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The 2000 NASA Aerospace Battery Workshop

J.C. Brewer, Compiler
Marshall Space Flight Center, Marshall Space Flight Center, Alabama

Proceeding of a workshop sponsored by the
NASA Aerospace Flight Battery Systems Program
and held in Huntsville, Alabama, November 14–16, 2000

National Aeronautics and
Space Administration

Marshall Space Flight Center • MSFC, Alabama 35812

March 2001

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Preface

This disk contains the proceedings of the 33rd annual NASA Aerospace Battery Workshop, hosted by the Marshall Space Flight Center on November 14-16, 2000. 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 silver-zinc technologies.

Introduction

The NASA Aerospace Battery Workshop is an annual event hosted by the Marshall Space Flight Center. The 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 2000 Workshop was held on three consecutive days and was divided into five sessions. The first day consisted of a General Session and a Focused Session (Status of Aerospace Battery Technology Heading into the 21st Century). The second day consisted of a short Nickel-Hydrogen Session followed by a Lithium / Lithium-Ion Session. The third and final day was a second Focused Session dealing with Lithium-Ion Cell and Battery Safety.

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;

Holiday Inn – Research Park, 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, and Rao Surampudi and Kumar Bugga, Jet Propulsion Laboratory, for organizing and conducting this year's focused 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.

Jeff Brewer
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13. ABSTRACT *(Maximum 200 words)*

This document contains the proceedings of the 33nd annual NASA Aerospace Battery Workshop, hosted by the Marshall Space Flight Center on November 14–16, 2000. 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 nickel-hydrogen, lithium-ion, lithium-sulfur, and silver-zinc technologies.

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Effects of AEA Cell-Bypass-Switch Closure on Charged EOS-Aqua NiH_2 Cell

2000 NASA Aerospace Battery Workshop

Denney Keys
Gopalakrishna M. Rao
David Sullivan
Harry Wannemacher*

NASA GODDARD SPACE FLIGHT CENTER
*QSS GROUP, INC

Objectives

- Verify the Performance of AEA Cell Bypass Protection Device (CBPD) under simulated EOS- Aqua/Aura flight hardware configuration
- Assess the Safety of the hardware under an inadvertent firing of CBPD switch, as well as the closing of CBPD switch under simulated high cell impedance
- Confirm that the mode of operation of CBPD switch is the formation of a continuous low impedance path (a homogeneous low melting point alloy)

EOS-Aqua Flight Hardware

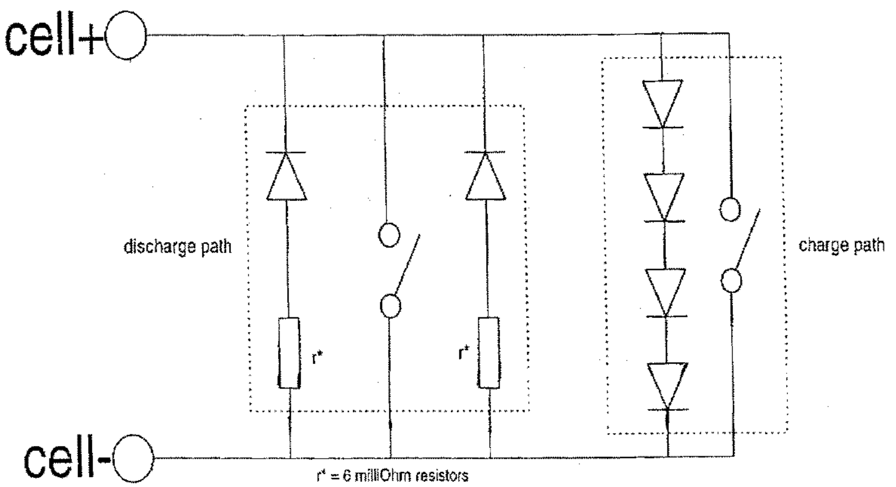
- Battery Cells:
  - Eagle-Picher 160 Ah NiH_2 (RNH 160-3)
  - Size: ~ 12cm Diameter
    ~ 32cm overall Height
  - Weight: ~ 4.3kg
- Cell-Bypass-Switch:
  - AEA Technology
    Cell Bypass Protection Device (CBPD)

AEA Hardware Tested

- A total of five (5) CBPDs were tested using the charged EOS Cell
  - Three FLIGHT devices
    (F01, F02 and F03)
  - Two ENGINEERING MODEL devices
    (EM01 & EM02)
- The two types of CBPDs are basically the same, with a change in separator and minor outer dimension changes

AEA Bypass Switch Schematic

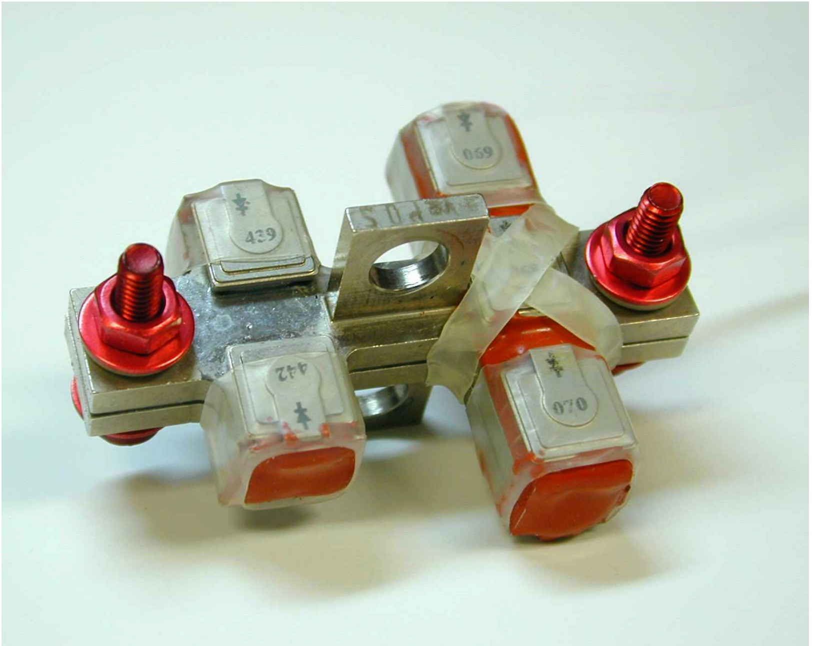
CBPD - LMPA Schematic
(Low Melting Point Alloy)



AEA
AEA Technology

Slide serial no 6

NOTE: Tested devices have 6 series diodes in charge path (not 4 as shown)



FLIGHT CBPD

AEA Cell-Bypass-Switch Spec

TRW spec for Aqua

90 grams

Icharge ~ 75A

R ~ 500 microOhms

CBPD - Specification

- 75grams
- Icharge < 35A
- I discharge < 235A
- Triggering - see operation summary
- R ~ 200 microOhms
- I operation < 400A - dependent on leads and mounting

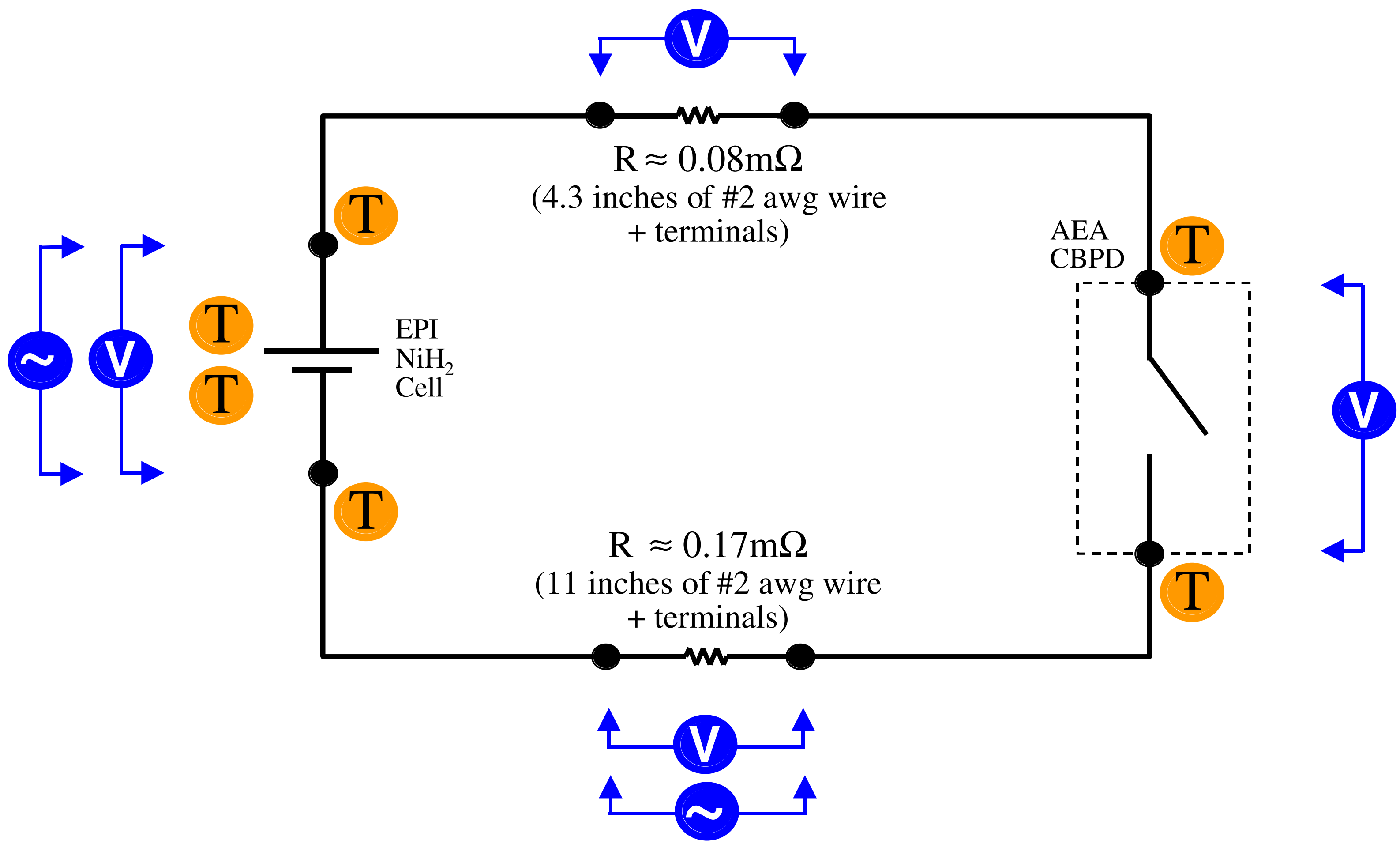
AEA
AEA Technology

Slide serial no 13

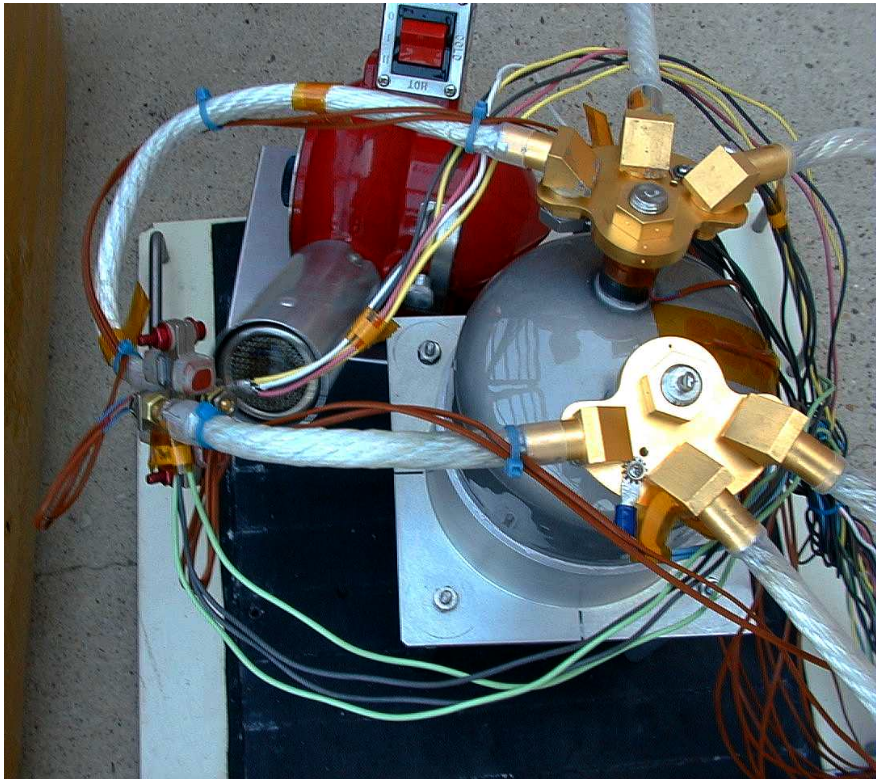
Tests Performed

- Test#1: CBPD F01
  Activated with heatgun
  Switch-axis ~45° from Horizontal
- Tests #2 & 3: CBPD EM01 & EM02
  Activated through charge diodes
  Switch -axis Vertical
- Test#4: CBPD F02
  Activated through charge diodes
  Switch-axis Horizontal (launch orientation)
- Test#5: CBPD F03
  same as Test#4, with added 50 mΩ resistance in current path

Test #1 setup (switch activated with heatgun)



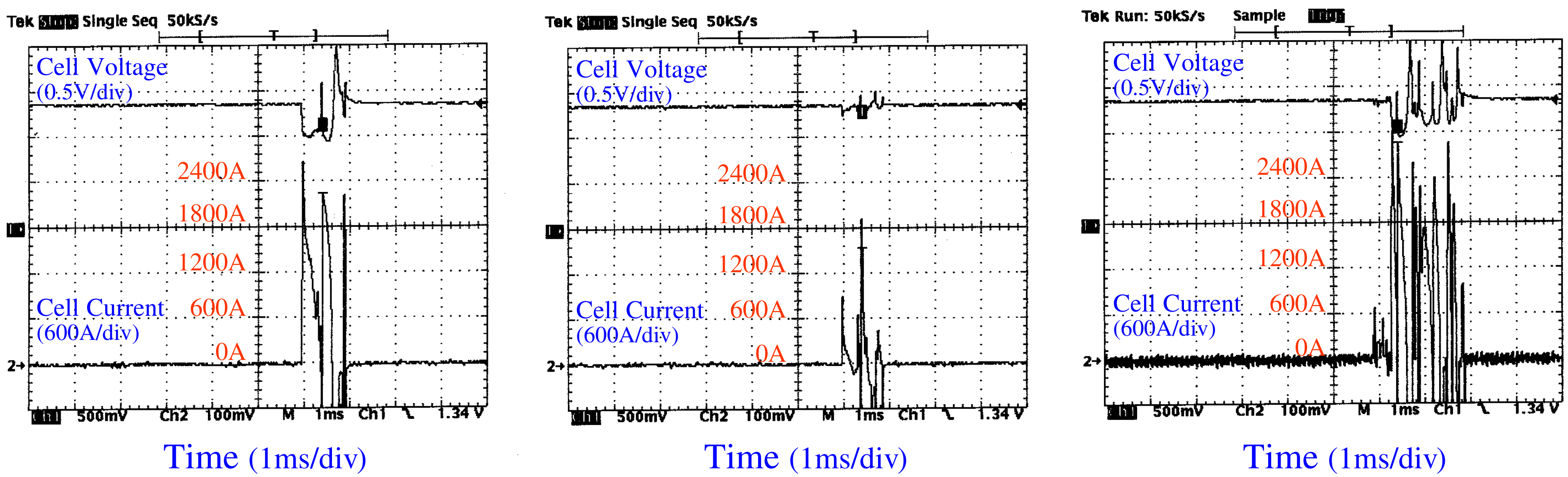
Test #1



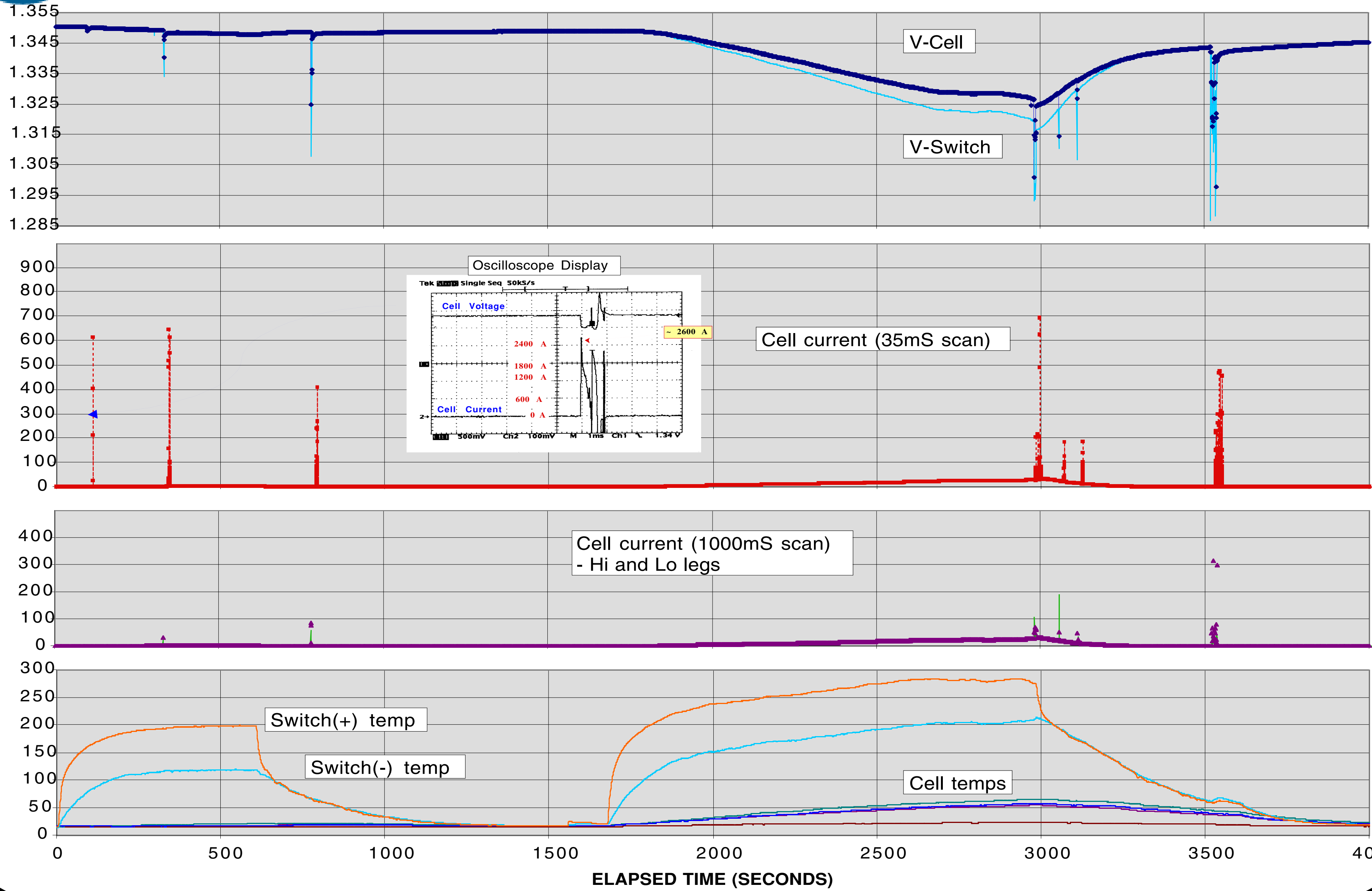
First application of heatgun

Heatgun repositioned for
second application

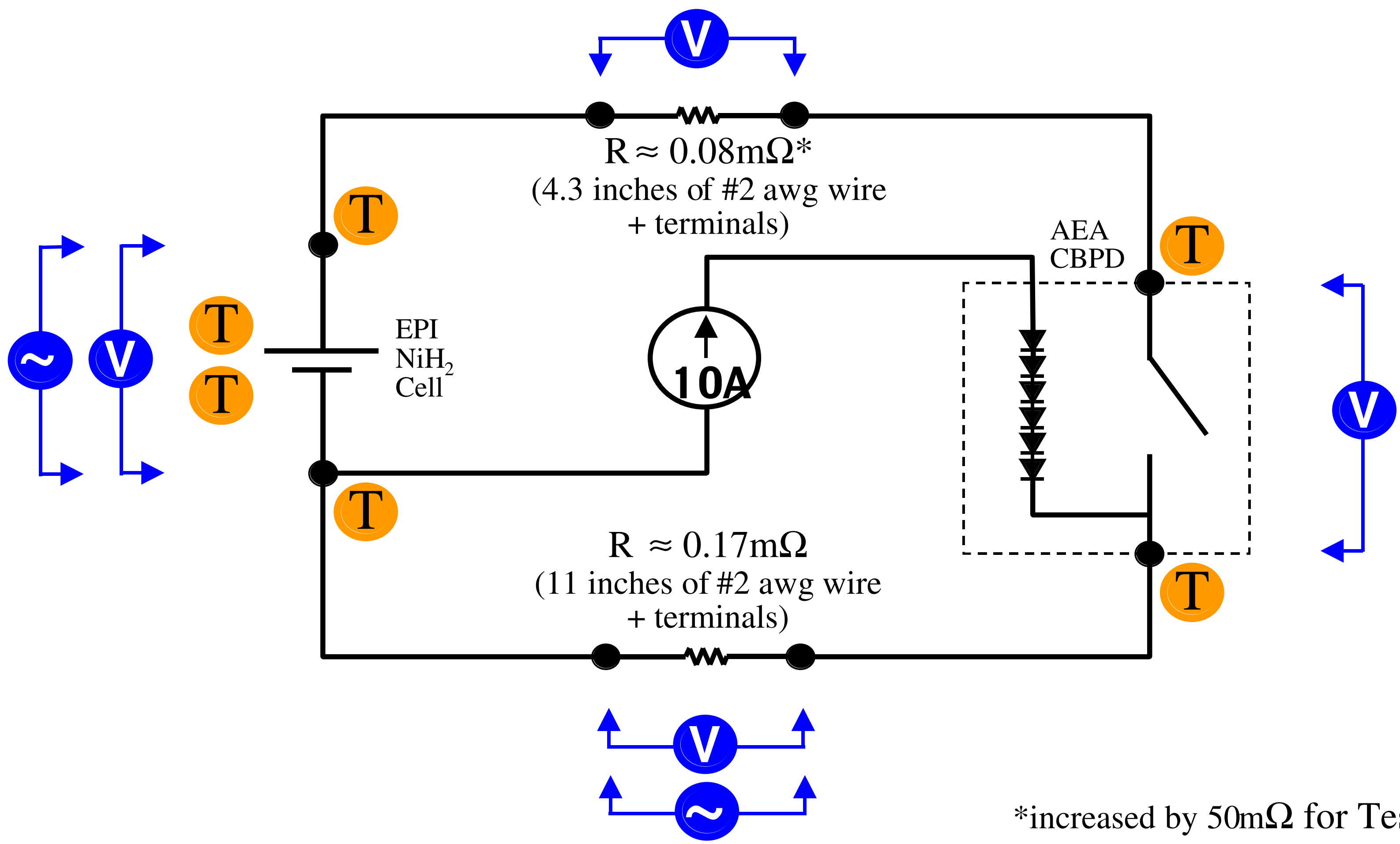
Test #1 Scope Traces



Test #1 Data

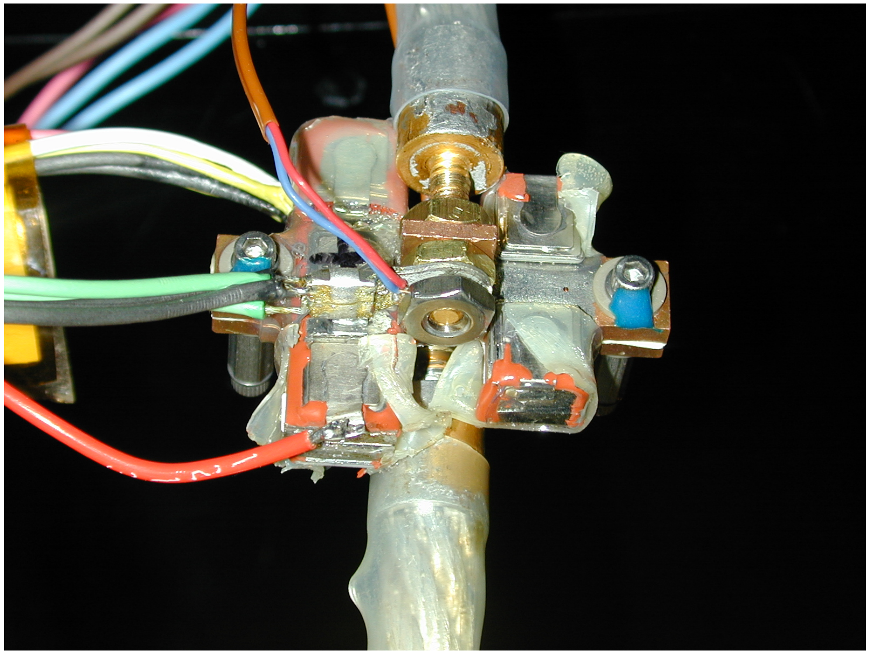

V-Cell
V-Switch
1.355
1.345
1.335
1.325
1.315
1.305
1.295
1.285
Oscilloscope Display
Cell Voltage
Cell Current
2600 A
2400 A
1800 A
1200 A
600 A
0 A
Cell current (35mS scan)
900
800
700
600
500
400
300
200
100
0
Cell current (1000mS scan)
- Hi and Lo legs
400
300
200
100
0
Switch(+) temp
Switch(-) temp
Cell temps
300
250
200
150
100
50
0
0
500
1000
1500
2000
2500
3000
3500
4000
ELAPSED TIME (SECONDS)

Test #2 thru 5 setup (switch activated through diodes)

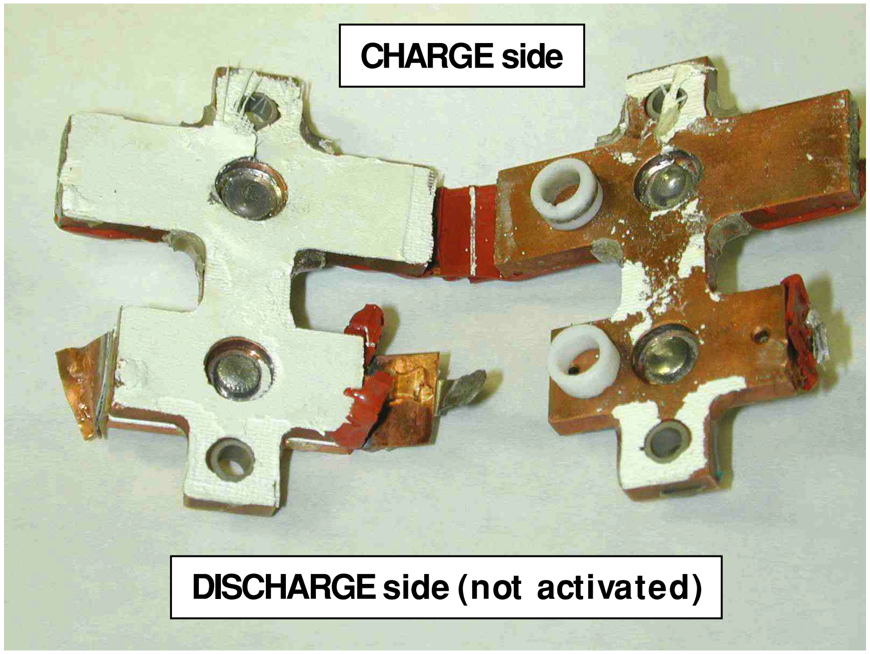


*increased by 50mΩ for Test #5

Test #2

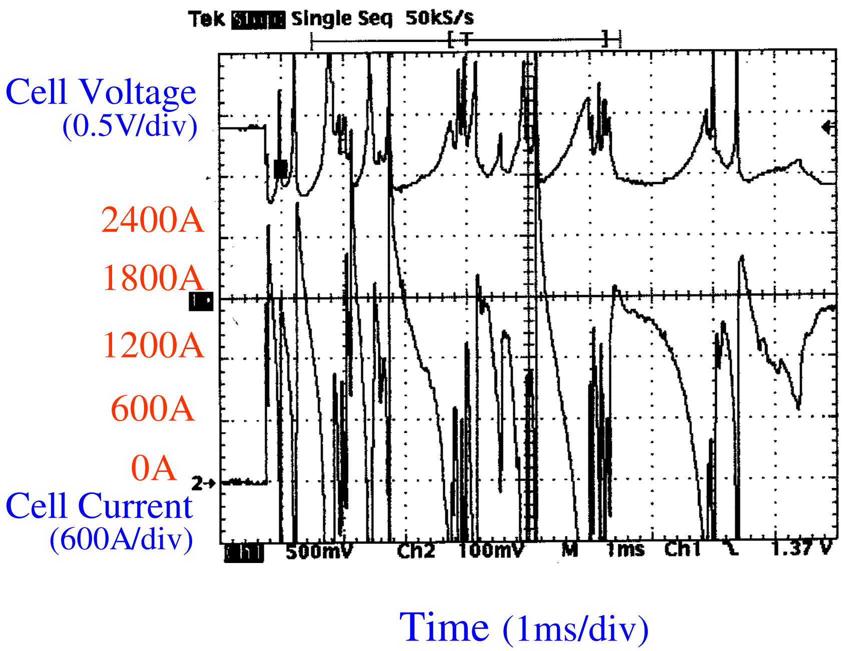


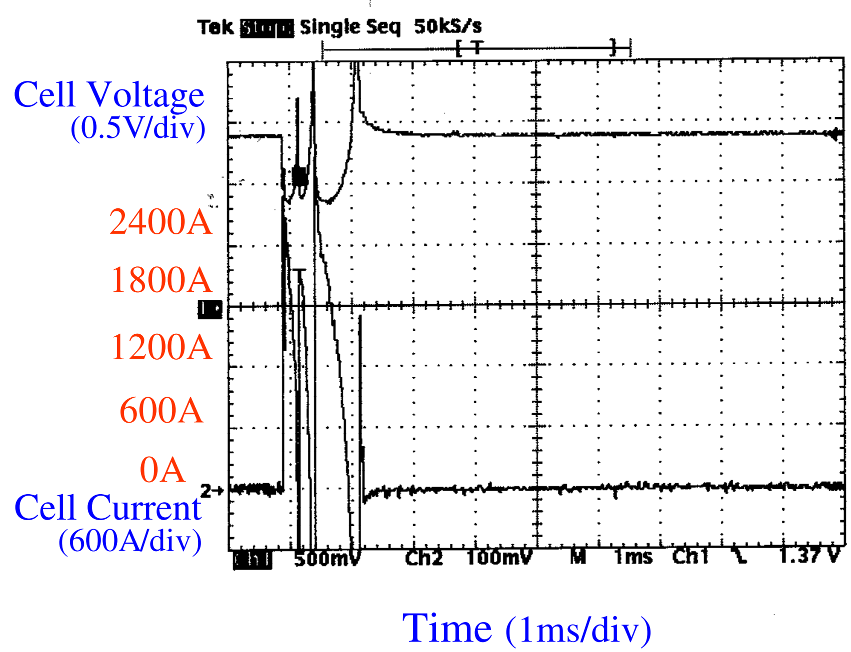
Engineering Model CBPD
after test



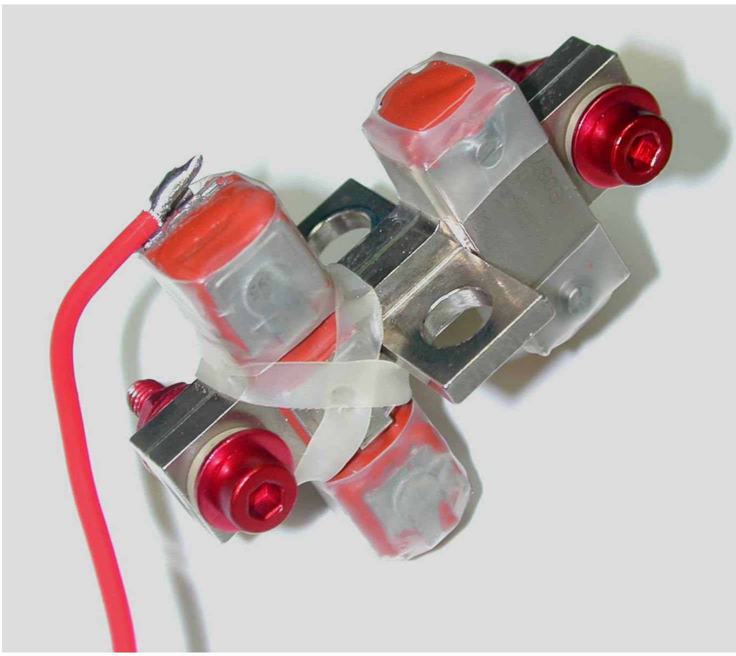
CBPD opened after test.

Test #2 & 3 Scope Traces

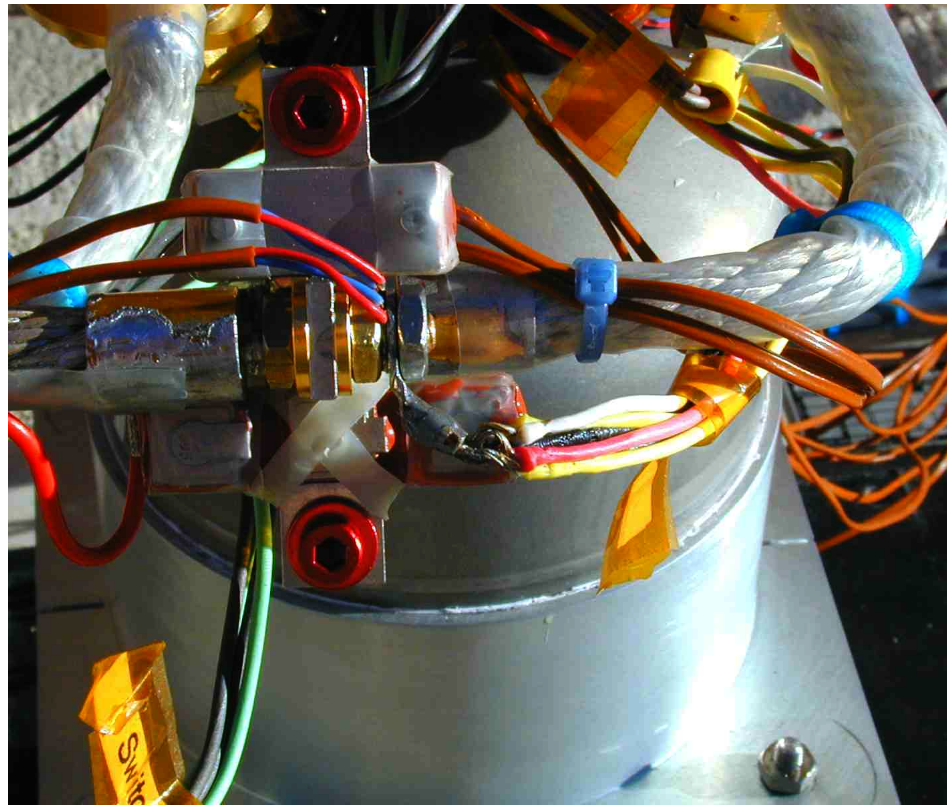




Test #4

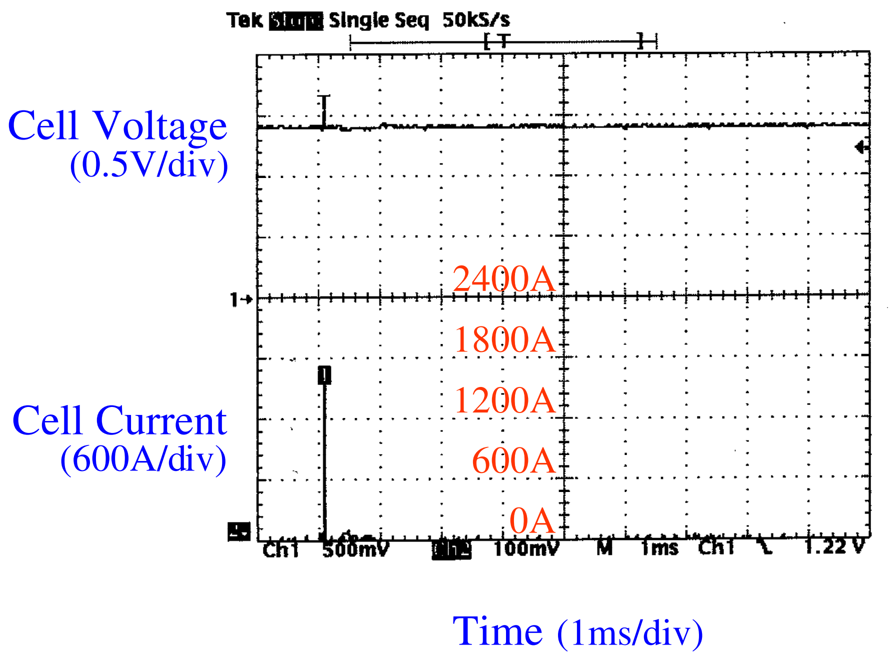


Charge diode string connection

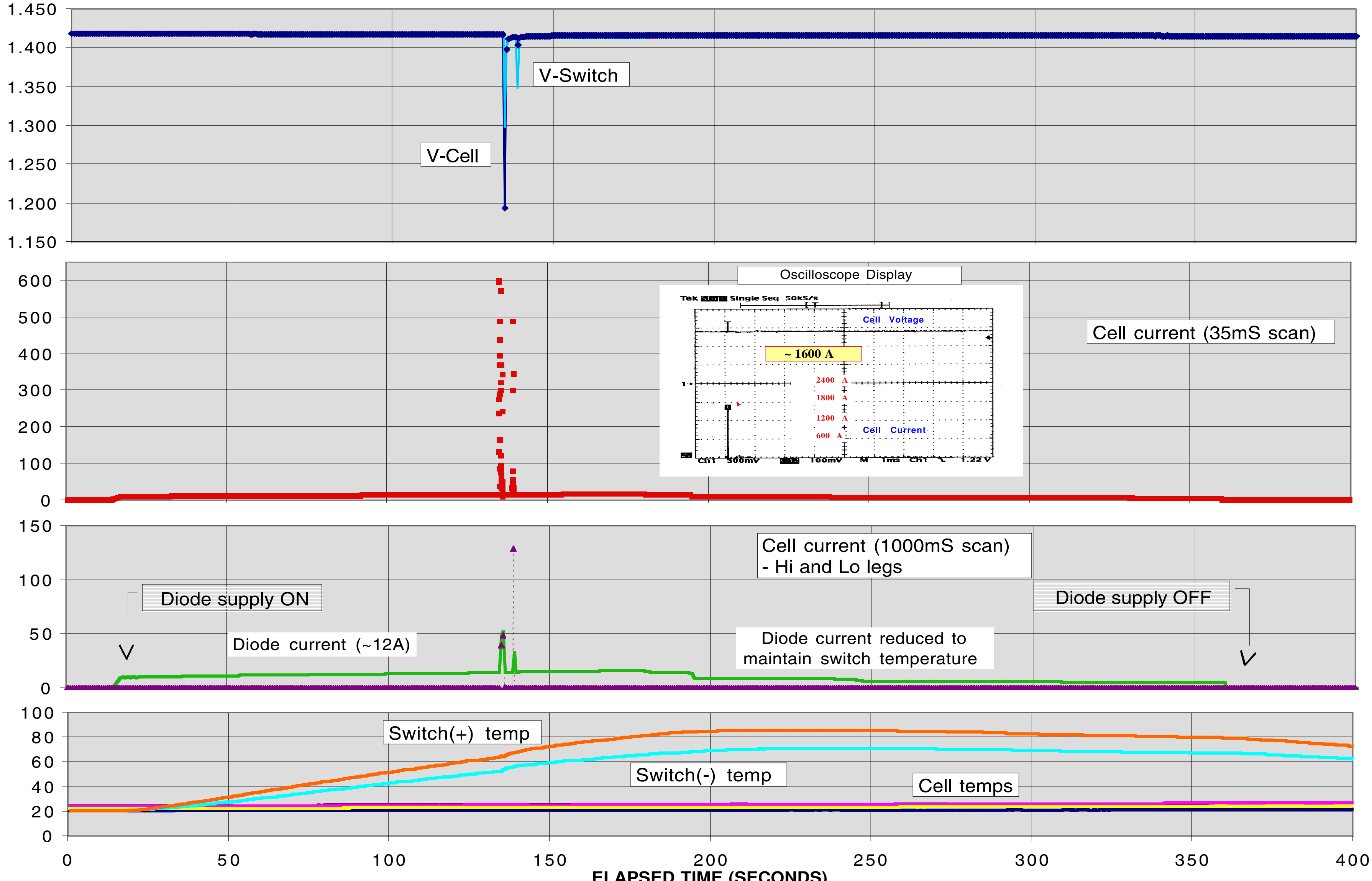


CBPD in launch orientation.

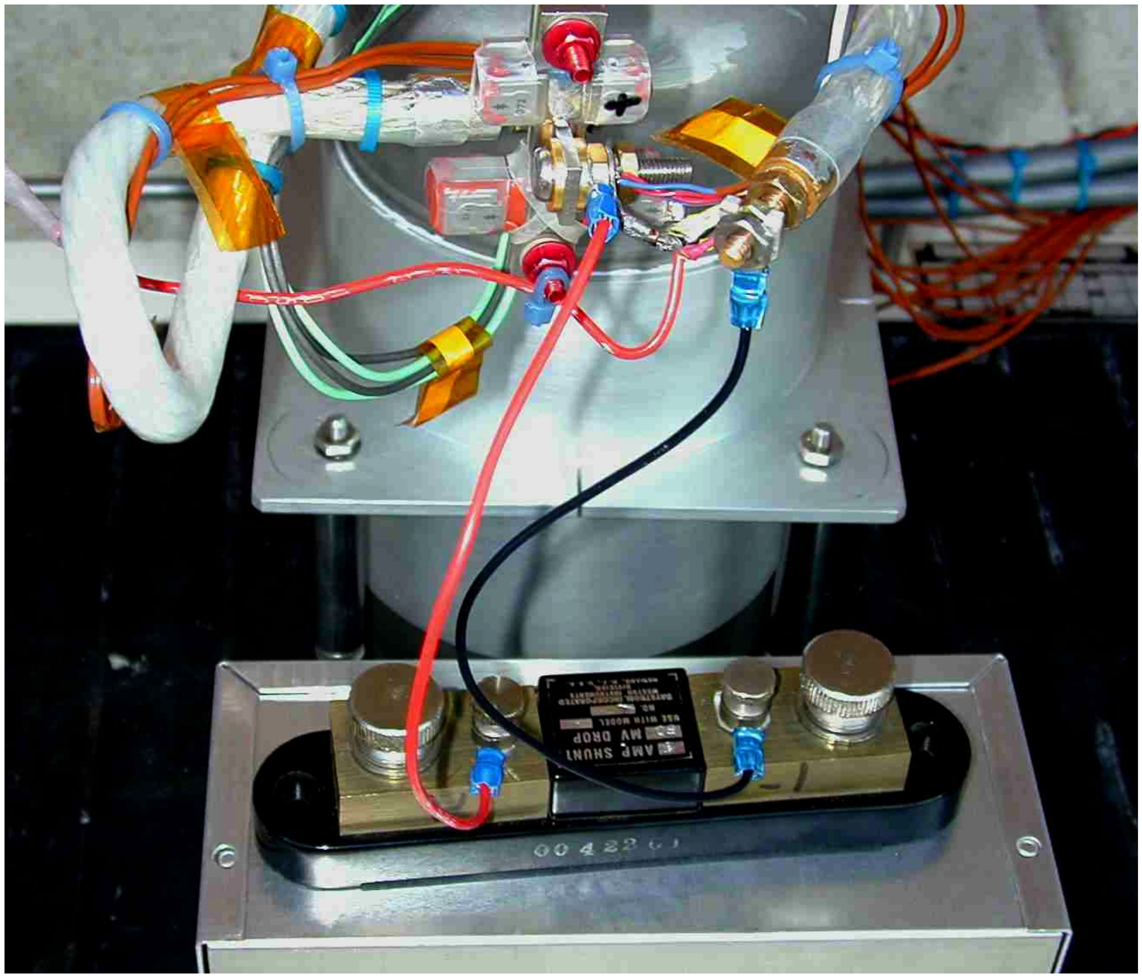
Test #4 Scope Trace



Test #4 Data

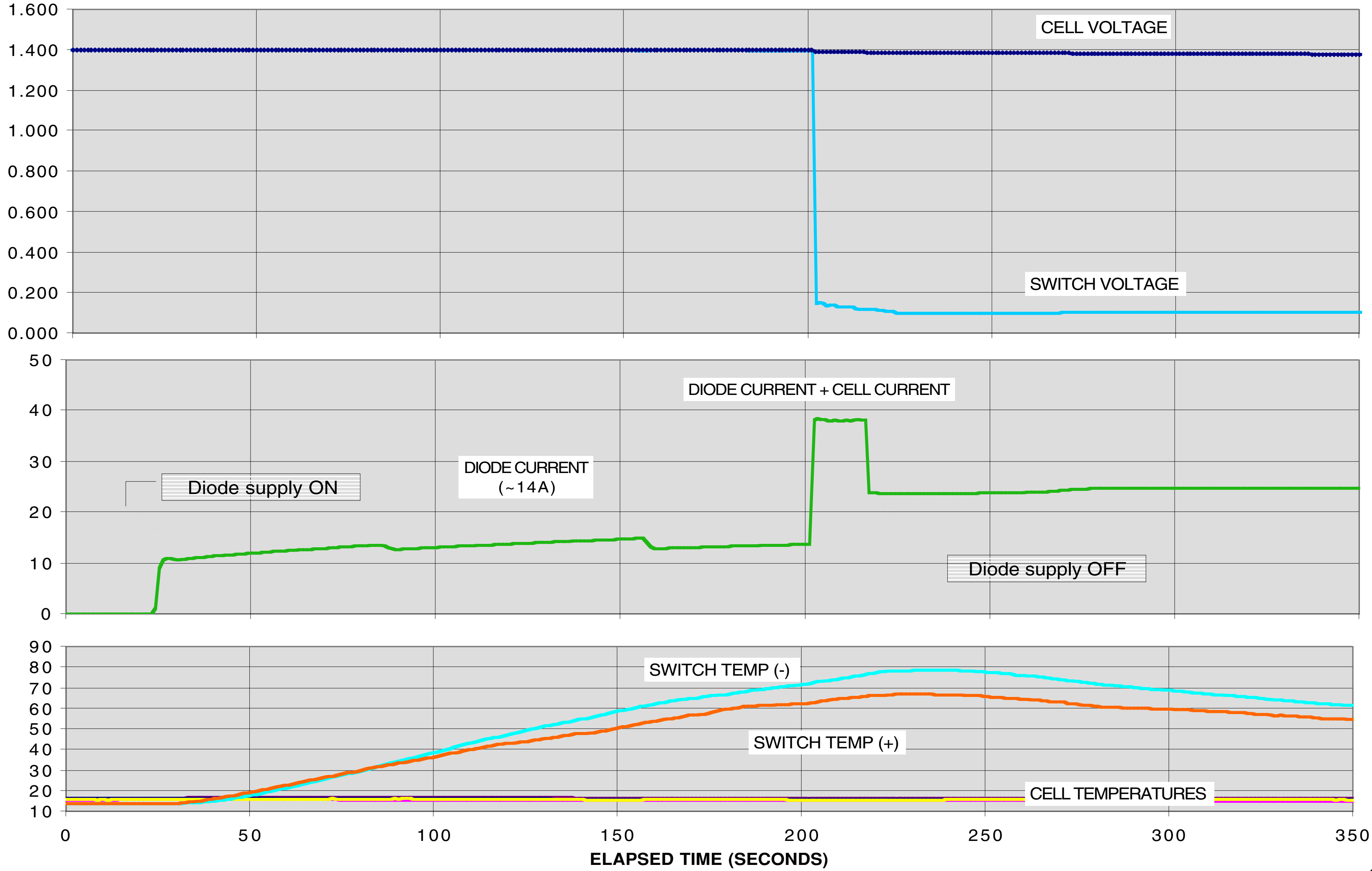

V-Switch
V-Cell
Oscilloscope Display
Cell Voltage
~ 1600 A
2400 A
1800 A
1200 A
600 A
Cell Current
Cell current (35mS scan)
Cell current (1000mS scan)
- Hi and Lo legs
Diode supply ON
Diode current (~12A)
Diode current reduced to
maintain switch temperature
Diode supply OFF
Switch(+) temp
Switch(-) temp
Cell temps
ELAPSED TIME (SECONDS)

Test #5

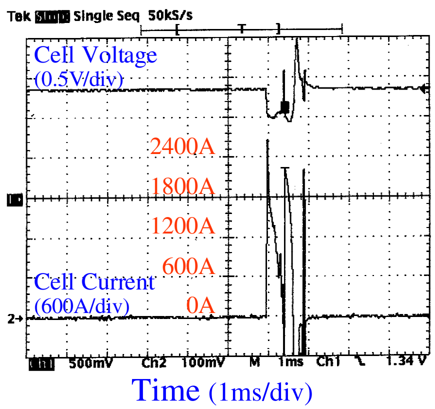


50 mΩ resistance added to positive current path

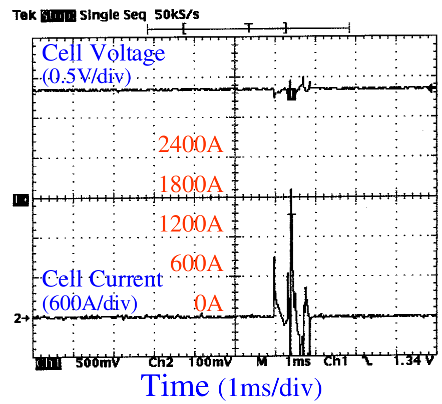
Test #5 Data (with added 50mΩ)



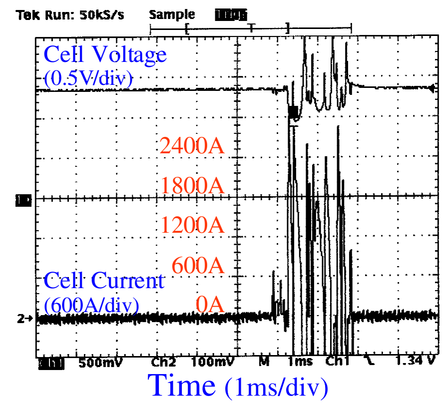
Scope traces for Tests #1 thru 4



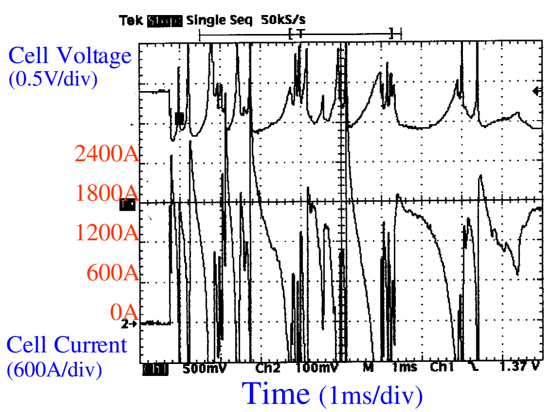
Test #1 (F01)



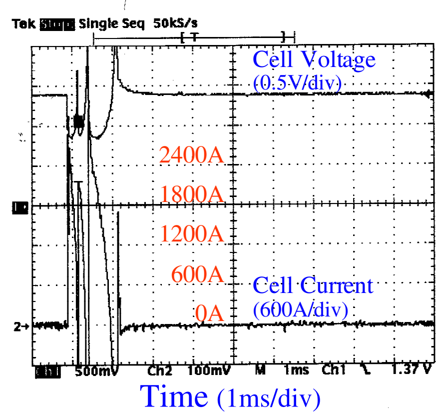
Test #1 (F01)



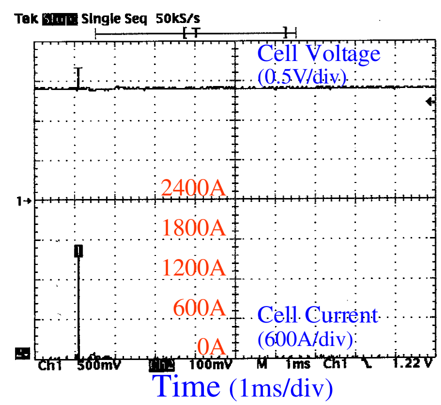
Test #1 (F01)



Test #2 (EM01)



Test #3 (EM02)



Test #4 (F02)

Test Summary

Test #	CBPD #	Result
1	F01	- Seven distinct current bursts were recorded - Switch failed to provide continuous short even after heating to near 300°C - It is expected that both charge and discharge switches were activated by the high temperature
2	EM01	- One distinct current burst was recorded - Switch failed to provide continuous short
3	EM02	- One distinct current burst was recorded - Switch failed to provide continuous short
4	F02	- One distinct current burst was recorded - Switch temperature was maintained over three minutes past the event, and switch still failed to provide continuous short
5	F03	- With 50 milliohms added to the current path, switch closed as expected, and maintained low impedance after diode current was removed and switch cooled

Conclusions

- The nominal performance of AEA CBPD under simulated EOS-Aqua/Aura flight hardware configuration has been demonstrated.
- There is no evidence of cell rupture or excessive heat production during or after CBPD switch activation under simulated high cell impedance (open-circuit cell failure mode).
- Inadvertent CBPD switch activation with a charged cell (low impedance path) intermittently closes and opens up the switch, therefore the device may or may not provide protection against future open-circuit cell failure.
  Further testing with switches F01 and F02 may provide clarification.
- The formation of a continuous low impedance path (a homogeneous low melting point alloy), has been confirmed - which is the expected mode of operation.

Further Work

- DPA of F03 (the only device to operate and carry continuous current) is in progress to confirm the formation of a stable, low impedance path
- Retest of F01 and F02 using added 50mΩ resistance is planned, with DPAs to follow

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- Mr. R. Stickle, GSFC, Technical Assistance
- Mr. H. Stintz, GSFC, Technical Support
- Mr. A. Teverovsky, GSFC, Technical Support
- Mr. D. Wise, GSFC, Technical Support

2000 NASA Aerospace Battery Workshop

Recent Developments in Silver/Zinc Rechargeable Cell Studies

Harlan L. Lewis
NAVSEA Crane

14-16 November 2000

Recent Developments In Silver/Zinc Rechargeable Cell Studies

- Introduction – History of cellophane and sausage casing model cell studies.
- Objective – Reduce number of layers of separation on cathode while maintaining cell performance.
- Experimental – Five cell sets of thirteen cells each. Eight cycle life and five wet life. Periodic cell removal for design performance analysis.

Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

- **Cell Separation Configurations;**
  - Set 1 – Reference standard set – six layer of 1-mil untreated Flexel clear cellophane provided by Yardney Technical Products (YTP), cathode wrap.
  - Set 2 – Reference standard set – six layers of 1-mil Flexel cellophane silver-treated (C-19) by YTP, cathode wrap.
  - Set 11 – Double layer SC set – one layer of 1-mil tubular SC followed by one layer of 2-mil PVA, followed by two layers of 2.3-mil SC from split SC tubing, cathode wrap.
  - Set 12 – Single layer SC set – one layer of 1-mil tubular SC followed by one layer of 2-mil PVA, followed by one layer of 2.3-mil SC from split SC tubing, cathode wrap. Cells were shimmed with cell case plastic to provide constant internal stack pressure vs. set 1.
  - Set 13 – Split wrap set – three layers of 1-mil Flexel cellophane silver-treated (C-19) by YTP, cathode wrap, plus three layers anode wrap. (The anodes were wrapped in a split L-configuration to seal the bottom of the anodes.)

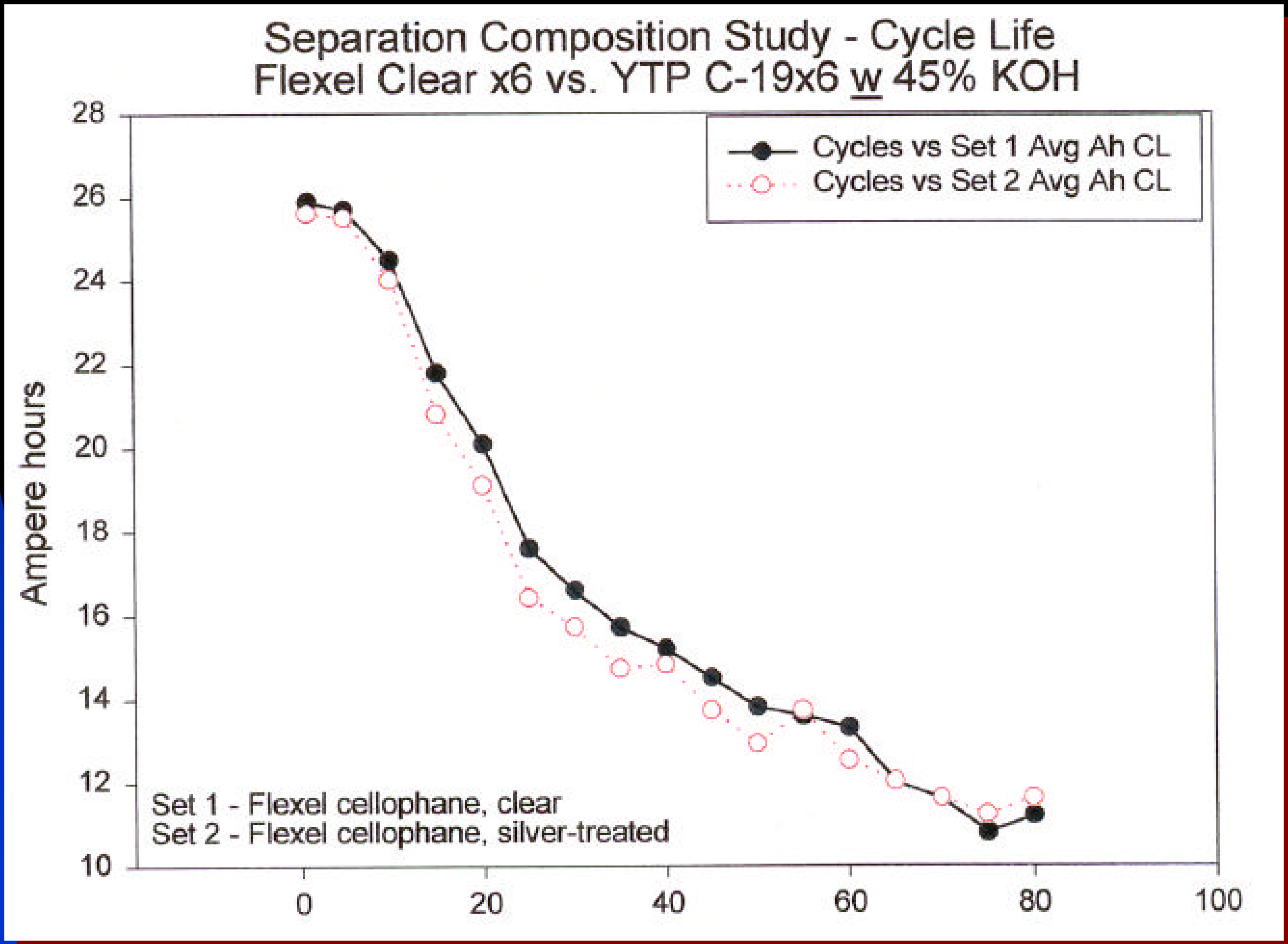
Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

- **Results and Discussion**
  - ✓ Discharge capacity comparisons
  - ✓ Silver migration comparisons

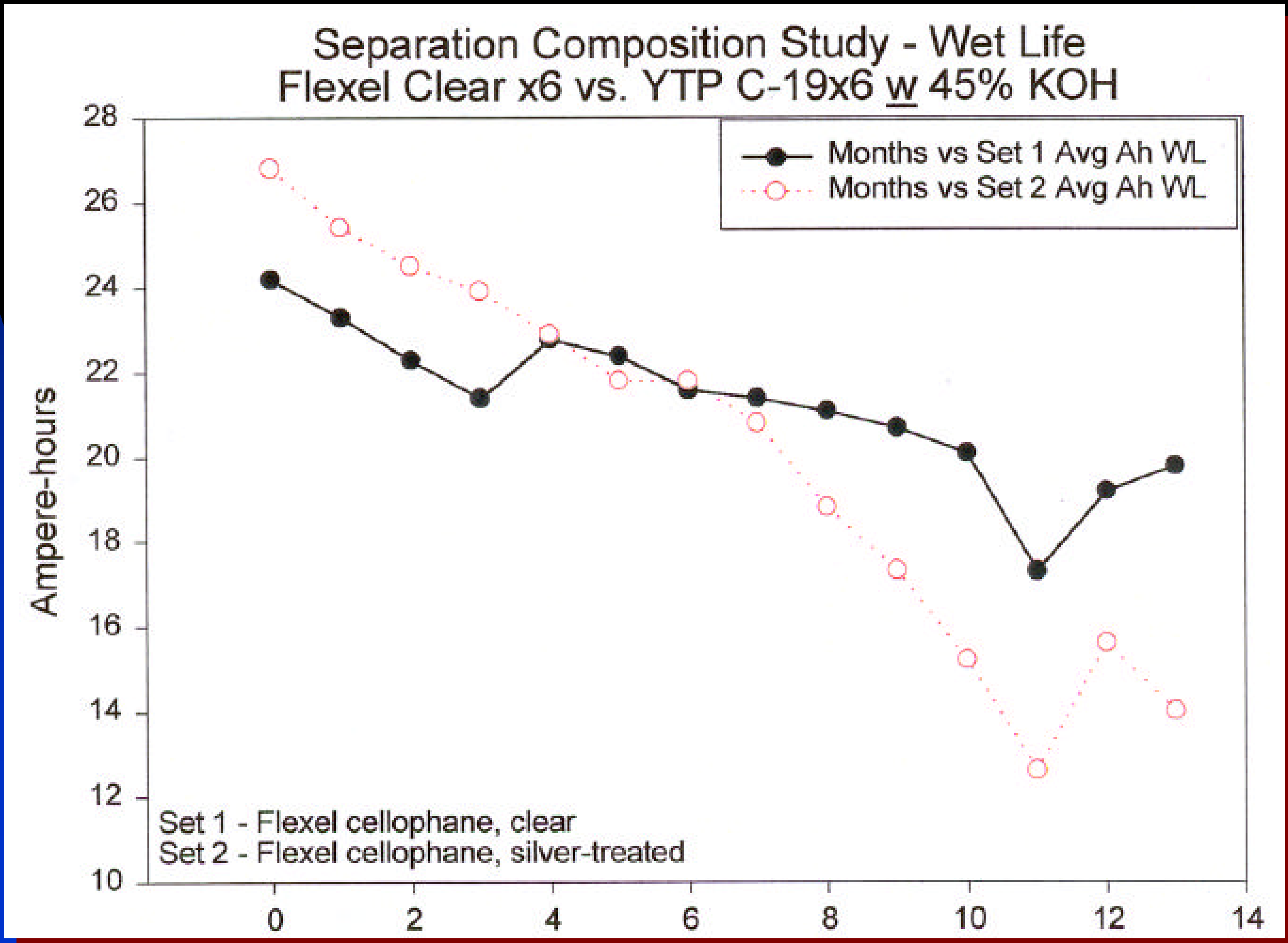
Recent Developments In Silver/Zinc Rechargeable Cell Studies

Cycle life data show approx. equivalent performance.



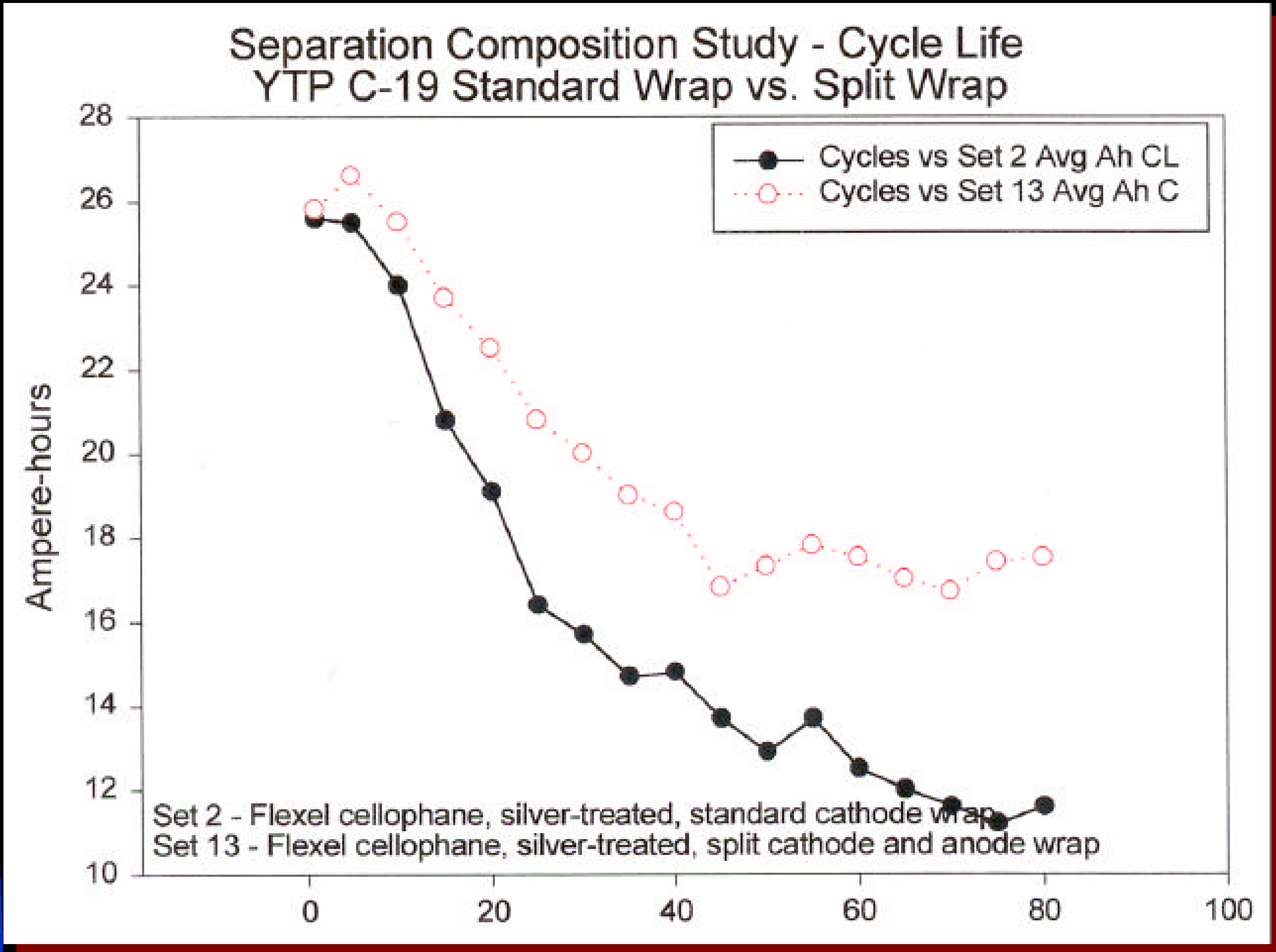
Recent Developments In Silver/Zinc Rechargeable Cell Studies

All but one of the clear Flexel wet life cells shorted out by the tenth month, while none of the C19 cells shorted, so comparison is flawed.



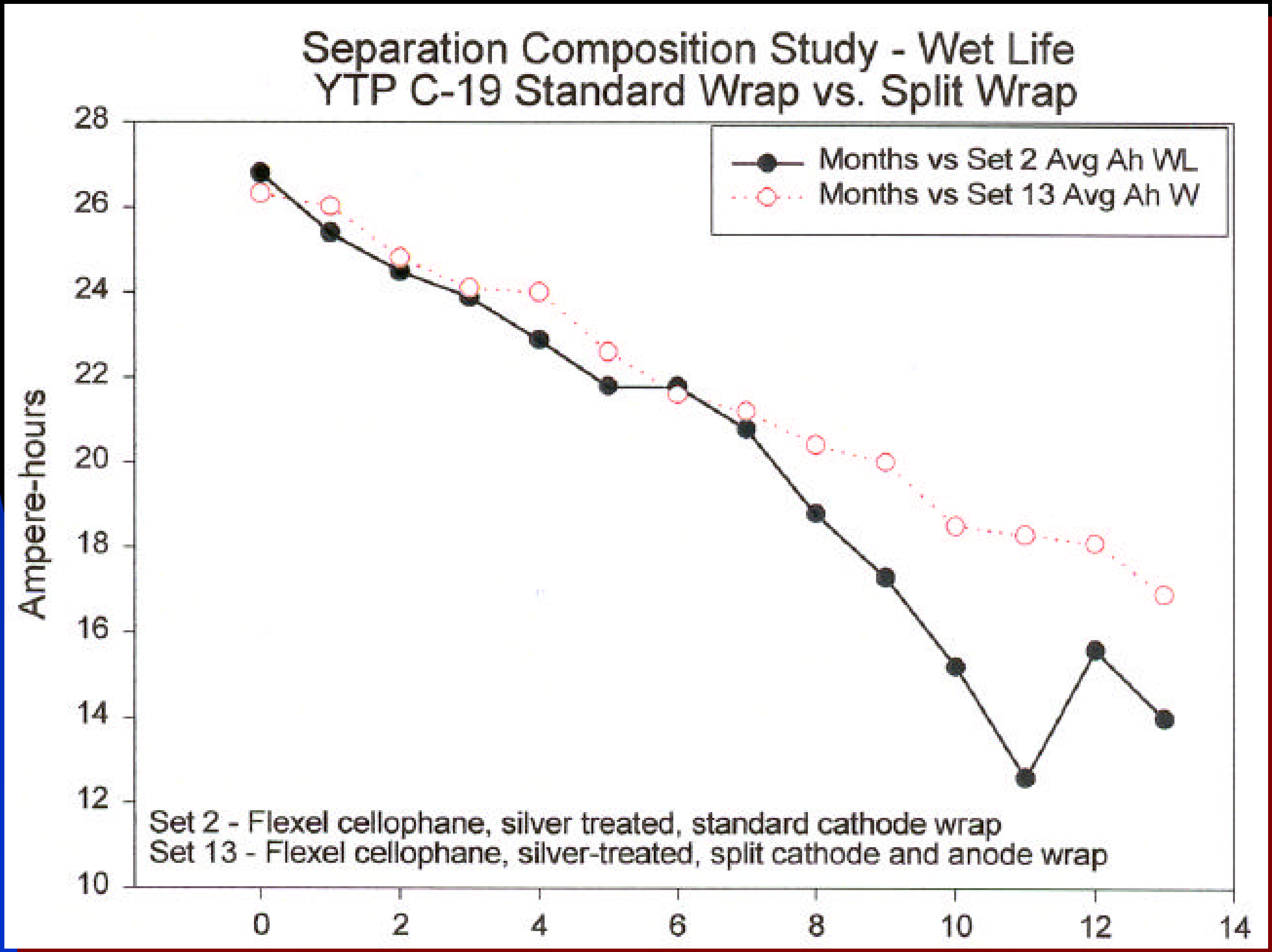
Recent Developments In Silver/Zinc Rechargeable Cell Studies

Cycle life data show a significant performance advantage for split wrap.



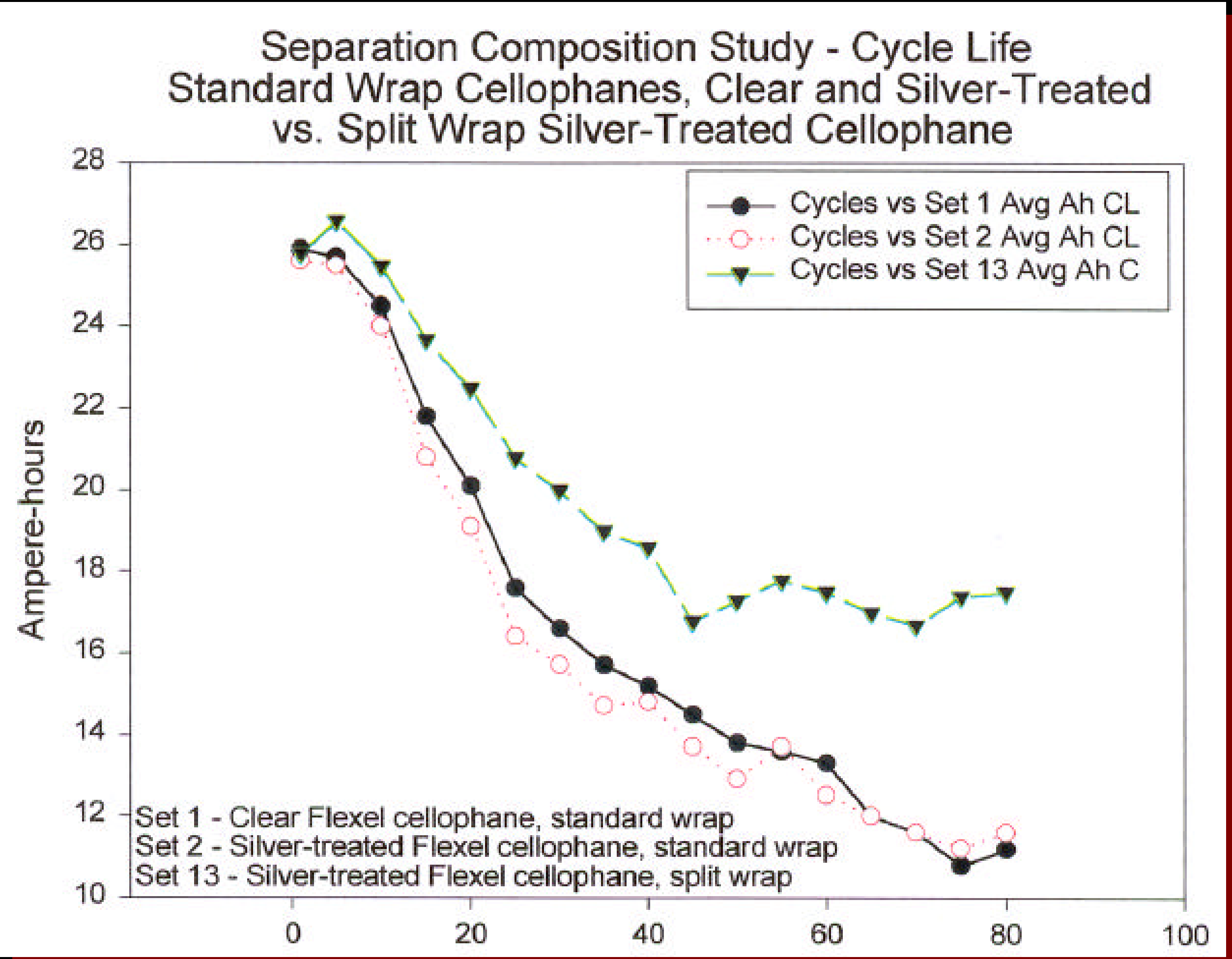
Recent Developments In Silver/Zinc Rechargeable Cell Studies

Wet life data also show a significant capacity advantage for split wrap.



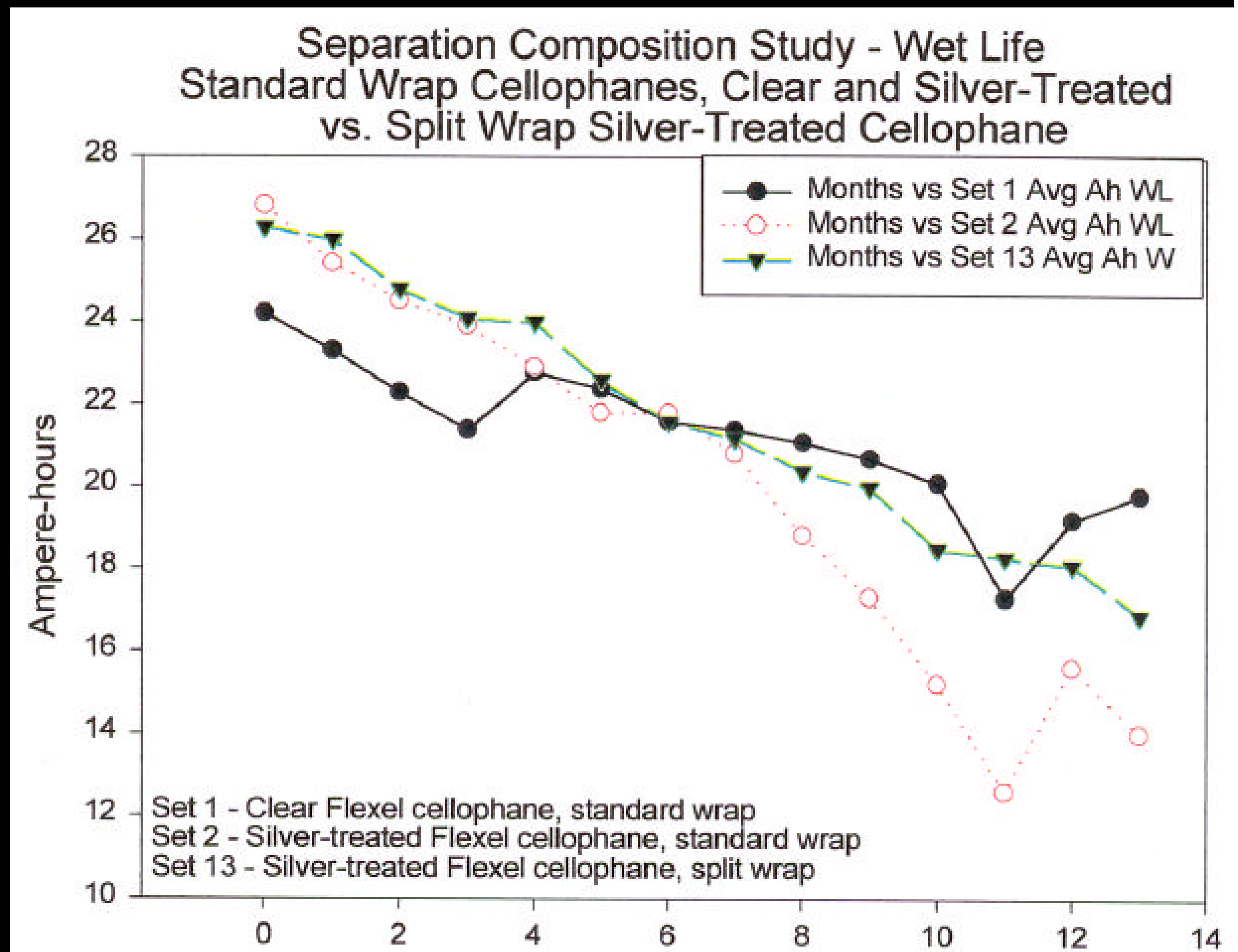
Recent Developments In Silver/Zinc Rechargeable Cell Studies

Combined plots for split wrap vs. both standard wraps in cycle life. The split wrap performance is clearly superior.



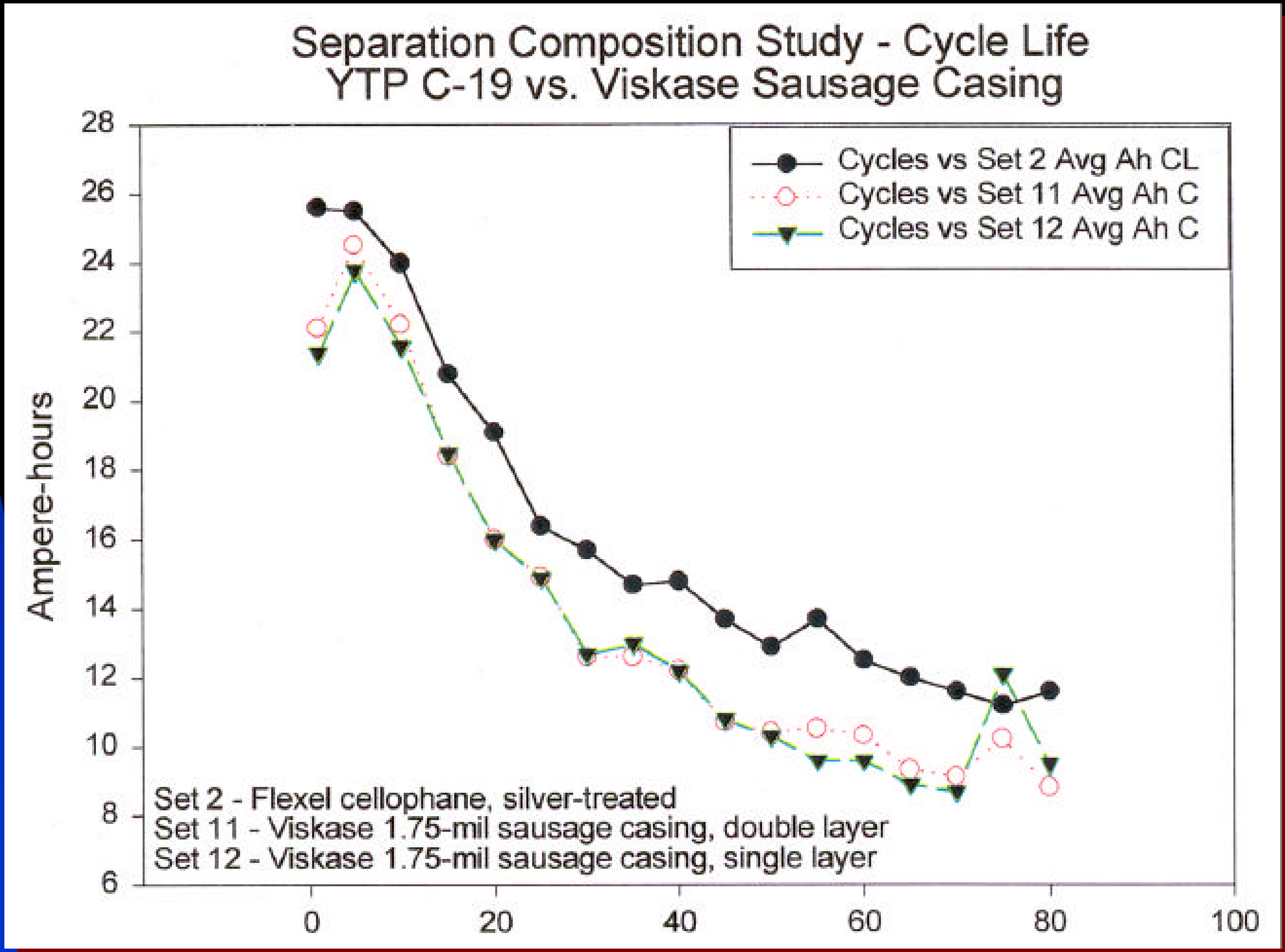
Recent Developments In Silver/Zinc Rechargeable Cell Studies

The Set 1 cells shorted out beginning at the 6th month, while no cells in Sets 2 and 13 shorted at all, so the discharge capacity averages do not reflect the actual performance adequately. Sets 2 and 13 were actually superior to Set 1, overall.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

Cycle life data for the two SC configurations exhibit slightly lowered capacity vs. C19, but no shorts occurred in any Set.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

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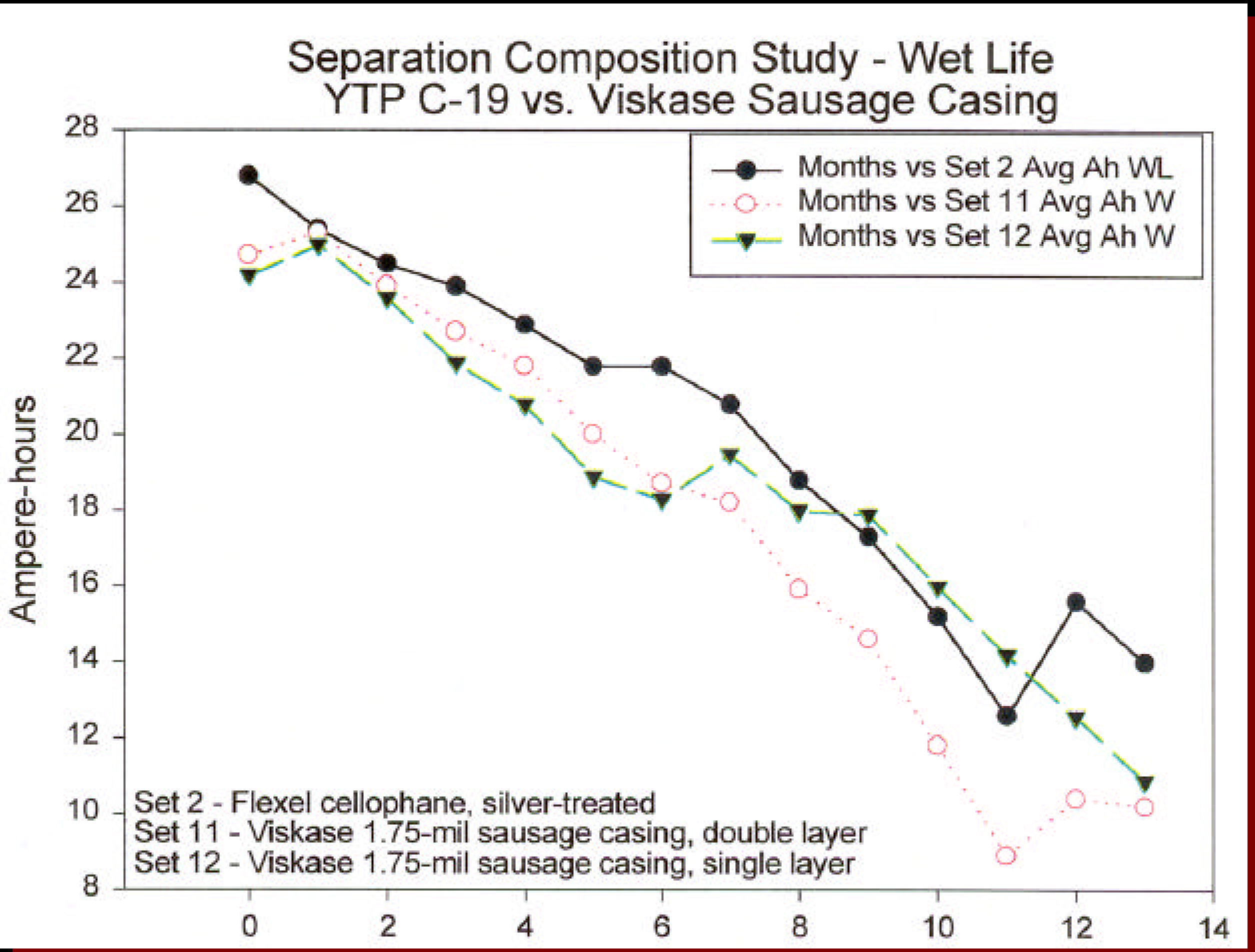
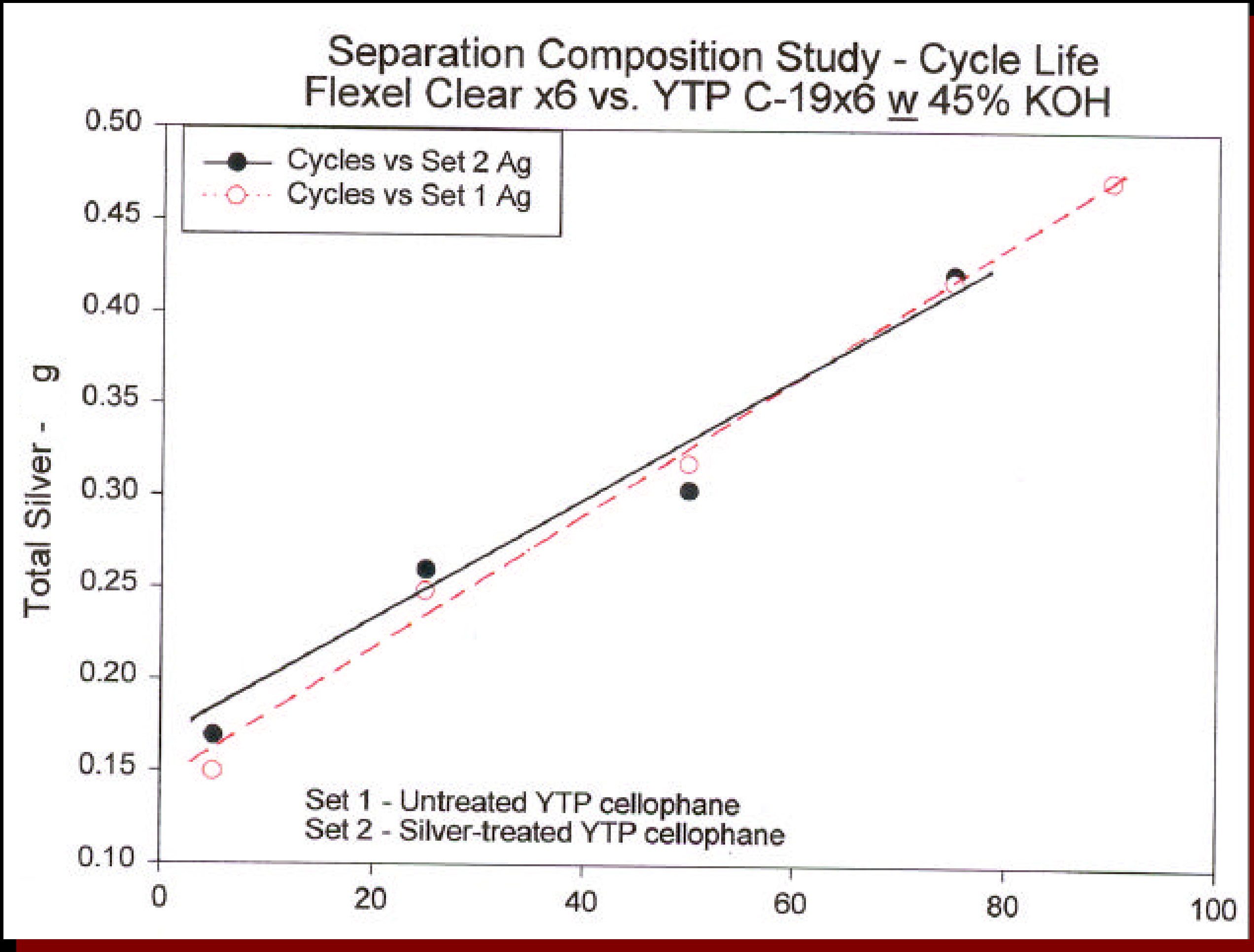
Wet life data indicate that single layer SC performed as well as C19 in late life.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

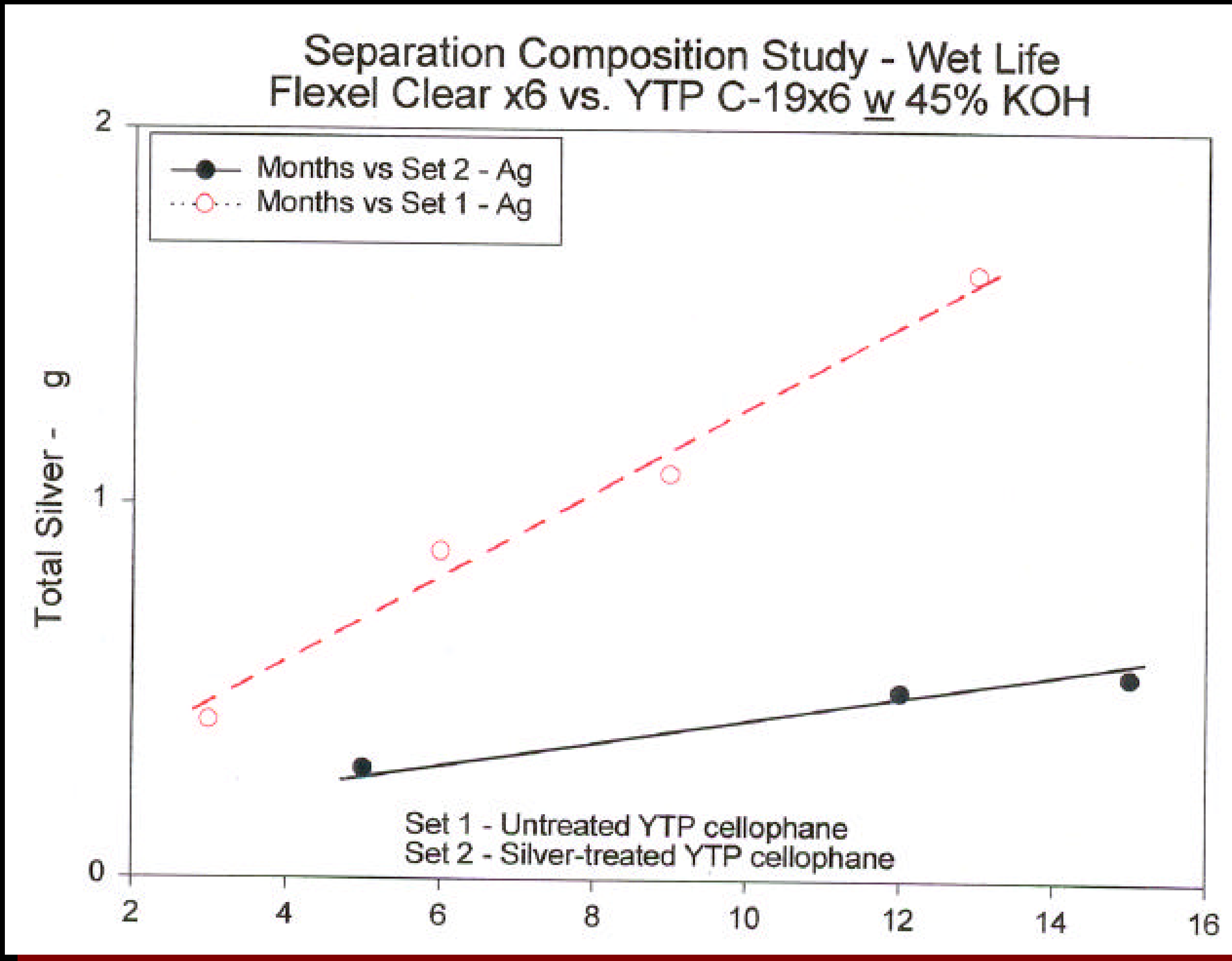
Silver migration in cycle life cells was identical for clear vs. silver-treated cellophane.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

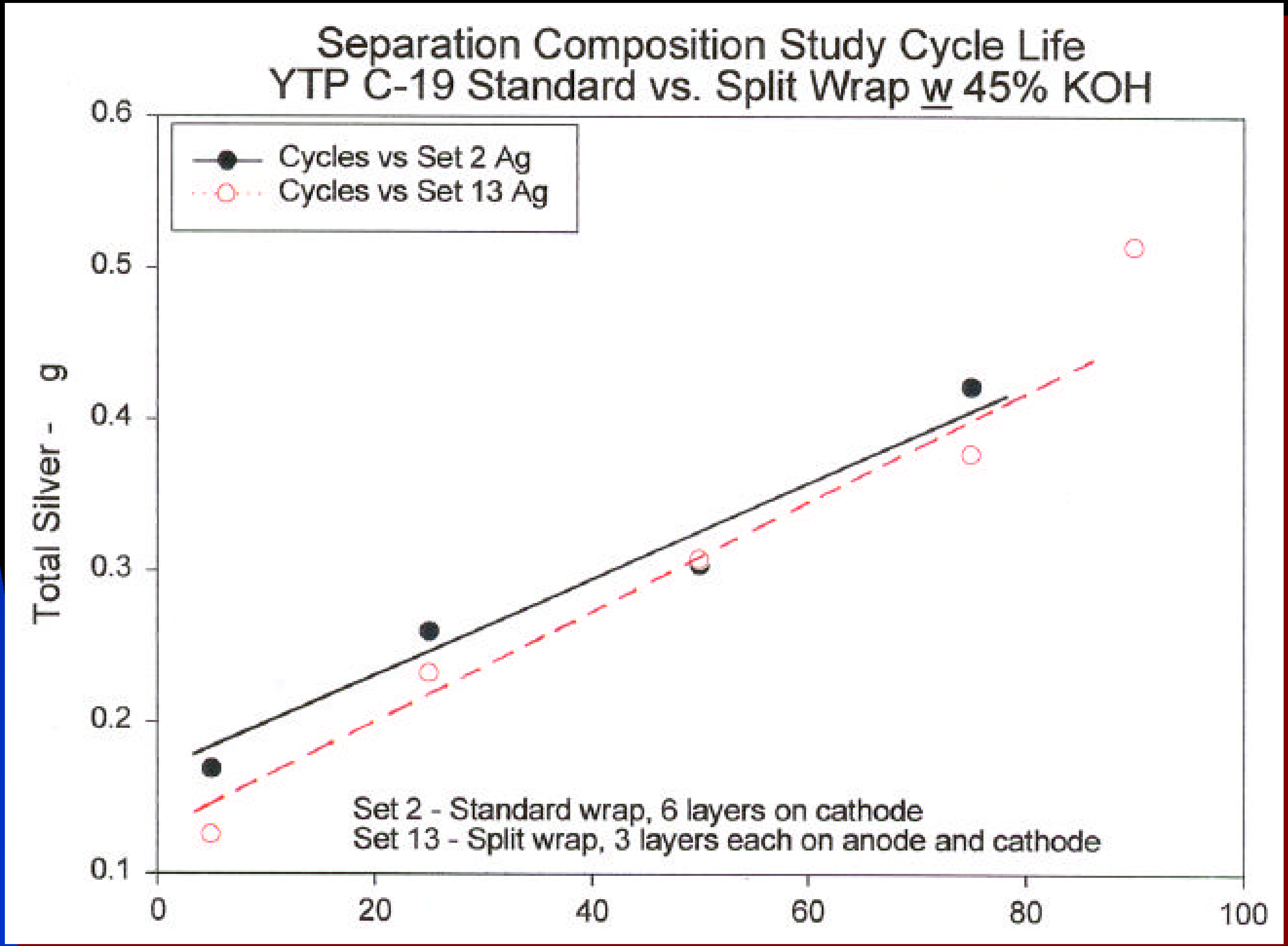
Silver migration in wet life cells occurred at a much lower rate for C19 cells.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

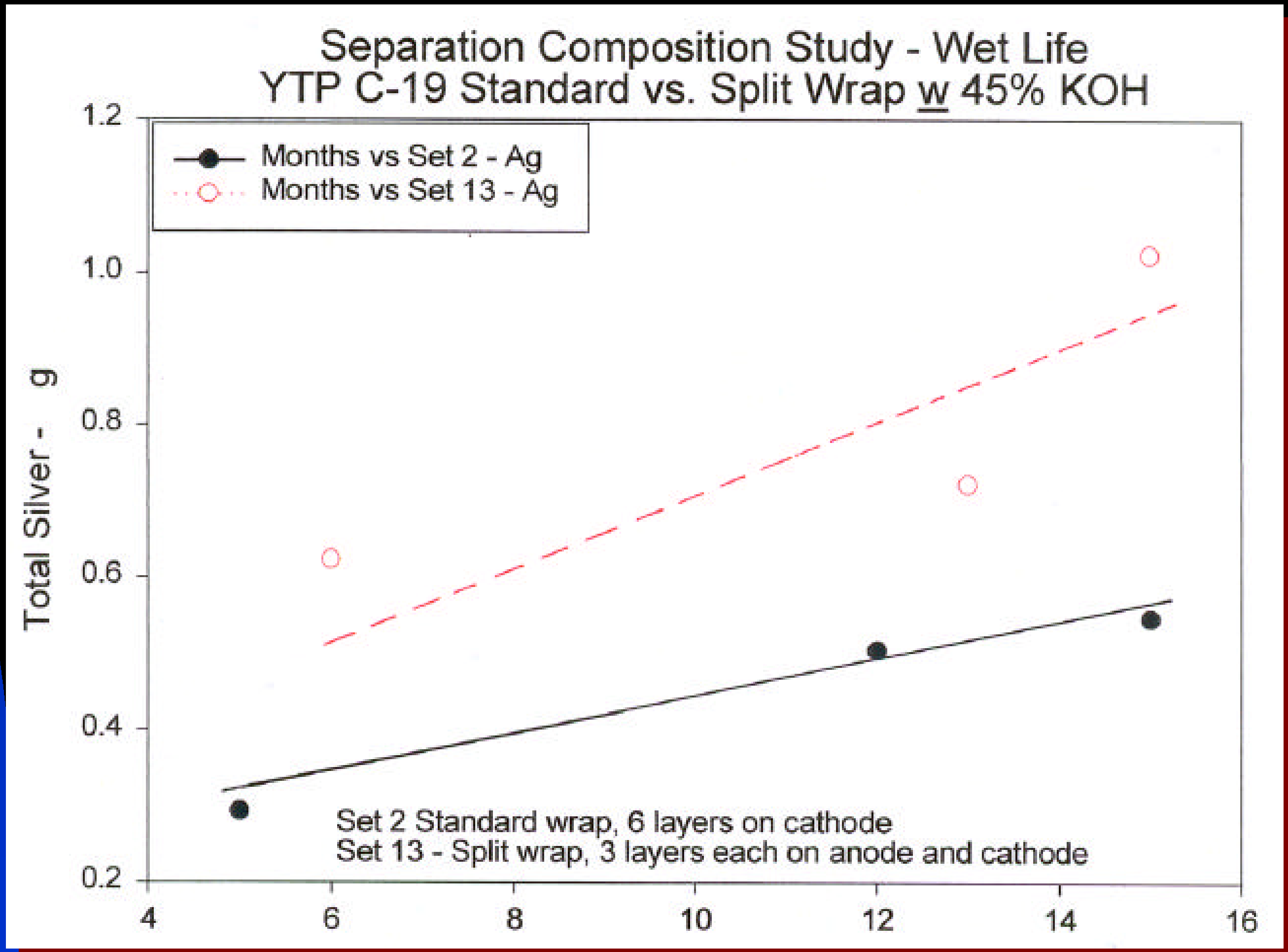
Silver migration for split wrap similar to standard wrap in cycle life.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

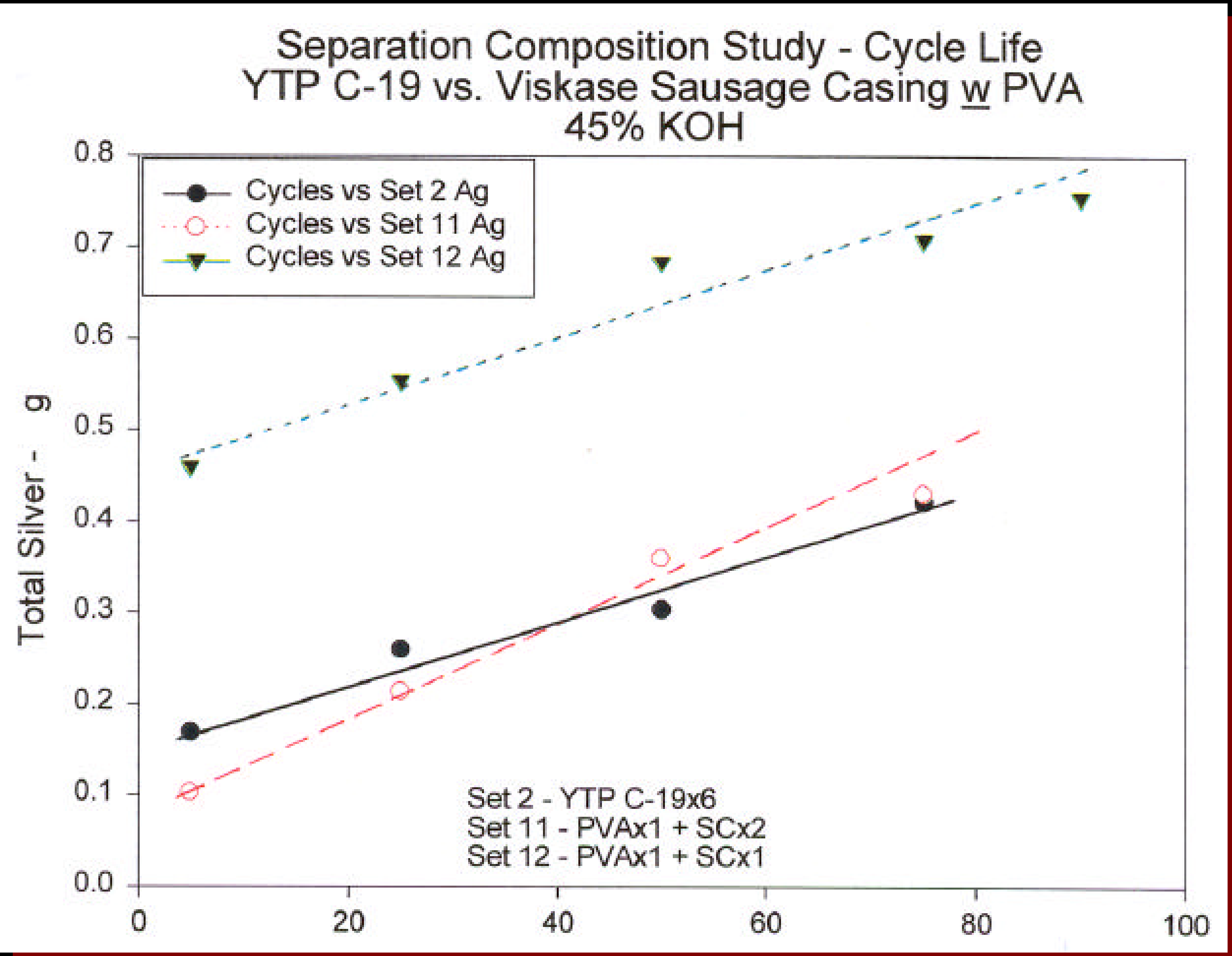
NAVSEA CRANE

Silver migration in split wrap cells occurred at a much greater rate than for standard wrap cells in wet life.



