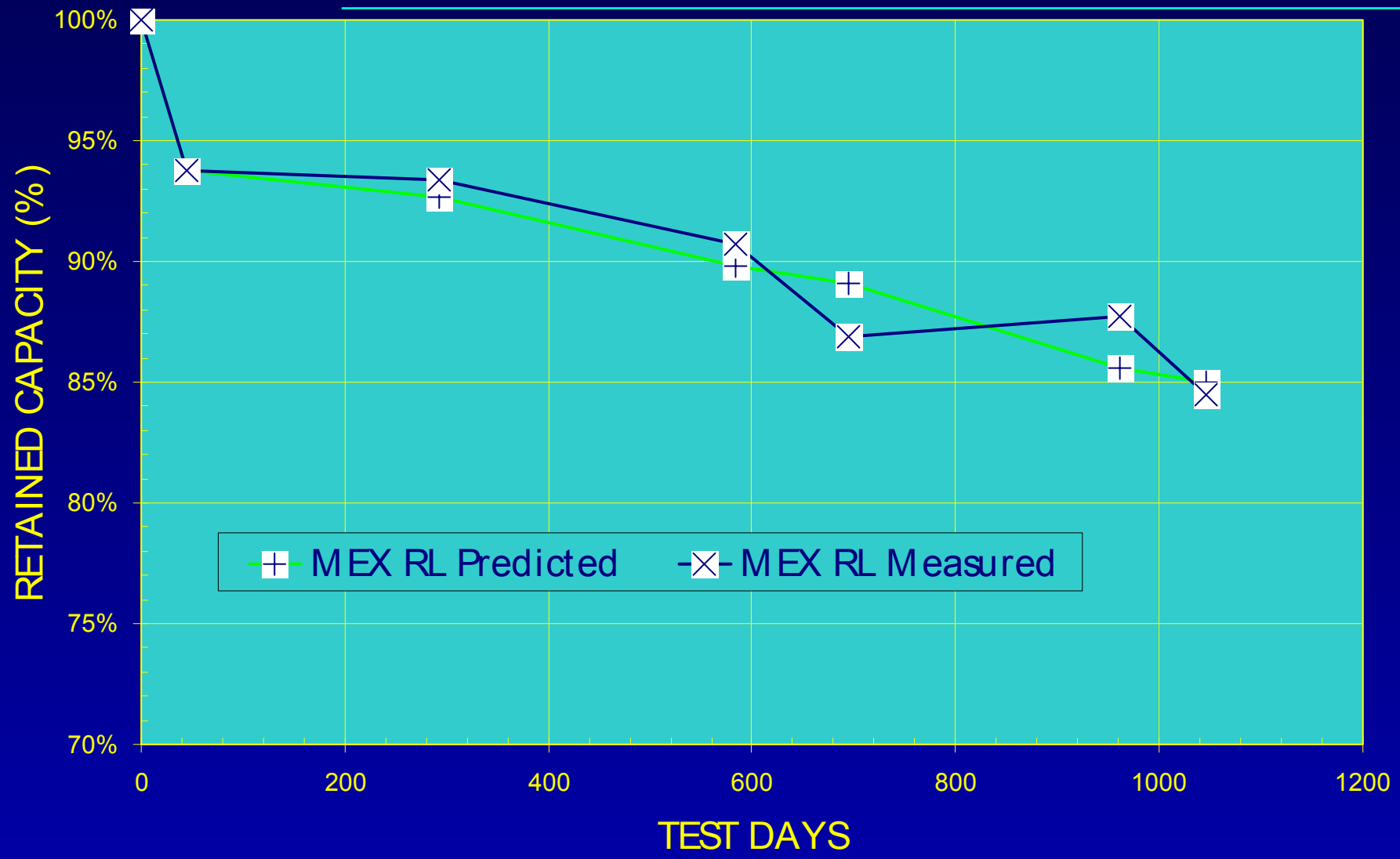
Battery Capacity



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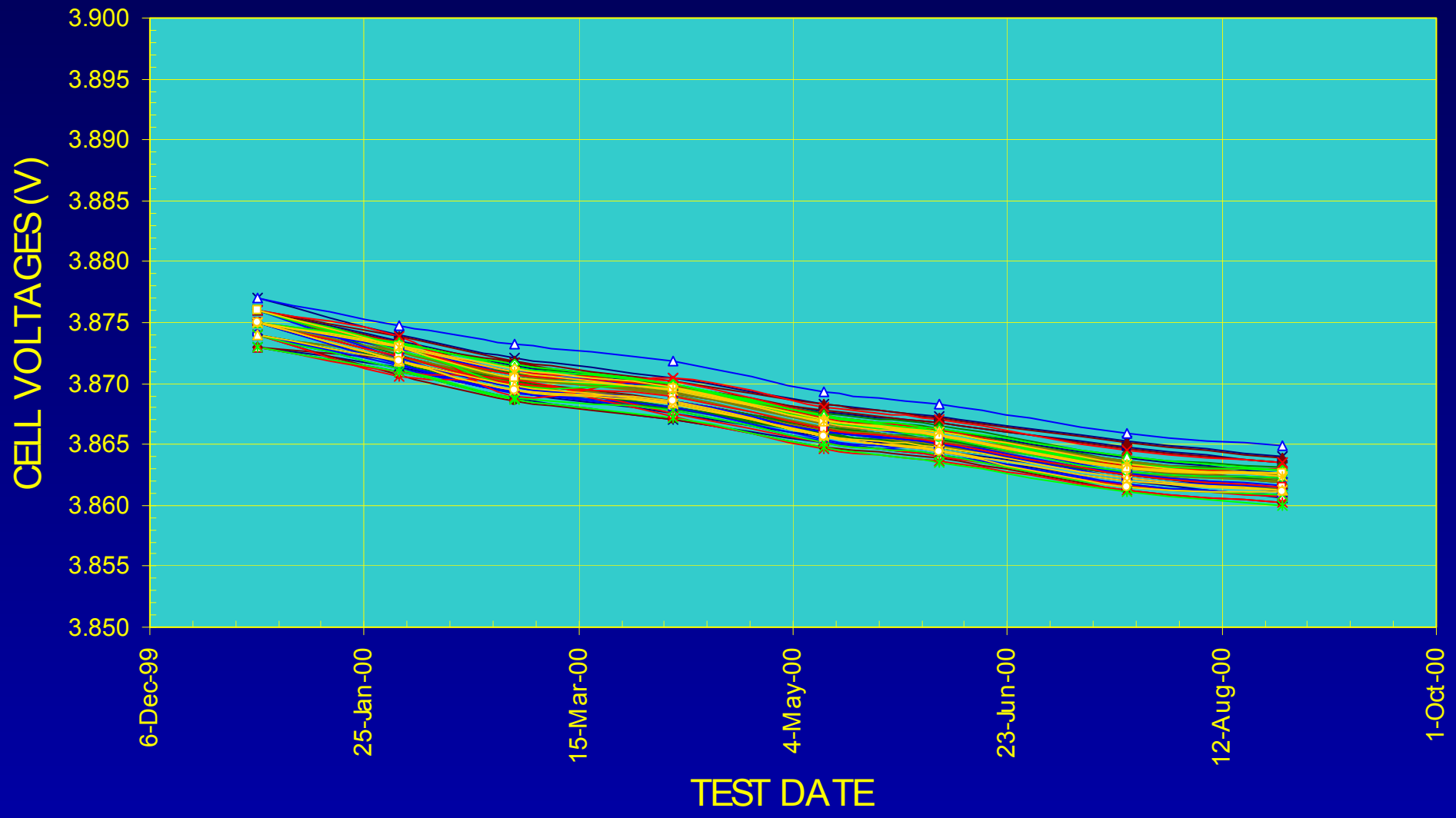
Cell Voltage - Cruise Phase



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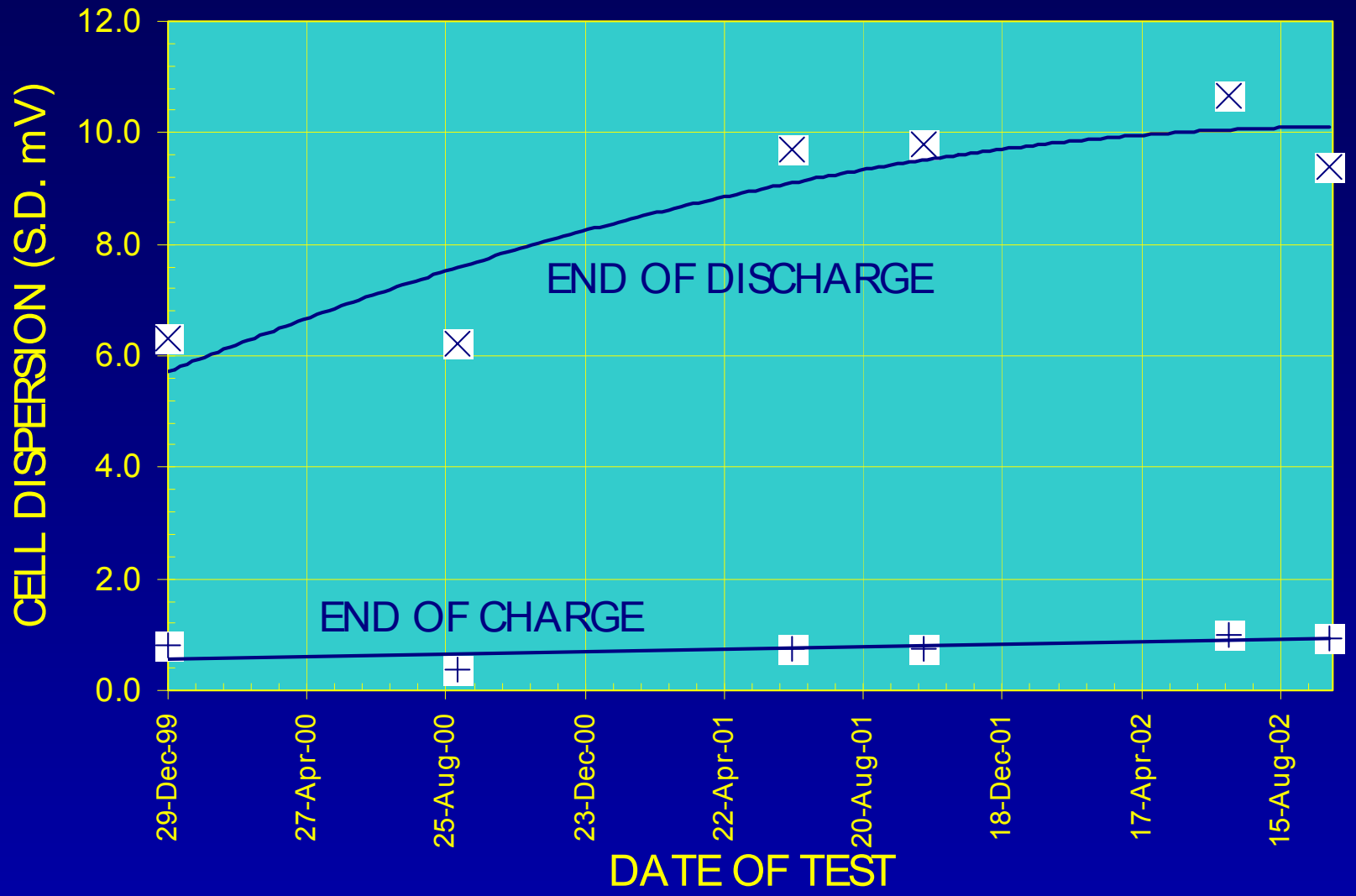
Cell Dispersion



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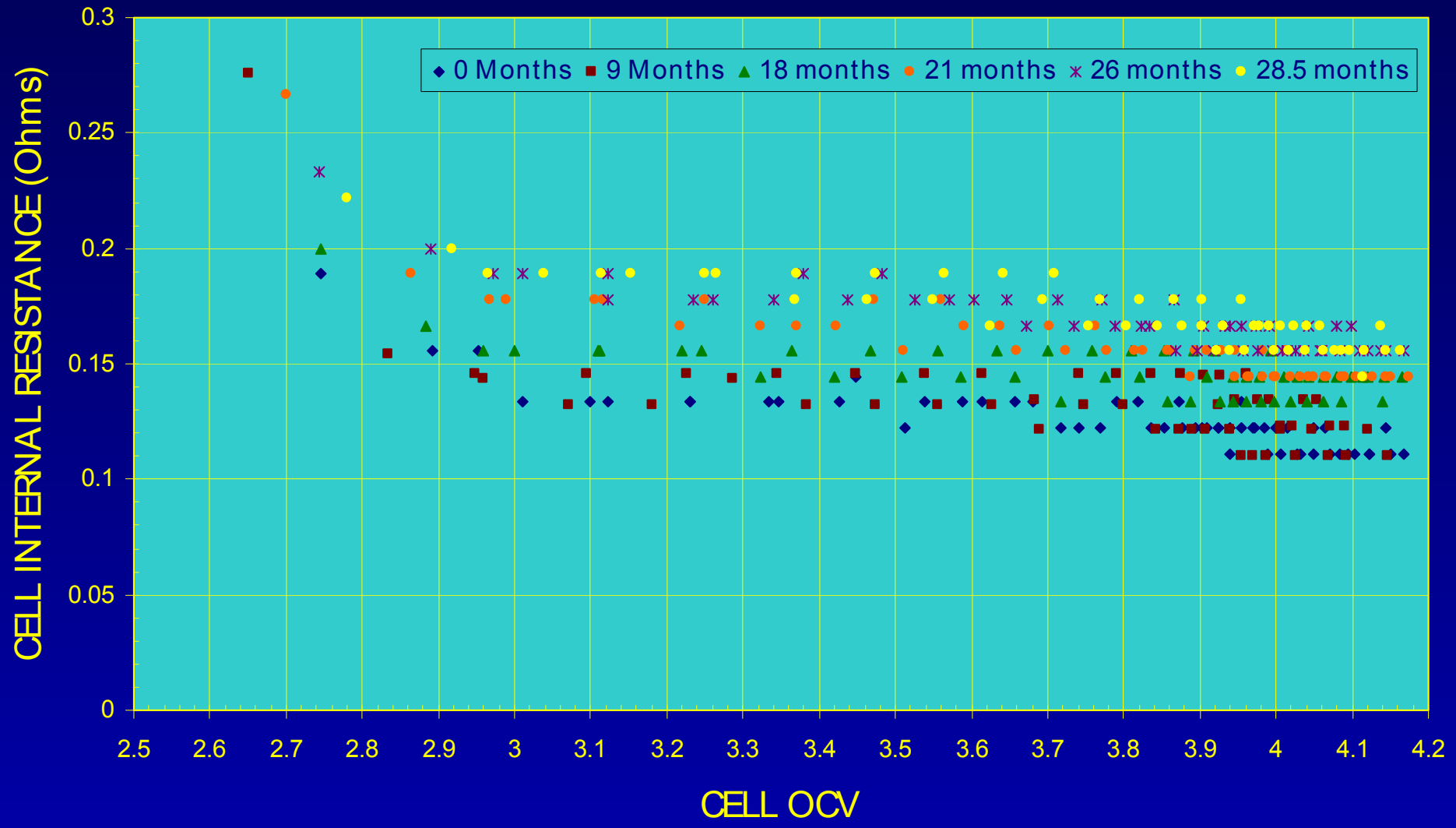
Cell Resistances