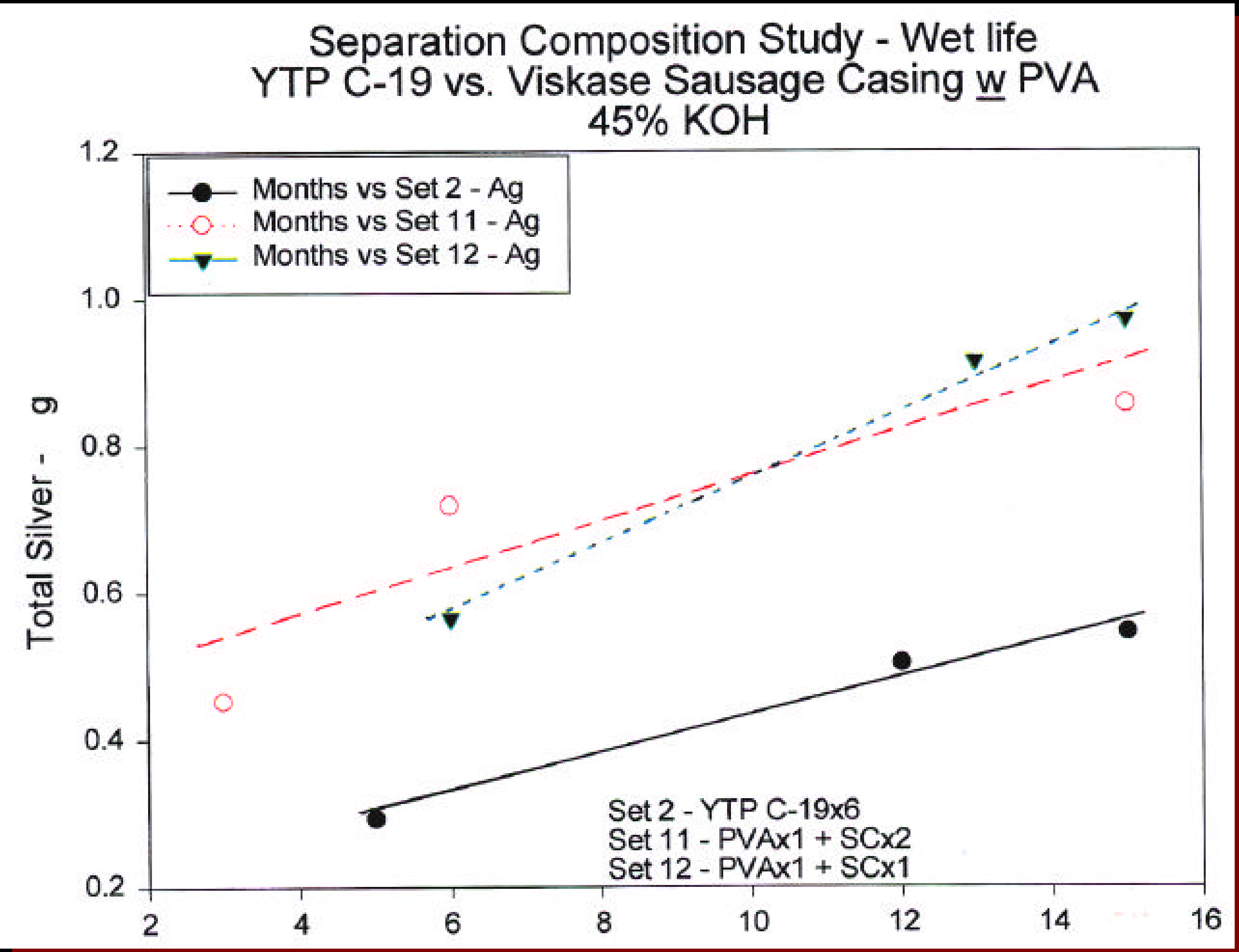
Recent Developments In Silver/Zinc Rechargeable Cell Studies

Although it appears that the single SC layer cells have a much higher silver migration rate than C19, layer-by-layer data show that all the silver in both SC sets was trapped at the PVA layer.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

As in the cycle life data, here also the layer-by- layer data show that all the silver in the SC cells was stopped by the PVA film.



Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

- **Conclusions**
  - Clear vs. Silver-Treated Cellophane
  - Split wrap vs. "Standard" Wrap
  - Cellophane vs. Sausage Casing

Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

- **Recommendations**
  - ✓ Use silver-treated cellophane instead of clear cellophane
  - ✓ Use split wrap for cellophane whenever possible
  - ✓ Strongly consider use of sausage casing with PVA film in the following configuration:

    1-mil (tubular) SC/1-mil PVA film/2.3-mil plain or 6-mil fiber-reinforced SC tubular

Recent Developments In Silver/Zinc Rechargeable Cell Studies

NAVSEA CRANE

- Acknowledgements
  - Cellophane film samples were purchased from Yardney Technical Products
  - Sausage Casing samples were furnished by Viskase Corporation
  - Funding support came from NAVSEA 03Z, SPECWARCOM, and Viskase Corporation

MOLTECH
CORPORATION

Advances in Lithium-Sulfur Rechargeable Batteries

Powering the Electronic Future

MOLTECH
CORPORATION

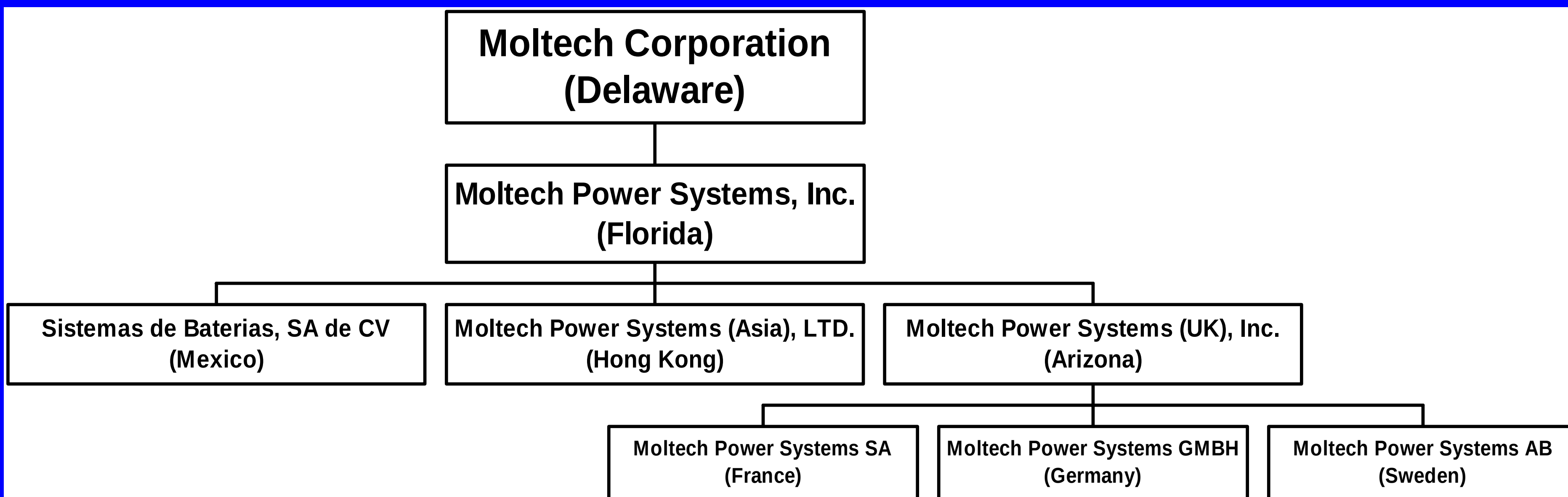
Corporate Overview

Moltech' s Mission

- To be the leader in Energy Storage Products

Moltech Corporate Offices, Tucson, Arizona

Corporate Structure



Moltech Corporation History

1988 Founded by Dr. Terje Skotheim as a spin-off from the Brookhaven National Laboratory

1994 First venture capital funding

1995 Signed development agreements with Ericsson, Atlas-Copco and Electrolux

1998-99 Development of Lithium Sulfur (Li-S^{TM}) sample cells

Moltech Power Systems History

1962	General Electric begins NiCd business in Gainesville, FL
1987	Gates Rubber acquires GE rechargeable business
1993	Eveready acquires Gates Nickel rechargeable business
Apr 99	Eveready decides to sell Energizer Power Systems (EPS)
Nov 99	Moltech acquires Energizer Power Systems and Energizer acquires equity in Moltech

Moltech Operating Structure

Gainesville, Florida
Corporate Headquarters
North & South American Marketing & Sales
NiCd / NiMH / Li-S Cell Manufacturing
NiCd / NiMH R & D
Intelligent Electronics
Development
Employees 675

Tucson, Arizona
Lithium Sulfur R & D
Employees 60

Newcastle**-Under-Lyme, UK**
European Marketing & Sales
Battery Design and Assembly
Employees 70

Juarez, Mexico
Battery Design & Assembly
NiCd / NiMH Cell Formation and Test
Employees 1400

Hong Kong
Asian Marketing & Sales
Battery Design & Assembly
Employees 70

Product Attributes

Rechargeable Li-S Cells

- *2 x Specific Energy vs Li-Ion*
- Lightweight (lithium & sulfur)
- Rate capability exceeds Li-Ion
- Environmentally benign
- Low Material Costs

Technology can be applied to:

- *Primary Batteries*
- *Supercapacitors*

Li-S Adapted Products

Mobile Phones

2.0 – 2.5 Amps

Laptop Computers

3.5 – 6.0 Amps

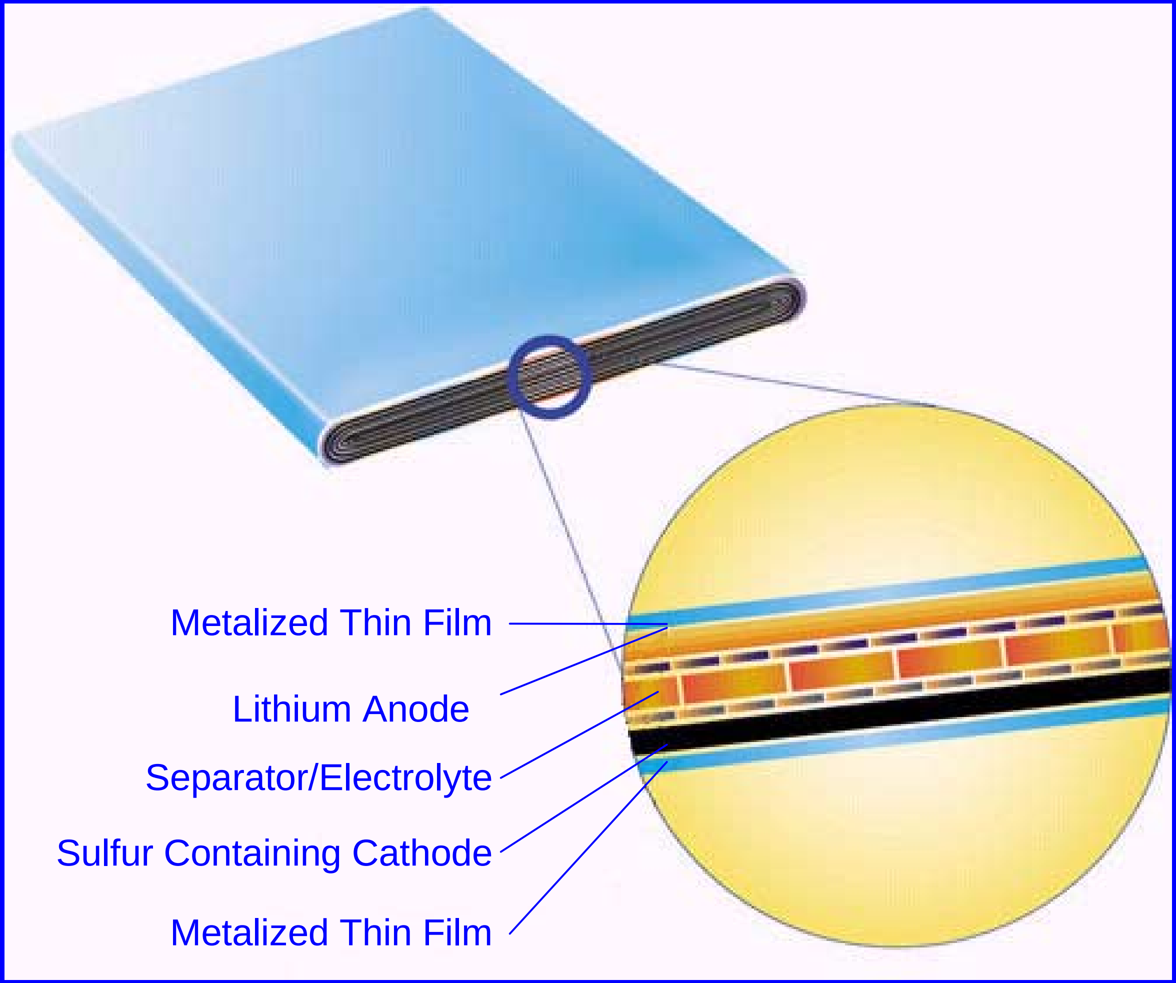
Cordless Grass Trimmer

14 Amps

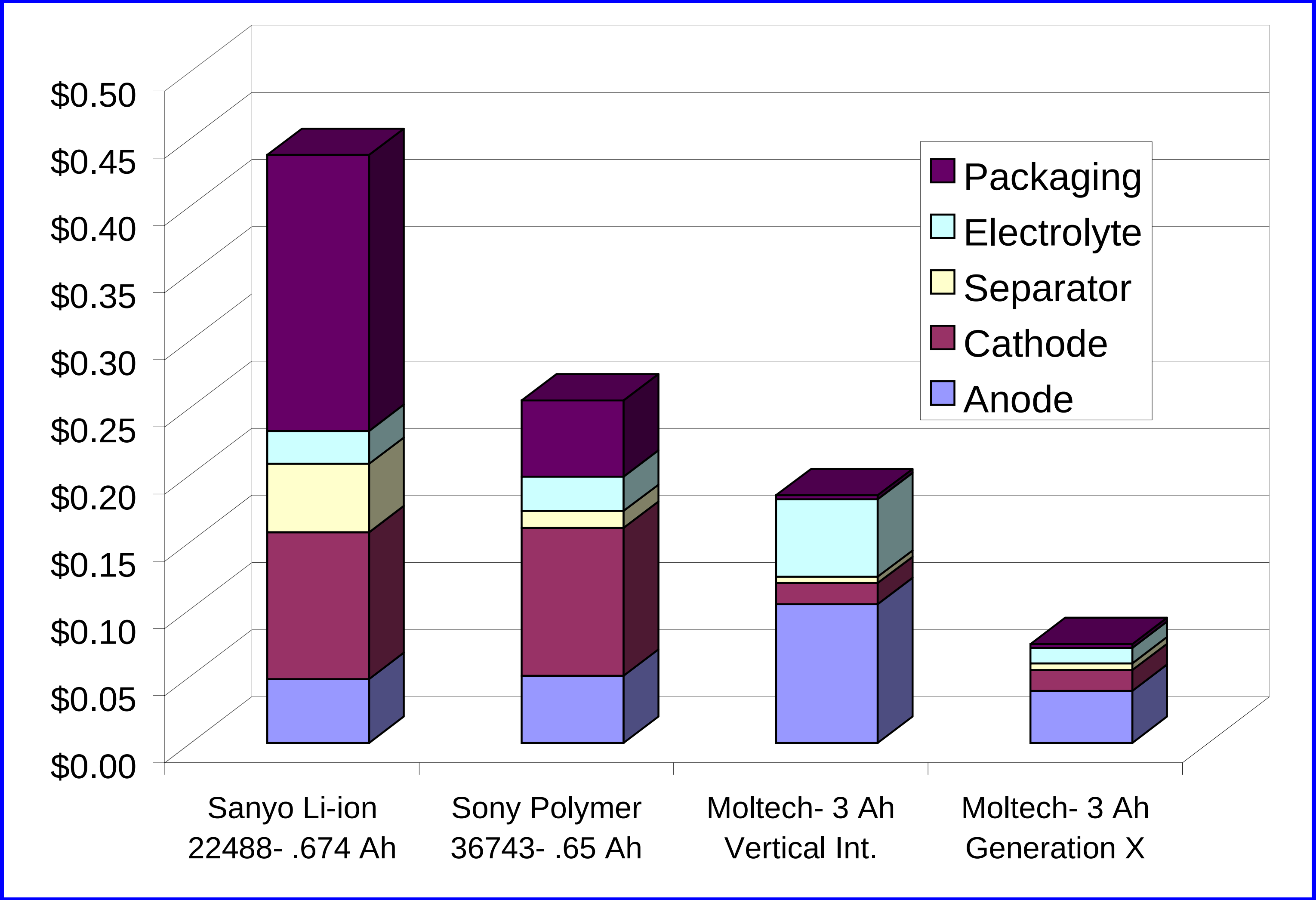
Cordless Drill

20 – 30 Amps

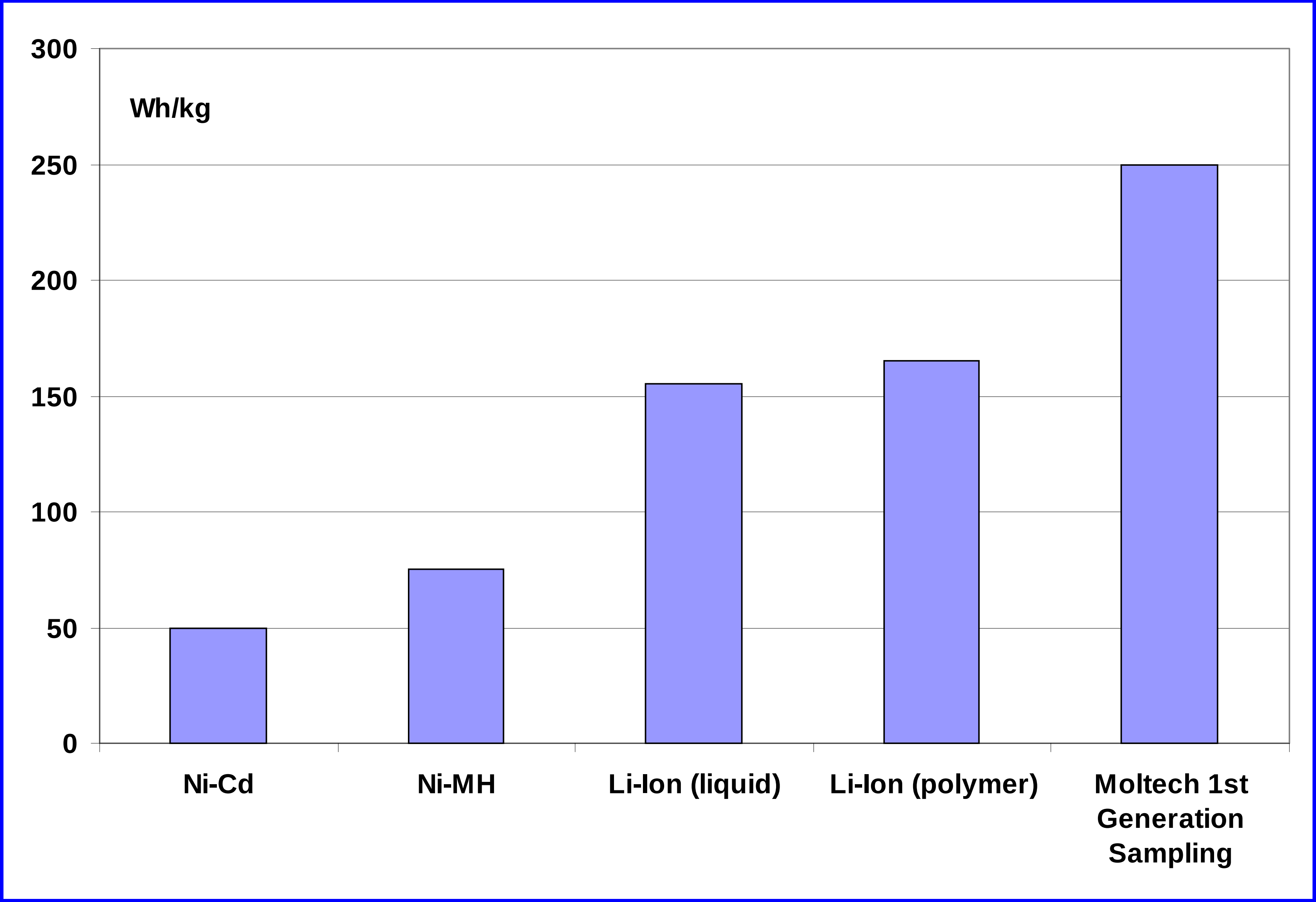
Cell Construction



Low Manufacturing Costs



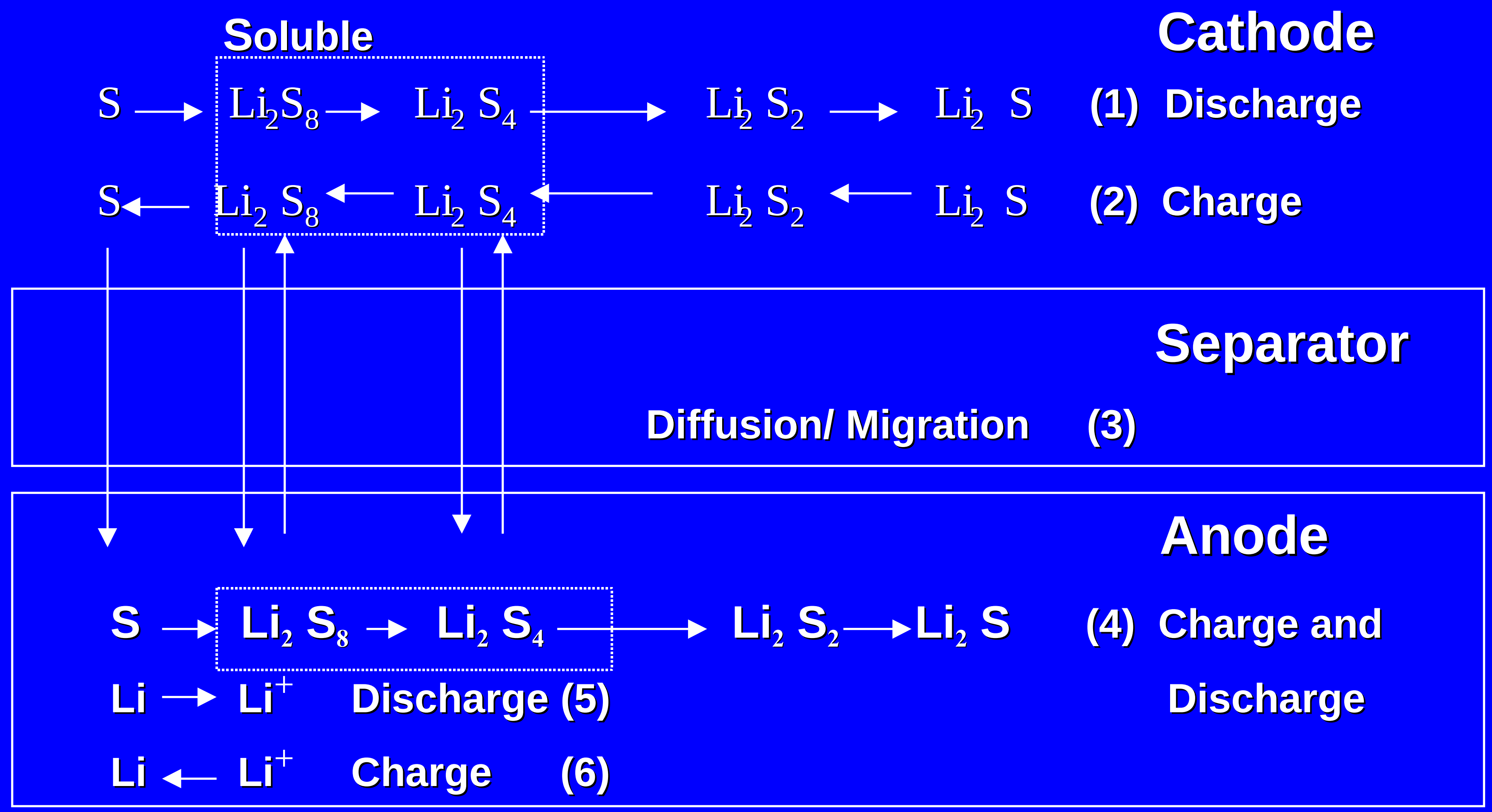
Specific Energy Comparisons



Product Requirements for Second Generation Li-S

- Cycle life to reach 300 at 80% of rated capacity
- Specific energy to 300 WH/Kg
- Volumetric energy to 400 WH/L
- Self-discharge <5%/month
- 70% of ambient capacity @ 1C at -10° C
- 90% of rated capacity at 3C at 25° C
- 80% of rated capacity at 5C at 25° C
- All safety requirements met

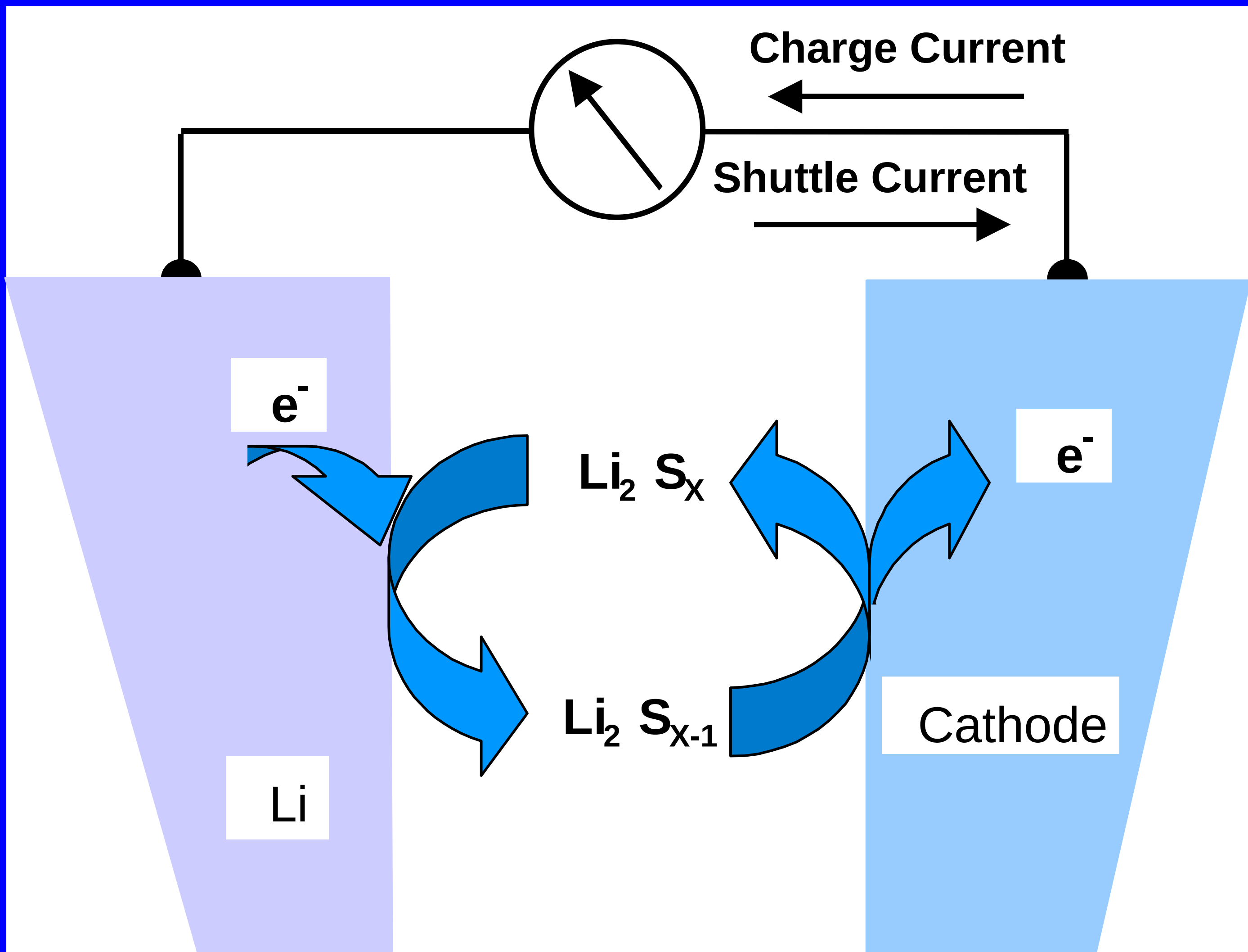
Active Materials Transformation Diagram



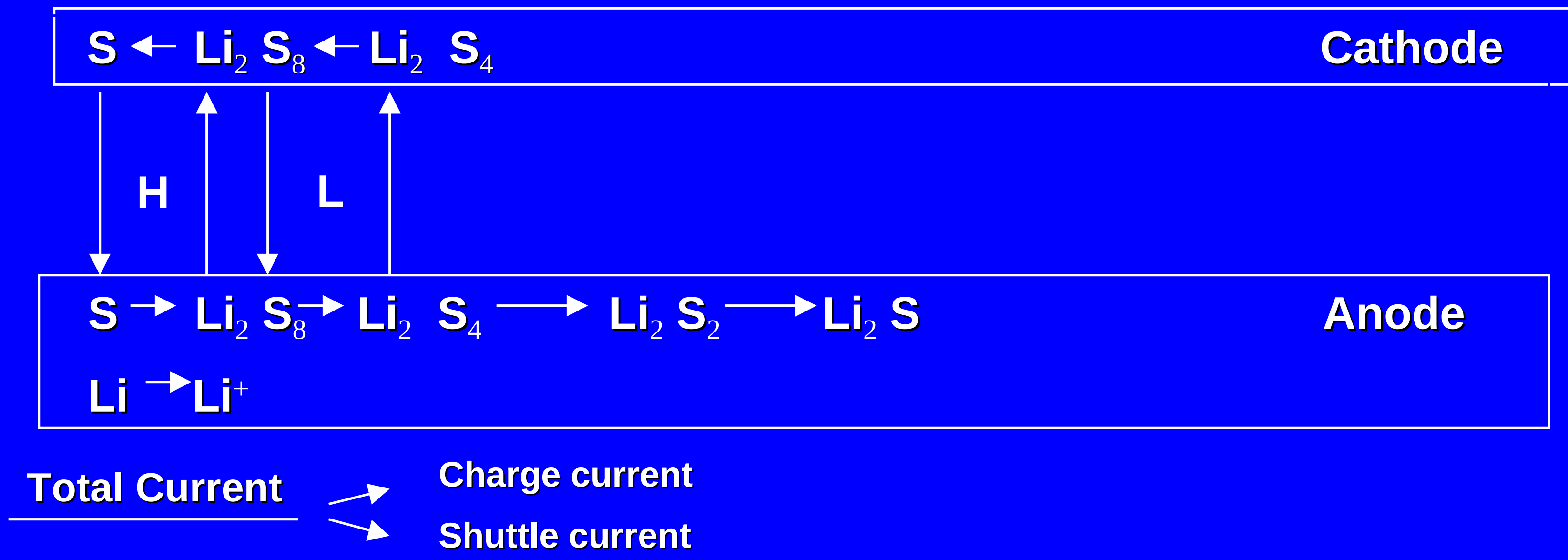
(1) (5) Discharge (4+5) (3) Self-discharge

(2) (6) Charge (4+5) (3) (2) Over-charge protection : Shuttle current

Internal Shuttle Protection



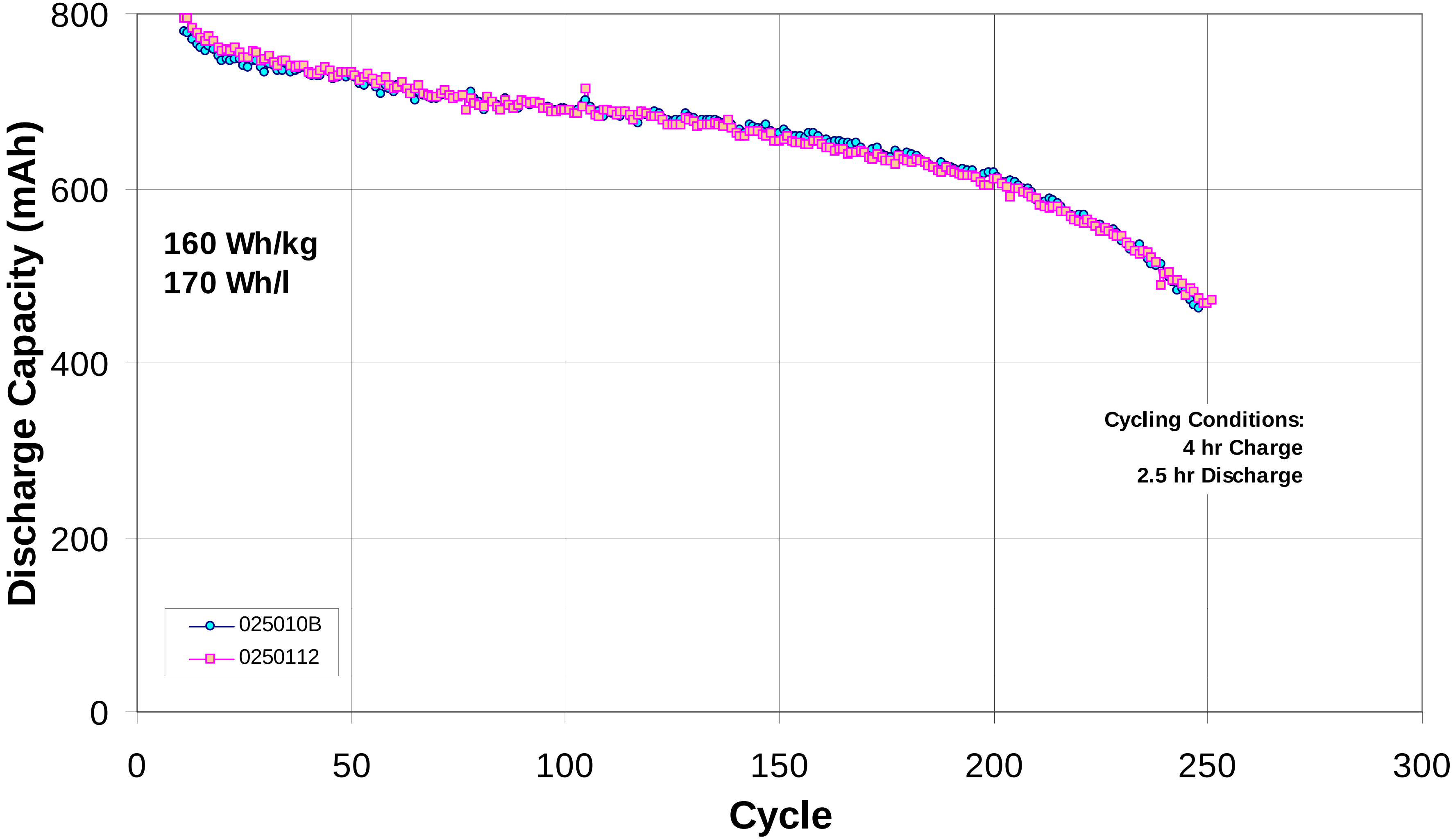
Overcharge protection - Shuttle current diagram



Cycle L	Voltage	
	Shuttle current	~ 0.05 mA/cm^2
	Charge efficiency	95 - 98%
Cycle H	Voltage	2.35 - 2.60 V
	Shuttle Current	0.1 - 0.2 mA/cm^2
	Charge efficiency	40 - 60%

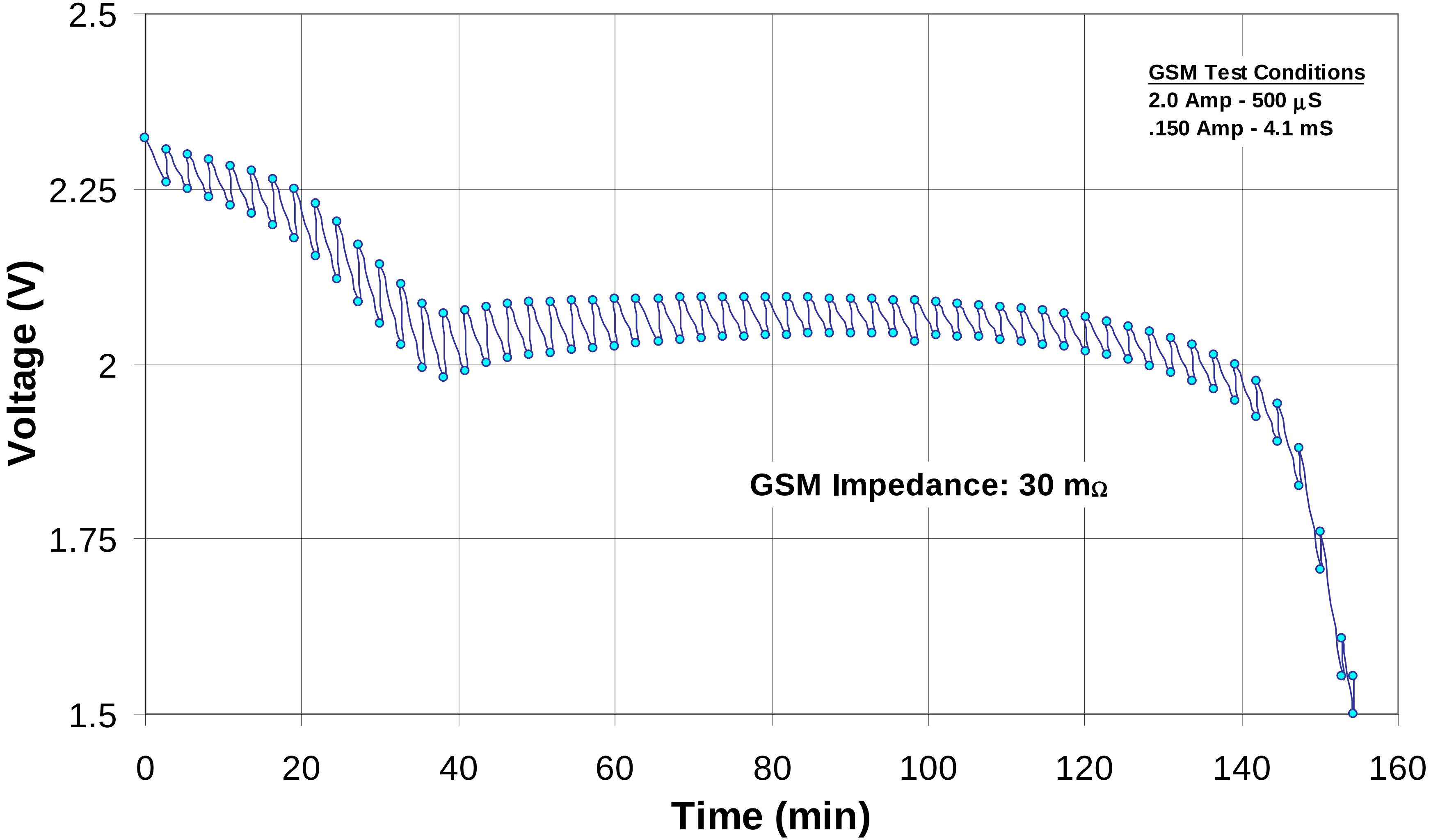
Typical Performance

Discharge Capacity vs Cycle Number

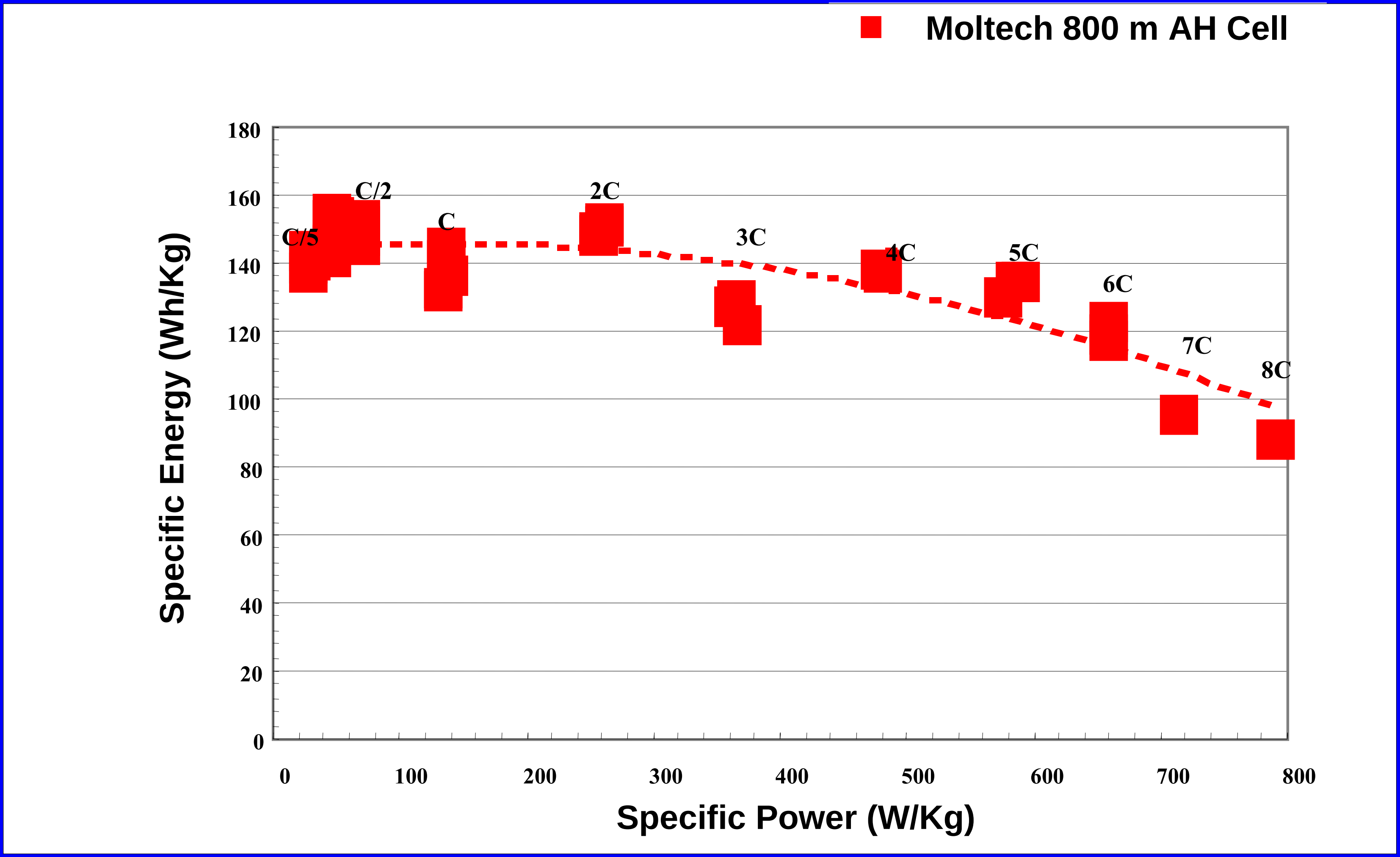


Typical Performance

GSM Discharge Profile



Ragone Plot

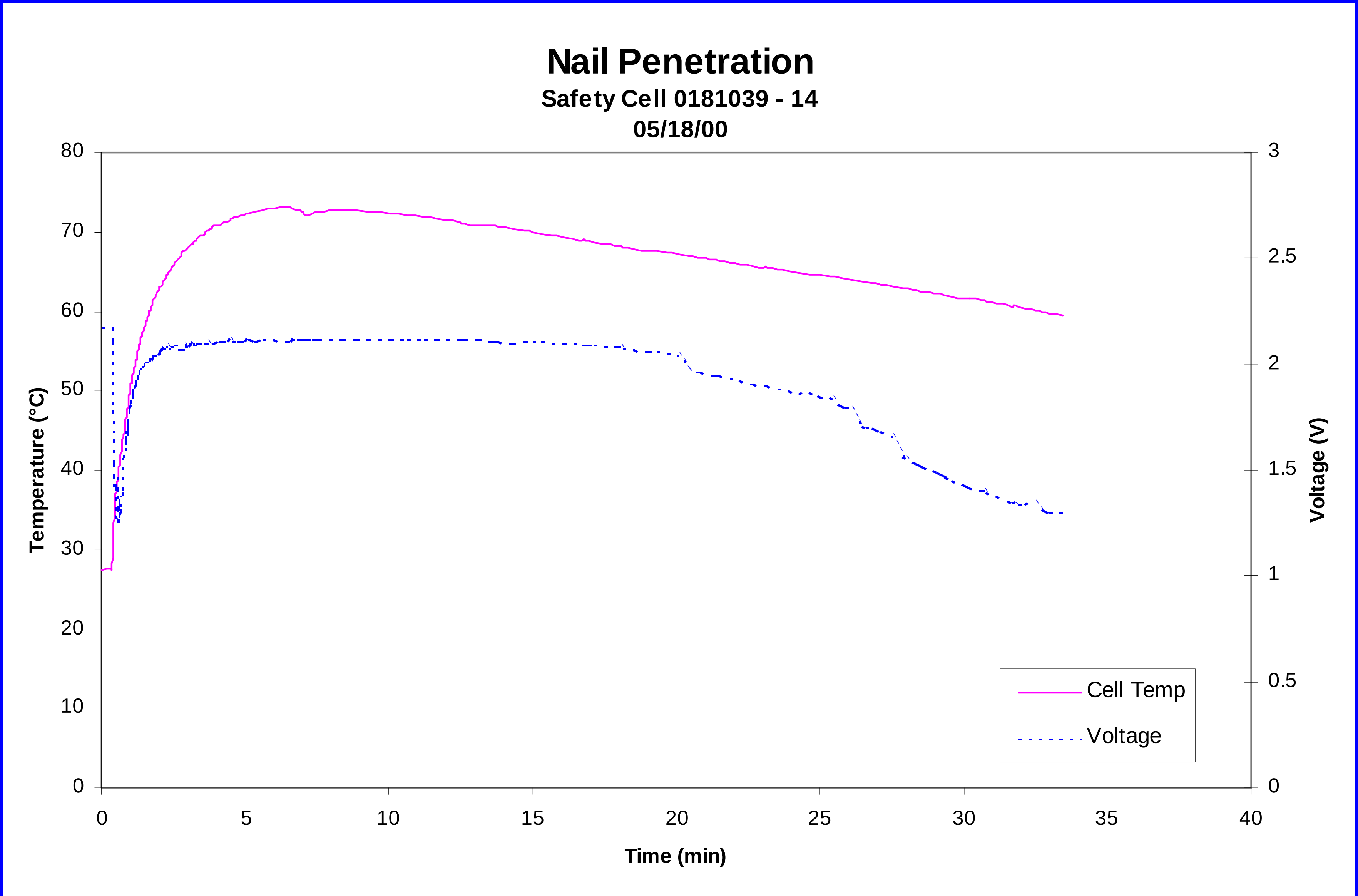


Moltech 800 m AH Cell
Specific Energy (Wh/Kg)
Specific Power (W/Kg)
180
160
140
120
100
80
60
40
20
0
0
100
200
300
400
500
600
700
800
C/5
C/2
C
2C
3C
4C
5C
6C
7C
8C

UL 1642 Safety Test Results on Lithium Sulfur Cells
No Safety Circuitry - Bare Cells

Test	UL	1 Cycle		50 Cycles		100 Cycles		150 Cycles	
	Required?	Passed	Failed	Passed	Failed	Passed	Failed	Passed	Failed
Short Circuit (60°C)	Yes	5	0	3	0	3	0		
Forced Discharge (.8Ax2.5h)	No	5	0						
Forced Discharge (.2Ax12.5h)	Yes			3	0	3	0		
Free Fall	Yes	5	0	3	0	3	0		
Flaming Particles (Fire Exposure)	Yes	5	0	3	0	5	0		
Projectile Test (Fire Exposure)	Yes	5	0	3	0	5	0		
Crush	Yes	5	0	3	0	3	0		
Impact	Yes	5	0	3	0	3	0		
Nail Penetration	No	5	0	3	0				
Overcharge (0.8A)	No	5	0						
Overcharge (0.2A)	Yes			6	0	5	0		
Thermal Exposure (Ramped)	Yes	0	5	5	0	5	0		
Thermal Exposure (Preheated Oven)	No	0	5						
High Rate Charge (2.4A)	No	4	1*						
High Rate Charge (.6Ax3.5h)	Yes	5	0	4	3*	5	1*		

* These failures could be interaction between cells and test equipment.



Nail Penetration
Safety Cell 0181039 - 14
05/18/00
Temperature (°C)
Voltage (V)
Time (min)
Cell Temp
Voltage
0
10
20
30
40
50
60
70
80
0.5
1
1.5
2
2.5
3
5
15
25
35

Core Intellectual Property

- Li-Sulfur Chemistry and Materials
- Advanced Materials and Processing
- Thin Film Technology
- Product Design and Manufacturing

Patent Portfolio Status

- 140 Patents & Applications
- Cover all aspects of materials, product design & manufacturing
- Control of Intellectual Property
- Protection in major battery markets

Battery Patents

- Organo-sulfur polymers
- Cathode compositions
- New separator technology
- Electrolyte compositions
- Anode stabilization and cycleability
- Cell design and engineering
- Cell assembly and manufacturing processes

Moltech Corporation
Li-S Commercialization

- Technology Research & Engineering Development
  - Tucson, AZ
- Production infrastructure in Gainesville, FL
  - Buildings
  - Land
  - Equipment
  - People
- UL Certified Test Laboratory
  - Gainesville, FL
- Electronics Design & Development Laboratory
  - Gainesville, FL

Moltech Corporation
Li-S Commercialization

- Battery Pack Design & Development Laboratory
  - Gainesville, FL
- Battery Pack Assembly
  - Juarez, Mexico
  - Hong Kong
  - UK
  - Malaysia
- Global Marketing/Sales Force

Summary

- Technology advancement from 150 cycles @ 50% rated capacity to 200 cycles@ 80% of rated capacity from January 2000 to September 2000.
- Current Status of development represents 40% of potential for cycle life and energy densities.
- Chemistry today shows safety performance compatible with commercialization.
- Moltech Corporation has all infrastructure required for commercialization.

MOLTECH
CORPORATION

Advanced Rechargeable Lithium Batteries

Powering the Electronic Future

SAFT

GEO AND LEO LIFE TEST RESULTS ON VES140 SAFT Li-Ion

Y. Borthomieu, J.P. Planchat

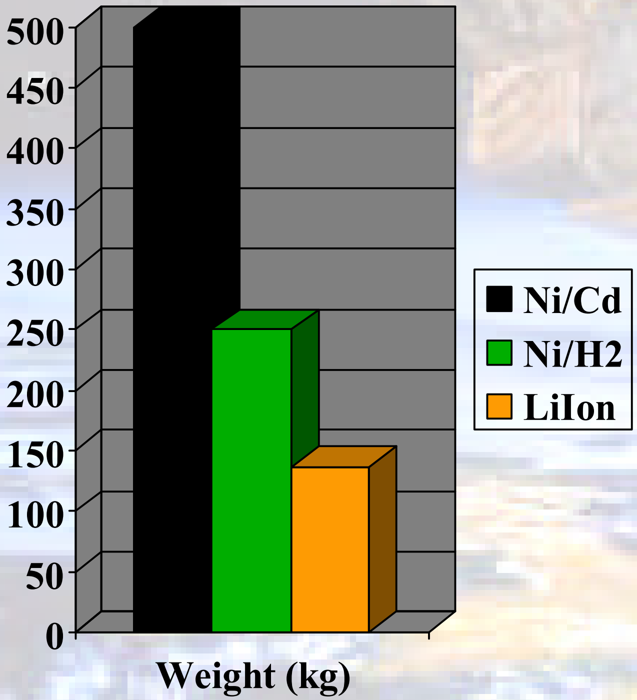
Defense and Space Division

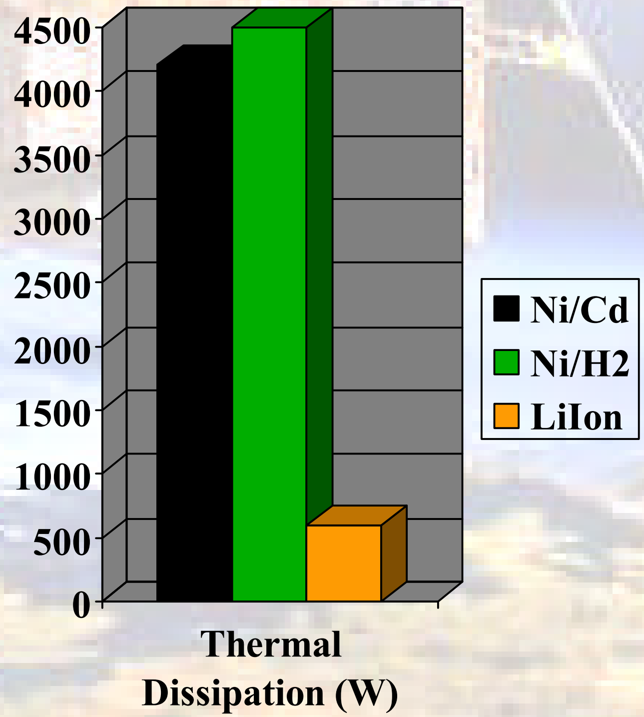
SAFT POITIERS

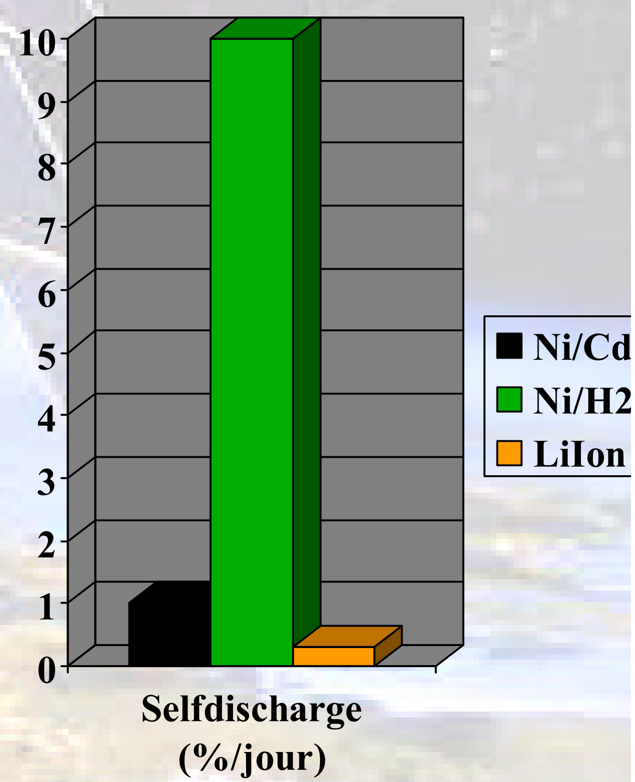
AGENDA

- VES140 Cell Design
- Qualification Status
- Calendar Effect Results
- Life Test Results
- Conclusions

Lithium-Ion Advantages for Space Applicatio

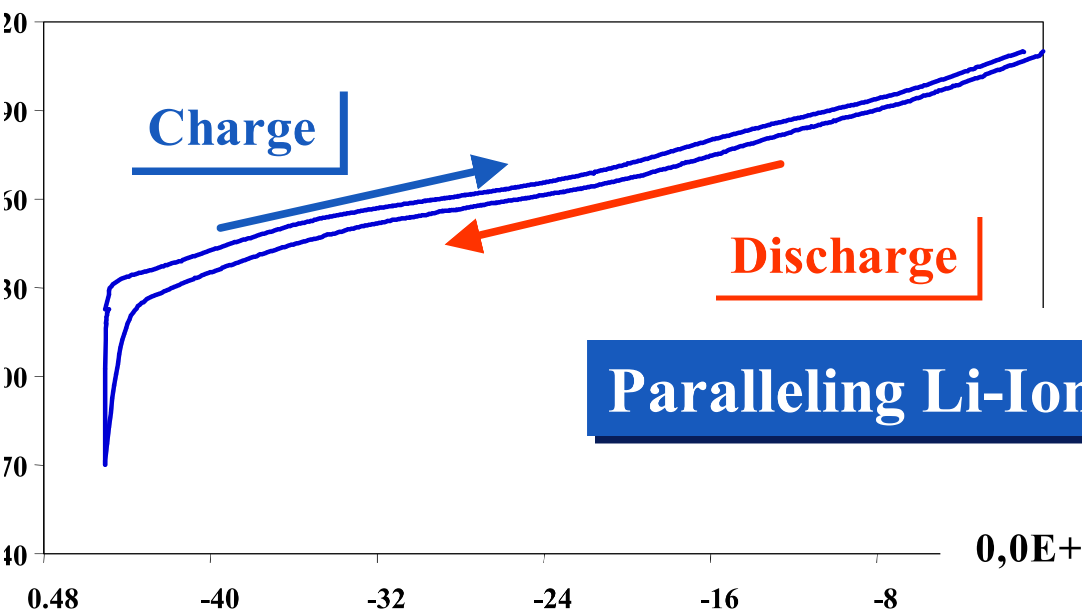






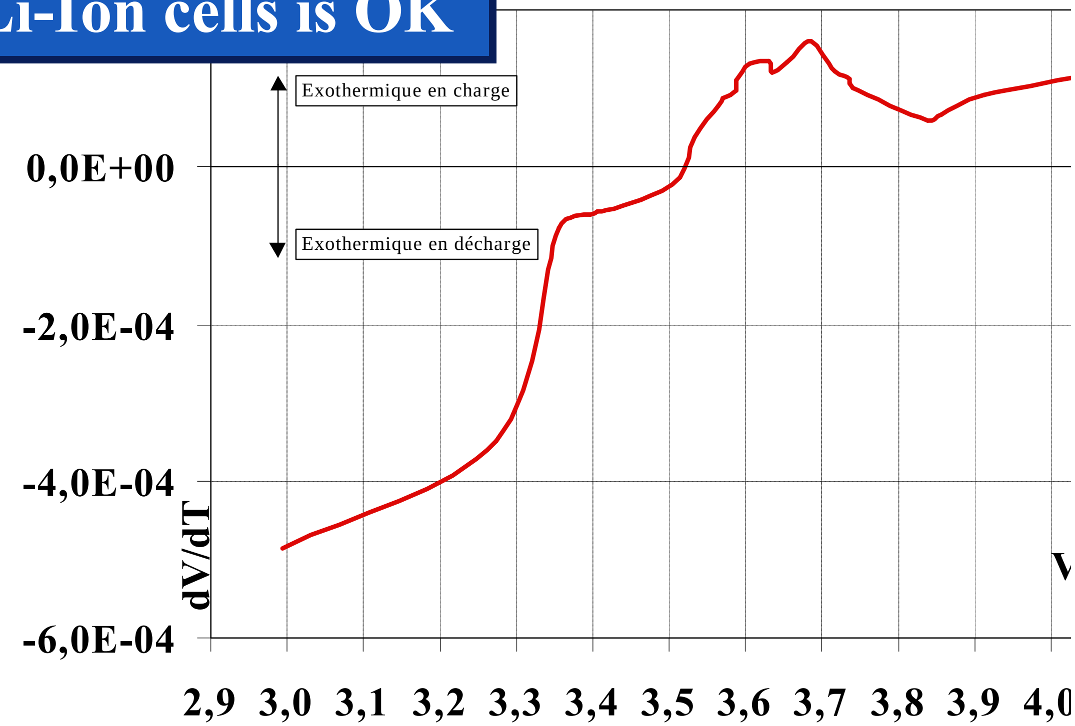
For 12 kW Battery

Li-Ion cells in parallel



Low impact of Temperature on OC

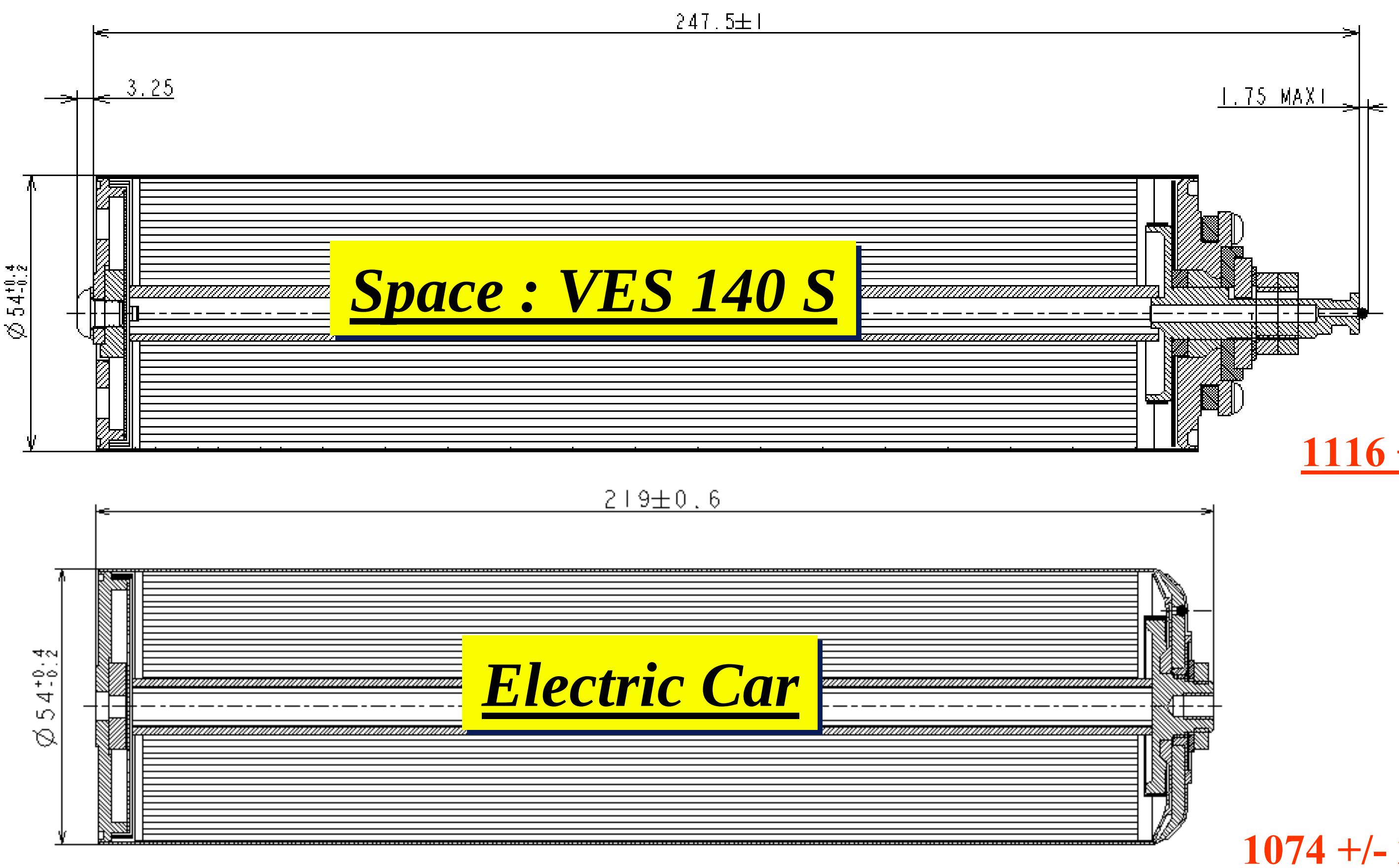
Paralleling Li-Ion cells is OK



Voltages is function of intercalated Lithium ions

$Li_{0.85}Ni_{(1-Y)}M_YO_2 + 3C \leftrightarrow Li_{0.35}Ni_{(1-Y)}M_YO_2 + 0.5LiC_6$

VES 140 S Cell design



1116 +/- 25 g

1074 +/- 25 g

Qualification Program

- GEO real time life test
- GEO Accelerated life test
- BOL Qualification
- Calendar Test
- LEO Accelerated life test
- LEO real time life test

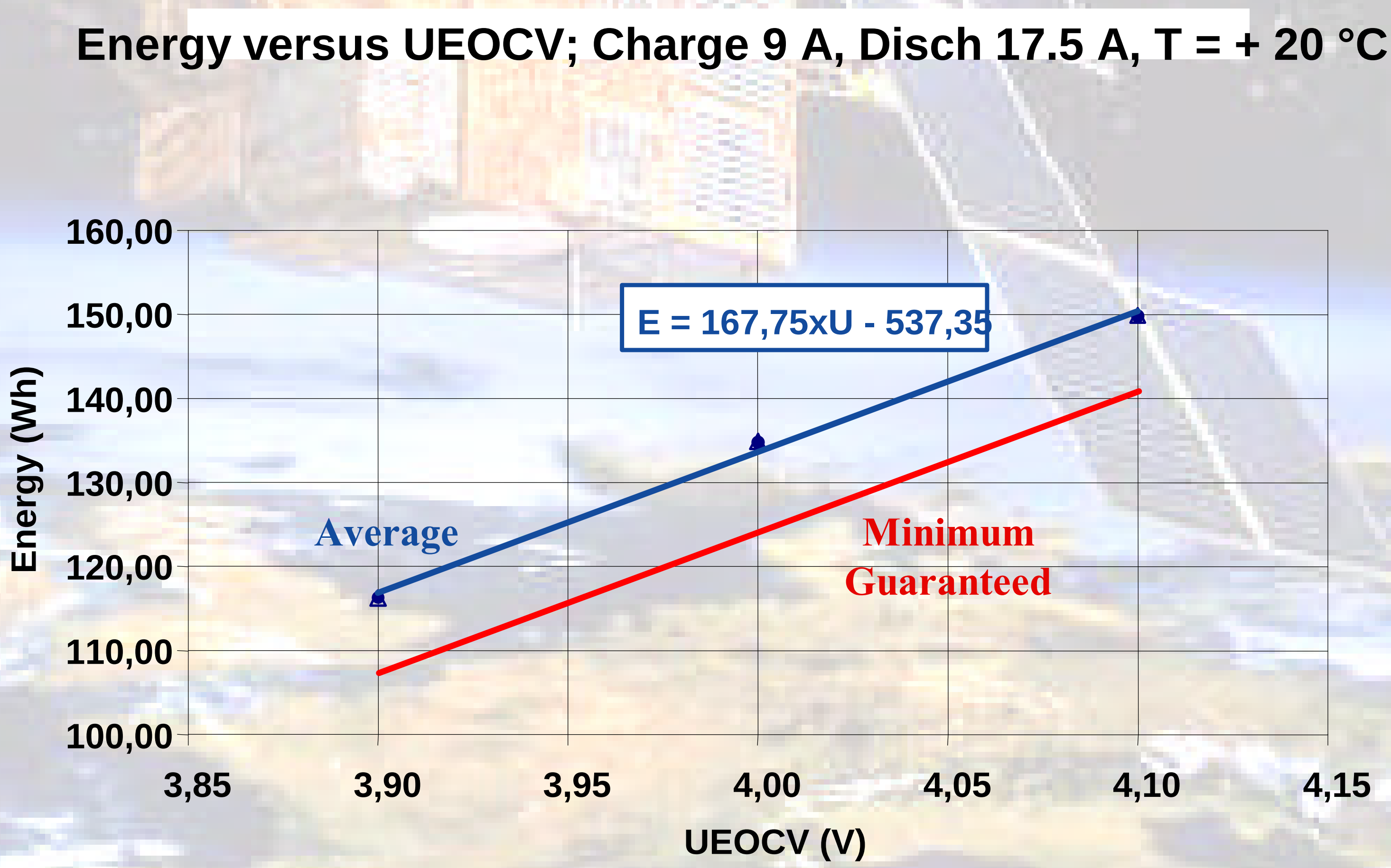
Qualification GEO (GEO real time life test, GEO Accelerated life test, BOL Qualification, Calendar Test)

Qualification LEO (BOL Qualification, Calendar Test, LEO Accelerated life test, LEO real time life test)

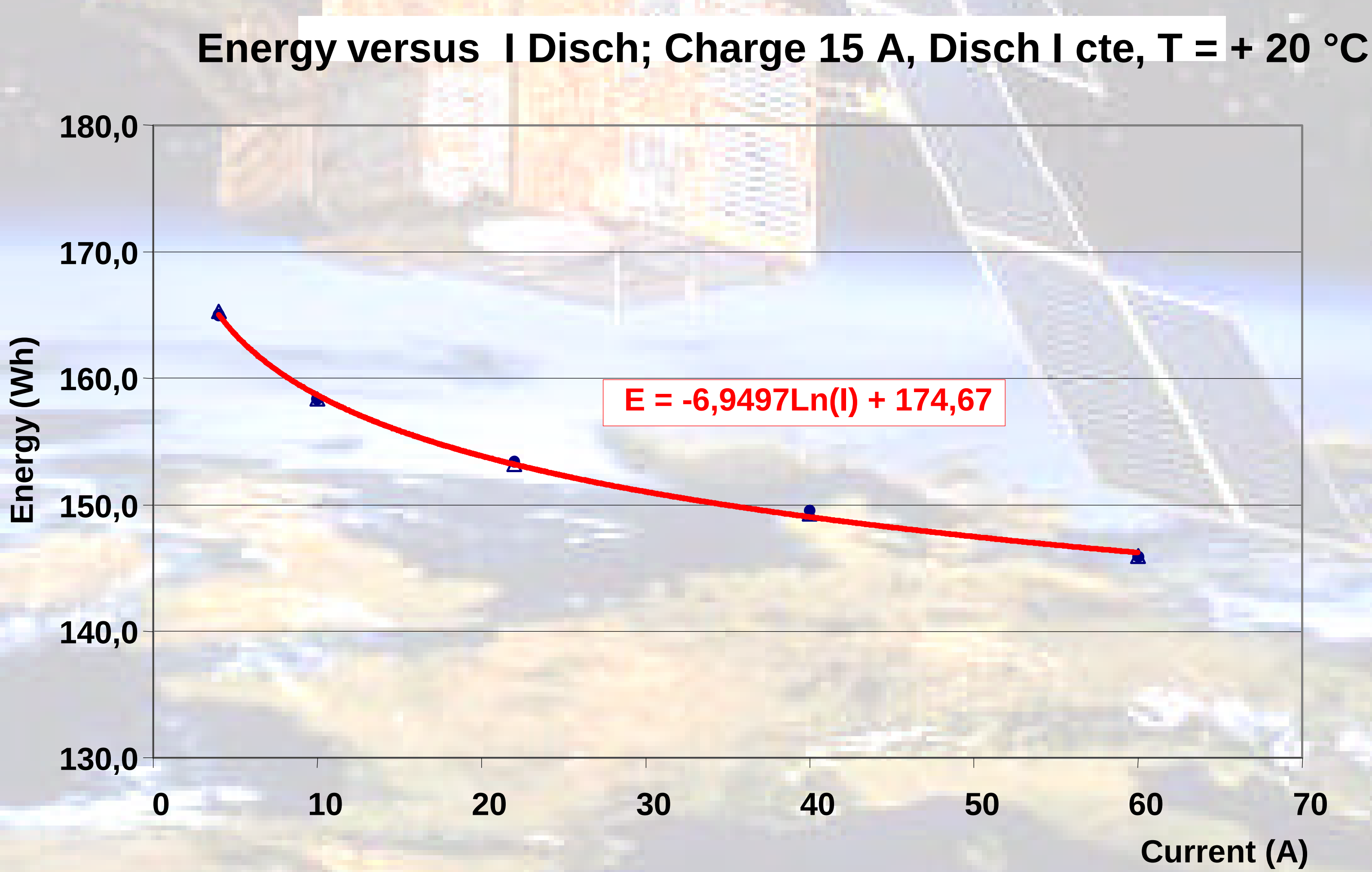
Qualification

- Qualification Review the 21st June 00 with CNES, ESA ASTRIUM and ASPI :
  - Electrical tests
  - Mechanical tests
  - Abuse tests
    - « overcharge » : charge up to 4.5 V
    - « overdischarge »
    - short circuit
    - high temperature test

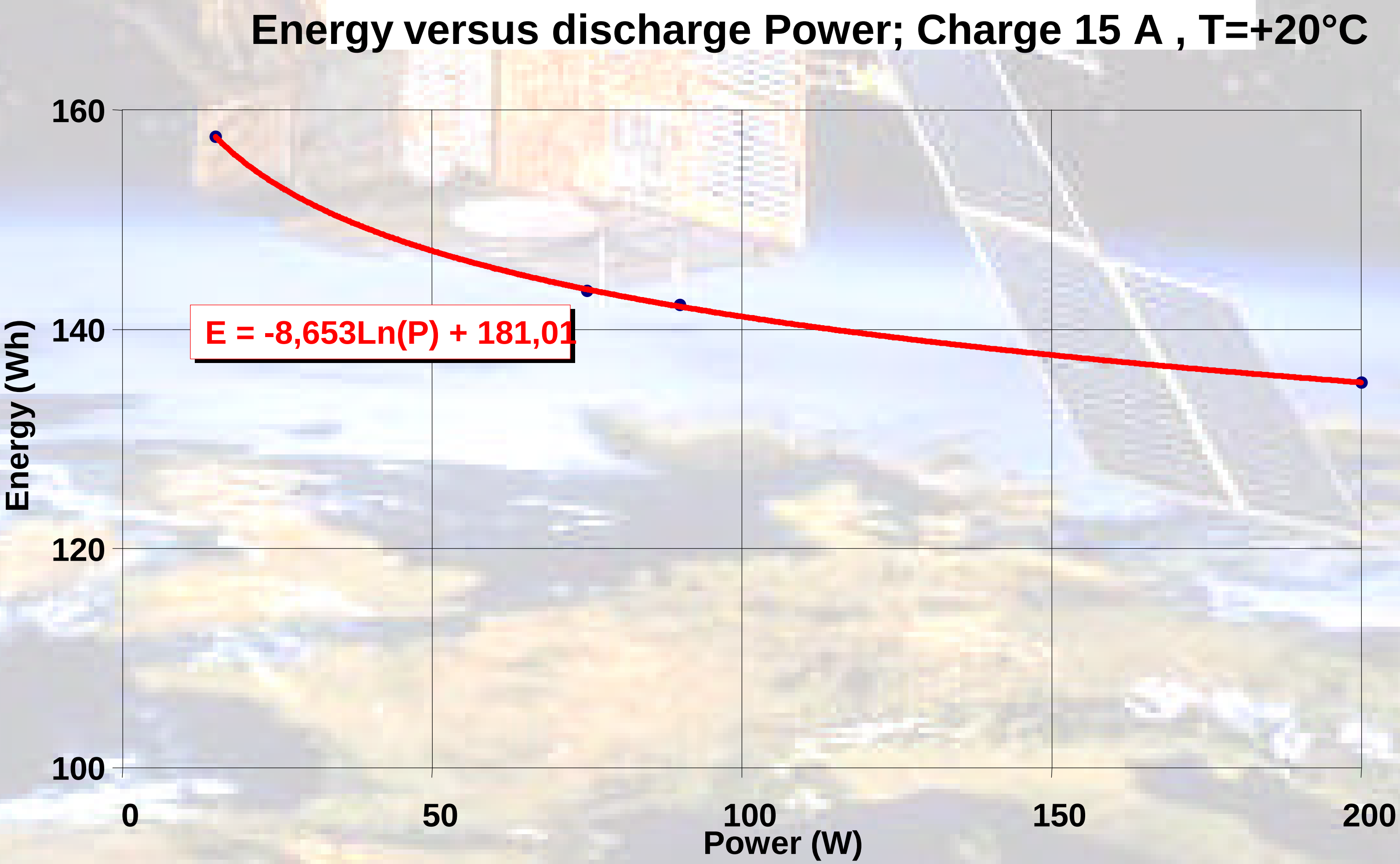
Energy versus EOCV



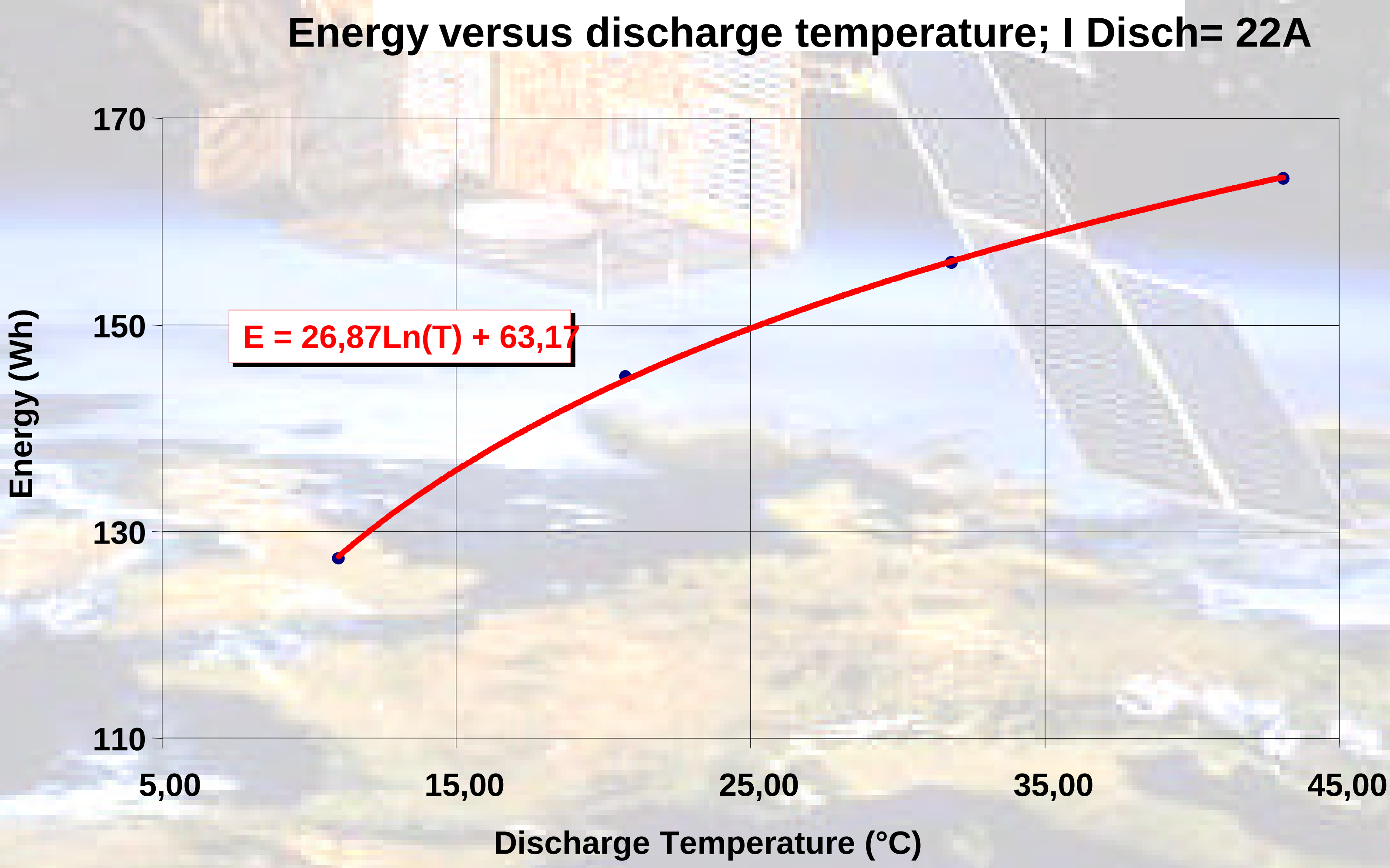
Energy versus I discharge



Energy versus Power



Energy versus discharge temperature



Sine Vibrations

- Vibrations performed on 3 cells :
  - charged at 3.8 V

Sweep rate, 2 octave / min, in OX and OZ.

Frequency	Level
5 to 24 Hz	± 11 mm
24 to 100 Hz	25 g

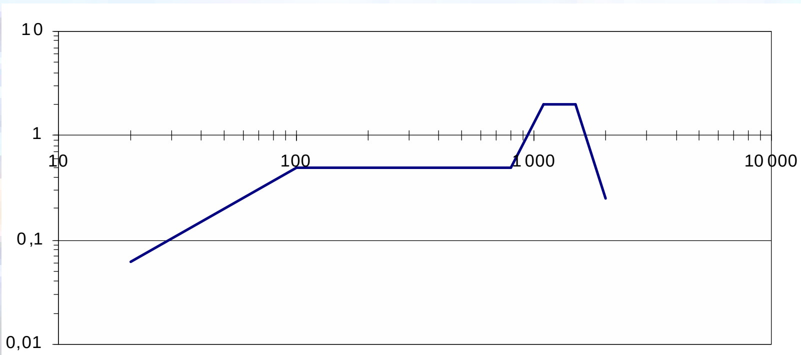
Random Vibrations

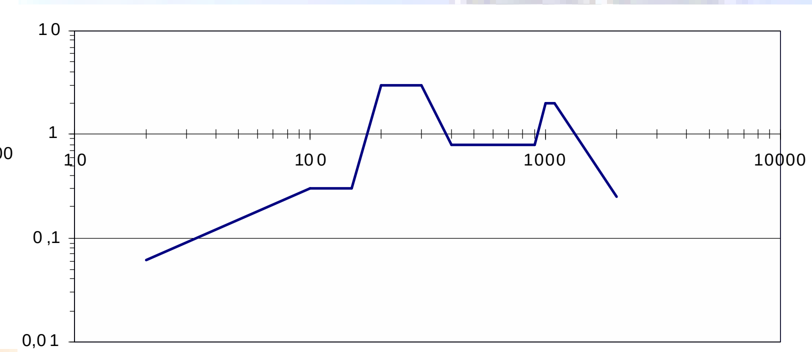
OZ axe level (3 min):	
Frequency	Level
20 to 100 Hz	+6 dB/Oct
100 to 800 Hz	0.5 g²/Hz
800 to 1100 Hz	slope
1100 to 1500 Hz	2 g²/Hz
1500 to 2000 Hz	-6 dB/Oct

Global 44.34 gRms

OX & OY axe level (6 min):	
Frequency	Level
20 to 100 Hz	+ 3 dB/Oct
100 to 150 Hz	0.3 g²/Hz
150 to 200 Hz	slope
200 to 300 Hz	3 g²/Hz
300 to 400 Hz	slope
400 to 900 Hz	0.8g²/Hz
900 to 1000 Hz	slope
1000 to 1100 Hz	2g²/Hz
1100 to 2000 Hz	- 9 dB/Oct

Global 45.32. gRms





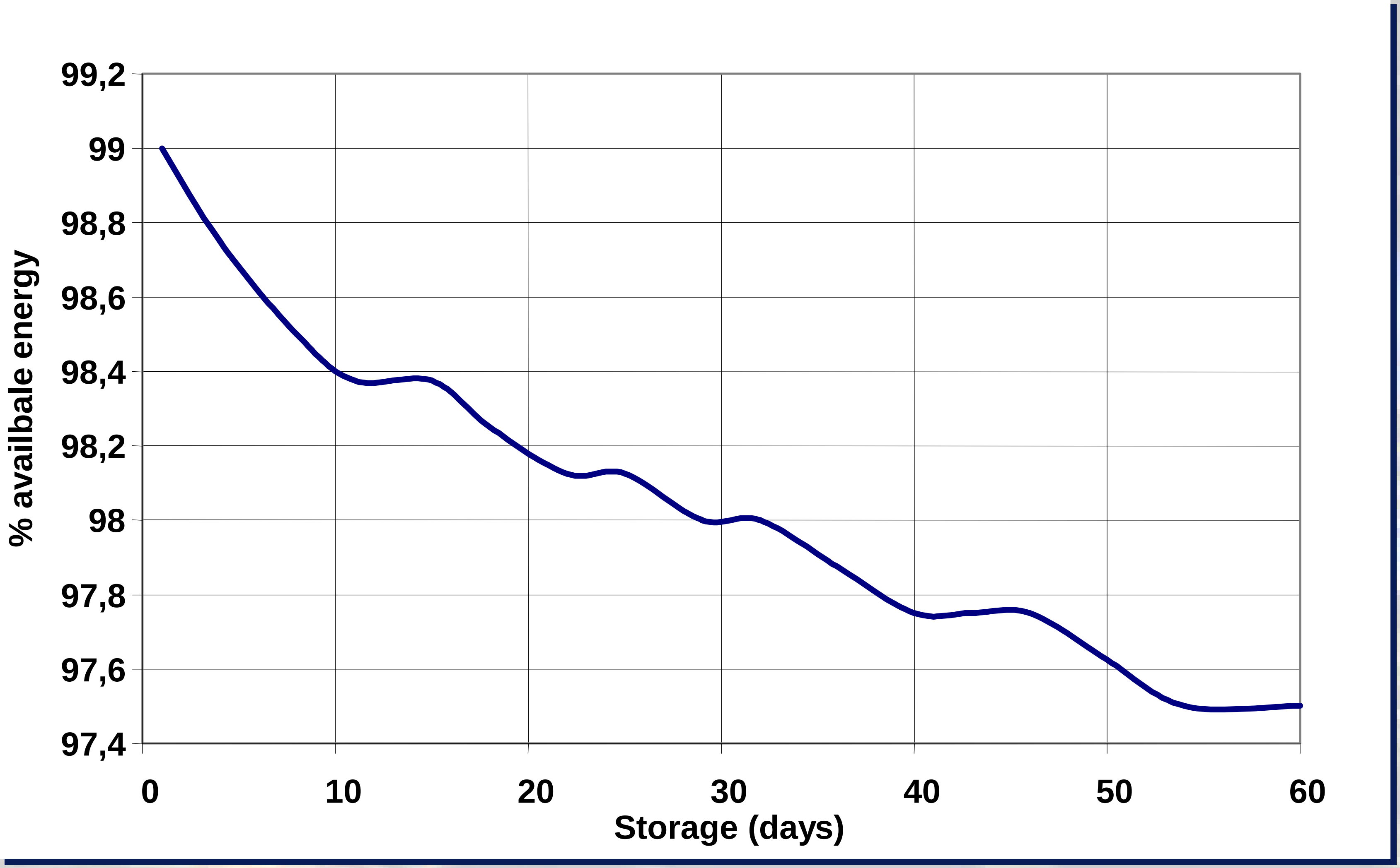
No modification on resonance frequency > 140 hz

No voltage evolution during test

No change on energy and integrity (DPA)

Self Discharge

% available Energy versus storage time



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Peak Discharge

- 150 Amps (2 secondes)

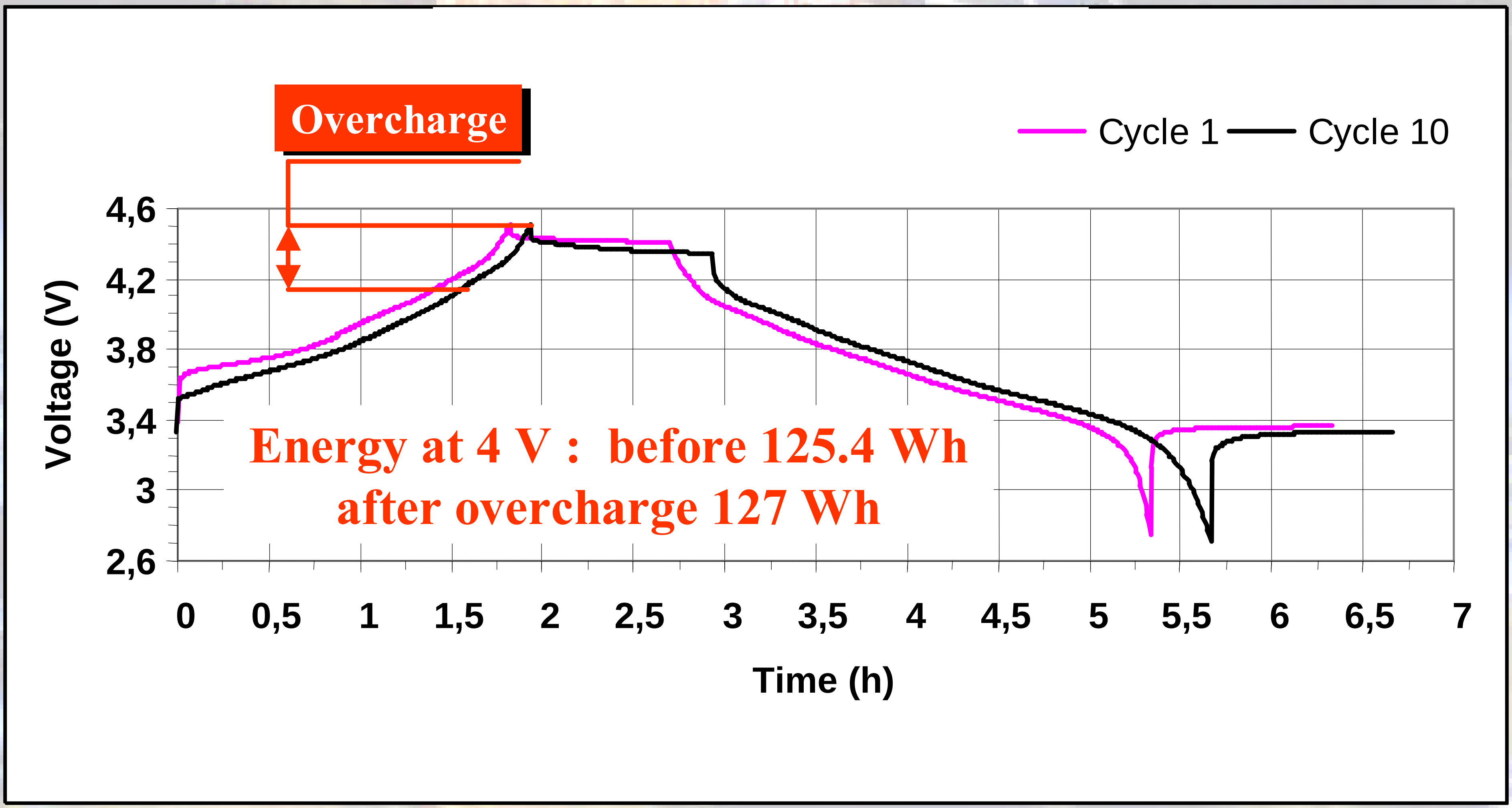
C/2 discharge

	30 min	60 min	93 min
Cell voltage UEOC = 4.0V	3.348	3.172	2.864
Cell voltage UEOC = 3.8V	3.168	2.887	

- 500 Amps (1 seconde)

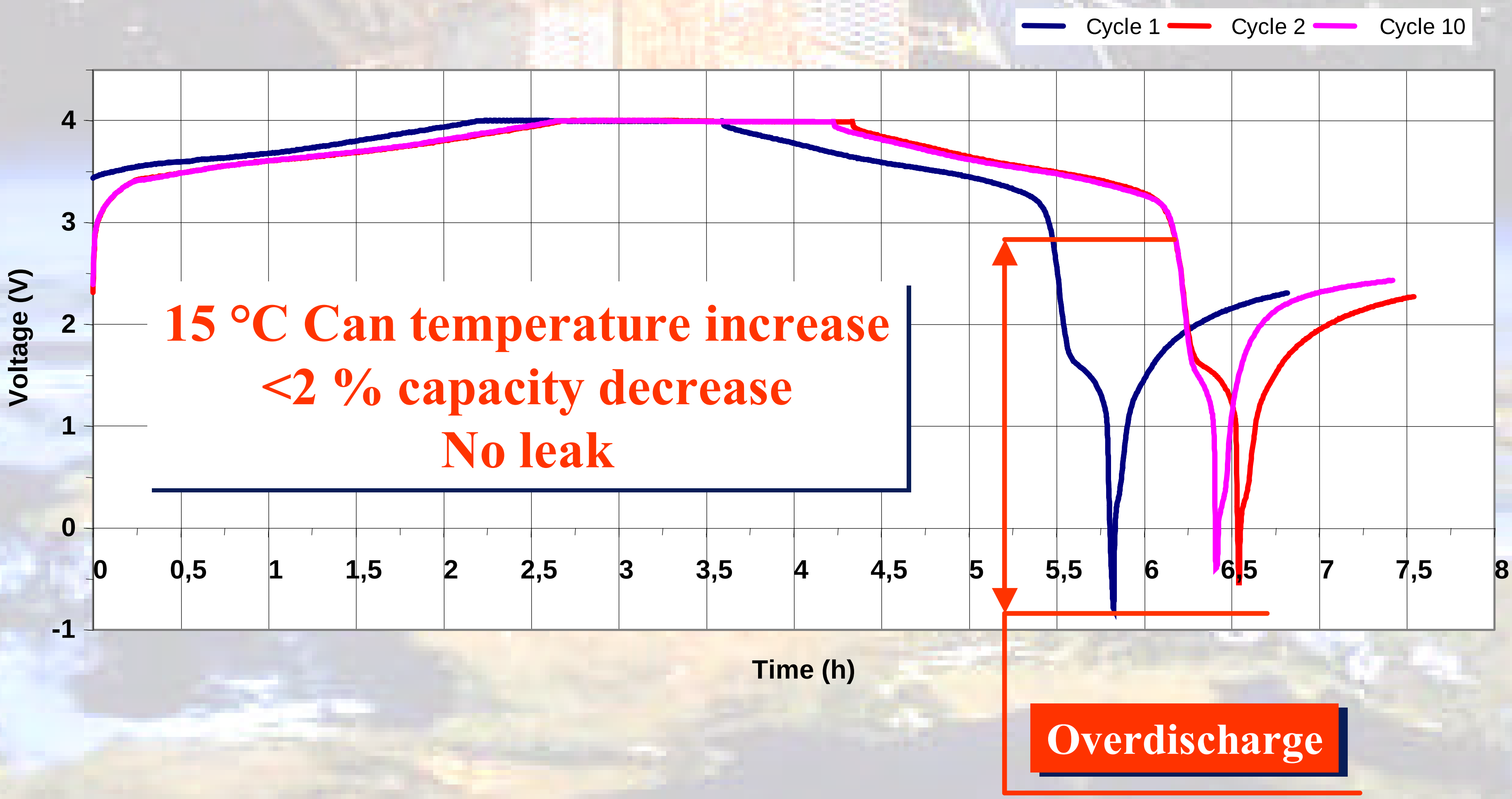
	30 min	60 min	93 min
Cell voltage UEOC = 4.0V	2.784	2.593	

Overcharge 25 amps @ 4.5 V



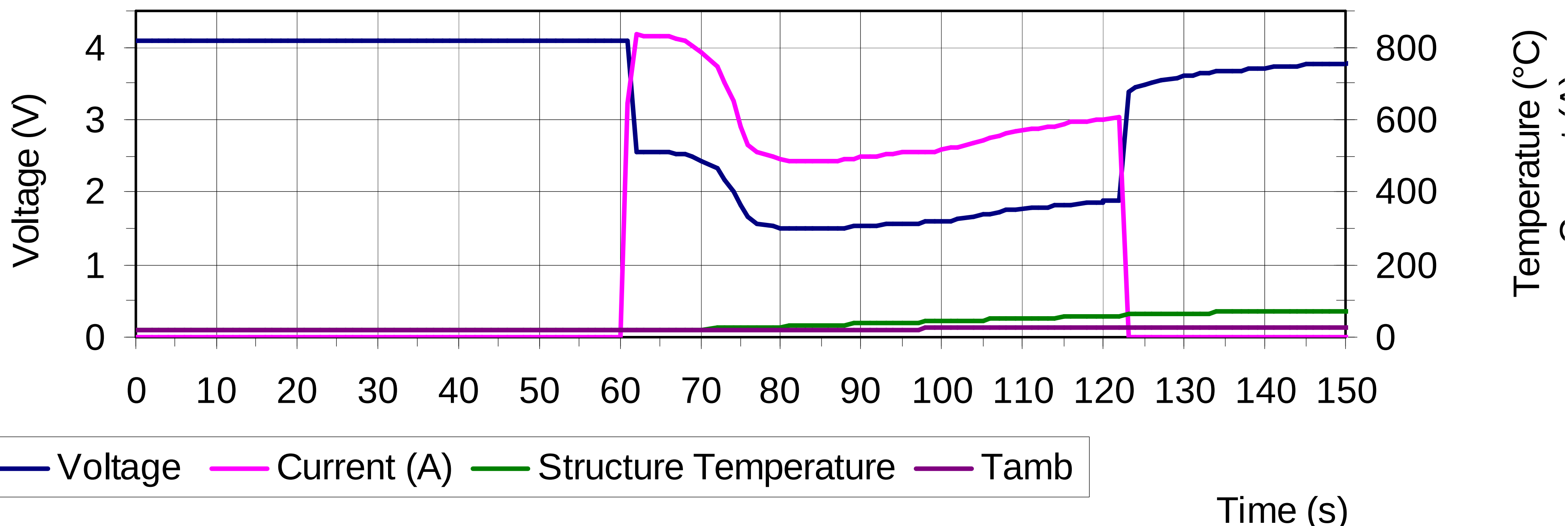
Overdischarge

Charge 15.5A EOCV 4.0V, Discharge 20A EODV -0.8V



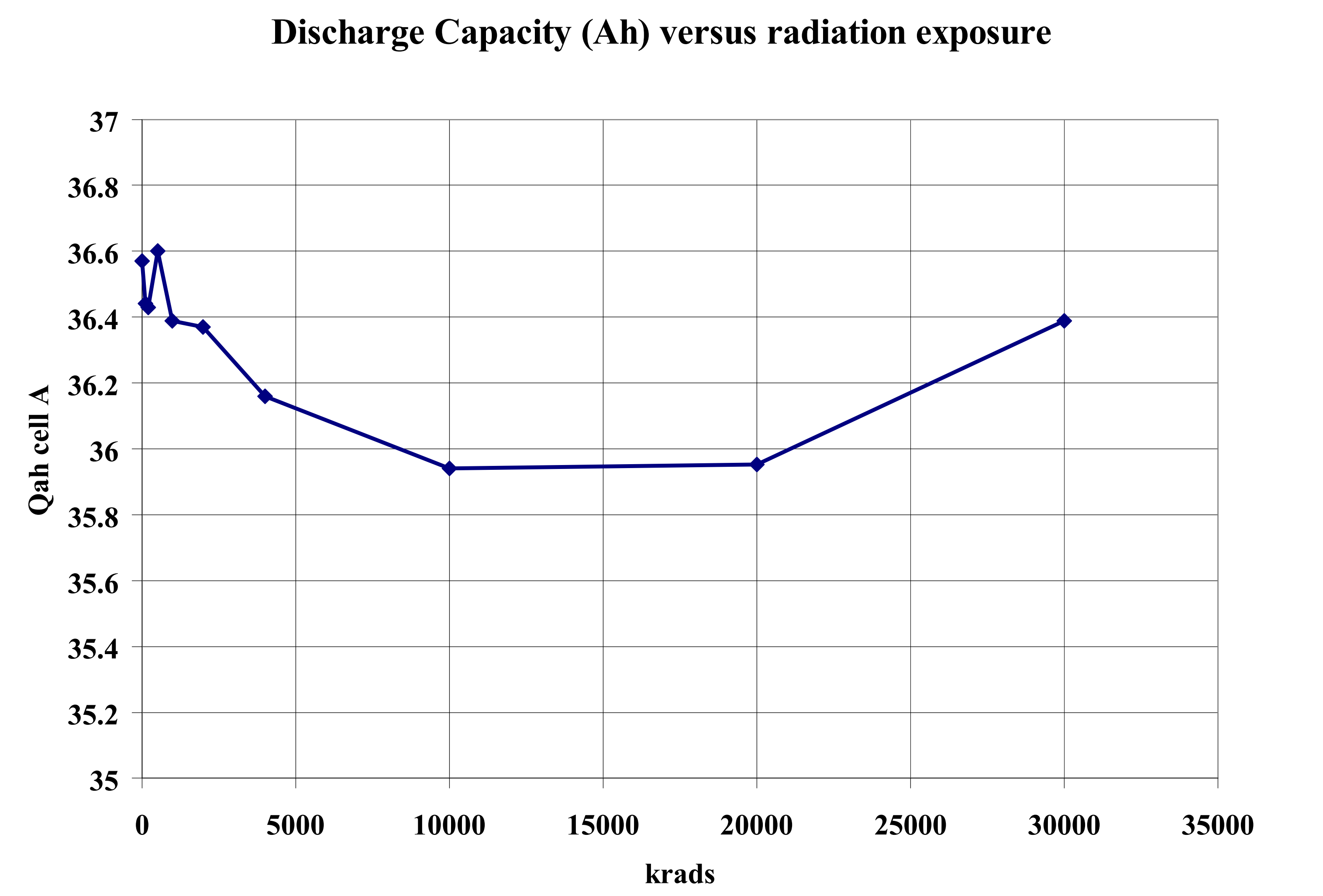
Short circuit

SHORT-CIRCUIT R = 3 mOhms
Cell L 369, U EOC = 4,10 V

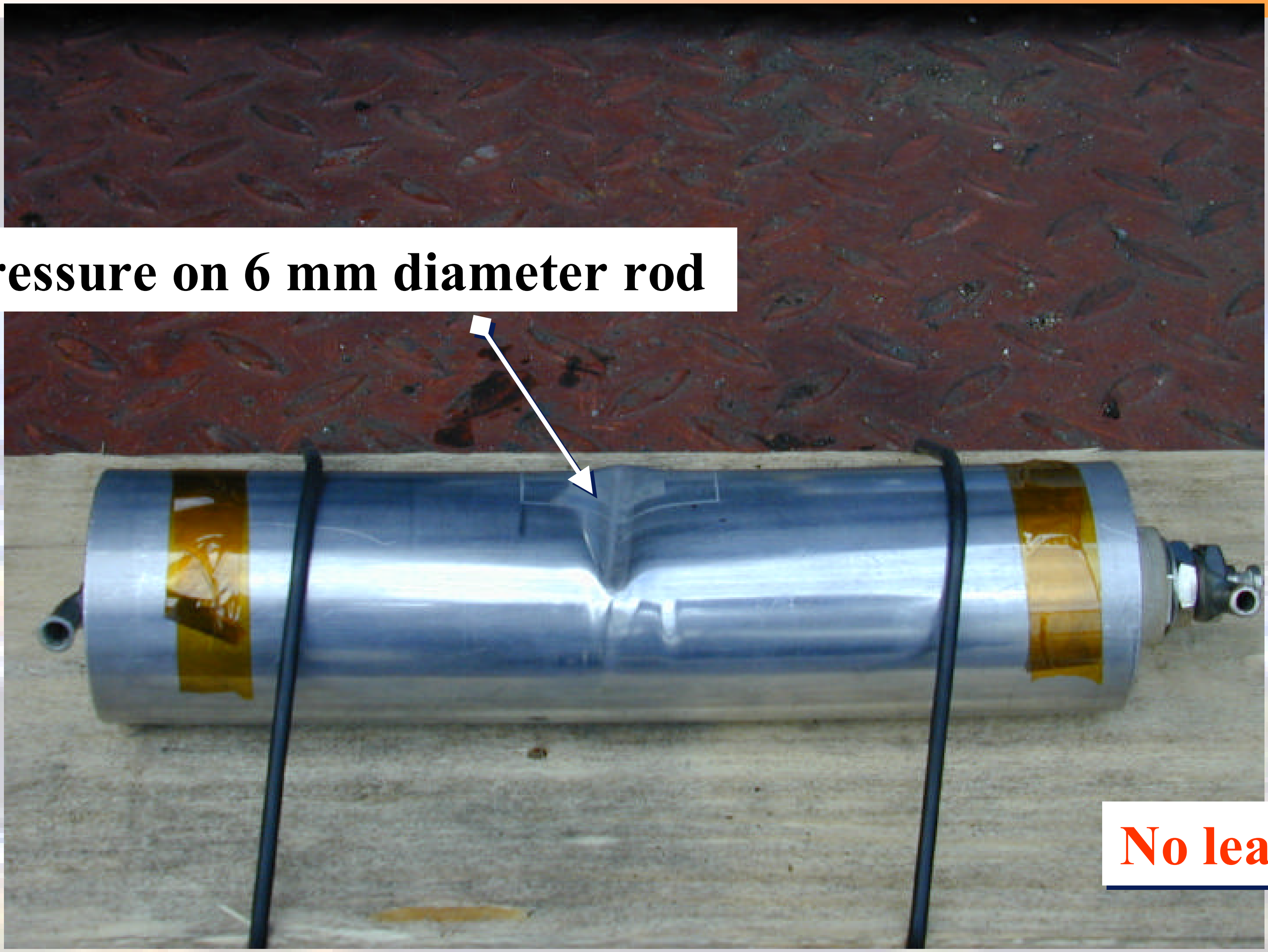


No energy change before and after short circuit test

Radiation Test



Crush Test



1 ton pressure on 6 mm diameter rod

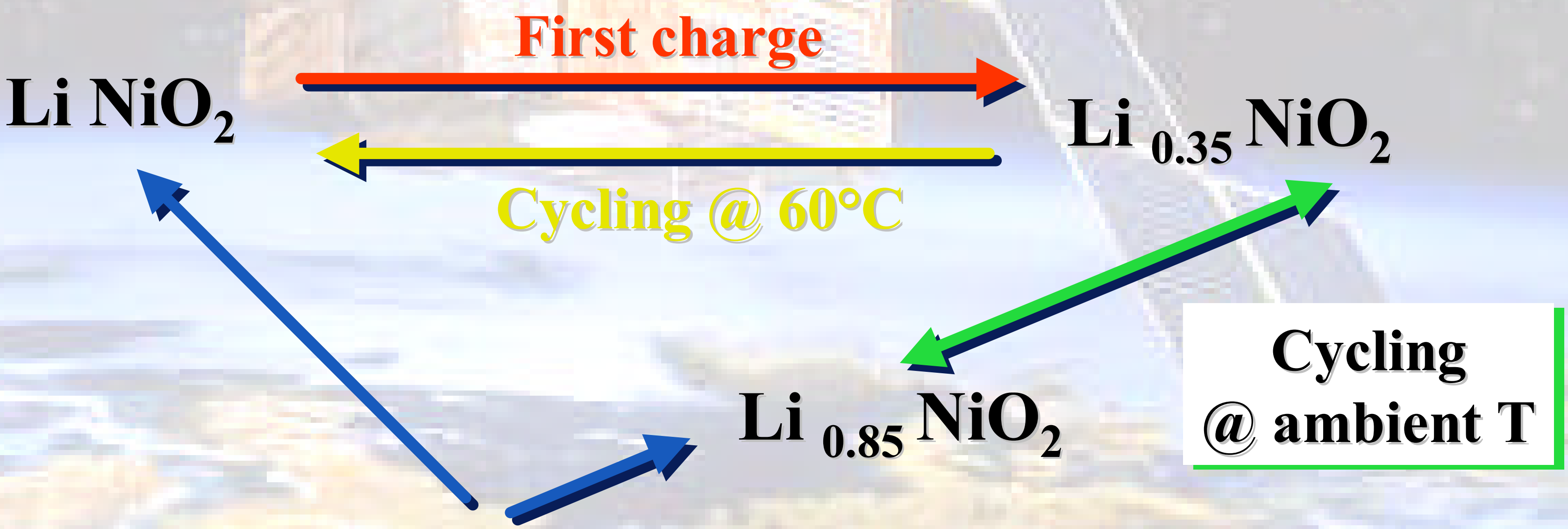
No leak, no sho

Calendar Test Plan

Test Plan

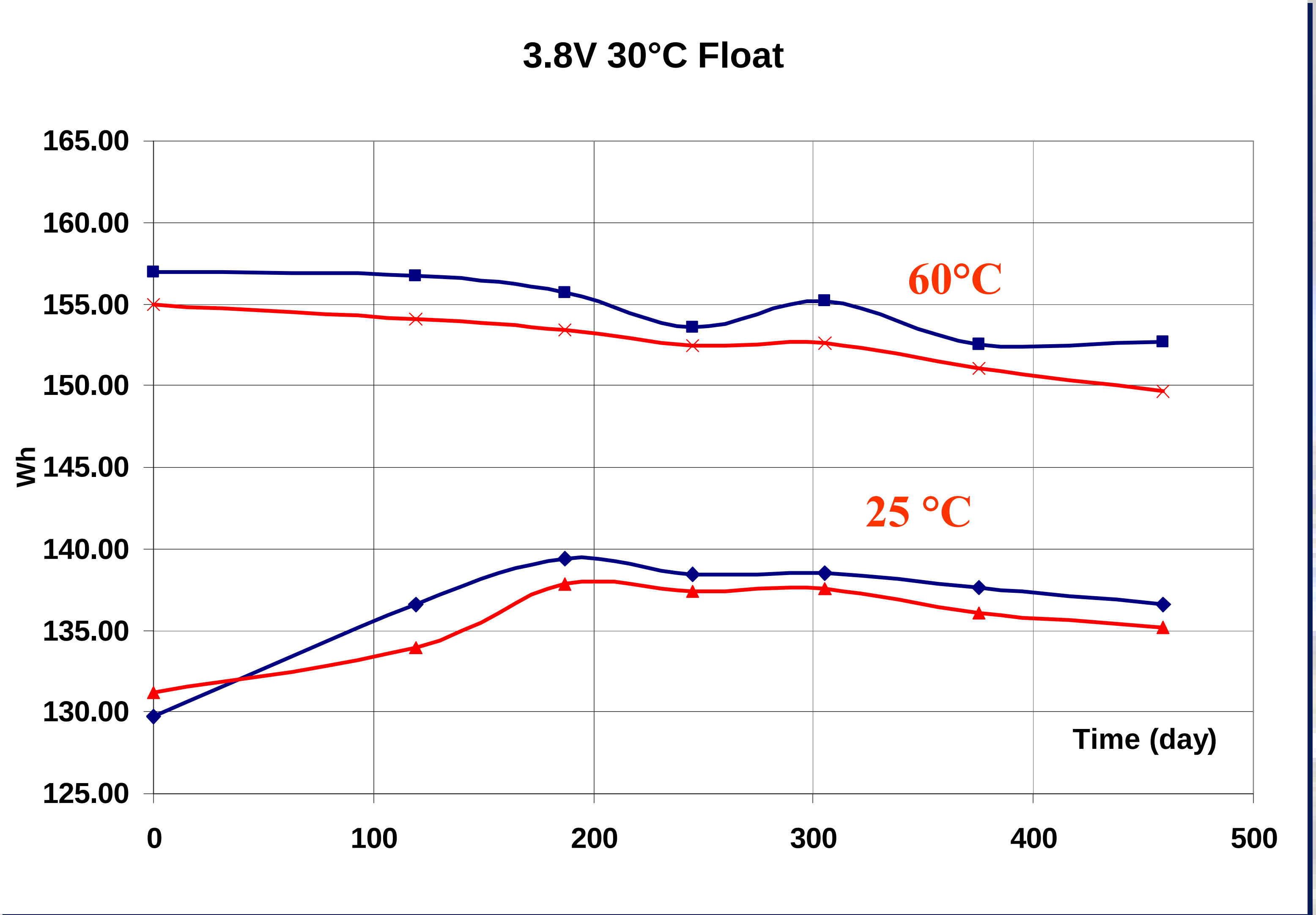
- Storage Temperature
  - From 0°C to 60°C
- EOCV
  - From 3.70 V to 4.10V
- Conditions
  - OCV and floating

Nickel based alloy specificities

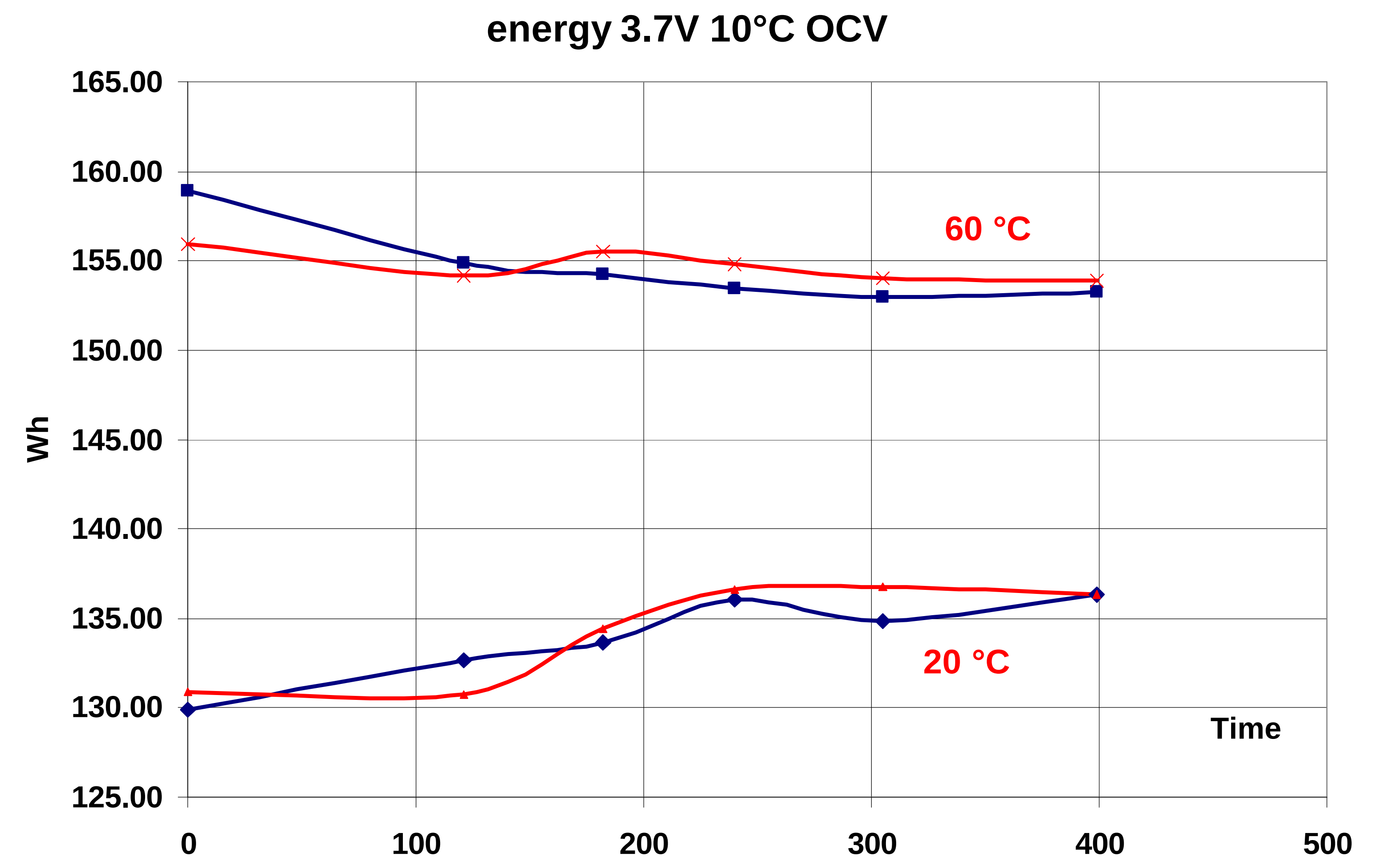


Lithium reserve = 12% within negative electrode

3.8V ,30°C, Floating



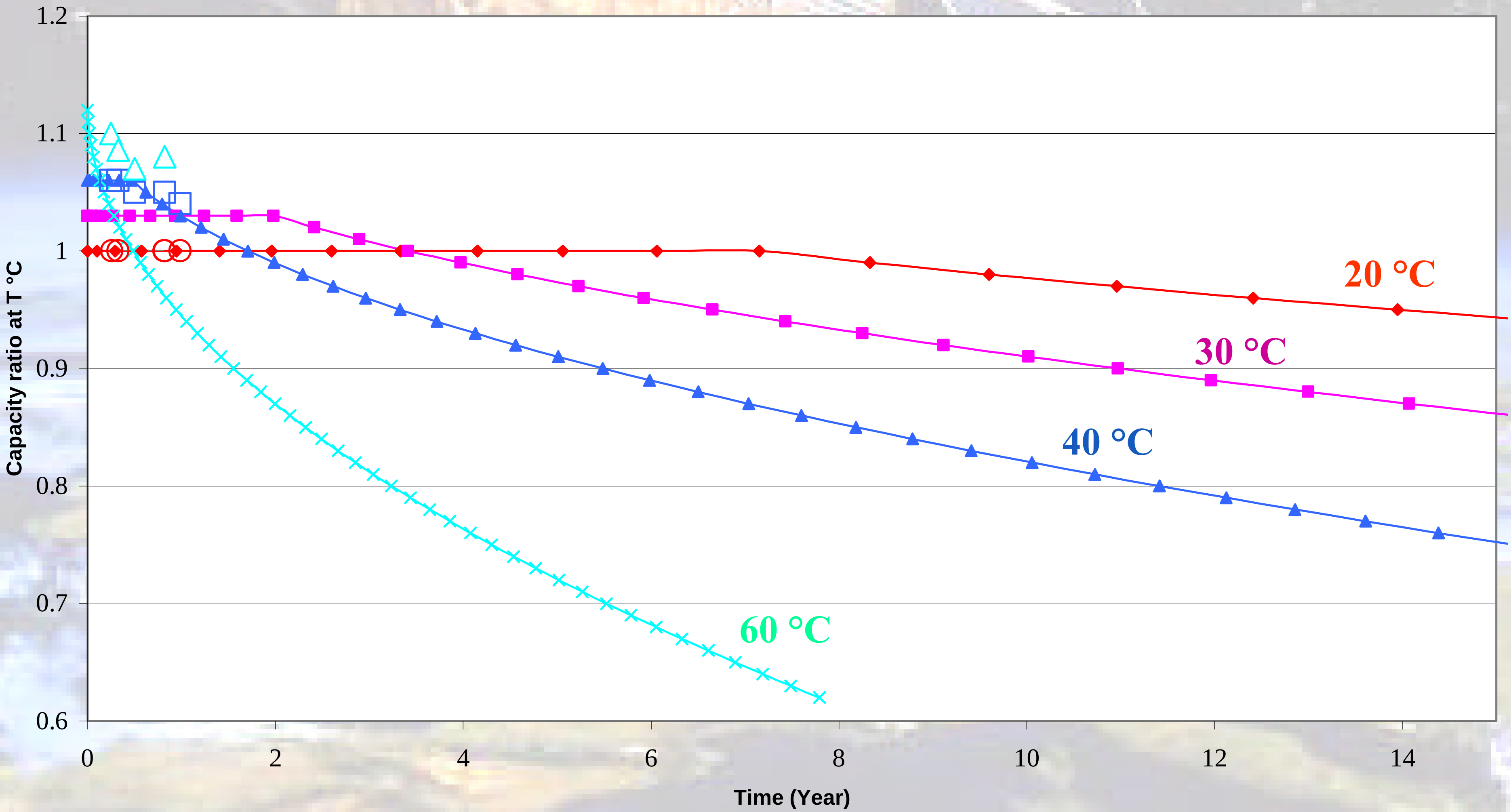
3.70V ,10°C, OCV



energy 3.7V 10°C OCV
165.00
160.00
155.00
150.00
145.00
140.00
135.00
130.00
125.00
Wh
0
100
200
300
400
500
Time
60 °C
20 °C

Calendar Effect

Capacity Loss due to Calendar Effect vs Temperature



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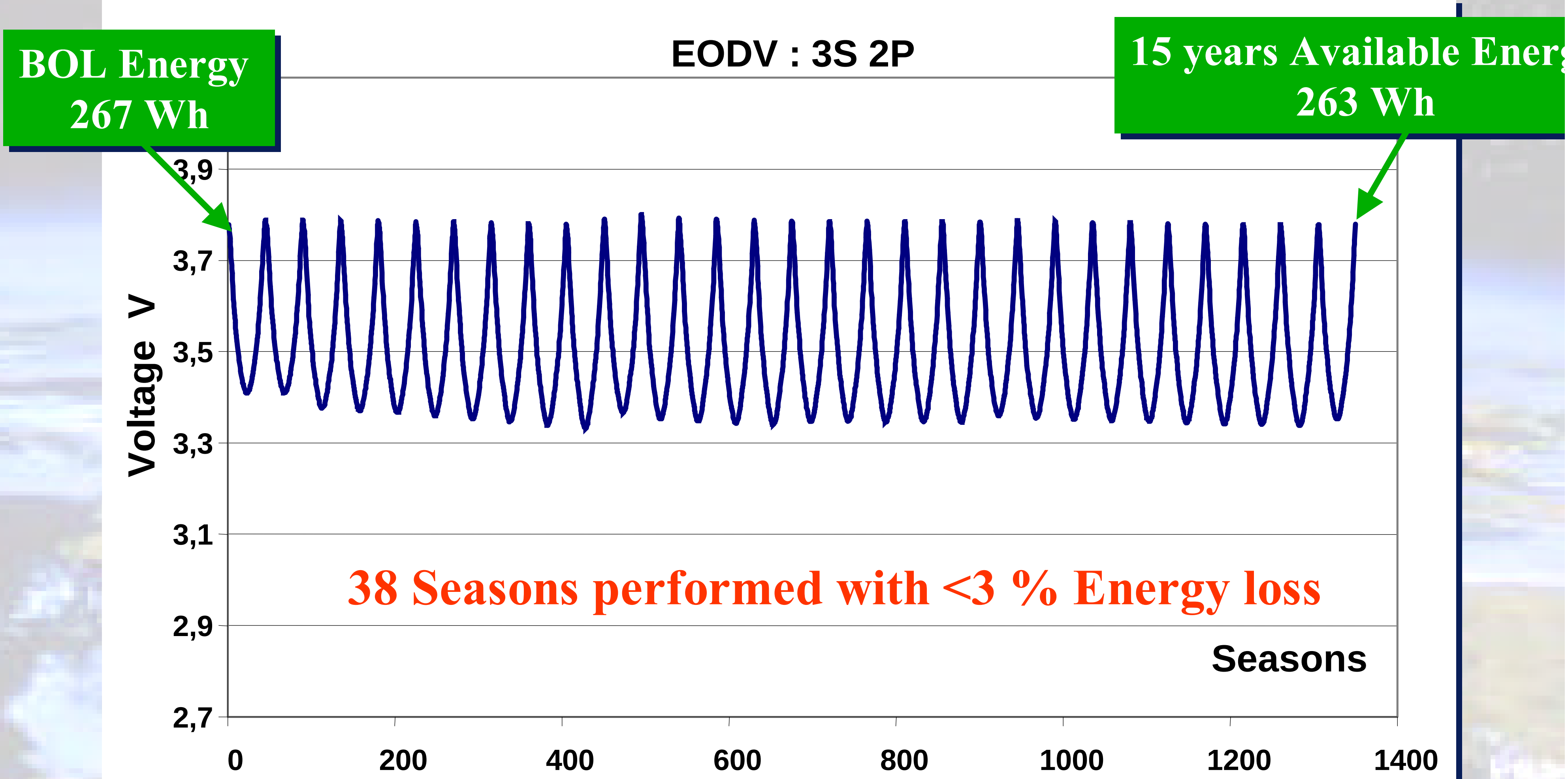
Cycling Test

TEST CONDITIONS

- GEO Cycling
  - From 60 to 85% DOD
  - EOCV from 4.00V to 4.1V
  - Charge current from 4 to 12 Amps
  - >30 cells in test

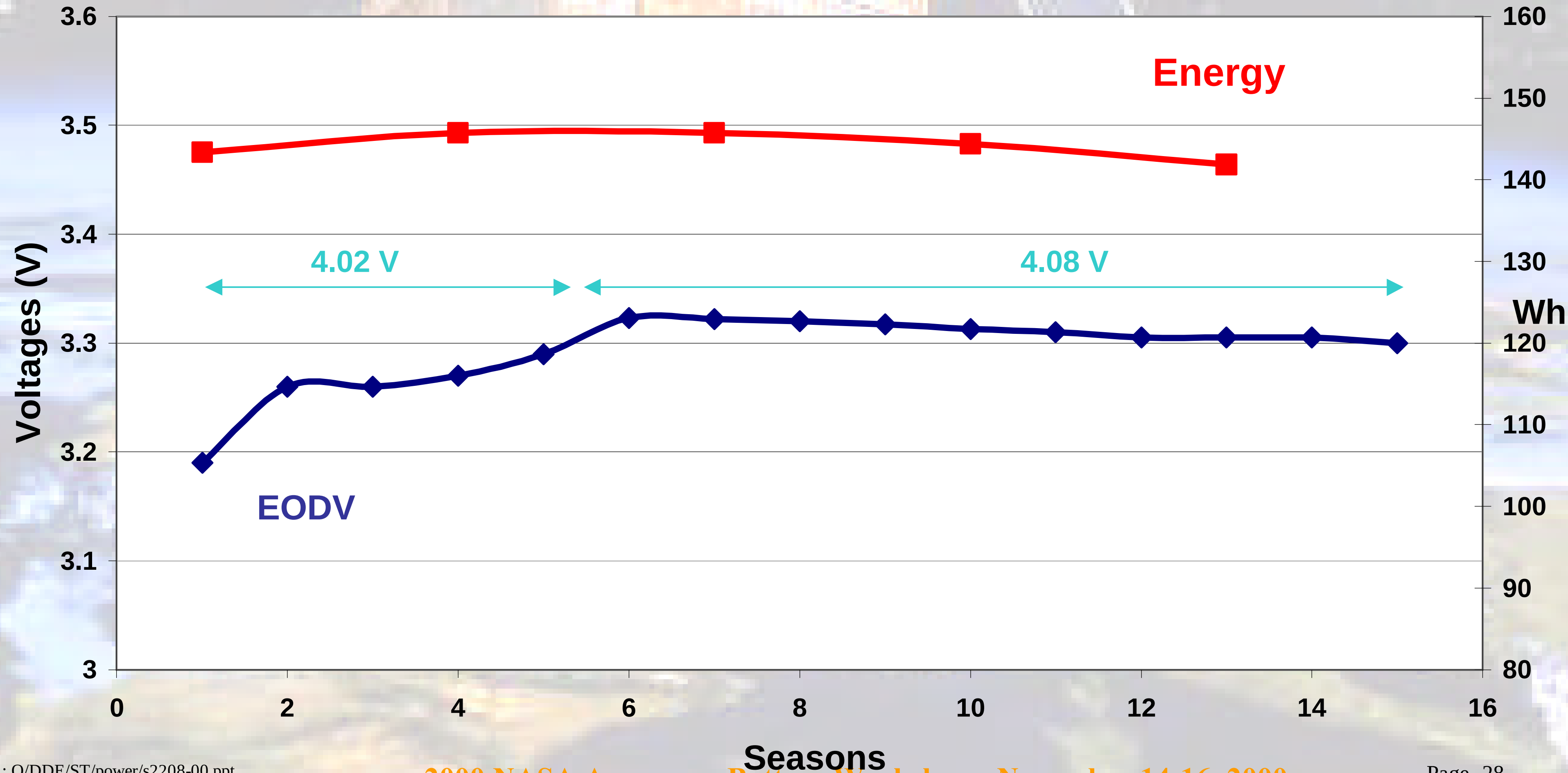
- LEO Cycling
  - From 10 to 40% DOD
  - EOCV from 3.80V to 3.90V
  - 16 to 70 cycles per day
  - >40 cells in test

Accelerated 80 % DOD GEO cycling



Accelerated 85 % DOD GEO cycling

UEODV at cycle 23 and Energy versus nb seasons
3S 2P T=25 °C



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GEO Life tests

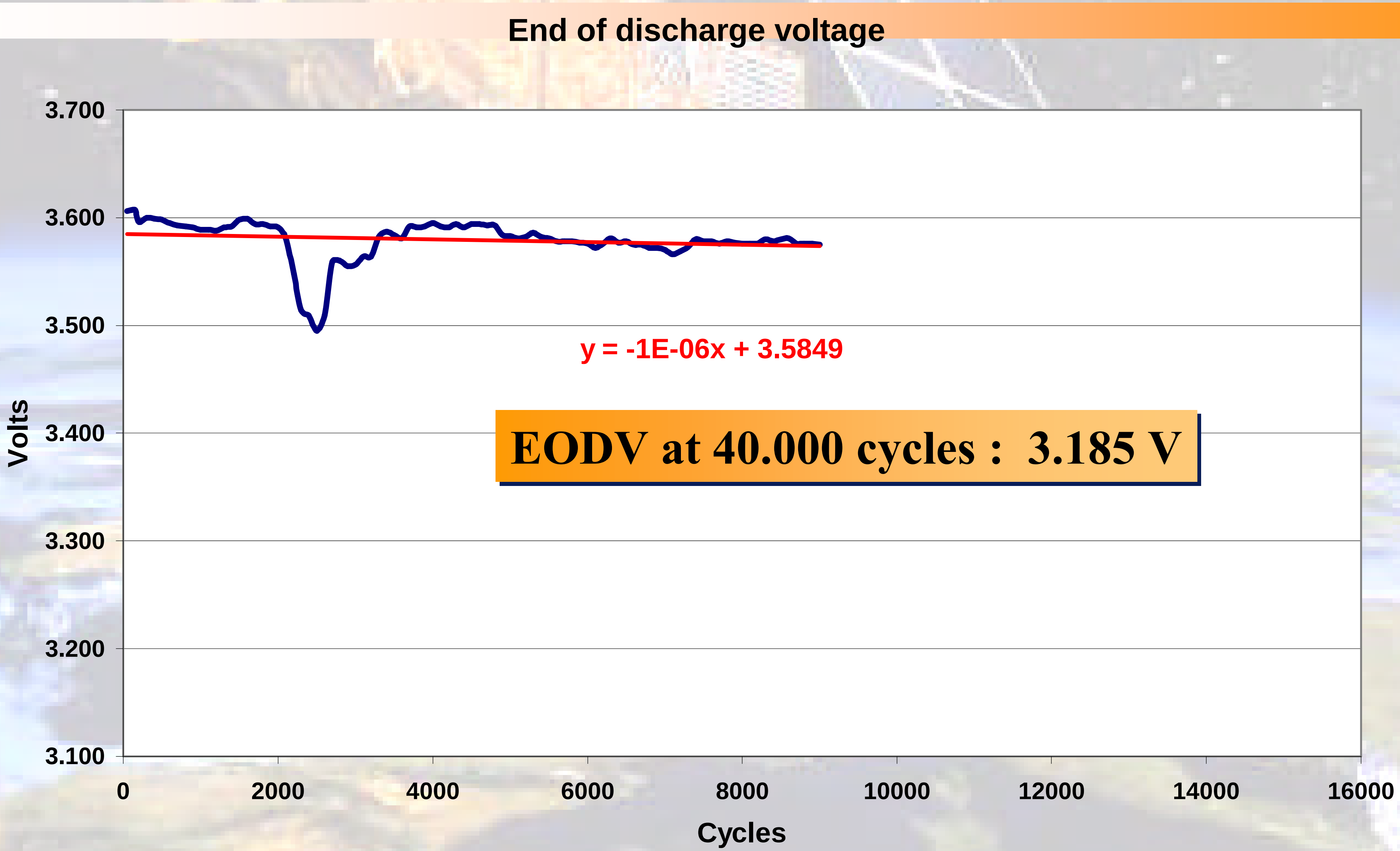
SYNTHESIS OF GEO TESTING ON SAFT CELLS

Cell Version	Test	DOD	Nb Cells Tested	Nb Seasons Performed	Fading Measured	Fading @15 years
Prototype	Semi accelerated 2c/day +PPS	40%	6 S Module	18	15%	**25%**
Prototype	Constant (charge C/5, disch : C/1.5)	60%	1	42 (1960 cycl)	17%	**12%**
Stentor	Semi accelerated 2c/day +PPS	40%	6 S Module	32	8%	**8%**
Stentor	Accelerated	80%	2S2P Module	30	11%	**11%**
VES140 0	Accelerated	80%	3S2P Module	36	3%	**2.5%**
VES140 0	Semi accelerated	85%	3S2P Module	18	0%	**-**
VES140 0	Accelerated	70% 60%	2 cells 4 cells	16 (710 cycles) 16 (706 cycles)	1.0% 1.0%	**3.0%** **2.9%**

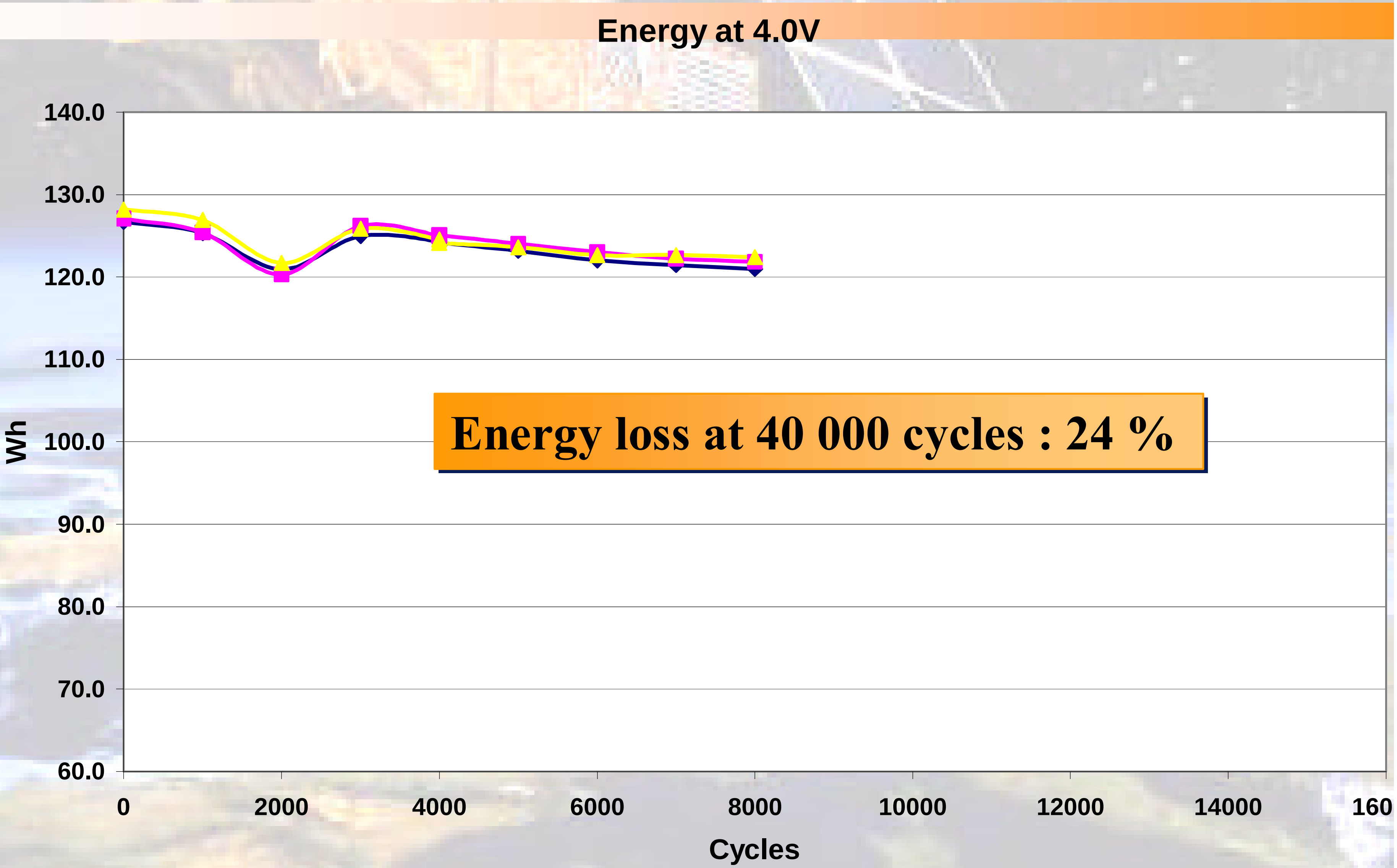
15 YEARS GEO FADING ENERGY <3%

Accelerated LEO Cycling : 20 % DOD, 3.9 V

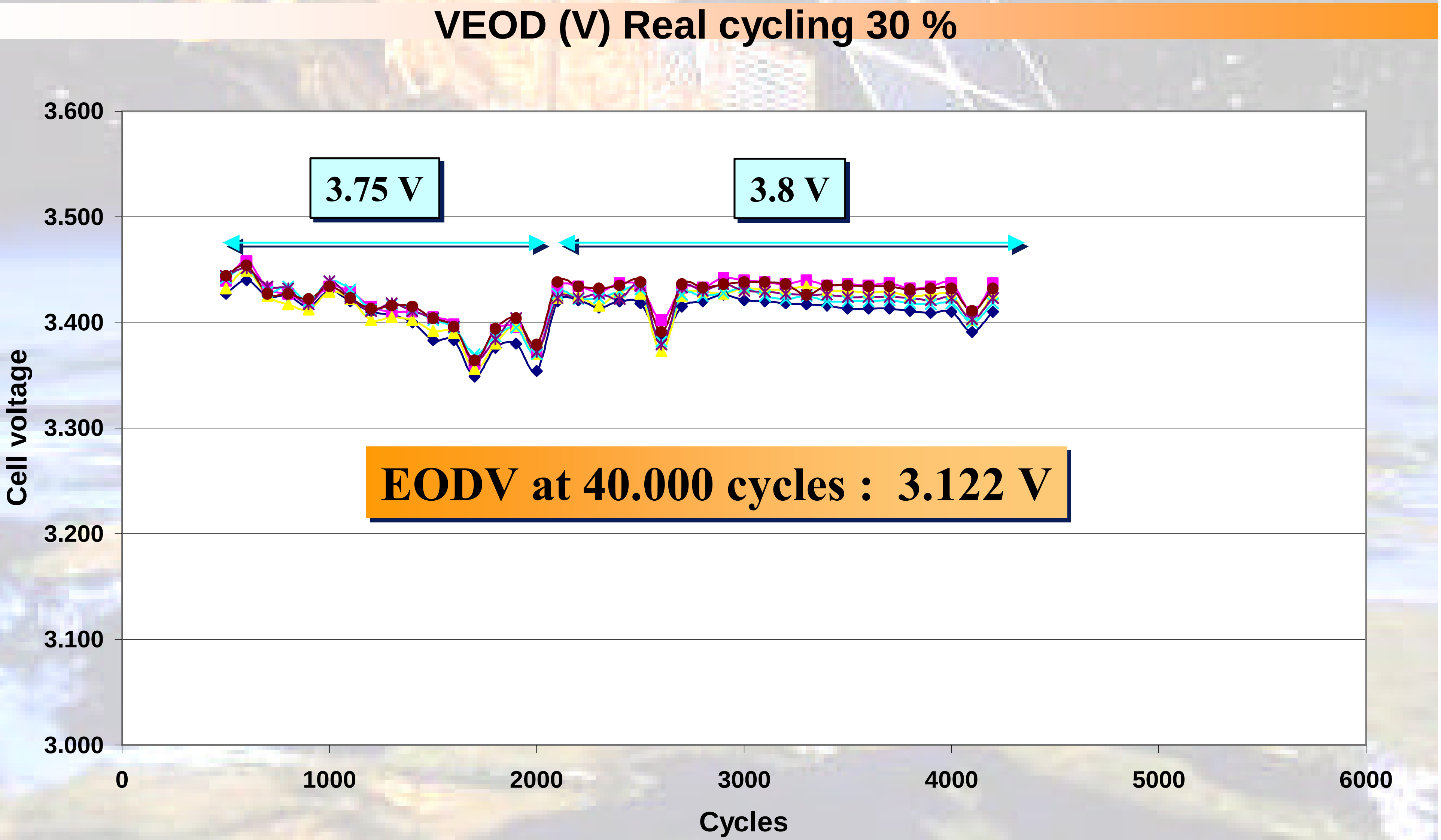
SAFT



Accelerated LEO Cycling : 20 % DOD, 3.9 V

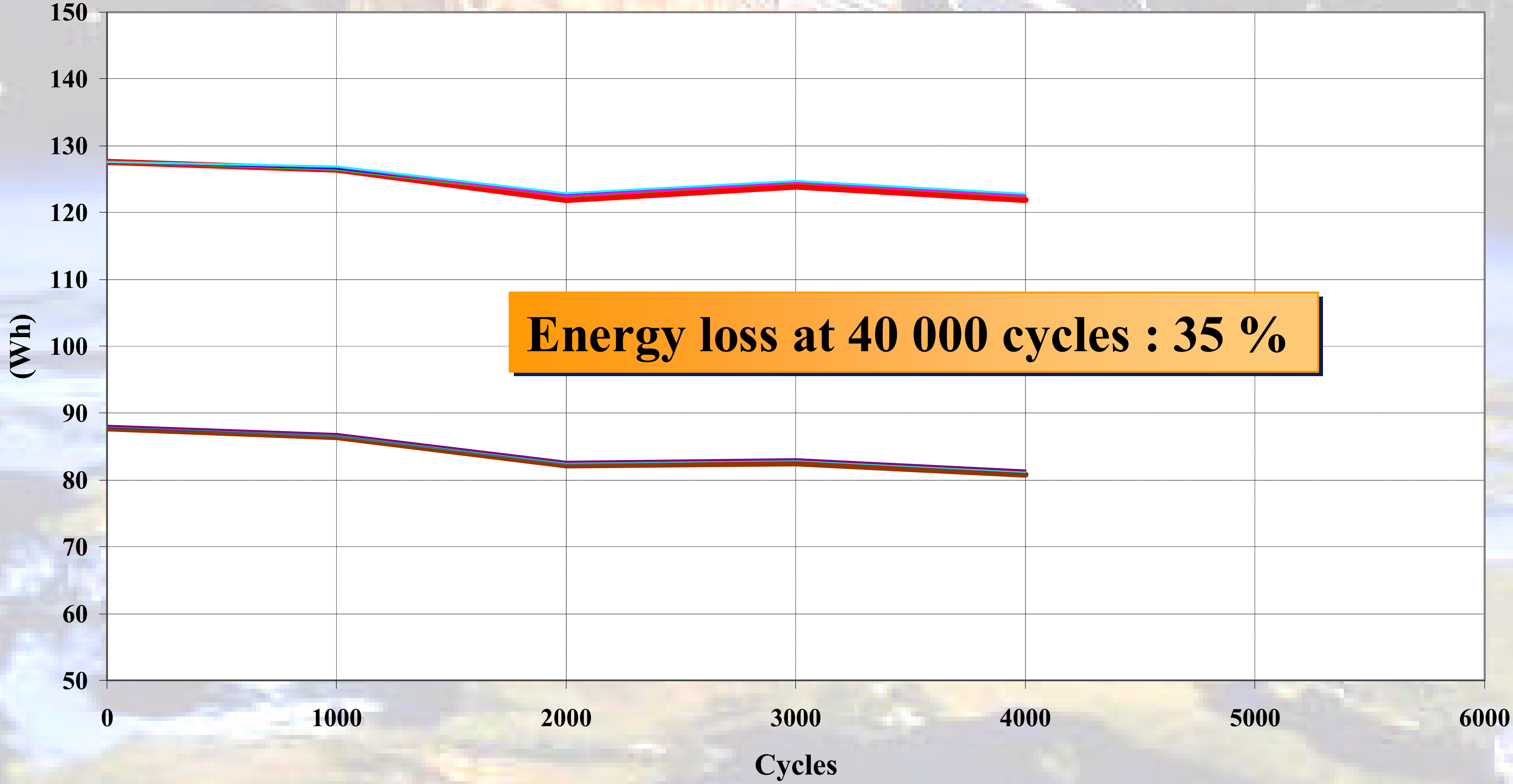


Real LEO Cycling : 30 % DOD, 3.8 V

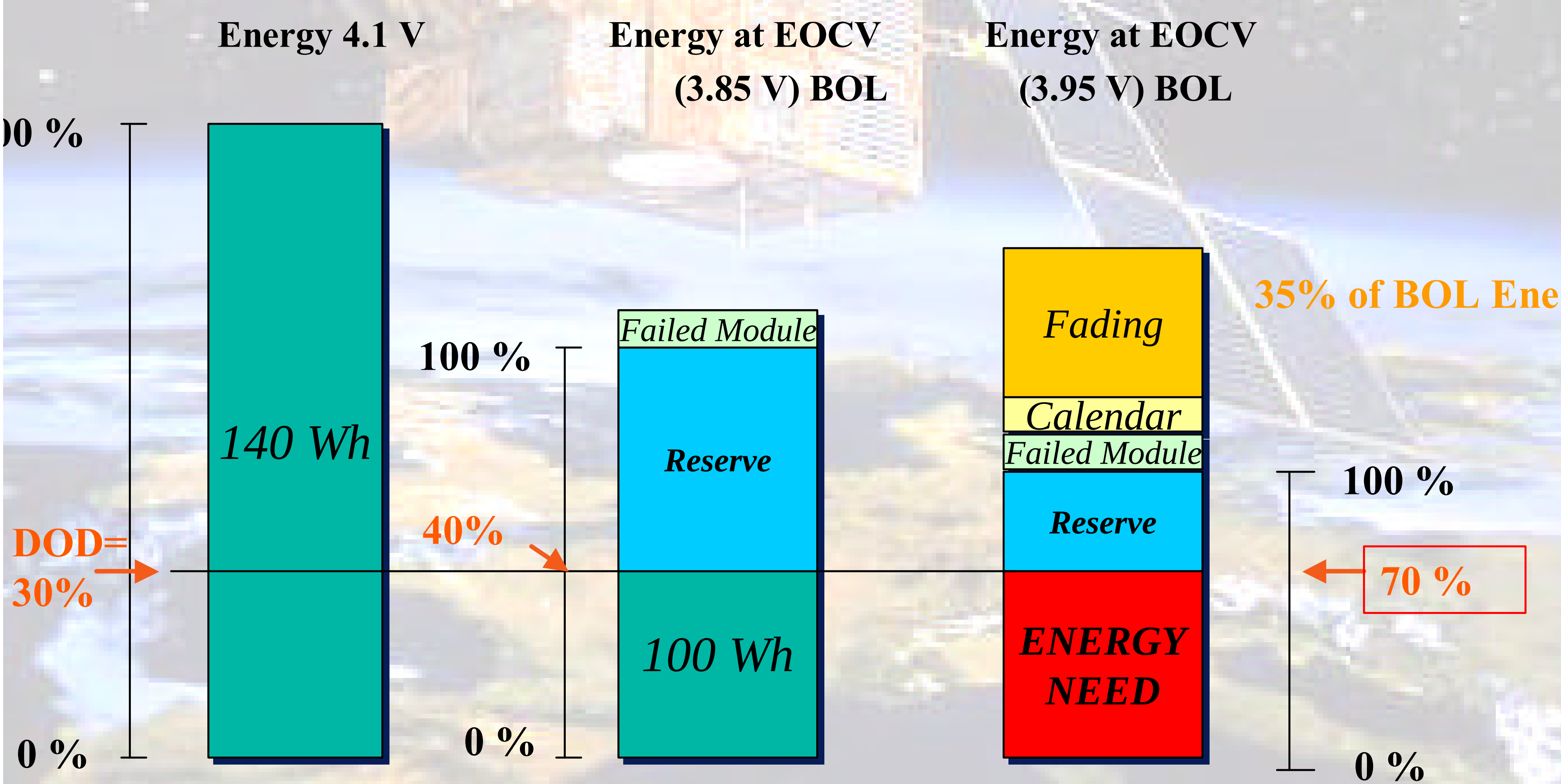


Real LEO Cycling : 30 % DOD, 3.8 V

ENERGY @ 4.00V & 3.80V



LEO BATTERY DESIGN



Conclusion

- VES 140 S cell :
  - Qualified by ESA, CNES, ASTRIUM and ASPI
  - Weight <1142g
  - Dimensions : Diameter 54, length 250 mm
  - Min Guaranteed Energy>132 Wh (Average 140 Wh) @ 4.10 V
  - Calendar Effect $t=X^2.e^{(6680/T-20.24)}+X.e^{(6989/T-20.59)}$
  - Cycling law $N=1.5*10^6*e^{-0.0846*DOD}$
    - 18 equivalent GEO years results at 80 % DOD (< 3 % fading)
    - 10.000 LEO cycles at 30 % DOD

Conclusion (Cont 'd)

- Negative Excess (Lithium) : 12%
- Self discharge < 3 mA
- Impédance <3 mOhm @ 20 et 60% DOD
- Air Transportation Autorization   N° 903-99
- Actual Industrial Line Capability :32 cells per day

VES 140 S qualified for Space use
Will fly on Stentor
>18 years GEO life test 80 % DOD
>2 years LEO life test 30 % DOD

High Specific Energy NiH_2 Batteries for GEO Satellites

Y. Borthomieu*, M.Fabre**

*** Defense and Space Division SAFT POITIERS**

**** Alcatel Space Industries CANNES**

AGENDA

- Qualification Status
- Cell modifications
- Battery changes
- Conclusions

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Qualification Status

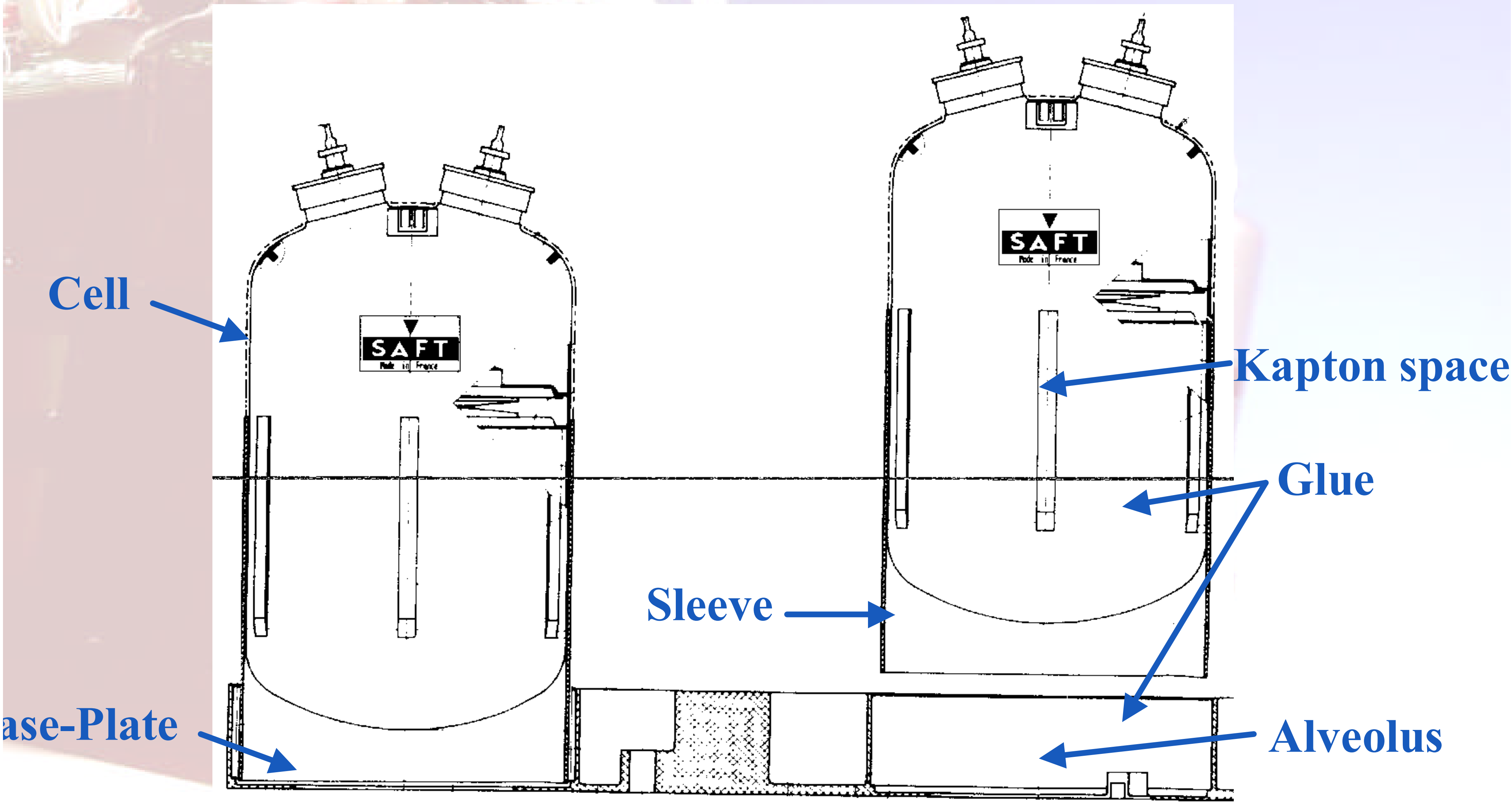
- Development started in 91
- Based on VHS design
- Qualification acquired in November 93
  - 3.5 inches cells
  - 12 to 32 cells per battery
  - 50 to 104 Ah
  - Adaptation to AN cells in 95

Qualification Status

Battery concept :

- Cell equipped with tubular aluminum sleeve
- Aluminum base-plate with alveolus
- From 12 to 32 cells
- Individual by-pass system
- Two redundant heater circuits
- Cells equipped with strain gages
- Thermistor and connectors
- Aluminum or Copper wiring

NiH_2 Battery for GEO



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Main characteristics

- Specific energy : 48 Wh/kg for 27 cells of 63 Ah
- Weight ratio cell/battery : 82 %
- Volume : 61*44*21 cm3 (2.4*1.7*0.82 inch3) for 27 cells battery
- DOD max : 80 % with one failed cell
- Thermal gradient (in failed case conditions) :
  - → Maximum Internal cell : 2.5 °C
  - → Maximum Between 2 cells : 9 °C
- Vibration : qualification up to 20 G both sine and random

S A F T

NiH_2 Battery for GEO

PROGRAMS

Satellite	Battery Type	Nb Battery per Satellite	Status
ARABSAT 2A	27*50 VHS	4+1 QM	Launched
ARABSAT 2B	27*50 VHS	4	Launched
ARTEMIS	23*60 VHS	2+1QM	Delivered
INDOSTAR (CAKRAWARTA)	22*52AN	2+2 IM	Launched
SINOSAT	27*56AN	4	Launched
SIRIUS 2 A	27*63AN	4 including 1 PFM	Launched
SIRIUS 2 B	27*63AN	4	Launched on EutelsatW4
ARABSAT 3A FM1	27*71AN	4 including 1 PFM	Launched
ATLANTIC BIRD 2	27*71AN	4	in manufacturing
HISPASAT1C	27*63AN	4	Launched
EURASIASAT	27*93AN	4 including 1 PFM	Delivered
ATLANTIC BIRD 1	23*97AN	2	In manufacturing
HOT BIRD 6	27*101AN	4 including 1PFM	In Design
STELLAT	27*93AN	4	In Design
GE12	27*89AN	4	In Design

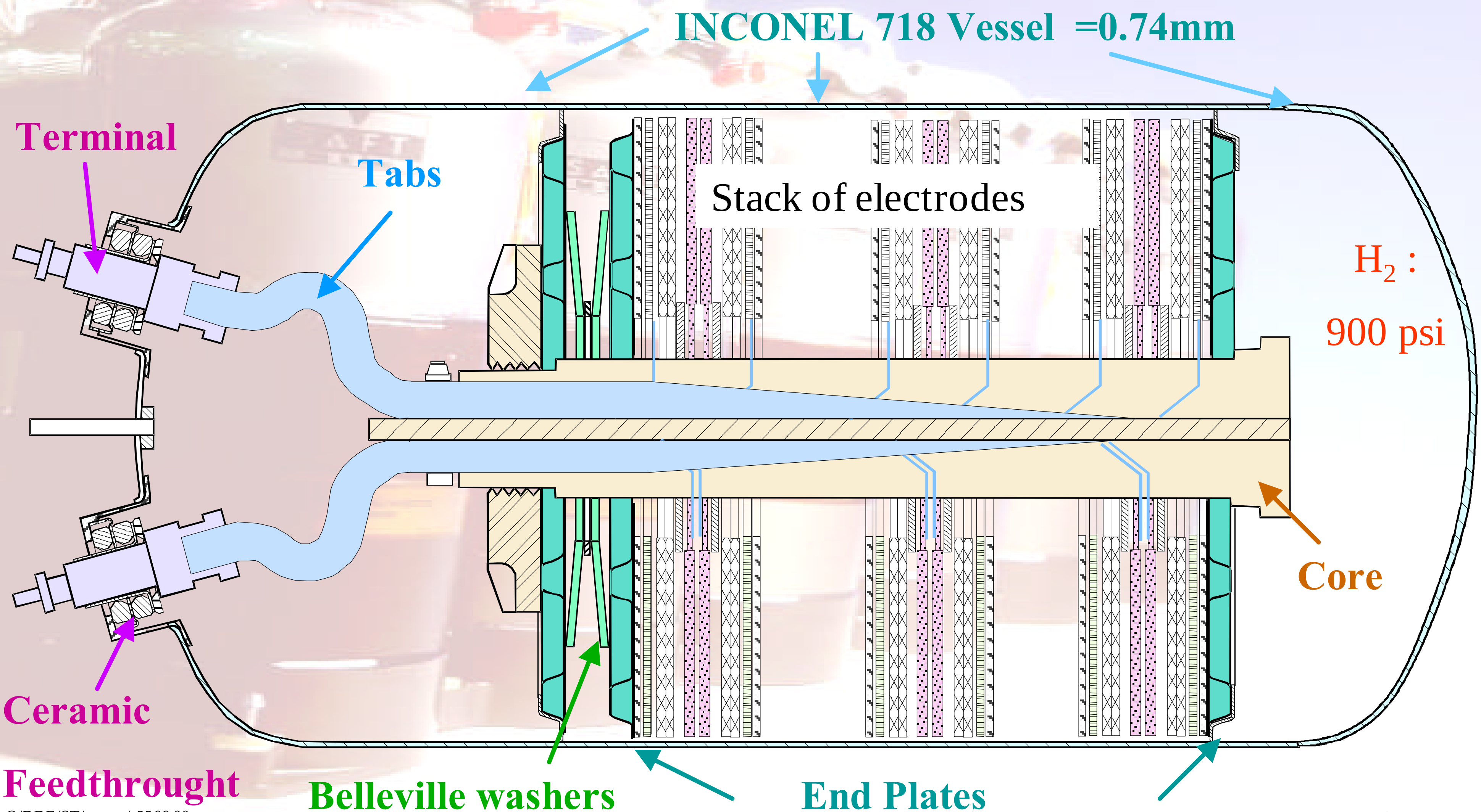
32 Batteries in operation

NiH_2 Battery for GEO

To Improve specific energy at battery level :

- Increase cell specific energy
- Optimize battery mounting

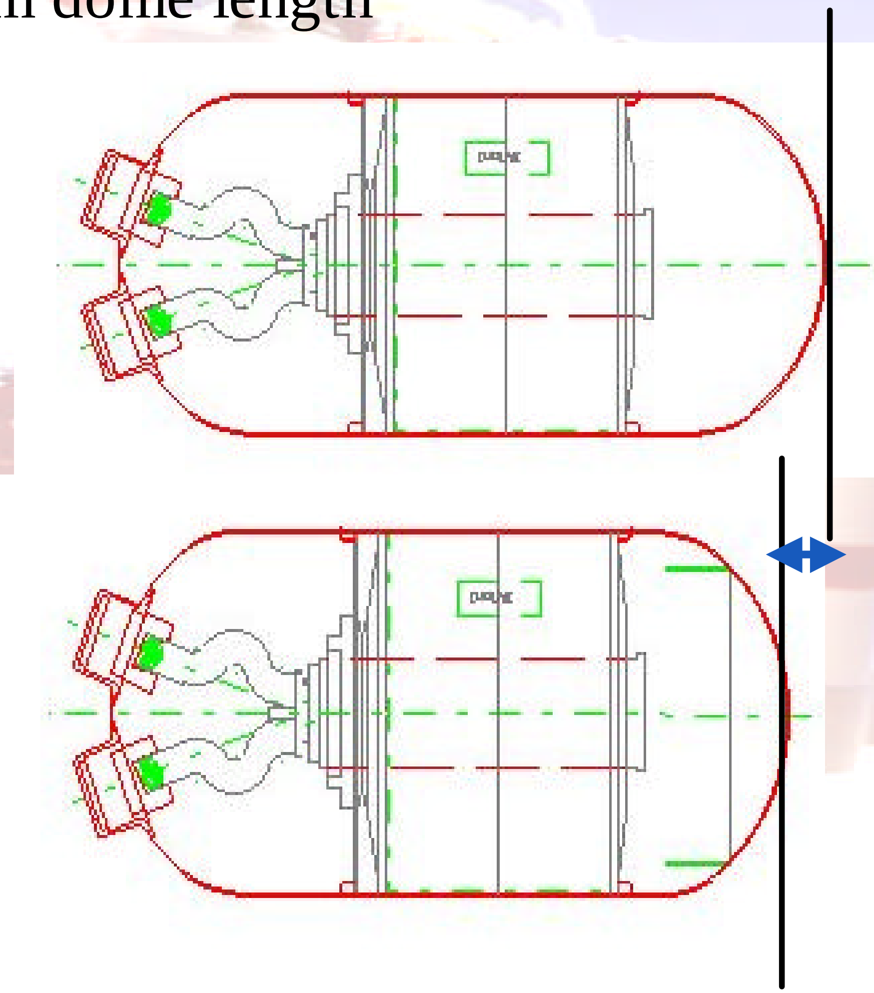
NiH_2 Cell


INCONEL 718 Vessel =0.74mm
Terminal
Tabs
Stack of electrodes
H_2 :
900 psi
Core
Ceramic
Feedthrought
Belleville washers
End Plates

NiH_2 Cell change 1

- Reduction bottom dome length

900 PSI
k=3.2



1000 PSI
k=2.8

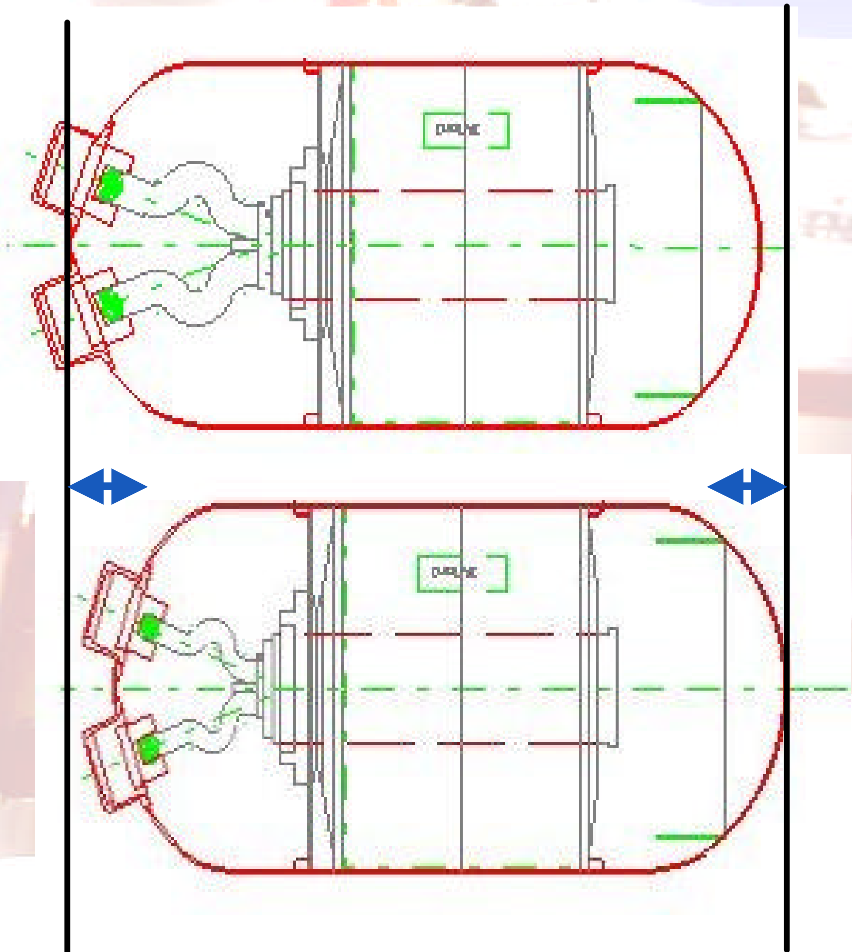
Already use on 4.

NiH_2 Cell change 1

- Impact of bottom dome length reduction:
  - At cell level for AN 101 :
    - 2.5 % Weight reduction over 2 294 g
  - At battery level for 9 kW satellite with 4 packs of 27AN101 :
    - 2.2 % Weight reduction over 291.6 kg

NiH$_2$ Cell change 2

- Transfert from top dome cyclindrical part to bottom dome



Reduction of tabs length

NiH_2 Cell change 2

- Impact of transfering top dome cyclindrical part to bottom dome

  - At cell level for AN 101 :
    - 5.8 % Weight reduction over 2 236 g

  - At battery level for 9 kW satellite with 4 packs of 27AN101 :
    - 4 % Weight reduction over 285 kg

NiH_2 Cell change 3

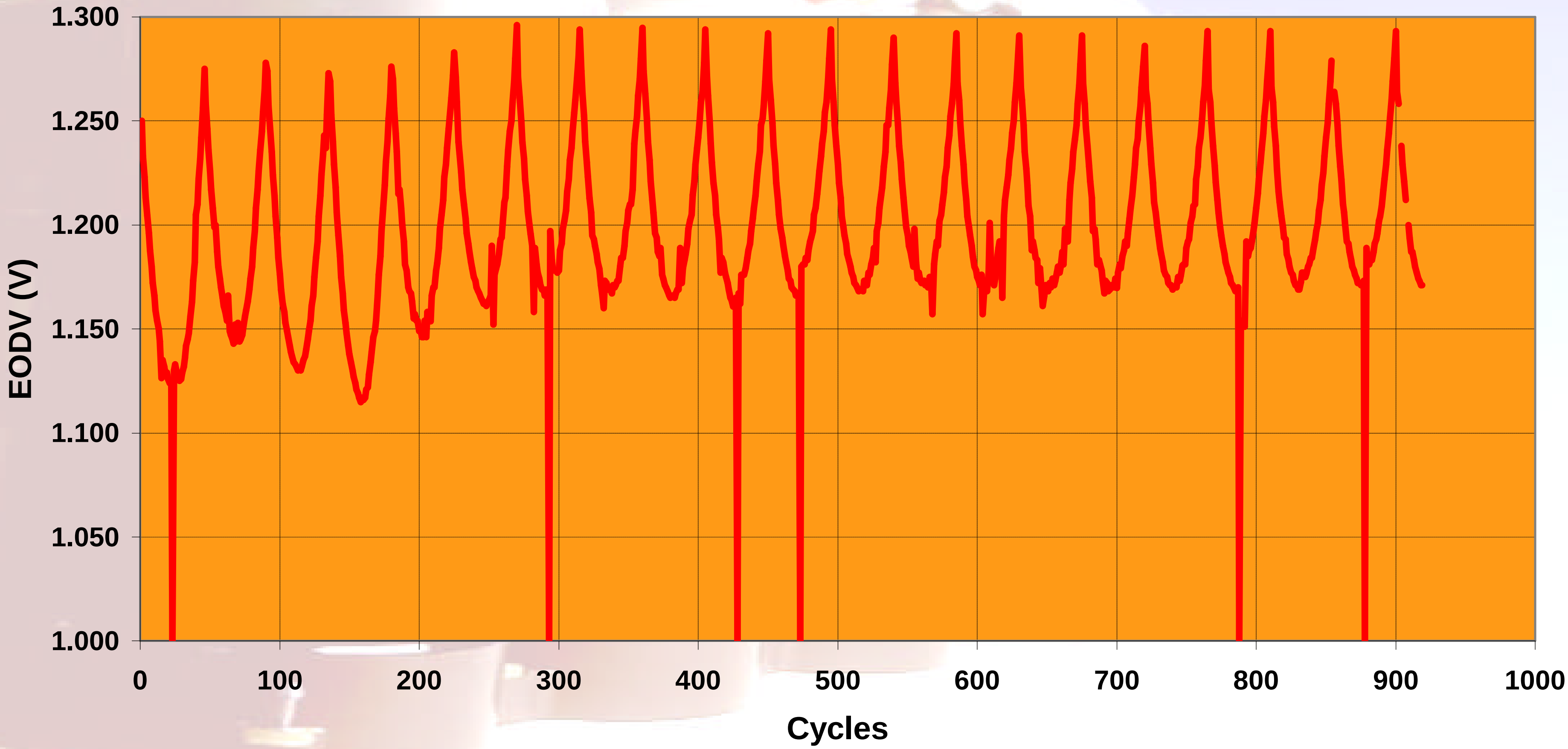
- Decrease of width and/or thickness of tabs
  - Tabs were oversized considering current
    - Criteria : voltage drop less than 45 mV at C rate
  - At cell level for AN 101 :
    - 2 % Weight reduction over 2 105 g
  - At battery level for 9 kW satellite with 4 packs of 27AN101 :
    - 1.7 % Weight reduction over 274 kg

NiH_2 Cell changes

- Change 1 and 2 have been used for Eurasiasat batteries
  - Life test performed to validate the change
    - 4 cells tested
    - Semi-accelerated conditions :
      - charge C/10 k=1.15 + Trickle charge C/100
      - discharge C/1.5, 72 min, 80 % DOD
      - 2 cycles per day
      - no solstice
- Change 3 is using on current programs
  - Life test will be performed on HB6

Eurasiasat life test

Average End of discharge voltage



Battery change 1

- Use of the Aluminum wiring instead of Copper
  - Qualification acquired in 96
  - Use of the ESA rules forderating
  - Weight saving at battery level for 9 kW :
    - 2.2 % over 280 kg

Battery change 2

- Charge management modification :
  - Decrease of the charge temperature from 0 °C to -10 °C
    - Increase of the delivered capacity
  - Weight saving at battery level for 9 kW :
    - 3 % over 274 kg
  - Is planned to be used on Hot Bird 6

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Battery Performances

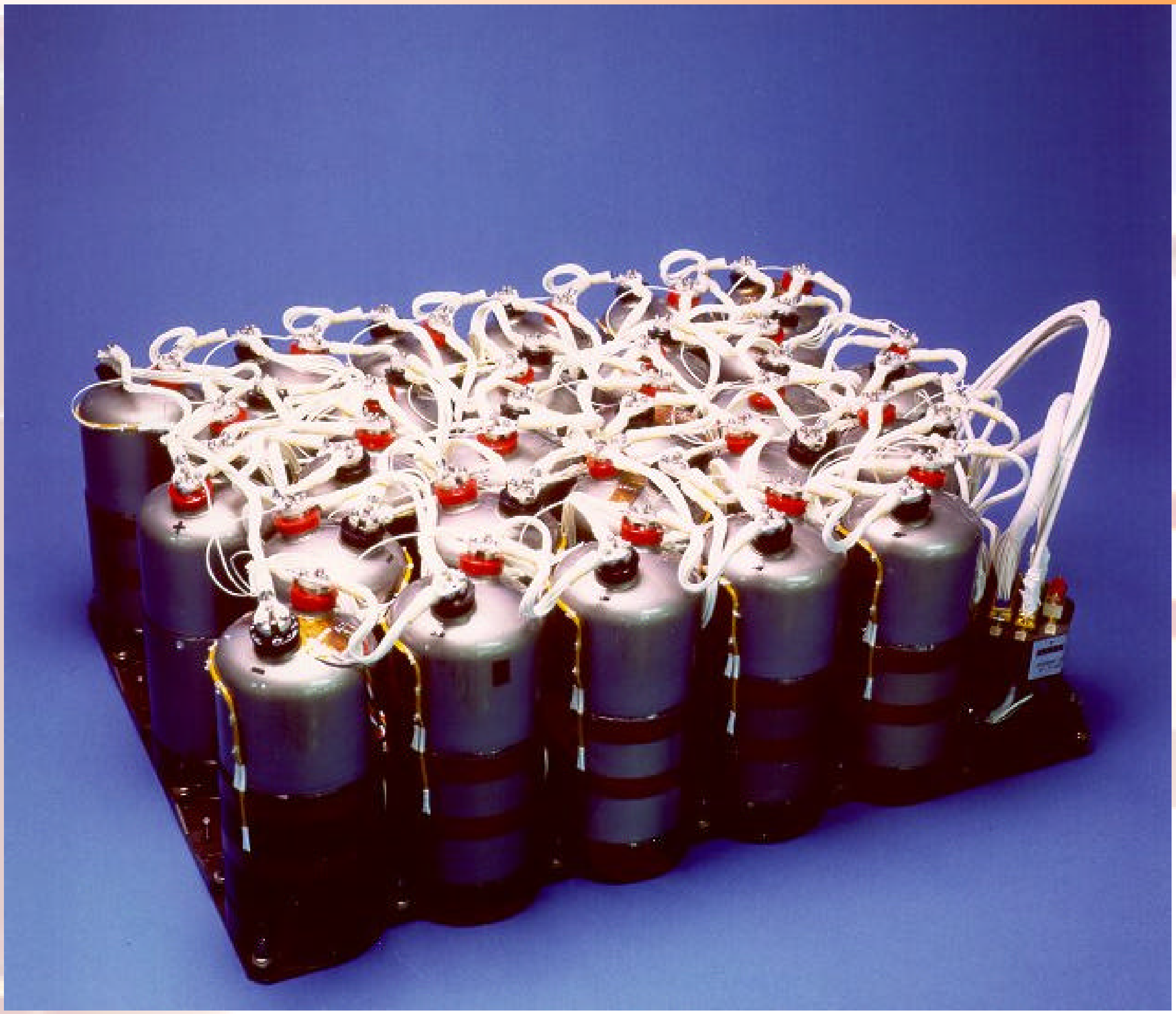
- By performing ASPI test :
  - One orbital cycle 80 % DOD
  - Recharge k=1.15 and discharge C/1.5 down to 1 V

FIRST DESIGN WITH ALUMINUM WIRING

	C Ah	T °C	Weight (kg)	**Sp En (Wh/kg)**
Sirius II : AN63	65.2	0 °C	186	**47.3**
Arabsat 3 : AN71	72	0 °C	204	**47.6**

Battery Performances : Arabsat 3 A

Battery Performances : Arabsat 3 A



Battery Performances

Battery Performances

DESIGN WITH CHANGES 1 and 2 AT CELL LEVEL

(MOP and Upper Stack)
ALUMINUM WIRING

	C Ah	T °C	Weight (kg)	Sp En (Wh/kg)
Eurasiasat : AN93	99	-2.5 °C	255	**51**

MORE THAN 8 % SPECIFIC ENERGY INCREASE

CONCLUSION

- First phase of improvement done on EURASIASAT (changes on MOP and upper stack)
  - weight gain over the prediction (8 % over 6 %)
- Second phase in validation on current programs, Hot Bird 6, (changes on tabs, charge management) will give 5 % weight gain more to reach

53 Wh/kg at battery level

LITHIUM ION DD CELLS

EVALUATION FOR SPACE APPLICATION

HAIYAN CROFT

BOB STANIEWICZ

SAFT R&D CENTER

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OVERVIEW

- CHEMISTRY
- CHARACTERIZATION OF DD CELLS
- HOW ACCELERATED TESTING IS PERFORMED
- CALENDAR RESULTS
- TESTING RESULT AND PREDICTED CYCLE LIFE

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CHEMISTRY

- **CHEMISTRY**
  - **POSITIVE MATERIAL:** $LiNi_{1-x-y}Co_xM_yO_2$
  - **NEGATIVE IS ADMIXTURE OF TWO GRAPHITES WITH NON-PVDF BINDER**
- **CAPACITY:** 9.2 AH
- **ENERGY DENSITY:** 135 WH/KG

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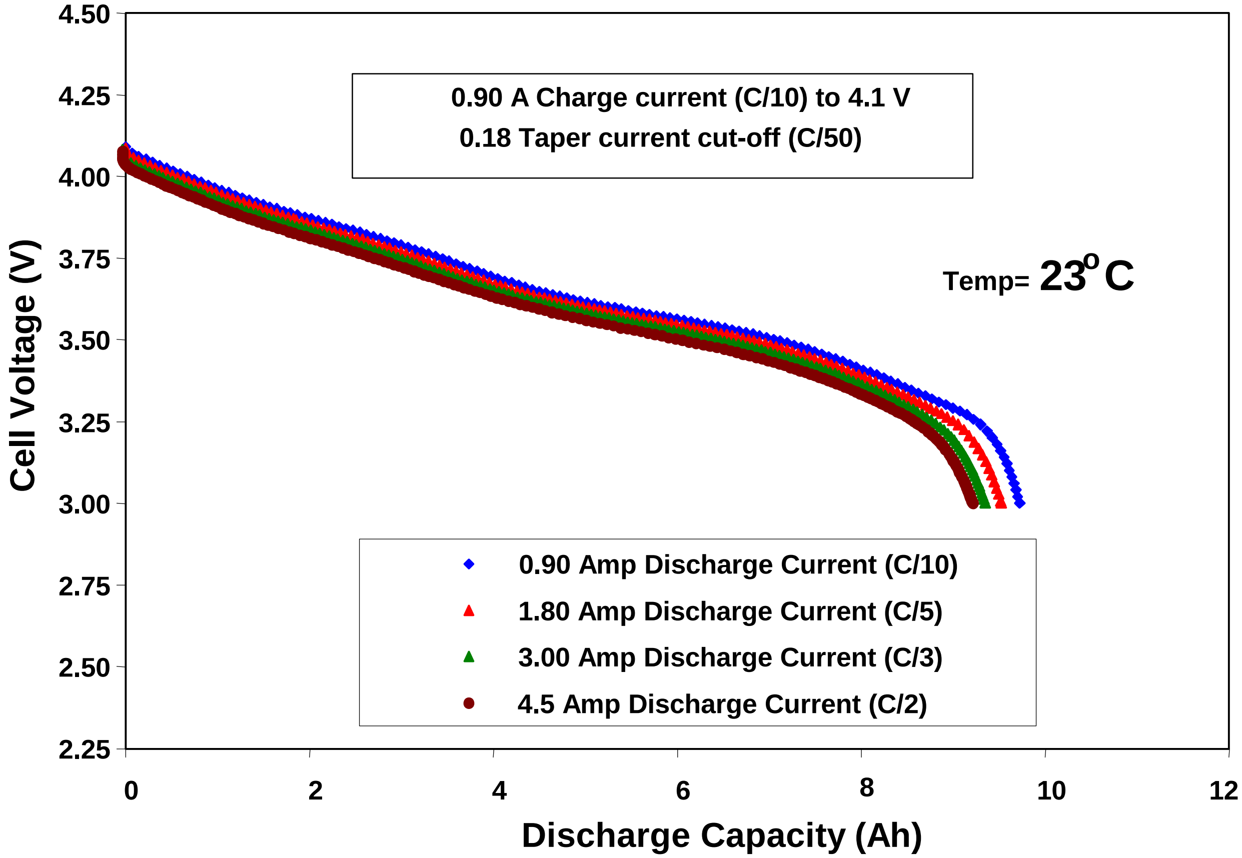
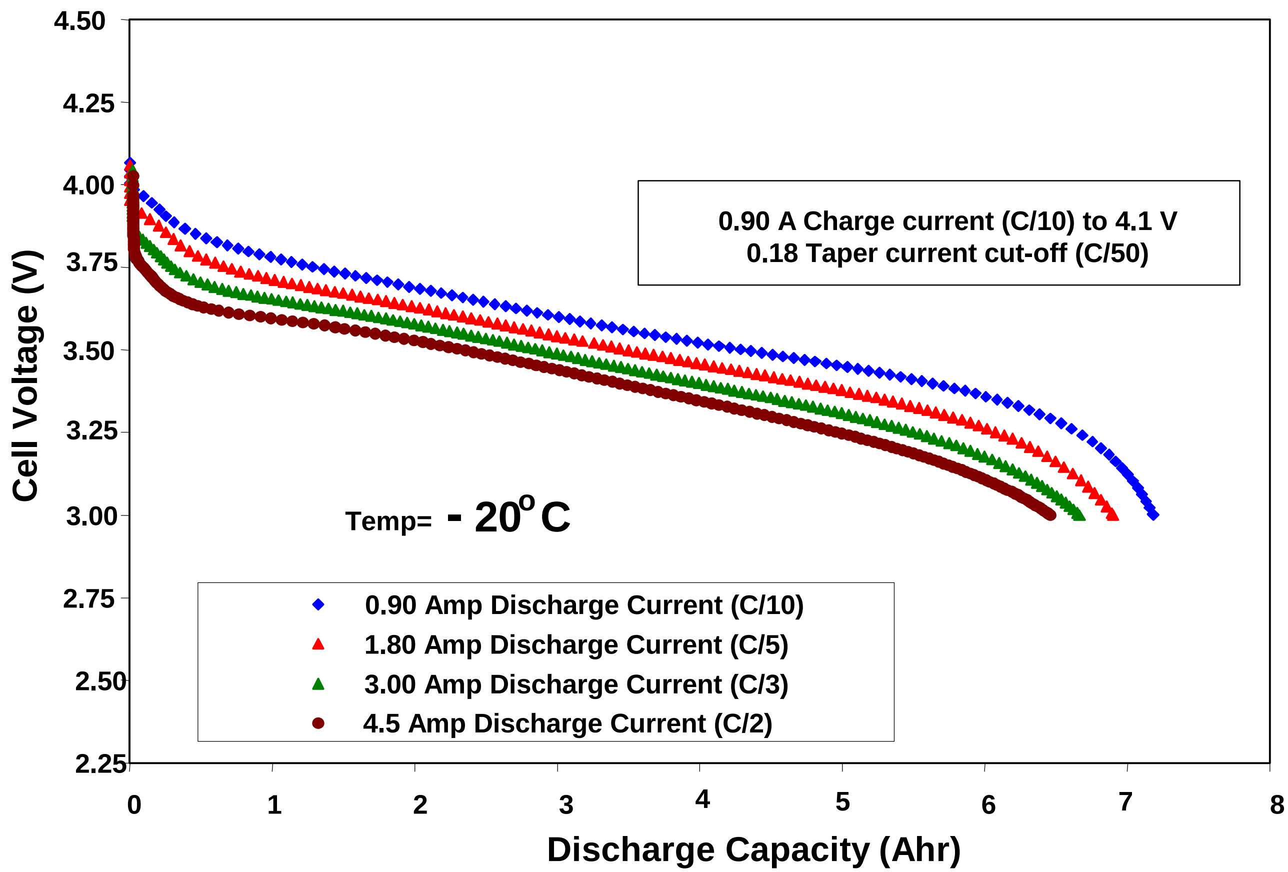
HARDWARE

- 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

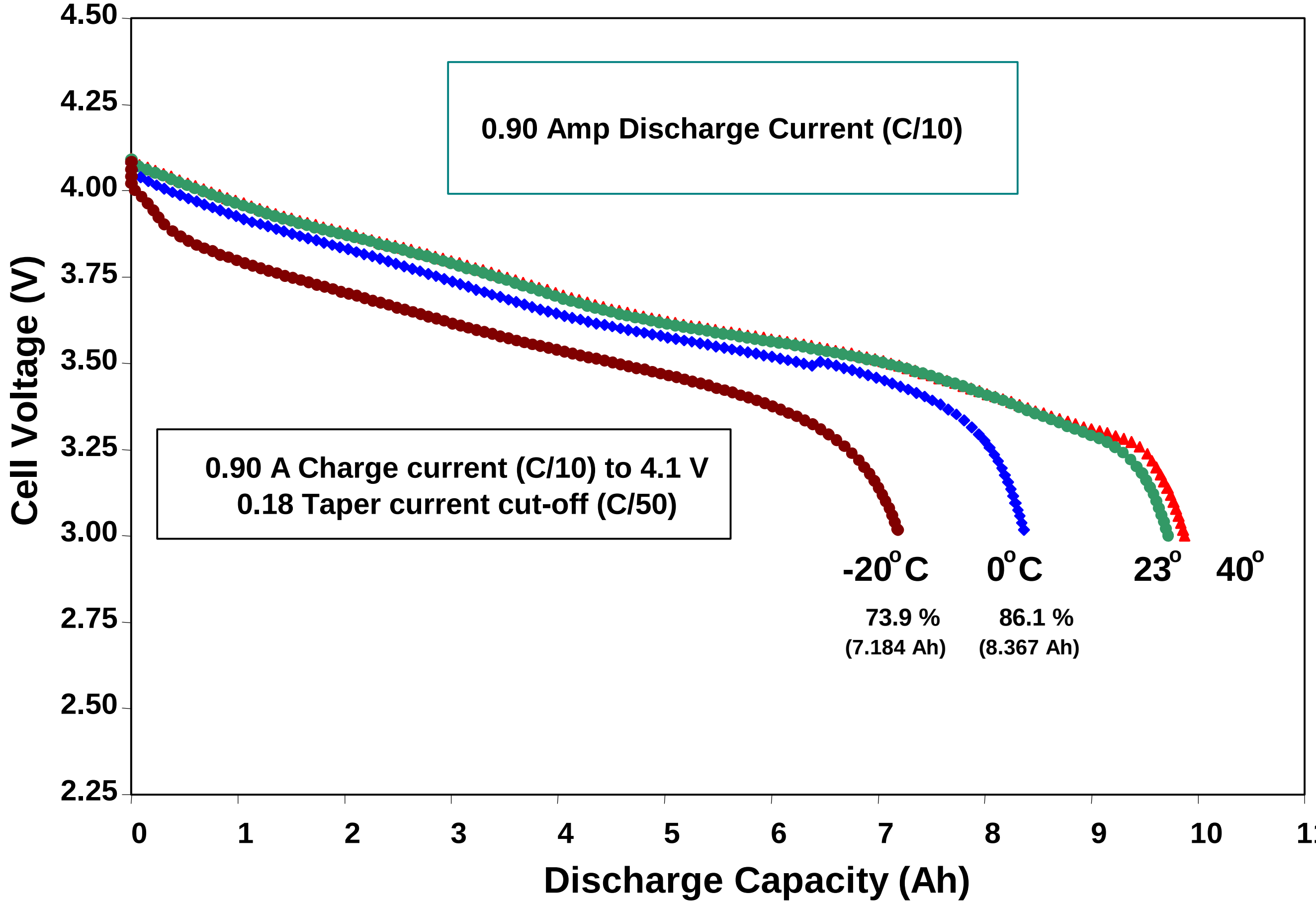
Discharge Rate characterization at 23ºC



Discharge Rate characterization at -20°C



Discharge Performance at Various Temperatures



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- LEO AND GEO CYCLING DEMONSTRATING PERFORMANCES FOR PLANETARY AND INTERPLANETARY APPLICATIONS

DEPTH OF DISCHARGE	CYCLES ACHIEVED TO DATE	RESULTS
30%	10,000	PREDICTED FOR 40K CYCLES
60%	1500	

ACCELERATED TESTING METHODS

WE JUDGED WHAT MIGHT BE REASONABLE, ACCELERATED TRADE-OFFS OF <u>TIME</u> AND <u>CURRENT</u> 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