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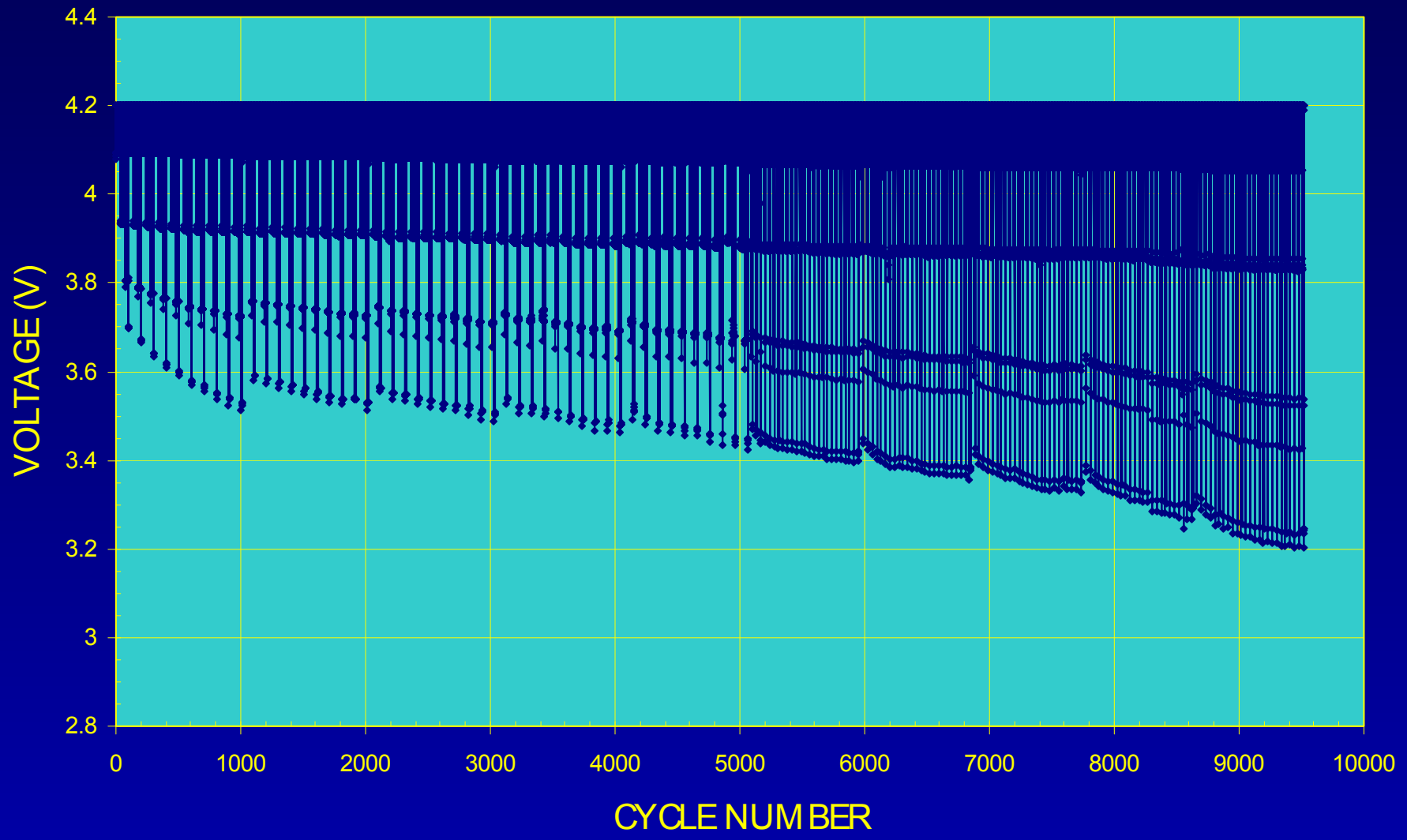
Accelerated Test Results

PA Test Voltages



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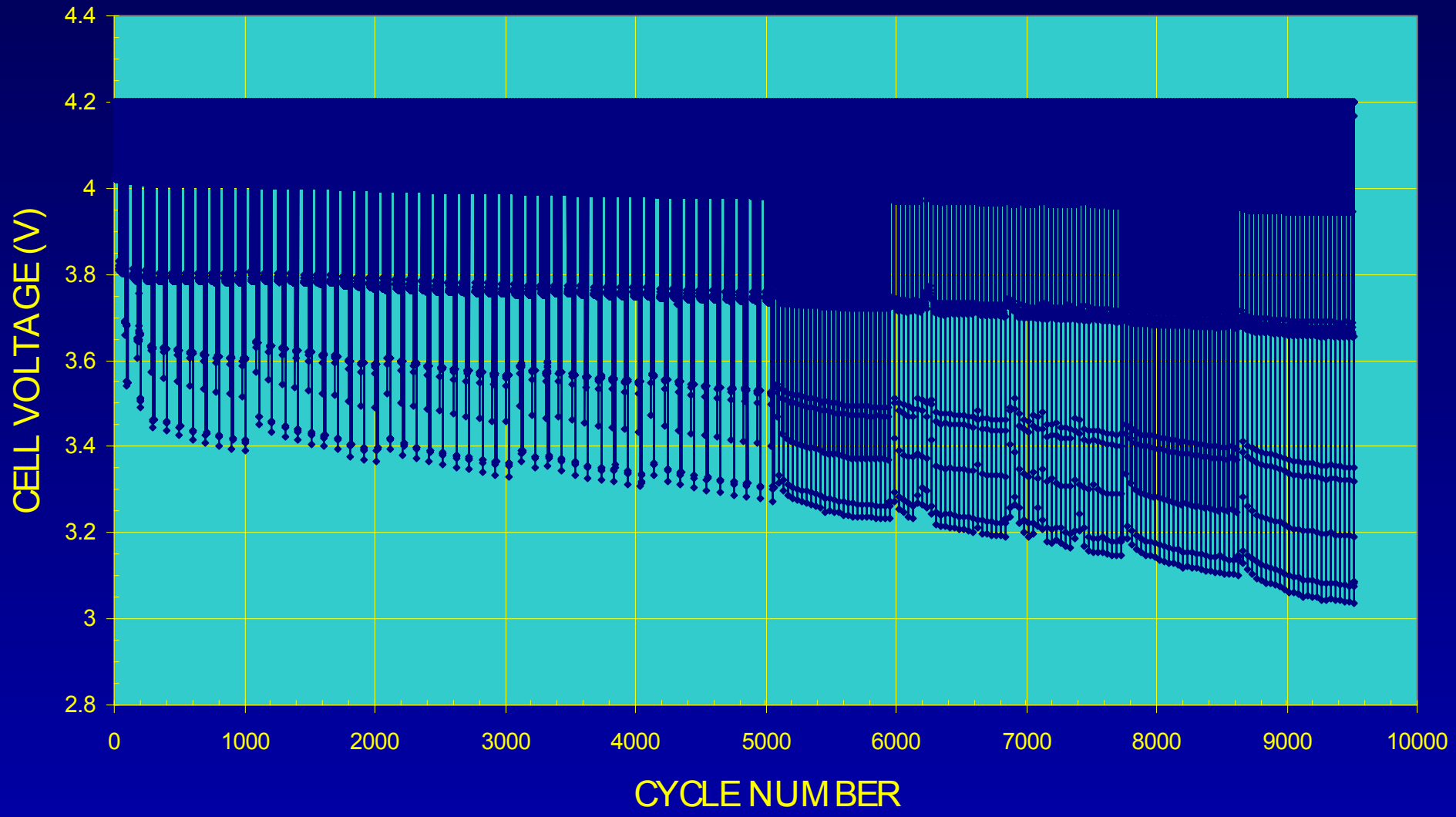
FA Test Voltages



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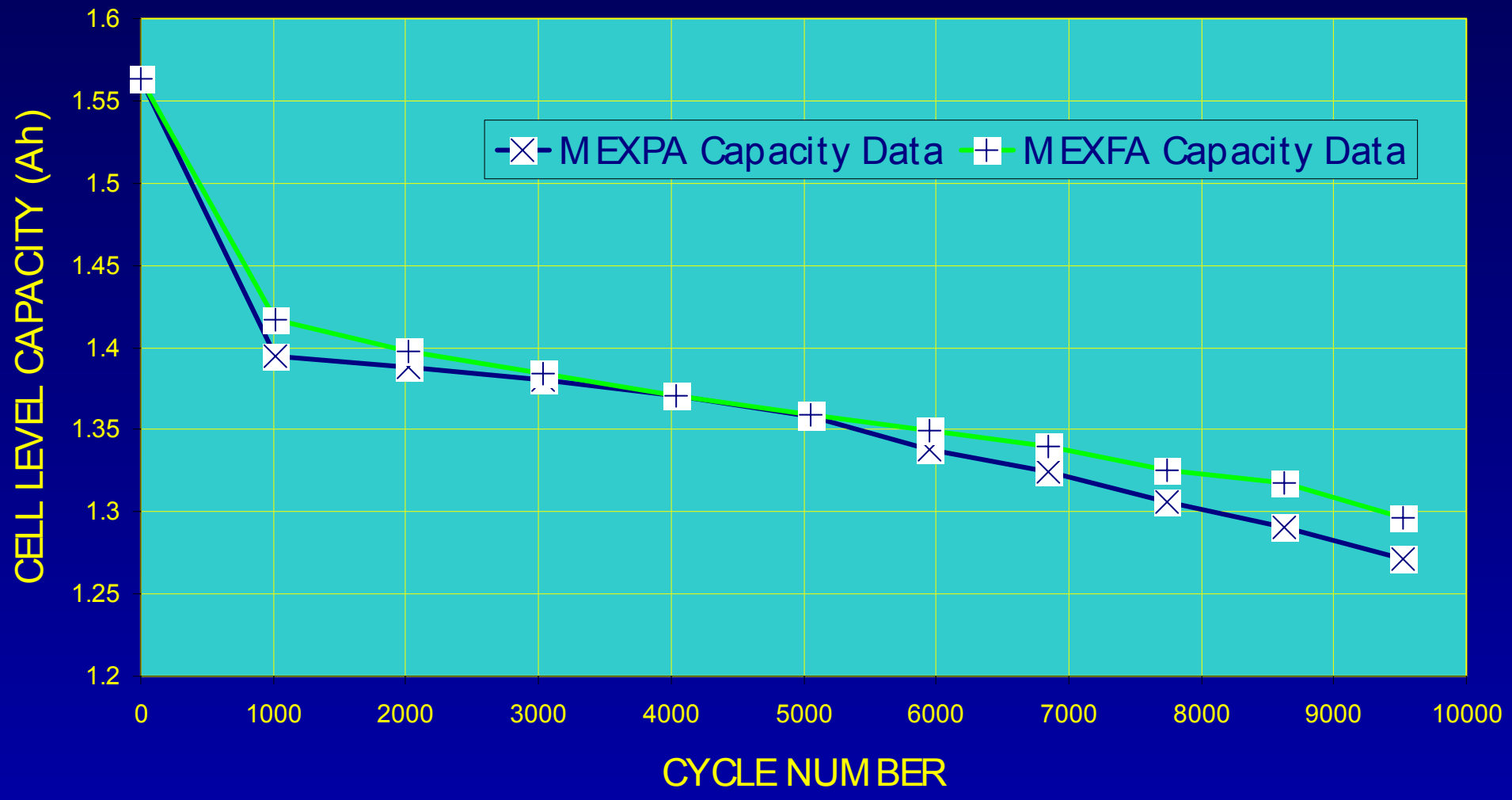
Capacity v. Cycle