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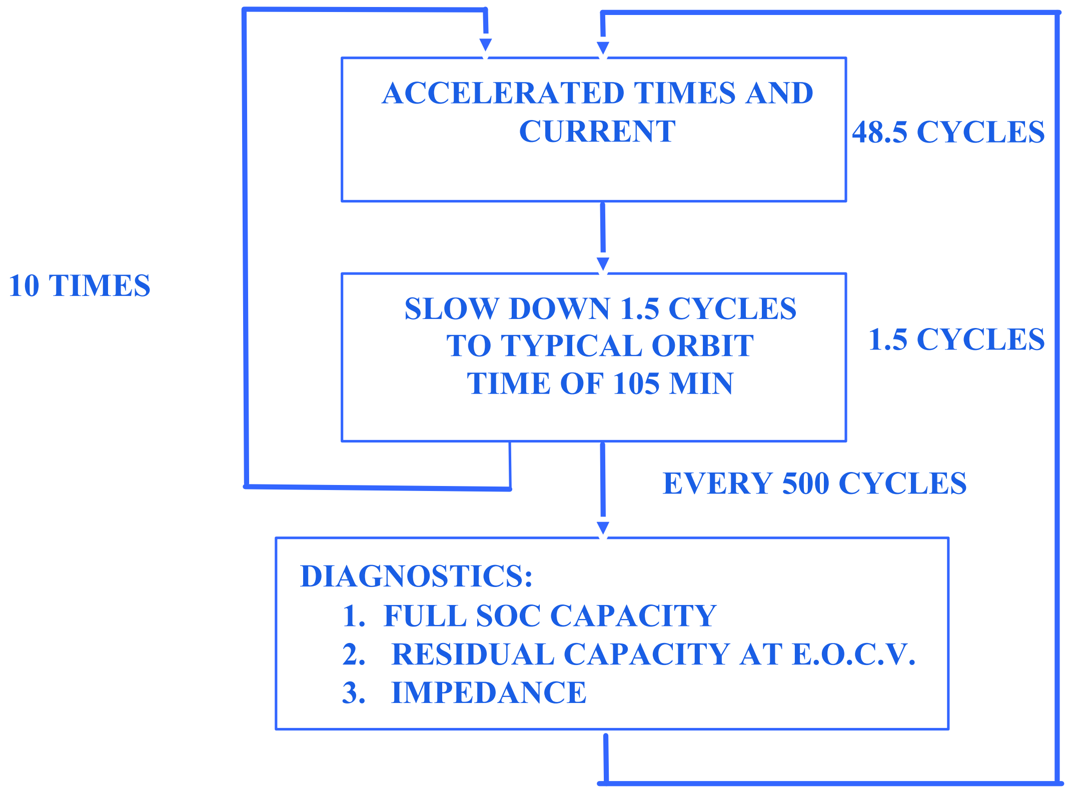
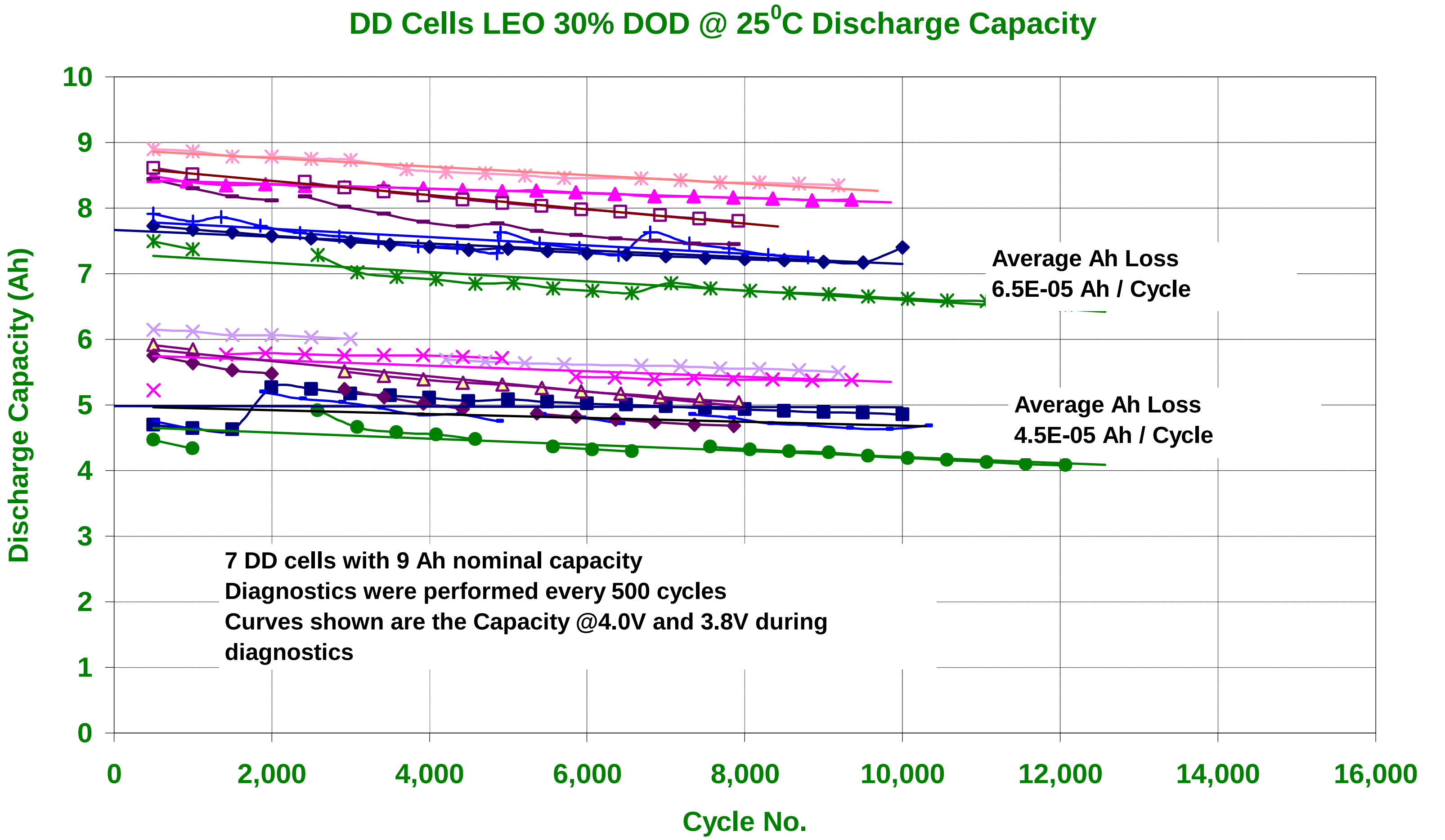
LEO TESTING



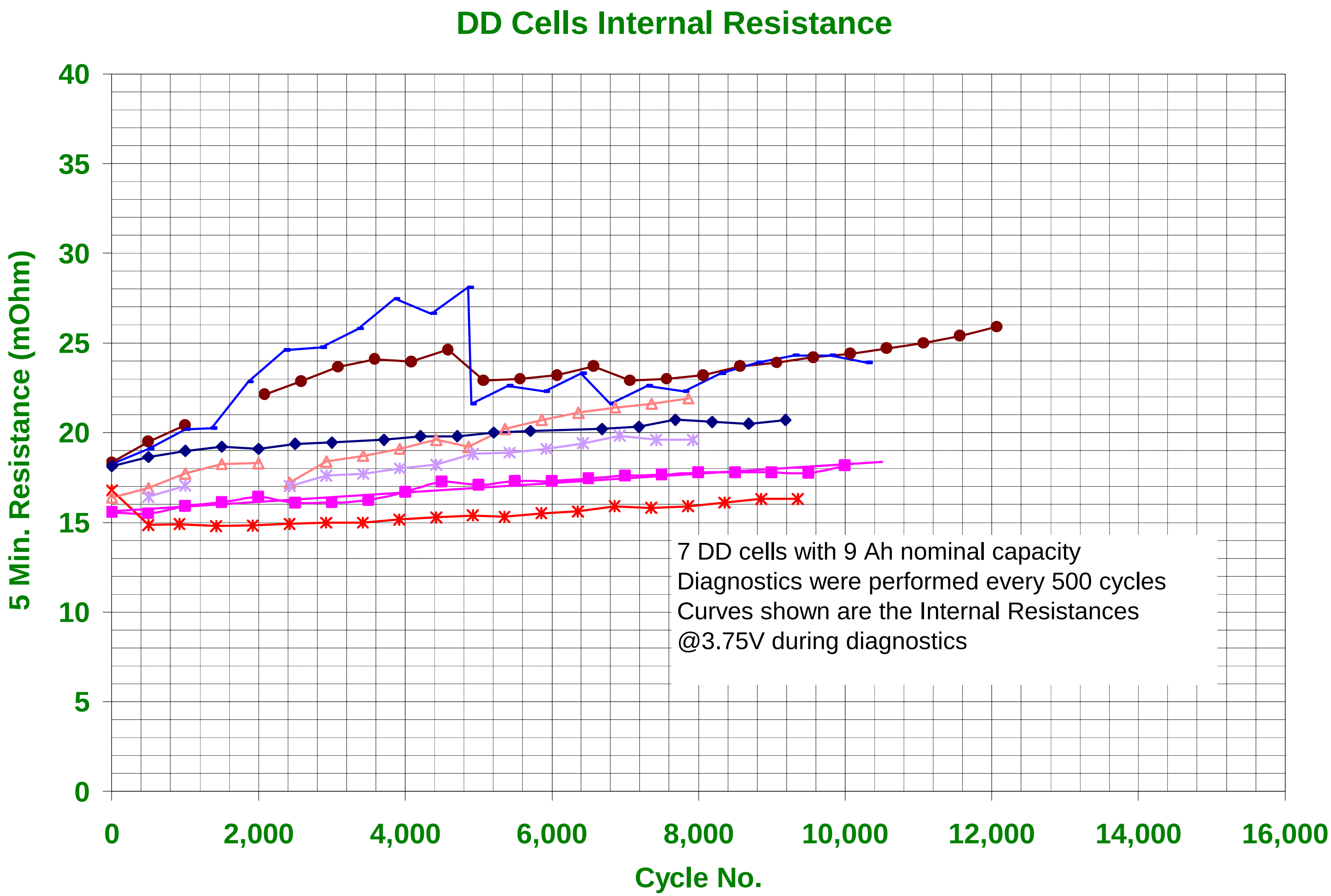
SLOWING DOWN TO REAL TIME ORBIT RATES OF 105 MIN. EVERY 50 CYCLES IS ESSENTIAL SO THAT E.O.D.V. REFLECTS TRUE ORBIT CONDITIONS

LEO TESTING

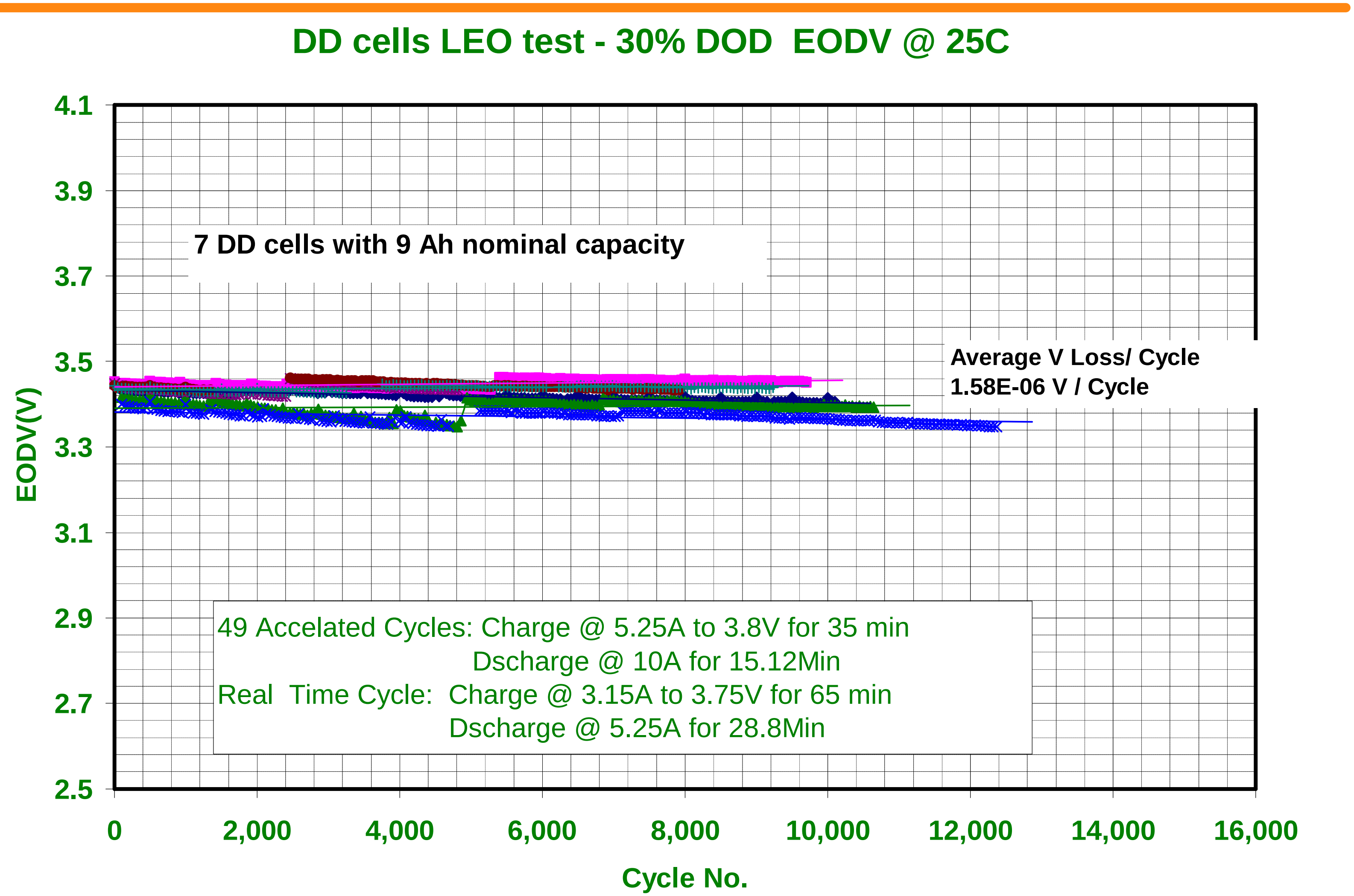


DD Cells LEO 30% DOD @ 25⁰C Discharge Capacity
Discharge Capacity (Ah)
Cycle No.
10
9
8
7
6
5
4
3
2
1
0
0
2,000
4,000
6,000
8,000
10,000
12,000
14,000
16,000
Average Ah Loss
6.5E-05 Ah / Cycle
Average Ah Loss
4.5E-05 Ah / Cycle
7 DD cells with 9 Ah nominal capacity
Diagnostics were performed every 500 cycles
Curves shown are the Capacity @4.0V and 3.8V during
diagnostics

LEO TESTING


DD Cells Internal Resistance
5 Min. Resistance (mOhm)
40
35
30
25
20
15
10
5
0
0
2,000
4,000
6,000
8,000
10,000
12,000
14,000
16,000
Cycle No.
7 DD cells with 9 Ah nominal capacity
Diagnostics were performed every 500 cycles
Curves shown are the Internal Resistances
@3.75V during diagnostics

LEO TESTING


DD cells LEO test - 30% DOD EODV @ 25C
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
EODV(V)
0
2,000
4,000
6,000
8,000
10,000
12,000
14,000
16,000
Cycle No.
7 DD cells with 9 Ah nominal capacity
Average V Loss/ Cycle
1.58E-06 V / Cycle
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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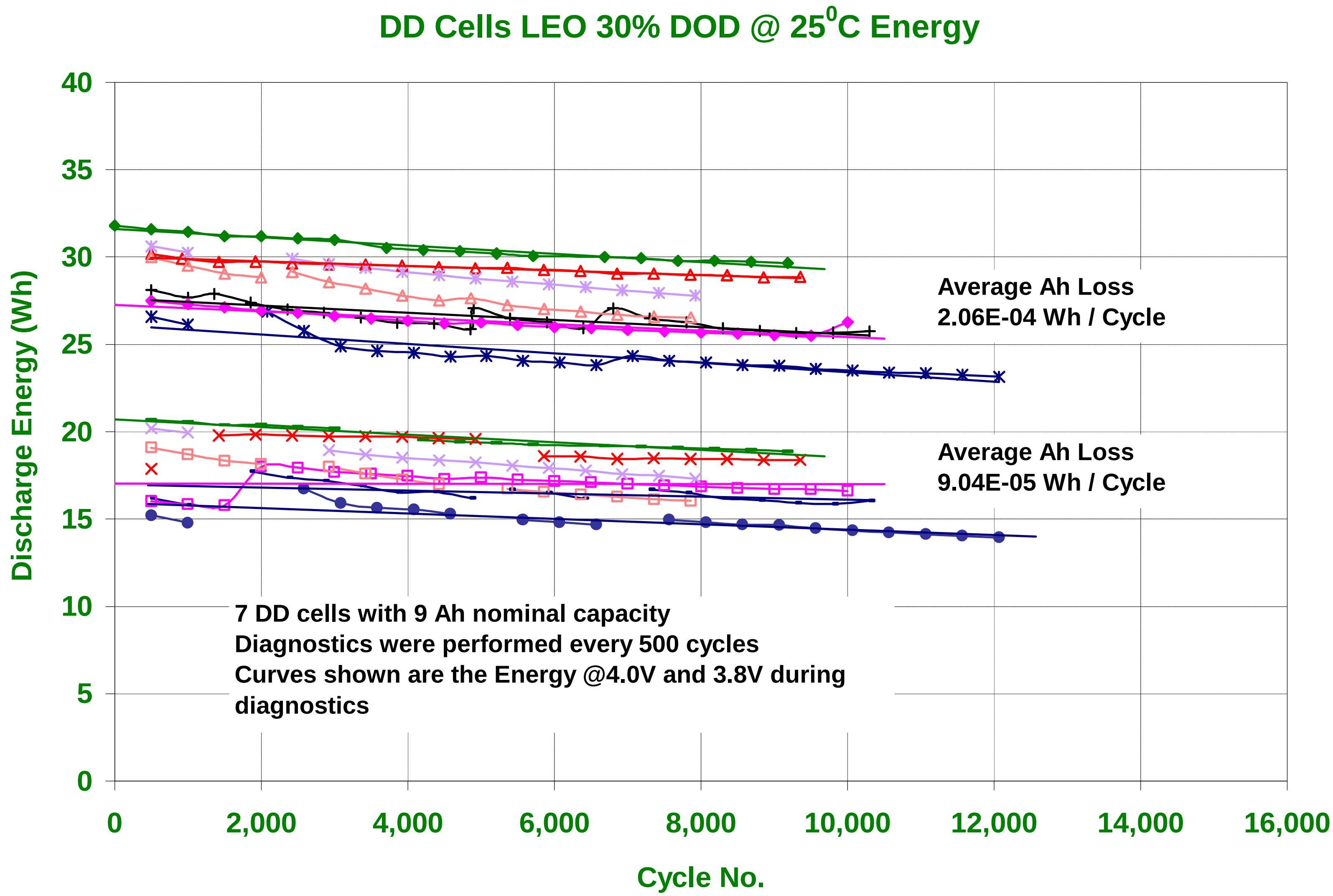
LEO TESTING



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CYCLE LIFE EXTRAPOLATION

PROTOTYPE DD CELLS (B.O.L. = 30 Wh)

Depth Of Discharge %	Cycles Achieved	Wh Fade Rate @ 4V % Per Cycle	Typical Req. For Cycles	E.O.M. Energy* Wh 25°C
30	12,000	.000206	40,000	21.8
60	1500	.0011	1,500	29.9

*NOT CORRECTED FOR CALENDAR LIFE

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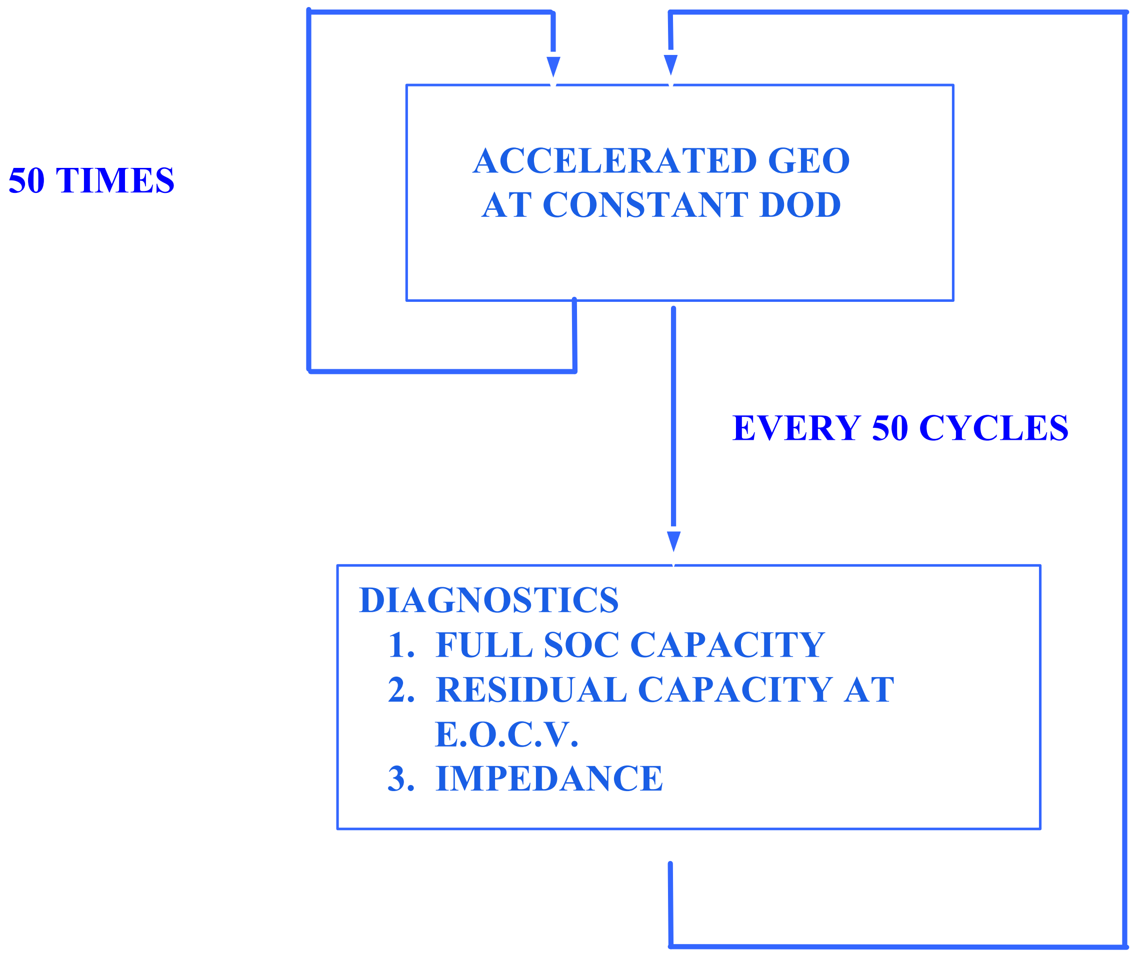
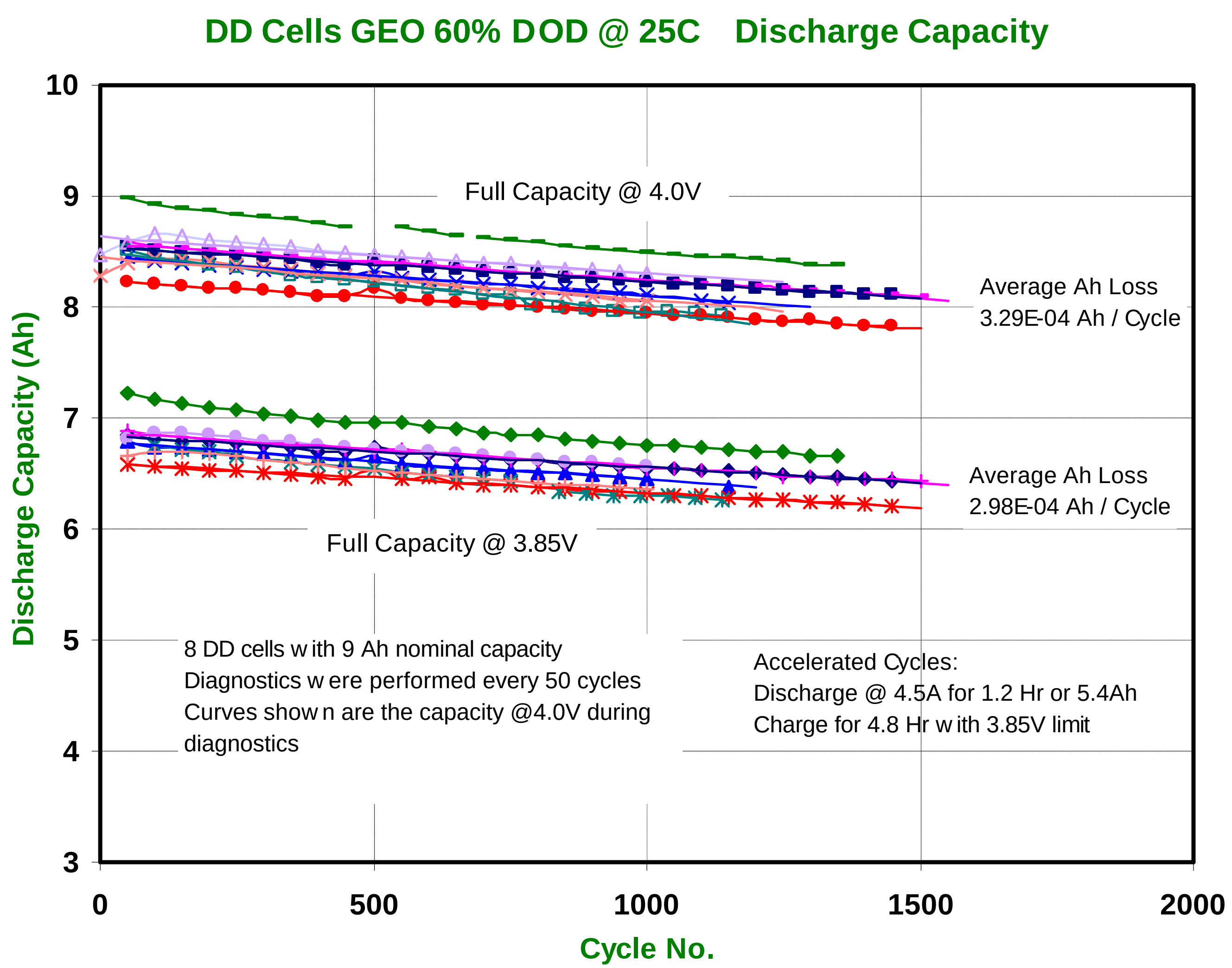
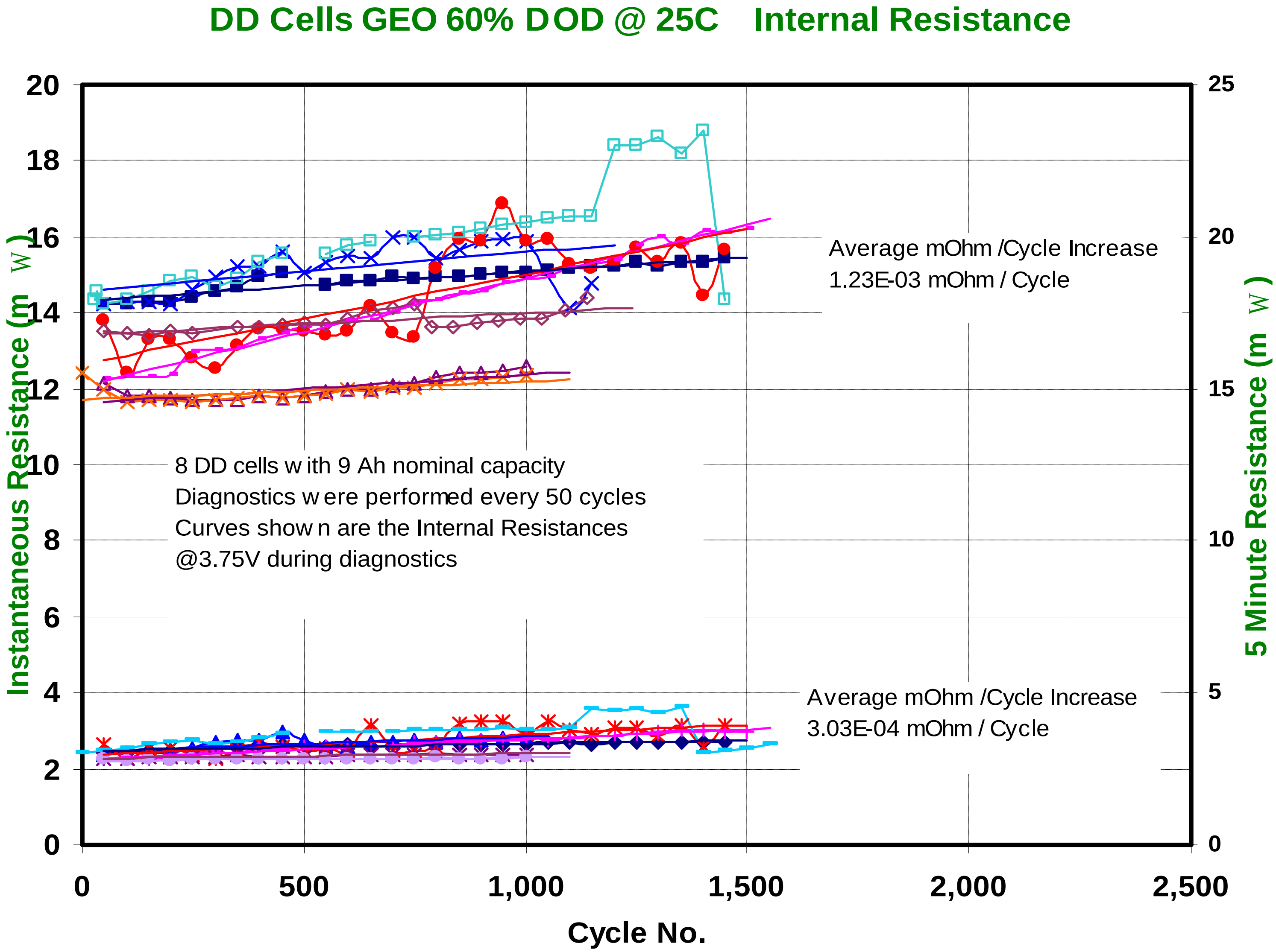
GEO TESTING



GEO TESTING

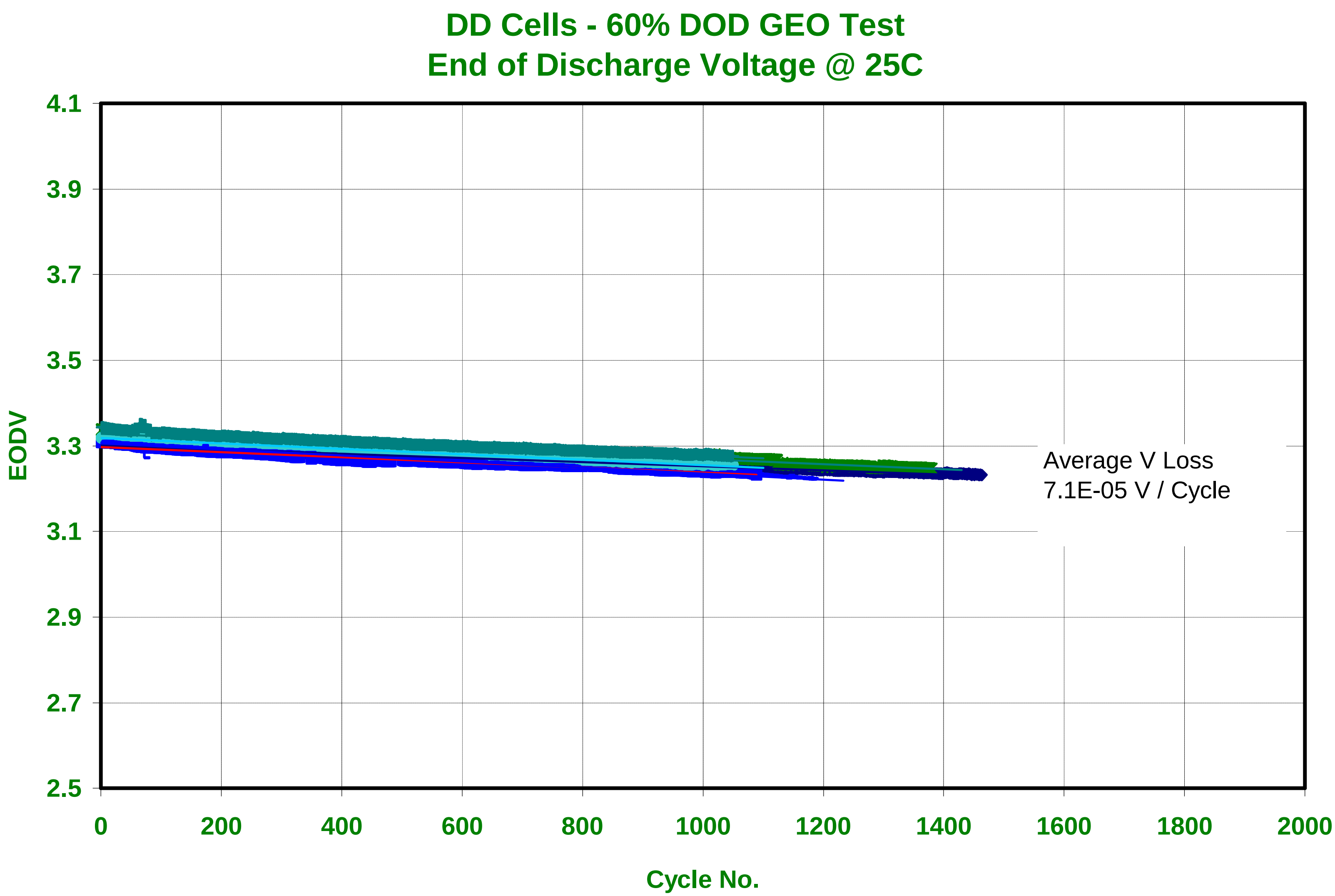

DD Cells GEO 60% DOD @ 25C Discharge Capacity
Discharge Capacity (Ah)
10
9
8
7
6
5
4
3
0
500
1000
1500
2000
Cycle No.
Full Capacity @ 4.0V
Average Ah Loss
3.29E-04 Ah / Cycle
Average Ah Loss
2.98E-04 Ah / Cycle
Full Capacity @ 3.85V
8 DD cells with 9 Ah nominal capacity
Diagnostics were performed every 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

GEO TESTING

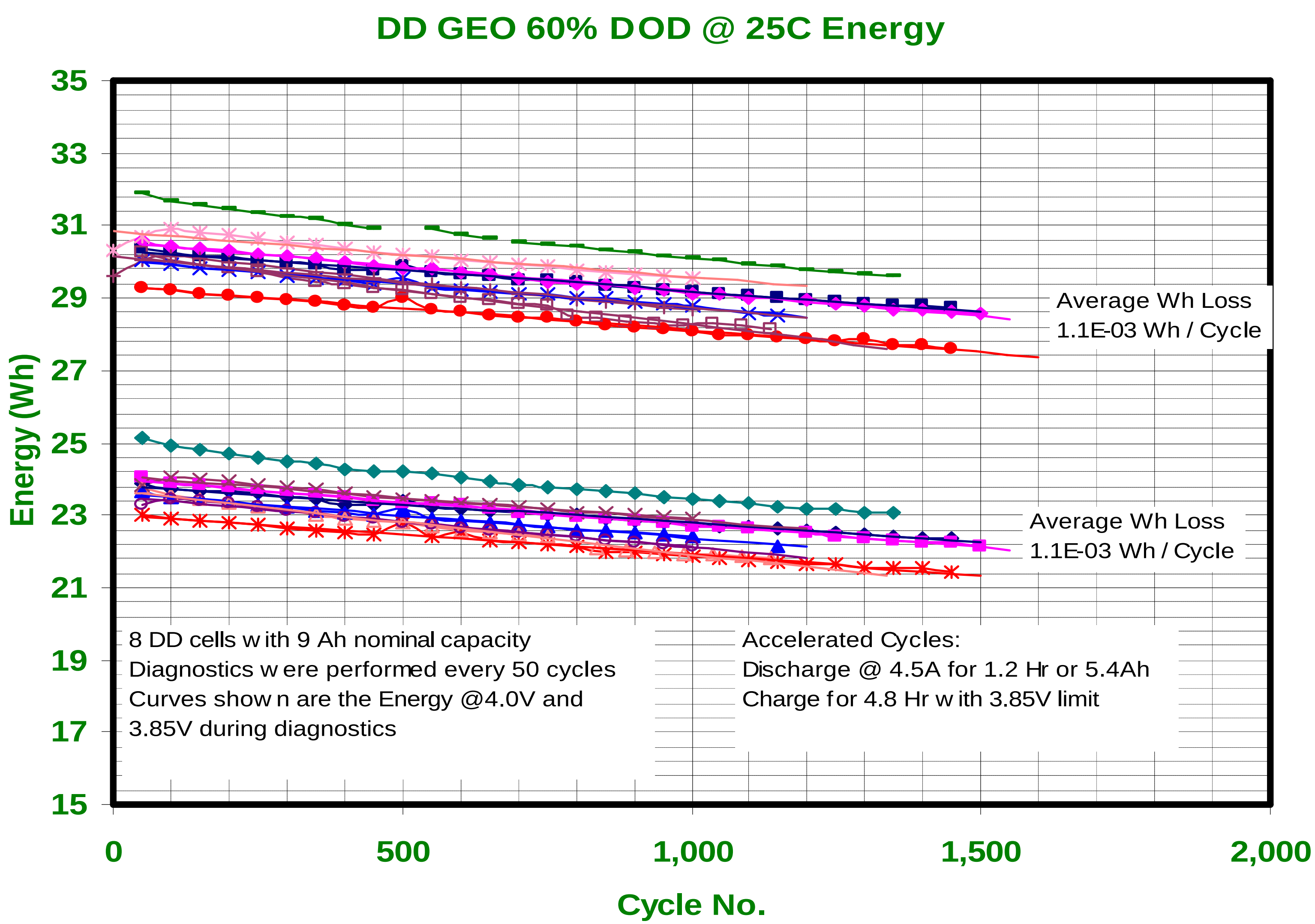


DD Cells GEO 60% DOD @ 25C Internal Resistance
Instantaneous Resistance (m W)
5 Minute Resistance (m W)
Cycle No.
Average mOhm /Cycle Increase
1.23E-03 mOhm / Cycle
8 DD cells w ith 9 Ah nominal capacity
Diagnostics w ere performed every 50 cycles
Curves show n are the Internal Resistances
@3.75V during diagnostics
Average mOhm /Cycle Increase
3.03E-04 mOhm / Cycle

GEO TESTING


DD Cells - 60% DOD GEO Test
End of Discharge Voltage @ 25C
EODV
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Cycle No.
Average V Loss
7.1E-05 V / Cycle

GEO TESTING


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
Cycle No.
Average Wh Loss
1.1E-03 Wh / Cycle
Average Wh Loss
1.1E-03 Wh / Cycle
8 DD cells with 9 Ah nominal capacity
Diagnostics were performed every 50 cycles
Curves shown are the Energy @4.0V and
3.85V 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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CALENDAR LIFE

Cell Fading Mechanisms

- Loss of lithium due to continuous SEI layer build up – parabolic function where fading rate decreases with time

- Degradation of active material properties – probably linear loss of capacity and impedance growth

CALENDAR LIFE

- Capacity measurement conducted at ambient temperature
- Cells stored on open circuit at 50% SOC in 45ºC and 60ºC, which is reasonable since a cycling cell is on average at 50% SOC
- Diagnostic tests performed every month for impedance and capacity

Calendar Life Projection

Capacity Loss	Expected Life of the Battery Updated for 32 weeks of data and normalized for temperature							
Years	1	3	5	7	10	12	14	15
Months	12	36	60	84	120	144	168	180
15°C	2.91%	3.63%	4.35%	5.07%	6.15%	6.87%	7.59%	7.95%
25°C	3.44%	5.21%	6.99%	8.77%	11.43%	13.21%	14.98%	15.87%

Equations	
Capacity Loss-Temperature relationships	$\%Loss = 8*10^{7}*e^{-7.5734*x}$ where $x = {}^{1000}/K$ used for projecting the loss of capacity
Linear loss of capacity after the 3rd month	$\%Loss = A + B*(\# \text{ of months})$ where A = 2.55% and B = 0.03% for 15°C where A = 2.55% and B = 0.074% for 25°C

CYCLE LIFE EXTRAPOLATION

CORRECTED FOR CALENDAR LIFE (8 YEARS FOR LEO; 15 YEARS GEO)

Depth Of Discharge %	Cycles Achieved	Wh Fade Rate @ 4V % Per Cycle	Typical Req. For Cycles	E.O.L. Energy* Wh 25ºC
30	12,000	.000704	40,000	21.8 - 2.6 = 19.1
60	1500	.0011	1,500	29.9- 4.49 = 25.4

Li-ion Battery Cell Balancing Requirements

NASA Aerospace Battery Workshop
Huntsville, Alabama
November 14, 2000

Mark J. Isaacson and Vincent L. Teofilo
Lockheed Martin Space Systems
Sunnyvale, CA 94089
mark.isaacson@lmco.com

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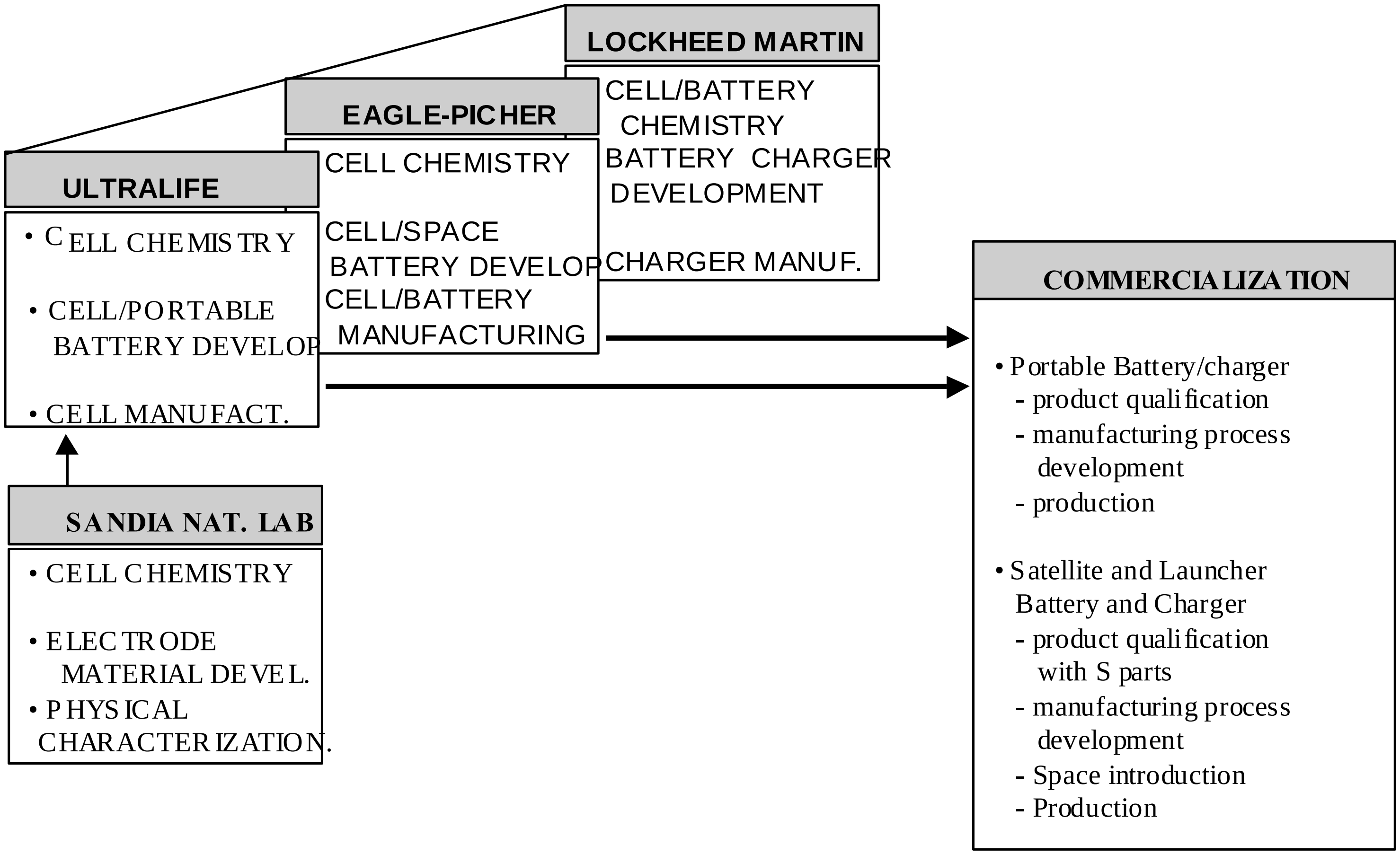
Outline

- ***Advanced Technology Program (ATP)***
- ***LI-ion Battery Management Requirements and Strategies***
- ***Li-ion Battery Management Architectures***
- ***Li-ion Cell Balancing Requirements for Portable Electronics Applications***
- ***Summary***

ATP Program Structure



Li-Ion Batteries

- High Energy Density and Specific Energy
- Long Cycle Life.
- Established Manufacturing Infrastructure for portable electronics.
- Battery/cell manufacturers developing Li-ion for satellite application.
- Sensitive to over-charge and over-discharge.

⇒ Battery Management Electronics for Portable Electronics and Aerospace applications?

ATP Testing

- ***ATP Program Testing***
  - ***LMSS focus is on cell characterization for evaluating charge balancing requirements***
- ***Ultralife (UBI) Cells***
  - ***700 mAmp-hour (nominal)***
  - ***made on production line***
  - ***graphitic anode***
  - ***$LiNi_{1-x}Co_xO2$ cathode***
  - ***polymer-gel electrolyte***
- ***A note on statistics***
  - ***test sample size must be sufficiently large to reach definitive conclusions***
  - ***only a few cells have been tested here to provide direction***
  - ***UBI will supply additional data***

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Li-ion Battery Management Strategies

- Battery Level Voltage Monitoring
- Cell Level Voltage Monitoring
- Dissipative Cell Level Voltage Management
- Non-Dissipative Cell Level Voltage Management

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Battery Level Voltage Monitoring

- Battery voltage is monitored.
- Cell voltages are not measured.
- Switched from Constant Current to Constant Voltage charge when Maximum *Battery* Voltage is reached.
- Battery voltage is maintained within specified limits.
- Cells voltages may exceed specified limits (I.e. be over-charged or over-discharged.) depending on cell-to-cell variations.
- Simple, inexpensive.

Cell Level Voltage Monitoring

- Cell voltages are monitored.
- Switched from Constant Current to Constant Voltage charge when first cell reaches Maximum *Cell* Voltage.
- Cell voltages are all maintained within specified limits.
- Cell state-of-charge is not actively managed.
- Battery capacity limited by lowest cell capacity.
- Minimum level of voltage management in commercial portable electronics.

Dissipative Cell Level Voltage Management

- Voltages of individual cells are monitored.
- State-of-charge of individual cells is actively managed by bypassing current around cells through a dissipative element such as a resistor.
- Voltage of all cells are maintained within specified limits.
- Operates only during charge.
- Battery capacity is limited by that of lowest capacity cell but all cells can be charged to maximum capacity.

Non-Dissipative Cell Level Voltage Management

- Voltages of individual cells are monitored.
- State-of-charge of individual cells is *managed* by transferring energy from cell to cell via a “nondissipative” element such as a capacitor.
- Voltage of all cells are maintained within specified limits.
- Can operates during both charge and discharge.
- Battery capacity is not limited by lowest capacity cell.

Li-ion Battery Charge Control Architectures

- Dissipative
  - Resistive Equalization
  - Analog Shunt Equalization
- Non-dissipative
  - Switched Capacitor Equalization
  - Resonant Equalization

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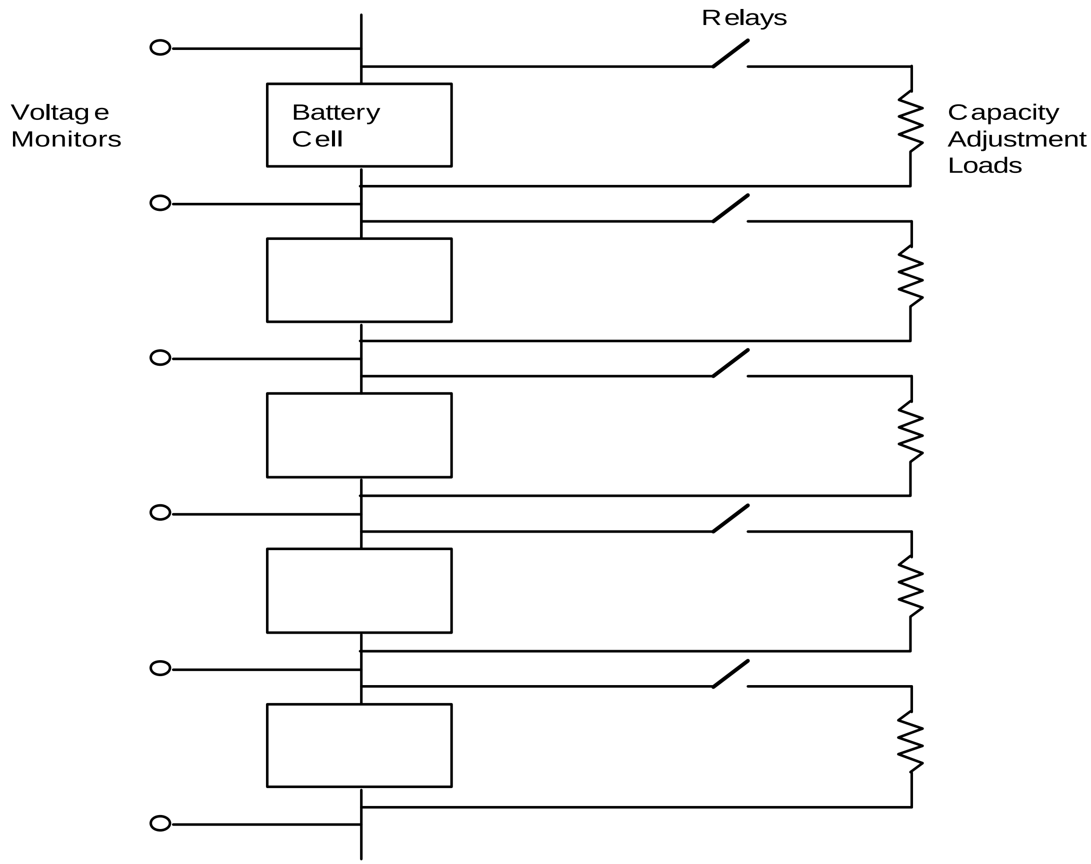
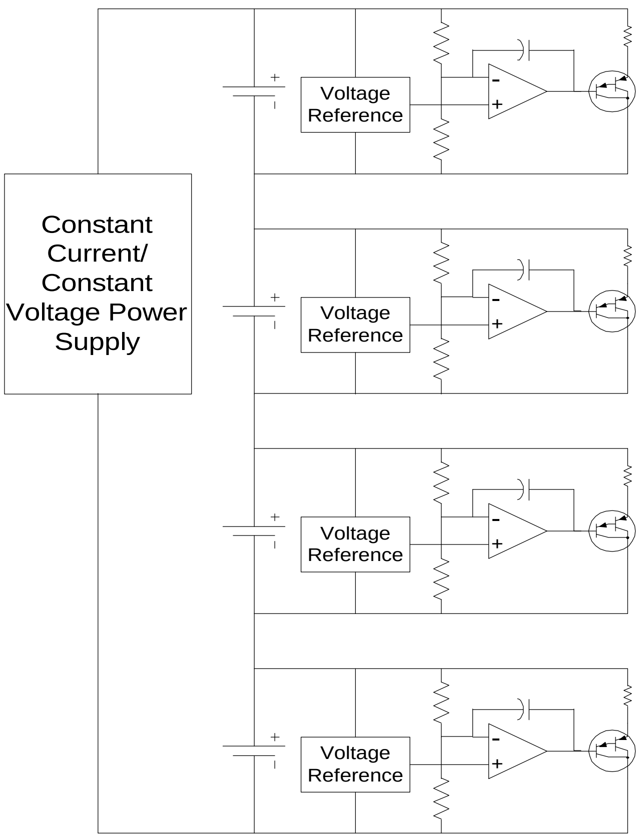
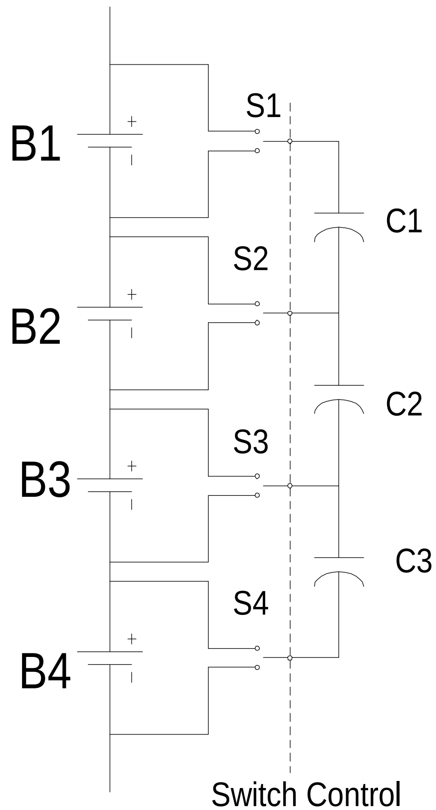
Resistive Equalization

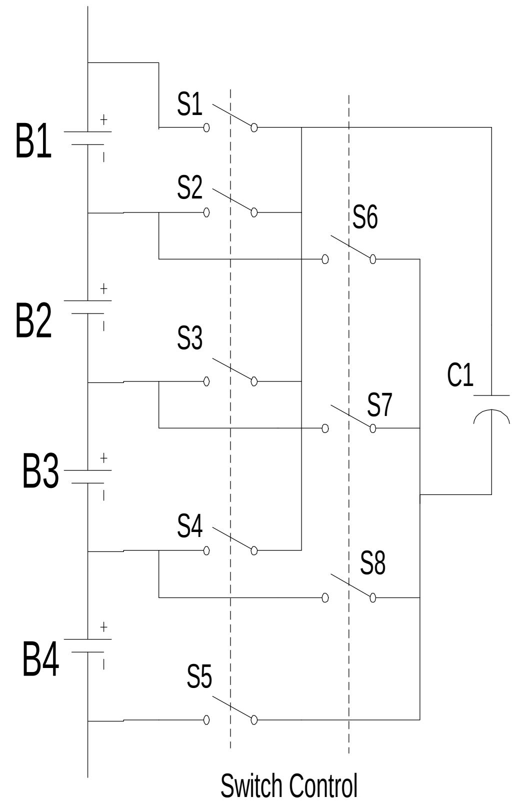


Analog Shunt Equalization



Switched Capacitor Equalization





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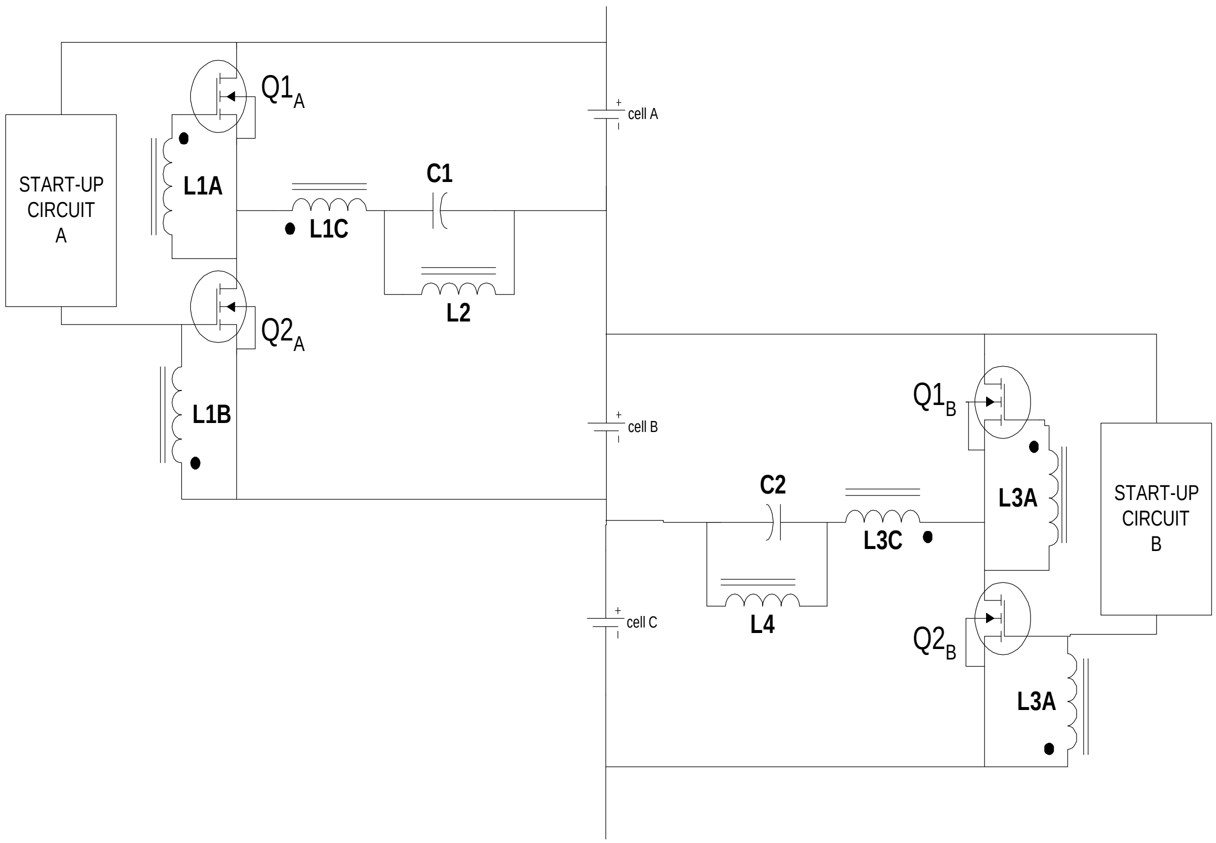
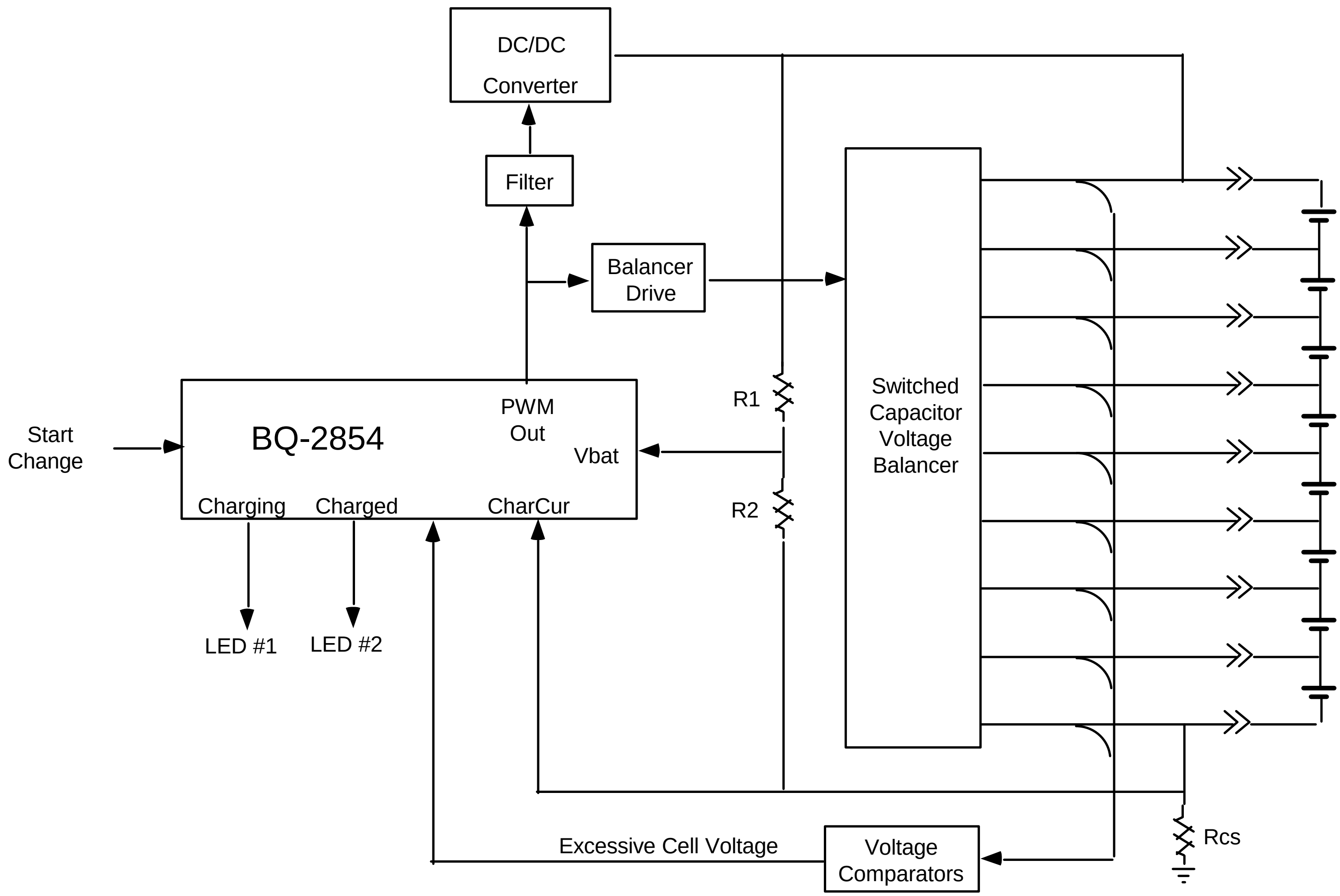
Resonant Equalization

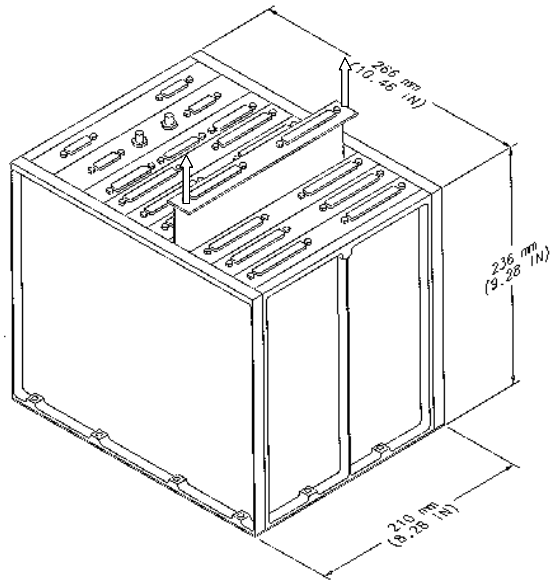


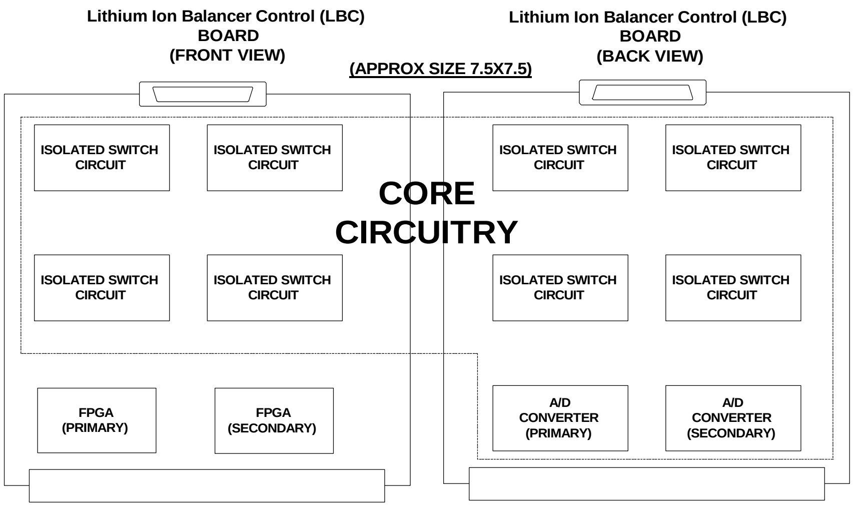
Portable Li-Ion Battery Management System Implementation

LOCKHEED MARTIN



Space Battery Management System Implementation





Desirable Features of Portable Electronics Batteries

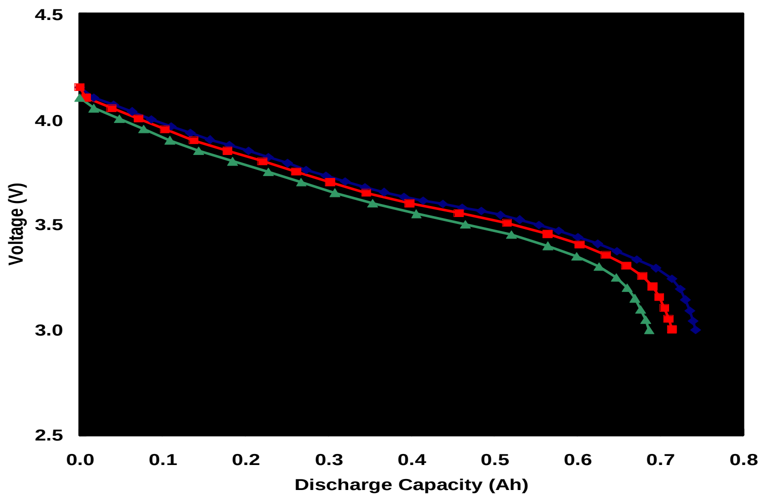
- ***Maximum Discharge Run Time***
- ***Minimum Charge Time***
- ***Increased Cycle Life***

⇒ ***Application requirements for portable electronics differ from those of Aerospace***

Testing Sequence

- ***Beginning-of-Life (BOL) Tests***
  - ***capacity characterization***
  - ***DC resistance***
  - ***self-discharge balance***
- ***Cycling***
- ***End-of-Life (EOL) Tests***
  - ***capacity characterization***
  - ***DC resistance***
  - ***self-discharge balance***

BOL Capacity Characterization



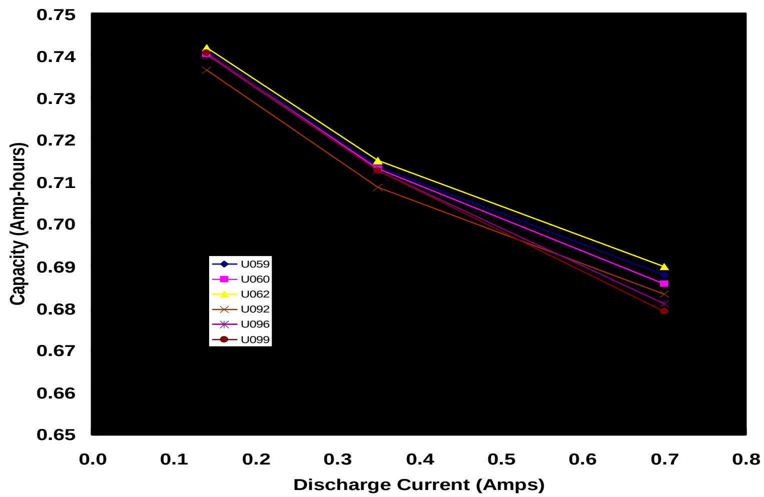


Table 2
Beginning-of-Life Cell Discharge Capacities

Cell	**Discharge Capacity (Amp-hours)**		
	0.14 Amps	**0.35 Amps**	**0.7 Amps**
U59	0.7411	0.7136	0.6879
U60	0.7405	0.7132	0.6857
U62	0.7419	0.7150	0.6898
U92	0.7366	0.7086	0.6833
U96	0.7402	0.7127	0.6810
U99	0.7406	0.7127	0.6792
Statistics (All Cells)			
Mean, Ah	0.7402	0.7126	0.6845
SD, Ah	0.0018	0.0022	0.0041
SE, %	0.2484	0.3018	0.5948
Statistics (w/o Cell U92)			
Mean, Ah	0.7409	0.7134	0.6847
SD, Ah	0.0007	0.0010	0.0045
SE, %	0.0898	0.1332	0.6580

Test Description

- C, C/2, C/5 discharges
- 20°C
- 4.15 V max, 3.0 V min

Test Results

- Tight capacity distribution. (Similar to Japanese manufacturers.)
- Wider capacity distribution at high discharge rates
- Cell U092 developed electrolyte leak because of improper handling

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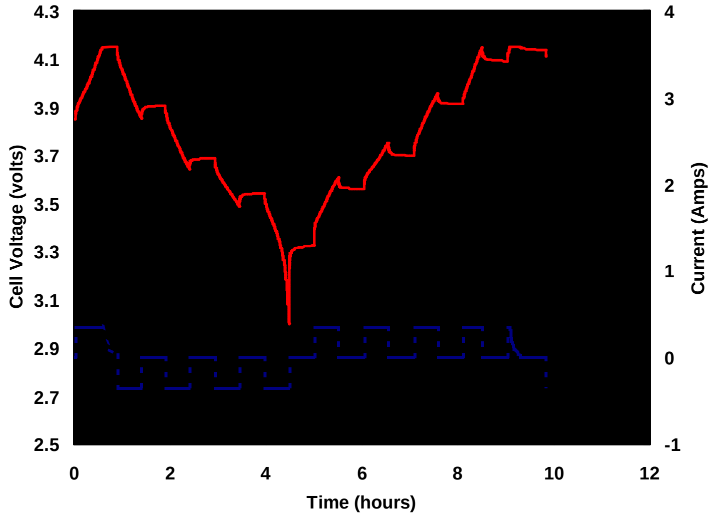
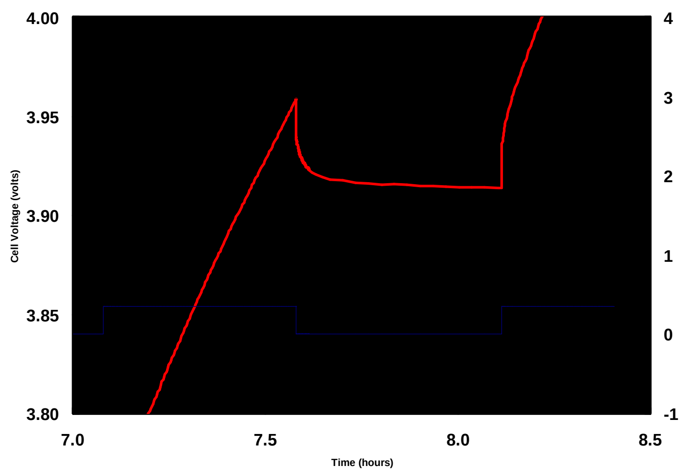
BOL DC Resistance Test Procedure





<u>Test Description</u>

- Charge and discharge at 350 mA (C/2).
- 30-minute OC at 75%, 50%, 25%, and 0% SOC on discharge and 25%, 50%, 75% and 10% SOC on charge.
- Polarization divided into two components, $?_{5s}$ and $?_{30m}$ based on AC impedance tests.
- $?_{5s}$ is dominated by faradaic resistance and ESR.
- $?_{30m}$ is dominated by concentration polarization.

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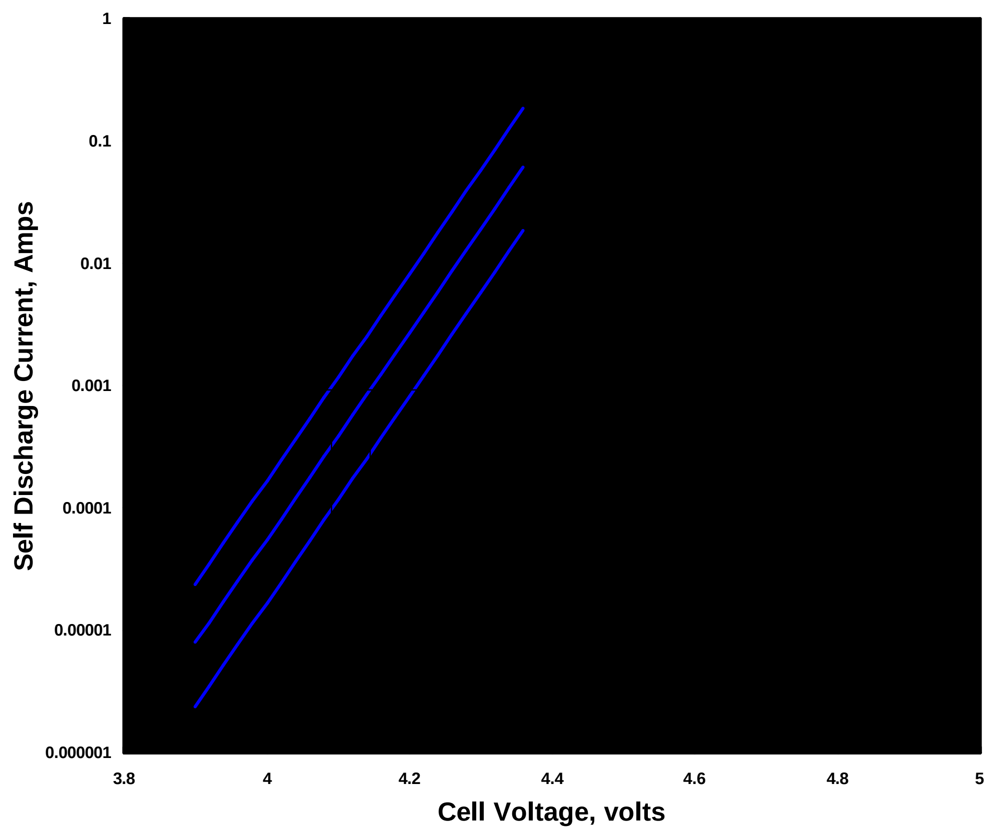
BOL DC Resistance Test Results

Table 3 Beginning-of-Life Cell Polarization			
Cell	**Cell Polarization (mV)** **(All values are negative but the sign has been omitted.)**		
	?$_{5s}$	?$_{30m}$	Total Polarization
U59	24.8	30.2	55.0
U60	24.8	30.3	55.1
U62	25.1	31.4	56.5
U96	26.4	34.3	60.7
U99	23.9	36.6	60.5
Statistics (excluding Cell U92)			
Mean, mV	25.1	34.1	59.2
SD, mV	1.3	2.6	2.4
SE, %	5.0	7.6	4.0

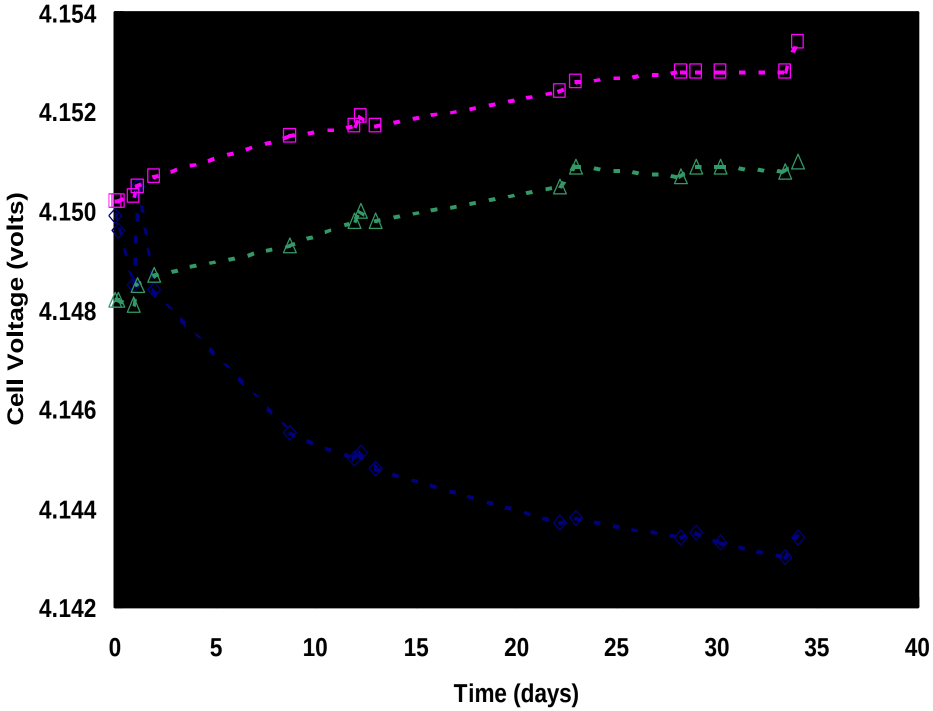
Test Description

- Cell polarization 50-60 mV.
- Standard deviation (1-3 mV) and standard error (5-10%) are small.

Equilibrium Voltages for Cells in Series with Unequal Self Discharge Rates



BOL Self Discharge Balancing Results



Test Results

- EOL voltage dispersion less than BOL voltage dispersion.
- Consistent with decrease in self discharge as cells age because of increase in internal resistance of cells.

Cell Cycling

- Three cells (U059, U062, U096) placed on cycle test
  - Test Regimen (100% DOD)
    - Constant current charge at C/2 to 4.15 V.
    - Constant voltage charge at 4.15 V to C/20.
    - Constant current discharge at C.
  - Test regimen similar to that used for portable electronics
- All cells cycles for an equal time
- Cells with lower capacity completed more cycles than those with a higher capacity
- Capacity characterization, DC resistance and self-discharge balance experiment repeated at end of cycle test to obtain end-of-life data (EOL)
- Cell-to-cell interactions in batteries?

Comparison of EOL and BOL Discharge Capacities

Table 2
Beginning-of-Life Cell Discharge Capacities

Cell	**Discharge Capacity (Amp-hours)**		
	0.14 Amps	**0.35 Amps**	**0.7 Amps**
U59	0.7411	0.7136	0.6879
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Statistics (All Cells)			
Mean, Ah	0.7402	0.7126	0.6845
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Statistics (w/o Cell U92)			
Mean, Ah	0.7409	0.7134	0.6847
SD, Ah	0.0007	0.0010	0.0045
SE, %	0.0898	0.1332	0.6580

Table 1
End-of-Life Cell Discharge Capacities

Cell	**Discharge Capacity (Amp-hours)**		
	0.14 Amps	**0.35 Amps**	**0.7 Amps**
U59	0.6063	(1)	0.574
U60	-	-	-
U62	0.5794	0.6049	0.5695
U92	-	-	--
U96	0.616	0.5856	0.5538
U99	-	-	-
Statistics			
Mean, Ah	0.6006	0.5953	0.5658
SD, Ah	0.0190	0.0136	0.0106
SE, %	3.1573	2.2927	1.8744

Test Results

- Cell capacities decrease as cells age.
- Cell capacity distribution increases as cells age.
- Capacity distribution is still relatively tight at EOL as well as at BOL.
- No evidence of need for balancing electronics.

Comparison of EOL and BOL DC Resistance Data

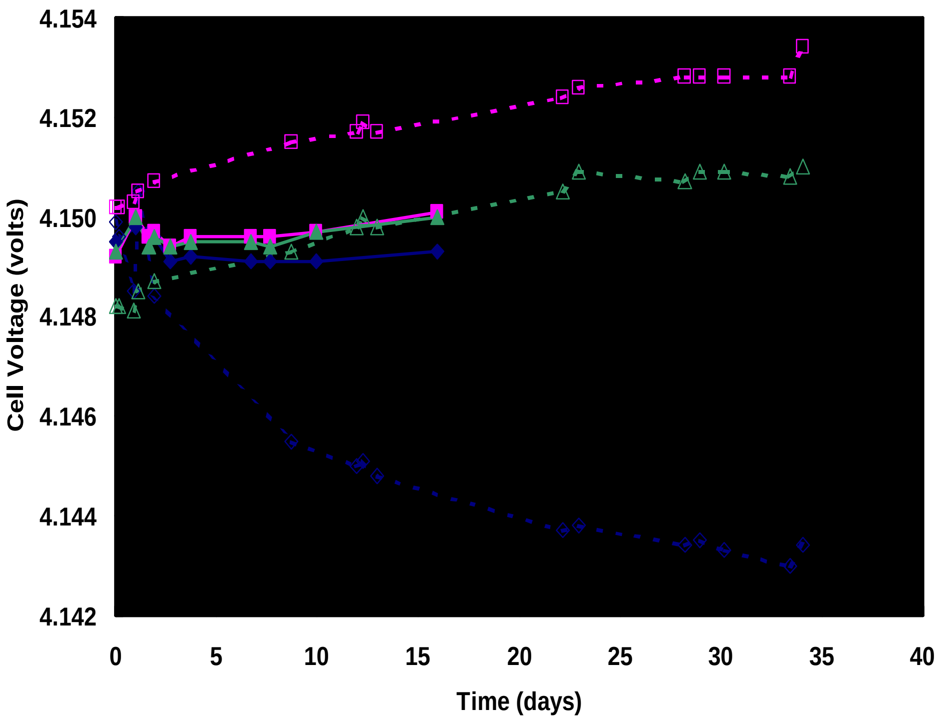
Table 4 Beginning-of-Life Cell Polarization			
Cell	**Cell Polarization (mV) (All values are negative but the sign has been omitted.)**		
	?5s	?30m	Total Polarization
U59	24.8	30.2	55.0
U60	24.8	30.3	55.1
U62	25.1	31.4	56.5
U96	26.4	34.3	60.7
U99	23.9	36.6	60.5
Statistics (excluding Cell U92)			
Mean, mV	25.1	34.1	59.2
SD, mV	1.3	2.6	2.4
SE, %	5.0	7.6	4.0

Table 3 End of Life Cell Polarization			
Cell	**Cell Polarization (mV) (All values are negative but the sign has been omitted.)**		
	?5s	?30m	Total Polarization
U59	33.0	77.9	110.9
U62	31.7	79.4	111.1
U96	35.7	87.0	122.7
Statistics			
Mean, mV	33.5	81.4	114.9
SD, mV	2.0	4.9	6.8
SE, %	6.1	6.0	5.9

<u>Test Results</u>

- Cell internal resistances increase as cells age.
- Cell internal resistance distribution increases as cells age.
- Internal resistance distribution is still relatively tight at EOL.
- No evidence of need for balancing electronics.

Comparison of EOL and BOL Self Discharge Balancing Data



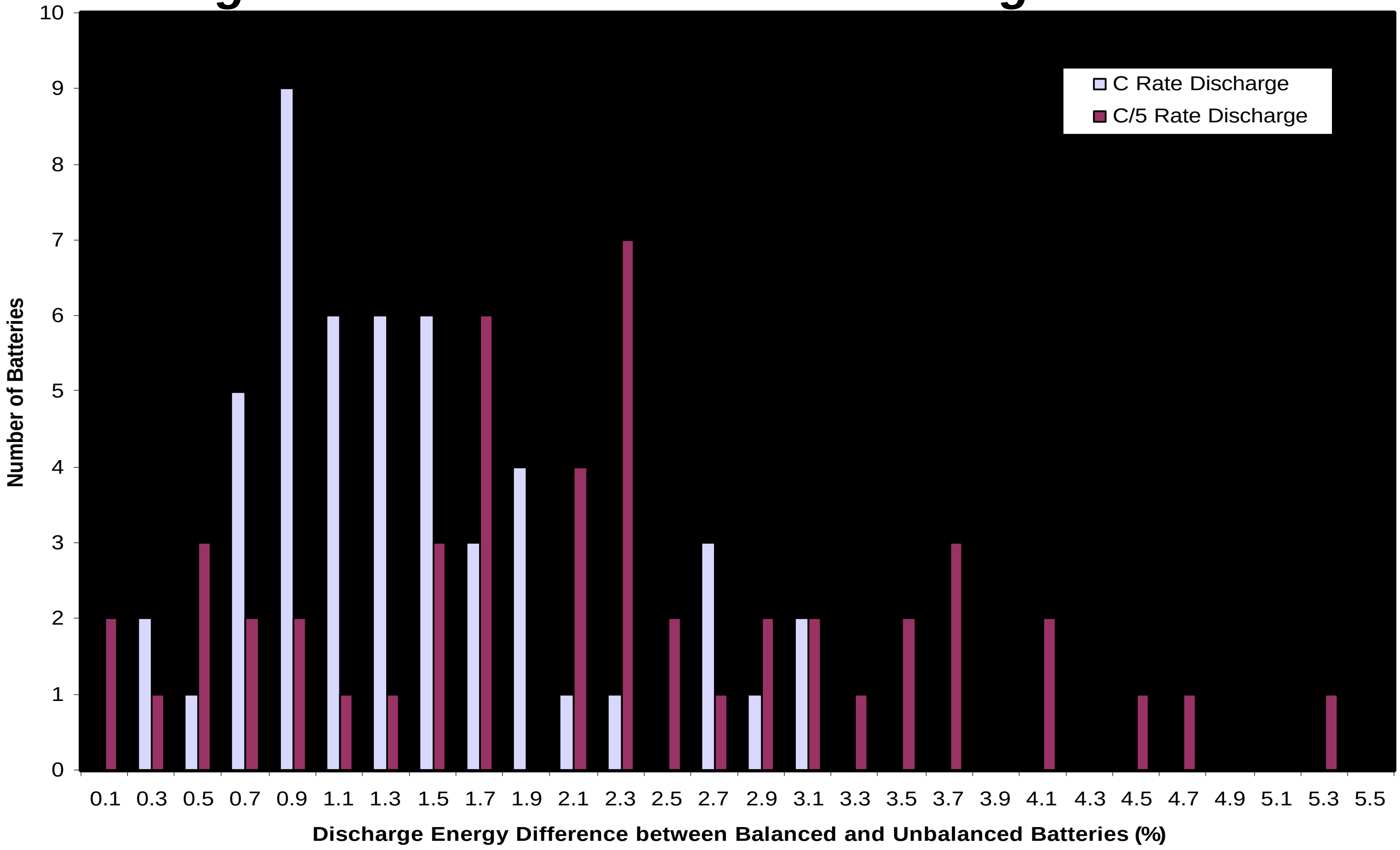
Test Results

- EOL voltage dispersion less than BOL voltage dispersion.
- Consistent with decrease in self discharge as cells age because of increase in internal resistance of cells.
- No evidence of need for balancing electronics.

“Monte Carlo” Calculations

- Generate (with computer) 150 cells
  - standard deviations from experimental capacity characterization
  - random number generator
  - normal capacity distribution as weighting function
- Randomly assemble 50 three-cell batteries
  - No matching
  - Three cells in series is a typical configuration for lap tops
- Calculate Discharge Energy for Unbalanced batteries
  - assume discharge energy is limited by cell with lowest discharge energy
  - battery discharge energy is three time discharge energy of “weakest” cell
- Calculate Discharge Energy for Nondissipatively Balanced Battery
  - assume 100% efficiency or perfect balancing
  - battery discharge energy is sum of discharge energy of three cells
- Determine difference in discharge energy between balanced and unbalanced batteries

Histogram of Capacity Differences Distribution between Unbalanced and Non-Dissipatively Balanced Batteries containing Cells with Different Self Discharge Rates



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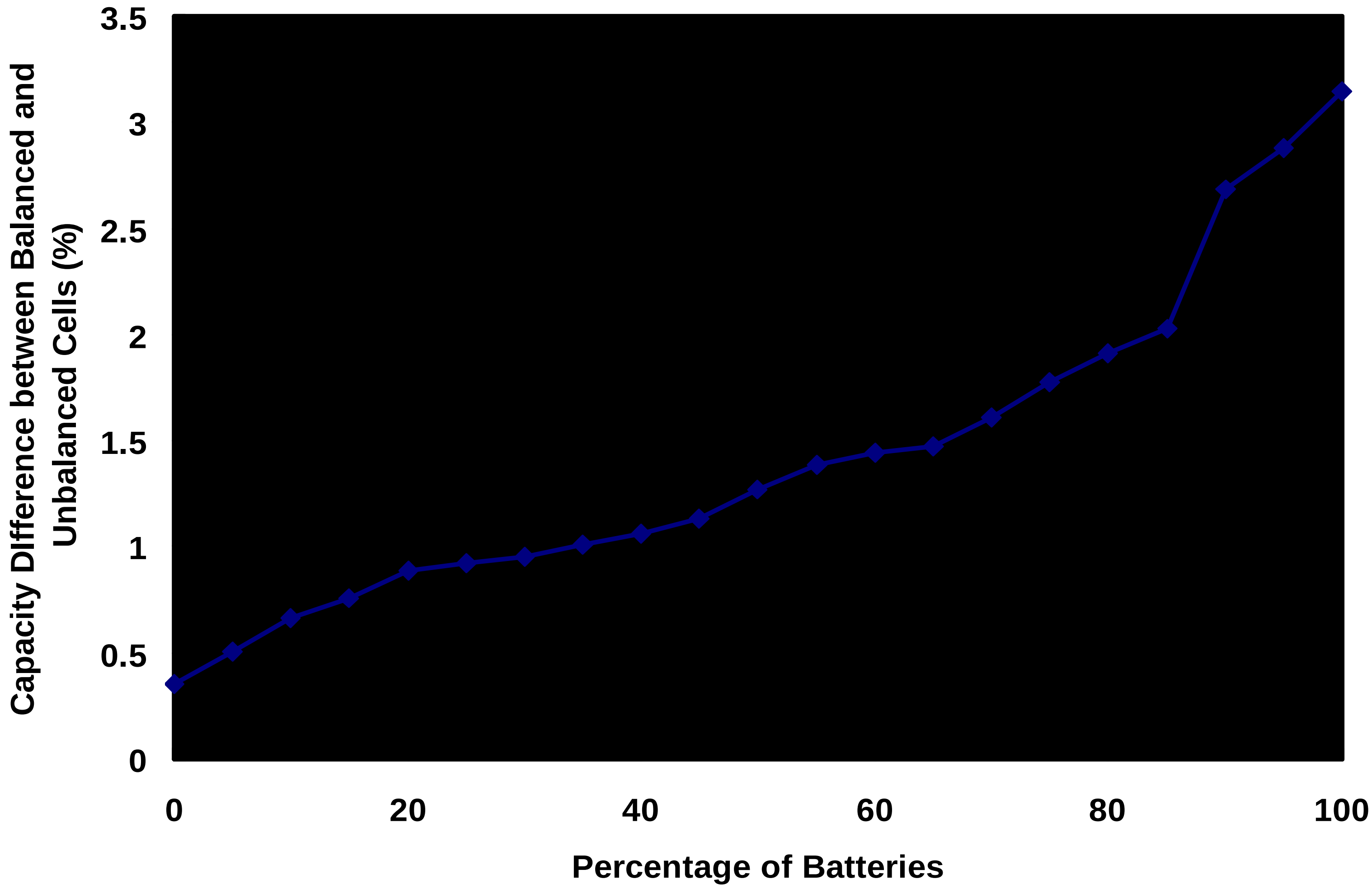
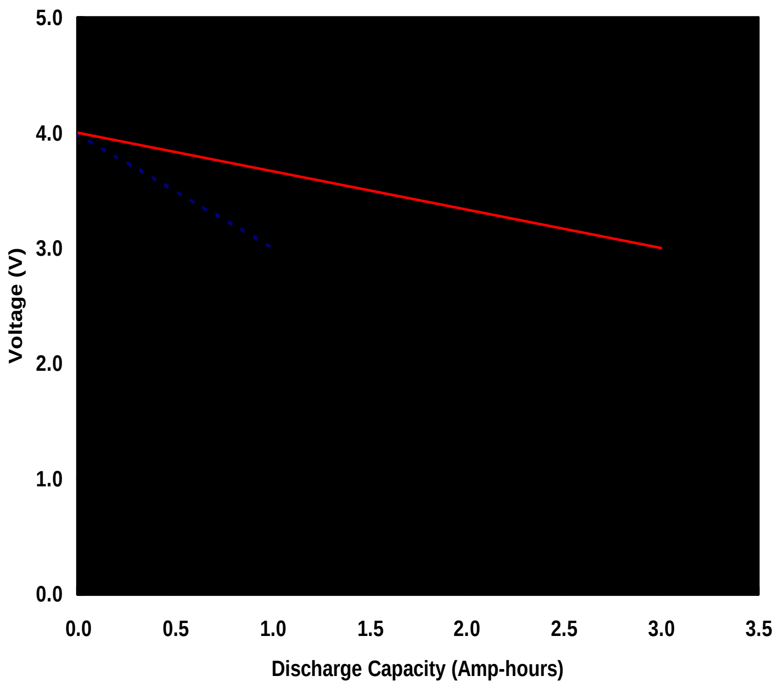
Monte Carlo Calculations of Capacity Difference Distribution between Unbalanced and Non-Dissipatively Balanced Batteries containing Cells with Different Self Discharge Rates



Available Discharge Energy Calculations for Unbalanced, Dissipative Balancing and



Assumptions

- **Battery with two cells in series**
- **Cell 1 Capacity: 1 Ah**
- **Cell 2 Capacity: 3 Ah**

Energy Calculations

- **Unbalanced (Worst Case)**

E = (3.17V)(3Ah)+(3.5V)(1Ah)= 6.67 Wh

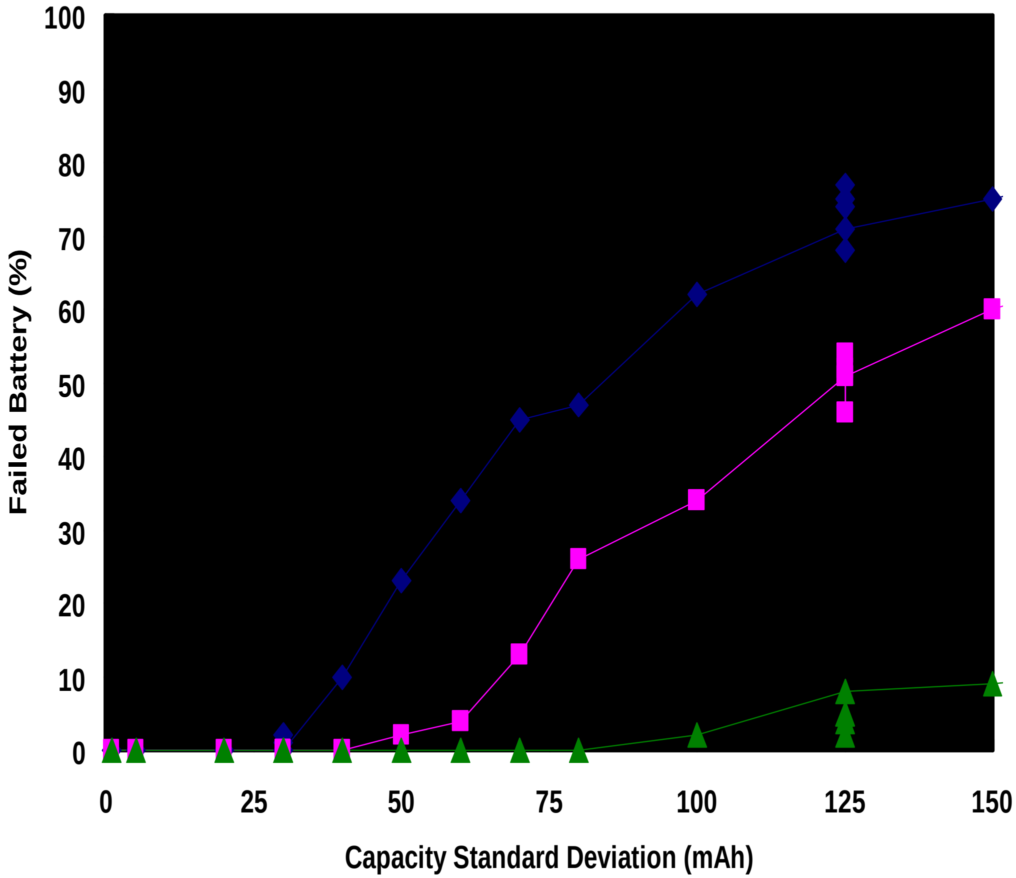
- **Dissipative Balancing (Best Case)**

E = (3.83V)(1Ah)+(3.5V)(1Ah)= 7.33 Wh

- **Non-Dissipative Balancing**

E = (3.5V)(3Ah)+(3.5V)(1Ah)= 14 Wh

Monte Carlo Calculations for Effect of Balancing Method on Battery Yield for Batteries containing Cells with Different Discharge Capacities



Input Data

- Nominal Capacity: 700 mAh
- Nominal Discharge Energy: 2520 Wh
- Failure Criteria: 2016 Wh/cell or 6048 Wh/battery (80% of BOL energy)
- Average EOL Discharge Energy: 2142 Wh/cell. 85% of BOL energy yielding 5% average margin.

Summary

- ***LI-ion Battery Management Requirements, Strategies and Architectures Reviewed.***
- ***UBI Li-ion cell testing under way to quantify Charge Balancing Requirements.***
- ***No evidence for Need for Cell Balancing for UBI Cells for Portable Commercial Electronics.***
- ***Conclusions for UBI portable electronics cells not necessarily applicable to other applications and other cell types.***

Acknowledgement

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Characterization and Simulated LEO Cycling of SAFT Lithium Ion Cells

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The 2000 NASA Aerospace Battery Workshop
Holiday Inn -- Research Park
Huntsville, Alabama
November 14 - 16, 2000

Scope

- This presentation summarizes test results, to date, obtained with SAFT MP commercial cells and prototype space cells.
- These tests are part of an ongoing program at TRW to evaluate lithium ion cells for space application.
- To facilitate development of a coherent data base, all cells in the program are subjected to similar test regimes:
  - Characterization
    - = Charge acceptance as a function of CVL and temperature
    - = Cell resistance as a function of SOC and temperature
  - Cycling
    - = LEO: 25% DOD, 15ºC and 25ºC, or
    - = GEO: 70% DOD, 15ºC and 25ºC

Test Plan

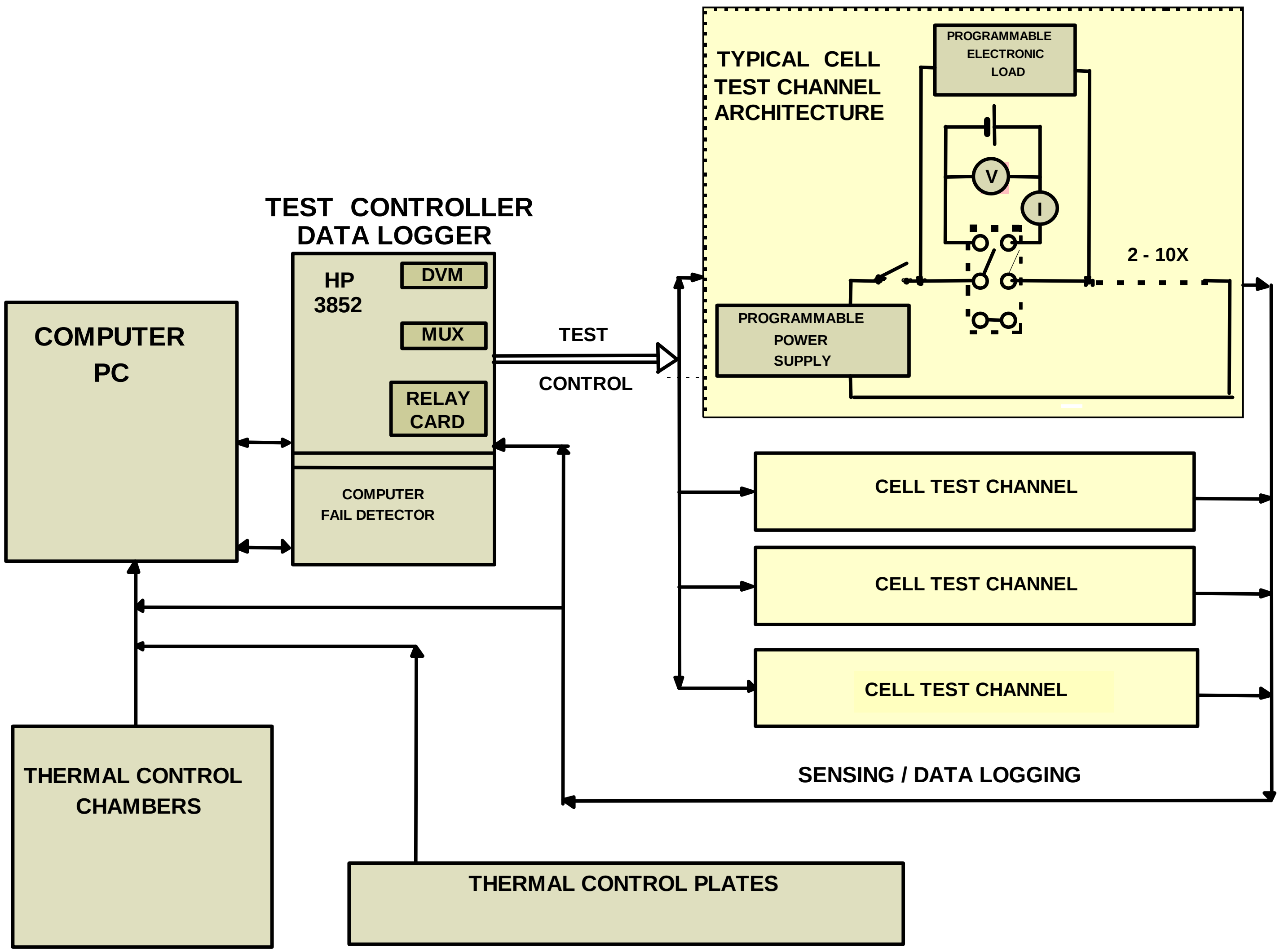
Characterization: Charge Acceptance, Cell Resistance

- **Charge Acceptance: determined as a function of CVL and temperature**
  - **Charge at C/5 to a CVL; taper charge until current is < C/100**
  - **Discharge at C/5 to 3.0 volts**
- **Cell Resistance: determined as a function of SOC, during charge and discharge**
  - **Impose 10% current pulses during C/5 charge and discharge**
  - **determine cell resistance as dV/dI**
- **All characterizations were performed at 15°C and 25°C**

Test Plan
Simulated Leo Cycling

- **Depth of Discharge: 25% (basis: capacity at 25ºC to a CVL of 4.0 volts and taper charge until the current is < C/100**
- **Orbit: 100 minutes with 36 minute eclipse periods**
- **Charge regime: 0.5C to CVL; taper until eclipse discharge**
- **Charge management: Individual cell control**
- **Discharge: 0.42C (36 minutes)**

Test Setup



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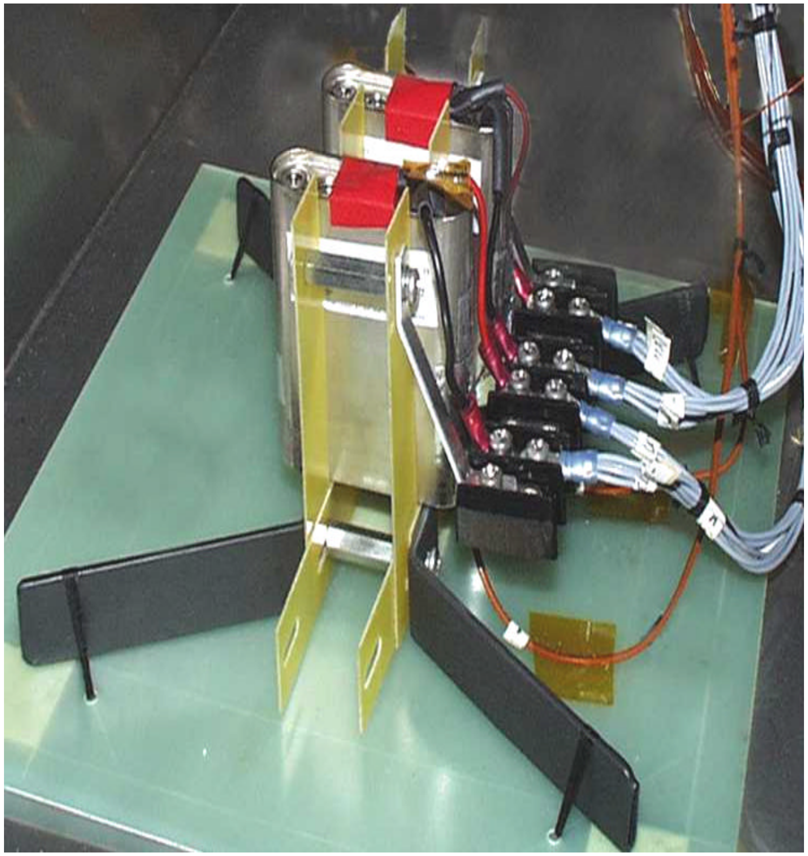
Test Facility

- **Accommodates lithium ion cell characteristics**
  - **Charge/discharge mgmt**
  - **Safety**
- **Autonomous test control and data logging**
- **Individual cell, cell pack, or battery control for all test articles**
- **Fail safe capability for test anomalies**

Test Articles

MP Cell



Prototype Cell

MP Cell Description

- Nomenclature: SAFT Li-Ion Prototype -- MP 176065
- Nominal Cell Capacity: 4.3 Ah
- Positive Electrode: $LiCoO_2$, PVDF binder
- Negative Electrode: Synthetic graphite, Non-fluorinated polymer binder
- Electrolyte: EC-DEC-DMC + VC additive
- Separator: PE/PP multilayer
- Stack: Wound prismatic
- Container: Stainless steel can, negative polarity
- Place of Manufacture: France

PROTOTYPE Cell Description

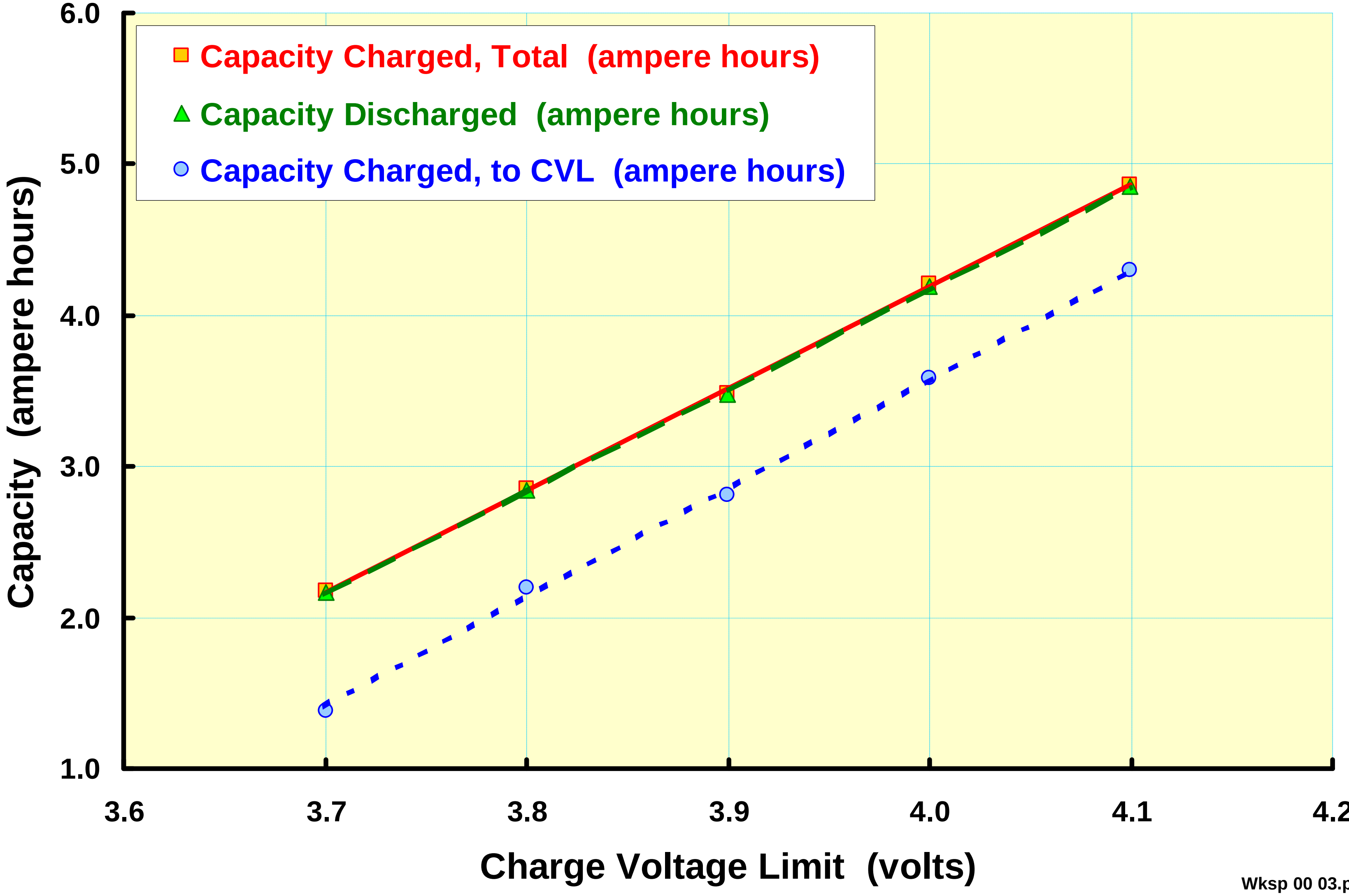
- Nomenclature: SAFT 400K Space Cell
- Nominal Cell Capacity: 42 Ah, 150 Wh
- Positive Electrode: $LiNiO_2$, PVDF binder
- Negative Electrode: Synthetic graphite, non-PVDF binder
- Electrolyte: 1M $LiPF_6$ PC/EC/3DMC
- Separator: PE/PP multilayer
- Stack: Wound cylindrical
- Container: Stainless steel can, negative polarity
- Place of Manufacture: USA

Test Results
(MP and Prototype Cells)

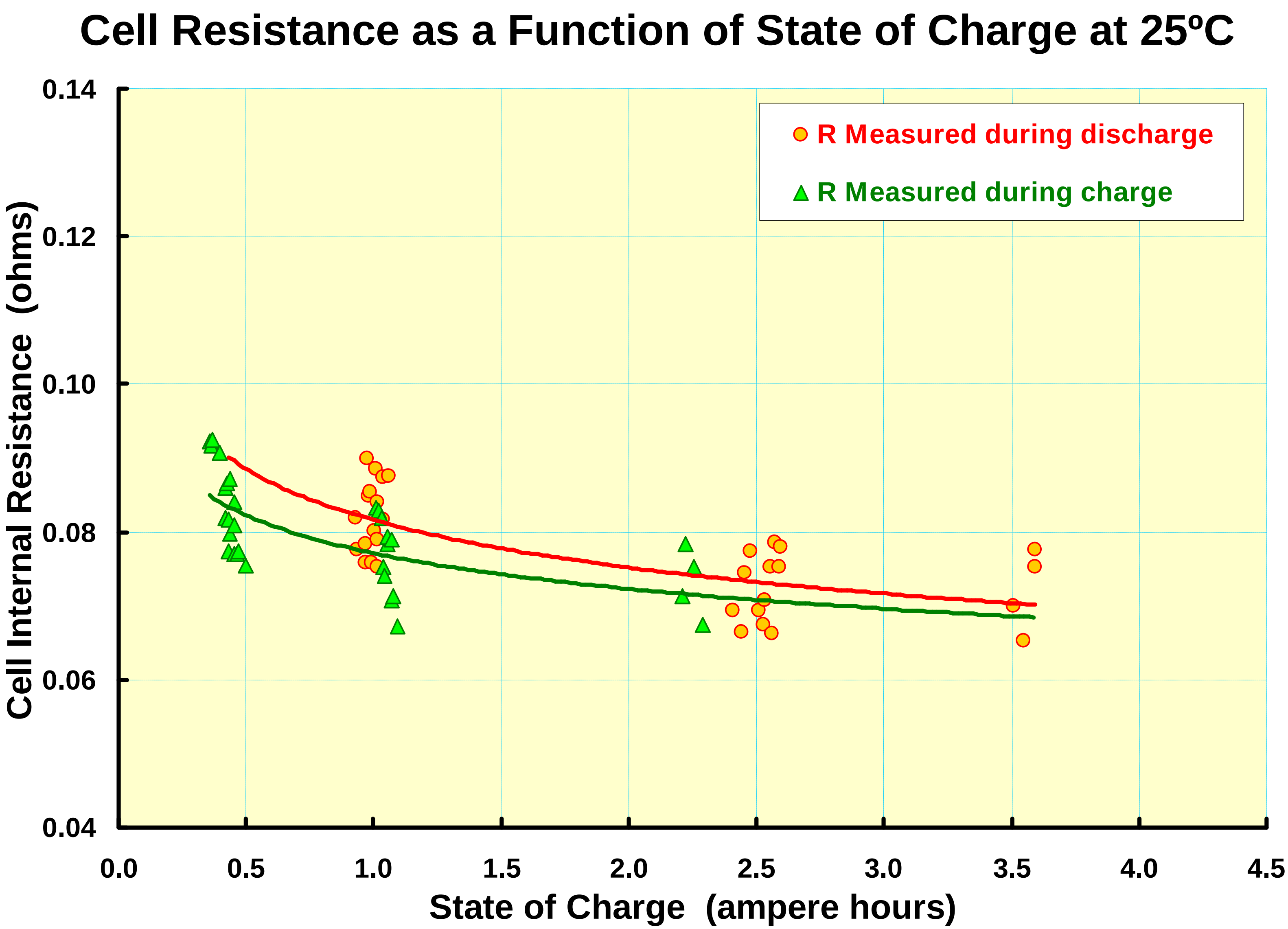
- Characterization
  - Charge acceptance
  - Cell resistance
- LEO Cycling
  - Typical 25% DOD cycle
  - EODV as a function of cycling at 25ºC
  - EODV as a function of cycling at 15ºC
  - Reserve capacity

MP Cell Characterization

Charge Acceptance as a Function of CVL at 25ºC

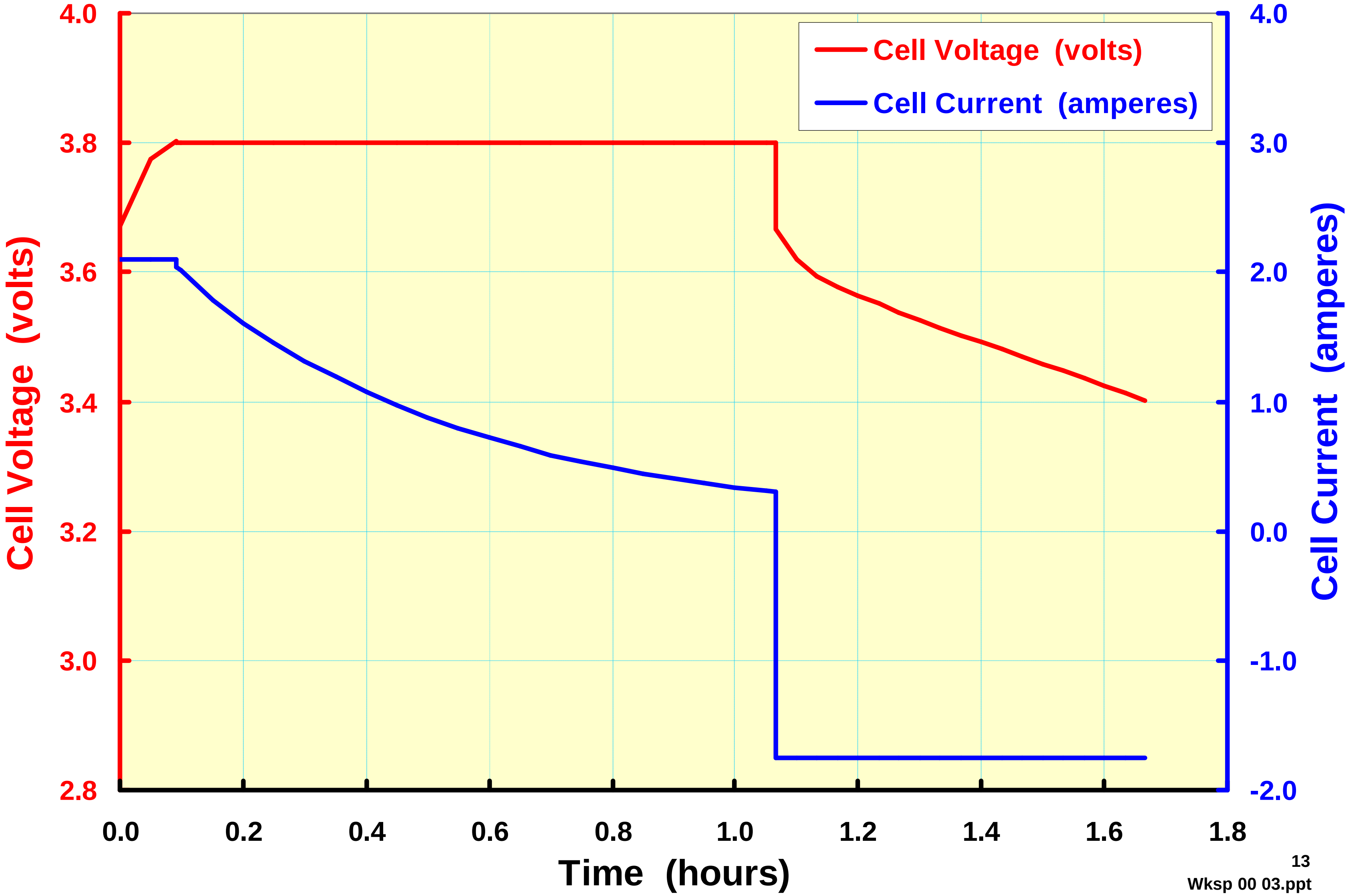


MP Cell Characterization



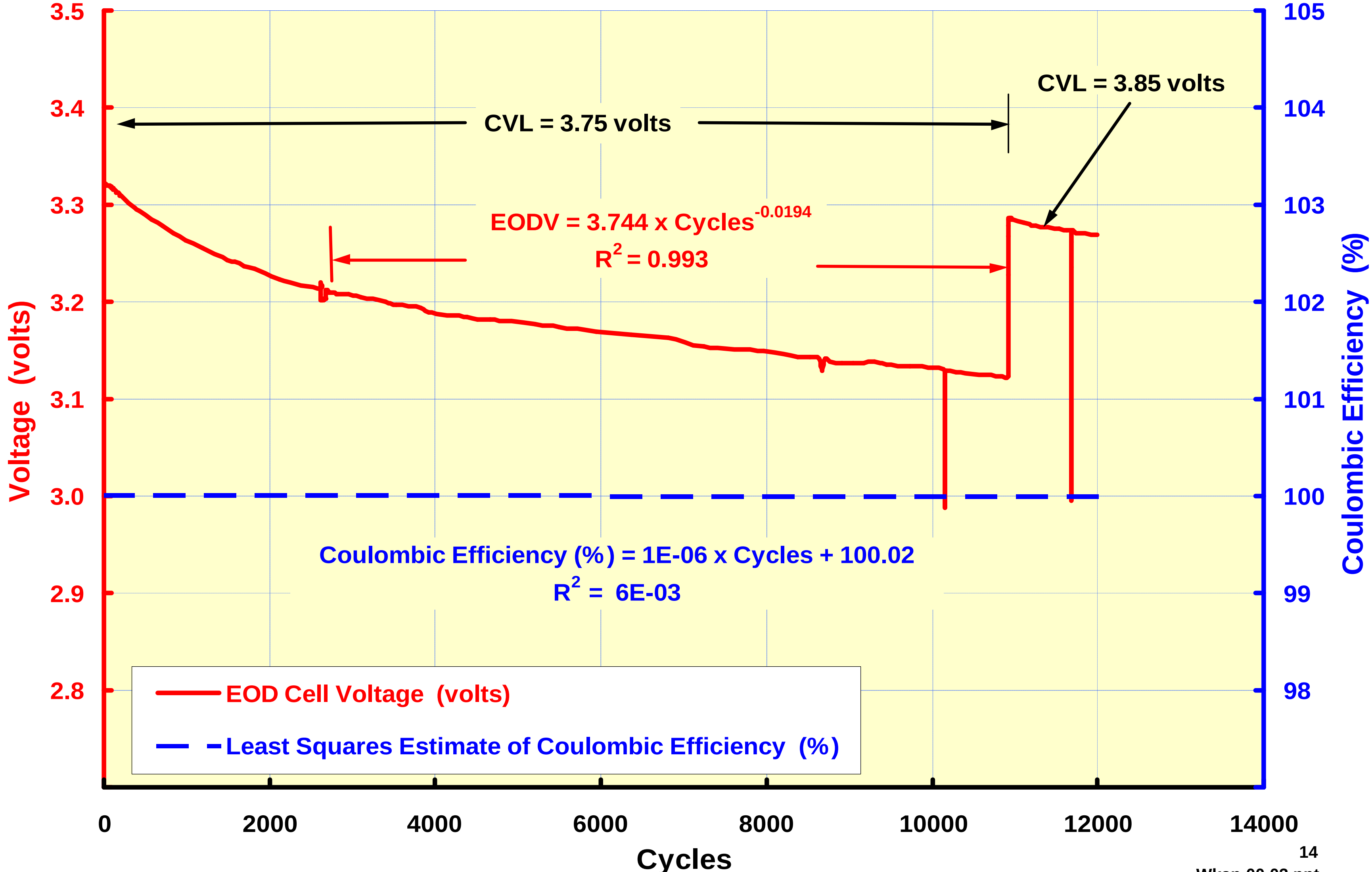
MP Cell LEO Cycling

Typical 25% DOD LEO Cycle (25ºC)



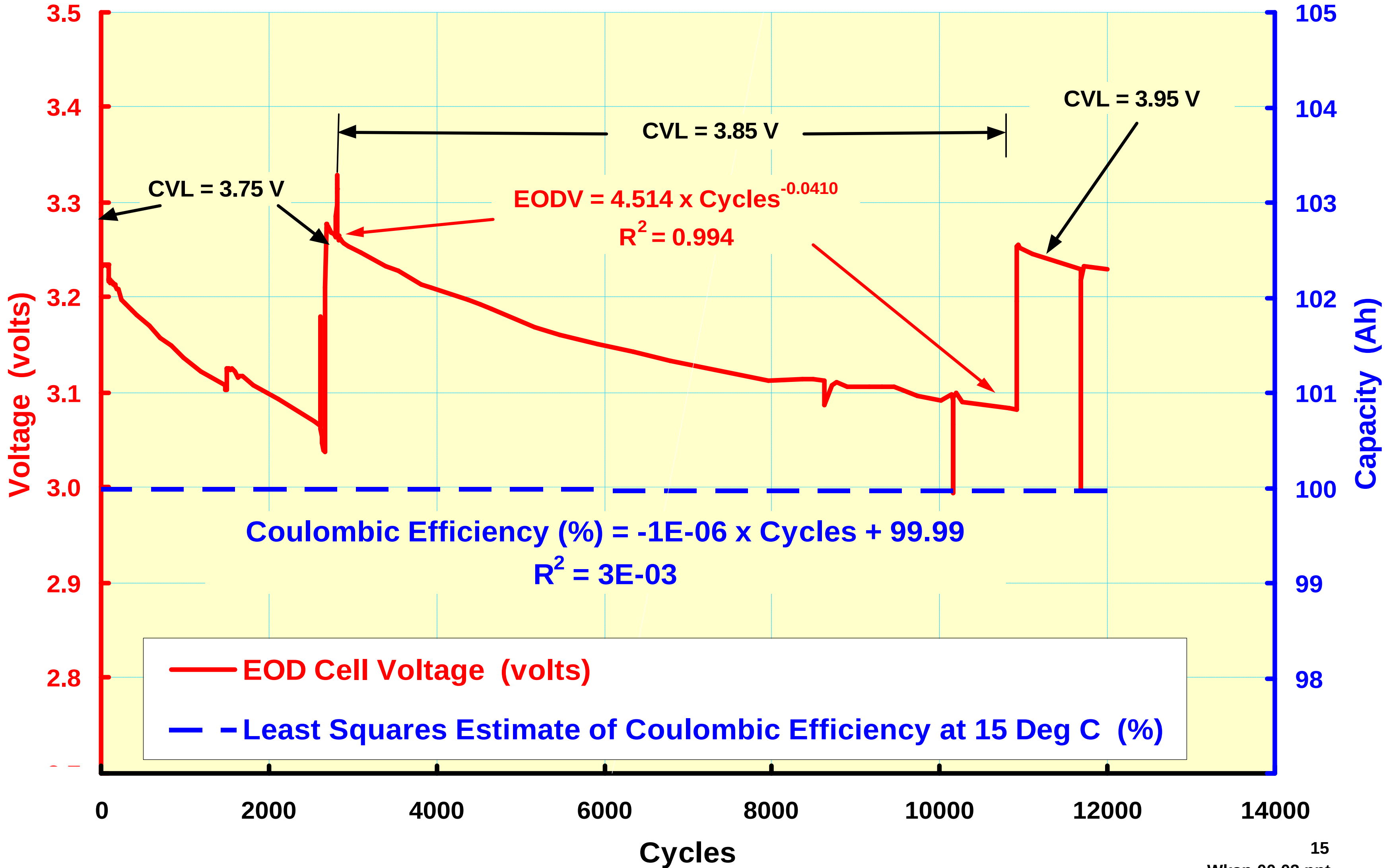
MP Cell LEO Cycling

EODV as a function of cycling at 25ºC



MP Cell LEO Cycling

EODV as a function of cycling at 15ºC



MP Cell LEO Cycling

Reserve Capacity Estimate (25 Deg C)

		Capacity (Ah) -- Charge: 3.75V CVL + taper			
Time (Years)	Temp (Deg C)	Discharge to 3.0V	Discharge to 25% of BOL 4.0V CVL capacity	Reserve	Loss
BOL	25	2.54	1.07	1.47	
2.0	25	1.35	1.07	0.28	1.19

Capacity (Reserve), 3.75V CVL (Ah) = Capacity (LEO to 3.0V) - Capacity (25% DOD)

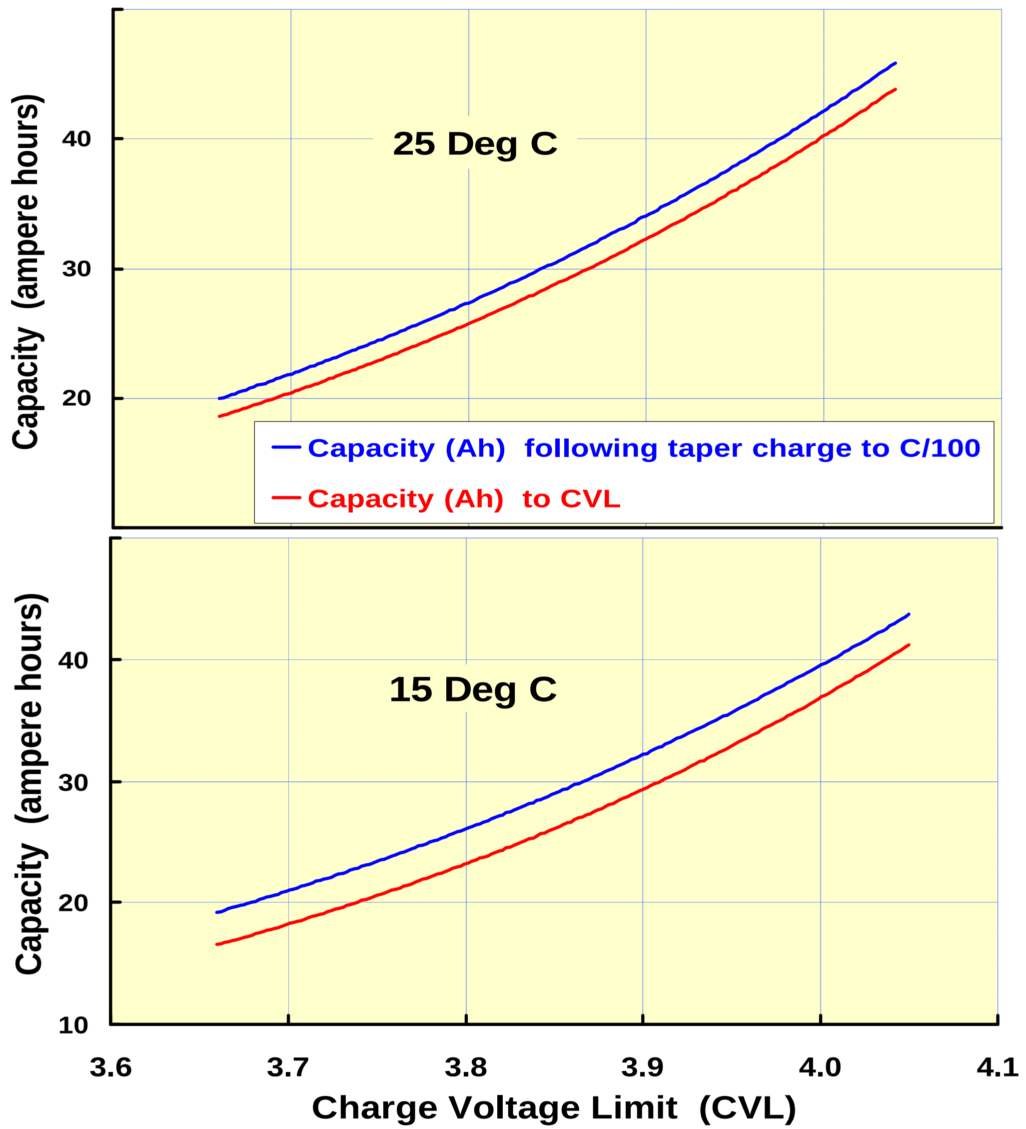
Capacity (Loss), 3.75V CVL (Ah) = Capacity (BOL) - Capacity (Time "t")

Reserve Capacity Estimate
Definition of Terms

- **Capacity (Reserve), 3.75V CVL (Ah):** The capacity remaining, to a 3.0V cutoff, following a 25% DOD discharge, during simulated LEO cycling.
- **Capacity (LEO to 3.0V):** Capacity to a 3.0V cutoff, following a simulated LEO charge to a 3.75V CVL and taper charge.
- **Capacity (BOL):** BOL capacity to a 3.0V cutoff, following charge, at C/5, to a specified CVL and taper charge until the current is <C/100.
- **Capacity (25% DOD):** 25% of the BOL capacity.
- **Capacity (Loss):** The difference between capacity at BOL and time "t", determined with comparable charge/discharge parameters..
- **Capacity (Time "t"):** The capacity observed at a time "t", to a 3.0V cutoff, following a simulated LEO cycle charge to a 3.75V CVL and taper.

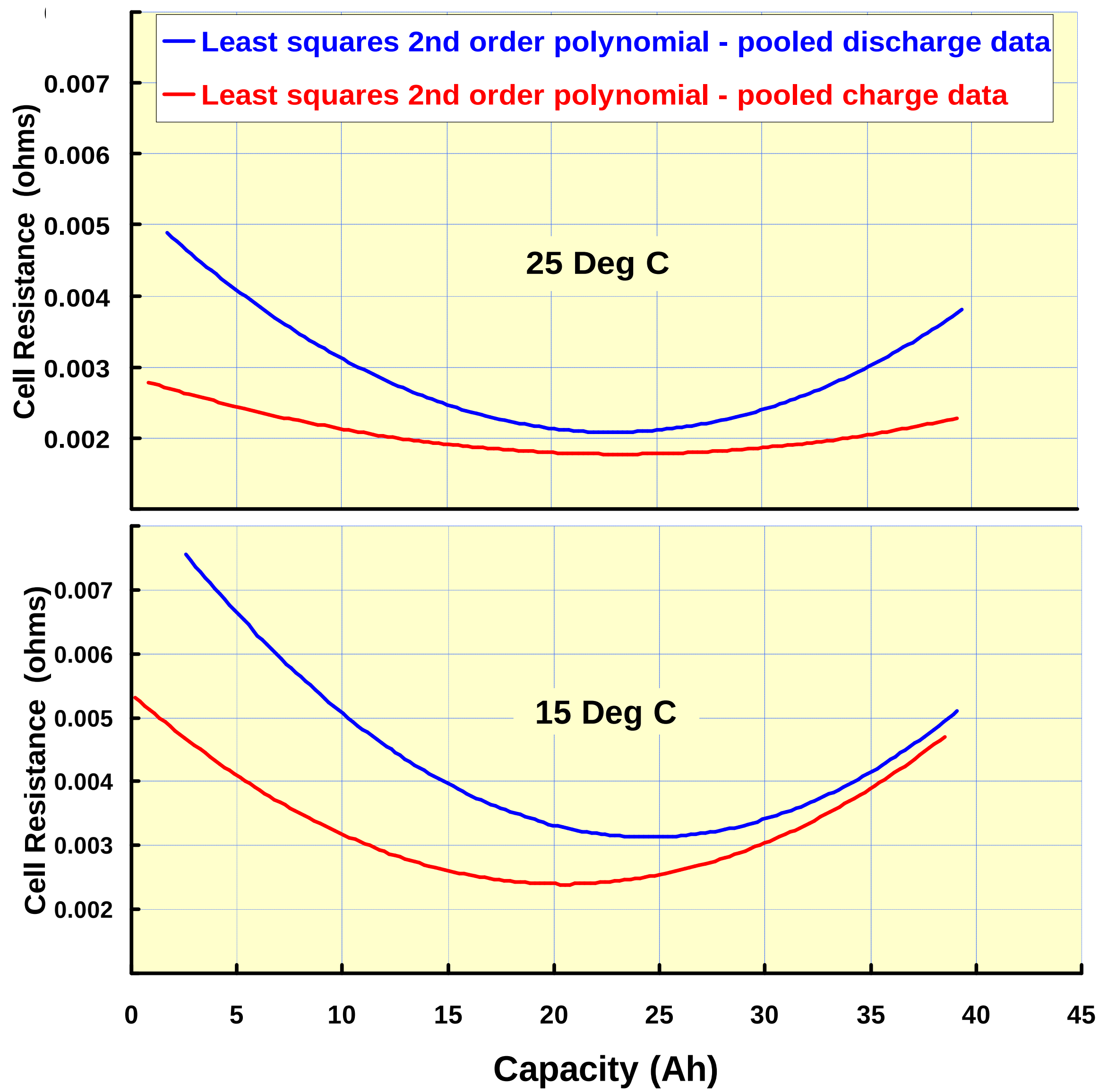
Prototype Cell Characterization

Charge Acceptance as a Function of CVL and Temperature



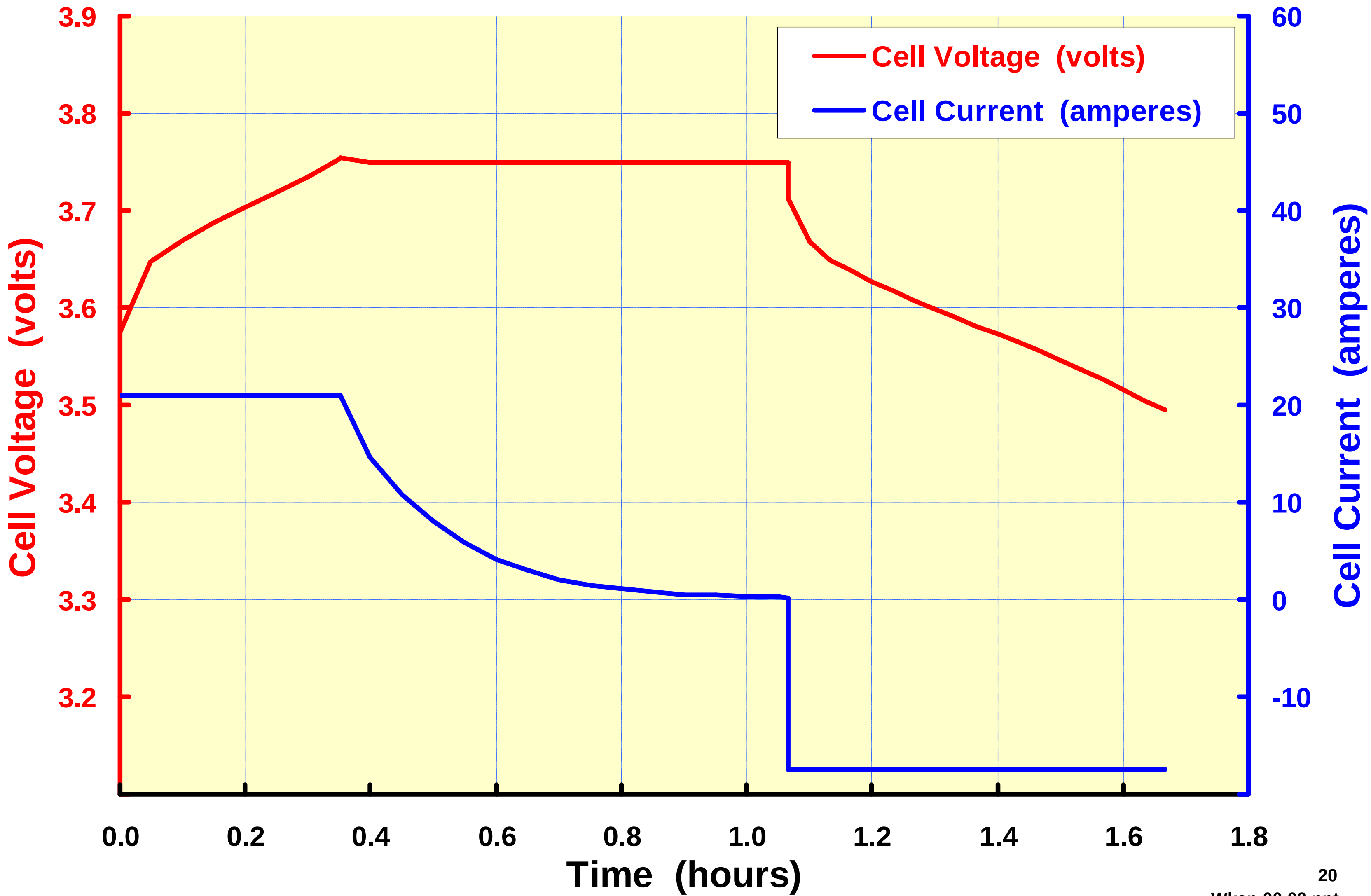
Prototype Cell Characterization

Cell Resistance as a Function of State of Charge and Temperature



Prototype Cell LEO Cycling

Typical 25% DOD LEO Cycle (25ºC)



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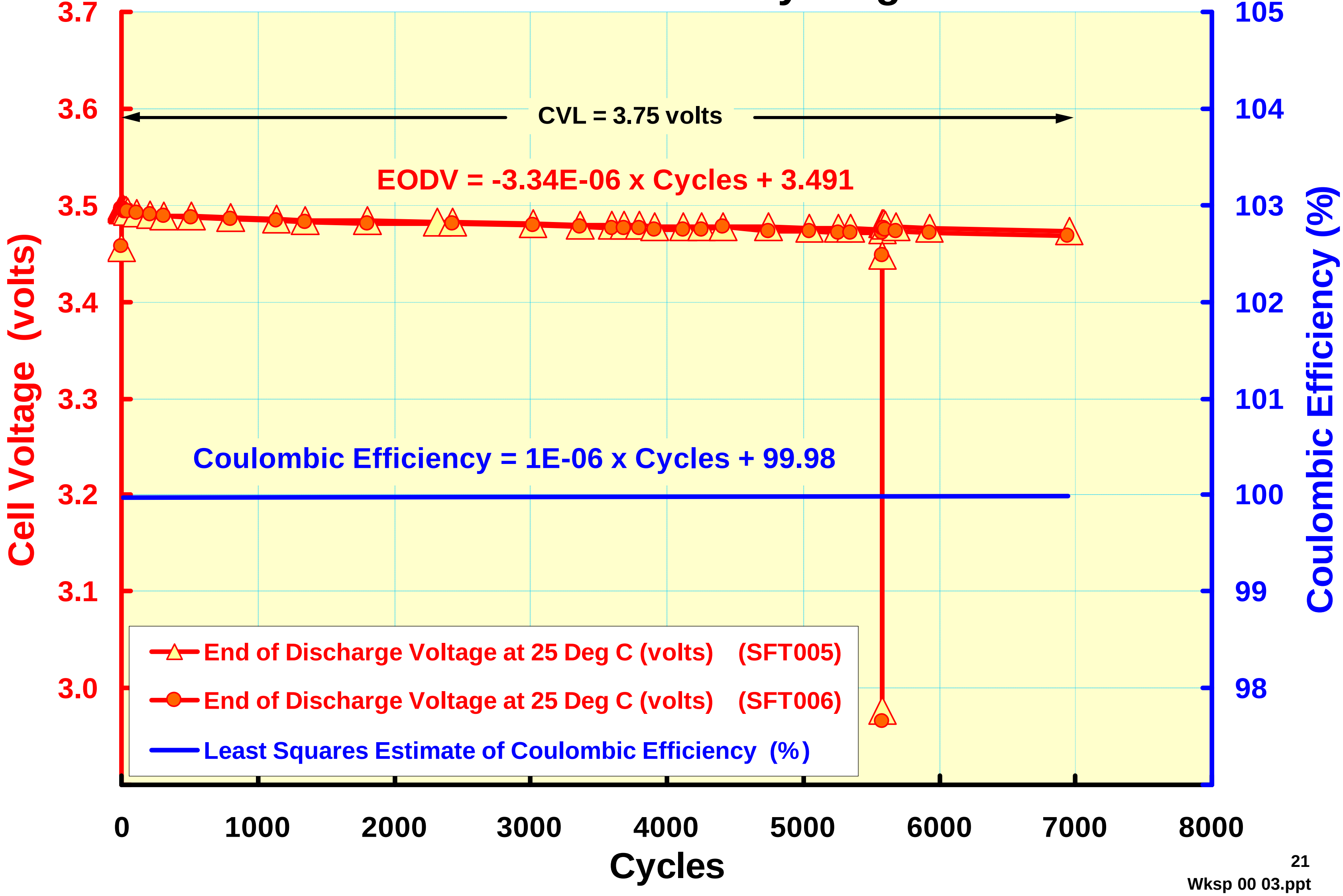
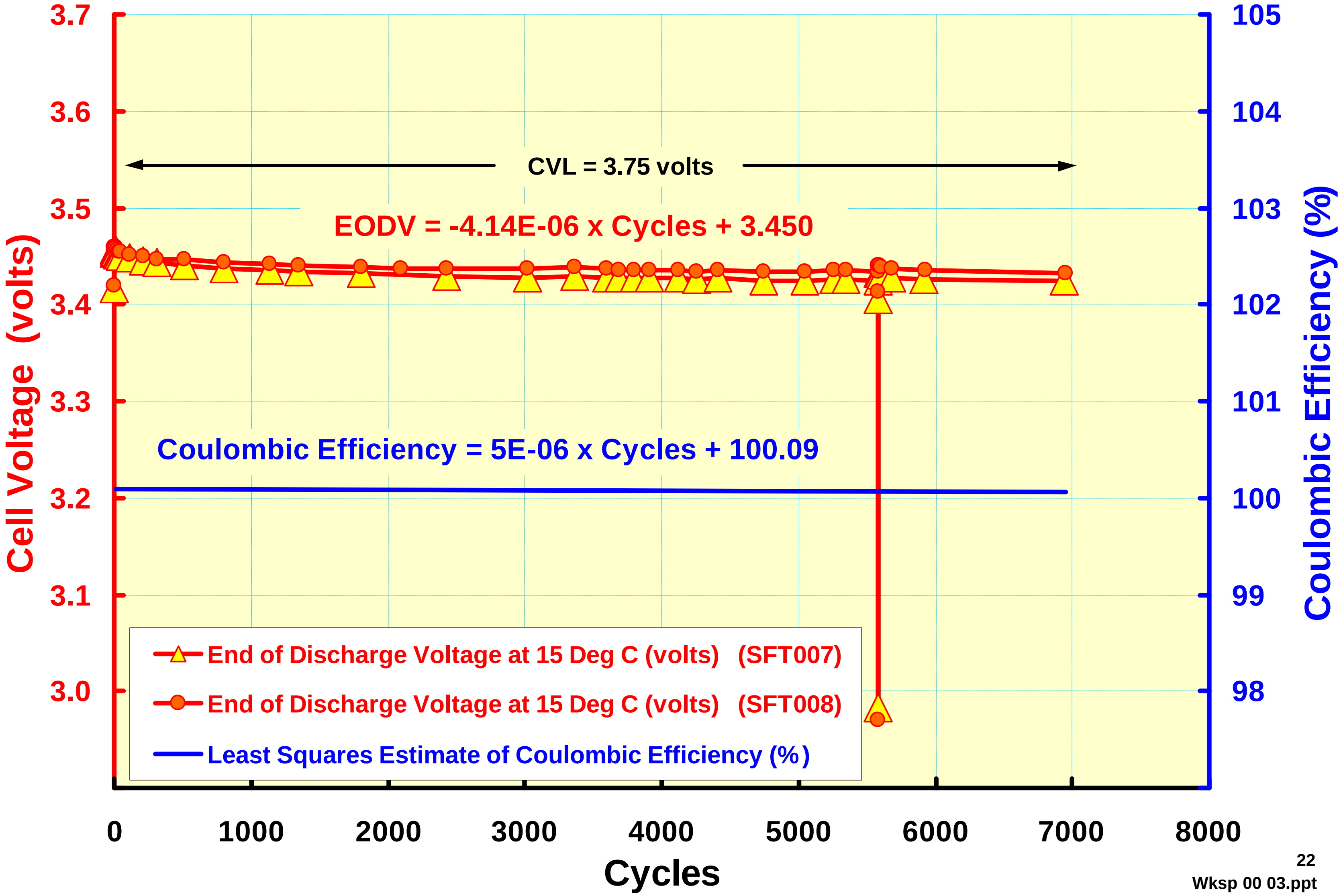
Prototype Cell LEO Cycling

EODV as a Function of cycling at 25ºC



Prototype Cell LEO Cycling

EODV as a Function of cycling at 15ºC



Prototype Cell LEO Cycling

Reserve Capacity Estimate

		Capacity (Ah) -- Charge: 3.75V CVL + taper			
Time (Months)	Temp (Deg C)	Discharge to 3.0V	Discharge to 25% of BOL 4.0V CVL capacity	Reserve	Loss
BOL	25	24.5	10.5	13.9	
13 Months	25	23.8	10.5	13.3	0.7
BOL	15	23.4	10.5	12.9	
13 Months	15	21.4	10.5	10.9	2.0

Capacity (Reserve), 3.75V CVL (Ah) = Capacity (LEO to 3.0V) - Capacity (25% DOD)

Capacity (Loss), 3.75V CVL (Ah) = Capacity (BOL) - Capacity (Time "t")

Summary

- SAFT MP 176065 and 42Ah space prototype cells are on test
- Testing includes initial characterization, and simulated, real time 25% DOD LEO cycling
- Initial characterization testing is complete
- MP cells have successfully completed > 2 years of LEO cycling
- 42 Ah cells have successfully completed > 1 year of LEO cycling and the low fade observed is encouraging; results are consistent with approximately 10-year life
- No anomalies have been observed
- Testing is continuing

CAPACITY MANAGEMENT AND WALKDOWN DURING LEO CYCLING OF NICKEL-HYDROGEN CELLS AND BATTERIES

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and Gloria To

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Presented at:

The 2000 NASA Aerospace Battery Workshop

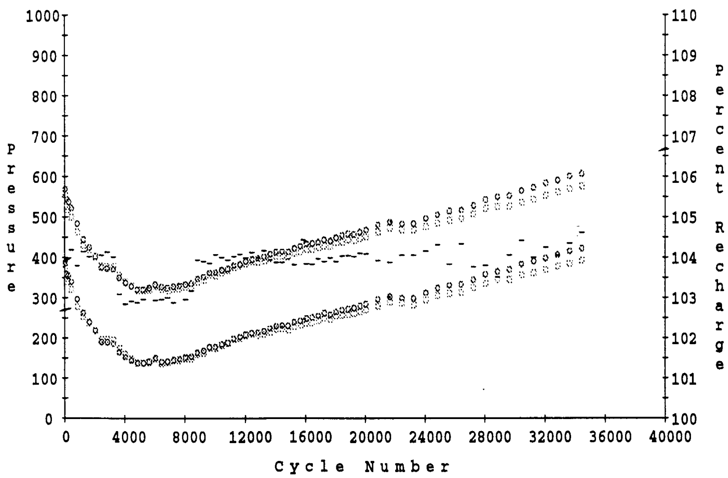
Huntsville, Alabama

November 14-16, 2000

OUTLINE OF PRESENTATION

- CAPACITY WALKDOWN DEFINED AND ILLUSTRATED
- IMPORTANCE OF CAPACITY WALKDOWN
- FOUR APPROACHES TO UNDERSTANDING THE PHENOMENON
  - Pressure Trend Studies
  - Charging Curve Studies
  - Electrochemical Voltage Spectroscopy Studies
  - Destructive Physical Analysis Studies
- RESULTS OF THE INTERRELATED STUDIES
- SUGGESTED MECHANISM FOR CAPACITY WALKDOWN
- CHARGING PROTOCOLS TO AVOID THE PROBLEM
- SUMMARY STATEMENTS

CAPACITY WALKDOWN



Characteristics

- Very Slow
- 2000 - 8000 Cycles
- Recoverable
- 30% to 40%Capacity Loss
- Monitored Using Strain Gauge

IMPORTANCE OF CAPACITY WALKDOWN

- **RESULTS IN A SIGNIFICANT REDUCTION IN THE RESERVE CAPACITY FOLLOWING A NORMAL DISCHARGE**
  - **The Gradual Drop in State of Charge for a Fixed Depth of Discharge will Result in Less and Less Reserve Capacity Following a Discharge**
- **WHEN THE CHARGEING PROTOCOL IS BASED ON A FIXED RECHARGE RATIO ADJUSTMENTS ARE REQUIED AS CYCLING CONTINUES**
  - **Accuracy to the Nearest One Tenth of a Percent May be Needed**

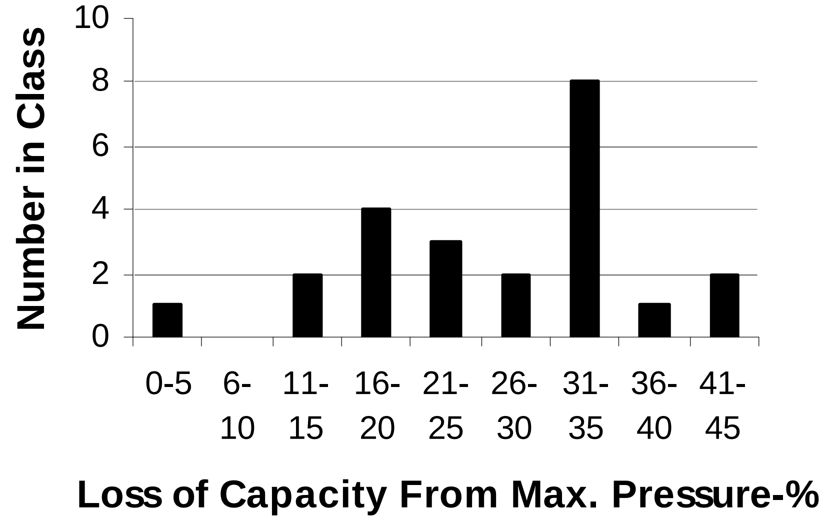
APPROACHES USED TO QUANTIFY AND UNDERSTAND CAPACITY WALKDOWN

- **PRESSURE TRENDS DURING LEO CYCLING AT THE NAVY FACILITY AT CRANE INDANA**
  - **Air Force, NASA Glenn, and NASA Space Station Tests**
- **CHARGING CURVES OF SELECTED AIR FORCE AND NASA SPONSORED LEO TESTS**
- **ELECTROCHEMICAL VOLTAGE SPECTROSCOPY STUDIES OF SELECTED SAMPLES OF PLATE MATERIAL FROM A VARIETY OF SOURCES**
- **EXTENSIVE DESTRUCTIVE PHYSICAL ANALYSES ON SIMILAR CELLS**
  - **One Cycled Under Conditions With No Walkdown**
  - **One Cycled Under Conditions With Significant Amount of Walkdown**

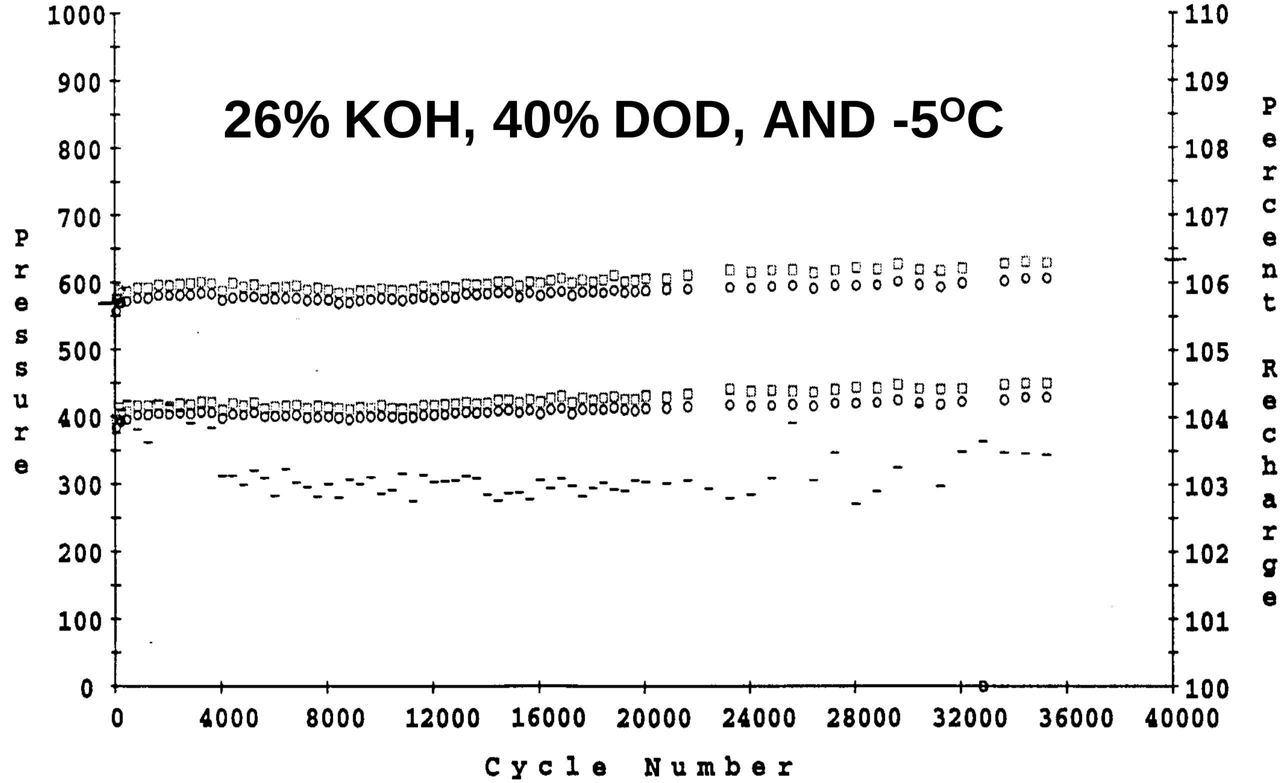
WALKDOWN AS A FUNCTION OF CYCLING CONDITIONS

- CELLS CYCLED AT 40% DOD AND -5^{O}C DID NOT SHOW WALKDOWN
- CELLS CYCLED AT 40% DOD AND +10^{O}C SHOWED VARIABLE AMOUNTS OF WALKDOWN
- CELLS CYCLED AT 60% DOD AND +10^{O}C SHOWED NO WALKDOWN
- CELLS CYCLED AT 60% DOD AND -5^{O}C SHOWED NO WALKDOWN BUT VERY SHORT CYCLE LIVES

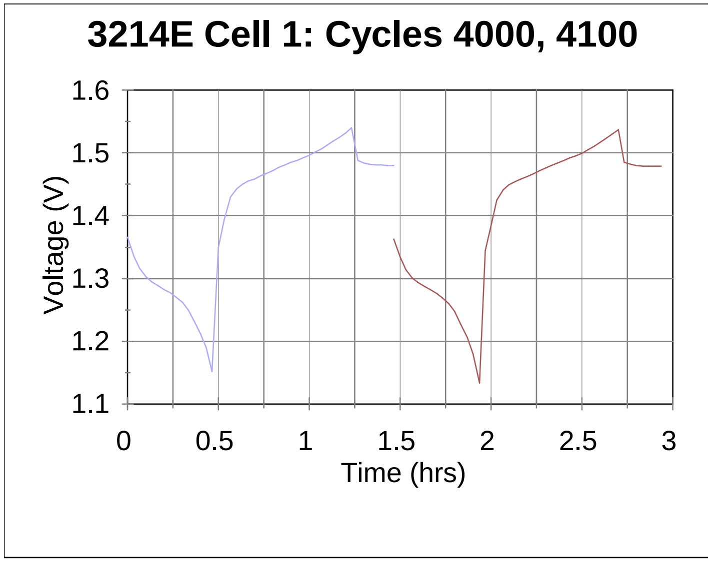
CAPACITY LOSS AT 40% DOD AND +10^{O}C



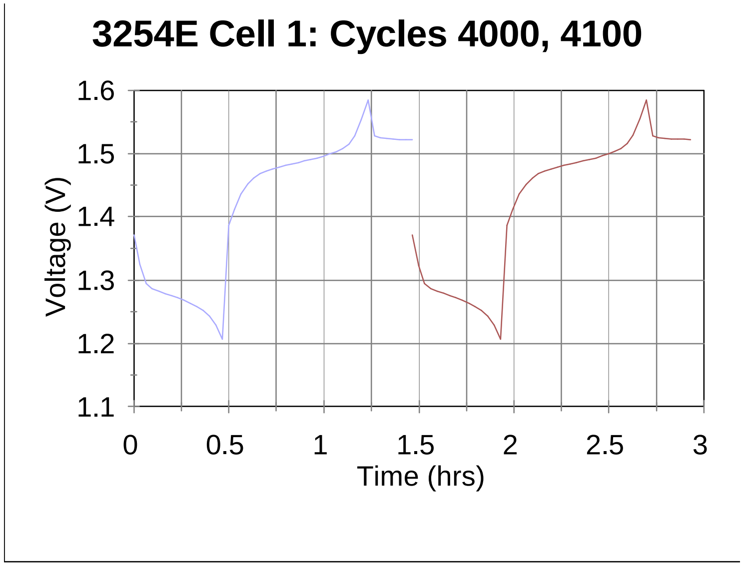
TYPICAL TEST SHOWING NO WALKDOWN



CHARGE CURVES FOR TWO CELLS: ONE AT +10^{O}C AND ONE AT -5^{O}C



+10^{O}C, 40% DOD, RR = 1.04

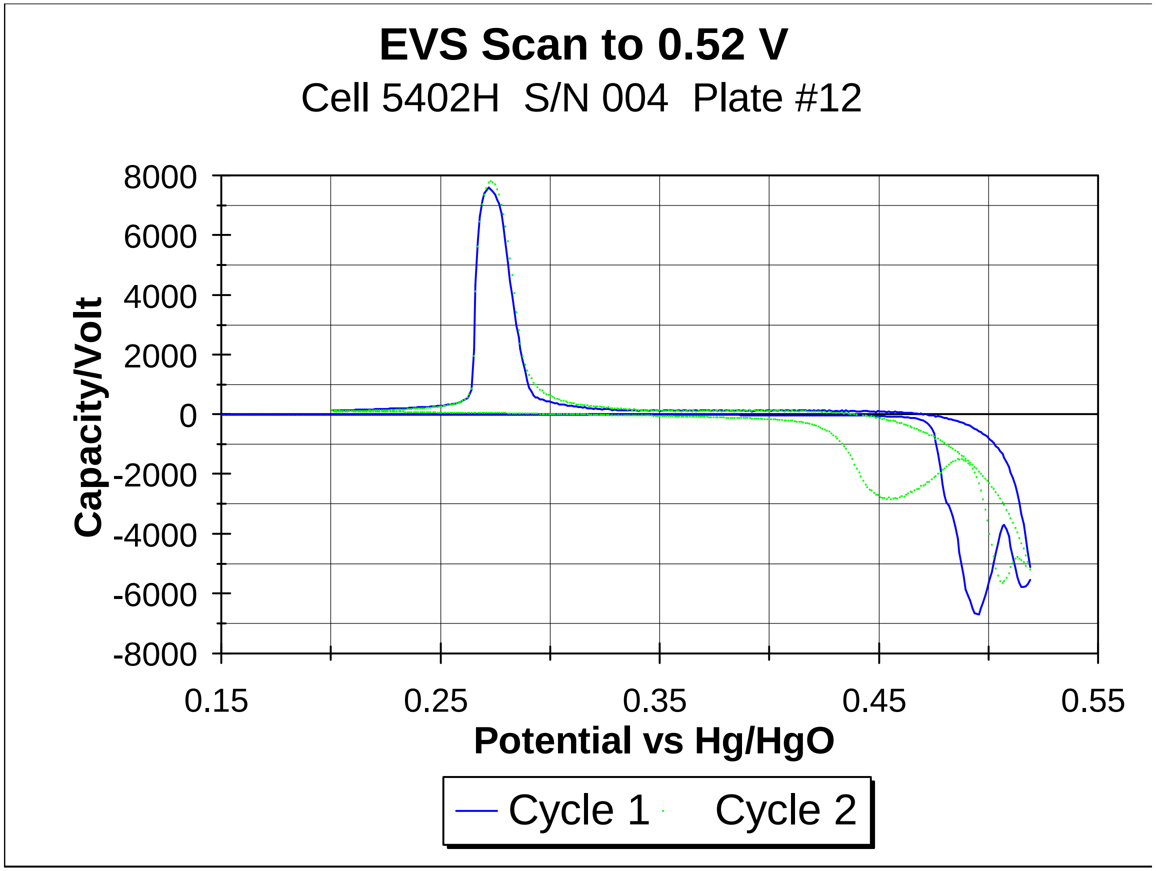


-5^{O}C, 40% DOD, RR = 1.03

DIFFERENCES IN CHARGING CURVES

- CYCLE 4000 WAS NEAR THE MINIMUM OF PRESSURE FOLLOWING WALKDOWN FOR CELLS IN PACK 3214E
- CELL #1 IN PACK 3214E DOES NOT SHOW THE SHARP ROLLUP AT THE END OF THE CHARGING PROCESS
- CELL #1 IN PACK 3254E HAS A SHARP ROLLUP INDICATIVE OF LESS OXYGEN EVOLUTION
  - This Results in a Higher Charging Efficiency and Therefore a Higher State of Charge at the End of the Charging Process for the Cell Cycled at -5^{o}C

ELECTROCHEMICAL VOLTAGE SPECTROSCOPY STUDIES



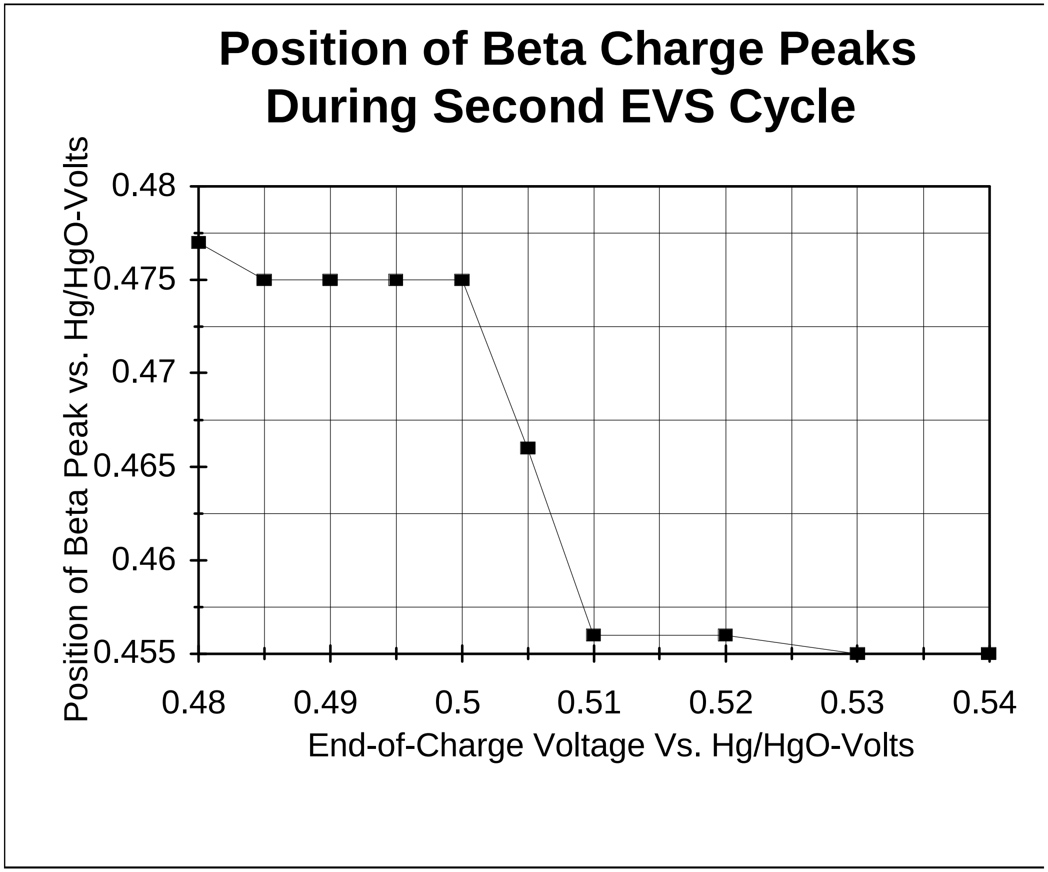
EVS REVEALED THE SOURCE OF THE WALKDOWN PHENOMENON

- THE BETA MATERIAL DURING THE FIRST CYCLE IS MORE DIFFICULT TO CHARGE BY 30 TO 40 MILLIVOLTS
- AFTER CHARGING TO THE GAMMA PHASE AND ONE FULL DISCHARGE, THE BETA MATERIAL IS REFERRED TO A BEING IN THE 'ACTIVE' FORM
- THE POSITION OF THE CHARGING PEAKS OF THE SECOND CYCLE IS INDICATIVE OF A DIFFERENT ACTIVE SPECIE
- IT HAS BEEN SUGGESTED THAT THEY ARE DIFFERENT CRYSTALINE FORMS OF BETA NICKEL HYDROXIDE
- WE HAVE NOT BEEN ABLE TO DESCERN ANY IDENTIFICABLE DIFFERENCES IN THE TWO DIFFERENT FORMS

RESULTS OF EVS SCANS TO DIFFERENT END OF CHARGE VOLTAGES

- MULTIPLE ~1.0 CM^2 SAMPLES SELECTED FROM THE SAME PLATE TAKEN FROM A GOOD CELL WITH ONLY 100 CYCLES
- TWO COMPLETE CHARGE DISCHARGE CYLES WERE USED AS PER THE PREVIOUS CHART
- THE END OF CHARGE VOLTAGE RANGED FROM 0.48 V vs. Hg/HgO REFERENCE ELECTRODE TO 0.54 V
- THE VOLTAGE PEAK FOR CHARGING THE BETA $Ni(OH)_2$ DURING THE SECOND CYCLE WAS RECORDED
- IT WAS FOUND THAT IF THE END OF CHARGE VOLTAGE WAS BELOW A CERTAIN VALUE, THE DISCHARGED FORM OF THE ACTIVE MATERIAL WAS NOT CONVERTED TO THE ACTIVE FORM
- FOR THIS ELECTRODE THE DIFFERENCE IN POTENTIAL OF THE TWO FORMS WAS 20 MILLIVOLTS

POSITION OF THE BETA PEAK DURING THE SECOND EVS SCAN



EXTENSIVE EVS STUDIES REVEALED THE FOLLOWING

- THE DEACTIVATED FORM OF NICKEL HYDROXIDE IS THE THERMDYNAMICALLY STABLE FORM
- THE ACTIVATED FORM OF NICKEL HYDROXIDE CAN BEGINE TO CONVERT BACK TO THE STABLE INACTIVE FORM IN ONLY A FEW DAYS
- ONCE IN THE ACTIVATED FORM, THE MATERIAL WILL REMAIN IN THE ACIVATED FORM AS LONG AS IT IS CHARGED ABOVE THE CRITICAL TRANSITION VOLTAGE
- THE DISCHARGE BETA AND GAMMA PEAKS SEPARATE AS ONE OR THE OTHER MATERIAL DOMINATES THE DISCHARGE TRACE

POST TEST AND DPA STUDIES ON SIMILAR CELLS

- CELL FROM PACK 3214E
  - +10 Degrees, 1.04 Recharge Ratio, 26% KOH
- CELL FROM PACK 3254E
  - -5 Degrees, 1.03 Recharge Ratio, 26% KOH
- CELLS WERE 50 Ah, DOUBLE LAYER ZIRCAR, SLURRY, BACK TO BACK CELLS CYCLING UNDER AIR FORCE SPONSORSHIP
- CELLS WITHDRAWN FROM ONGOING TESTS FOR OUR FURTHER STUDIES
- CRANE CONDUCTED TWO POST CEST CYCLES

SUMMARY OF CRANE POST TEST EVALUATION

Discharge	Charge	+10°C Cells	-5°C Cells
	Normal	1.04 recharge ratio	1.03 recharge ratio
C-rate		21.7 Ah discharged	46.8 Ah discharged
C/10-rate		11.3 Ah discharged	7.7 Ah discharged
Total 1st discharge		33.0 Ah discharged	54.5 Ah discharged
	C/2-rate	48.9 Ah charged	48.9 Ah charged
	C/10-rate	14.8 Ah charged	14.9 Ah charged
	Total 1st charge	63.7 Ah charged	63.8 Ah charged
C-rate		49.9 Ah discharged	50.2 Ah discharged
C/10-rate		7.7 Ah discharged	9.0 Ah discharged
Total 2ed Discharge		57.6 Ah discharged	59.2 Ah discharged

AEROSPACE DPA ACTIVITIES

- **CELLS PUNCTURED IN SPECIAL CHAMBER TO MEASURE RESIDUAL GAS PRESSURE AND COMPARE WITH STRAIN GAUGE READINGS OF OTHER CELLS WITHIN THE PACK**
- **RESIDUAL GAS SAMPLES SENT FOR MASS SPEC. ANALYSIS**
- **FLOODED UTILIZATION AND EVS TESTING OF PLATE SAMPLES FROM FOUR SECTORS OF THE CELLS**
- **CHEMICAL ANALYSIS CARRIED OUT ON SINTER AND ACTIVE MATERIAL**

RESIDUAL PRESSURE AND GAS ANALYSIS

Cell Pack	3214 E	3254 E
Cycling Temp. - ^{o}C	+ 10	-5
Residual Pressure - psia	118.0	1.3
Composition - %		
Hydrogen	97.8	3.0
Water Vapor	1.8	16.3
Nitrogen	0.3	77.9
Average Plate Expansion - %	15.7	15.0

SUGGESTED MECHANISM

- CHARGING TO HIGHER VOLTAGES CONVERTS BETA NICKEL OXYHYDROXIDE TO THE GAMMA PHASE
- UPON DISCHARGE, THE UNSTABLE ALPHA FORM OF NICKEL HYDROXIDE IS FORMED
- THIS MATERIAL DISSOLVES IN KOH AND PRECIPITATES AS A VERY SMALL CRYSTALINE FORM OF BETA NICKEL HYDROXIDE
- THIS IS THE ACTIVATED FORM AND CAN EASILY BE CHARGED TO THE GAMMA FORM VIA THE BETA NICKEL OXYHYDROXIDE
- OSTWOLD RIPENING CONVERTS THE ACTIVATED FORM BACK TO THE DEACTIVATED FORM
- LOWER TEMPERATURES FACILITATE THE CHARGING TO THE GAMMA PHASE AND RETARDS THE RATE OF COVERSION BACK TO THE DEACTIVATED FORM

SUGGEST RECHARGE PROTOCOL TO AVOID OR MINIMIZE WALKDOWN

- **CYCLING TEMPERATURE MUST BE LOW ENOUGH TO PERMIT CHARGING TO THE GAMMA PHASE**
- **DETERMINE MINIMUM VOLTAGE REQUIRED TO CONVERT MATERIAL TO THE ACTIVE FORM**
- **CHARGE TO A CUTOFF PRESSURE OR MONITOR THE END OF CHARGE PRESSURE**
- **CORRECT PRESSURE READING FOR STRAIN GAUGE DRIFT AND SINTER CORROSION VIA RECONDITIONING**

SUMMARY

- CAPACITY WALKDOWN A CONSEQUENCE OF THE INABILITY TO MAINTAIN A HIGHT STATE OF CHARGE
- CAPACITY LOSS IS TYPICALLY 35% WHICH WOULD BE EXPECTED BY THE VALENCE DIFFERNCE BETWEEN GAMMA AND BETA NICKEL OXYHYDROXIDE
- CYCLING AT -5 DEGREES FACILITATES THE FORMATION OF THE GAMMA PHASE
- EXCESSIVE OVERCHARGE CAN ALSO FACILITATE GAMMA PHASE FORMATION AT THE EXPENCE OF CYCLE LIFE
- CONDITIONS CAN NOW BE SUGGESTED TO HELP MINIMIZE CAPACITY WALKDOWN

Mathematical Modeling of Ni/H_2 and Li-Ion Batteries

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Department of Chemical Engineering
and
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Department of Electrical Engineering

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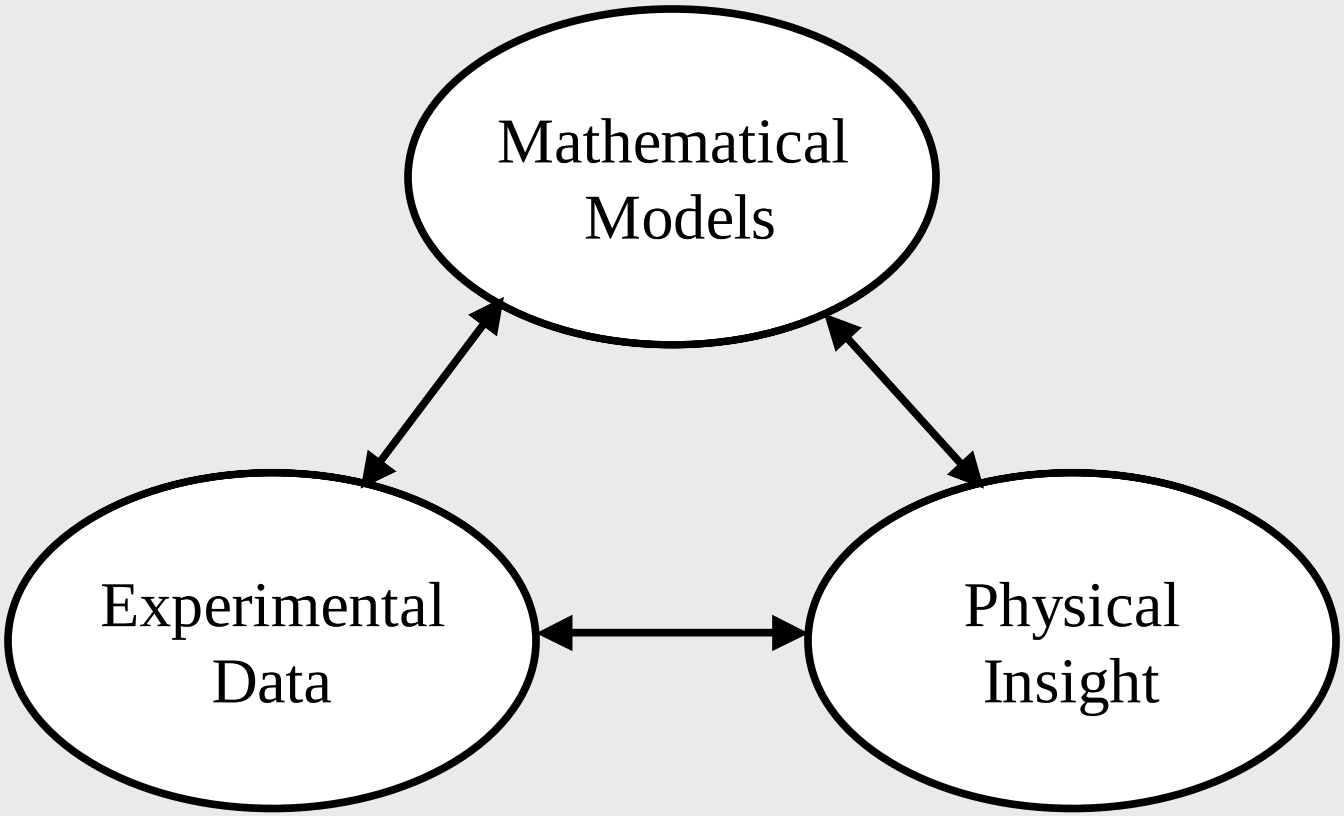
Analysis of Battery Systems



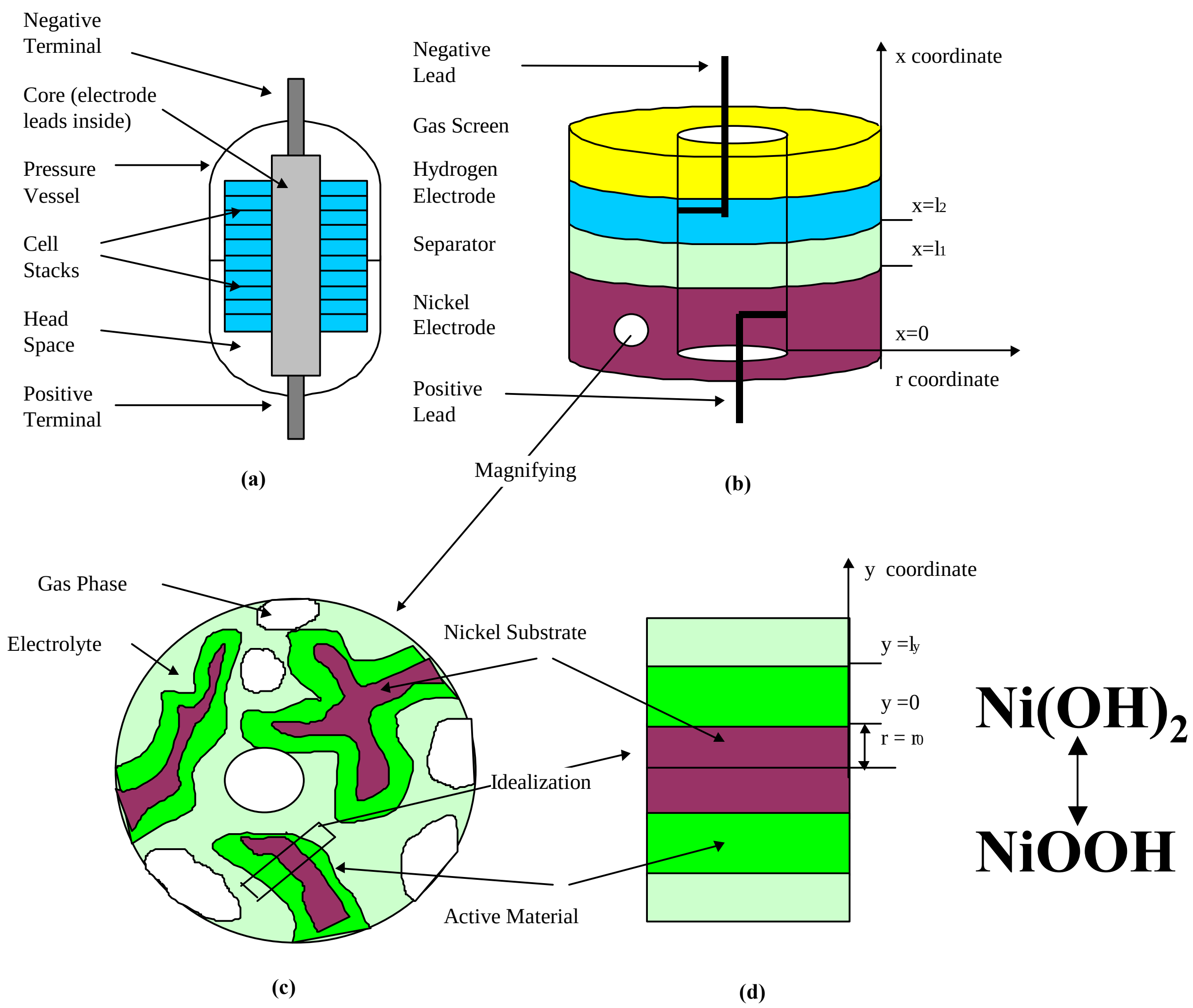
Modeling Effort

- Electrochemical Deposition of Nickel Hydroxide
  - Deposition rates of thin films
  - Impregnation of porous electrodes
- Experimental Characterization of Nickel Hydroxide
  - Diffusion coefficients of protons
  - Self-discharge rates (*i.e.*, oxygen-evolution kinetics)
  - Hysteresis between charge and discharge
  - Capacity loss on cycling

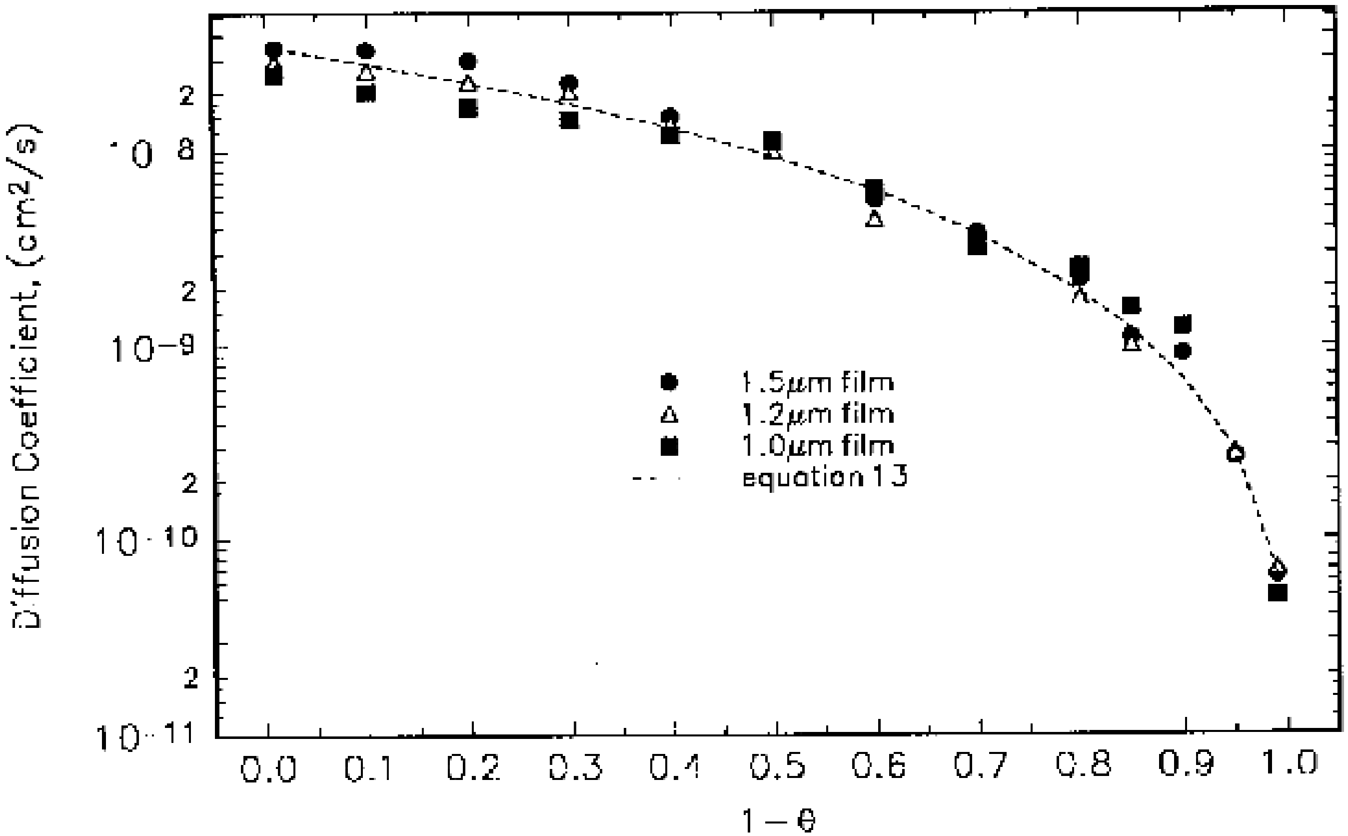
Modeling Effort

- Mathematical Modeling of Ni/H_2 Batteries
- Experimental Verification of the Ni/H_2 Battery Model
- Mathematical Modeling Li-Ion Batteries
- Experimental Verification of the Li-Ion Battery Model
- Integrated Power System Models for Satellites
- Experimental Verification of Integrated-Systems Model

Schematic of Ni/H_2 Battery

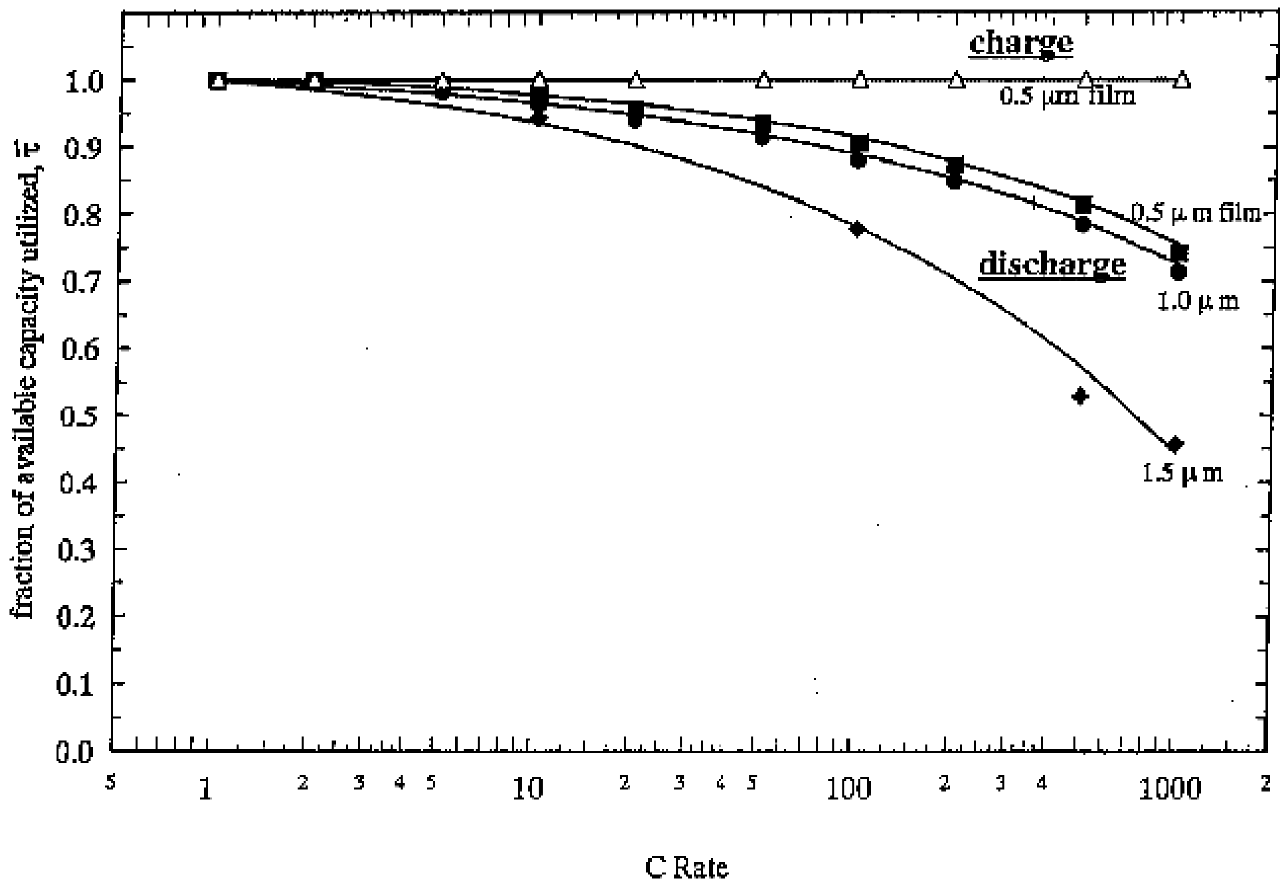


Proton Diffusion Coefficient



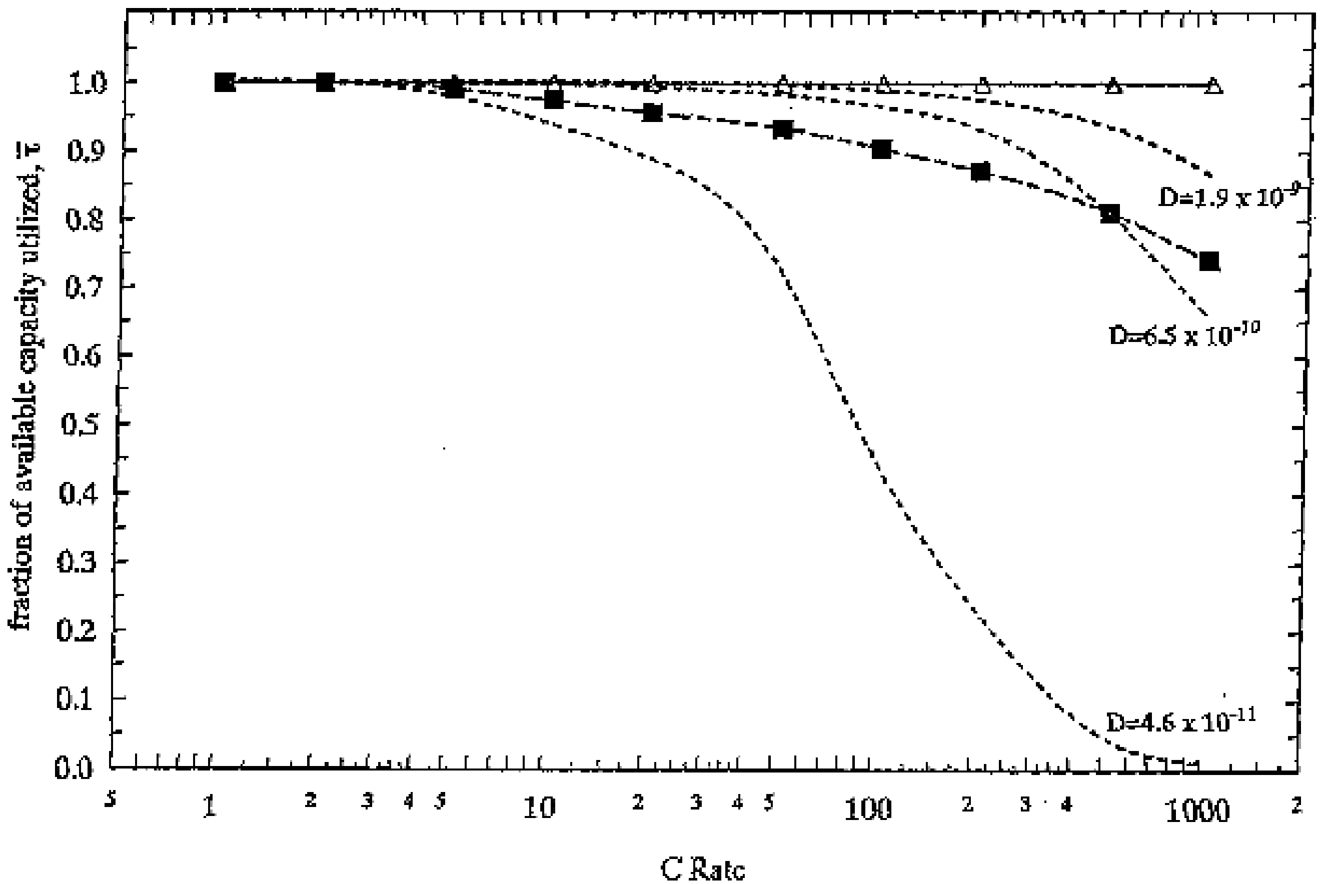
S. Motupally, C. C. Streinz, and J. W. Weidner, *J. Electrochem. Soc.*, **142**, 1401-1408 (1995).

Utilization of the NiOOH



S. Motupally, C. C. Streinz, and J. W. Weidner, *J. Electrochem. Soc.*, **145**, 29-34 (1998).

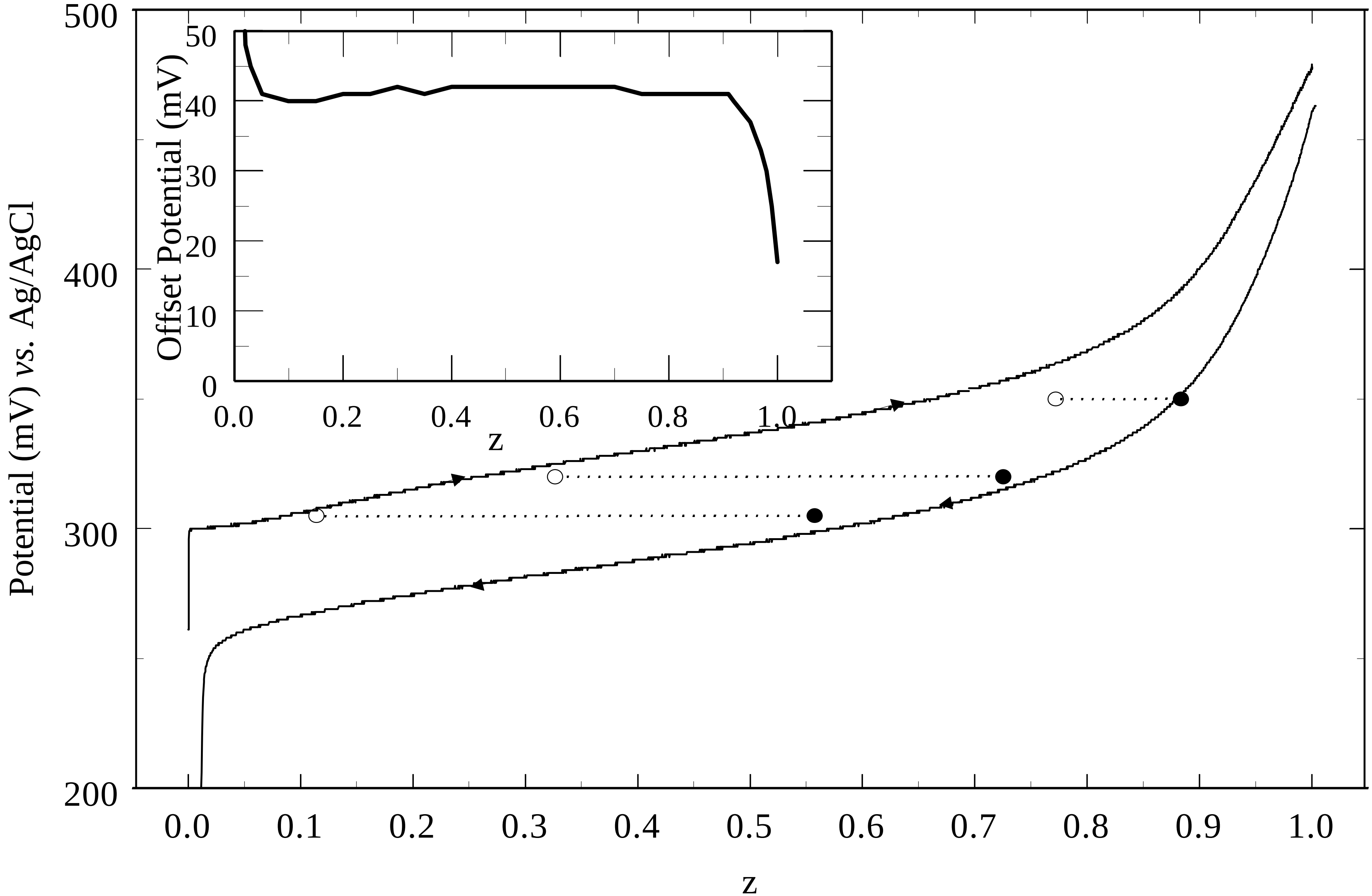
Utilization of the NiOOH



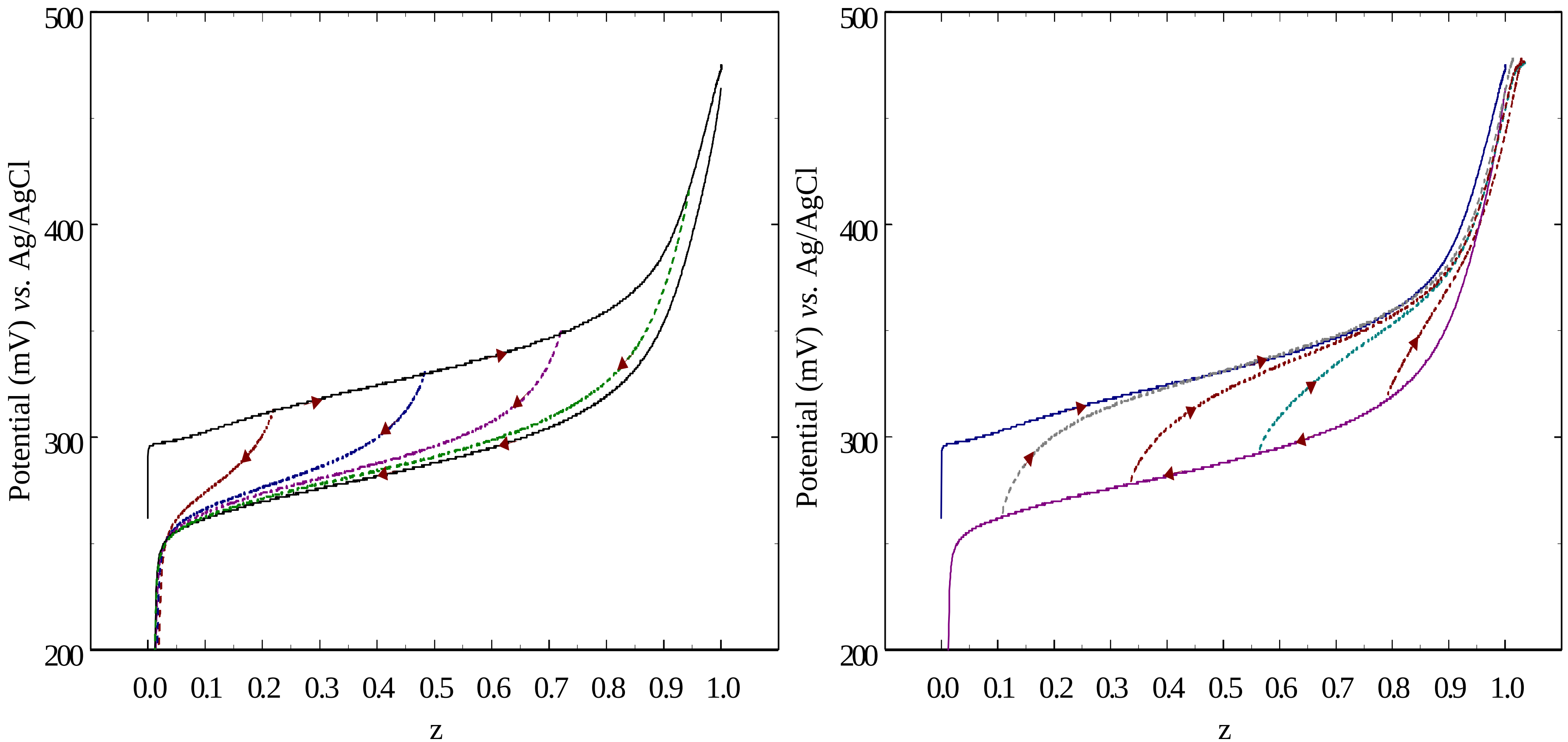
S. Motupally, C. C. Streinz, and J. W. Weidner, *J. Electrochem. Soc.*, **145**, 29-34 (1998).