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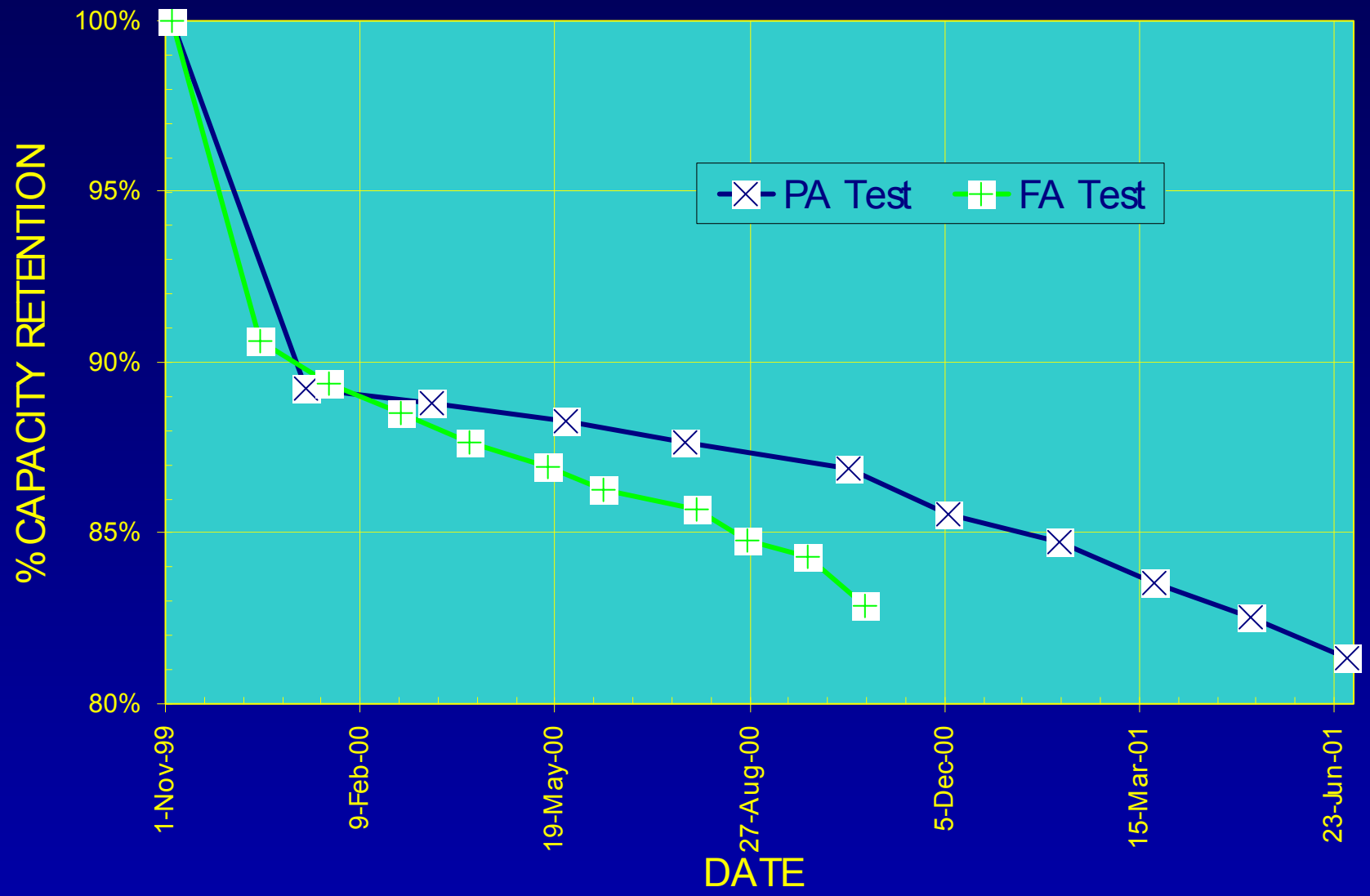
Capacity v. Test Time



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Conclusions

Conclusions

- The battery will exceed requirements for the extended mission
- Good agreement between the pre-test predictions and the measured results for the realistic test
- Fundamental principles of prediction algorithm proven
- Care must be taken interpreting accelerated tests due to calendar life
- Lots more to be learnt from this data set

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Acknowledgements

- We gratefully acknowledge our customers:
  - Dieter Kolbe, Astrium, Germany
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  - The ESA Mars Express Team at ESTEC
- BNSC for their support and encouragement
- ESA for the use of the artists impressions

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BAE SYSTEMS Applied Technologies

Battery Technology Center

Effects of LEO Cycling on Li-Ion Pouch Cell Electrodes

NASA Space Power Workshop

James C Massingill

11/21/02

Objective

- Identify the limiting electrode(s)
- Gain understanding of failure mechanism

Experimental Overview

- Pouch Cells
  - Bring Pouch cells to “complete” state of discharge.
  - Open pouch cells in glovebox.
  - Observe condition of electrodes and other components.

Experimental Overview (contd.)

- Coin Cells
  - Build coin “half-cells” using portions of pouch cell’s electrode
  - Cycle at low rate (C/10) and high rate (LEO rates)
    - Low rate to measure intrinsic capacity
    - High rate to determine rate capability loss.
  - Evaluate Data
    - Identify limiting pouch cell electrode (negative or positive)
      - **Intrinsic Capacity**
      - **Rate Capability**
    - Determine amount of cyclable lithium lost.

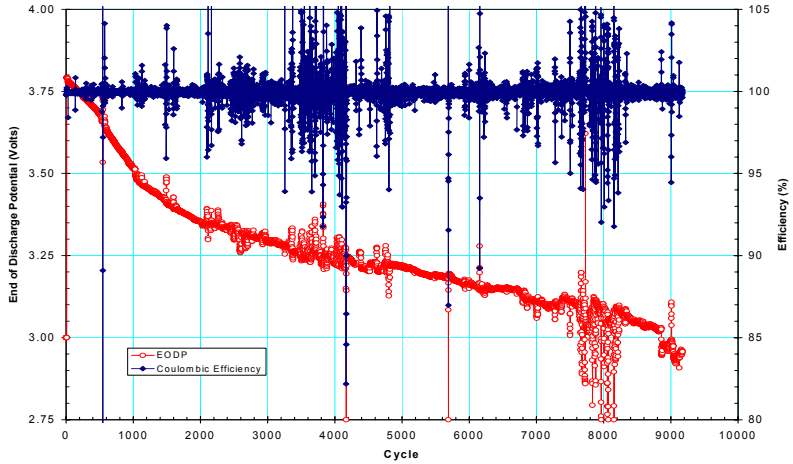
Experimental Overview (contd.)
Pouch Cell Build/DPA Summary

Pouch Cells	Positive	Negative	# Cycles
Cell #1	$LiCoO_2$ Vendor A	0.5% SP MCMB2528	~9000
Cell #2	LiCoO2 Vendor B	2% SP* MCMB2528	~4900
Cell #3	$LiCoO_2$ Vendor B	2% SP* MCMB2528	~4600
Cell #4	$LiCoO_2$ Vendor A	2% SP* MCMB2528	~4500
Cell #5	$LiCoO_2$ Vendor A	0.5% SP MCMB2528	~6000
Cell #6	$LiCoO_2$ Vendor A	0.5% SP MCMB2528	~7000
Cell #7	$LiCoO_2$ Vendor A	2% SP* MCMB2528	~6500

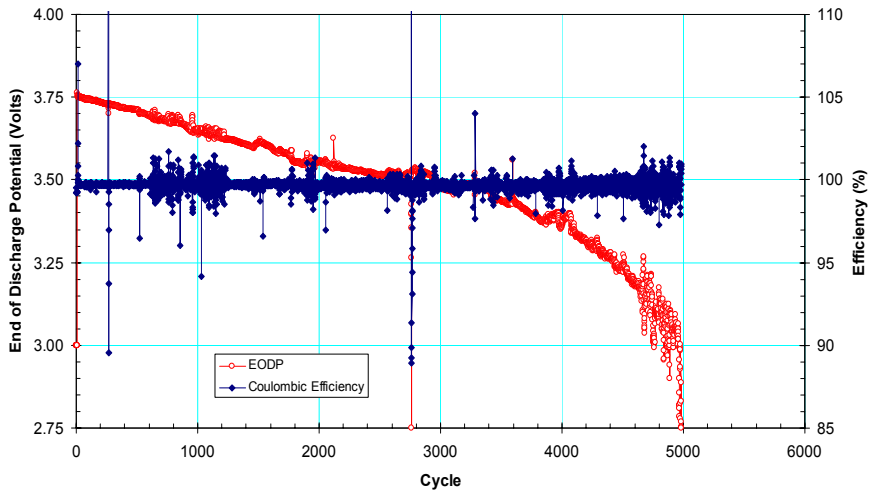
*Non-uniform Coating Porosity

Cycle Life Plots of Pouch Cells

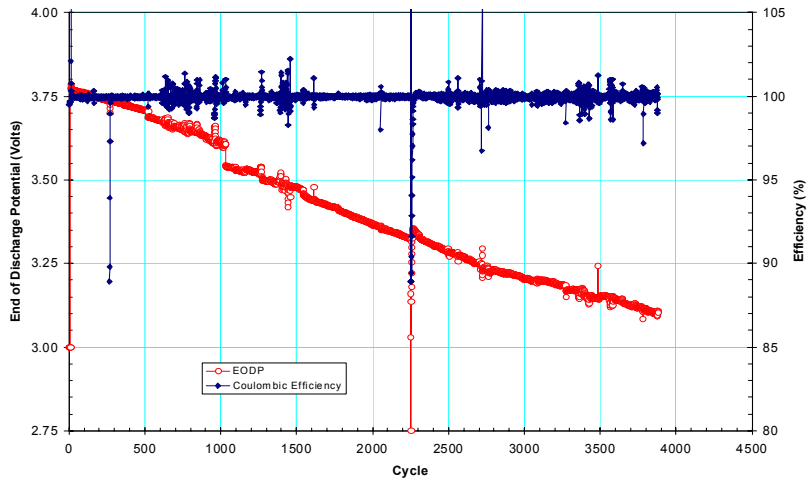
Cell #1



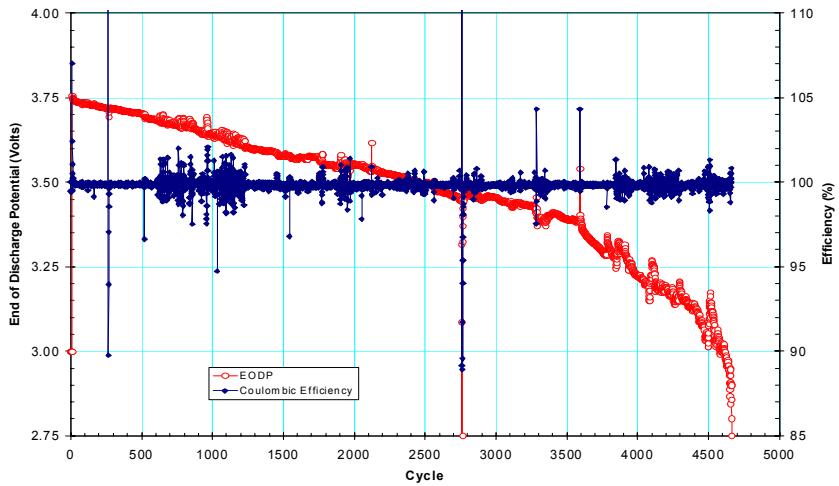
Cell #2



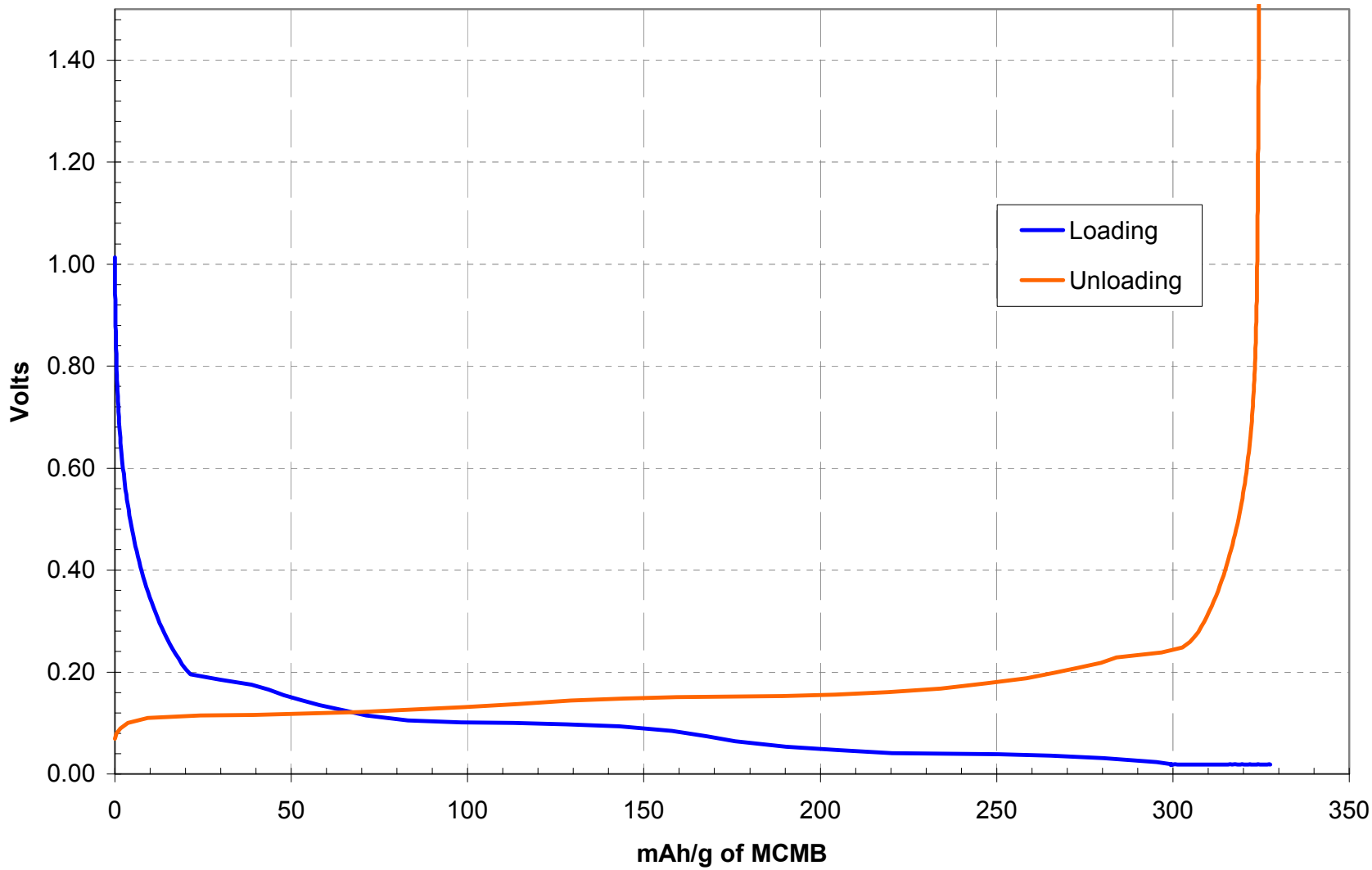
Cell #4



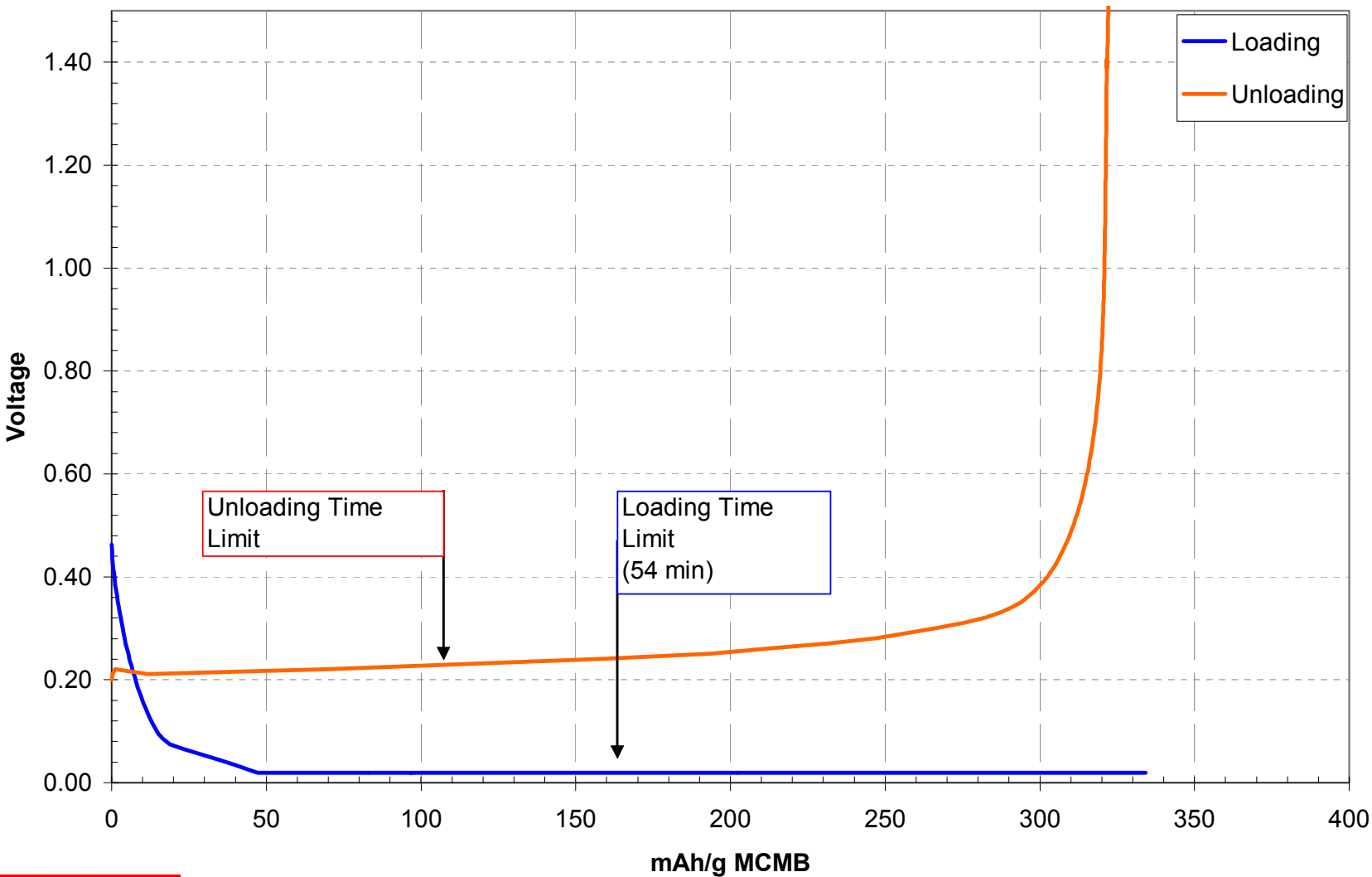
Cell #3



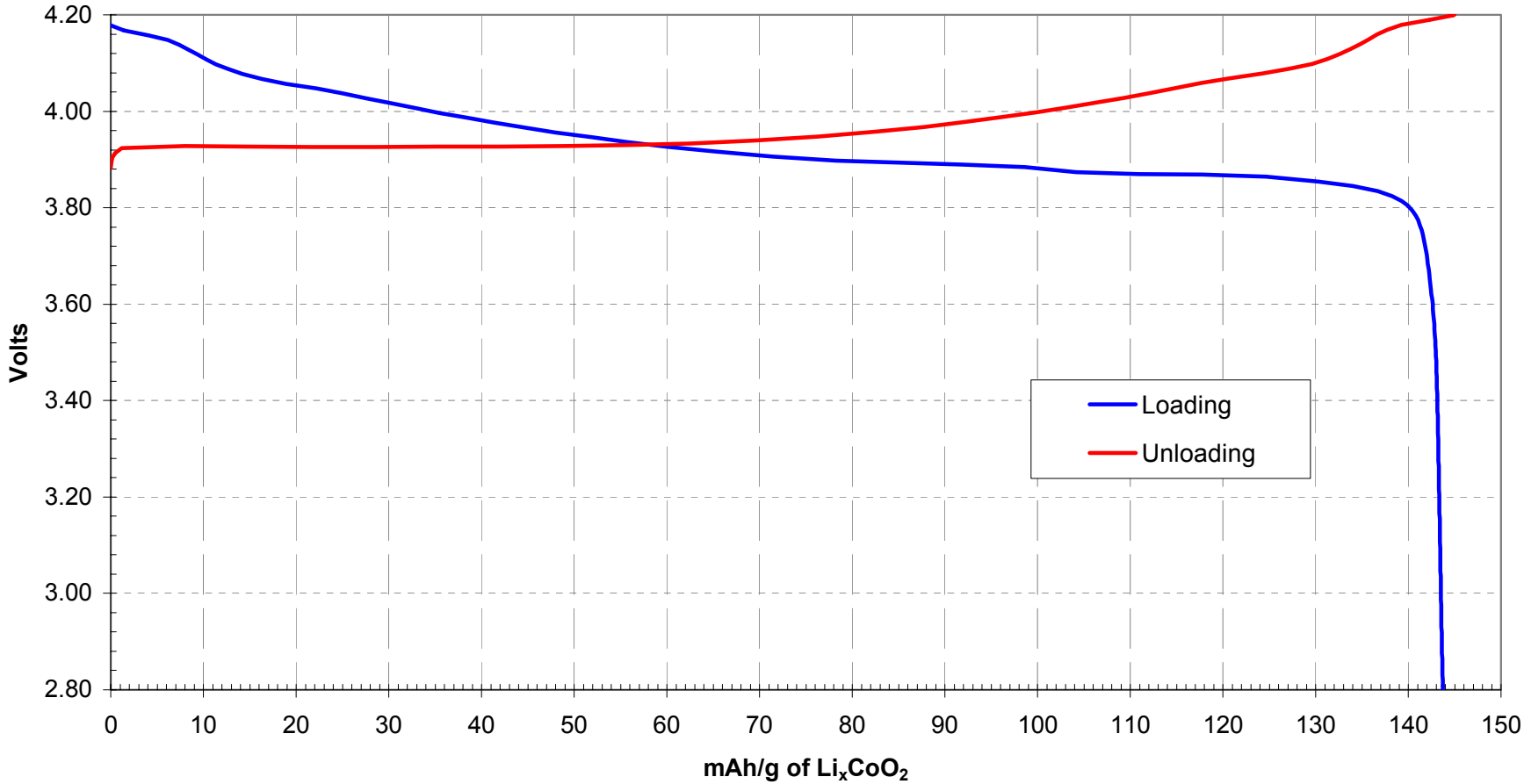
Coin Cell Results
Control Negative Electrode @ C/10



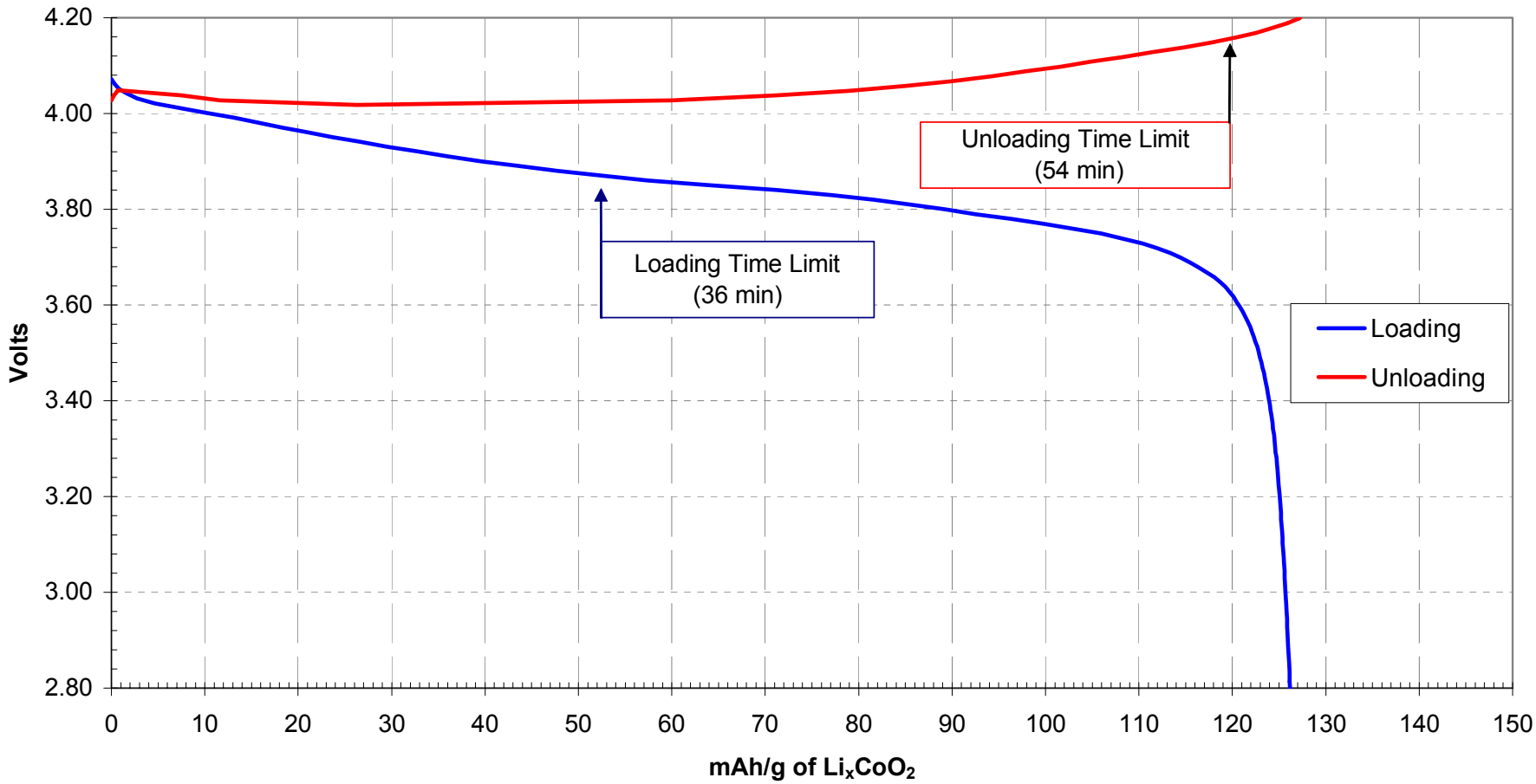
Coin Cell Results (contd.)
Control Negative Electrode @ LEO Rates