Hysteresis in the Nickel Electrode

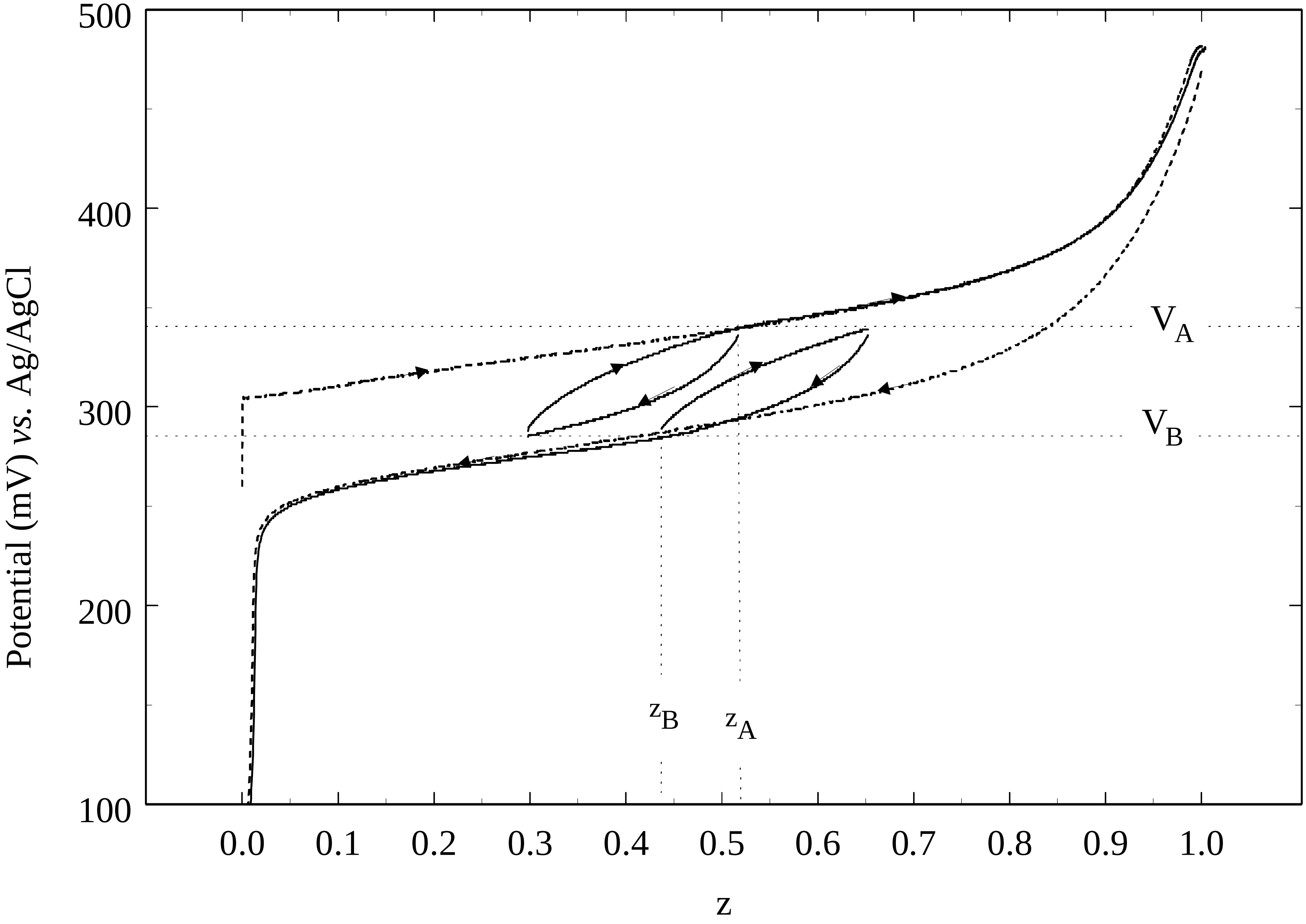
Constant Current *vs.* Constant Potential Experiments

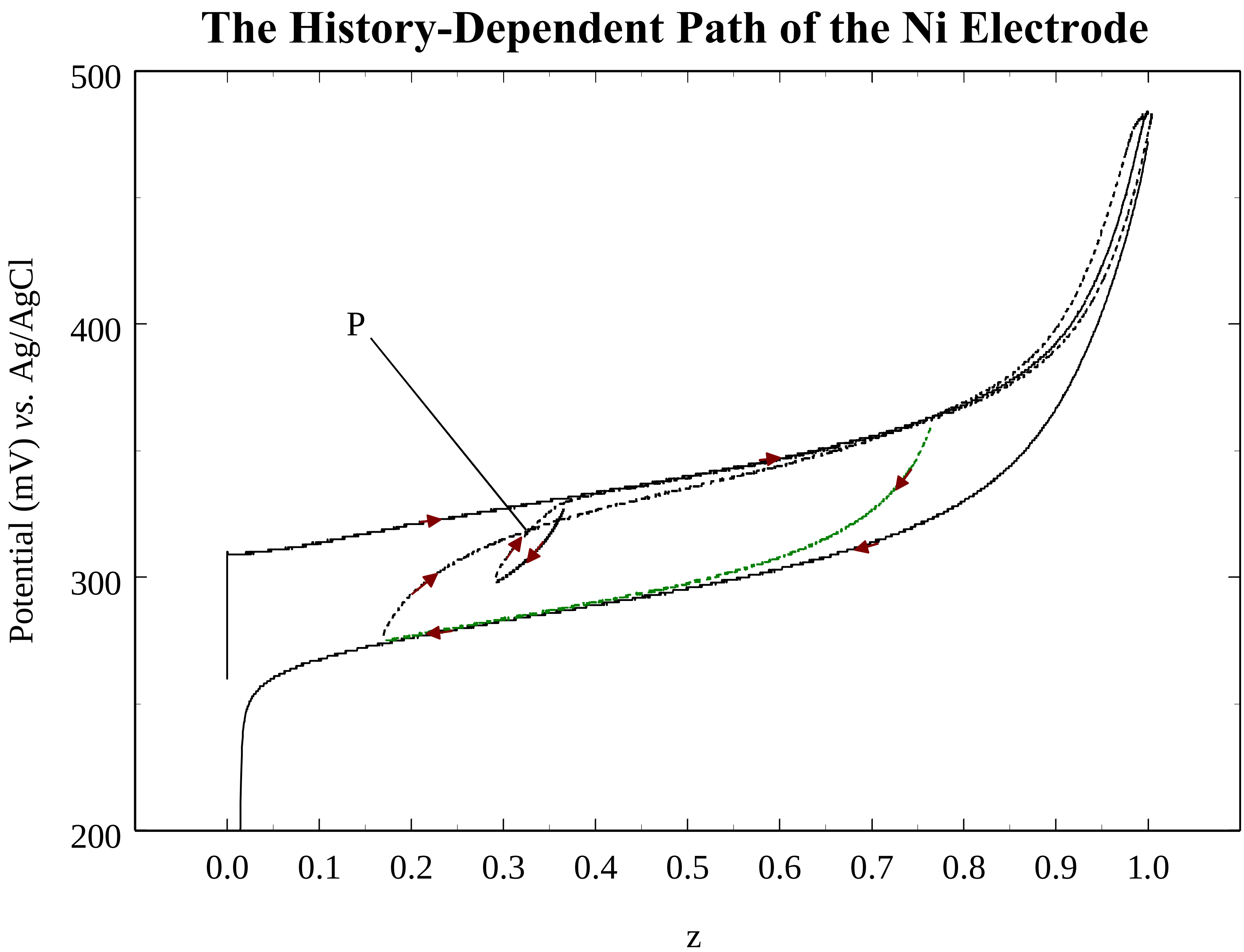


Boundary and Scanning Curves During Proton Intercalation/Extraction

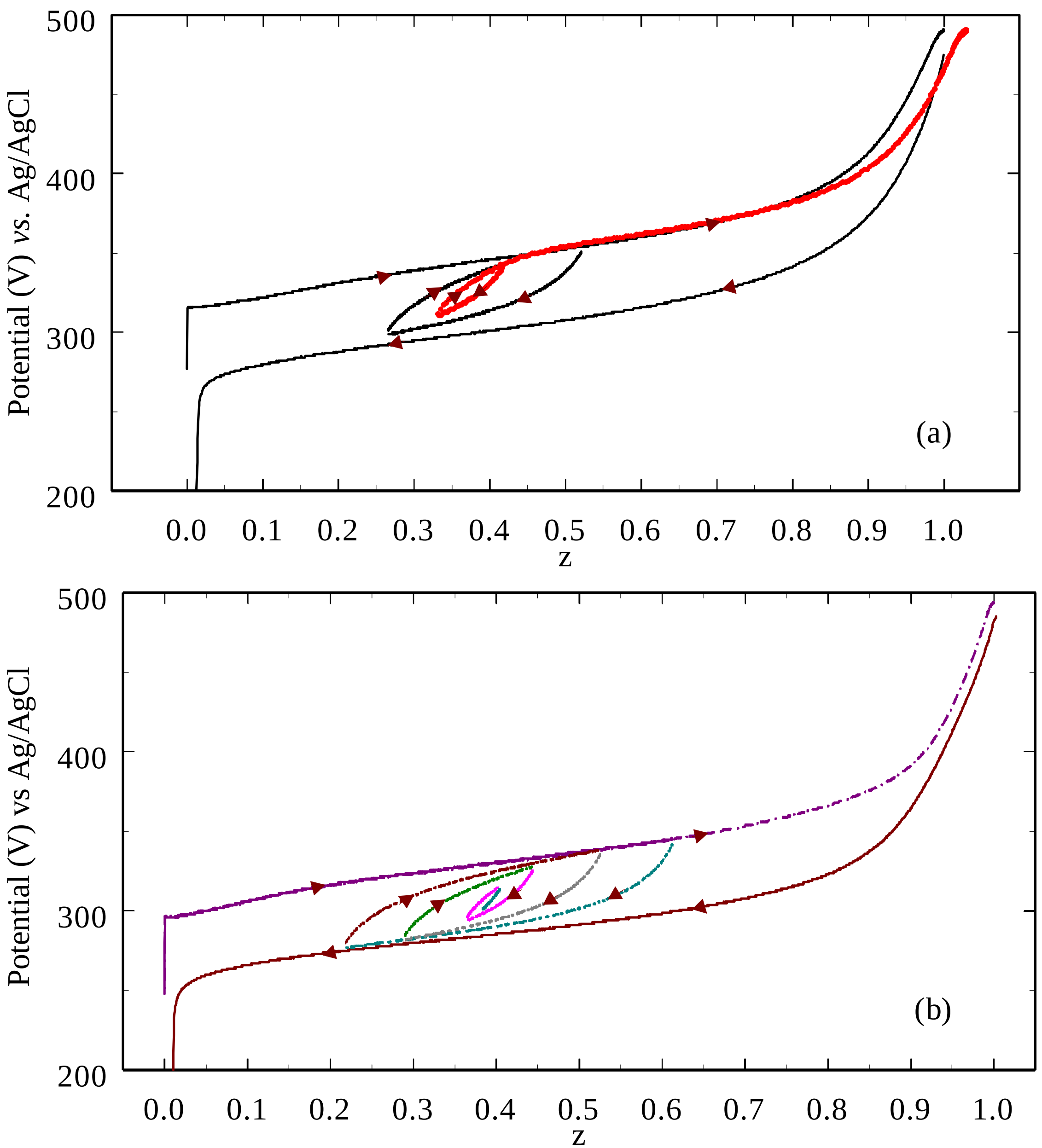


“Wiping-out” Property of Systems Exhibiting Hysteresis

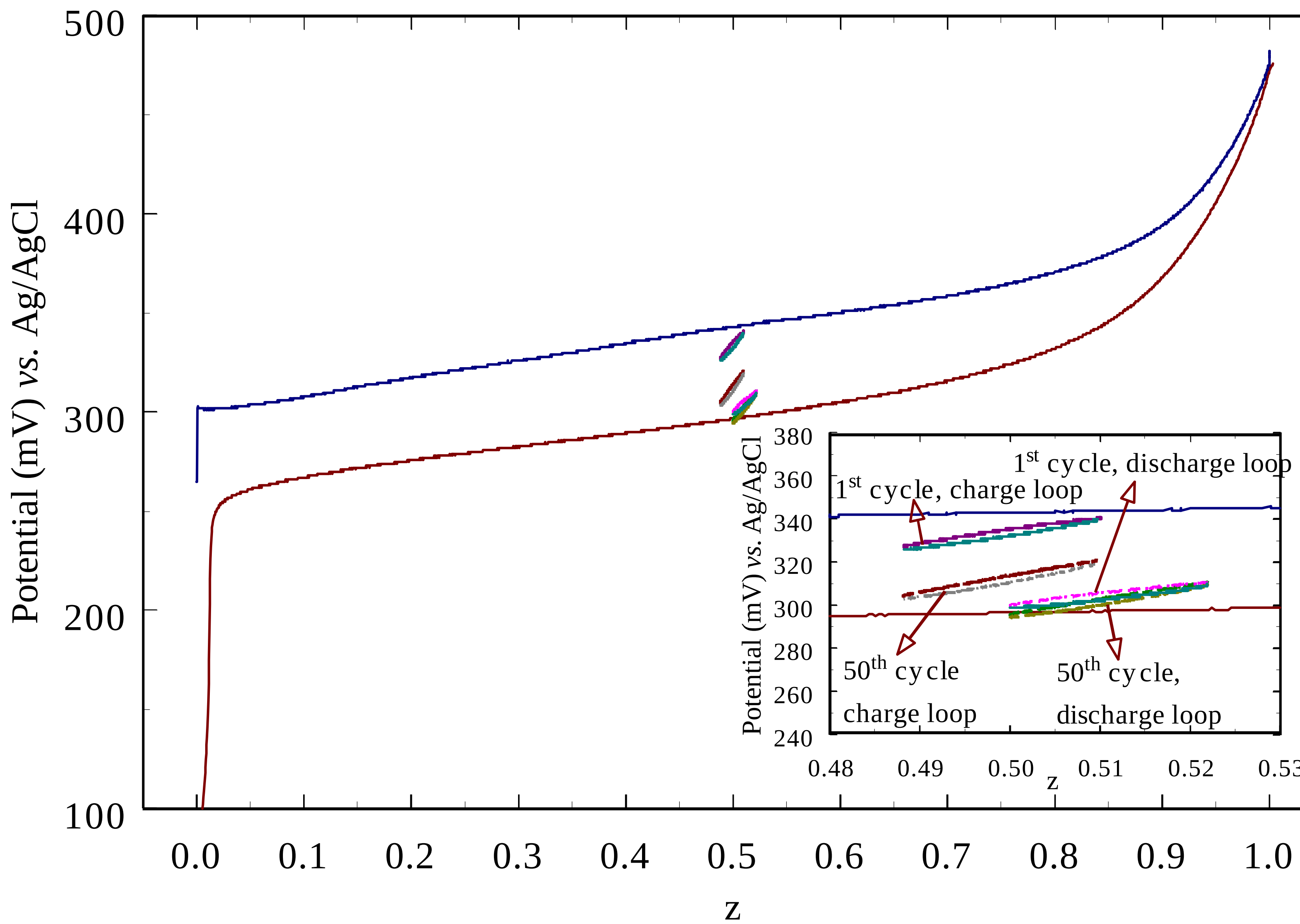



The History-Dependent Path of the Ni Electrode
500
400
300
200
Potential (mV) vs. Ag/AgCl
P
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
z

Internal Hysteresis Loops in The Ni Electrode

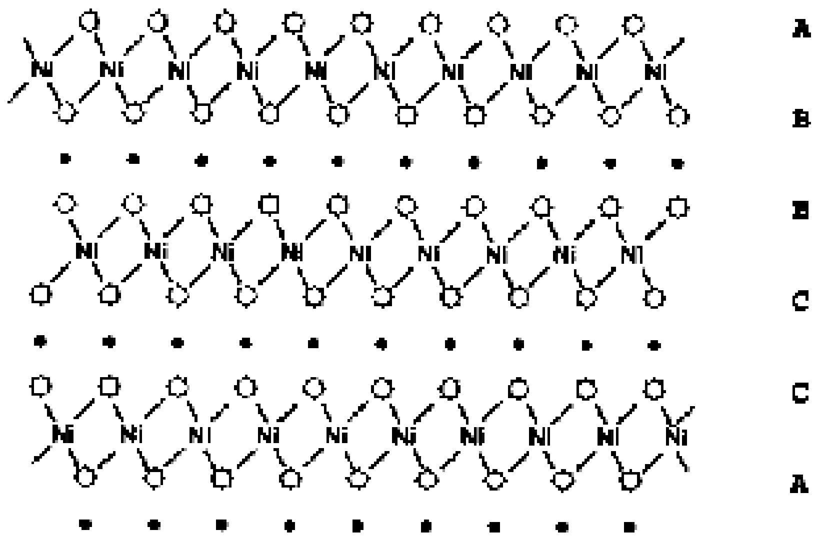


Path of the System During Continuous Cycling Over Small Z

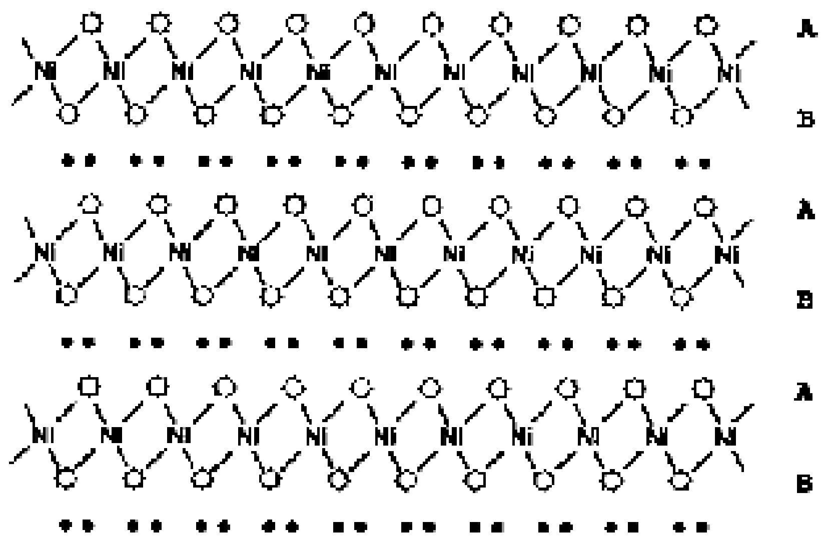


Crystal Structures for Nickel Hydroxide

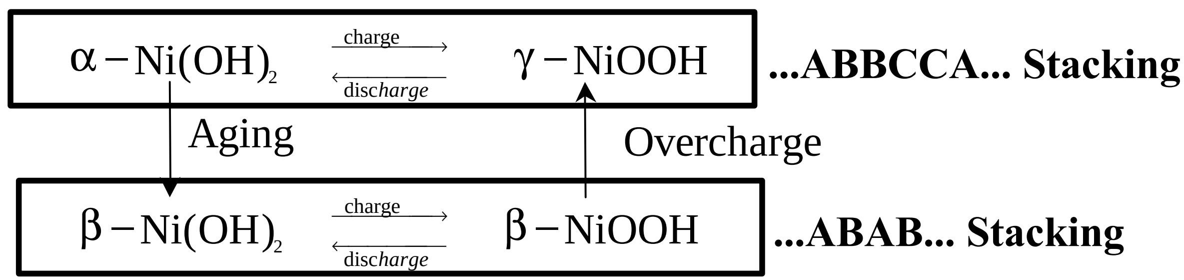
ABBCCA Structure: NiOOH



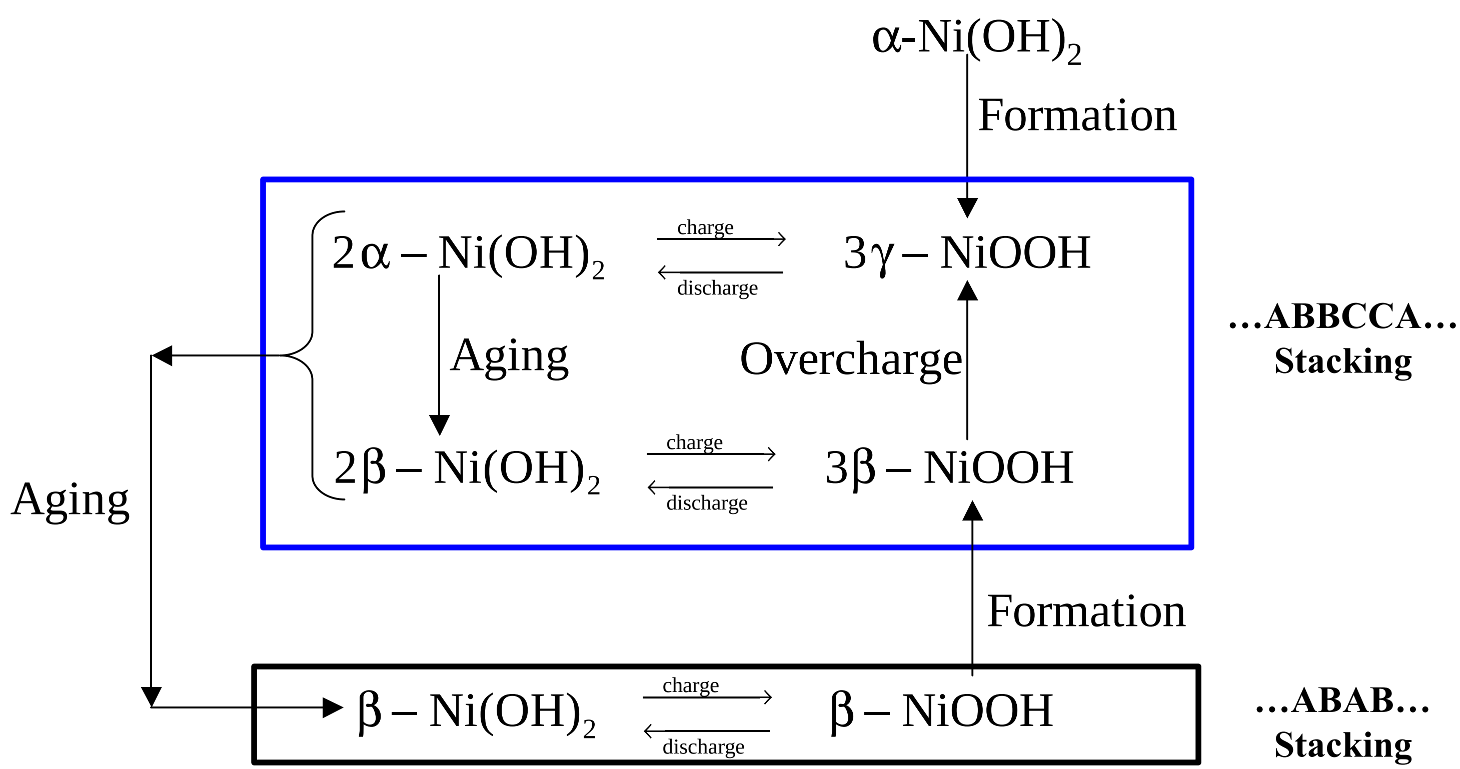
ABAB Structure: $Ni(OH)_2$



Bode Diagram



Modified Bode Diagram



Defect Representation of the Nickel Hydroxide Electrode

$$\left[Ni_{1-x}\, a K\, t_{y}\, a_{i}\, H\, t_{x-y}\right]OOH_{2-z} \cdot X_{w} H_{2}O$$

$$x = \frac{\text{number of Ni vacancies}}{\text{total number of Ni lattice sites}}$$

$$y = \frac{\text{number of Ni vacancies occupied by } K^{+}}{\text{total number of Ni lattice sites}}$$

$$n = \frac{\text{number of } H^{+}}{\text{number of Ni vacancies not occupied by } K^{+}}$$

$$X_{w} = \frac{\text{number of water molecules}}{\text{total number of Ni lattice sites}}$$

$$2 - z = \frac{\text{number of interlamellar protons}}{\text{total number of Ni lattice sites}}$$

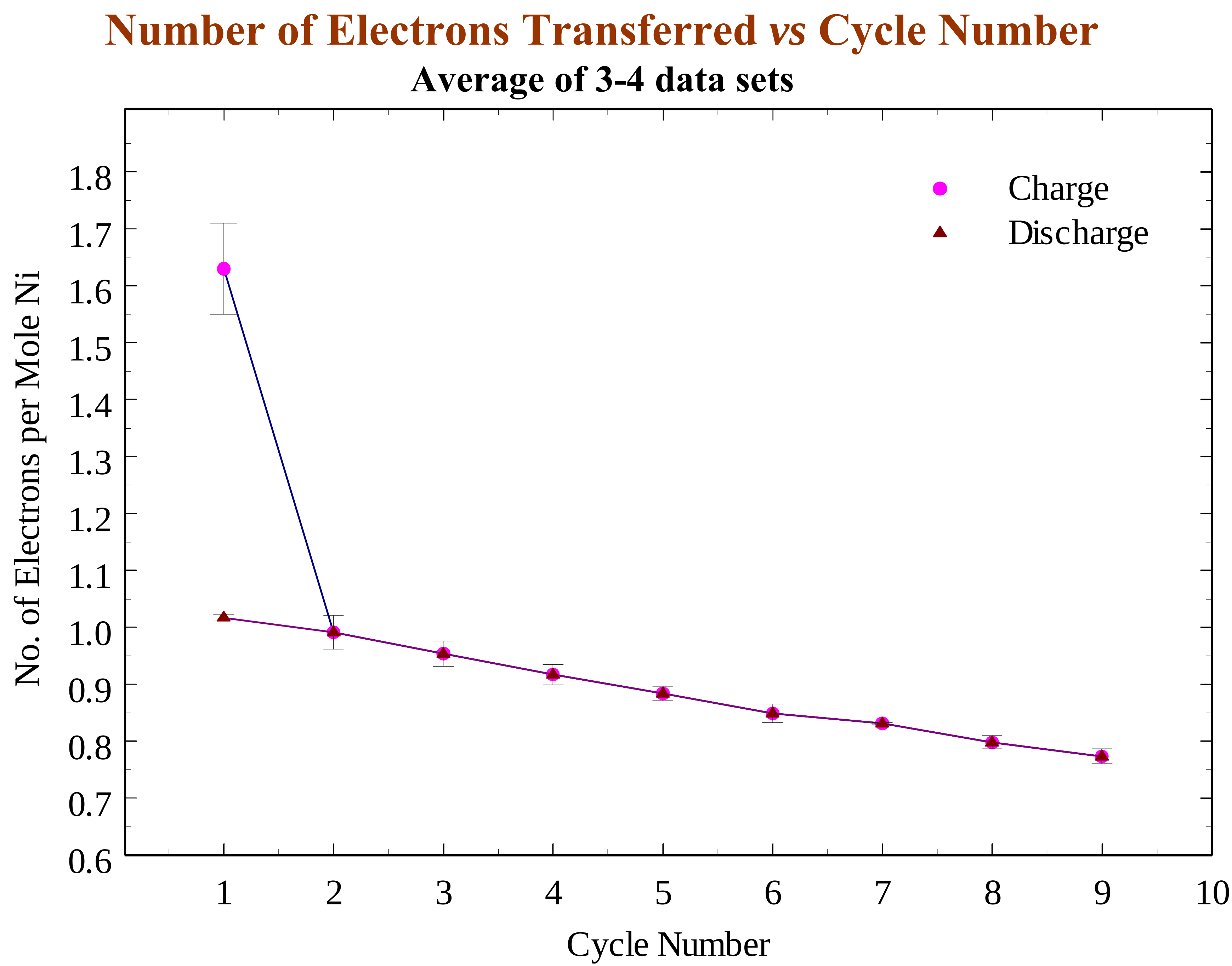
Nickel Hydroxide Redox Reaction

$$\left[\mathbf{Ni}\,(\mathbf{K})_{\frac{y_1}{(1-x_1)}}(\mathbf{n_1H})_{\frac{x_1-y_1}{1-x_1}}\right]\mathbf{O}_{\frac{2}{1-x_1}}\mathbf{H}_{\frac{2}{1-x_1}}\cdot \mathbf{X}_{w_1}\mathbf{H_2O} + \lambda_1\mathbf{OH}^- + \lambda_2\mathbf{K}^+$$

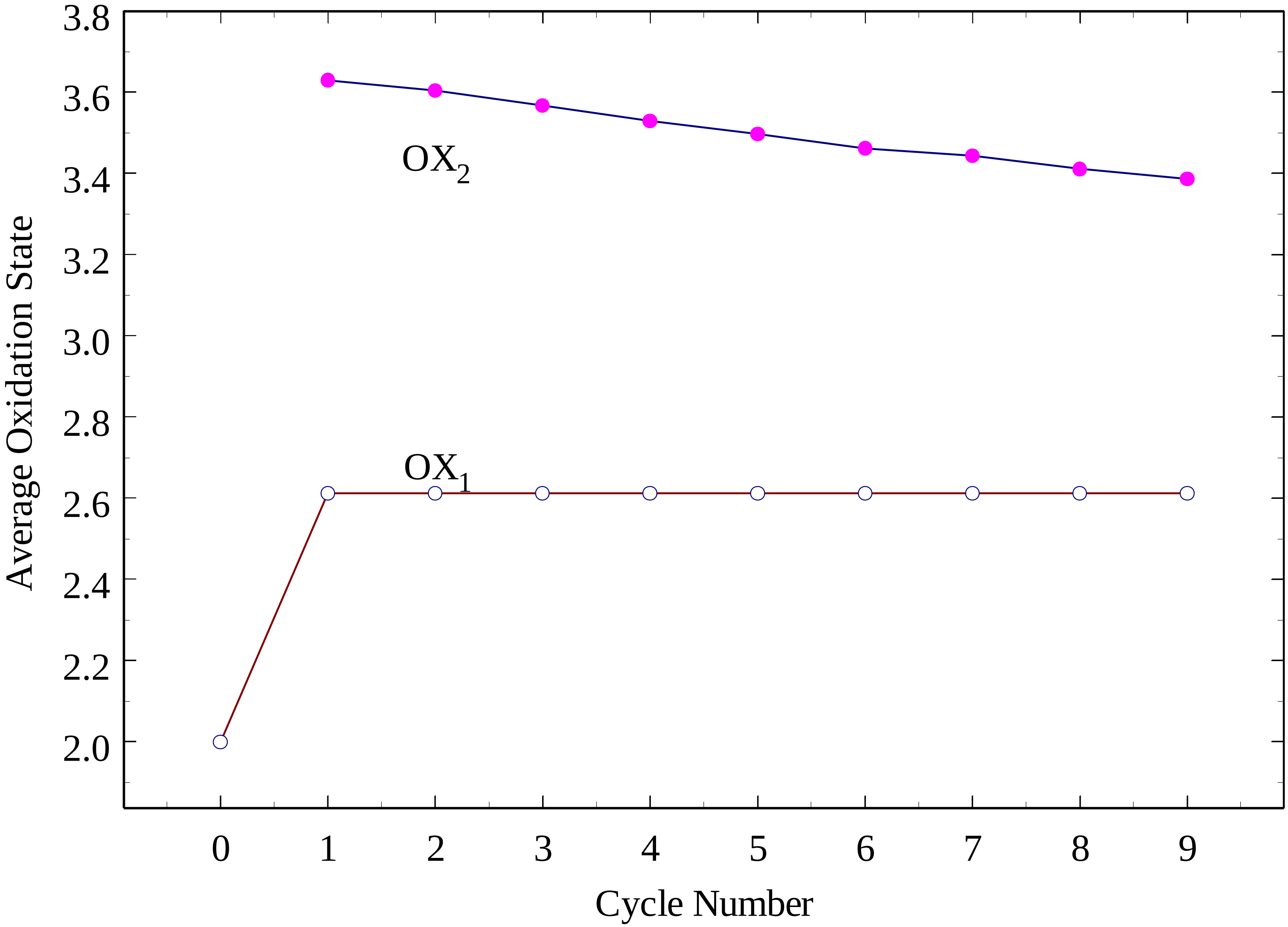
$$\underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \left[\mathbf{Ni}\,(\mathbf{K})_{\frac{y_2}{(1-x_2)}}(\mathbf{n_2H})_{\frac{x_2-y_2}{1-x_2}}\right]\mathbf{O}_{\frac{2}{1-x_2}}\mathbf{H}_{\frac{1}{1-x_2}}\cdot \mathbf{X}_{w_2}\mathbf{H_2O} + \lambda_3\mathbf{H_2O} + \lambda_4\mathbf{e}^-$$

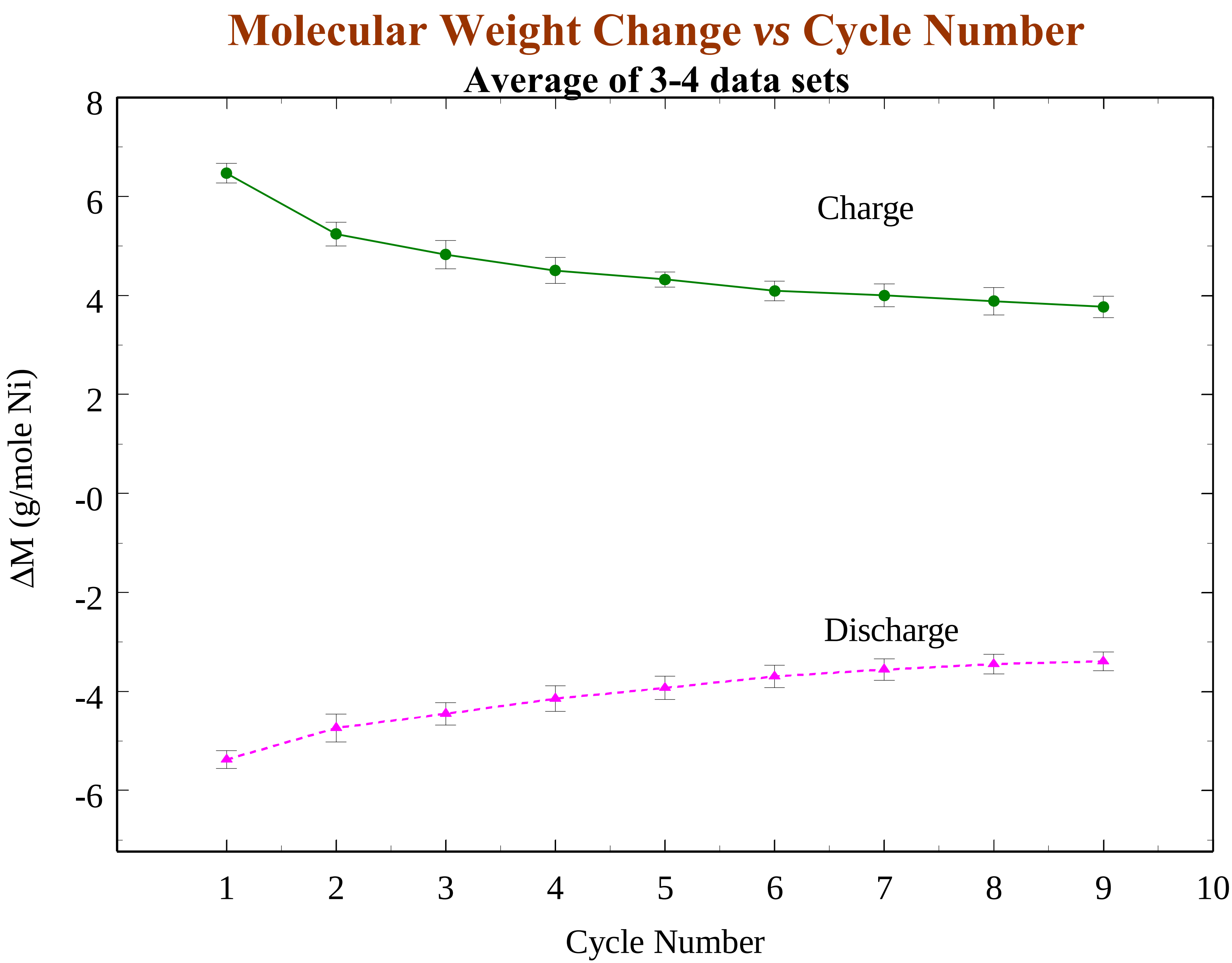
$$\lambda_1 = \left[\frac{n_1(x_1-y_1)-2}{(1-x_1)} - \frac{n_2(x_2-y_2)-3}{(1-x_2)}\right] \qquad \lambda_3 = \left[\frac{n_1(x_1-y_1)}{(1-x_1)} - \frac{n_2(x_2-y_2)-1}{(1-x_2)}\right] + X_{w_1} - X_{w_2}$$

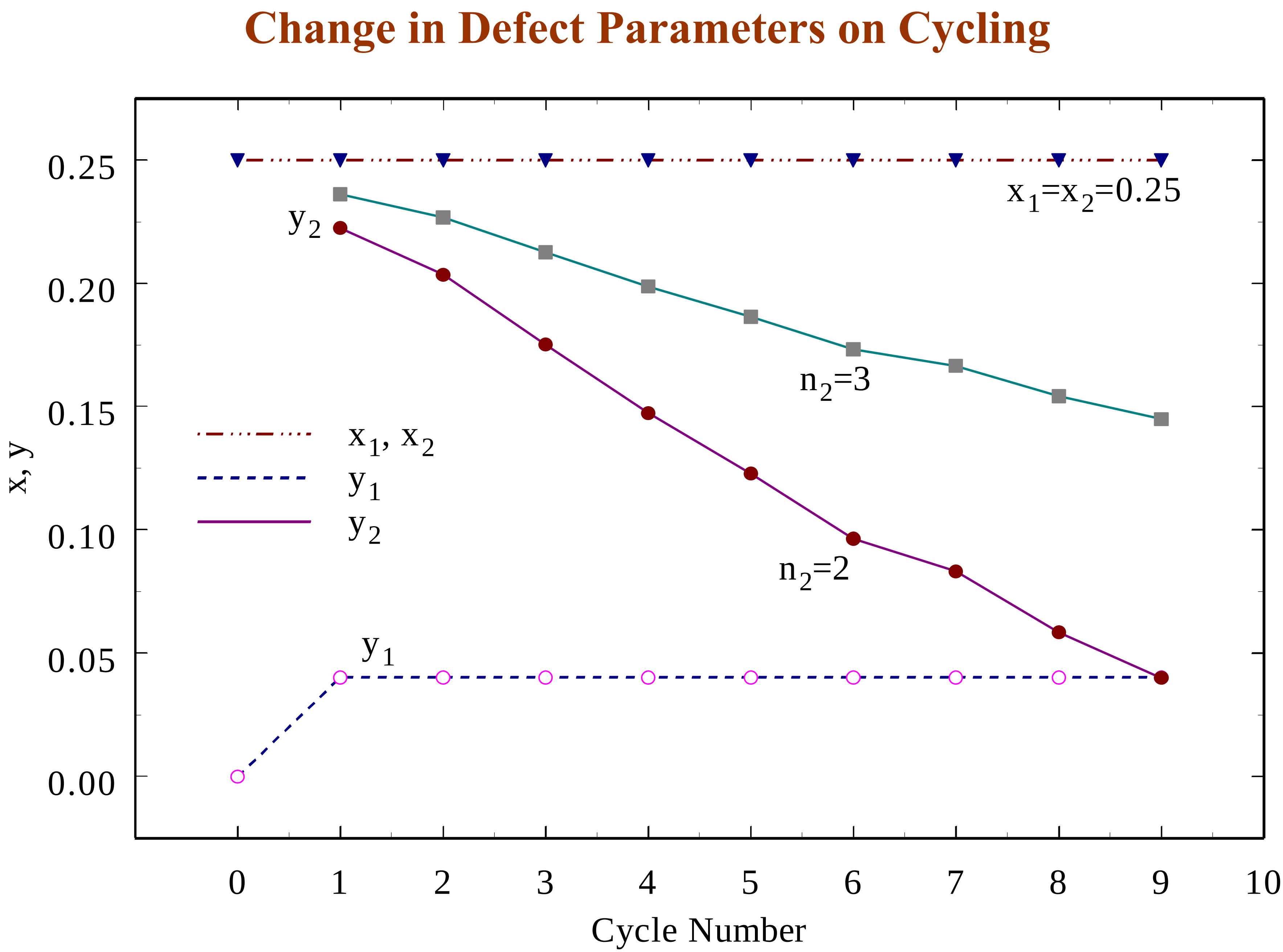
$$\lambda_2 = \left[\frac{y_2}{(1-x_2)} - \frac{y_1}{(1-x_1)}\right] \qquad \lambda_4 = \left[\frac{3-y_2-n_2(x_2-y_2)}{(1-x_2)} - \frac{2-y_1-n_1(x_1-y_1)}{(1-x_1)}\right]$$


Number of Electrons Transferred vs Cycle Number
Average of 3-4 data sets
Charge
Discharge
No. of Electrons per Mole Ni
Cycle Number
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1
2
3
4
5
6
7
8
9
10

Change in Oxidation State on Cycling




Molecular Weight Change *vs* Cycle Number
Average of 3-4 data sets
ΔM (g/mole Ni)
8
6
4
2
-0
-2
-4
-6
Charge
Discharge
1
2
3
4
5
6
7
8
9
10
Cycle Number



Change in Defect Parameters on Cycling
0.25
0.20
0.15
0.10
0.05
0.00
x, y
x1=x2=0.25
y2
n2=3
n2=2
y1
x1, x2
y1
y2
0
1
2
3
4
5
6
7
8
9
10
Cycle Number

Redox Reactions In the Nickel Electrode as Described by the Defect Model

x_1=x_2=y_2=0.25, n_1= 0 and y_1=0

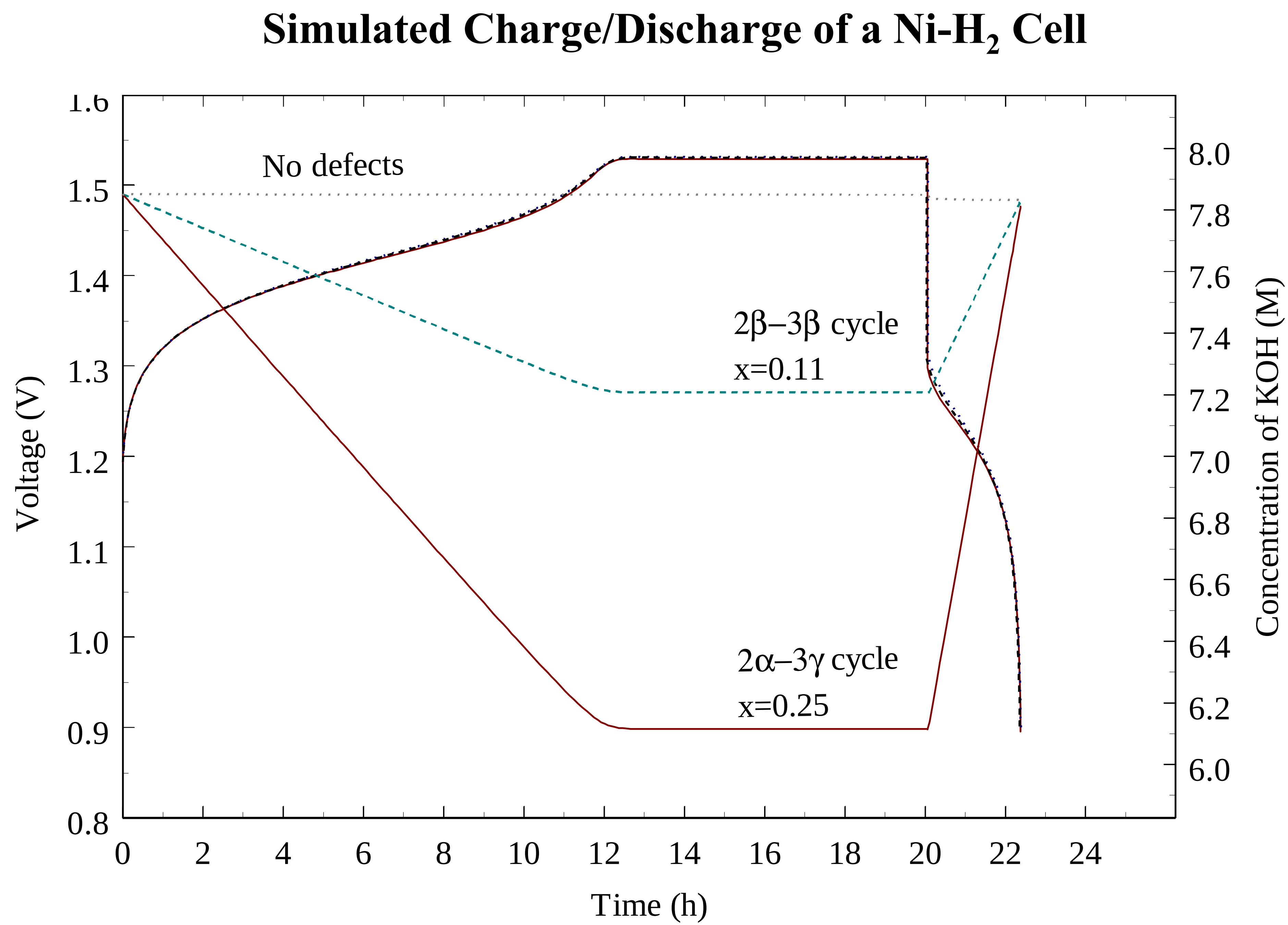
$$2\alpha-\left[Ni^{2.67}(V_{Ni})_{0.33}\right]O_{2.67}H_{2.67} + 1.33OH^- + 0.33K^+ \underset{discharge}{\overset{charge}{\rightleftarrows}} 3\gamma-\left[Ni^{3.67}(K)_{0.33}\right]O_{2.67}H_{1.33} + 1.33\,H_2O + 1\,e^-$$

x_1=x_2=0.11, n_1= 0, y_1=y_2=0 and n_2=1

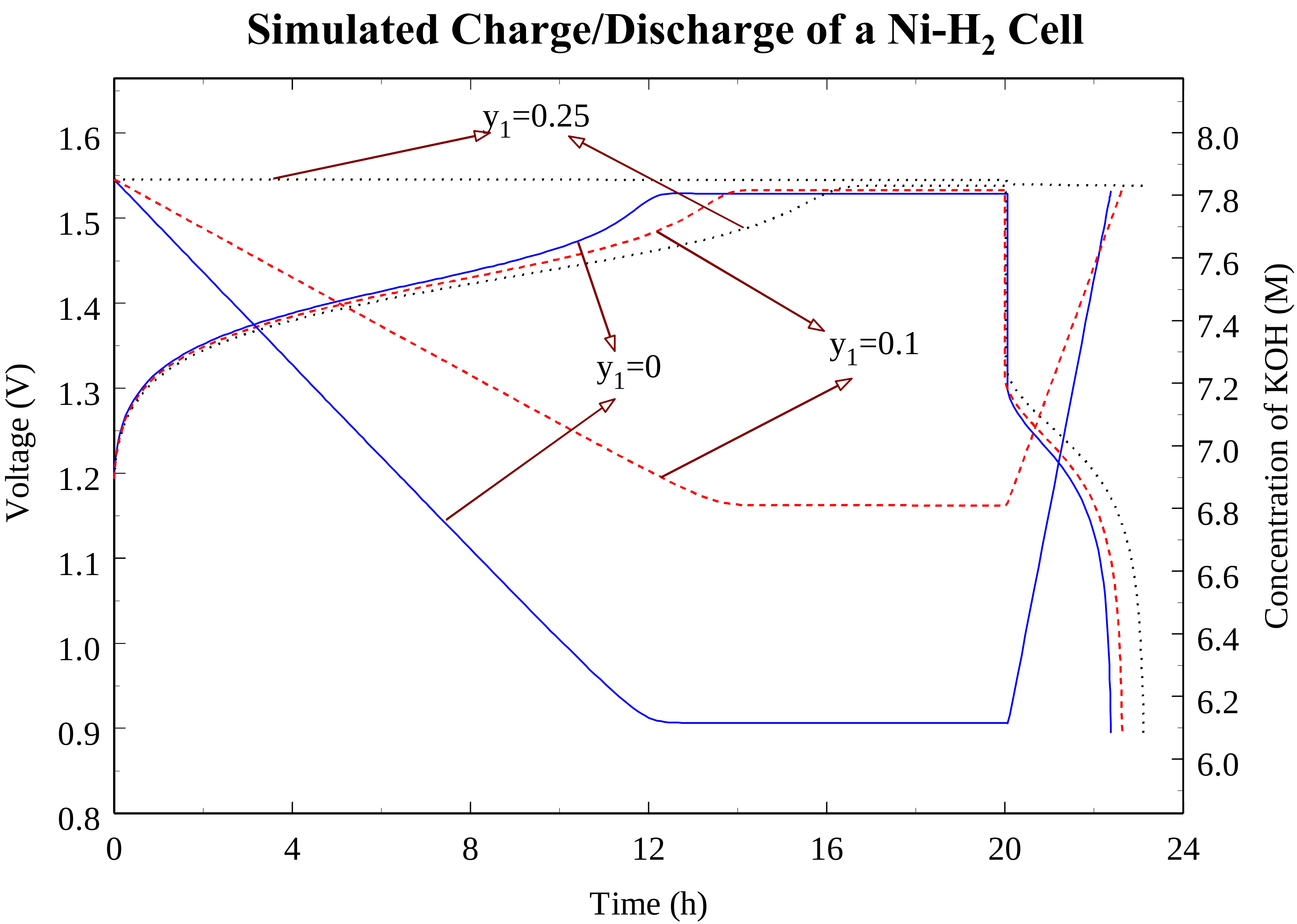
$$2\beta-\left[Ni^{2.25}(V_{Ni})_{0.12}\right]O_{2.25}H_{2.25} + OH^- \underset{discharge}{\overset{charge}{\rightleftarrows}} 3\beta-\left[Ni^{3.25}(H)_{0.12}\right]O_{2.25}H_{1.12} + H_2O + 1e^-$$

x_1=x_2=y_2=0.25, n_1= 2 and y_1=0

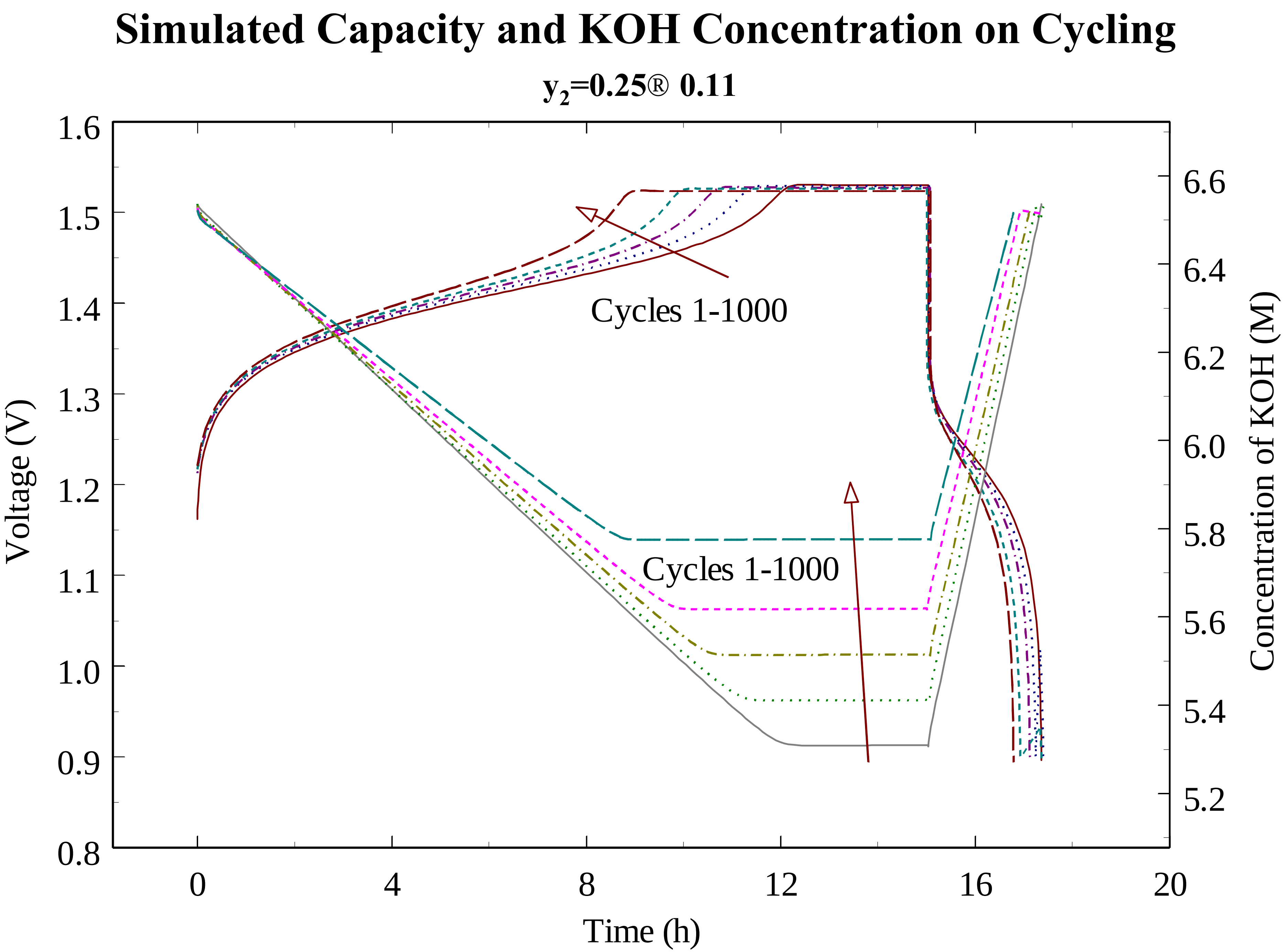
$$\alpha-\left[Ni^{2.0}(2H)_{0.33}\right]O_{2.67}H_{2.67} + 2OH^- + 0.33K^+ \xrightarrow{Formation} 3\gamma-\left[Ni^{3.67}(K)_{0.33}\right]O_{2.67}H_{1.33} + 2\,H_2O + 1.67\,e^-$$



Simulated Charge/Discharge of a Ni-H2 Cell
No defects
2β–3β cycle
x=0.11
2α–3γ cycle
x=0.25
Voltage (V)
Concentration of KOH (M)
Time (h)
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
0
2
4
6
8
10
12
14
16
18
20
22
24

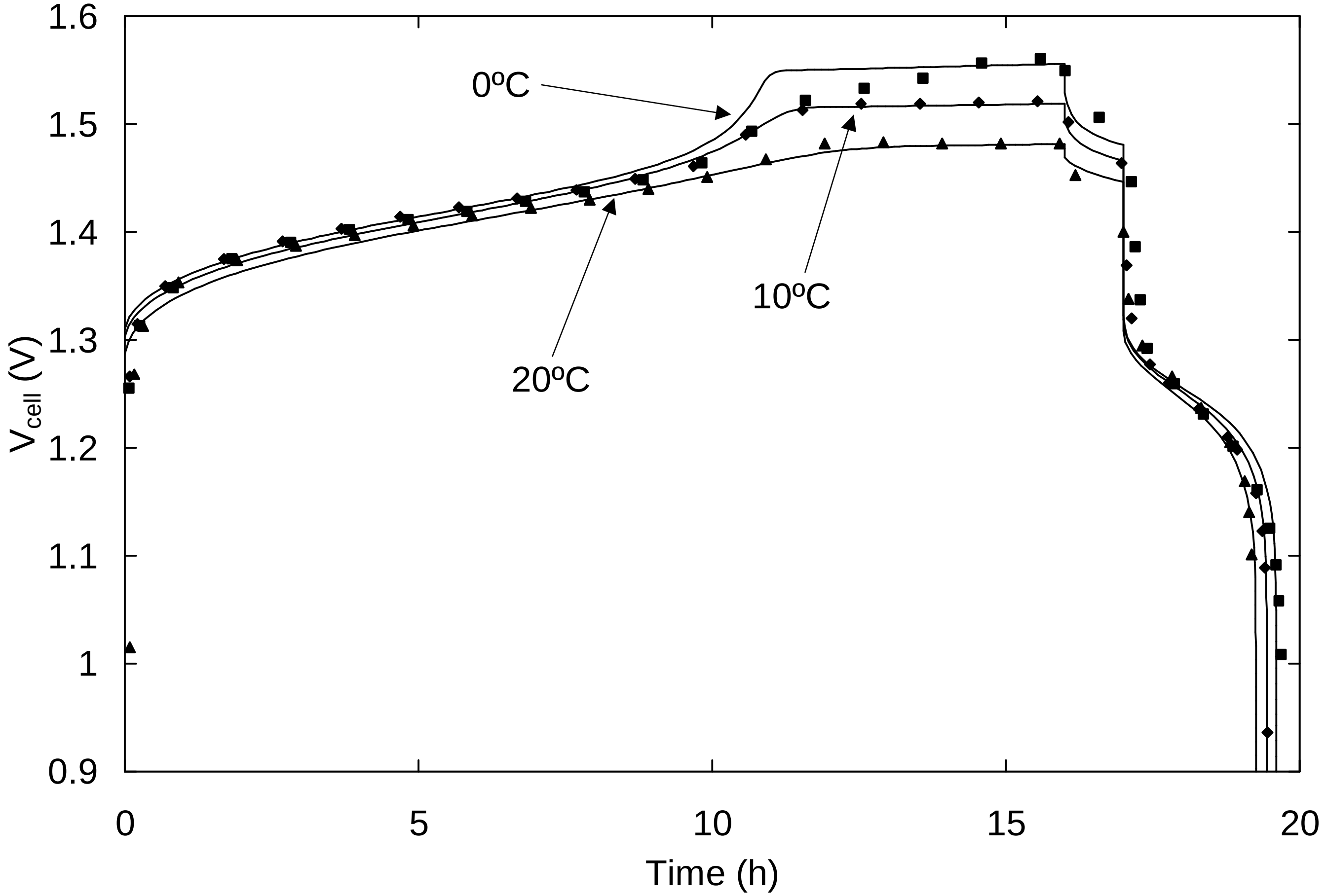


Simulated Charge/Discharge of a Ni-H2 Cell
y1=0.25
y1=0.1
y1=0
Voltage (V)
Concentration of KOH (M)
Time (h)
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
0
4
8
12
16
20
24



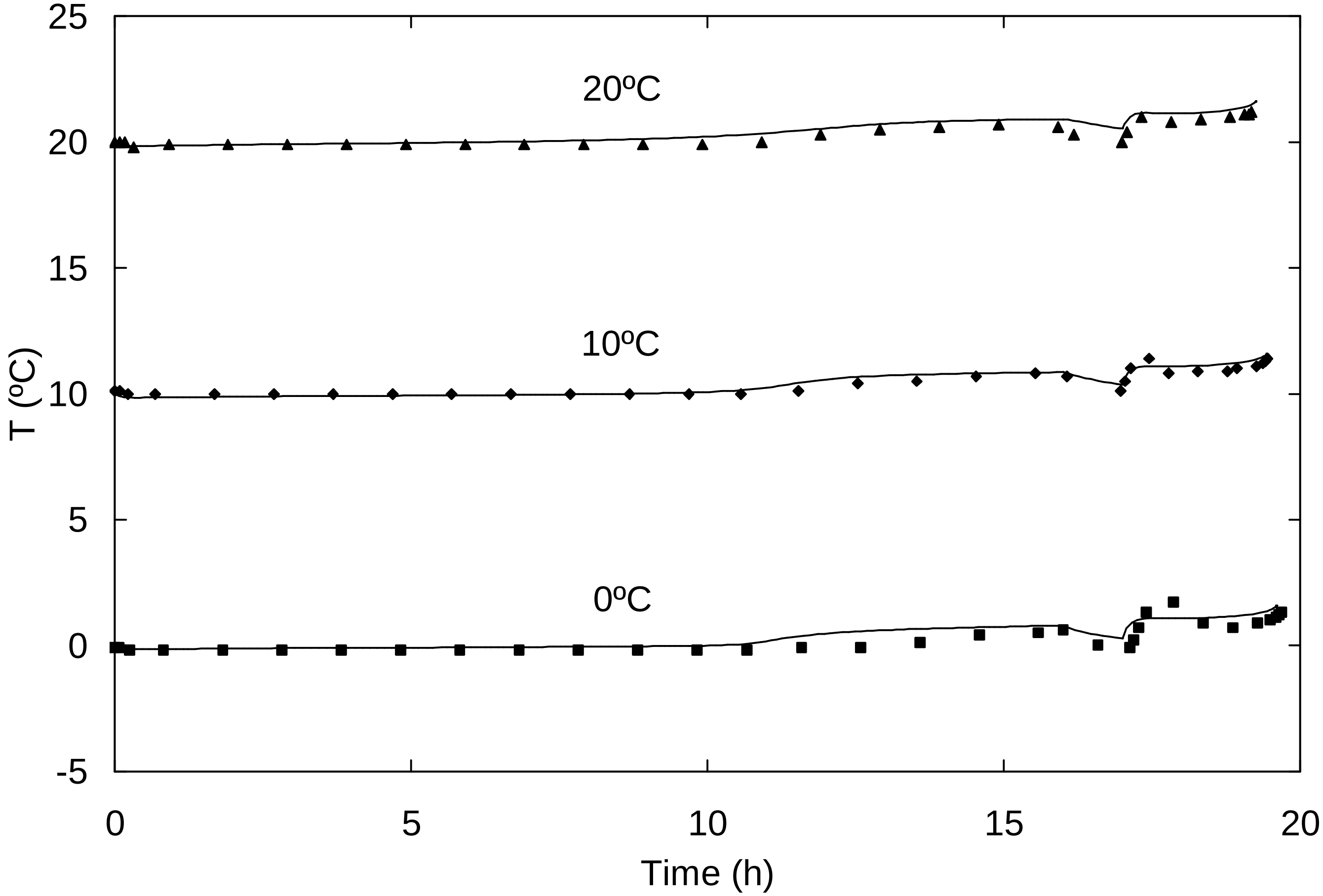
Simulated Capacity and KOH Concentration on Cycling
y2=0.25® 0.11
Cycles 1-1000
Cycles 1-1000
Voltage (V)
Concentration of KOH (M)
Time (h)
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
0
4
8
12
16
20

Comparison of Model Predicted Cell Potential with TRW Data



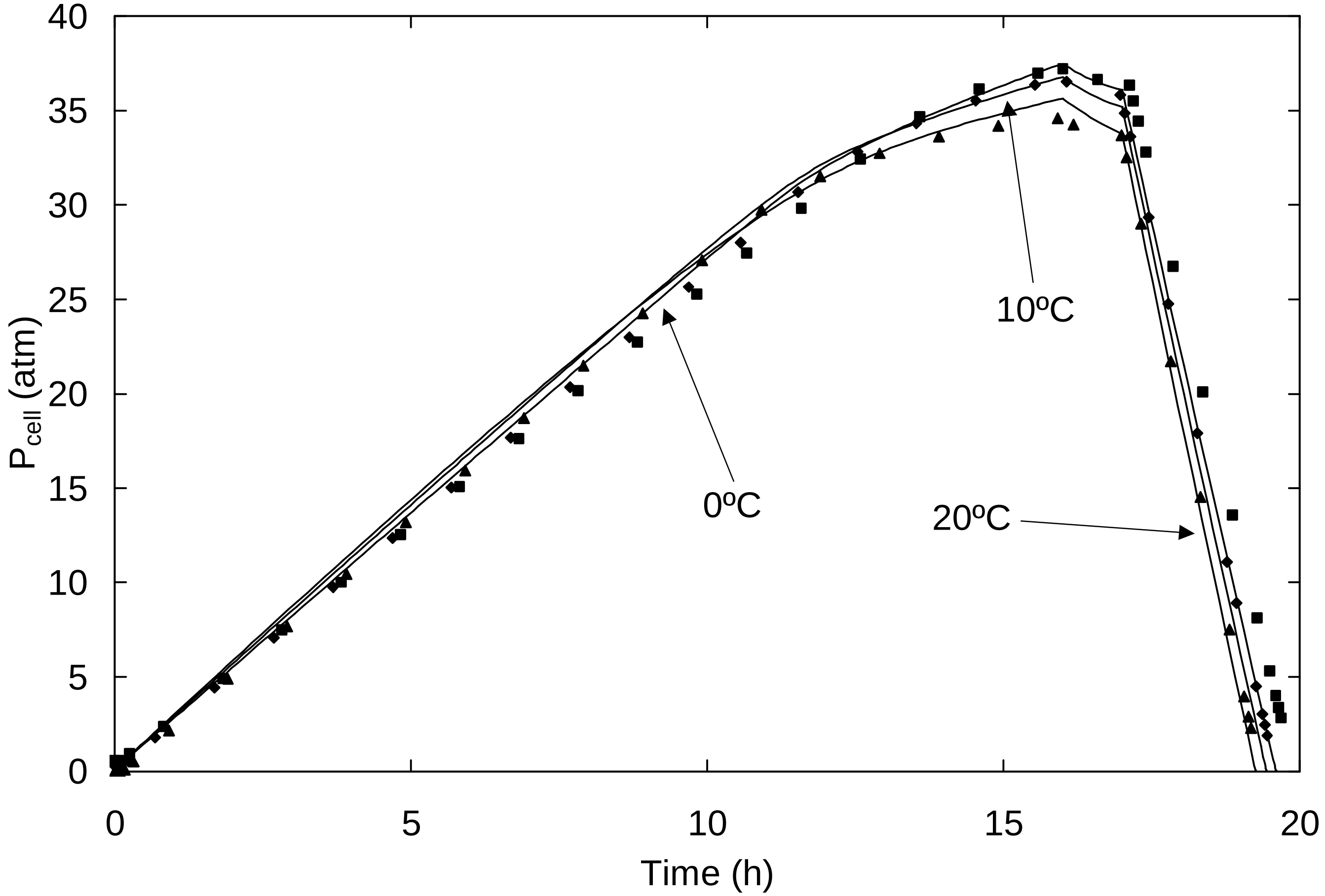
B. Wu and R. E. White, *J. Electrochem. Soc.*, in press (2000).

Comparison of Model Predicted Cell Temperature with TRW Data



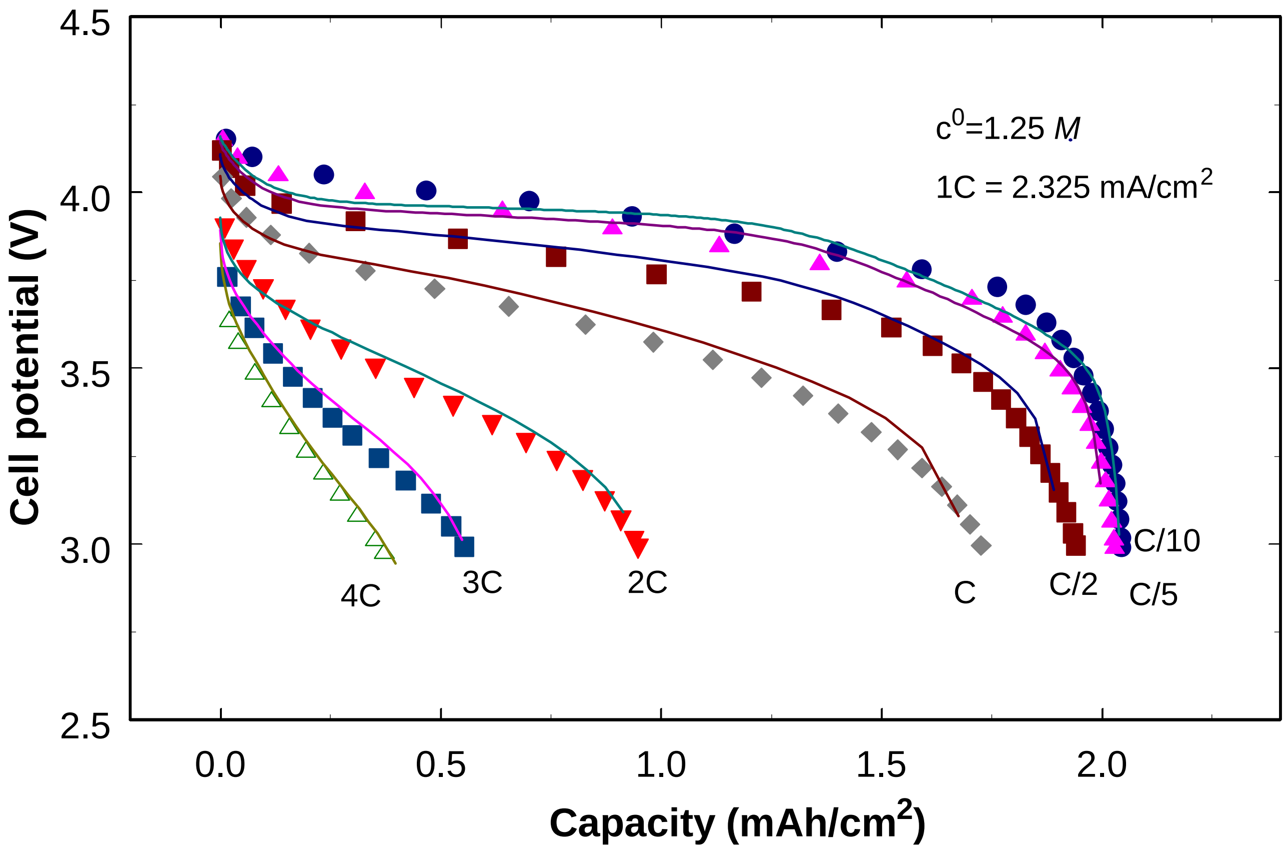
B. Wu and R. E. White, *J. Electrochem. Soc.*, in press (2000).

Comparison of Model Predicted Cell Pressure with TRW Data



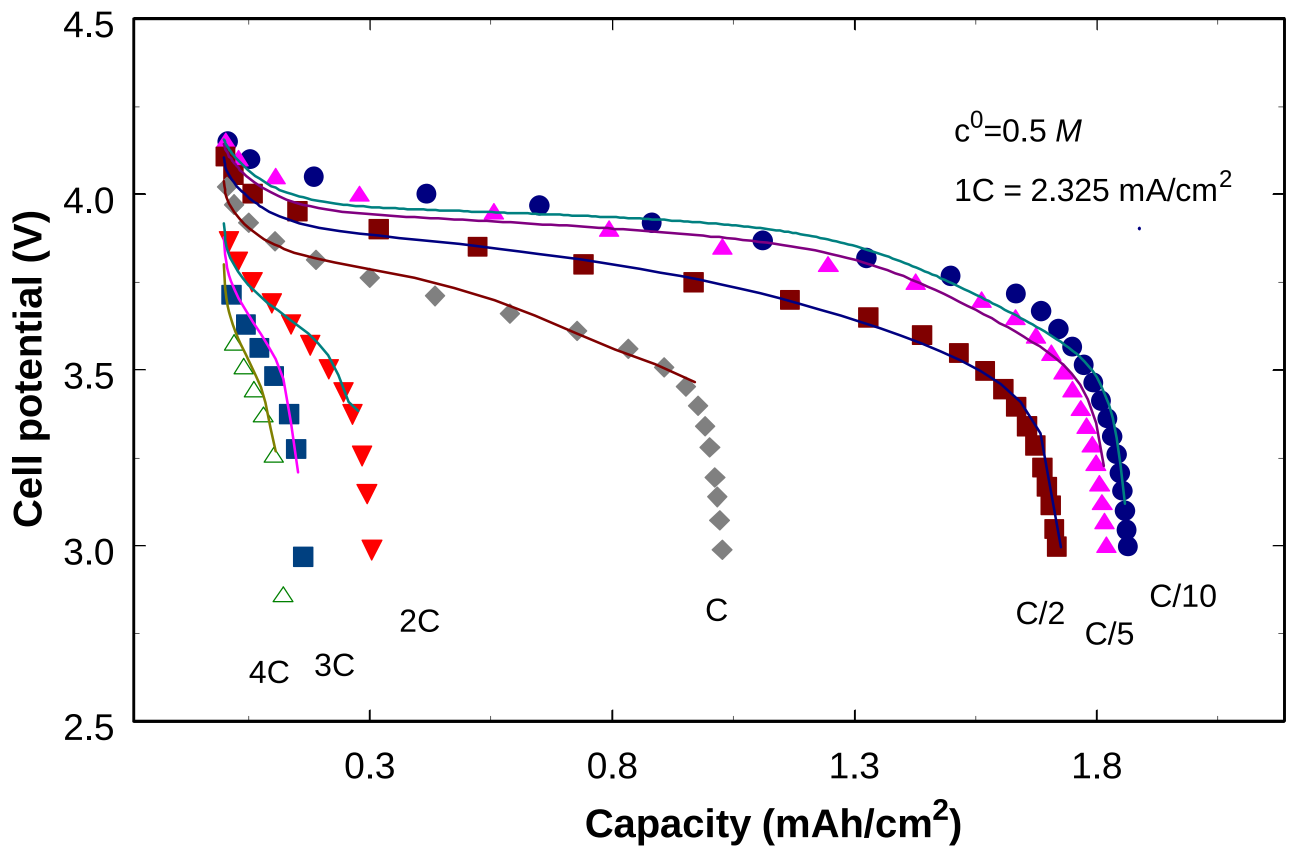
B. Wu and R. E. White, *J. Electrochem. Soc.*, in press (2000).

Experimental & Simulated Discharge Curves for a Li-Ion Cell with 1.25 M Initial Salt Concentration



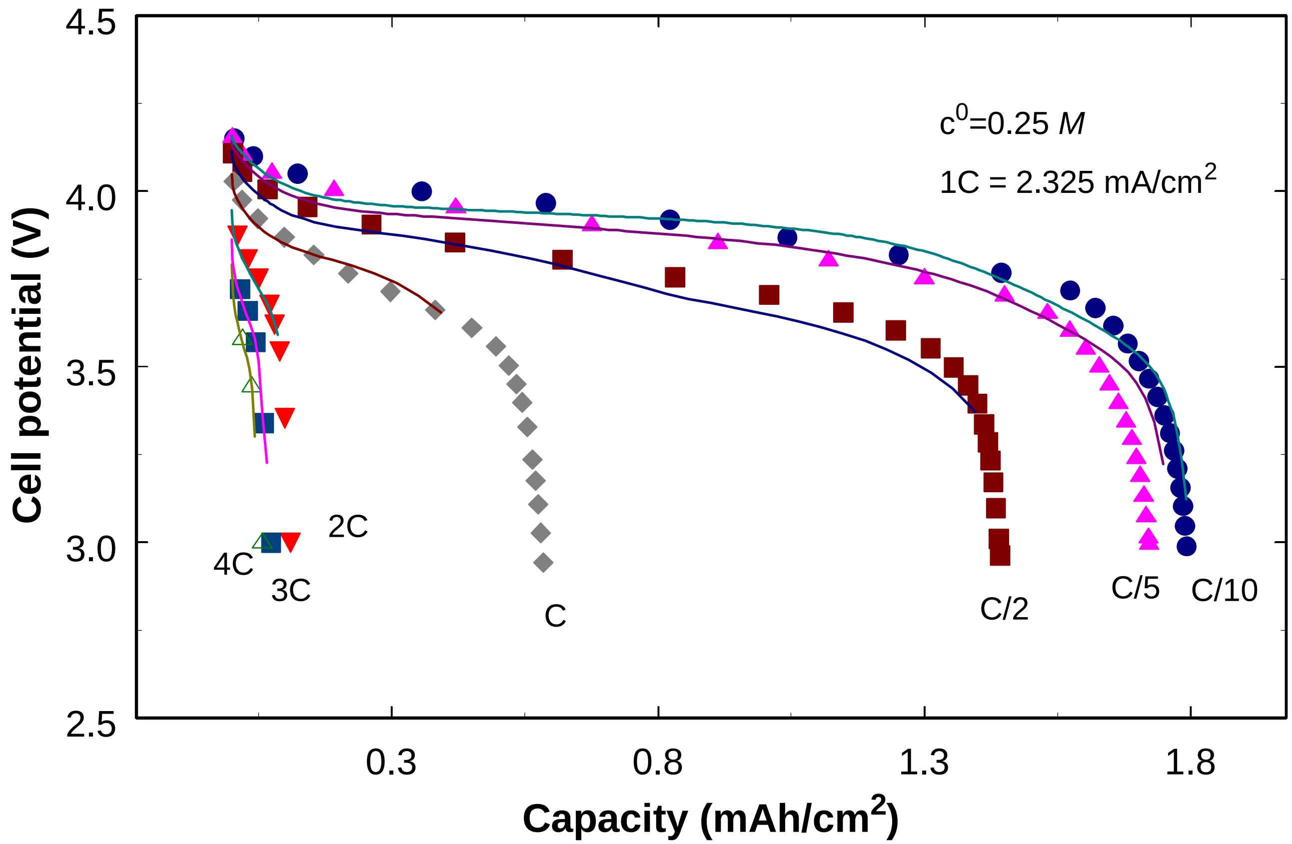
P. Arora, M. Doyle, A. S. Gozdz, R. E. White, and J. Newman, *J. Power Sources*., **88**, 219-231 (2000).

Experimental & Simulated Discharge Curves for a Li-Ion Cell with 0.5 M Initial Salt Concentration

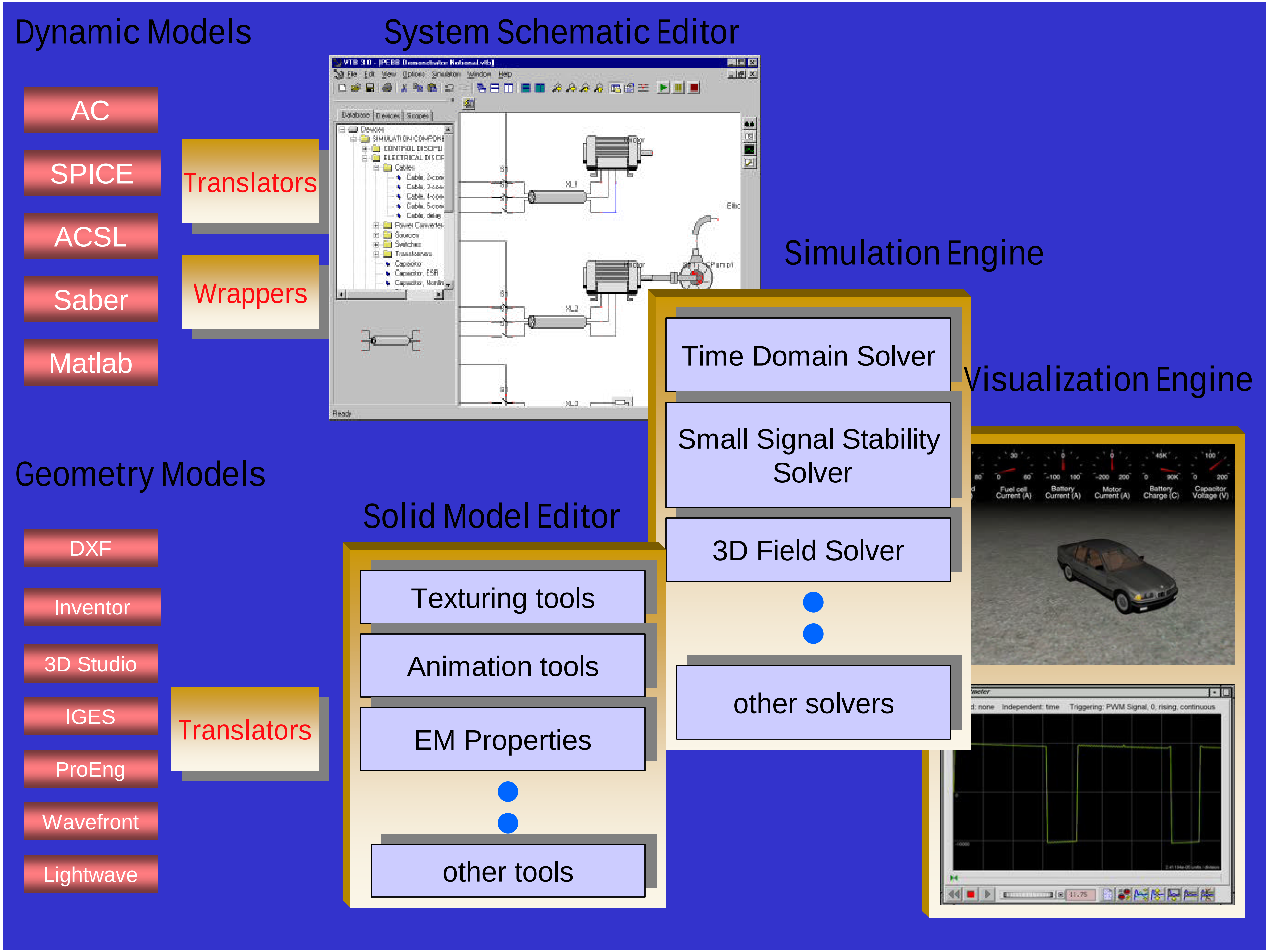


P. Arora, M. Doyle, A. S. Gozdz, R. E. White, and J. Newman, *J. Power Sources.*, **88**, 219-231 (2000).

Experimental & Simulated Discharge Curves for a Li-Ion Cell with 0.25 M Initial Salt Concentration

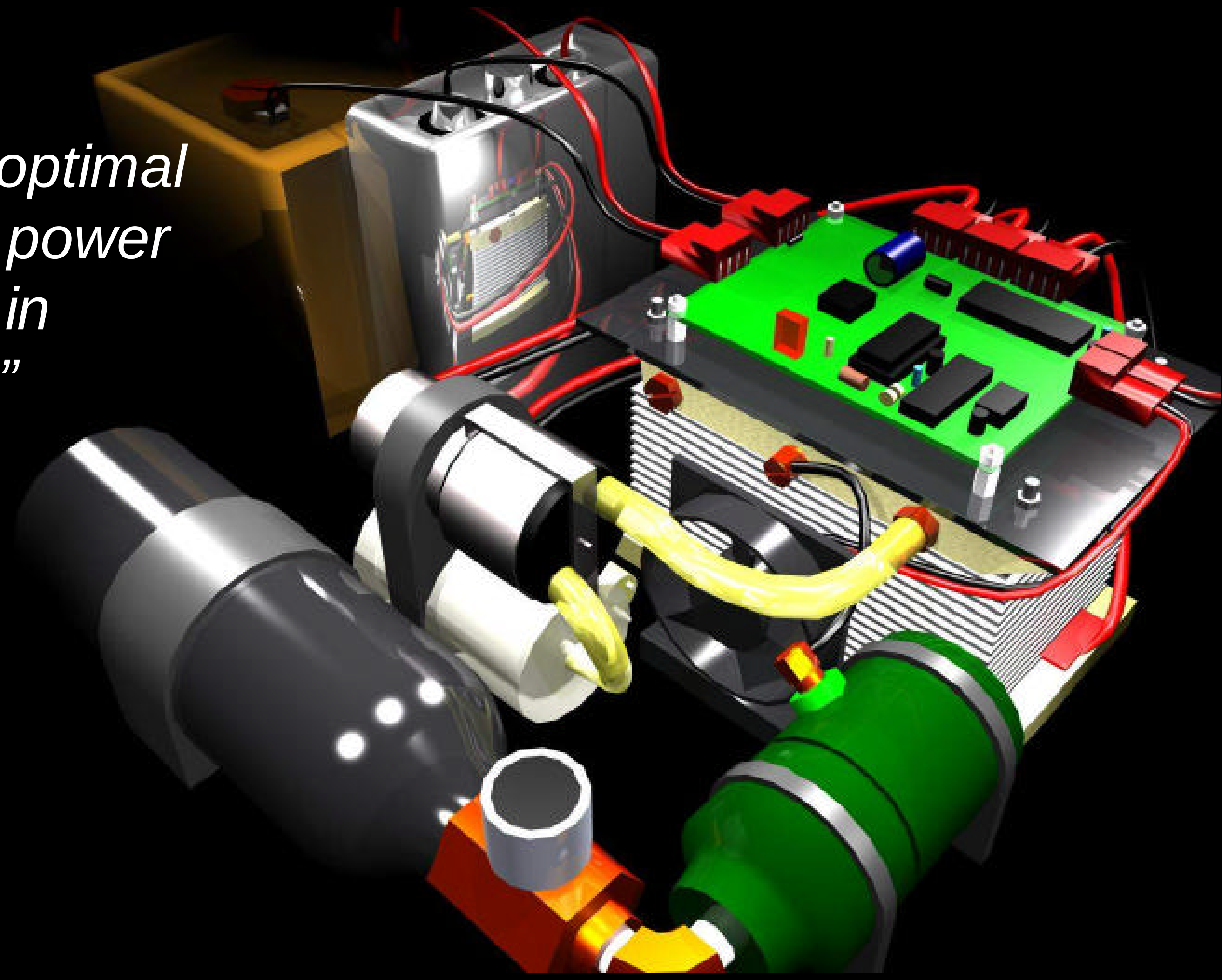


P. Arora, M. Doyle, A. S. Gozdz, R. E. White, and J. Newman, *J. Power Sources*., **88**, 219-231 (2000).

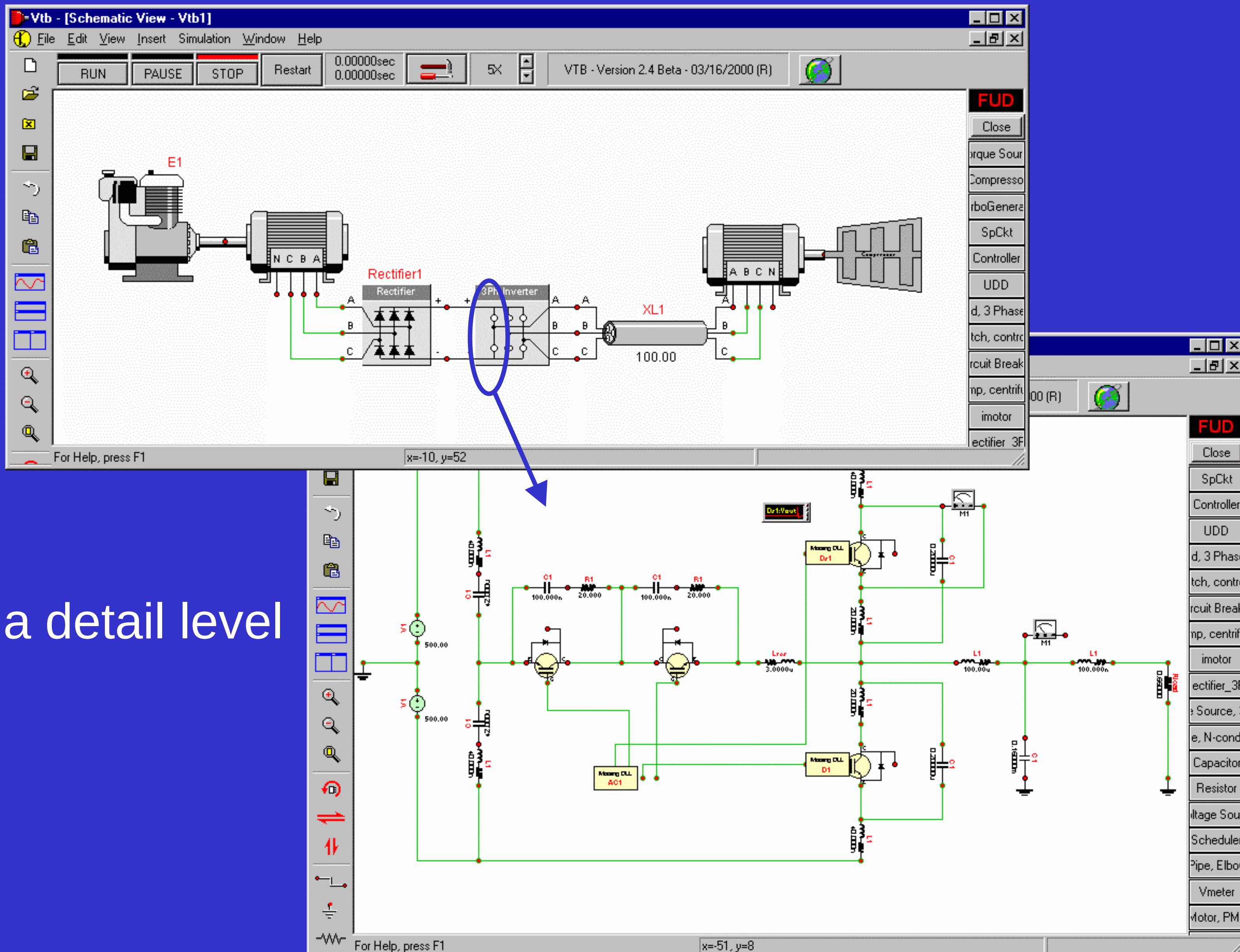

Dynamic Models
AC
SPICE
ACSL
Saber
Matlab
Translators
Wrappers
System Schematic Editor
Simulation Engine
Time Domain Solver
Small Signal Stability Solver
3D Field Solver
other solvers
Visualization Engine
Geometry Models
DXF
Inventor
3D Studio
IGES
ProEng
Wavefront
Lightwave
Translators
Solid Model Editor
Texturing tools
Animation tools
EM Properties
other tools

Project Objectives

"Investigate the optimal design of hybrid power systems for use in mobile systems."

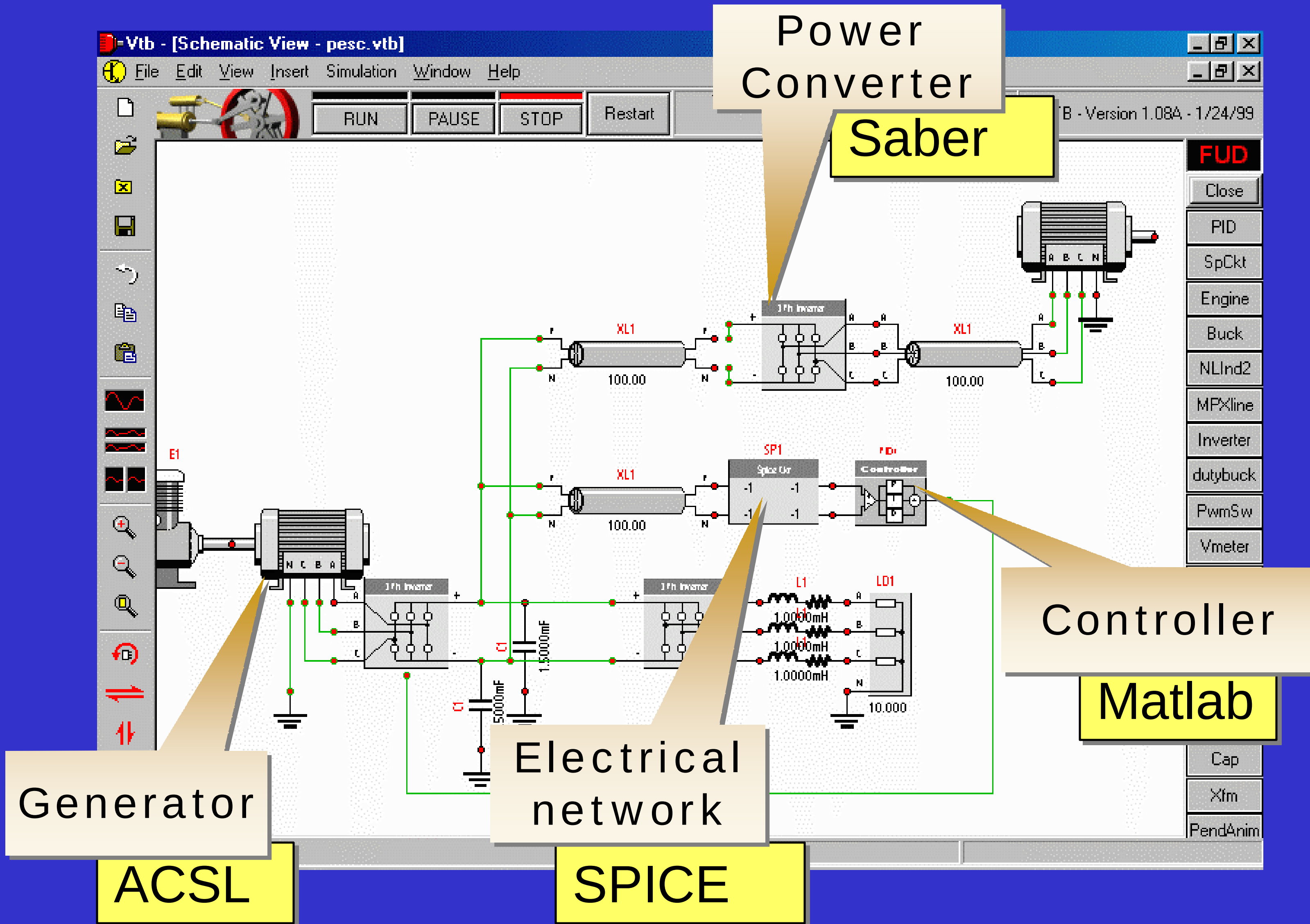


VTB supports analysis at the system level



And at a detail level

The VTB is a highly interactive environment for collaborative design and virtual prototyping of advanced power systems.



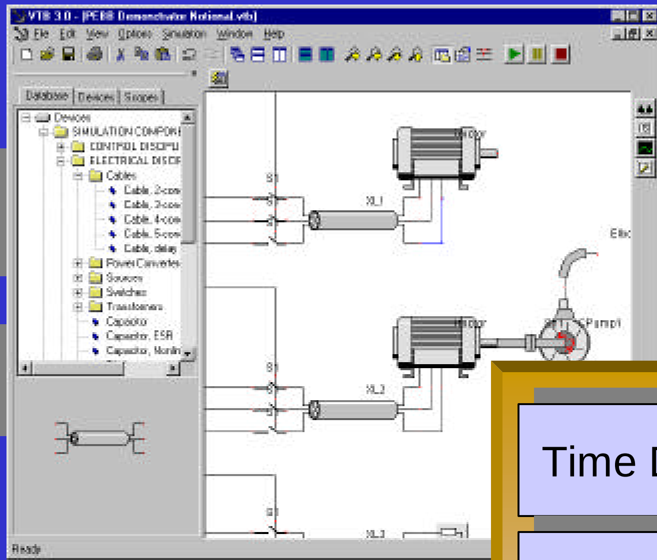
Dynamic Models

- AC
- SPICE
- ACSL
- Saber
- Matlab

Translators

Wrappers

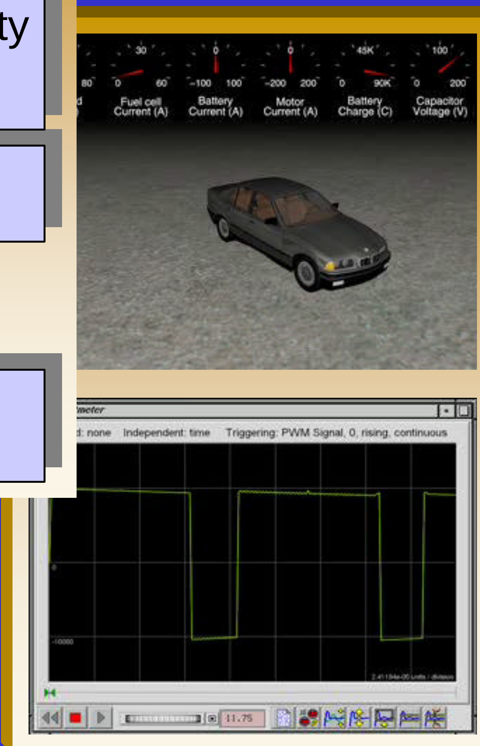
System Schematic Editor



Simulation Engine

- Time Domain Solver
- Small Signal Stability Solver
- 3D Field Solver
- other solvers

Visualization Engine



Geometry Models

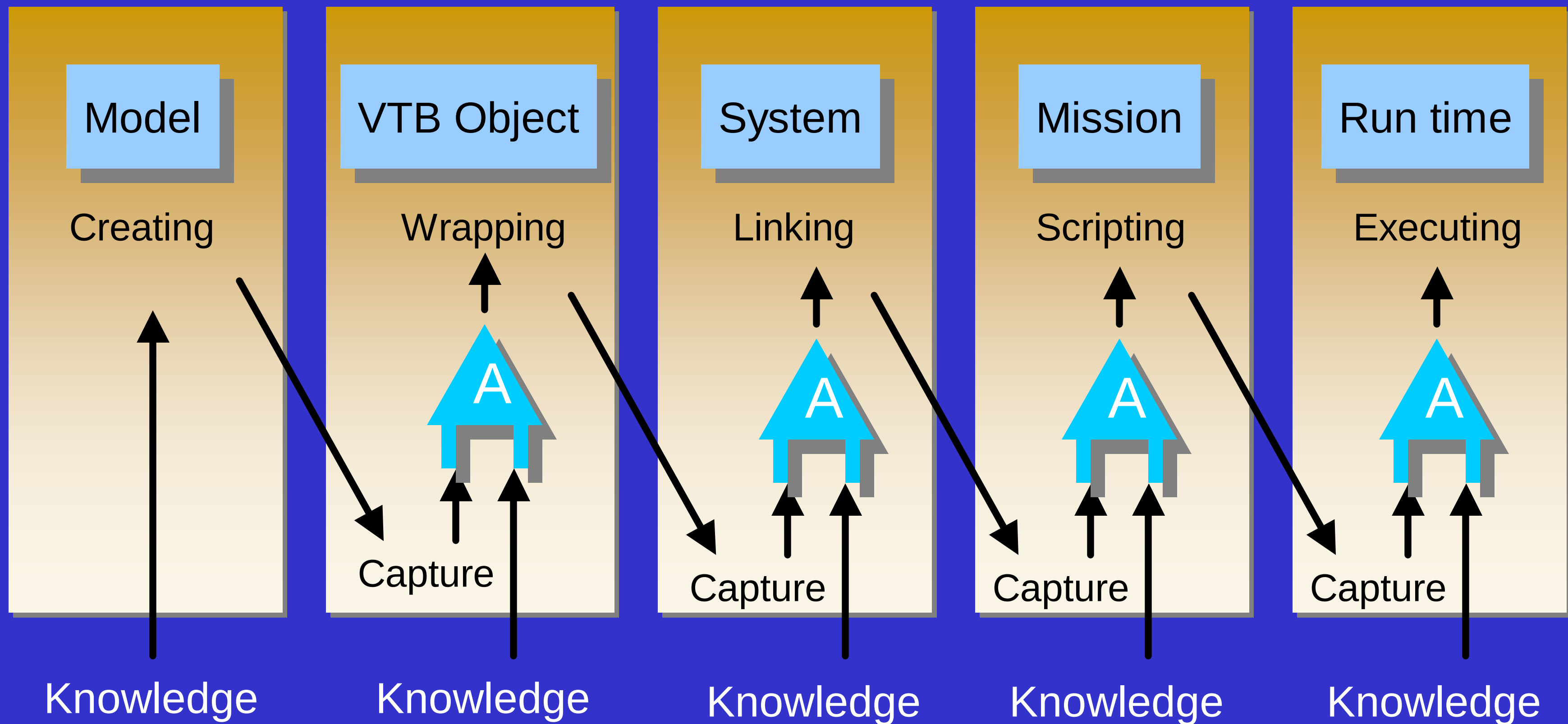
- DXF
- Inventor
- 3D Studio
- IGES
- ProEng
- Wavefront
- Lightwave

Translators

Solid Model Editor

- Texturing tools
- Animation tools
- EM Properties
- other tools

VTB facilitates interdisciplinary and distributed team work (and eliminates stovepipe work threading) by capturing and amplifying user knowledge at every step



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The author has respectfully requested that this paper be withheld from publication in these proceedings.