Coin Cell Results (contd.)
Control Positive Electrode @ C/10

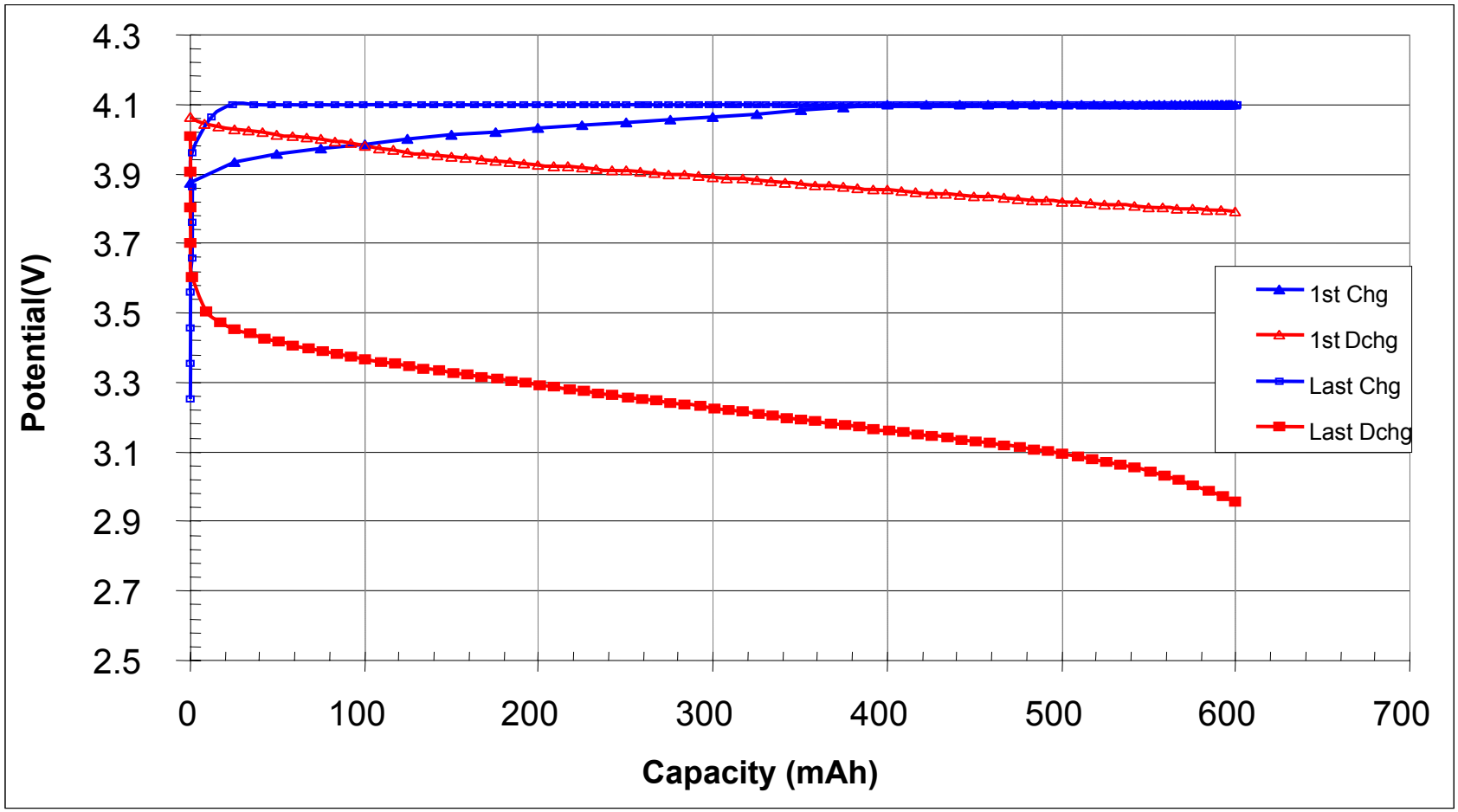


Coin Cell Results (contd.)
Control Positive Electrode @ LEO Rates

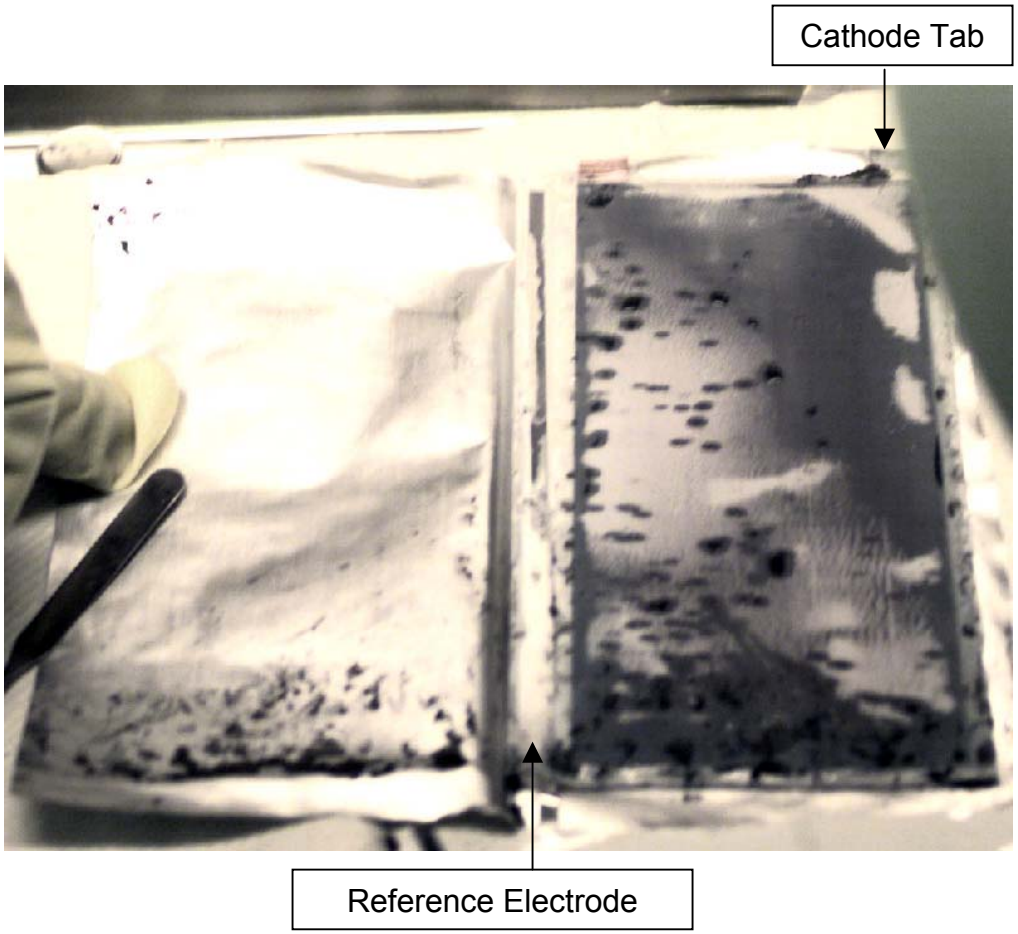


Pouch Cell #1 Results
1st Cycle vs. Last Cycle

Indicative of predominant cathode polarization



Pouch Cell #1 Results (contd.)
DPA Photos Pouch Material



Close-up of Cathode Tab

- Observations
  - Mossy Li deposits around perimeter of separator bag.
  - Mossy Li deposits on pouch surface.
  - Heavy deposits of mossy Li around cathode tab.
  - Most of Li missing from reference electrode.

Pouch Cell #1 Results (contd.)
DPA Photos of Negative Electrode

Edge #1 0.192 – 0.196 mm, 4k – 6k Ω

Edge #4
0.194 – 0.208 mm
1k – 5k Ω

Edge #2
0.192 – 0.202 mm
4k – 13k Ω

Edge #3 0.195 – 0.212 mm, 40k – 60k Ω

- Observations
  - Discoloration around perimeter of electrode
  - No visible Li deposits on electrode surface
  - Mossy Li deposits around perimeter of separator bag

Fresh Material
Thickness: 0.157 – 0.160 mm
Resistance: 5 – 10 Ω

Pouch Cell #1 Results (contd.)
DPA Photos of Positive Electrode

Cycled Cathode

Thickness: 0.160 – 0.165 mm

Resistance: 120 - 190 Ω

Fresh Cathode

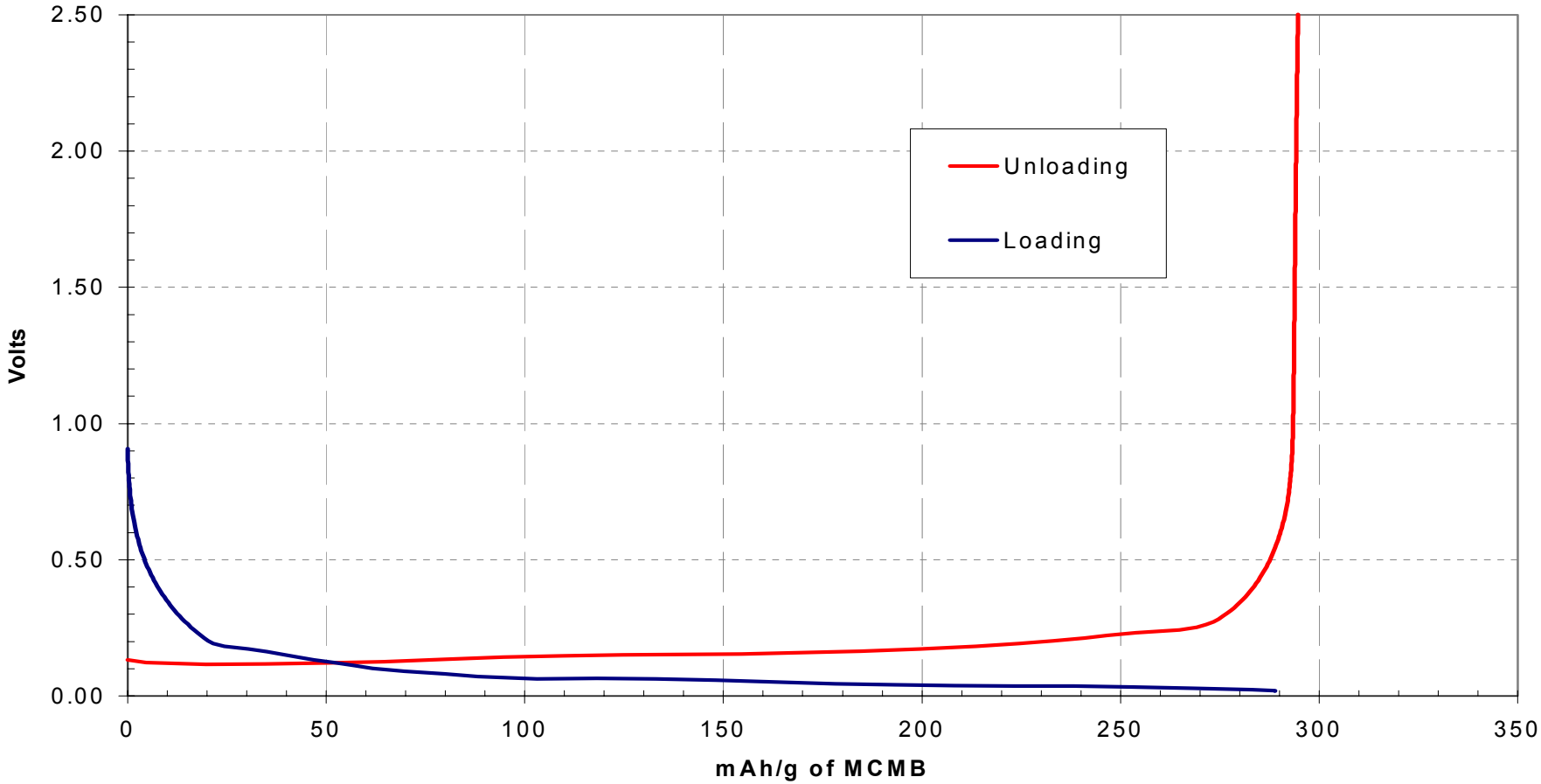
Thickness: 0.151 – 0.154 mm

Resistance: 70 – 90 Ω

- Observations
  - Cathode appeared “fresh”.
  - No visible Li deposits on electrode surface
  - Mossy Li deposits around perimeter of separator bag