Thermal and Cycle-Life Behavior of Commercial Li-ion and Li-Polymer Cells

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Abstract

Accelerated and real-time LEO cycle-life test data will be presented for a range of commercial Li-ion and Li-polymer (gel type) cells indicating the ranges of performance that can be obtained, and the performance screening tests that must be done to assure long life. The data show large performance variability between cells, as well as a highly variable degradation signature during non-cycling periods within the life tests. High-resolution Dynamic Calorimetry data will be presented showing the complex series of reactions occurring within these Li cells as they are cycled. Data will also be presented for cells being tested using an Adaptive Charge Control Algorithm (ACCA) that continuously adapts itself to changes in cell performance, operation, or environment to both find and maintain the optimum recharge over life. The ACCA has been used to prevent all unneeded overcharge for Li cells, NiCd cells and NiH_2 cells. While this is important for all these cell types, it is most critical for Li-ion cells, which are not designed with electrochemical tolerance for overcharge.

Introduction

The development of lithium-ion battery cells that are capable of long cycle-life for commercial applications has tempted satellite power-system engineers for years with the promise of smaller and lower weight battery systems. However, the accumulation of the performance history and databases necessary to assure high reliability over long-term space missions as well as the needed optimization of lithium-ion power systems, have made the anticipated transition to lithium-ion batteries in satellite systems quite slow. One of the leading satellite types expected to advantageously utilize lithium-ion technology is nanosatellites and picosatellites. These satellites are very small, typically in the 100g to 10 kg range. Because of their small size, very compact and lightweight batteries offer compelling advantages. Because of their relatively low cost and generally limited life requirements (1-3 years in low earth orbit is typical), commercial lithium-ion battery technology provides a promising power system option for these classes of satellites.

Here we will present performance data and thermal characteristics of selected commercial lithium-ion battery cells to illustrate some of the key advantages of these batteries for small satellites, as well as some of the issues that must be handled to reliably integrate these batteries into a successful power system.

Cycle-Life Measurements

The cycle life of a lithium-ion battery must be adequate to support worst-case mission needs with sufficient margin to assure high reliability when cell performance variability is considered. One issue that has been noted for lithium-ion battery cells is that cycle life performance can be highly variable, depending on the details of how cells are built and how they are tested. It should be pointed out that this experience matches that obtained early in the use of nickel cadmium and nickel hydrogen cells, where large variability in performance taught many lessons related to cell design and charge management practices. Given this situation, it is key to the use of lithium-ion batteries that appropriate test and screening regimens be developed to assure that all cells selected for satellite use will perform well with the anticipated charge control system. To this end we have developed an accelerated cycling test that will rapidly indicate the cycle-life capability of lithium-ion battery cells.

A key difficulty in assessing the cycle-life capability of lithium-ion cells is the strong coupling between cycle life and both charge-management and operational temperature. This kind of coupling is not really surprising, since it has also been found to be the rule for other kinds of battery cells, most notably nickel cadmium and nickel hydrogen. As for these other types of battery cells, databases must be developed that show precisely how temperature and different charge management variations affect cycle-life. To help gather such data we have developed a simple accelerated life test protocol that is based on a simple doubling of the cycle-times normally associated with low-earth-orbits. This test employs a 45-minute cycle consisting of 15 minutes for discharge and 30 minutes for recharge, and operates the cells at 20% depth-of-discharge (DOD). Recharge is at a C/2 rate, with a constant voltage limit of 4.0 or 4.1 volts, and test temperature is 20 deg C. Thus, this test applies the currents normally anticipated at 40% DOD in a standard 90-minute LEO cycle. The test is therefore very sensitive to the increases in resistance that have often been seen to accompany or forewarn premature cell degradation, while allowing a x2 acceleration factor in cycle numbers. Whether this acceleration factor of 2 applies to standard LEO orbital usage remains to be debated, and ultimately will be established based on the test data.

This accelerated life test has been applied to a range of commercial Li-ion cells to determine anticipated performance. Figure 1 shows the relative cycle life performance of two types of SONY 18650 cells. Cell type A was acquired in 1994 and remained stored in the laboratory until 1999, when the cells were put on test. Cell type B was acquired in 1999 and immediately put on test. These two types of cells reflect the changes in cell design over a 5-year period for SONY. It should be noted that the type B cells had at least a 10% greater beginning-of-life capacity relative to the type A cells. These cells are being tested at a 1.5 Ah nameplate capacity and recharge is to a 4.1-volt limit.

There are several noteworthy results in Figure 1. First, after about 16,000 cycles of testing, it has become clear that both the type A and the type B cells are capable of a very long cycle life. Extrapolation of the observed degradation slopes yields a cycle life in excess of 50,000 for all these cells. The other noteworthy result is that the degradation rate for the newer type B cells is about twice that of the older Type A cells, in spite of the greater capacity in the newer cells. This was expected, and is at least partially a result of the utilization of a graphitic carbon in the anodes of the newer cell design, thus providing higher voltage and capacity at the cost of more rapid degradation of the highly ordered graphite structure. These results, however, clearly demonstrate that it is important to routinely screen the performance of each lot of commercial cells acquired for space use so that such changes in design or performance will be detected prior to flight.

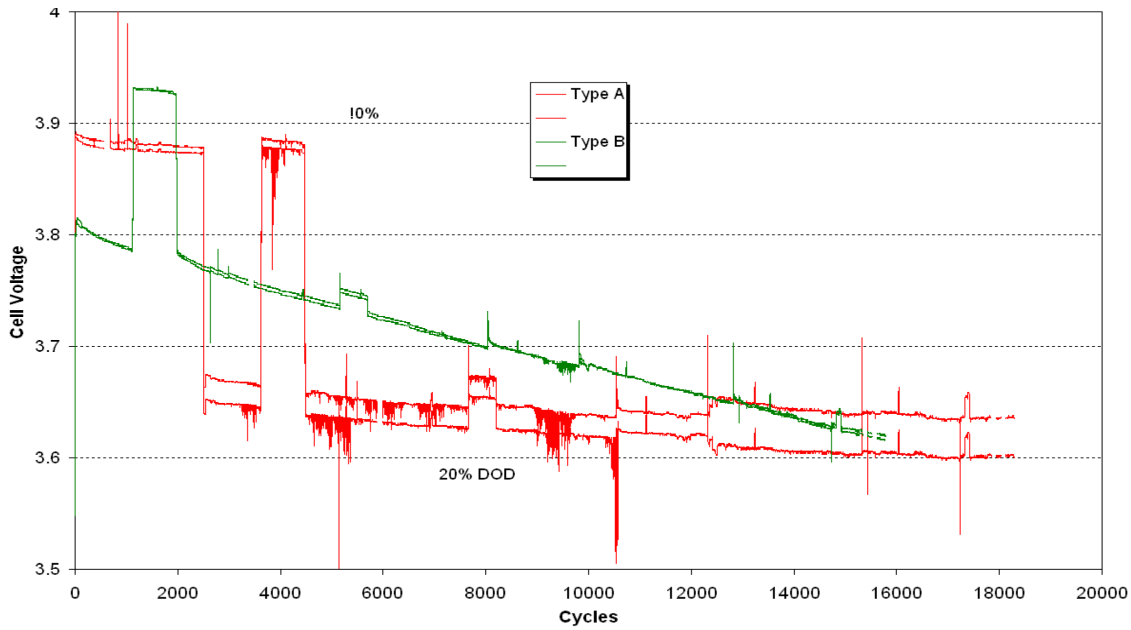


Figure 1. Comparison of Accelerated Cycling Performance for Type A and Type B SONY 18650 Cells.

The need for cell screening can be made dramatically clear by the results in Figure 2, which shows the relative performance obtained for cells from two different lots of cells that were built about 2 months apart. These are lithium-polymer cells, which are of significant interest in nanosatellites because they can be sandwiched into the satellite

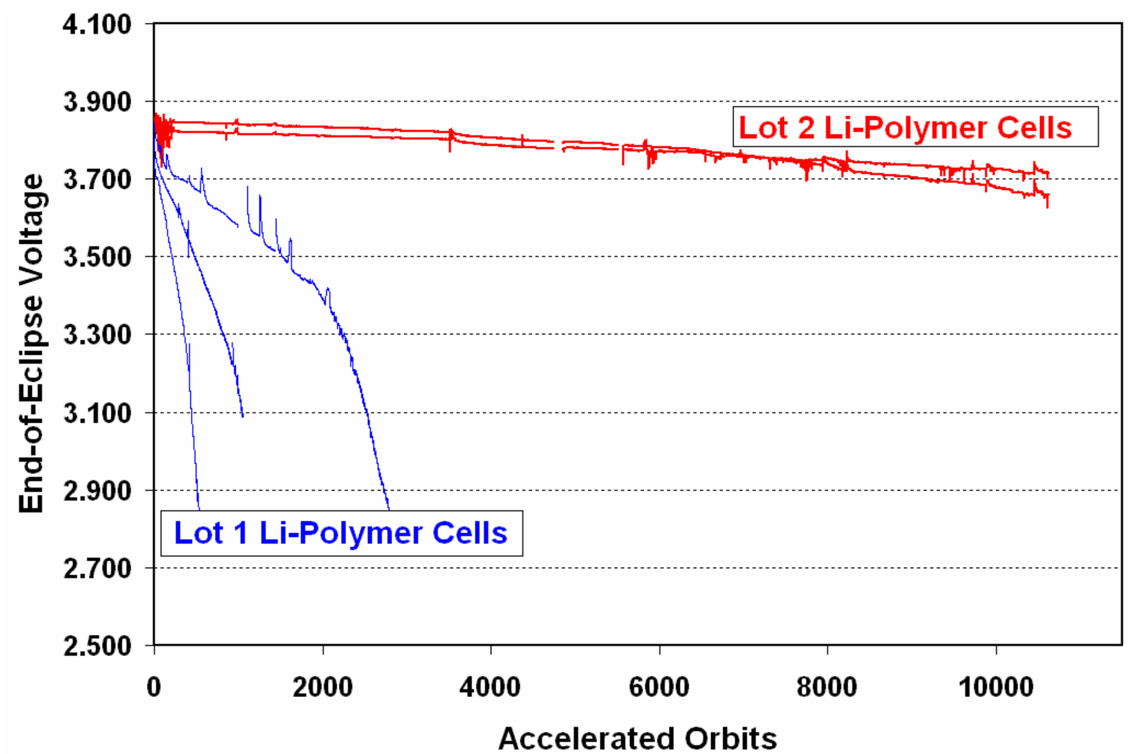


Figure 2. Relative Accelerated Test Performance of Two Lots of Li-Polymer Cells.

structure much more easily than the cylindrical 18650 cells. As noted in Figure 2, cells from the first lot operated only 1000 to 3000 cycles before failing, while cells from the second lot operated 15,000 cycles.

The issue of optimum charge control for lithium-ion cells is an area that has not been fully resolved. As indicated in Figure 1, simple recharge to 4.1 volts each cycle, then allowing the current to taper at the 4.1-volt limit can be very effective. However, the optimum recharge voltage level may not always be 4.1 volts. It may vary with the cell design, temperature, electrode degradation over life, recharge rates, or a variety of other parameters. One indication that this is indeed the case is shown in Figure 3, where the performance of four 1.5 Ah lithium polymer cells from the same build lot is indicated. Two of these cells were cycled with a 4.1-volt recharge limit and the other two were cycled with a 4.0-volt limit. The cells cycled to 4.1 volts started out with a much higher discharge voltage, however they did settle in on a more rapidly dropping voltage as cycling progressed. The cells cycled to 4.1 volts also developed a downwards curve to their end-of-discharge voltage that ultimately made them fail long before the cells that were only being recharged to 4.0 volts. It is noteworthy that the cells cycled to 4.0 volts have degraded with a slow linear slope to the end-of-discharge voltage, thus not displaying any tendency to develop a curving down drop-off.

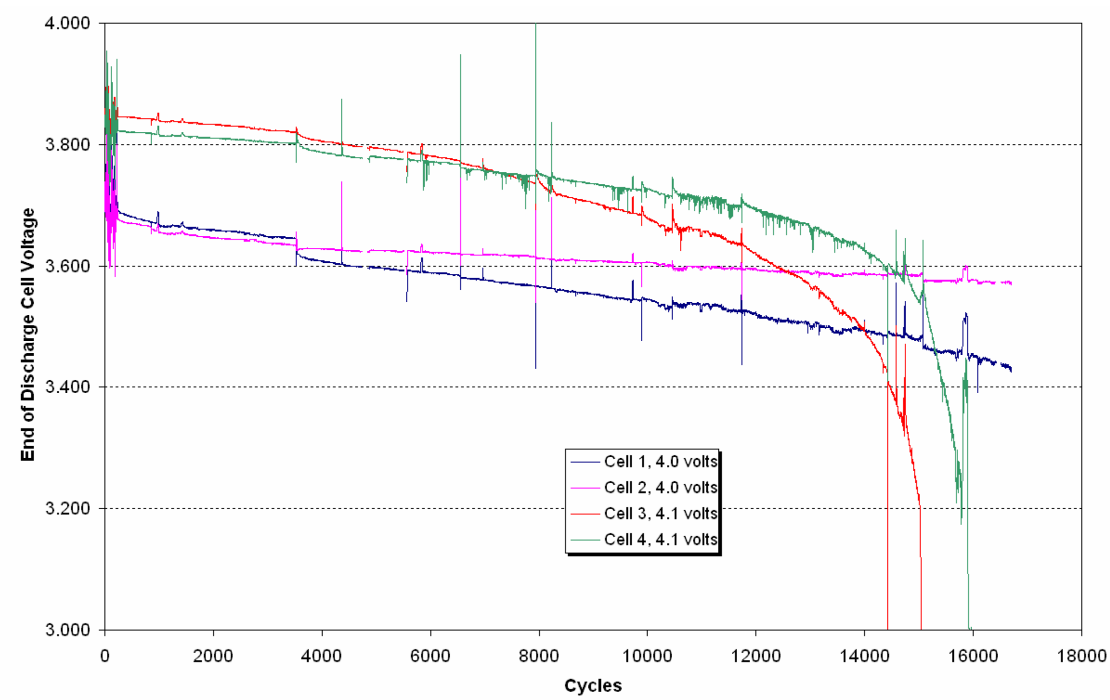


Figure 3. Relative Performance of Lithium-Polymer Cells Charged to Different Voltage Limits.

The results in Figure 3 can be interpreted to suggest a different failure mode coming into play when these cells were cycled to 4.1 volts, which was not the main degradation mode at a recharge limit of 4.0 volts. One suggestion is that the rapid and curving drop-off in end-of-discharge voltage is due to capacity loss, which was significantly accelerated by recharge to the higher voltage. This rapid and curving drop-off is superimposed on a more linear drop-off that is due to increases in the impedance of the electrodes and electrolyte as the cells are cycled. For the cells cycled to 4.0 volts, the increasing impedance of the cells appears to be the dominant degradation mode, explaining why no tendency has yet been seen for the end-of-discharge voltage to curve downwards. These results clearly suggest that limiting the added degradation mode at the higher voltages for these cells can significantly increase their expected performance life and reliability in a satellite power system, at the cost of some lesser performance at beginning of life.

The data in Figure 3 also show another potential issue with lithium ion cells. At about cycle 3500, a two-week test shutdown occurred due to the failure of some test equipment. During these two weeks the cells were left in the fully charged state (either at 4.0 or 4.1 volts). When the cycling resumed, all the cells adopted an increased degradation rate, except one of the cells being charged to 4.0 volts. In addition several of the cells displayed a step decrease in the end-of-discharge voltage in response to simply standing open circuited for two weeks in the fully charged state. Both the variability in how this stand period impacted the cells, as well as the performance loss itself are a significant concern. These results indicate that cells should be maintained at a less than fully charged state during known periods where no cycling or very shallow cycling is required. This is a charge management capability that must be built into the satellite power system, since in many low-earth-orbits there are sometimes periods of up to several weeks when no battery cycling is required.

The accelerated testing that has been done on a wide range of lithium-ion and lithium polymer cells suggests that the initial downward slope in the end-of-discharge voltage is a good relative indication of degradation rate and ultimate cycle life. If we examine the slope over the first 2500 cycles of test, those cells that failed most rapidly always had a higher slope. While simple extrapolation of slopes to a failure point could be deceiving due to the accelerating drop-off for some cells, in all cases these cells had a higher early slope than did cells that did not exhibit downwards curvature towards end-of-life. Thus, we propose a 2500-cycle accelerated screening test be performed on a sampling of commercial cells from each lot intended for use in satellites. While this test can be performed at any temperature, we recommend 20 deg C as a good standard temperature. The charge voltage limit for this test should be based on that anticipated in the power system, but based on our data a 4.0-volt limit is recommended.

Dynamic Calorimetry Results

The heat generation from lithium-ion cells is important both for designing a thermal control system that can adequately handle the end-of-life thermal environment, and for observing the electrochemical processes within an operating cell. The voltage of a lithium-ion cell typically does not clearly show steps and plateaus corresponding to the changing processes in the cell. However, the thermal behavior of a cell is capable of separating quite subtle changes in the cell reaction processes. Heat generation from lithium cells was measured here using dynamic calorimetry. This technique provides accurate heat generation rates or rapidly changing systems, and thus is applicable during high rate charge or discharge. Heat generation is sensed by the response of tiny thermistors attached to the sides of a cell. The cell is immersed in a fluid bath that is held at a constant temperature (to $\pm$0.0002 deg C), and heat generation is determined from the response of the thermistors which respond to the small region of the cell wall to which they are attached. Typical maximum thermal excursions for these thermistors are about 0.1 deg C for 1.5 Ah lithium-ion cells. This heat measurement system is calibrated by balancing electrical and thermal energy over a complete stabilized charge/discharge cycle, and typically has a thermal time constant of only several seconds.

Figure 4 shows a typical charge and discharge voltage, which has a number of subtle inflections during recharge and discharge, but no clear indication of changing electrochemistry as the cell is cycled. Figure 5 shows how the heat generation from a 1.5 Ah lithium-polymer cell varies during charge and discharge at 20 deg C, and compares

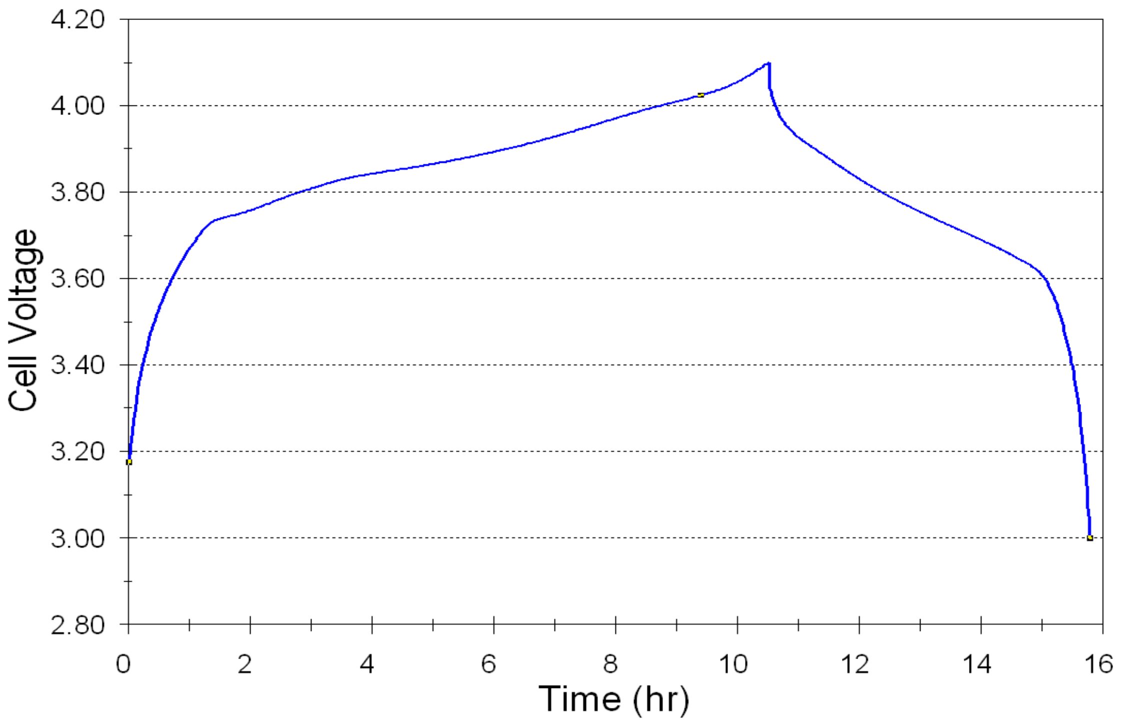


Figure 4. Typical Charge and Discharge Voltage for a Lithium-Polymer Cell.

the heat generation to the voltage profile. There are clearly a number of step changes in the heat production by this cell as it goes through several endothermic processes at the start of recharge, followed by several exothermic processes. All of these processes appear to be fully reversible, i.e. they appear during discharge as well as during recharge with the exception of the exothermic spike seen at the start of recharge. This exothermic spike is always seen for this particular type of cell, suggesting that some reactive material has been formed during recharge that is initially discharged. While this raises some concern regarding cycle life for this cell design, cells that are on test appear to be capable of about a 20,000 cycle life at 20% DOD.

The thermoneutral voltage of the cell may be determined during charge and discharge from the heat generation data. The thermoneutral voltage is the voltage at which no heat is generated during charge or discharge. Figure 6 indicates the thermoneutral voltage along with the cell voltage for a 1.5 Ah lithium-polymer cell. There are clearly a number of staging processes taking place during intercalation as the cell charges and discharges, and which correspond to the changes in heat generation seen in Figure 5.

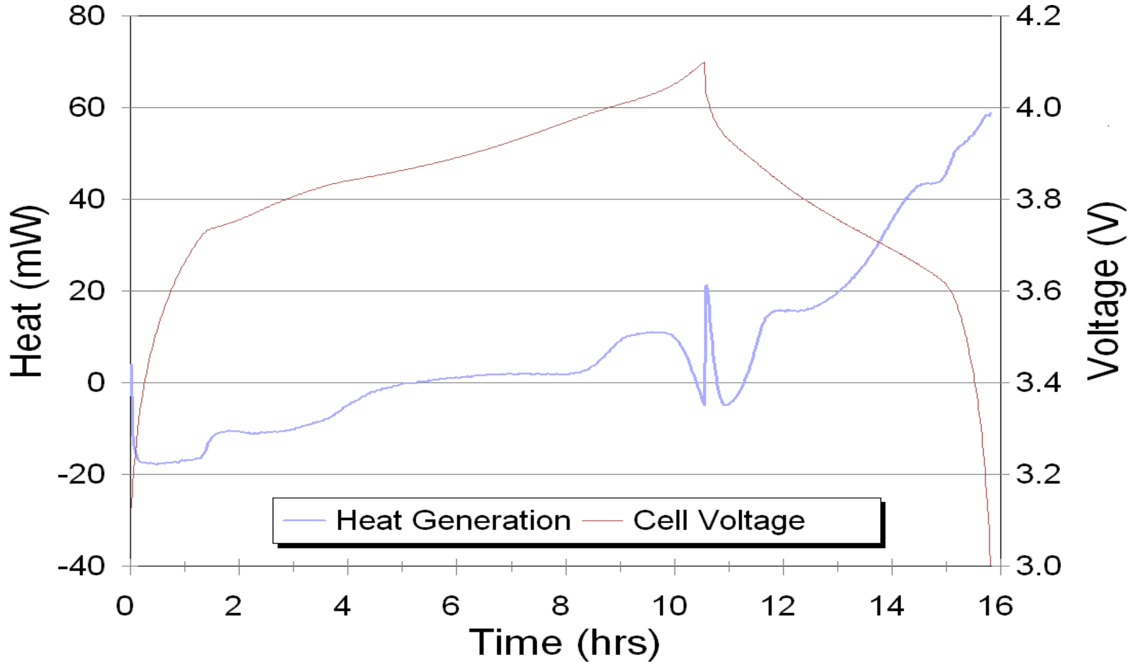


Figure 5. Lithium-Polymer Cell Heat Production during Charge and Discharge.

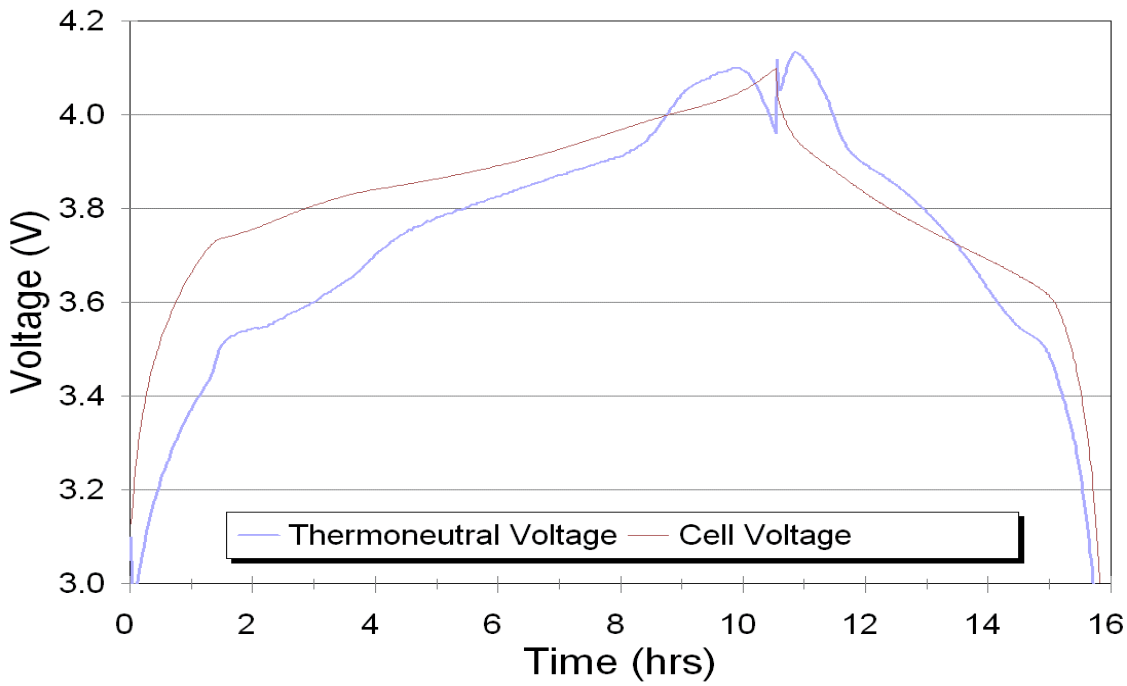


Figure 6. Lithium Polymer Cell Voltage and Thermoneutral Potential during Charge and Discharge.

Adaptive Charge Control Algorithm

The long-term performance of most rechargeable batteries is degraded by unnecessary overcharge. While nickel cadmium and nickel hydrogen cells can tolerate overcharge, any overcharge that is not needed to maintain the state-of-charge does indeed tend to diminish cycle life. Lithium-ion cells have no internal mechanism to allow them to tolerate overcharge, thus any overcharge not needed to keep them charged adequately should be avoided if long cycle life is required. We have developed an adaptive charge control algorithm that applies recharge based on keeping track of recharge ratio, and which continuously adjusts the applied recharge ratio to prevent any overcharge that is not needed to maintain the state of charge. This algorithm automatically adjusts for inaccuracies in the recharge ratio measurement, for temperature variations, electrode or cell degradation, as well as current or DOD changes. In this way this algorithm seeks to prevent any unneeded overcharge over cycle life, which should optimize the cycle life from a given lithium-ion cell design.

Figure 7 indicates a test of this algorithm on a pair of NiCd cells. The algorithm required about 550 cycles to adapt itself to the needs of a NiCd cell, settling out with a recharge ratio of about 101% in this 20% DOD test. Figure 8 indicates another test of this algorithm for a 0.75 Ah commercial lithium-ion cell pair operated in a thermal vacuum environment that simulated low-earth orbit operation at 20% DOD. These cells operated for over 2200 cycles with little evidence of significant degradation. The dithering of the voltages in Figure 8 is due to the continuous adjustments in the cell recharge as the adaptive algorithm verifies that it is maintaining the optimum recharge conditions. Figure 9 shows a similar simulated low-earth orbit test of two 1.5 Ah lithium-polymer cells in a nanosatellite mass simulator operated in a thermal vacuum chamber. In Figure 9 we again see the dithering as the algorithm continuously adjusts the amount of recharge applied to the cells, which is controlled on an independent cell basis. These two cells do show some evidence of degradation after about 3000 cycles, which is recognized by the gradual decrease in the average end-of-discharge voltage and increase in the end-of-charge voltage. In this test the end of life will occur when the average end of discharge voltage reaches 3.0 volts and the peak recharge voltage reaches 4.1 volts.

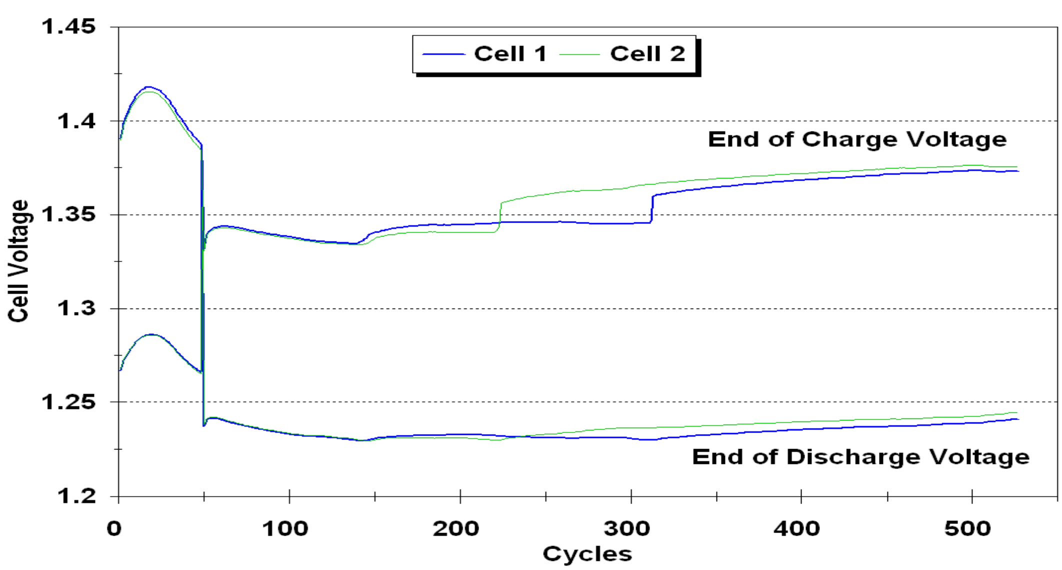


Figure 7. Adaptive Charge Control Test for 2 NiCd Cells.

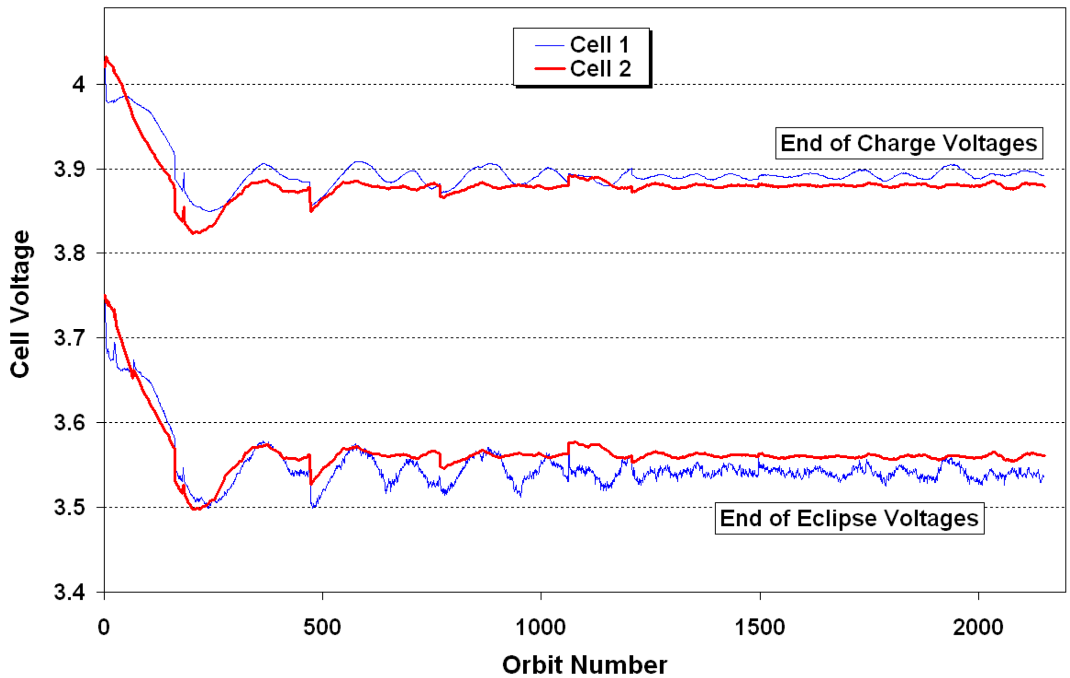


Figure 8. Adaptive Charge Control Test for Two Lithium-ion Cells.

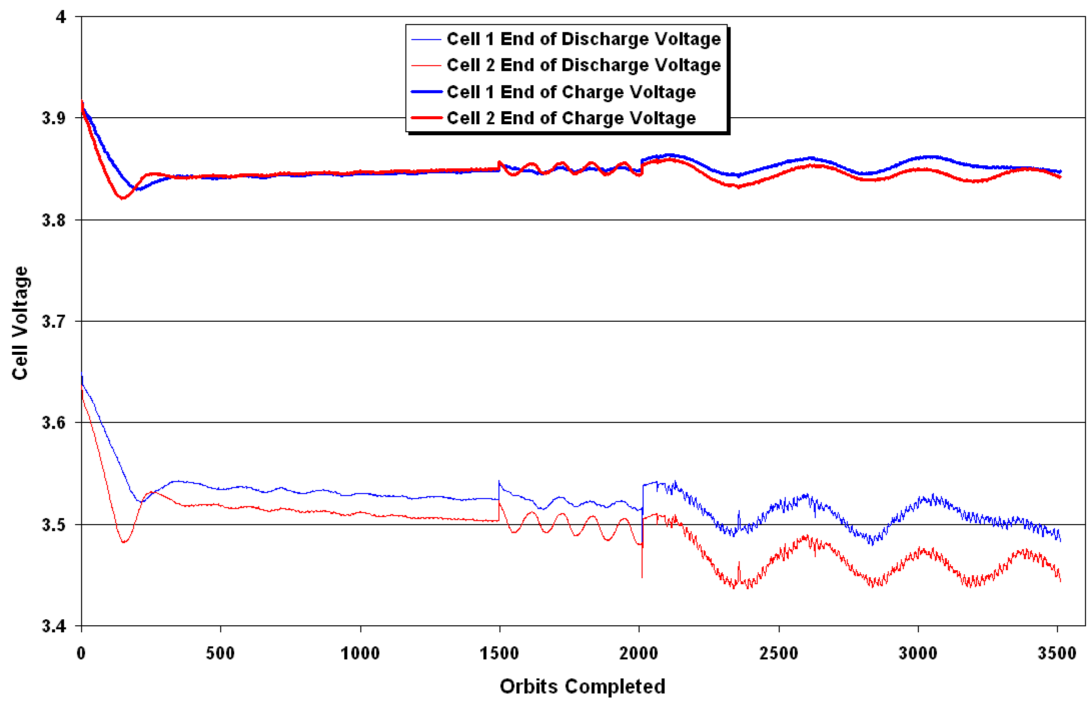


Figure 9. Adaptive Charge Control Test for Two Lithium-polymer Cells.

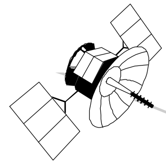
The Adaptive Charge Control Algorithm method for the charge management of lithium ion batteries can offer a minimum stress cycling regime that will change in response to changes in the cell electrodes, resistance, or environment to maintain minimum stress. This approach is capable of actually optimizing the cycle life of a lithium-ion battery. Additional testing of this algorithm with spacecraft type lithium-ion cells is expected to begin shortly.

Conclusions

An accelerated cycling test has been developed that can screen lithium-ion test cells from a given lot in 2-3 months of test time, and is based on the degradation seen in cell voltages over the first 2500 cycles. Evidence has also been seen suggesting that some lithium-ion cells do not respond well to periods of stand in a highly charged state. Calorimetry measurements on a wide range of lithium-ion and lithium polymer cells invariably show a rich chemistry of staging processes as lithium ions undergo stepwise intercalation into the electrodes. Calorimetry can also provide an extremely sensitive method for detecting changes in cell design or chemistry over time, as well as verifying the thermal design of a satellite for a given type of cell at end of life.

An Adaptive Charge Control Algorithm has been discussed that is capable of automatically adapting to the charge needs of a battery cell so as to maintain an optimized recharge protocol for minimizing stress due to cycling. Data have been presented demonstrating the functioning of this algorithm for NiCd, lithium-ion, and lithium-polymer batteries.

Eagle-Picher Technologies, LLC



Large Capacity Single Pressure Vessel (SPV) Battery Development

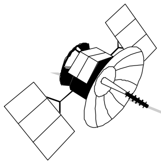
Jeff Dermott

Jack Brill

Eagle-Picher Technologies, LLC

Joplin, Missouri

Eagle-Picher Technologies, LLC

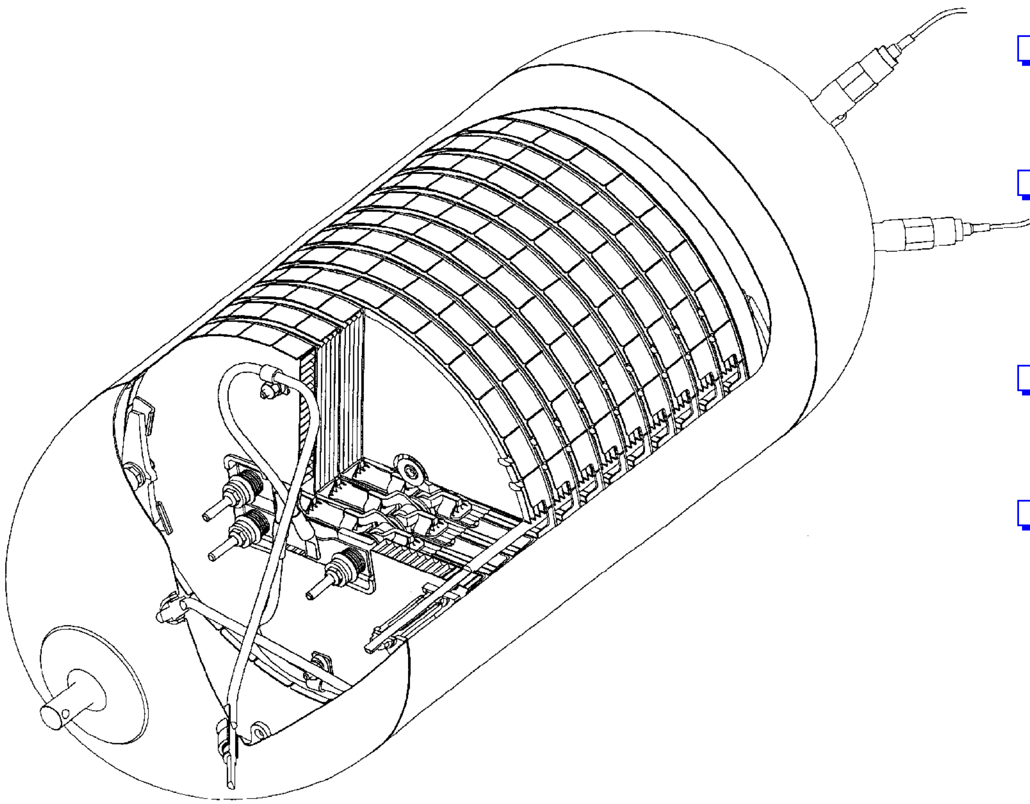


Single Pressure Vessel (SPV) Background

- **Originally Developed for the Iridium® Program**
- **104 Batteries Produced**
- **92 Batteries Launched**
- **Flights Included Batteries Having Capacities of 50 Ah and 60 Ah**
  - **Iridium®, Ikonos, STEX**
  - **50 Ah --- 24 Flights**
  - **60 Ah --- 68 Flights**

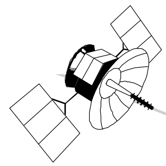
EAGLE EP PICHER
Eagle-Picher Technologies, LLC

Single Pressure Vessel (SPV) Battery Characteristics



- **All Cells in One Pressure Vessel**
- **Pressure Monitored by Two Transducers for Redundancy**
- **Heat Conducted by Ni-coated Al Plates**
- **Cell Terminals Connected by Mechanical Pressure**

Eagle-Picher Technologies, LLC



SPV Design Heritage

- **Qualified Batteries In the 10 inch Diameter Pressure Vessel:**
  - **30 Ah --- SAR 10107**
    - **Length 19.44 inches**
    - **MEOP 400 psig**
    - **Weight 43 lbs**
  - **50 Ah --- SAR 10065**
    - **Length 24.7 inches**
    - **MEOP 500 psig**
    - **Weight 67 lbs**
  - **60 Ah --- SAR 10081**
    - **Length 25.2 inches**
    - **MEOP 640 psig**
    - **Weight 80 lbs**

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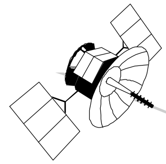
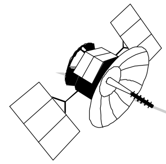


Designs in Development

- Two Battery Designs in Development with 13 inch Diameter Pressure Vessels
- Scaled From the 10 Inch Designs
- Lessons Learned From 10 Inch SPV Applied to 13 Inch Diameter Battery Designs
- Cell Terminal/ECS Seal Design Modified Due to the Need for a Larger Current Conductor

EAGLE PICHER
Eagle-Picher Technologies, LLC



SPV Design Comparison

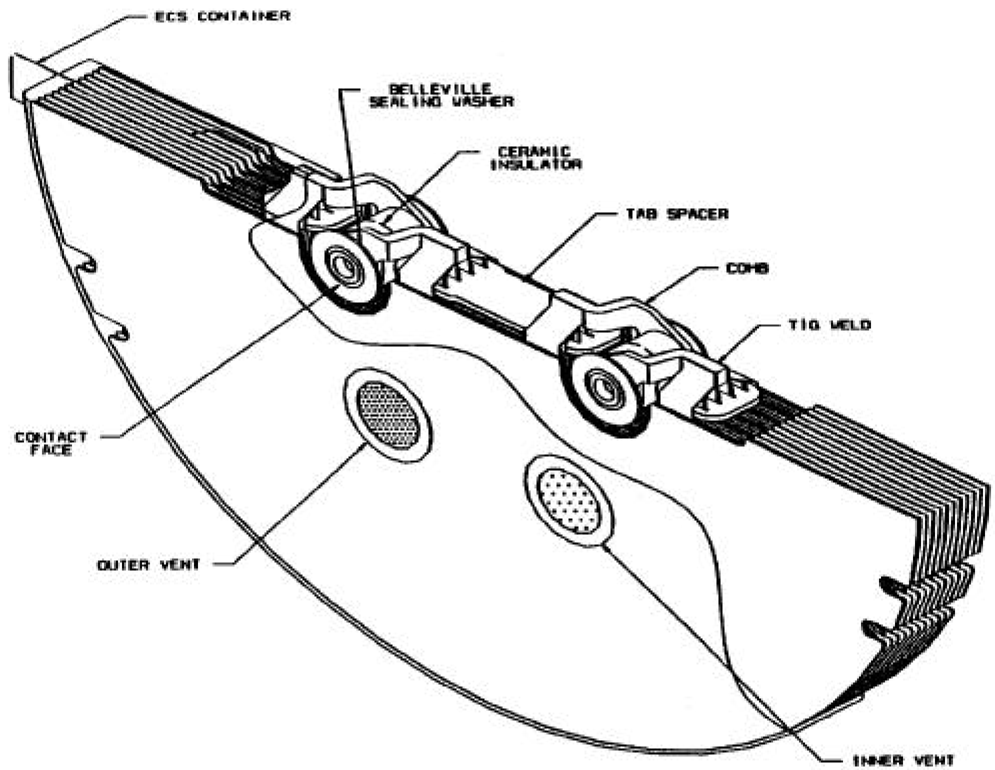
Modules Per Cell	Resulting 10" Design Capacity (AH)	Resulting 13" Design Capacity (AH)
3	30	N/E
4	40	80
5	50	100
6	60	120

- **30 Ah, 50 Ah, & 60 Ah 10" Battery Designs Proven by Flight Heritage.**
- **80 Ah & 120 Ah 13" Battery Designs Are Currently in Development.**

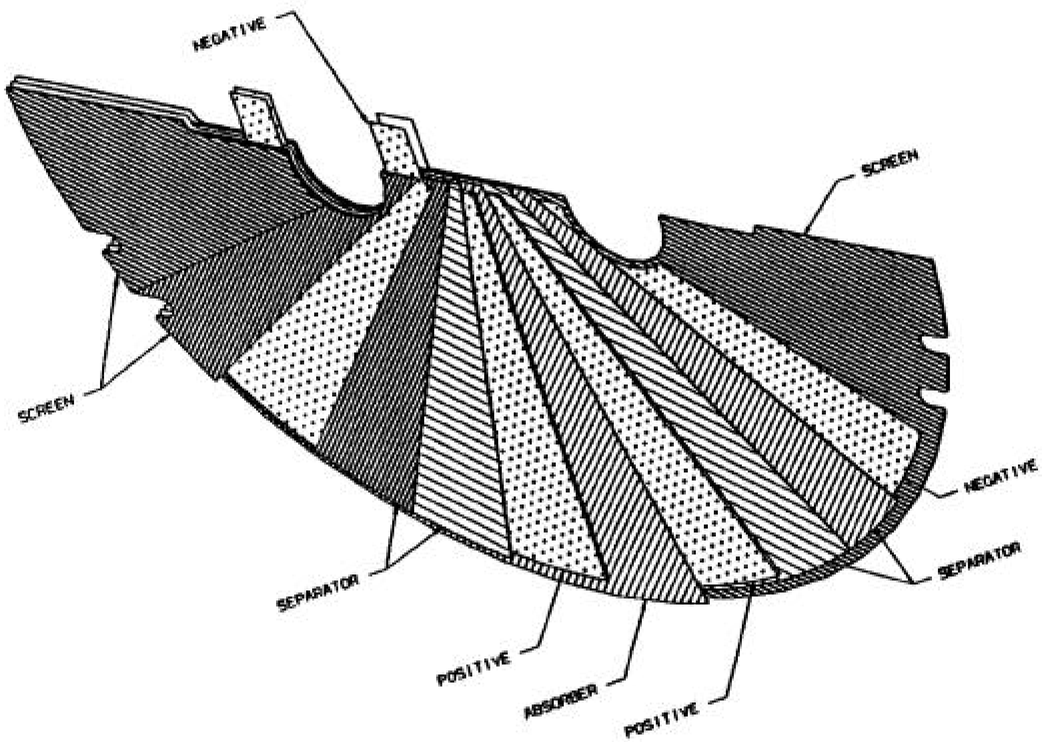
Eagle-Picher Technologies, LLC

SPV Cell Design

- Same Cell Design As Was Used in 10" Design
- Dual Layer Electrolyte Containment System
- Microporous Vent Allows Gas to Flow, but Not Liquid



SPV Module features



- "Half-Moon" Module Shape Identical to 10" Design
- Nickel Plaque Identical to Original 10" Design
- Two Tabs Per Electrode for Low Impedance and Redundancy
- Absorber Functions As an Electrolyte Reservoir

SPV Pressure Vessel Characteristics

- **Pressure Vessel Manufactured From Inconel 718 by the Same Processes Used in the 10” Design**

- **Boss and Trunion Welds Are LASER Welds**

- **Girth Weld Is LASER Weld by In-house System**

- **Pressure Vessel Qualified With Cycle-burst Sample in Same Manner As 10” Designs**

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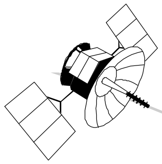

13” Battery Design Improvements

- Most Changes to SPV Design Are Necessary to Incorporate the Larger Electrode Size or Higher Current Rates.
- ECS-Comb Seal Redesign Completed and Verified Through Development Test
- Benefits of ECS-Comb Seal Redesign
  - Fewer Parts Necessary to Seal Simplifies Comb Seal
  - ECS Hermetically Sealed and Tested Prior to Battery Stack
  - Restacking Battery Will Not Automatically Require a Rebagging of Cells
  - Allows Larger Surface Area for Intercell Electrical Connections
  - Fewer Electrical Tie Rods Reduces Mass Associated With Electrical Connections

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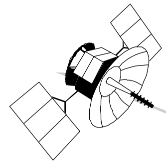
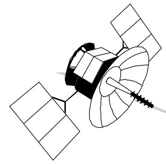


SPV Battery Performance Similarities

- **Battery Impedance Similar to That of the 10” Design (<35 mW) – Measured 21 mW**
- **Charge Retention Efficiency Is Same As 10” Design (85-90%) – Measured 87.5%**
- **Hydrogen Leak Rate Same as Level Experienced in 10”design (< 5 X 10^{-6} cc/sec)**

Eagle-Picher Technologies, LLC



80 AH SPV Battery Design Summary

Battery Type	SAR 10121
Nominal Voltage (volts)	27.7
Rated Capacity (Ah)	80
Actual Capacity (Ah)	90.6
Specific Energy (WHr/kg)	55.3
Energy Density (WHr/liter)	70.9
Weight (lb)	100
Diameter (inches)	13.06
Length (inches)	26.4
MEOP (psig)	540

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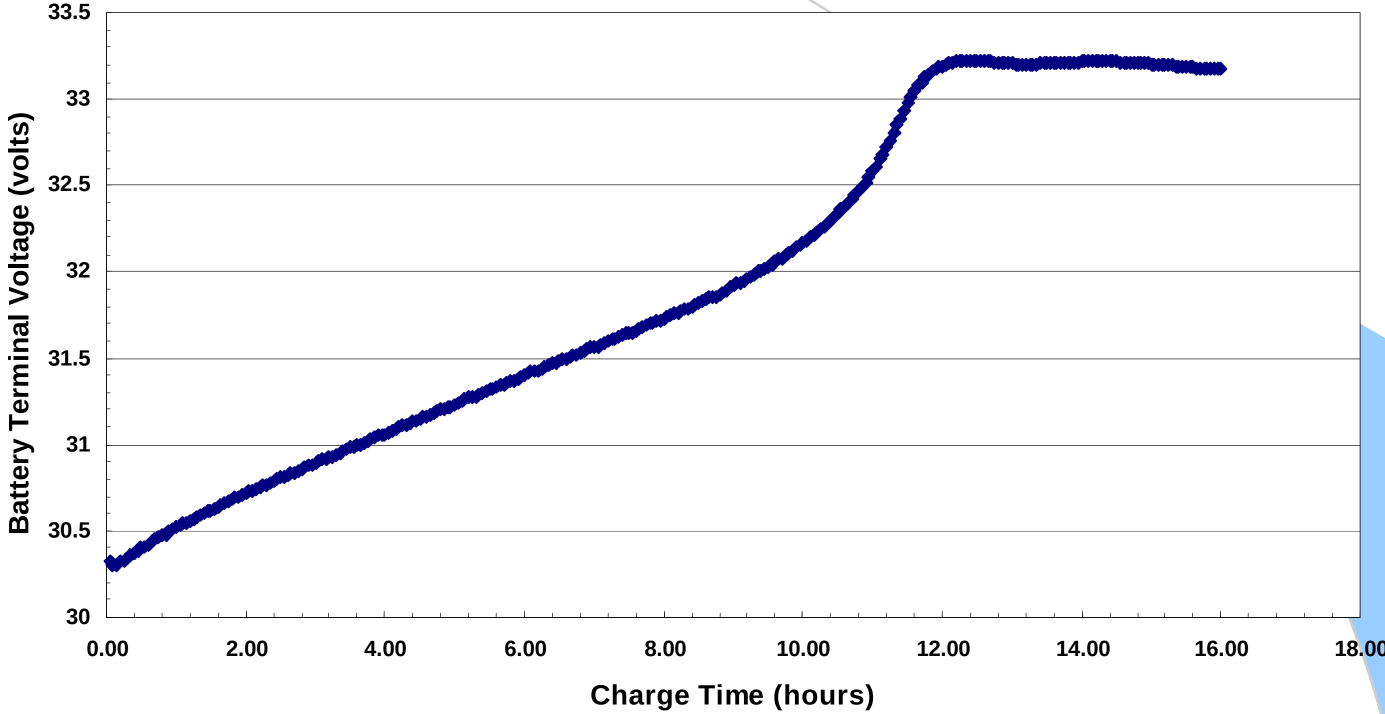
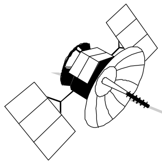
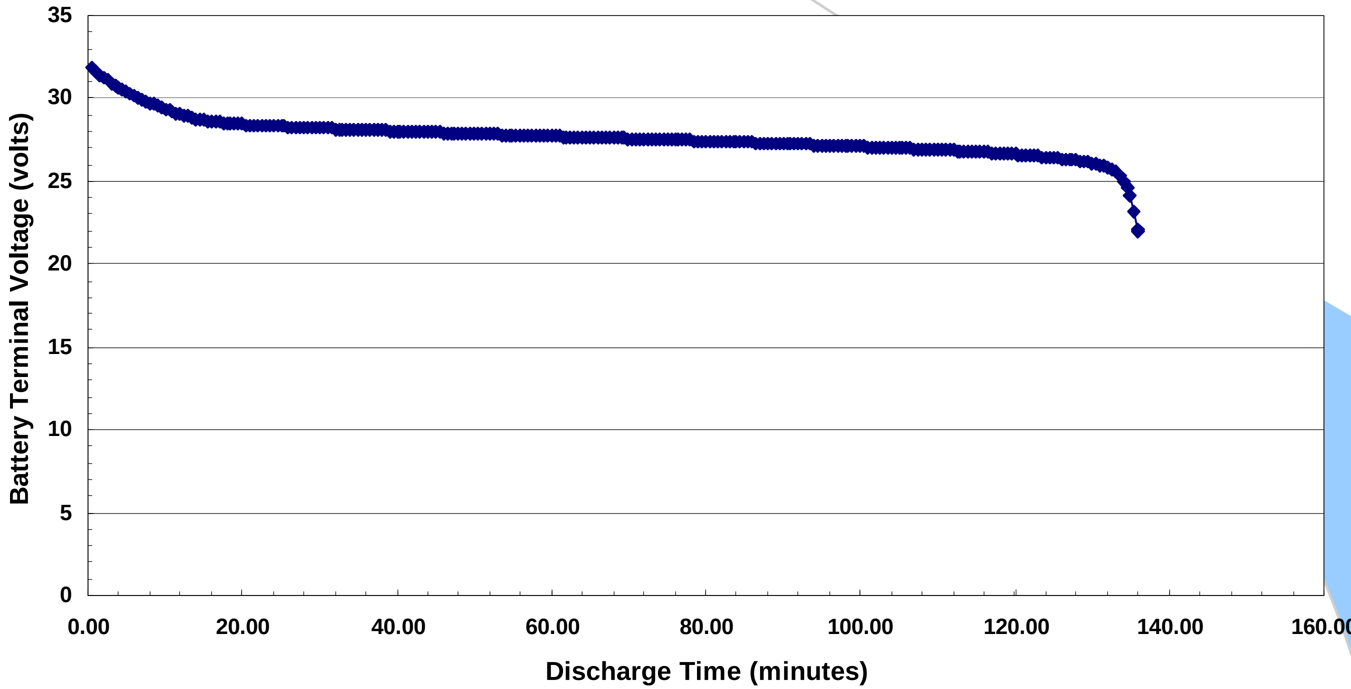
C/10 Charge for SAR 10121



Eagle-Picher Technologies, LLC



C/2 Discharge for SAR 10121



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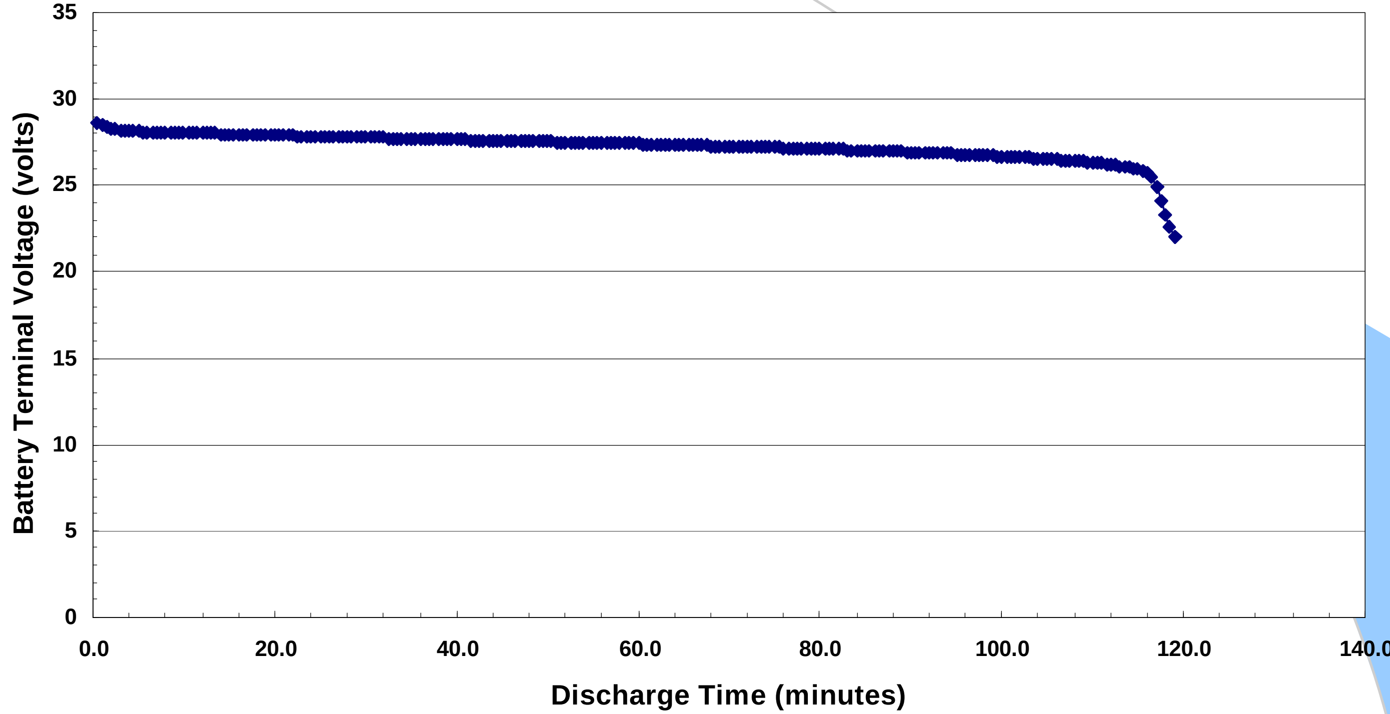
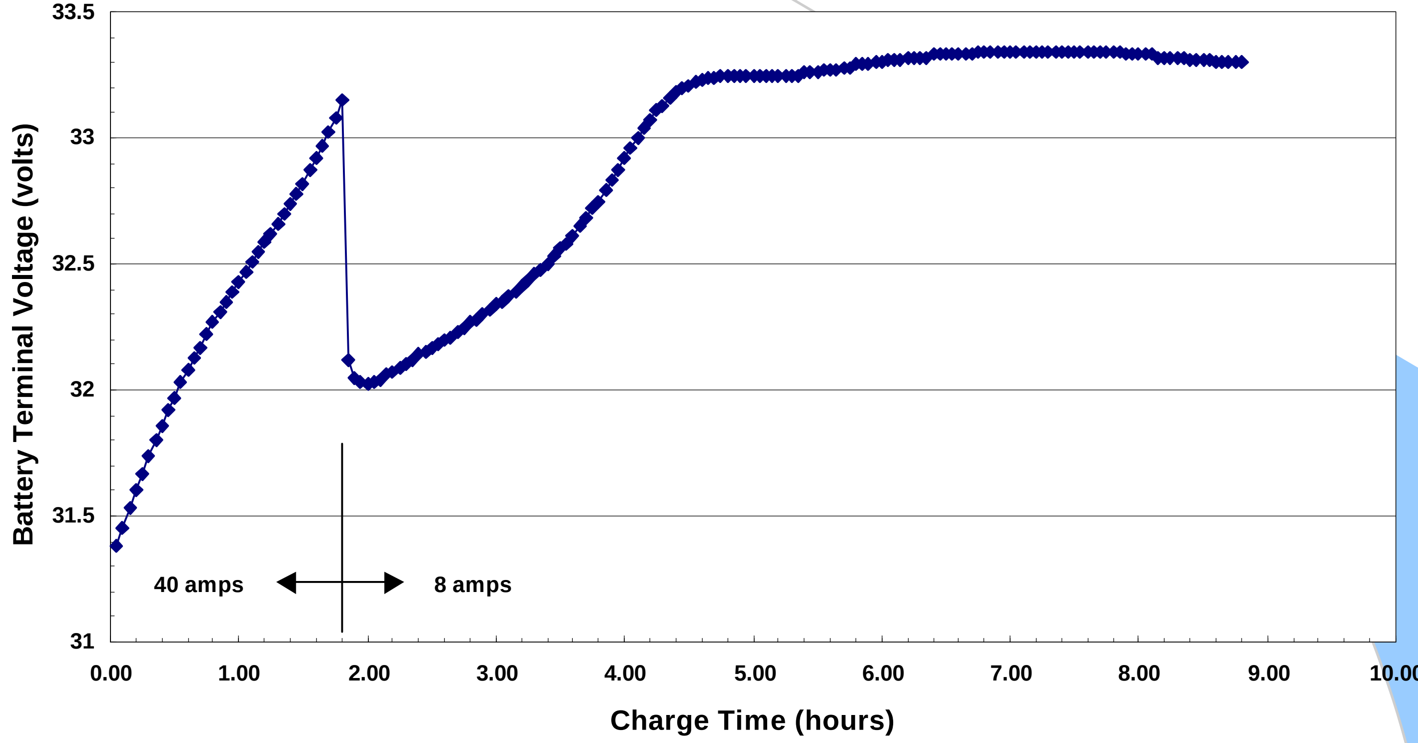
C/2 Discharge for SAR 10121 After 72 Hr OCV



Eagle-Picher Technologies, LLC

Step Charge for SAR 10121



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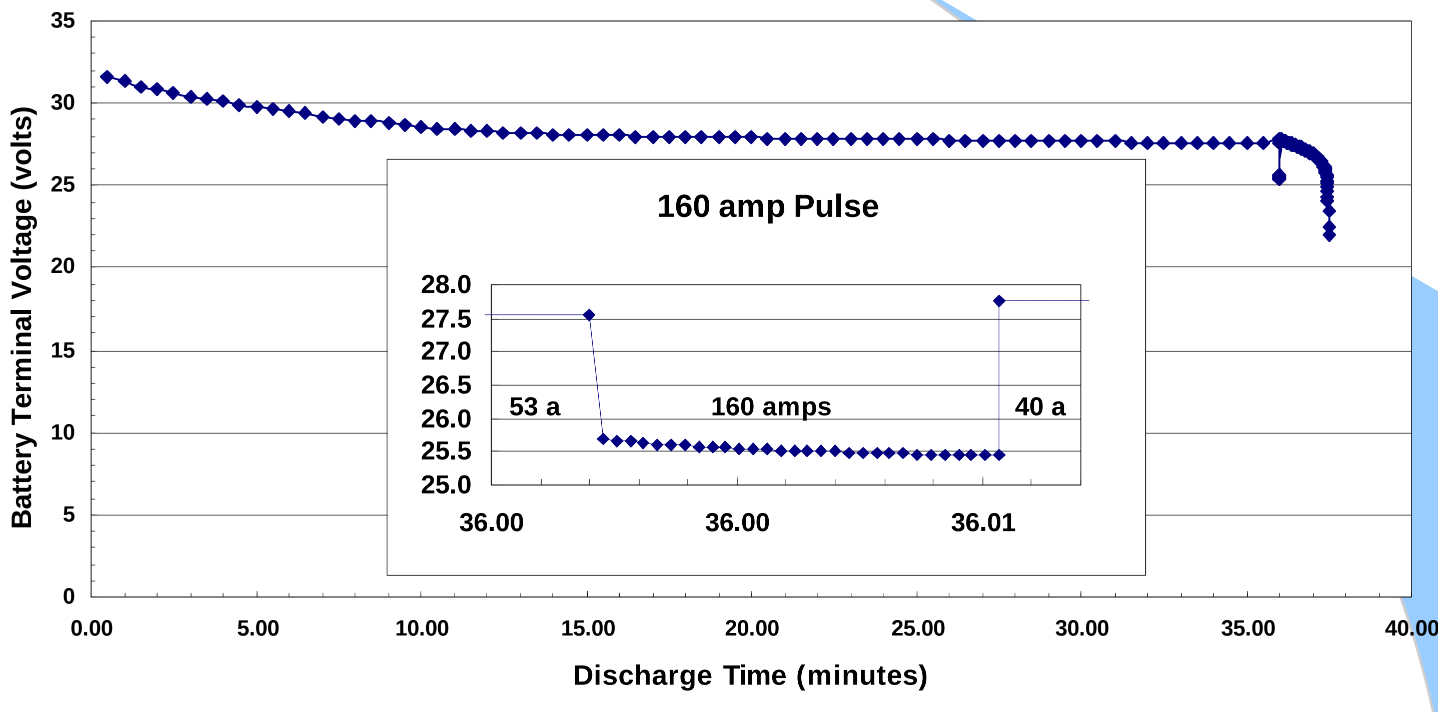
Discharge with 160 amp Pulse SAR 10121



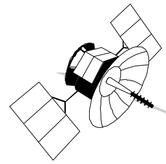
EAGLE EP PICHER

Eagle-Picher Technologies, LLC

120 AH SPV Battery Proposed Design Summary

❑ Battery Type	SAR 10125
❑ Nominal Voltage (volts)	27.7
❑ Rated Capacity (Ah)	120
❑ Actual Capacity (Ah)	132
❑ Specific Energy (WHr/kg)	53.7
❑ Energy Density (WHr/liter)	64.3
❑ Weight (lb)	150
❑ Diameter (inches)	13.06
❑ Length (inches)	36.2
❑ MEOP (psig)	540

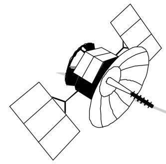
Eagle-Picher Technologies, LLC



Planned 13” Battery Design Qualification Tests

- **Pressure Vessel Qualification (Cycle & Burst Sample)**
- **Random Vibration to 12.9 Grms**
- **Sinusoidal Vibration to 10.5 G**
- **Pyrotechnic Shock**
- **Electrical Testing**
  - **Standard Capacity @ -10°C to 30°C**
  - **LEO Operational Profile**
  - **GEO Operational Profile**
  - **Charge/Discharge Rates (pulse)**
  - **Charge Retention @ 10°C**
  - **Impedance**
  - **Insulation Resistance**

Eagle-Picher Technologies, LLC



Summary

- Two Battery Designs Are Being Developed in the 13 Inch Diameter
- Both Designs Utilize the Basic Technology Qualified and Flown on the Iridium® Program
- 80 Ah Design Is Being Completed for Qualification Test with Planned Completion of March 2001
- 120 Ah Design Will Be Completed by November 2001

CRANE CELL TESTING SUPPORT OF NASA/GODDARD SPACE FLIGHT CENTER: AN UPDATE

Mike Strawn and Jerry David
NAVSURFWARCENDIV Crane, Indiana
Gopalakrishna M. Rao
NASA Goddard Space Flight Center
Greenbelt, Maryland

OBJECTIVE

- Verify the Quality and Reliability of aerospace battery cells and batteries for NASA flight programs
- Disseminate the data
  - to develop a Plan for in-orbit battery management
  - to Design a cell/battery for future NASA spacecraft
- Establish a cell test Data Base for rechargeable cell/batteries

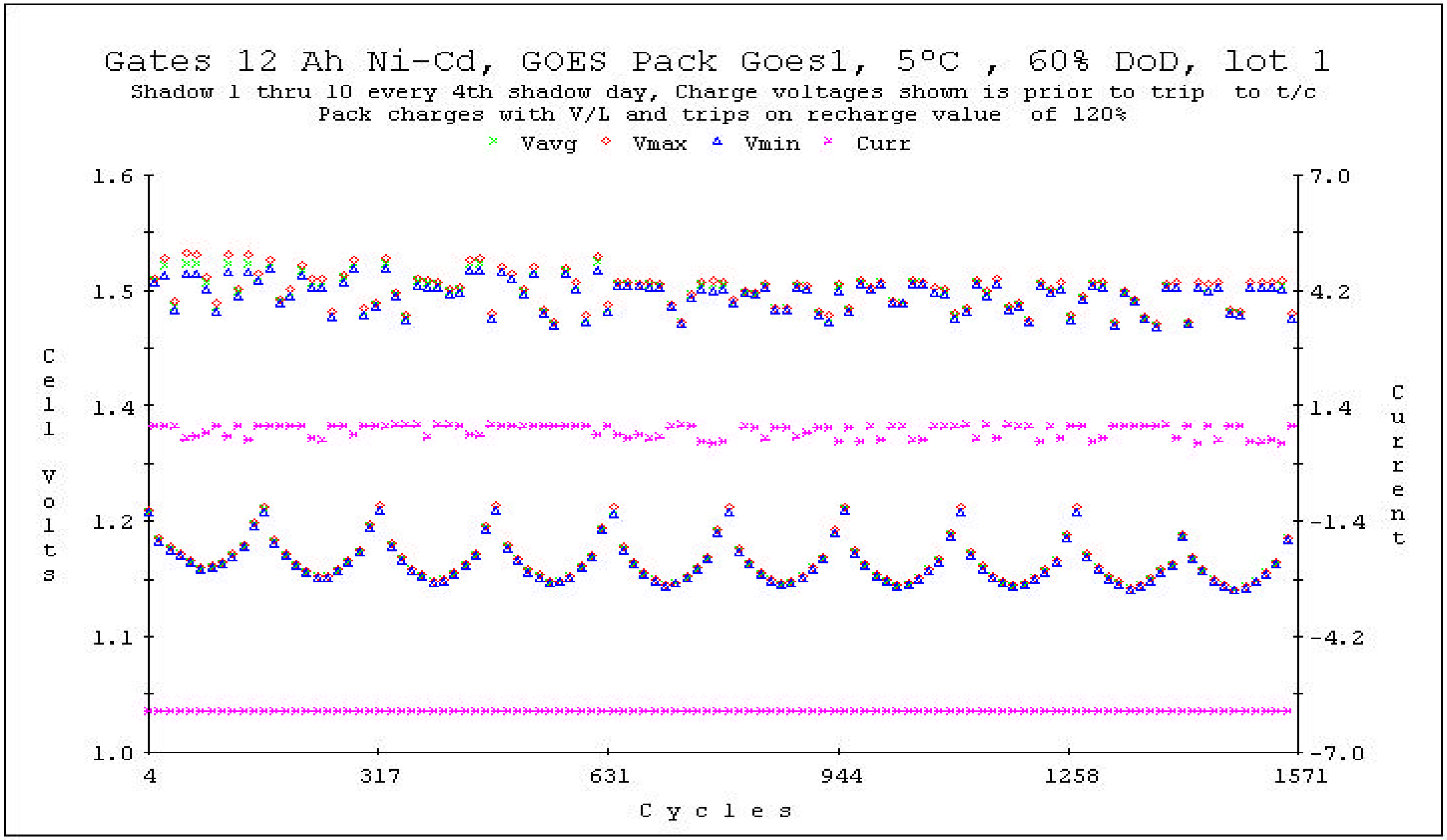
PACKS

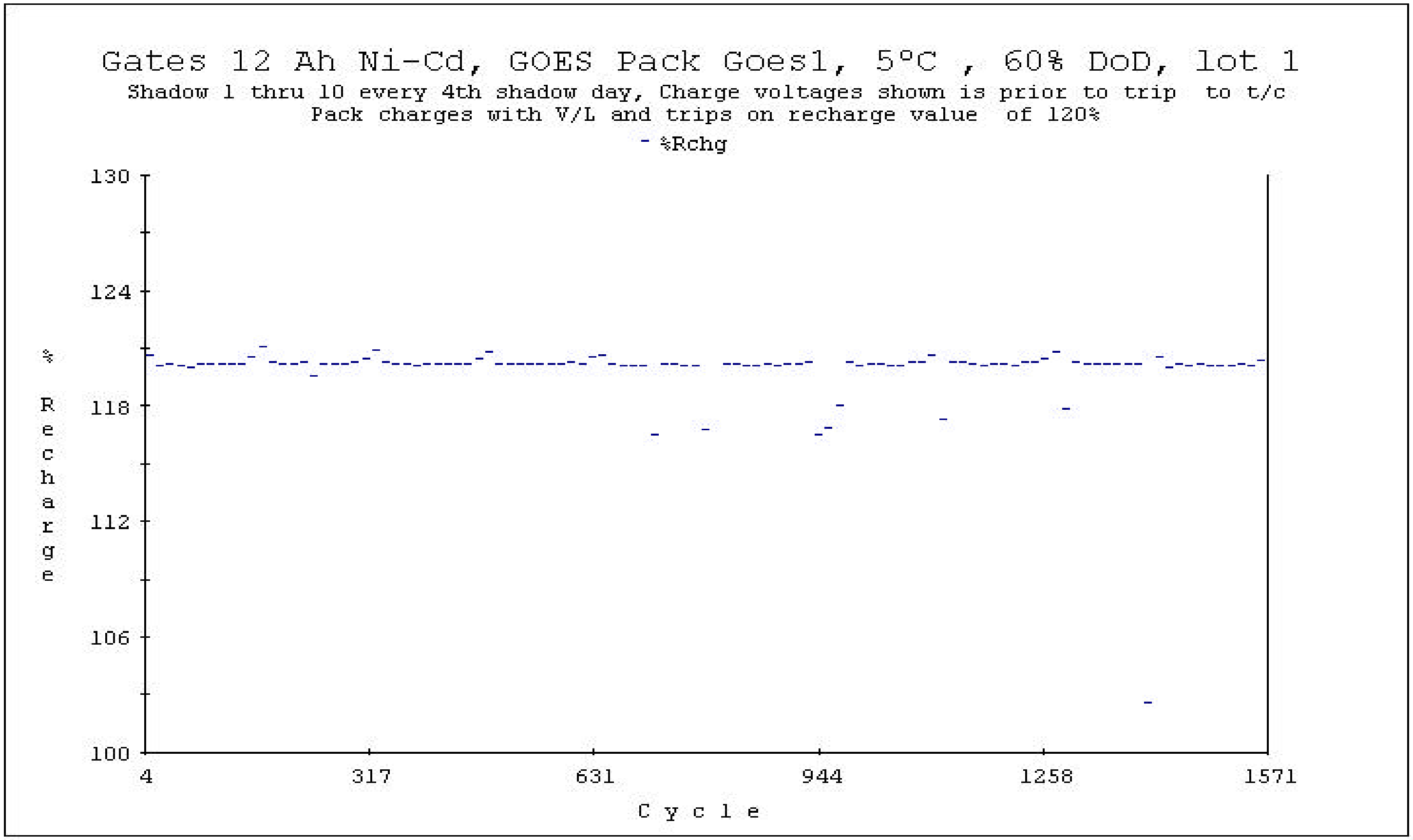
Orbit	Pack	Type	Ah	Start Date	DoD	°C	K Cycles
Stress	0021H	Super	21	10/98	50	20	10.9
Mission	0040P	Saft Ni-Cd	40	7/96	21	5	20.4
Mission	0044P	Saft Ni-Cd	40	1/99	21	5	9.0
Mission	0045P	Saft Ni-Cd	40	1/00	21	5	3.2
Mission	0052T	Super	50	3/95	14.4	10	28.9
Mission	0053T	Super	50	5/95	17	0	27.9
Mission	6151T	Super	50	6/96	25	10	22.4
Stress	6152T	Super	50	6/96	17	0	24.6
Stress	3023M	EPT-CPV	23	11/98	60	10	1.3
Stress	3023T	EPT-CPV	23	12/98	60	10	10.4
Mission	3050S	EPT	50	1/00	60	10	4.1
Mission	3050H	EPT	50	10/95	20	5	25.6
Mission	3600H	EPT	93	1/92	11	-5	42.7
Mission	3601H	EPT	93	1/92	11	-5	42.2

DISCONTINUED PACKS

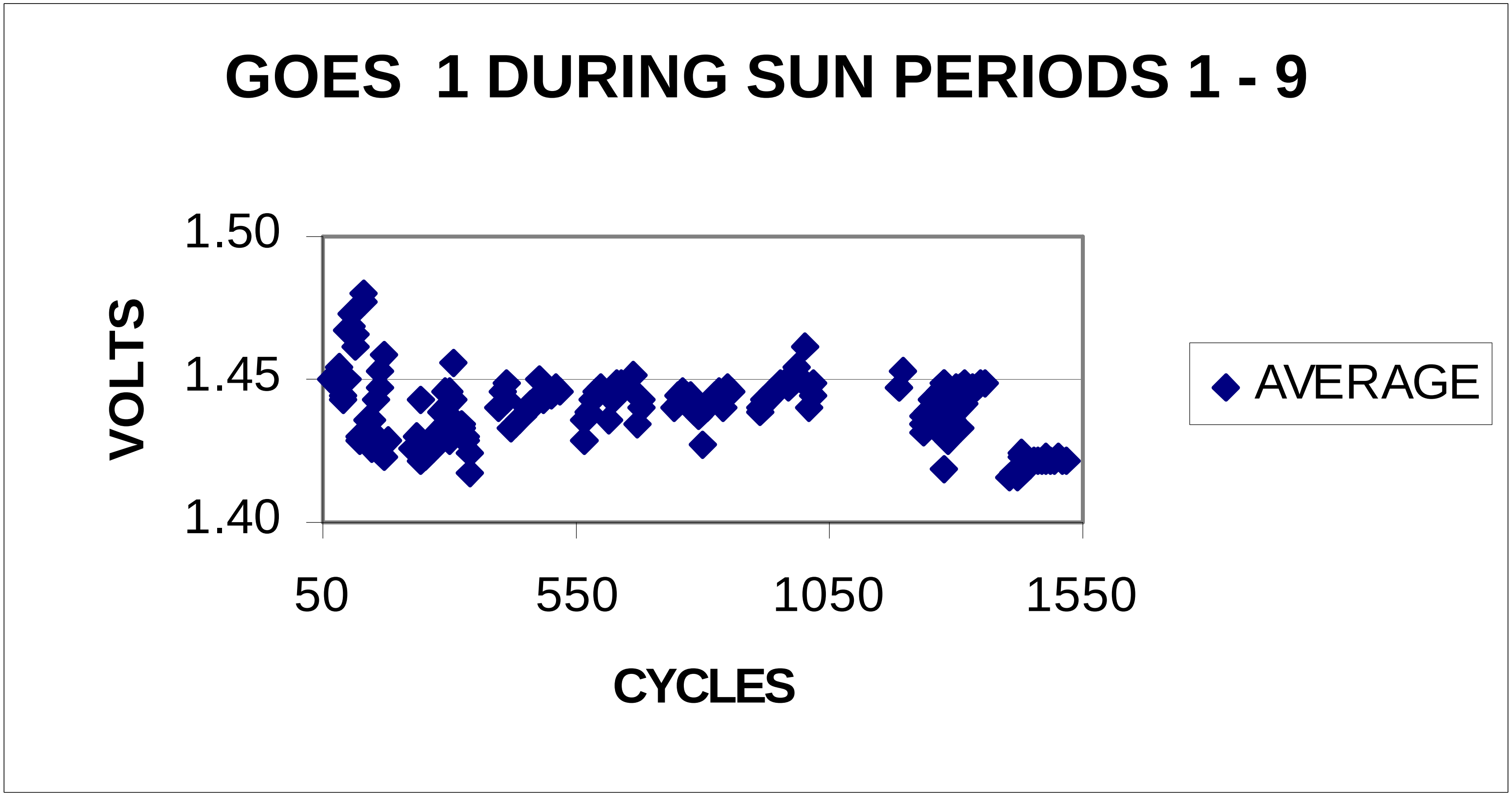
Orbit	Pack	Type	Ah	Date Start/ End	DoD	ºC	K Cycles
Stress	0042P	Saft Ni-Cd	40	7/97 3/00	40	20	15.1
Stress	0043P	Saft Ni-Cd	40	10/97 2/00	40	20	13.1
Mission	B300A	Super	21	3/99 2/00	pulse	5	0.5
GEO REAL	GOES 1	Saft Ni-Cd	12	10/95 7/00	60	0	Sh#10

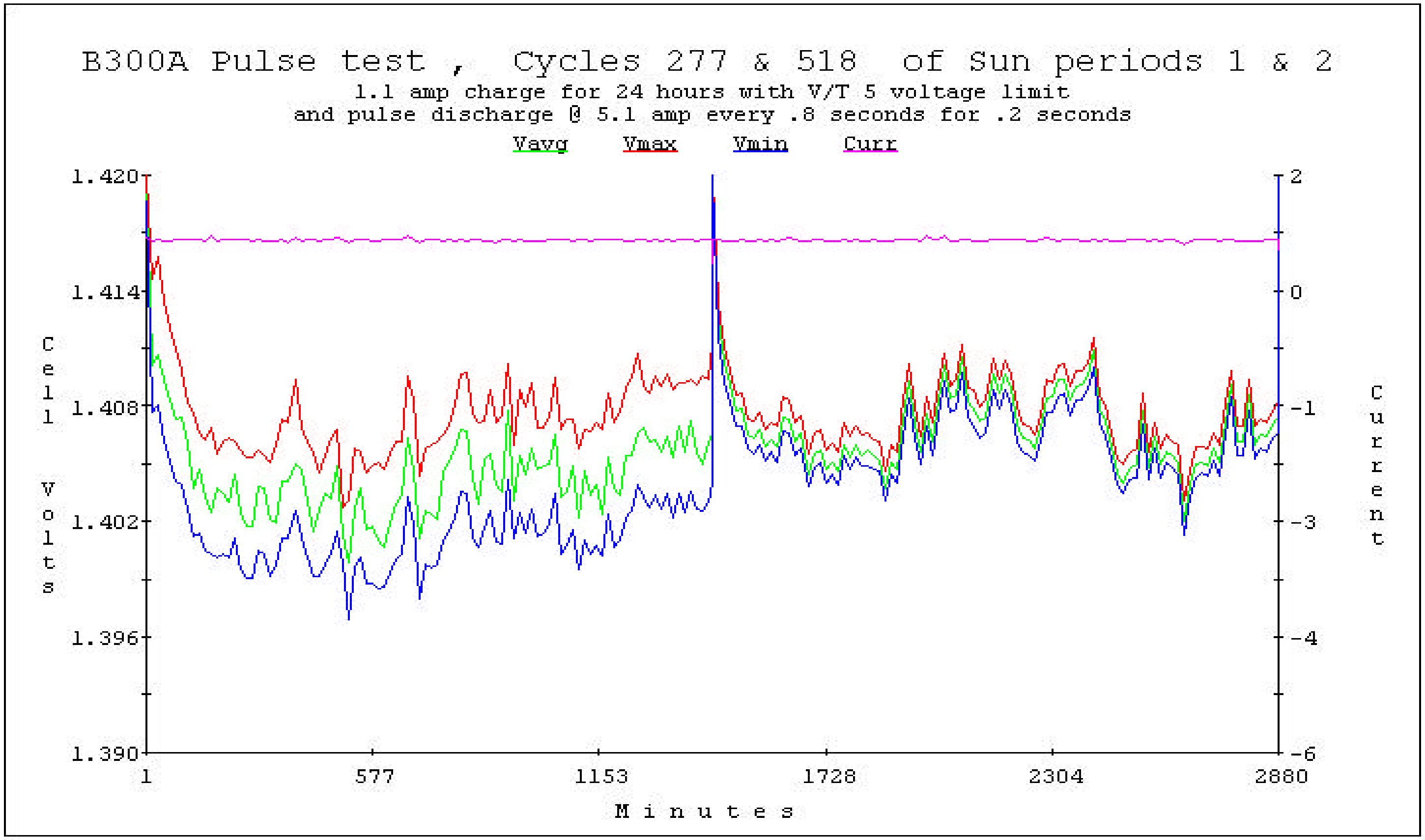
Packs discontinued during FY00


Gates 12 Ah Ni-Cd, GOES Pack Goes1, 5°C , 60% DoD, lot 1
Shadow 1 thru 10 every 4th shadow day, Charge voltages shown is prior to trip to t/c
Pack charges with V/L and trips on recharge value of 120%
Vavg
Vmax
Vmin
Curr
1.6
1.5
1.4
1.2
1.1
1.0
7.0
4.2
1.4
-1.4
-4.2
-7.0
Cell Volts
Current
4
317
631
944
1258
1571
Cycles

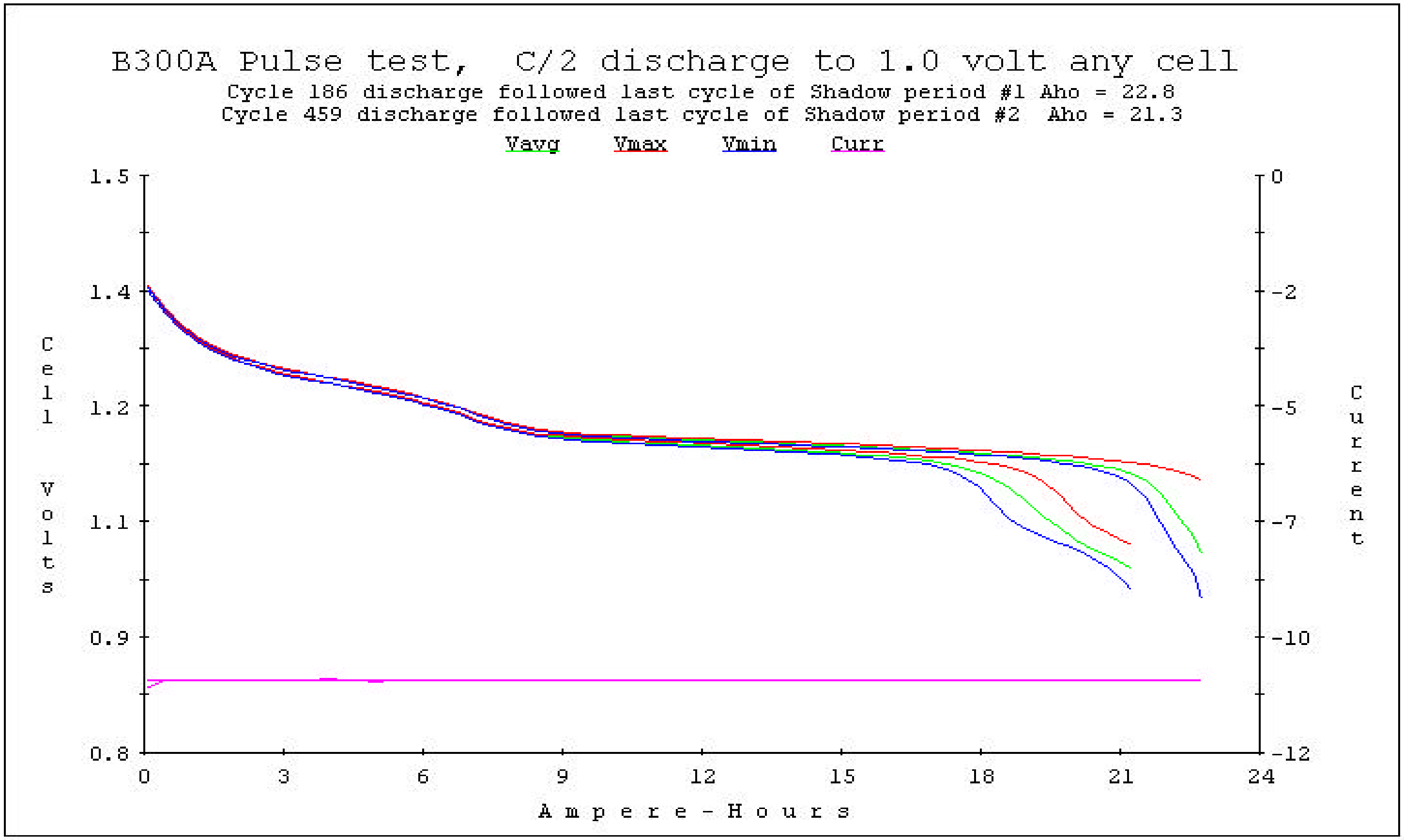


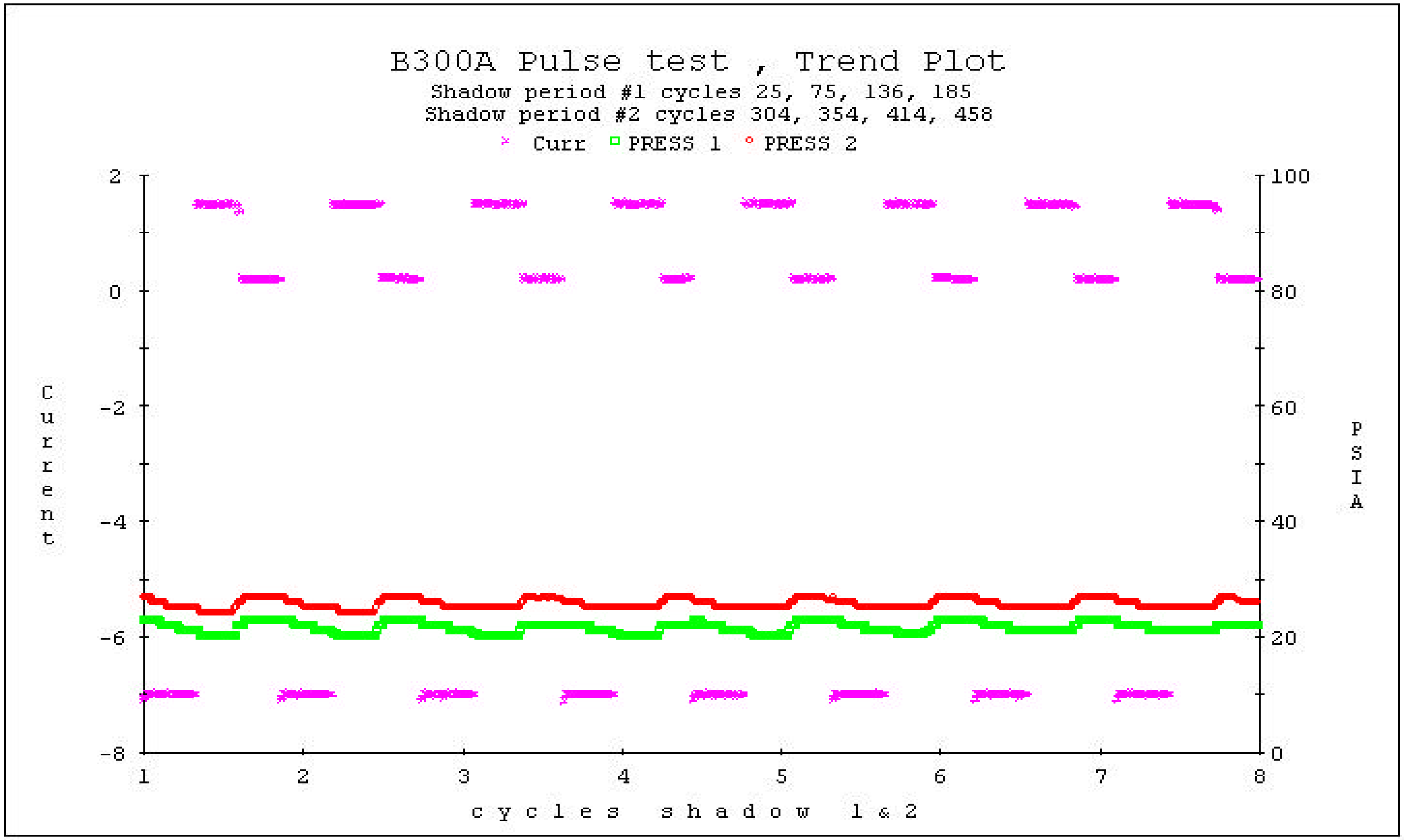
Gates 12 Ah Ni-Cd, GOES Pack Goes1, 5°C , 60% DoD, lot 1
Shadow 1 thru 10 every 4th shadow day, Charge voltages shown is prior to trip to t/c
Pack charges with V/L and trips on recharge value of 120%
%Rchg
% Recharge
130
124
118
112
106
100
4
317
631
944
1258
1571
Cycle