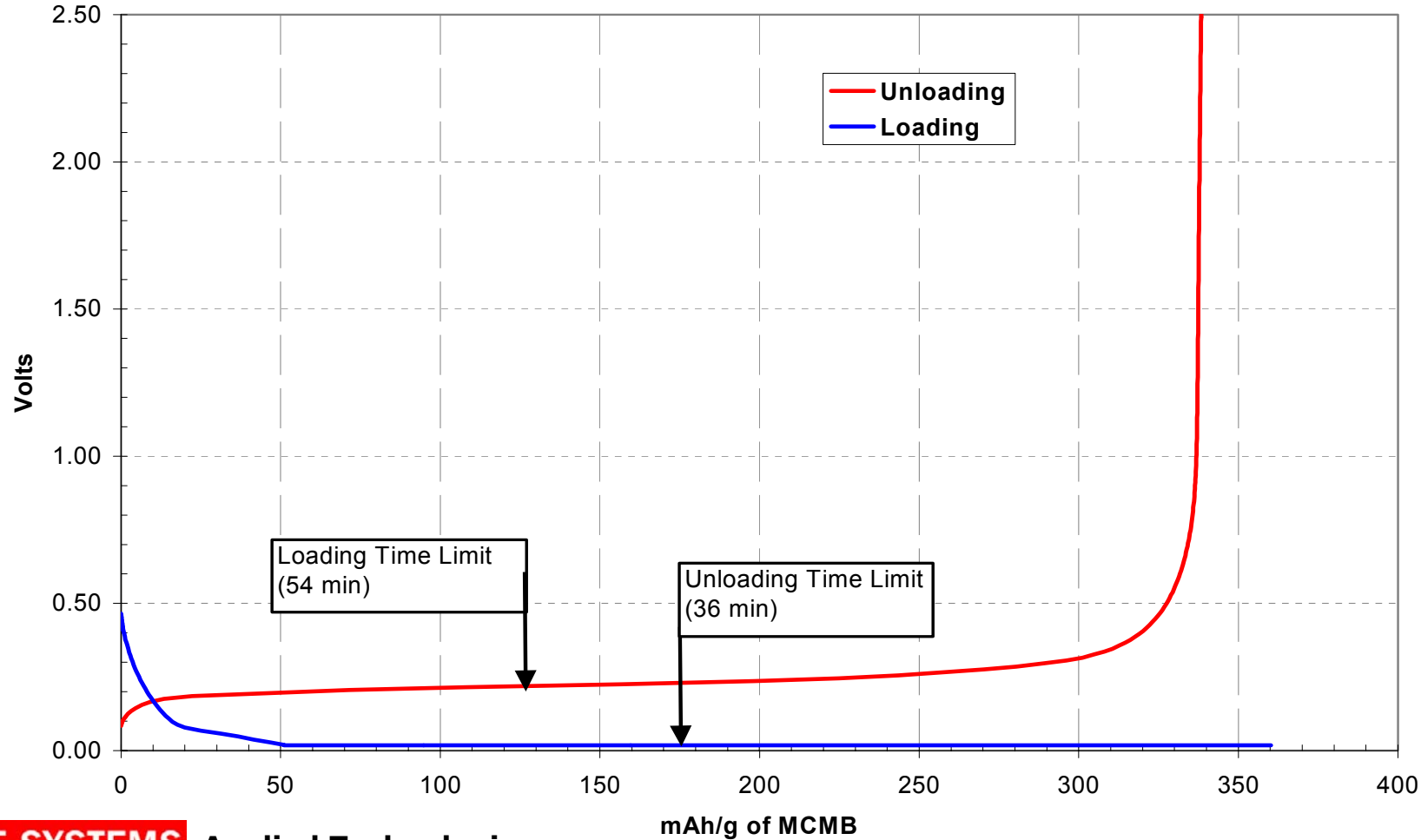
Coin Cell #1 Results
Negative Electrode @ C/10

Slight Loss of Intrinsic Capacity



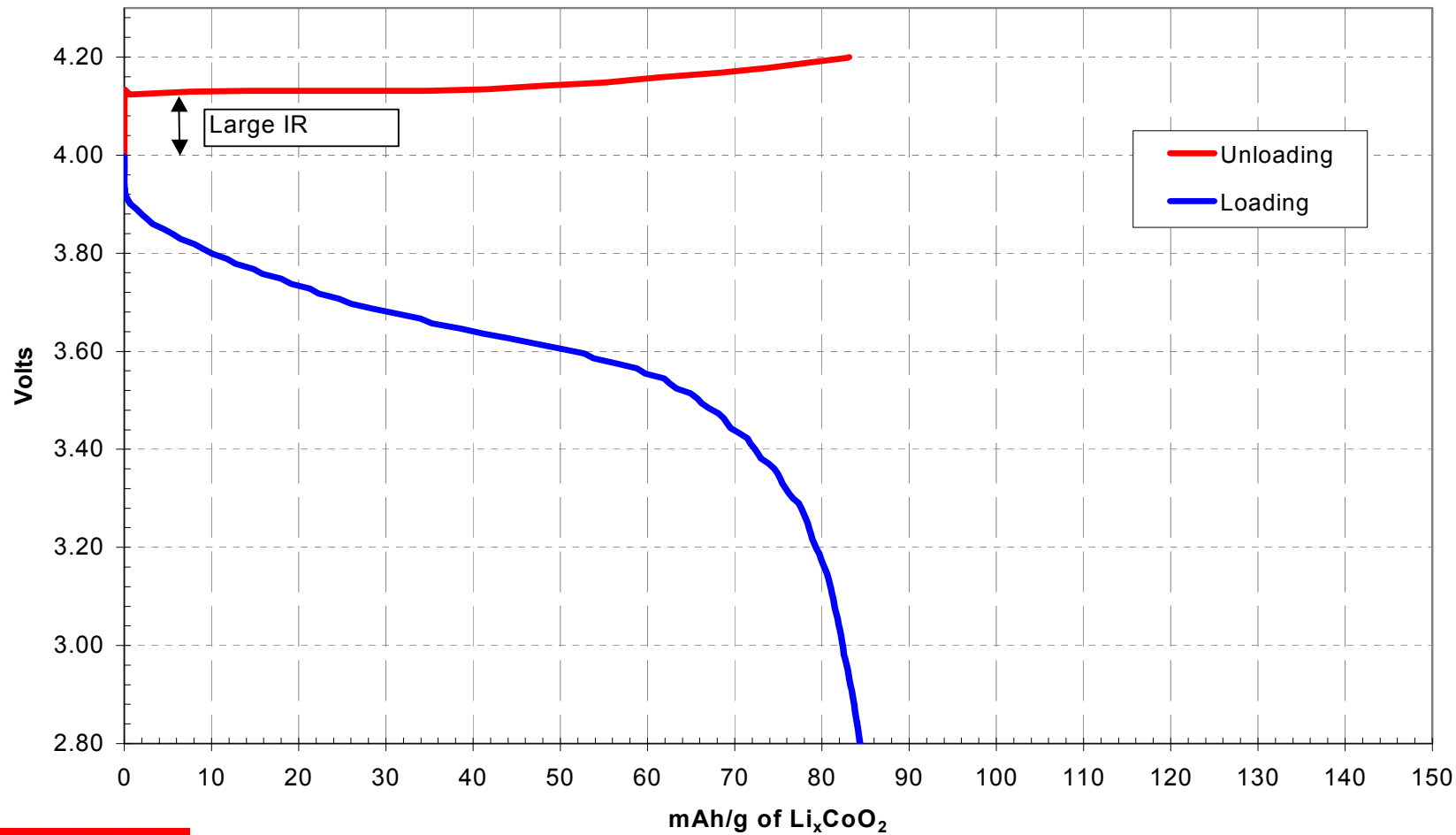
Coin Cell #1 Results (contd.)
Negative Electrode @ LEO Rates

No Loss of Rate Capability



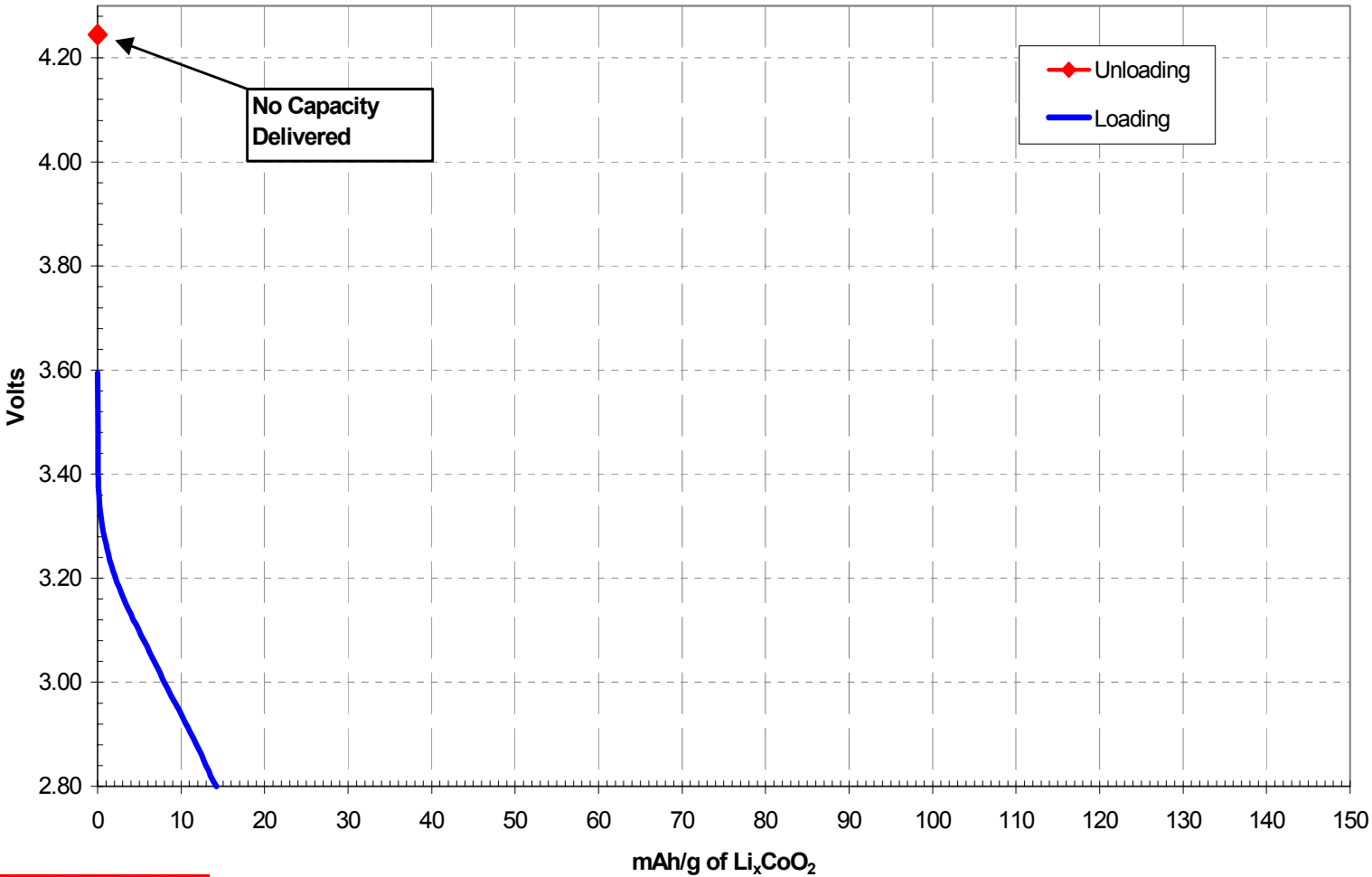
Coin Cell #1 Results (contd.)
Positive Electrode @ C/10

Significant Loss of Intrinsic Capacity

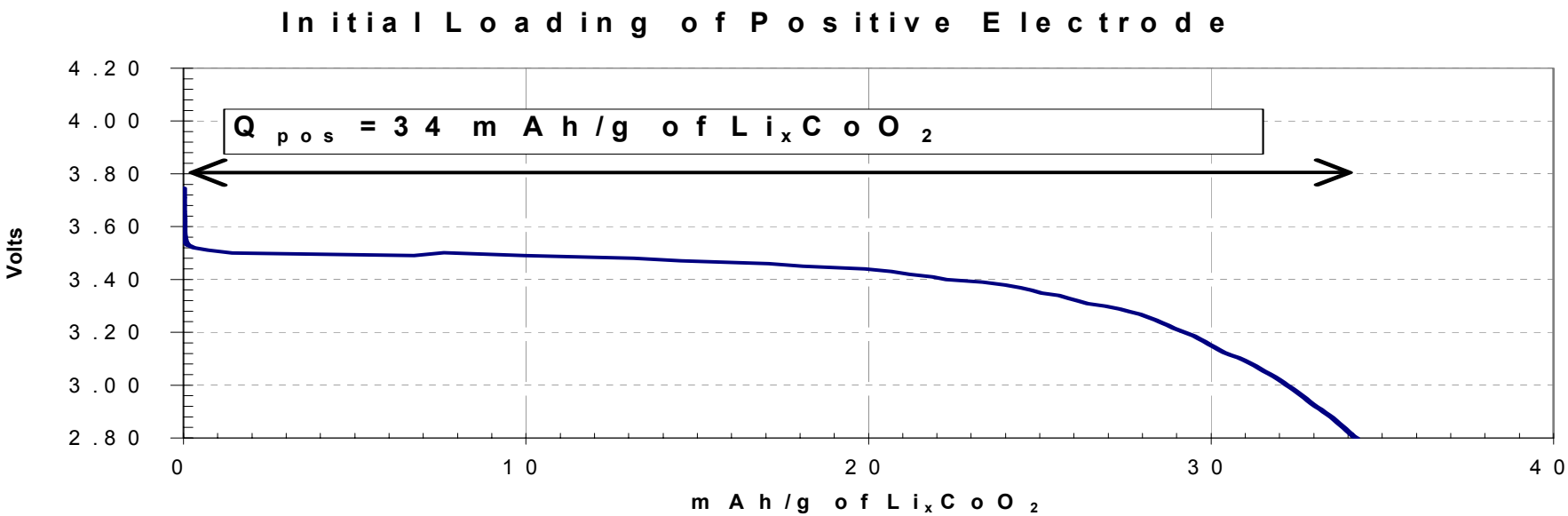


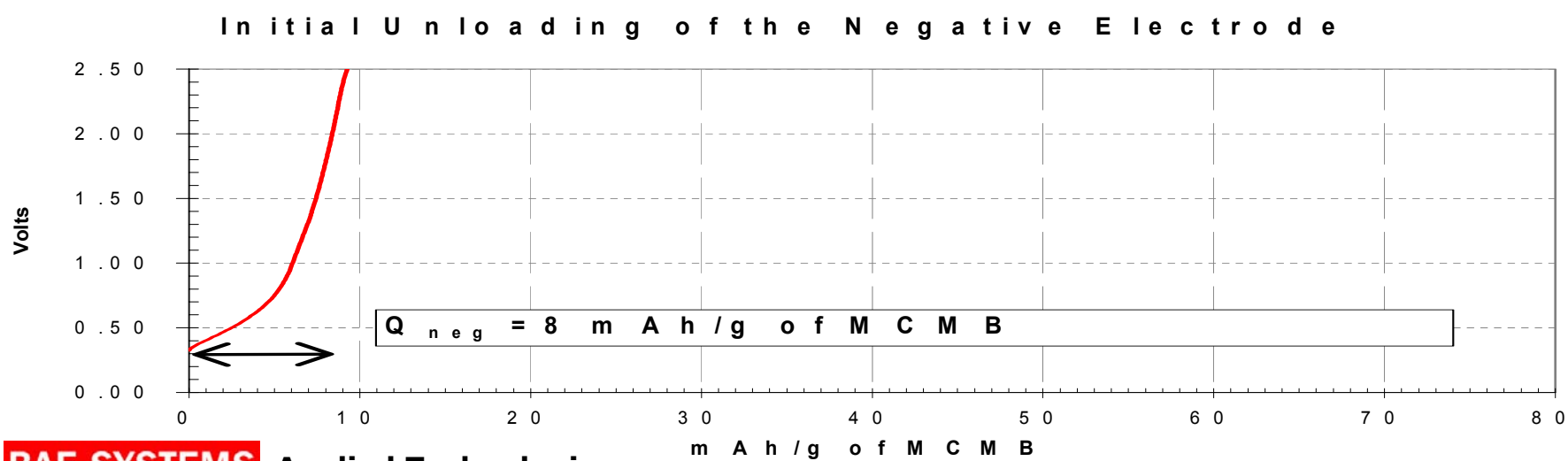
Coin Cell #1 Results (contd.)
Positive Electrode @ LEO Rates

Severe Loss of Rate Capability



Coin Cell Results
Cell #1 Cyclable Lithium Loss





Lithium Accounting Calculations

1. Cyclable Li Lost =

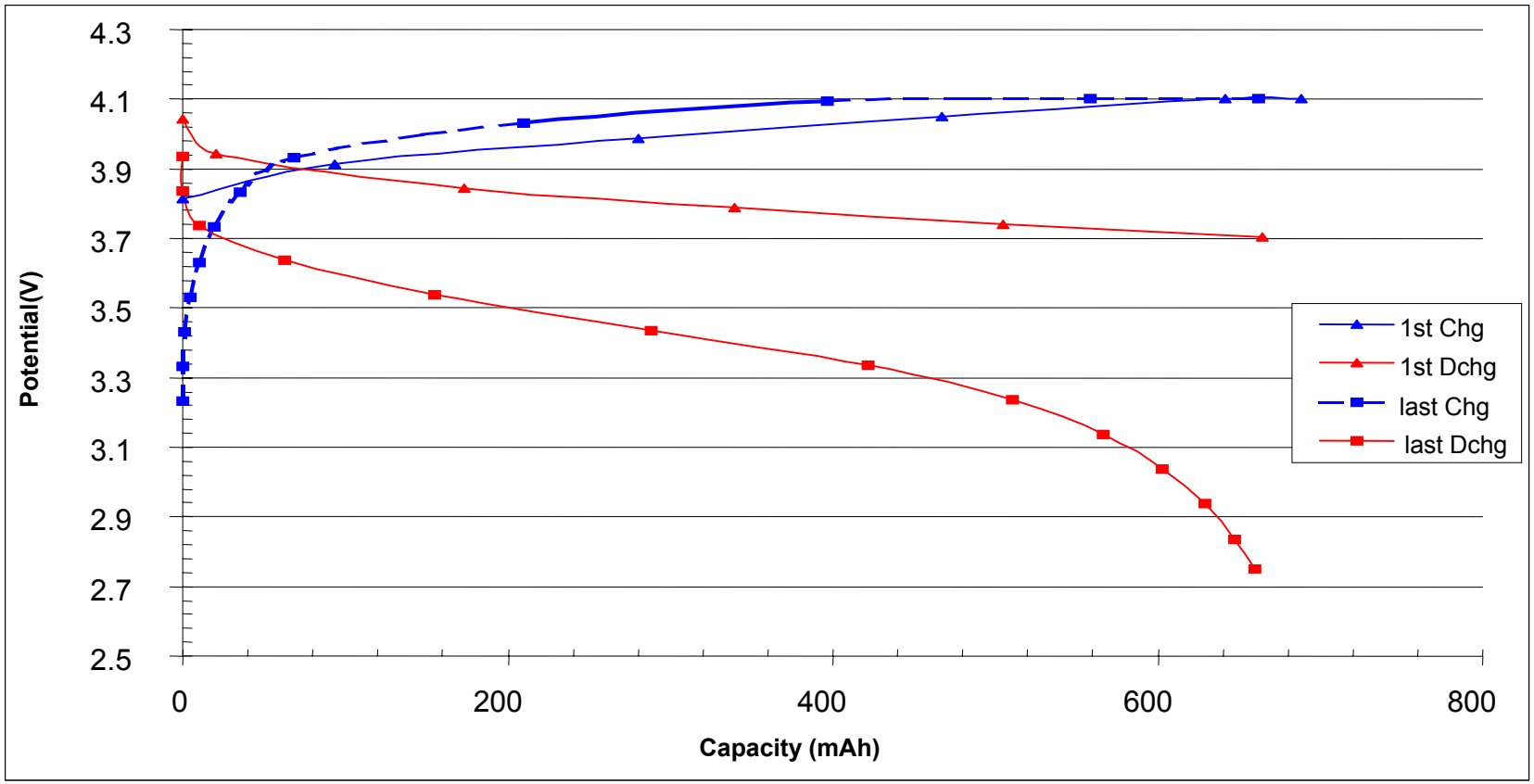
[Li Lost from Li_xCoO_2 – Li for SEI] – Li Remaining in MCMB

2. Li Lost from Li_xCoO_2 = $\mathbf{Q_{pos}}$/273 mAh/g
3. Li for SEI = 0.054
4. Li Remaining in MCMB = $\mathbf{Q_{neg}}$/372 mAh/g

For Cell #1	
0.124	
0.054	
0.022	
0.048	Cyclable Li lost

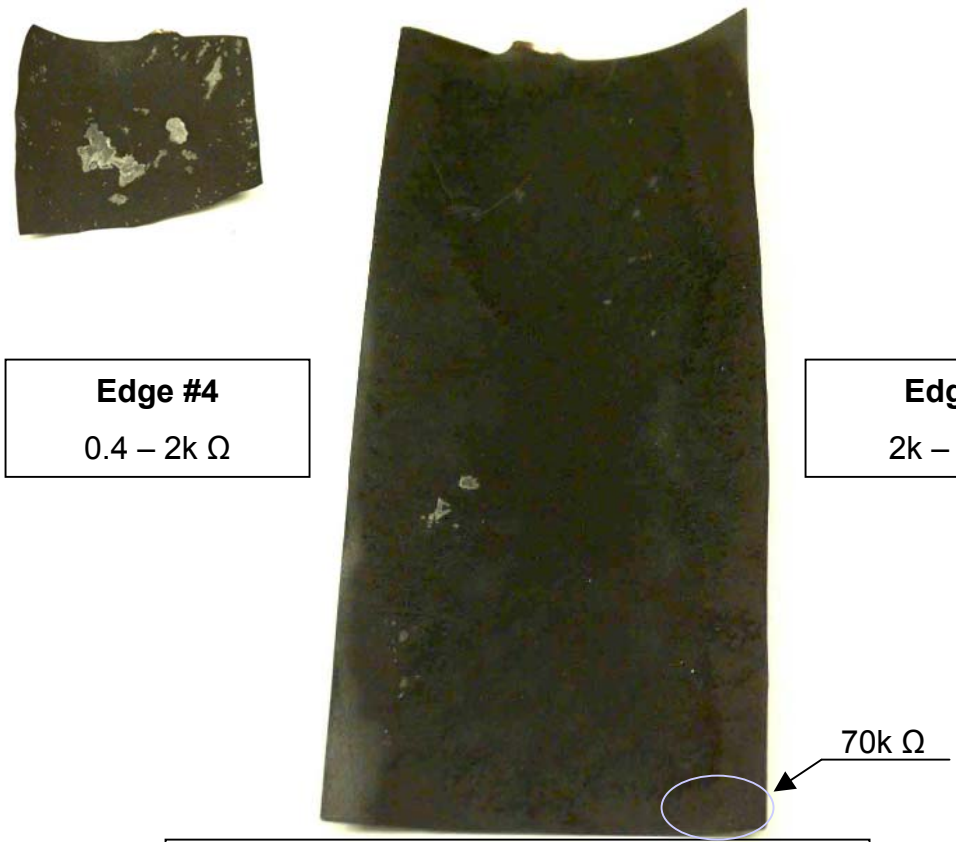
Pouch Cell #3 Results
1st Cycle vs. Last Cycle

Indicative of cathode & anode polarizations



Pouch Cell #3 Results
DPA Photos of Negative Electrode

Edge #1 1k – 4k Ω



Edge #4
0.4 – 2k Ω

Edge #2
2k – 40k Ω

Edge #3 1k – 3k Ω

- Observations
  - Blotched areas
    - smooth hard texture
    - raised deposits
    - 20k - 40k Ω
    - reacted with H_2O

Fresh Material
Resistance: 5 – 10 Ω

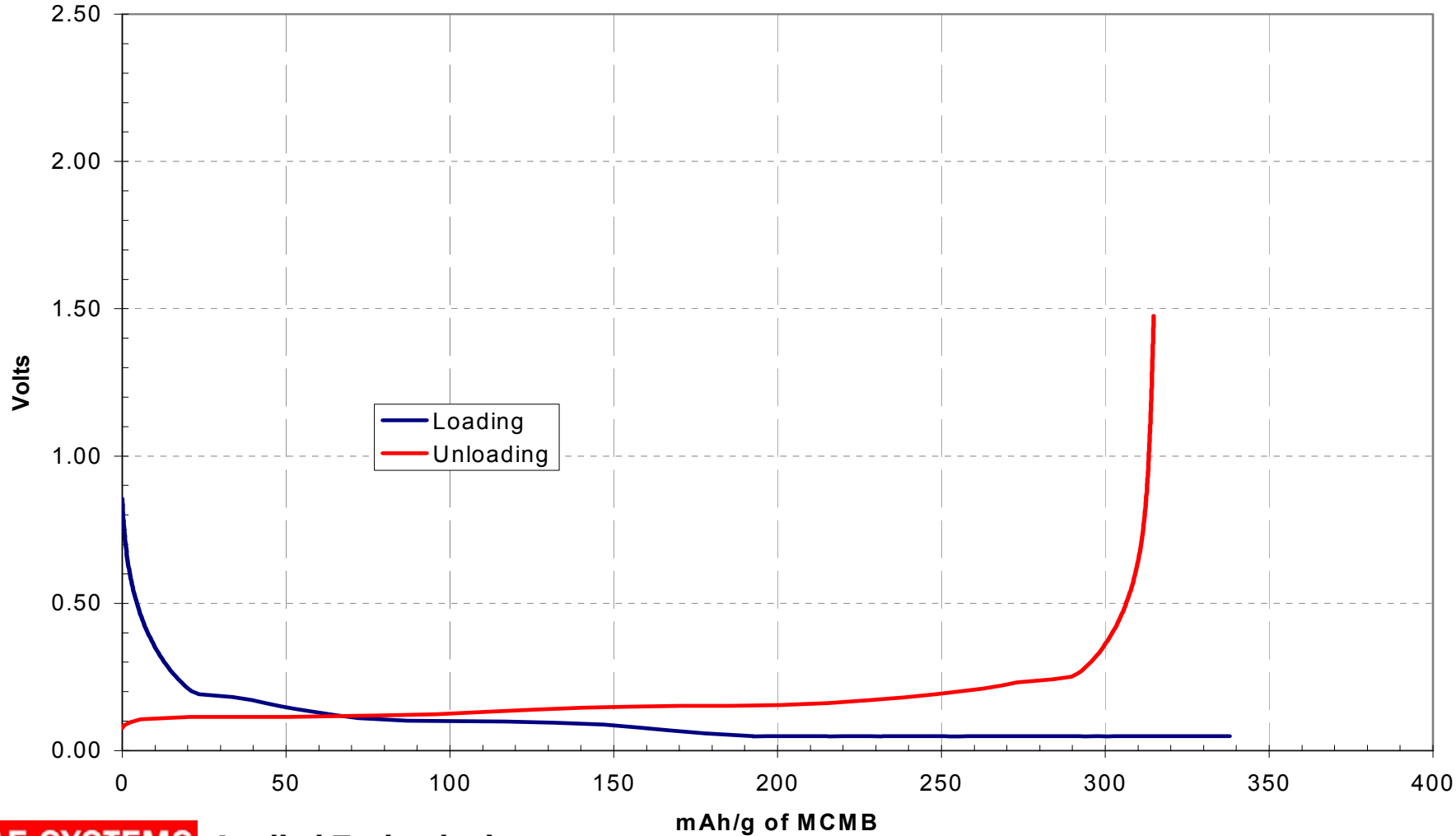
Pouch Cell #3 Results (contd.)
DPA Photos of Positive Electrode

- Observations
  - Areas with dark discoloration (300 – 400 Ω)
  - Side A (170 - 200 Ω)
  - Side B (80 - 100 Ω)

* Note: Color not accurate. Coloration altered to highlight discolored areas.

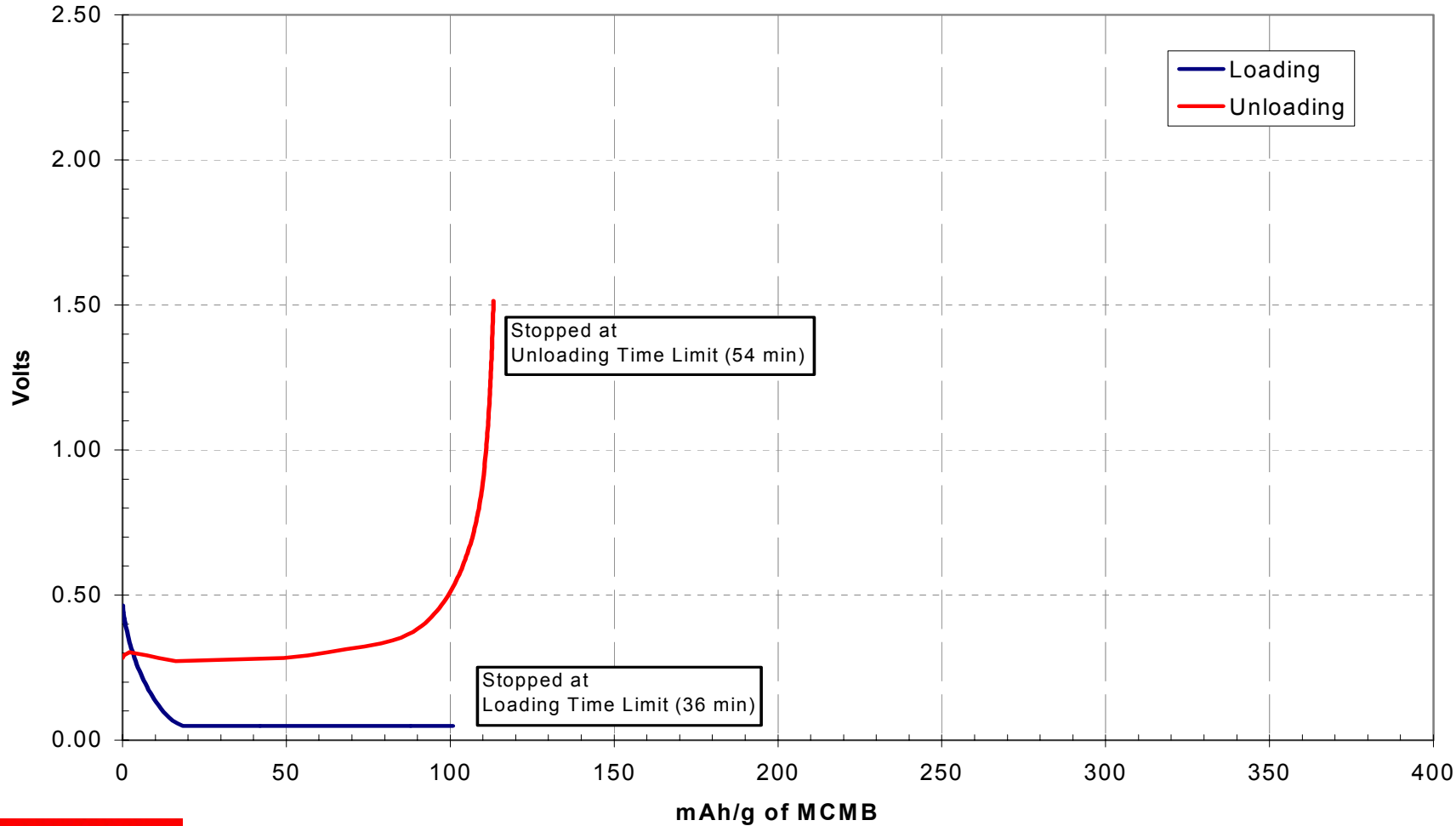
Coin Cell #3 Results
Negative Electrode @ C/10

No Loss of Intrinsic Capacity



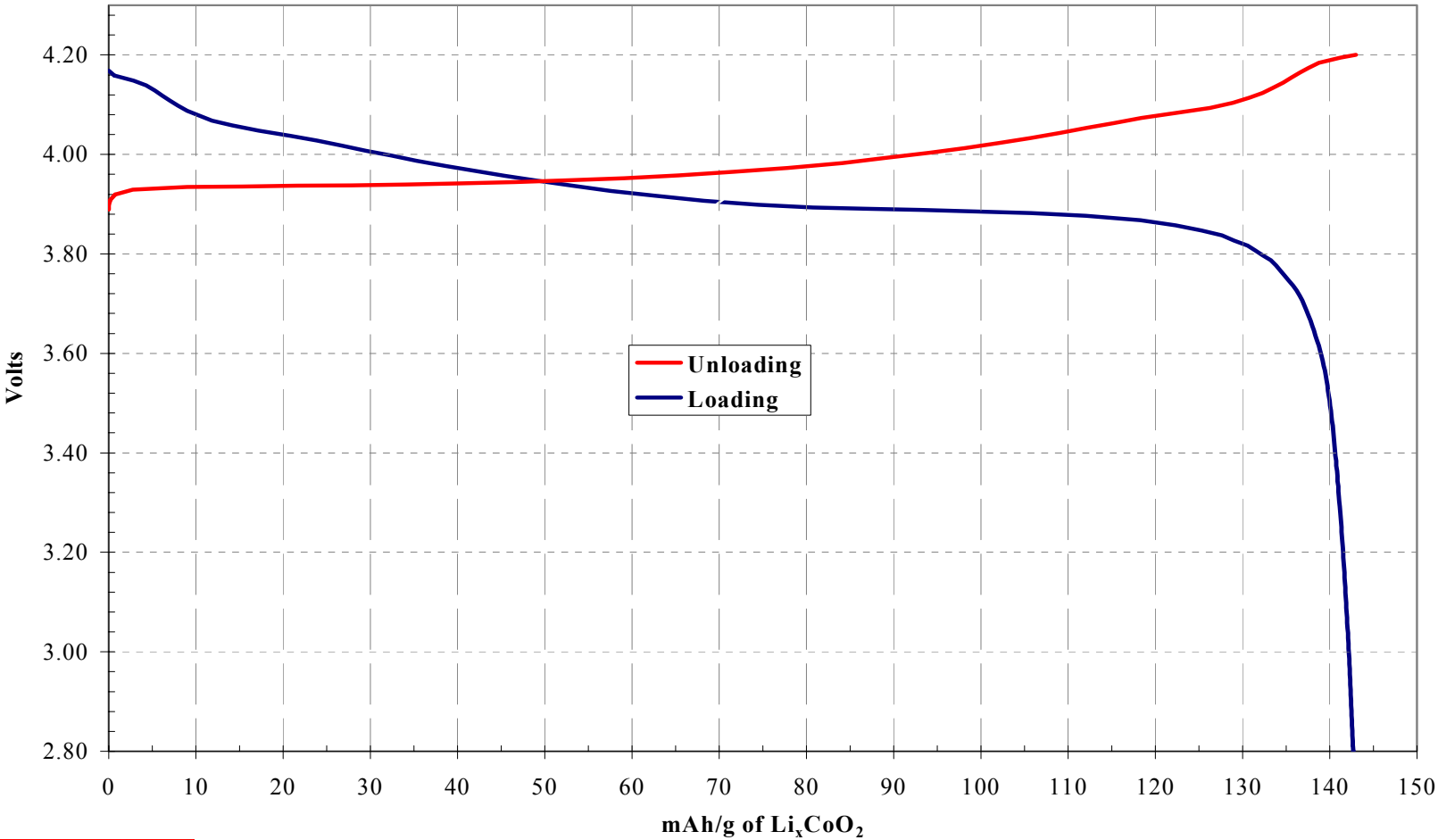
Coin Cell #3 Results (contd.)
Negative Electrode @ LEO Rates

Degradation of Rate Capability



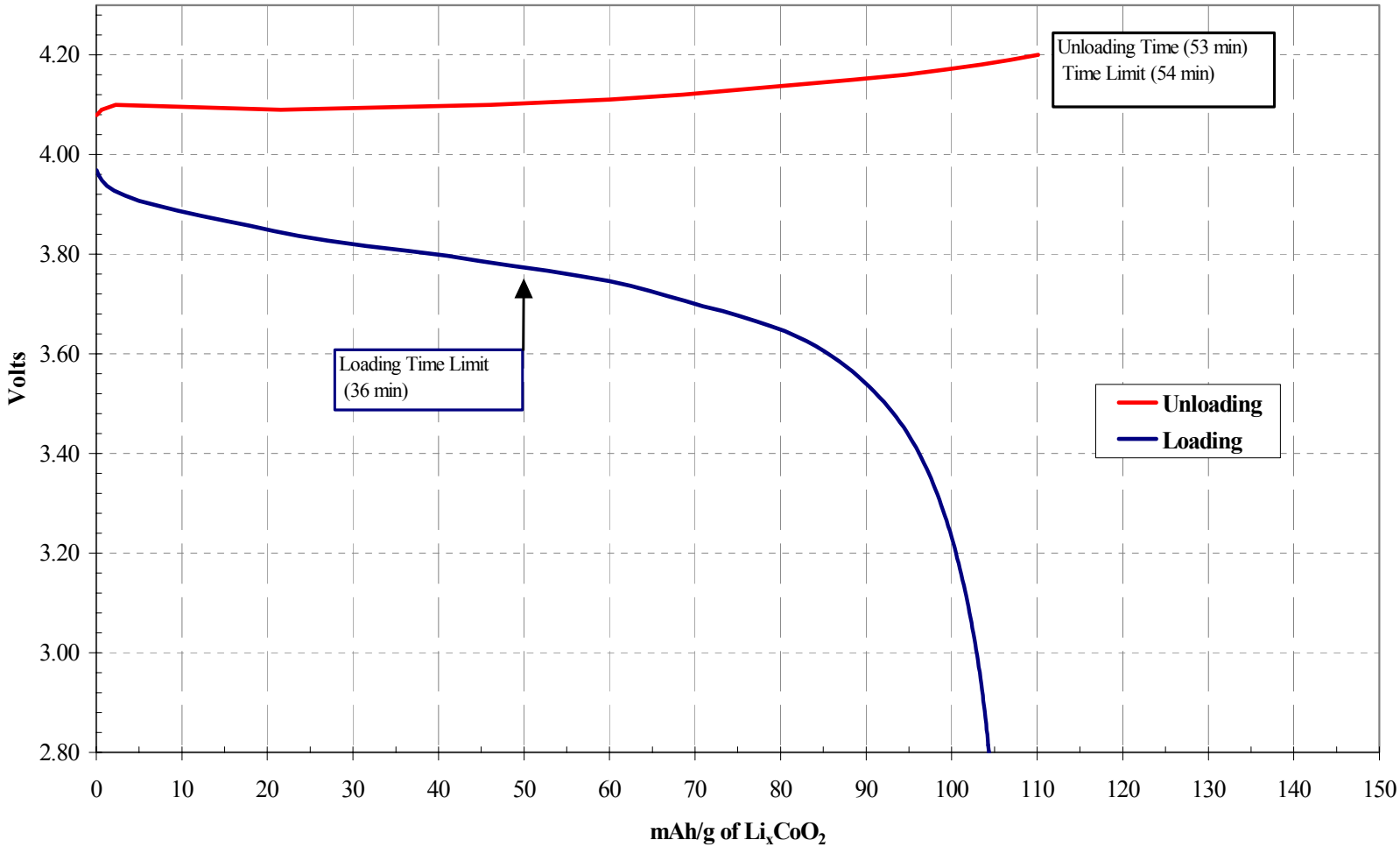
Coin Cell #3 Results (contd.)
Positive Electrode @ C/10

No loss of Intrinsic Capacity



Coin Cell #3 Results (contd.)
Positive Electrode @ LEO Rates

Slight degradation of Rate Capability



Lithium Accounting Calculations

1. Cyclable Li Lost =

[Li Lost from Li_xCoO_2 – Li for SEI] – Li Remaining in MCMB

2. Li Lost from Li_xCoO_2 = $\mathbf{Q_{pos}}$/273 mAh/g
3. Li for SEI = 0.054
4. Li Remaining in MCMB = $\mathbf{Q_{neg}}$/372 mAh/g

For Cell #3	
0.253	
0.054	
0.022	
0.177	Cyclable Li lost

Results Summary

Cell ID	Electrode	Intrinsic Capacity (mAh/g)		LEO Capacity (mAh/g)		Li Loss (x)
Control	Positive	145 U	145 L	121 U	56 L	NA
	Negative	336 L	332	209 L	120 U	
#1	Positive	85 U	84 L	**0 U**	**14 L**	0.048
	Negative	315 L	299 U	169 L	122 U	
#2	Positive	128 U	126 L	78 U	54 L	0.031
	Negative	299 L	314 U	128 L	113 U	
#3	Positive	143 U	143 L	110 U	54 L	**0.177**
	Negative	337 L	317 U	101 L	113 U	
#4	Positive	121 U	121 L	**0 U**	**0 L**	0.040
	Negative	316 L	312 U	105 L	108 U	
#5	Positive	115 U	115 L	**0 U**	**0 L**	**
	Negative	273 L	266 U	137 L	130 U	
#6	Positive	112 U	112 L	**0 U**	**0 L**	**
	Negative	322 L	318 U	137 L	122 U	
#7	Positive	84 U	84 L	**0 U**	**0 L**	**
	Negative	296 L	293 U	163 L	120 U	

** No Measurable Loss

Conclusions

- Two major failure modes
  - Cathode severely polarized due to either structural degradation or passivation film
    - XRD of post-mortem Li_xCoO_2 electrodes indicated structural degradation
    - TEM in progress
  - Anode polarized due to possible SEI destruction/repassivation
    - Loss of cyclable lithium