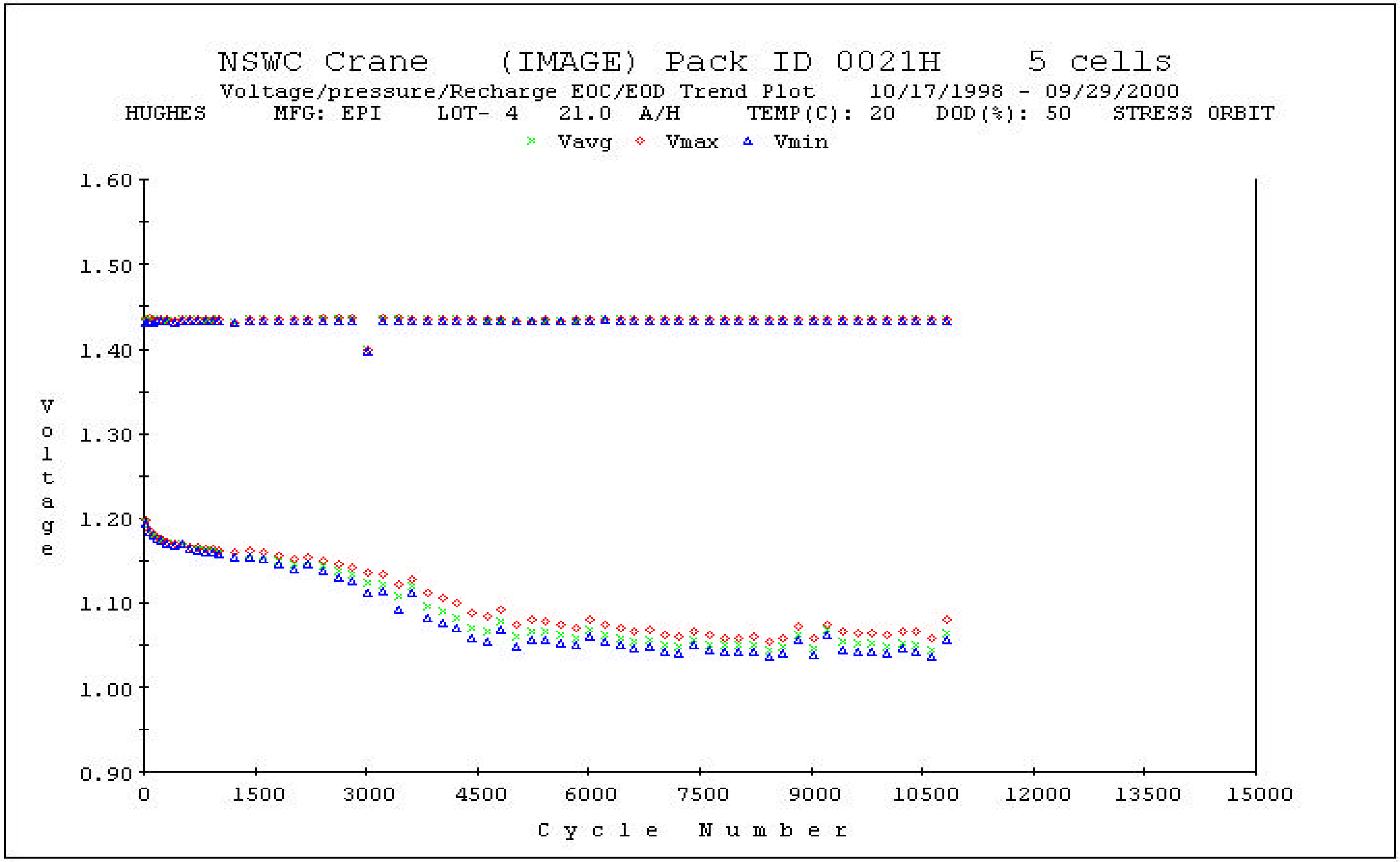

GOES 1 DURING SUN PERIODS 1 - 9
VOLTS
1.50
1.45
1.40
50
550
1050
1550
CYCLES
AVERAGE

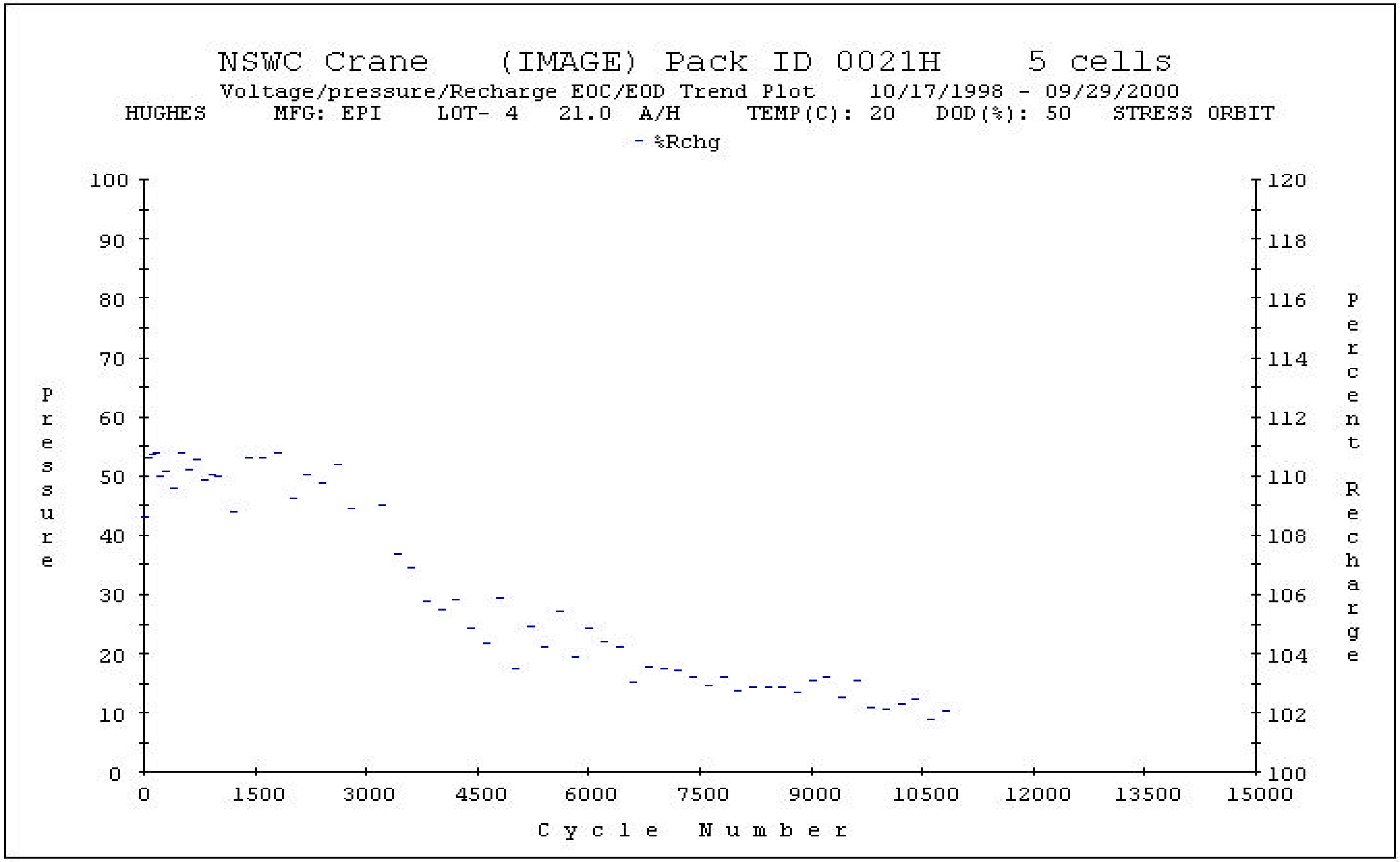

B300A Pulse test , Cycles 277 & 518 of Sun periods 1 & 2
1.1 amp charge for 24 hours with V/T 5 voltage limit
and pulse discharge @ 5.1 amp every .8 seconds for .2 seconds
Vavg
Vmax
Vmin
Curr
Cell Volts
1.420
1.414
1.408
1.402
1.396
1.390
Current
2
0
-1
-3
-4
-6
1
577
1153
1728
2304
2880
Minutes

o

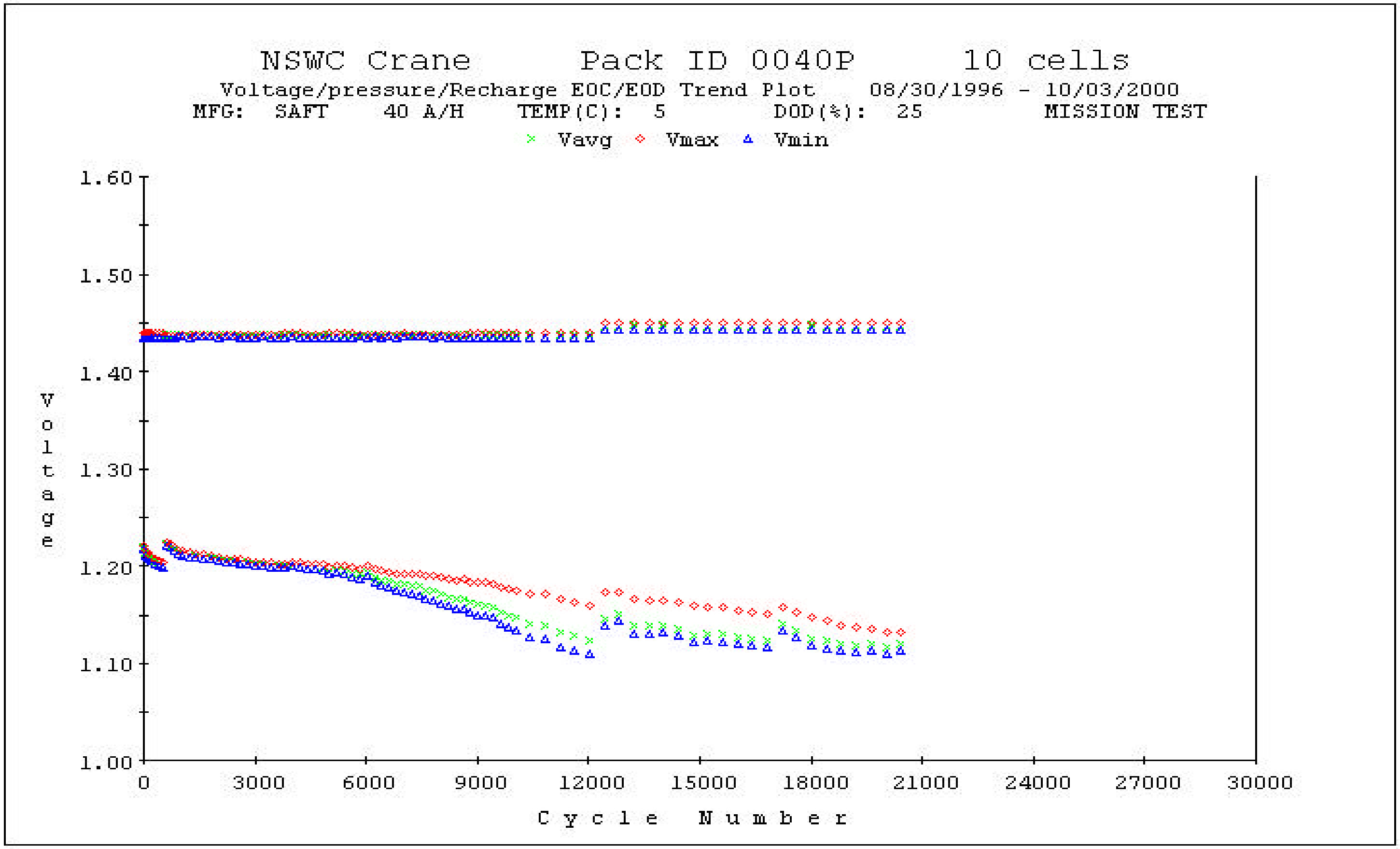

B300A Pulse test, C/2 discharge to 1.0 volt any cell
Cycle 186 discharge followed last cycle of Shadow period #1 Aho = 22.8
Cycle 459 discharge followed last cycle of Shadow period #2 Aho = 21.3
Vavg
Vmax
Vmin
Curr
Cell Volts
1.5
1.4
1.2
1.1
0.9
0.8
0
-2
-5
-7
-10
-12
Current
0
3
6
9
12
15
18
21
24
Ampere-Hours

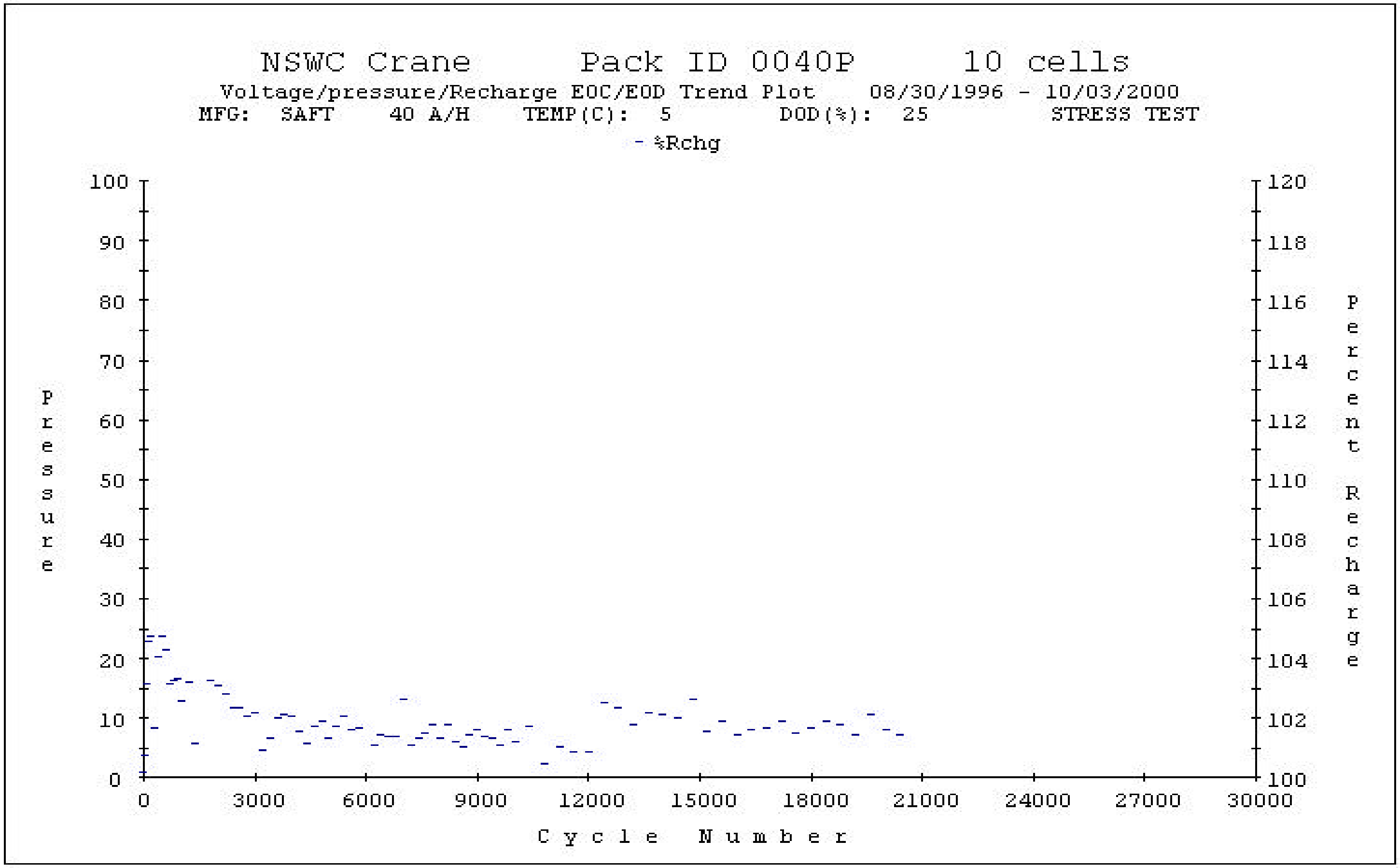

B300A Pulse test , Trend Plot
Shadow period #1 cycles 25, 75, 136, 185
Shadow period #2 cycles 304, 354, 414, 458
Curr
PRESS 1
PRESS 2
Current
PSIA
cycles shadow 1 & 2
2
0
-2
-4
-6
-8
100
80
60
40
20
0
1
2
3
4
5
6
7
8

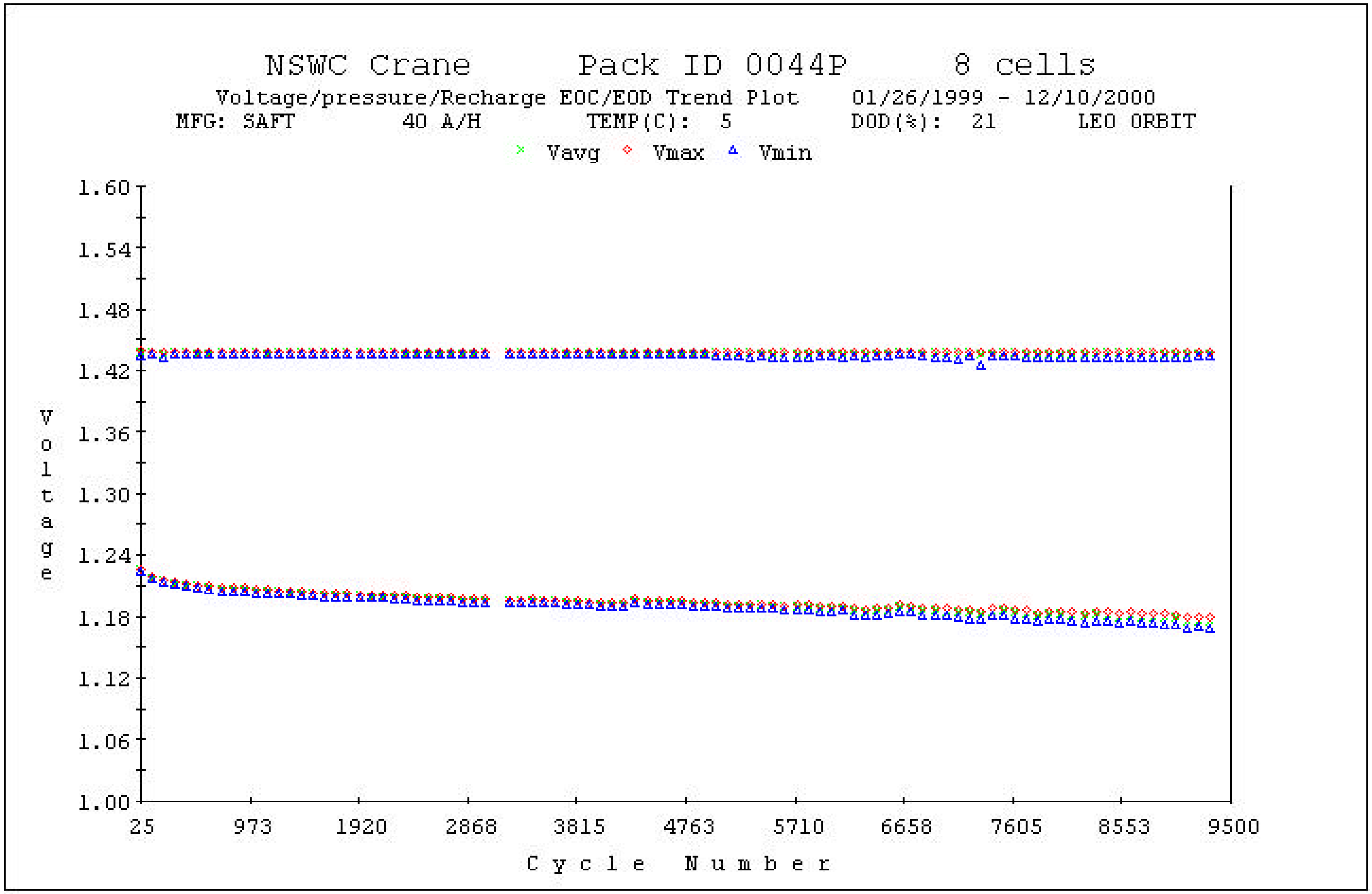

NSWC Crane (IMAGE) Pack ID 0021H 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 10/17/1998 - 09/29/2000
HUGHES MFG: EPI LOT- 4 21.0 A/H TEMP(C): 20 DOD(%): 50 STRESS ORBIT
Vavg Vmax Vmin
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
Voltage
0
1500
3000
4500
6000
7500
9000
10500
12000
13500
15000
Cycle Number



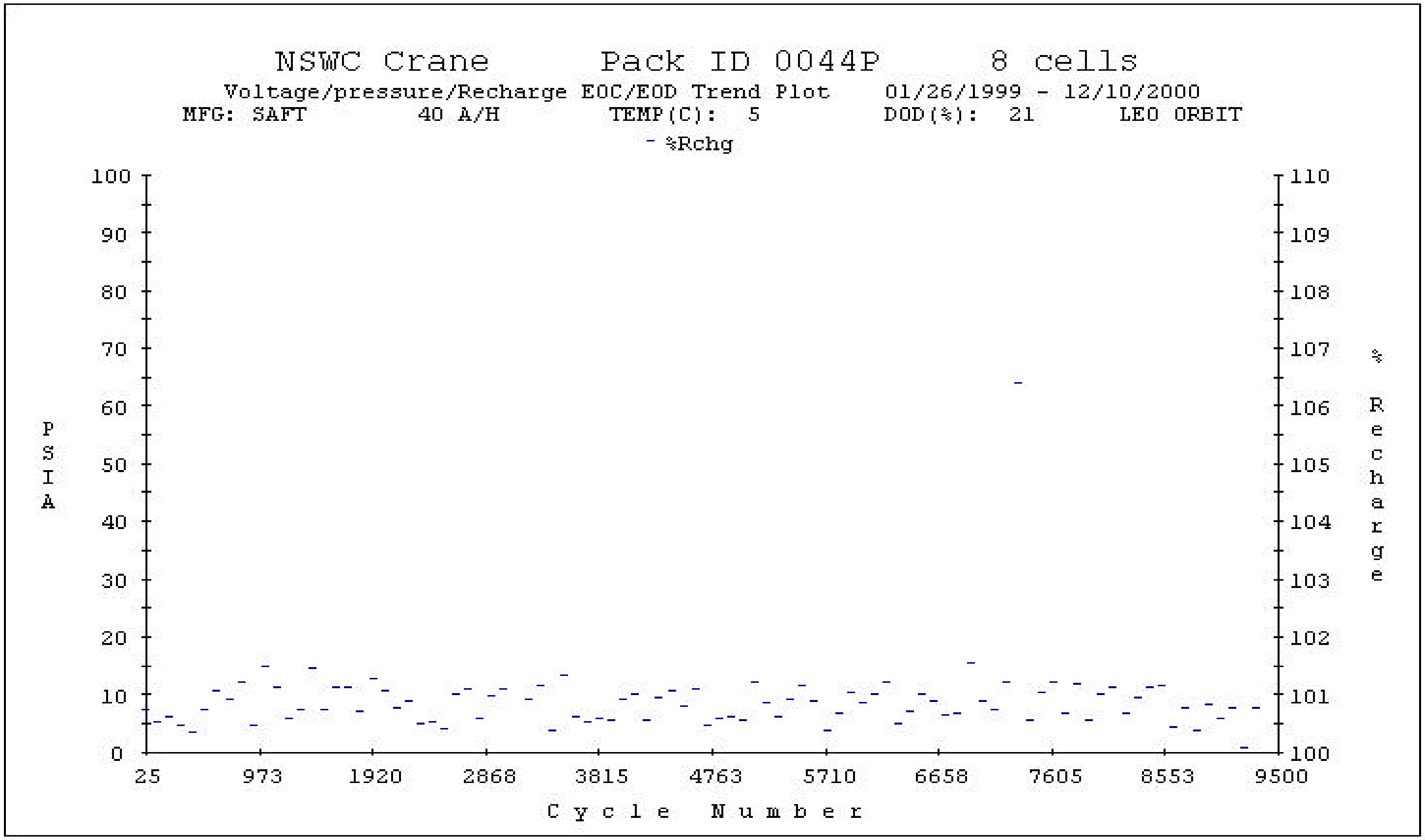
NSWC Crane (IMAGE) Pack ID 0021H 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 10/17/1998 - 09/29/2000
HUGHES MFG: EPI LOT- 4 21.0 A/H TEMP(C): 20 DOD(%): 50 STRESS ORBIT
- %Rchg
Pressure
Percent Recharge
Cycle Number
0
1500
3000
4500
6000
7500
9000
10500
12000
13500
15000
0
10
20
30
40
50
60
70
80
90
100
100
102
104
106
108
110
112
114
116
118
120

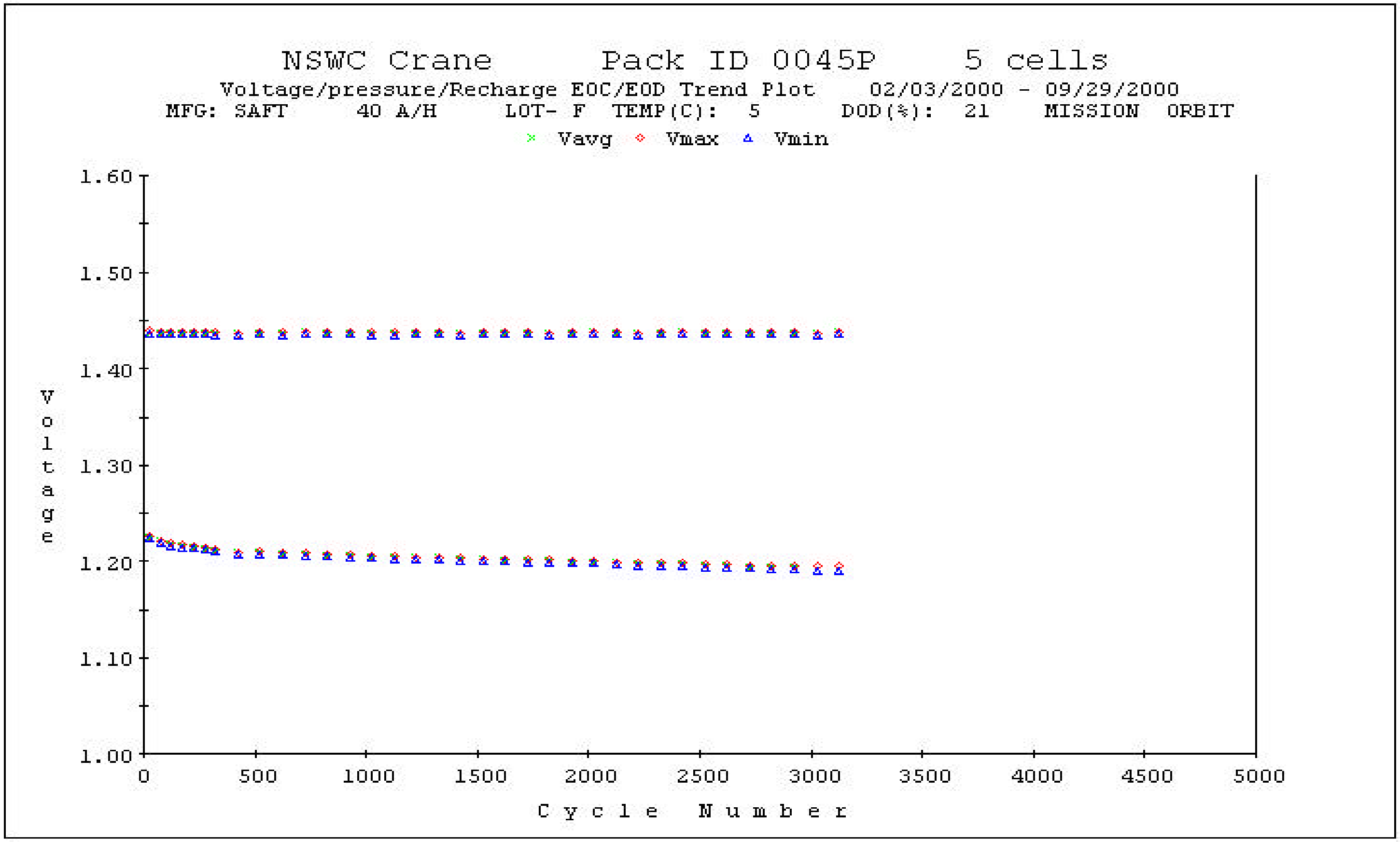

NSWC Crane Pack ID 0040P 10 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 08/30/1996 - 10/03/2000
MFG: SAFT 40 A/H TEMP(C): 5 DOD(%): 25 MISSION TEST
Vavg Vmax Vmin
Voltage
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000
Cycle Number

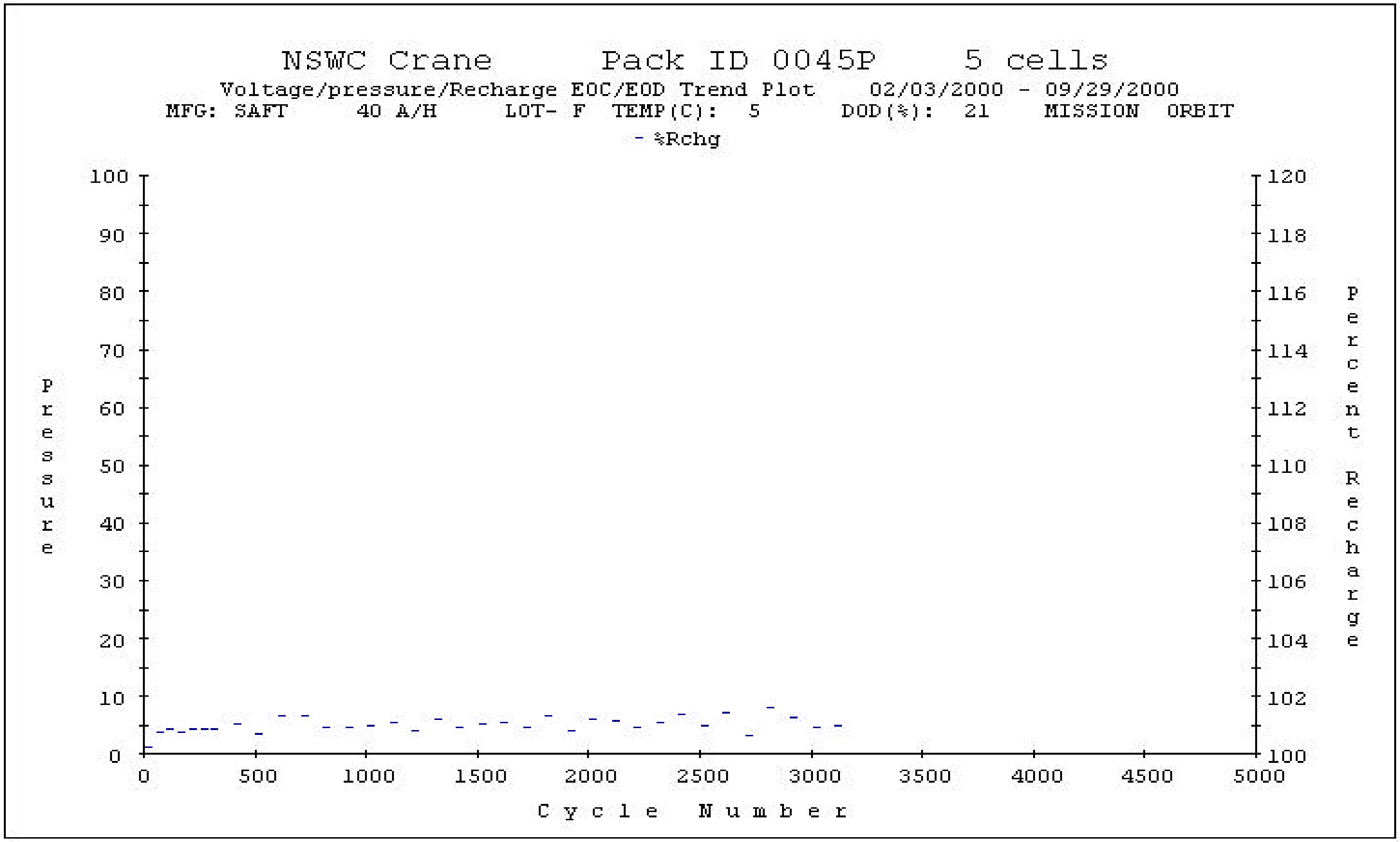

NSWC Crane Pack ID 0040P 10 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 08/30/1996 - 10/03/2000
MFG: SAFT 40 A/H TEMP(C): 5 DOD(%): 25 STRESS TEST
%Rchg
Pressure
Percent Recharge
Cycle Number
0
10
20
30
40
50
60
70
80
90
100
120
118
116
114
112
110
108
106
104
102
100
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000

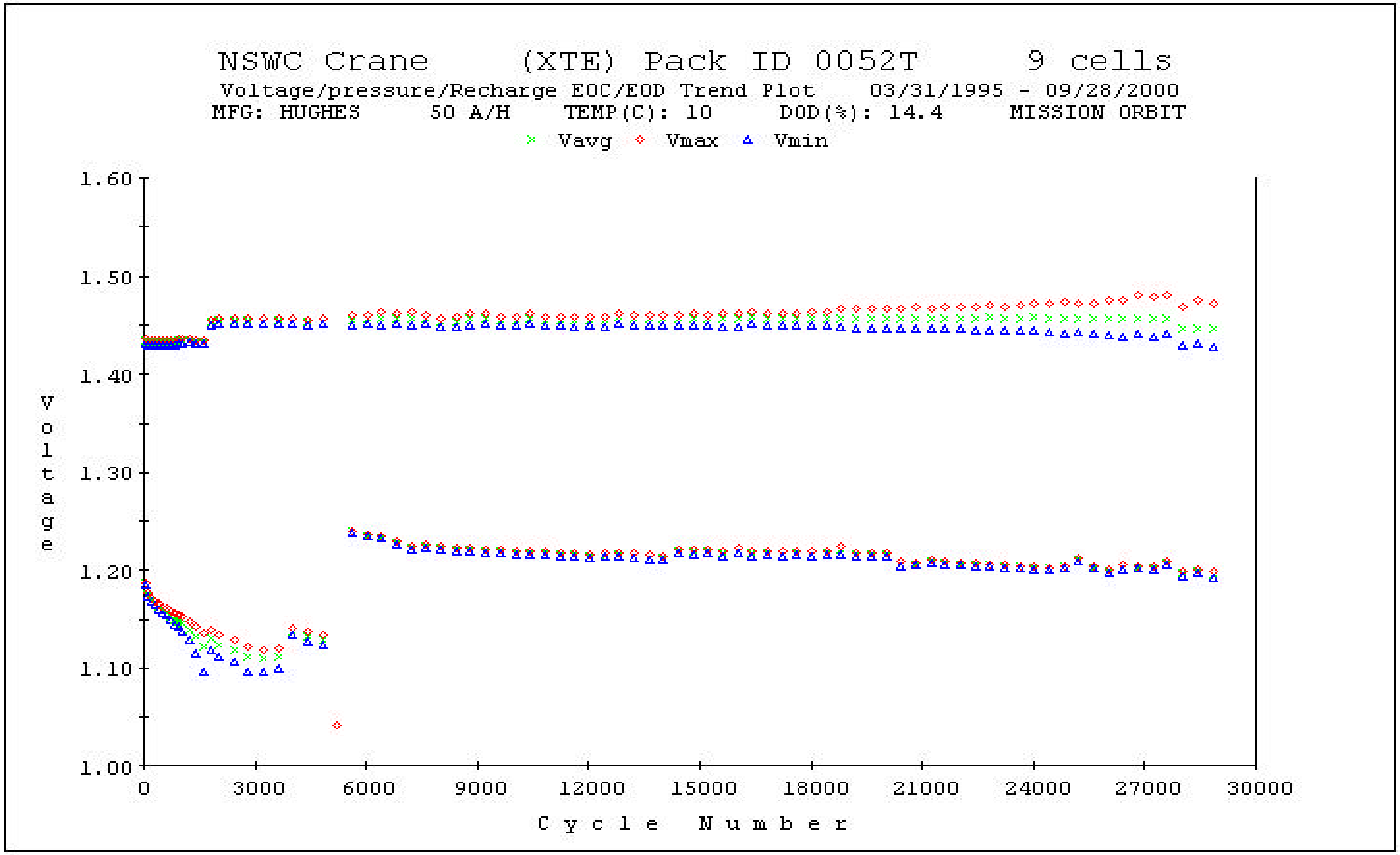


NSWC Crane Pack ID 0044P 8 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 01/26/1999 - 12/10/2000
MFG: SAFT 40 A/H TEMP(C): 5 DOD(%): 21 LEO ORBIT
Vavg Vmax Vmin
1.60
1.54
1.48
1.42
1.36
1.30
1.24
1.18
1.12
1.06
1.00
Voltage
25
973
1920
2868
3815
4763
5710
6658
7605
8553
9500
Cycle Number

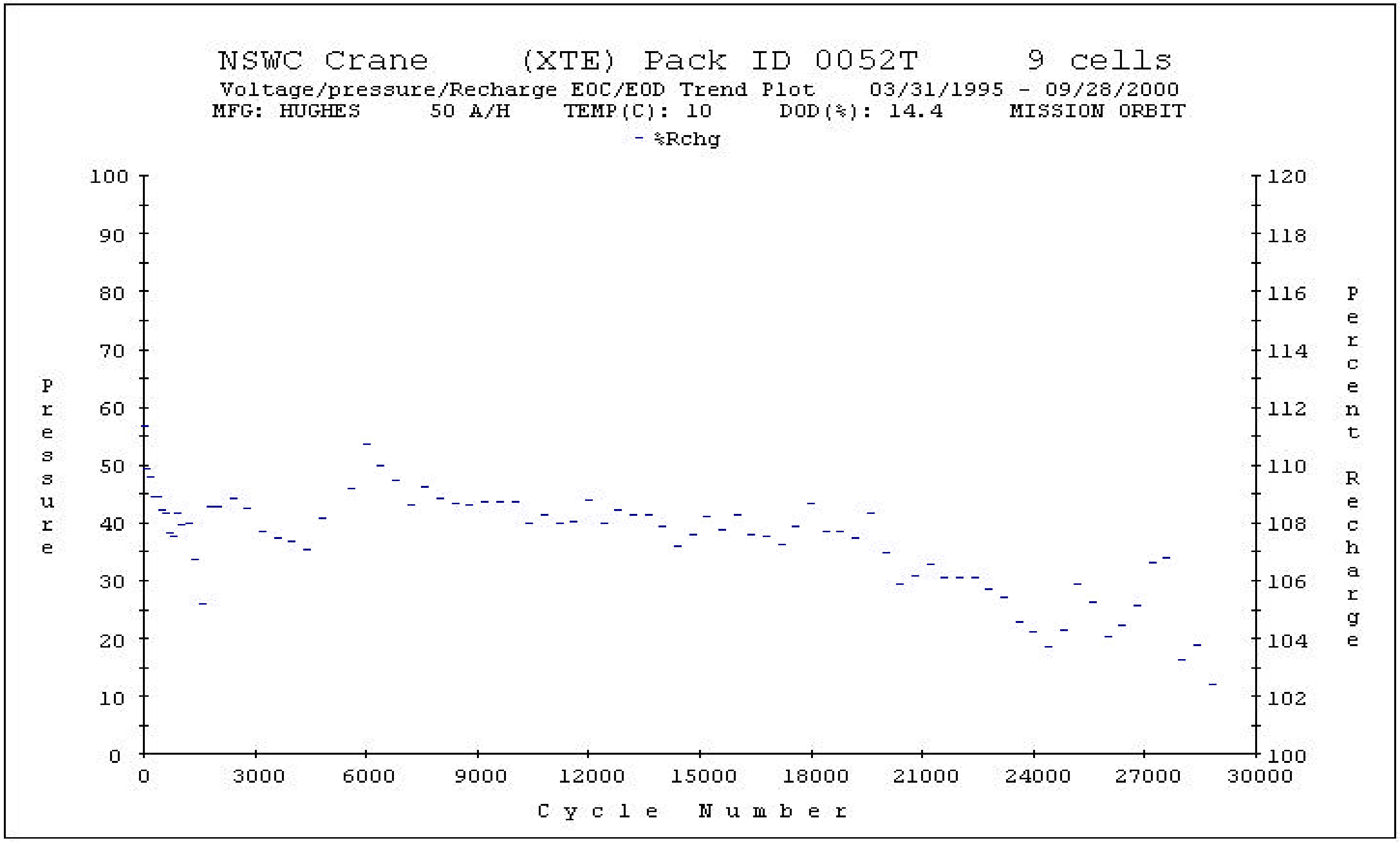

NSWC Crane Pack ID 0044P 8 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 01/26/1999 - 12/10/2000
MFG: SAFT 40 A/H TEMP(C): 5 DOD(%): 21 LEO ORBIT
%Rchg
P S I A
% Recharge
100
90
80
70
60
50
40
30
20
10
0
110
109
108
107
106
105
104
103
102
101
100
25
973
1920
2868
3815
4763
5710
6658
7605
8553
9500
Cycle Number

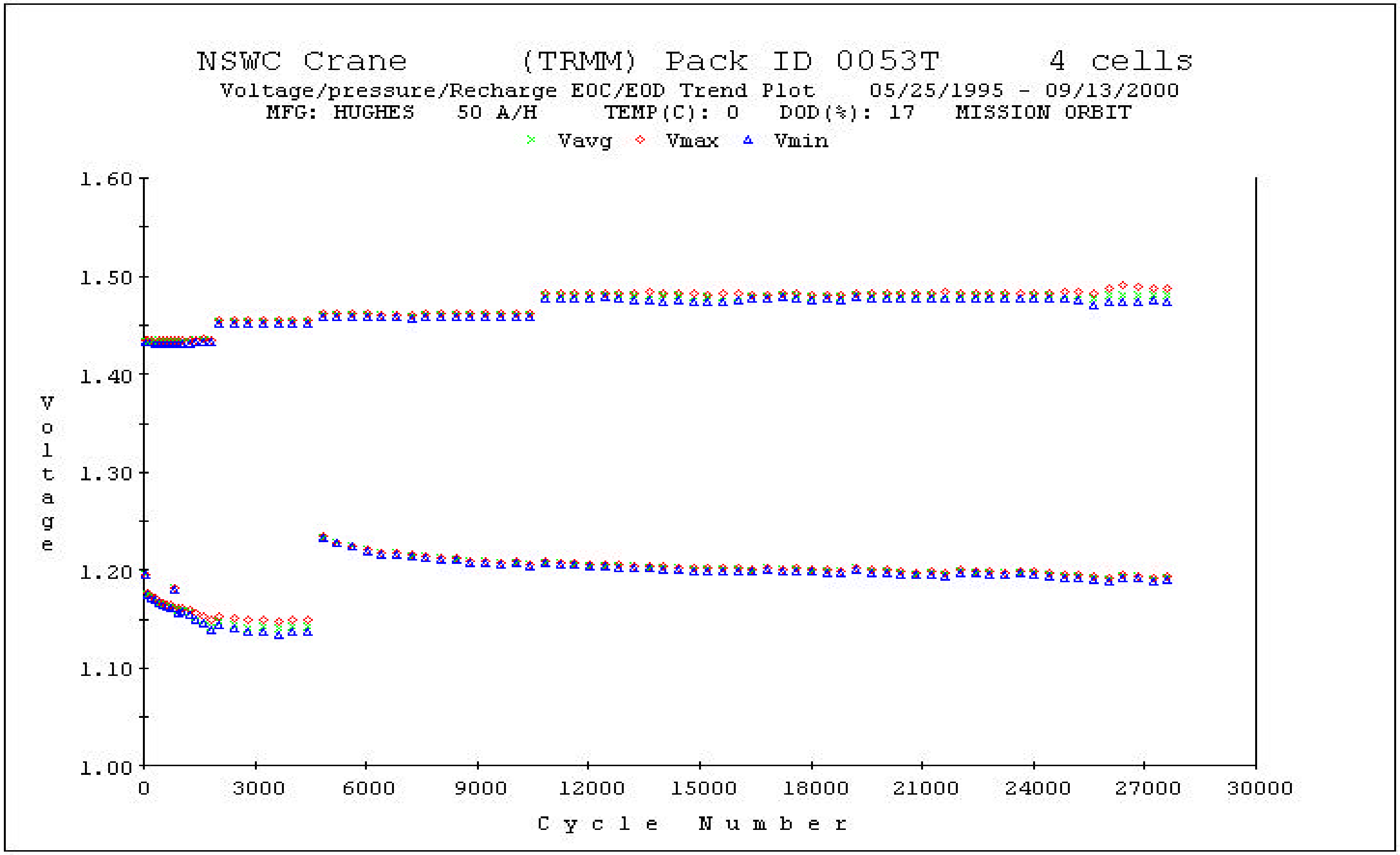

NSWC Crane Pack ID 0045P 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 02/03/2000 - 09/29/2000
MFG: SAFT 40 A/H LOT- F TEMP(C): 5 DOD(%): 21 MISSION ORBIT
Vavg Vmax Vmin
Voltage
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Cycle Number

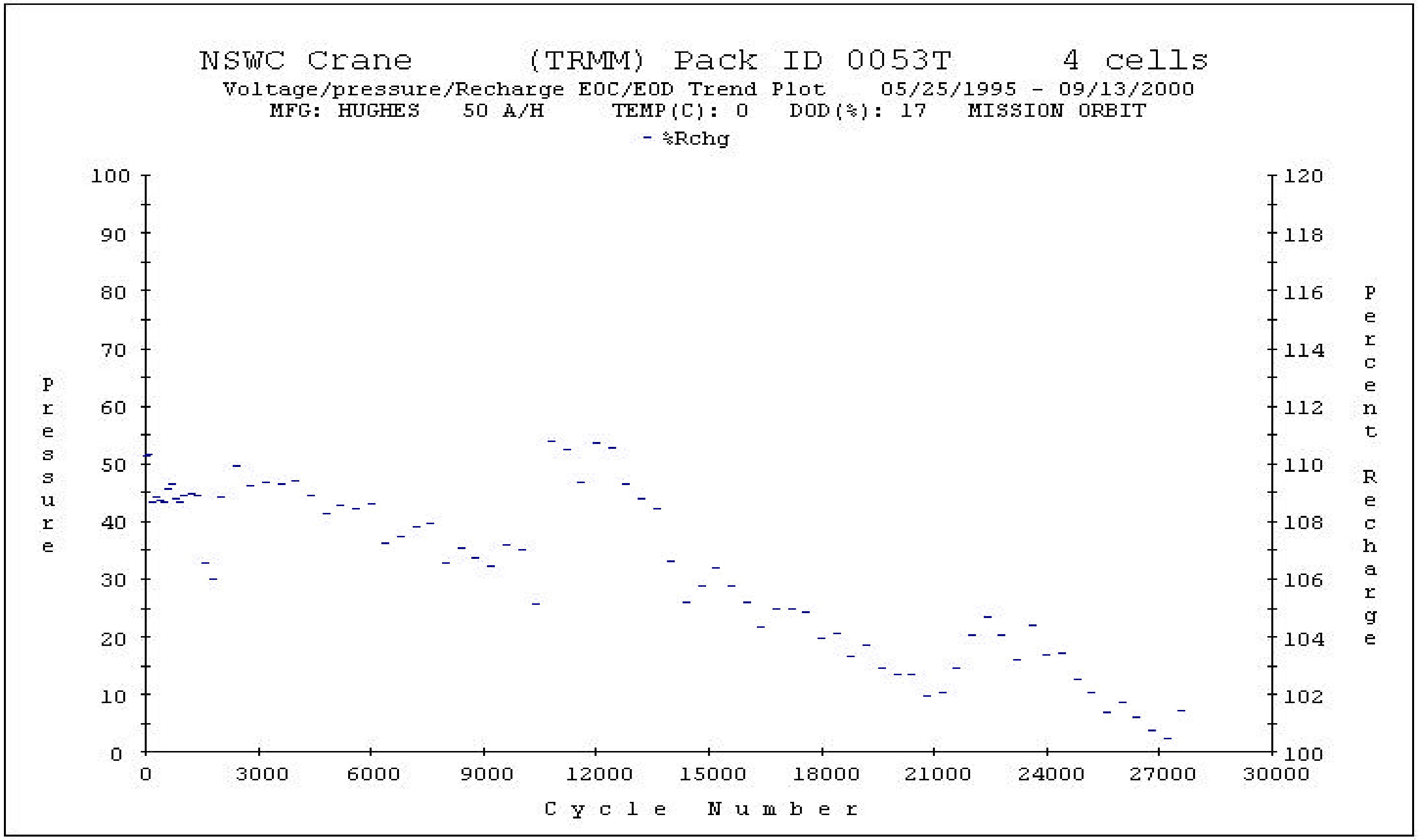

NSWC Crane Pack ID 0045P 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 02/03/2000 - 09/29/2000
MFG: SAFT 40 A/H LOT- F TEMP(C): 5 DOD(%): 21 MISSION ORBIT
- %Rchg
Pressure
Percent Recharge
0
10
20
30
40
50
60
70
80
90
100
100
102
104
106
108
110
112
114
116
118
120
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Cycle Number

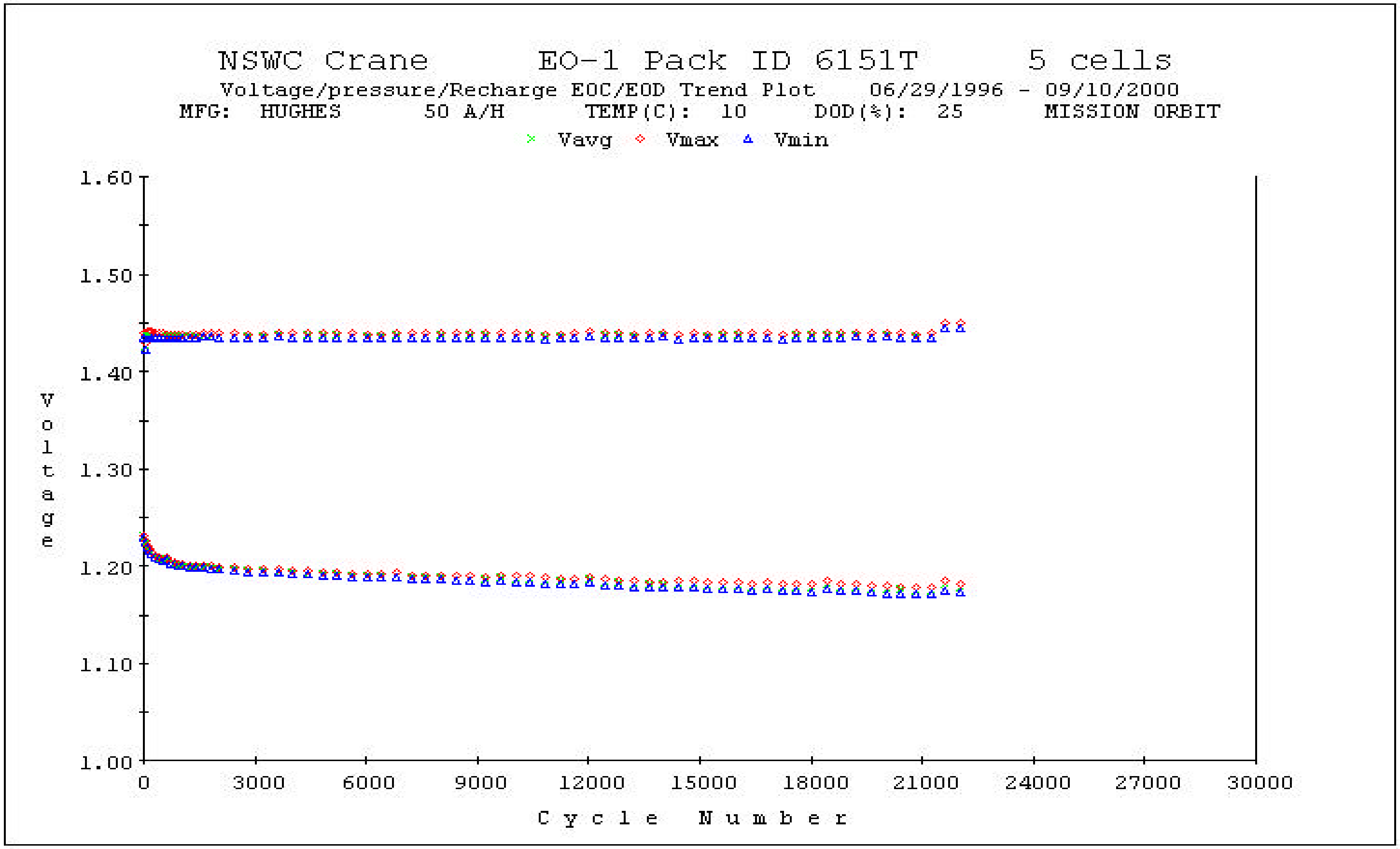


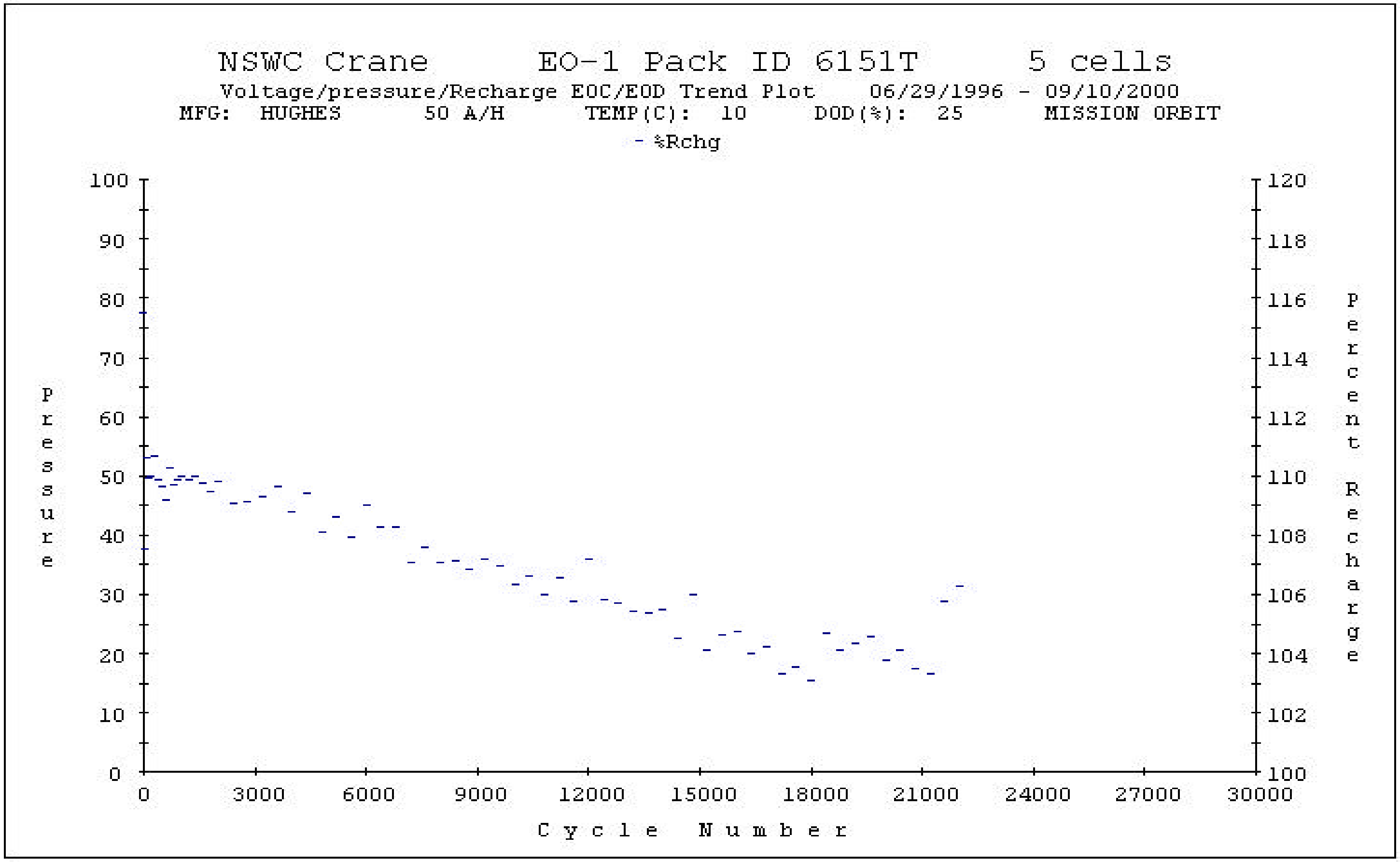
NSWC Crane (XTE) Pack ID 0052T 9 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 03/31/1995 - 09/28/2000
MFG: HUGHES 50 A/H TEMP(C): 10 DOD(%): 14.4 MISSION ORBIT
Vavg Vmax Vmin
1.60
1.50
1.40
1.30
1.20
1.10
1.00
Voltage
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000
Cycle Number

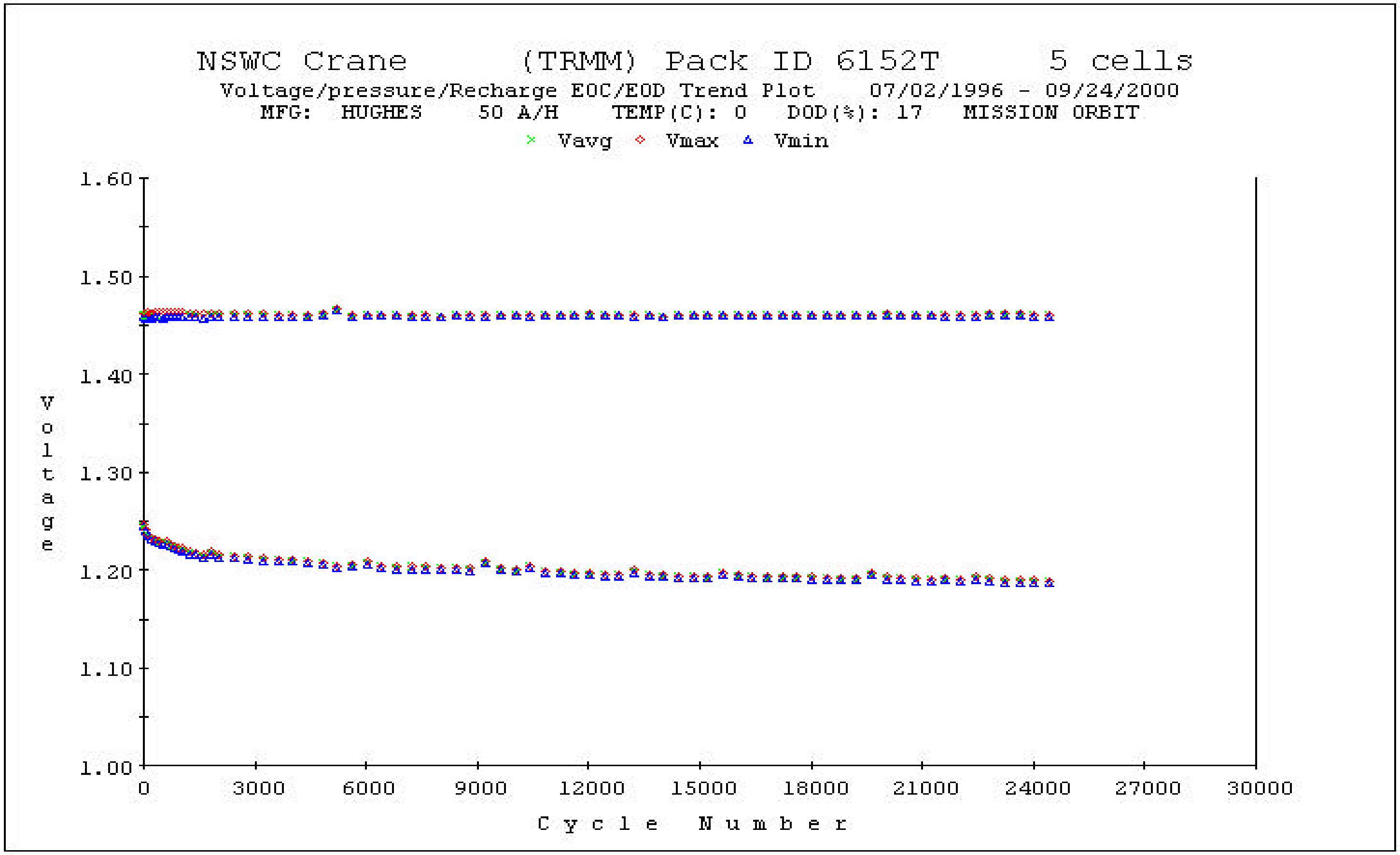

NSWC Crane (XTE) Pack ID 0052T 9 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 03/31/1995 - 09/28/2000
MFG: HUGHES 50 A/H TEMP(C): 10 DOD(%): 14.4 MISSION ORBIT
%Rchg
Pressure
Percent Recharge
Cycle Number
0 10 20 30 40 50 60 70 80 90 100
100 102 104 106 108 110 112 114 116 118 120
0 3000 6000 9000 12000 15000 18000 21000 24000 27000 30000

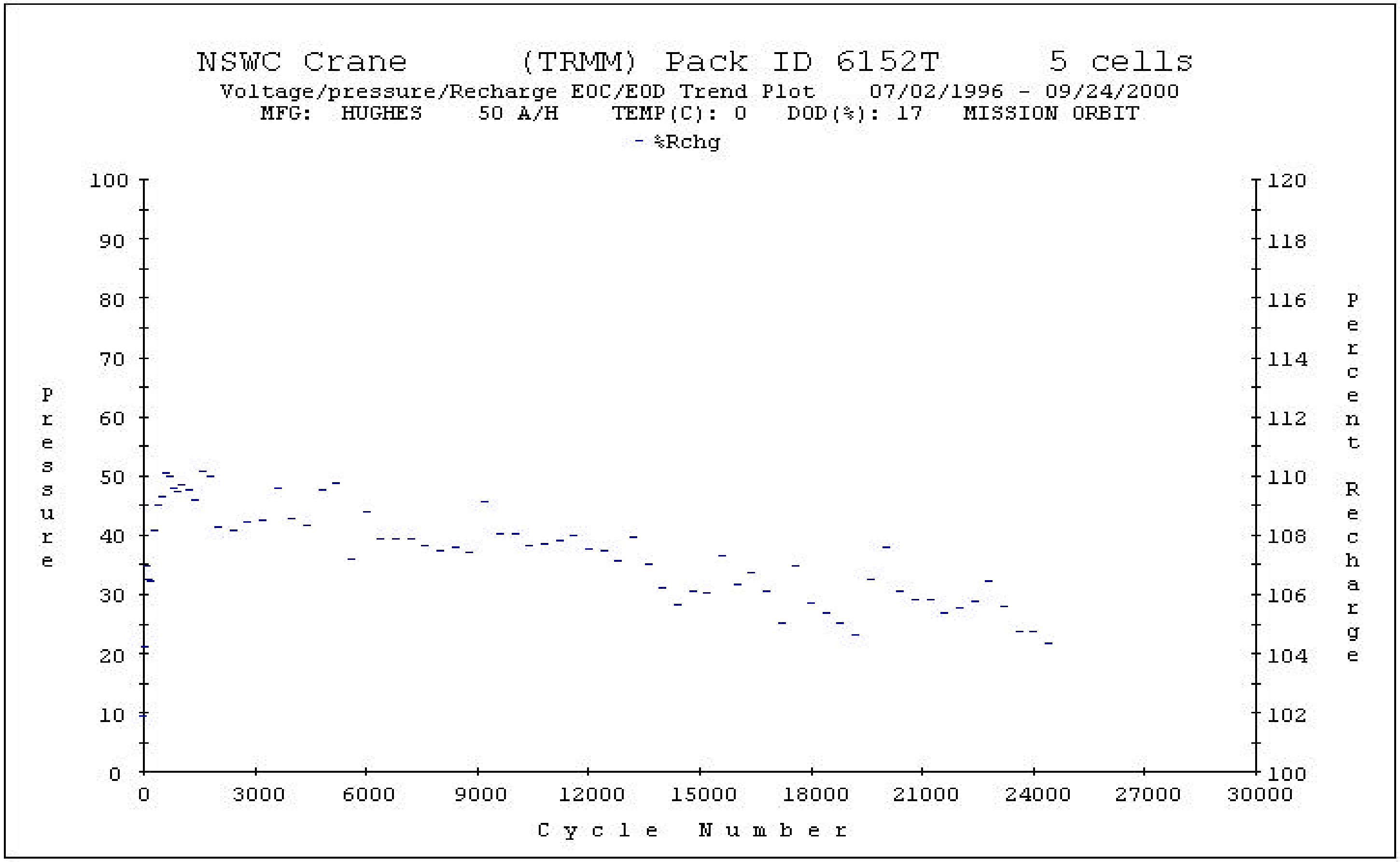

NSWC Crane (TRMM) Pack ID 0053T 4 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 05/25/1995 - 09/13/2000
MFG: HUGHES 50 A/H TEMP(C): 0 DOD(%): 17 MISSION ORBIT
Vavg Vmax Vmin
Voltage
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000
Cycle Number

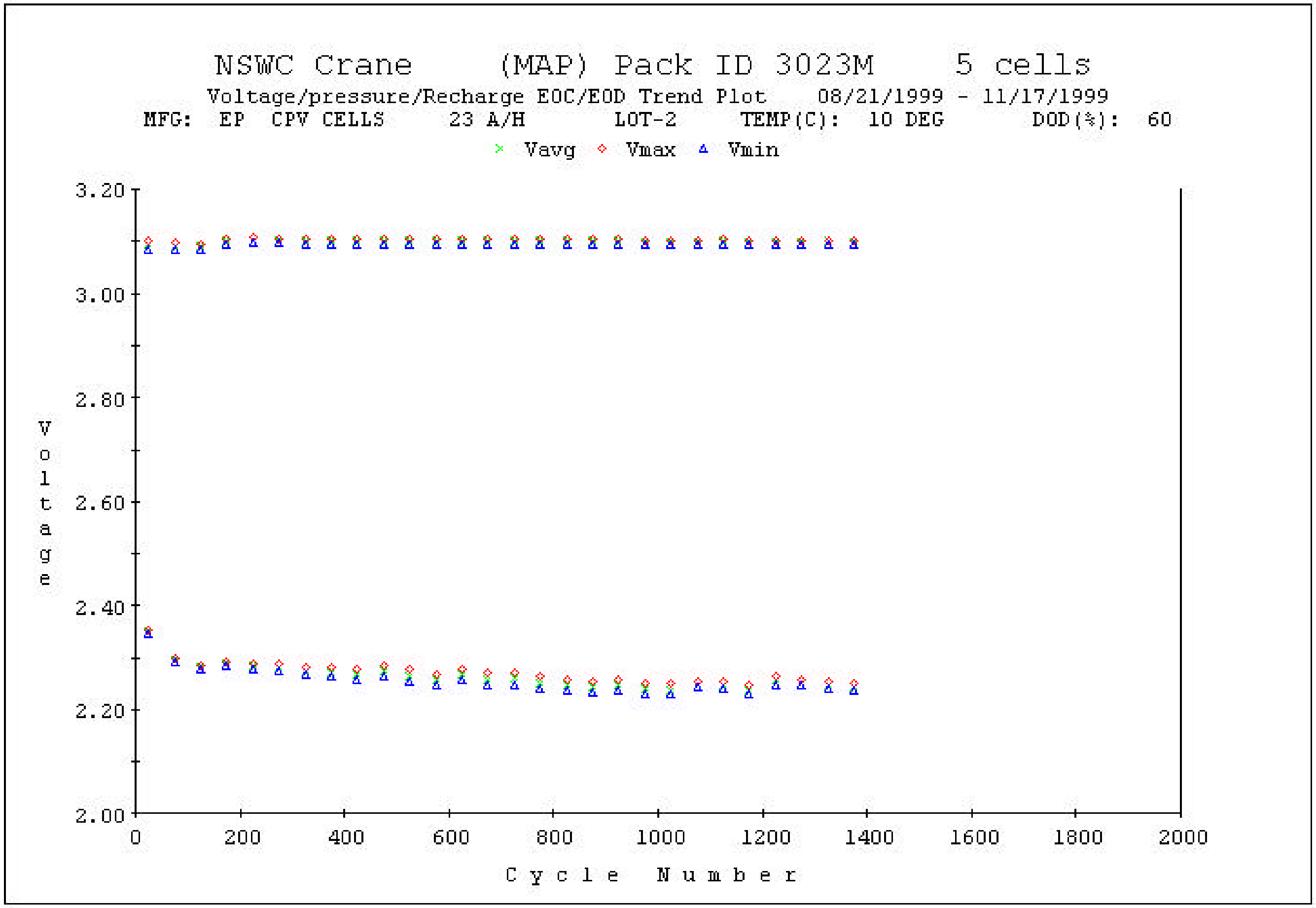

NSWC Crane (TRMM) Pack ID 0053T 4 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 05/25/1995 - 09/13/2000
MFG: HUGHES 50 A/H TEMP(C): 0 DOD(%): 17 MISSION ORBIT
%Rchg
Pressure
Percent Recharge
Cycle Number
0
10
20
30
40
50
60
70
80
90
100
100
102
104
106
108
110
112
114
116
118
120
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000

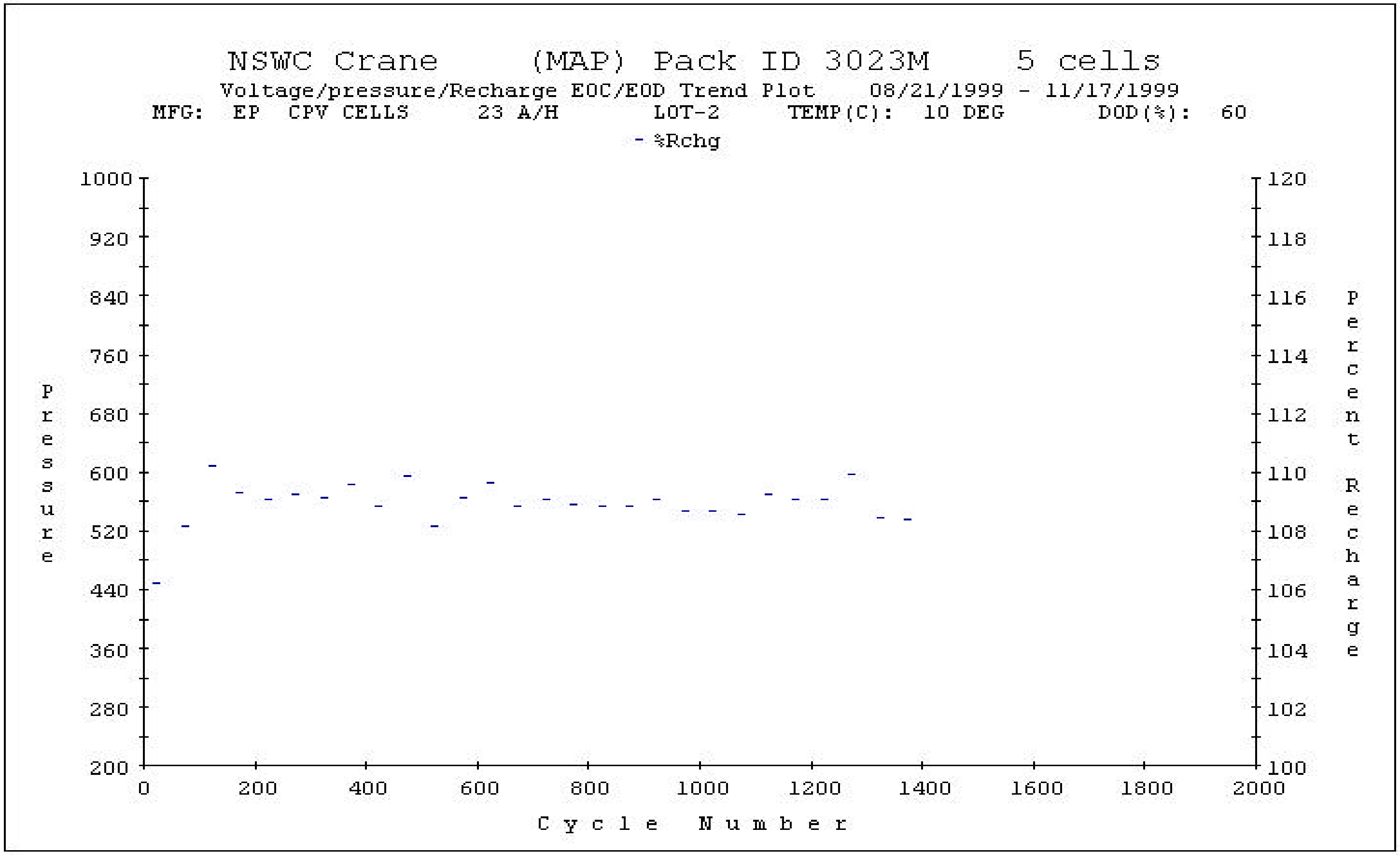

NSWC Crane EO-1 Pack ID 6151T 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 06/29/1996 - 09/10/2000
MFG: HUGHES 50 A/H TEMP(C): 10 DOD(%): 25 MISSION ORBIT
Vavg Vmax Vmin
Voltage
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000
Cycle Number


NSWC Crane EO-1 Pack ID 6151T 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 06/29/1996 - 09/10/2000
MFG: HUGHES 50 A/H TEMP(C): 10 DOD(%): 25 MISSION ORBIT
%Rchg
Pressure
Percent Recharge
Cycle Number
0
10
20
30
40
50
60
70
80
90
100
100
102
104
106
108
110
112
114
116
118
120
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000

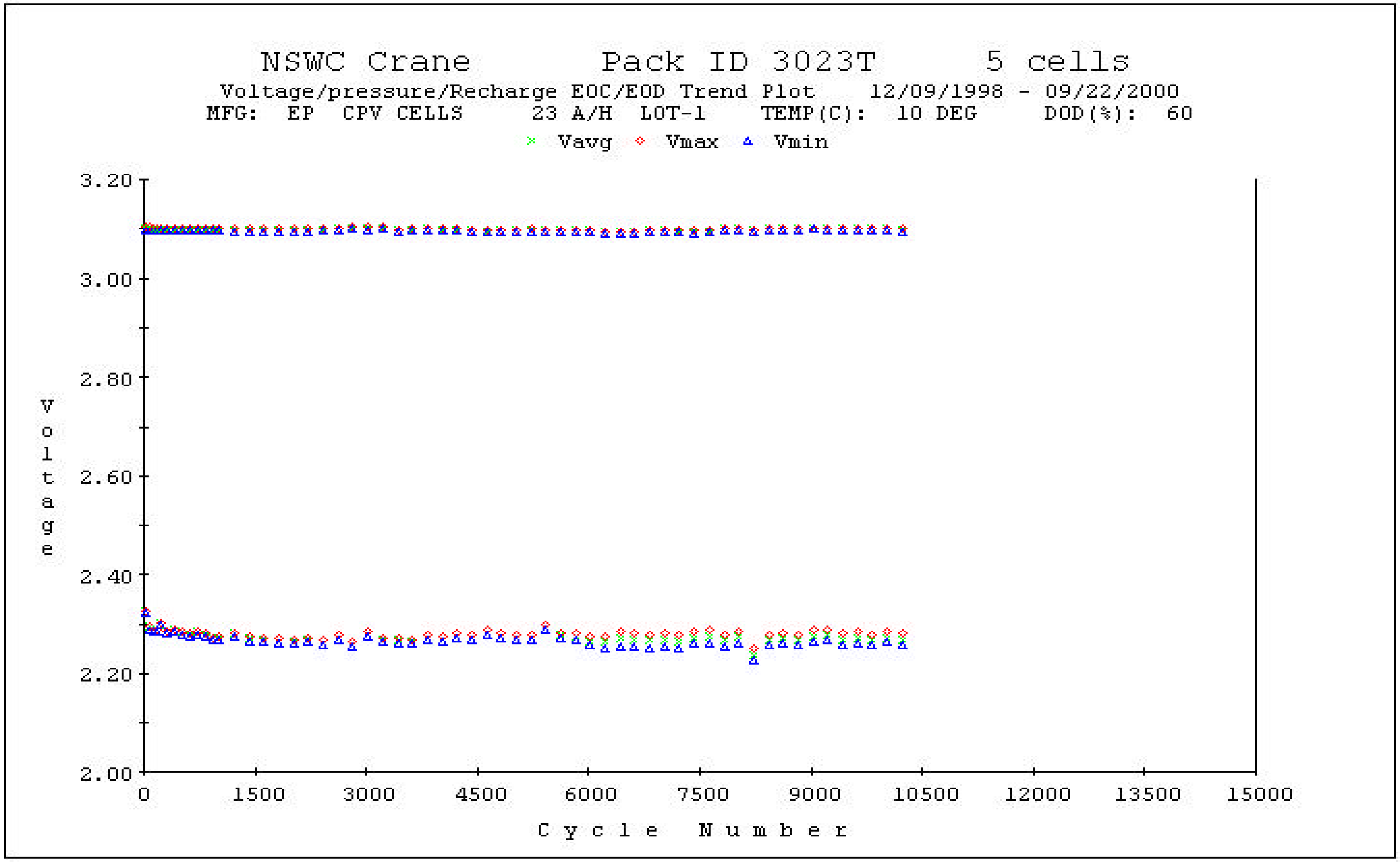

NSWC Crane (TRMM) Pack ID 6152T 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 07/02/1996 - 09/24/2000
MFG: HUGHES 50 A/H TEMP(C): 0 DOD(%): 17 MISSION ORBIT
Vavg Vmax Vmin
1.60
1.50
1.40
1.30
1.20
1.10
1.00
Voltage
0 3000 6000 9000 12000 15000 18000 21000 24000 27000 30000
Cycle Number

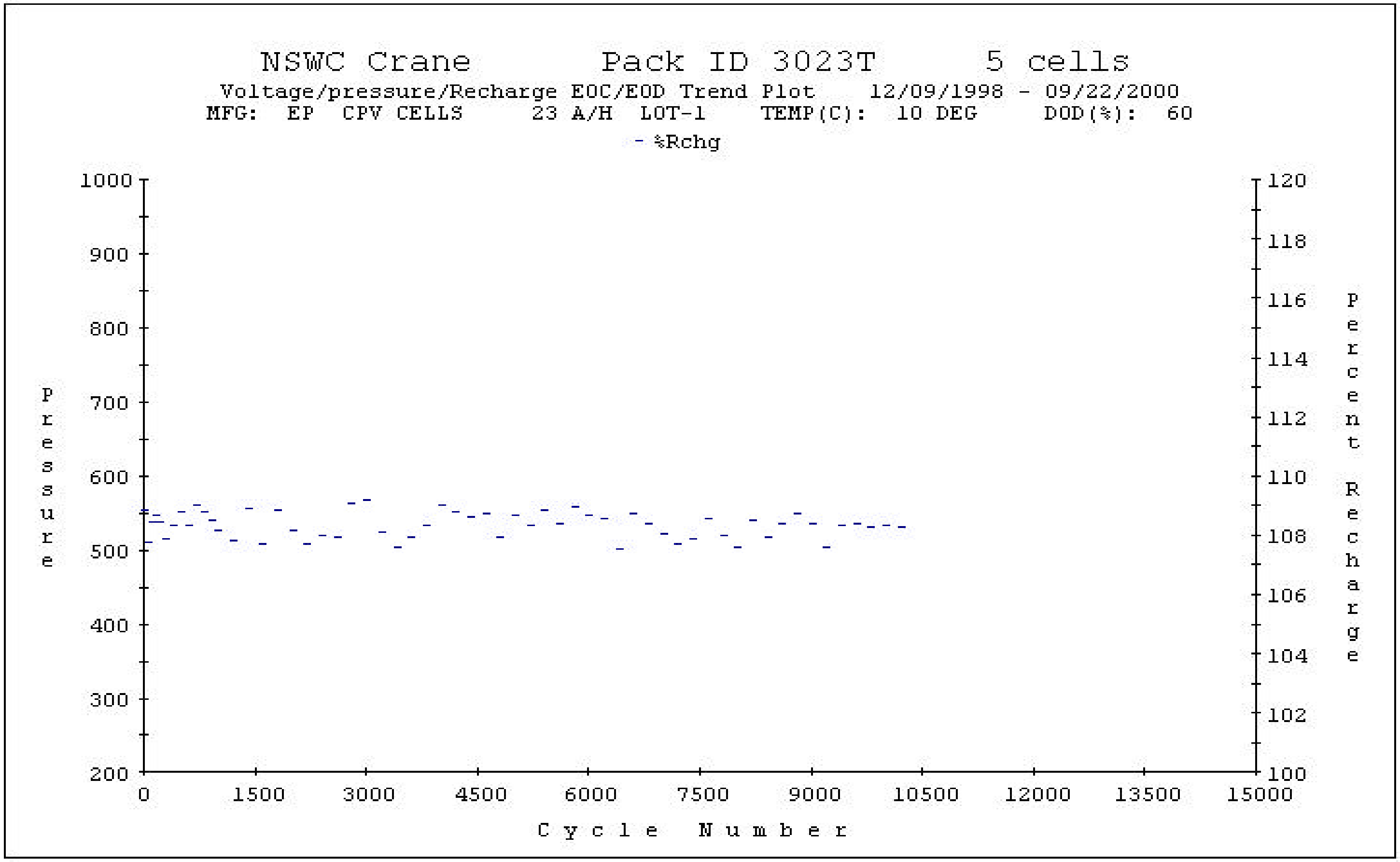

NSWC Crane (TRMM) Pack ID 6152T 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 07/02/1996 - 09/24/2000
MFG: HUGHES 50 A/H TEMP(C): 0 DOD(%): 17 MISSION ORBIT
%Rchg
Pressure
Percent Recharge
Cycle Number
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000
0
10
20
30
40
50
60
70
80
90
100
100
102
104
106
108
110
112
114
116
118
120

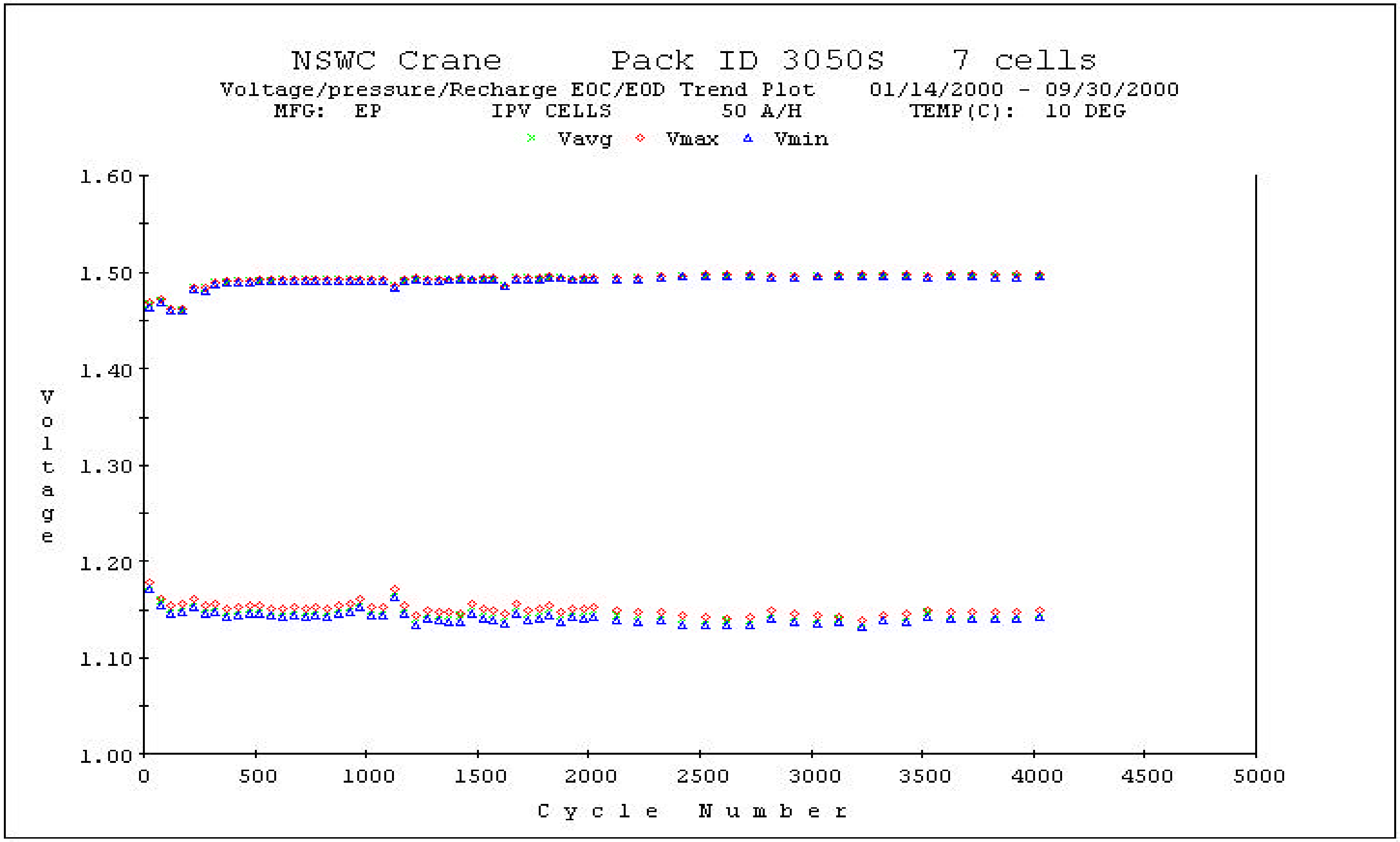

NSWC Crane (MAP) Pack ID 3023M 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 08/21/1999 - 11/17/1999
MFG: EP CPV CELLS 23 A/H LOT-2 TEMP(C): 10 DEG DOD(%): 60
Vavg Vmax Vmin
3.20
3.00
2.80
2.60
2.40
2.20
2.00
Voltage
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Cycle Number



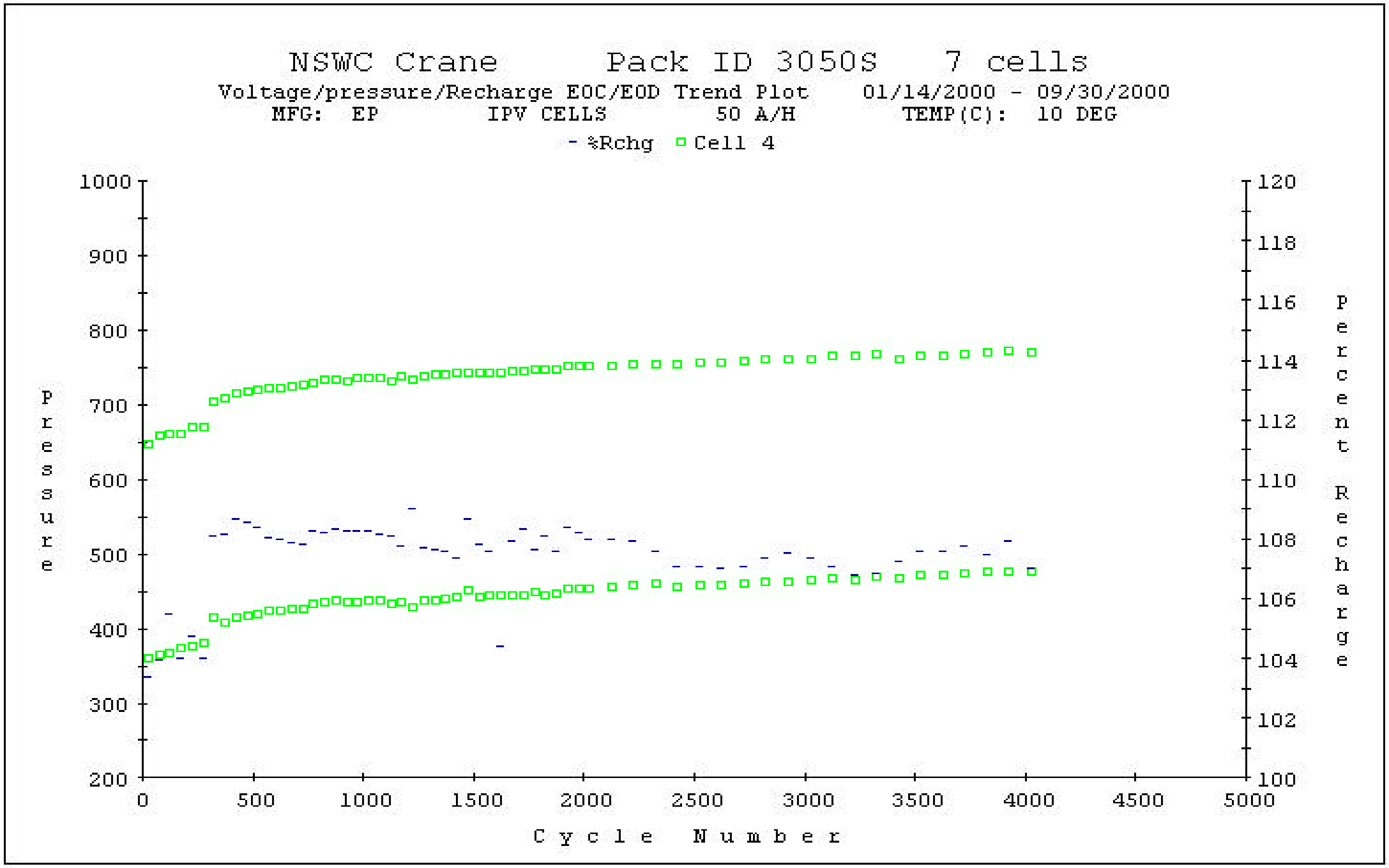
NSWC Crane (MAP) Pack ID 3023M 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 08/21/1999 - 11/17/1999
MFG: EP CPV CELLS 23 A/H LOT-2 TEMP(C): 10 DEG DOD(%): 60
- %Rchg
Pressure
Percent Recharge
Cycle Number
1000
920
840
760
680
600
520
440
360
280
200
120
118
116
114
112
110
108
106
104
102
100
0
200
400
600
800
1000
1200
1400
1600
1800
2000

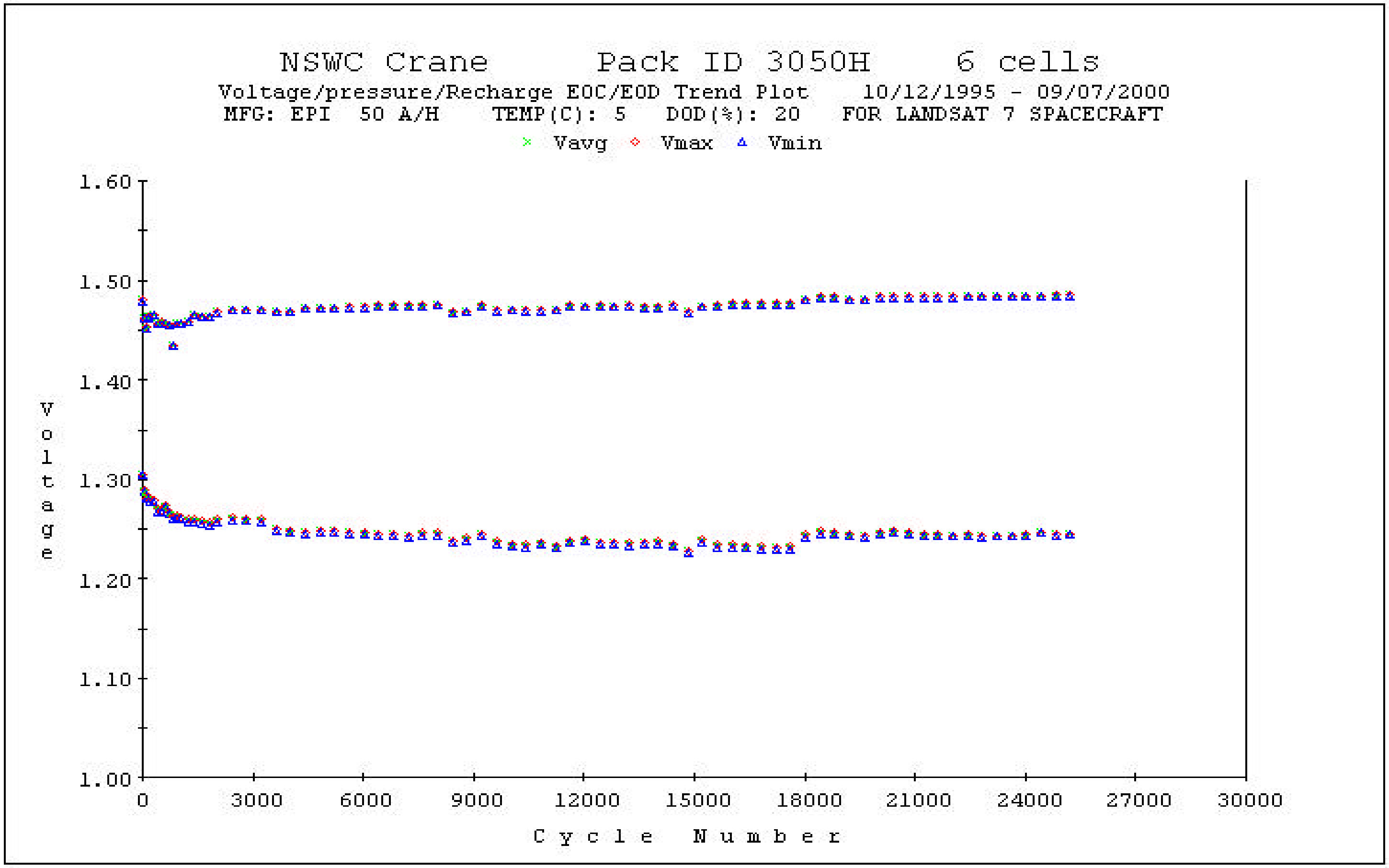

NSWC Crane Pack ID 3023T 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 12/09/1998 - 09/22/2000
MFG: EP CPV CELLS 23 A/H LOT-1 TEMP(C): 10 DEG DOD(%): 60
Vavg Vmax Vmin
Voltage
3.20
3.00
2.80
2.60
2.40
2.20
2.00
0
1500
3000
4500
6000
7500
9000
10500
12000
13500
15000
Cycle Number

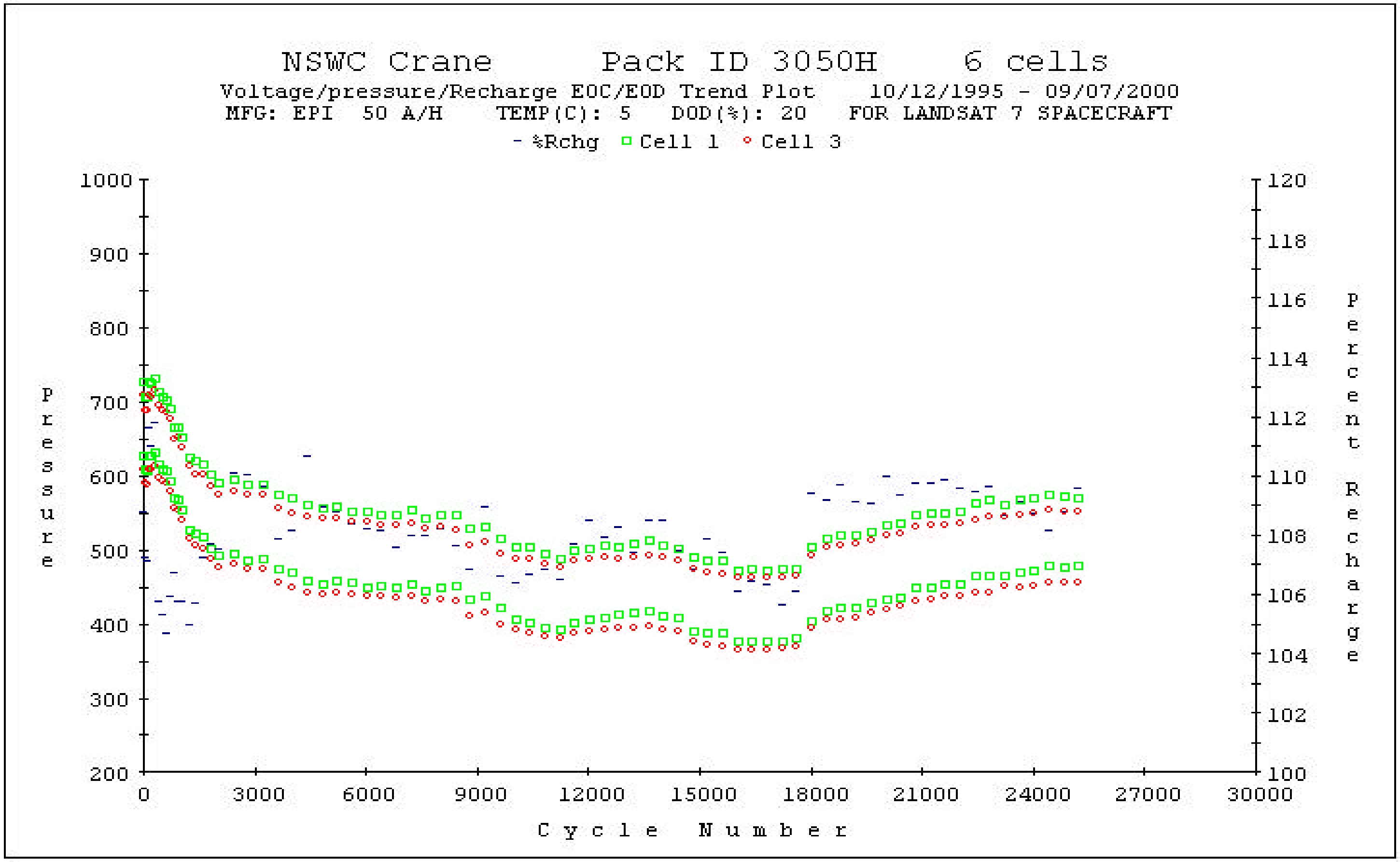

NSWC Crane Pack ID 3023T 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 12/09/1998 - 09/22/2000
MFG: EP CPV CELLS 23 A/H LOT-1 TEMP(C): 10 DEG DOD(%): 60
- %Rchg
Pressure
1000
900
800
700
600
500
400
300
200
0
1500
3000
4500
6000
7500
9000
10500
12000
13500
15000
Cycle Number
120
118
116
114
112
110
108
106
104
102
100
Percent Recharge

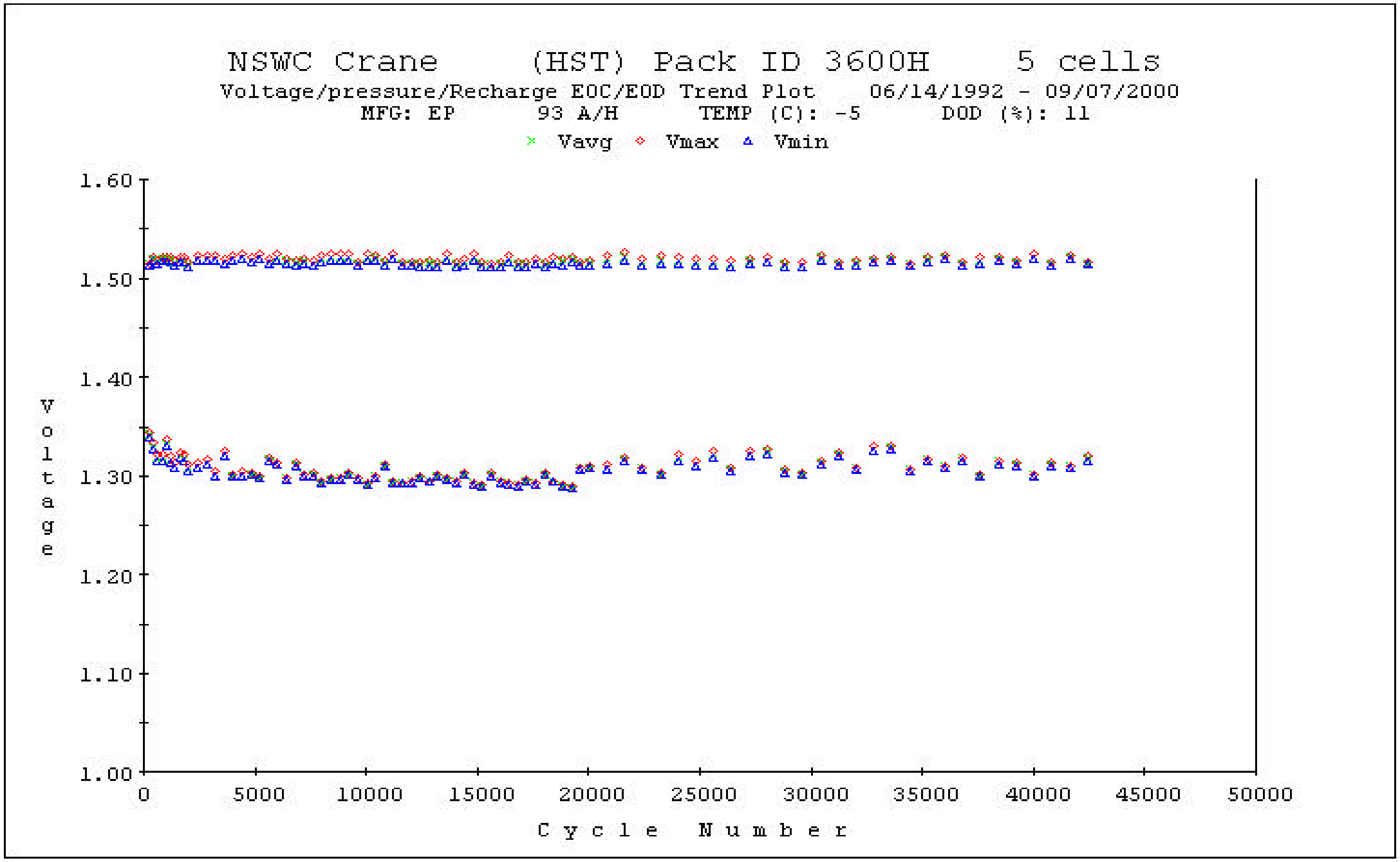


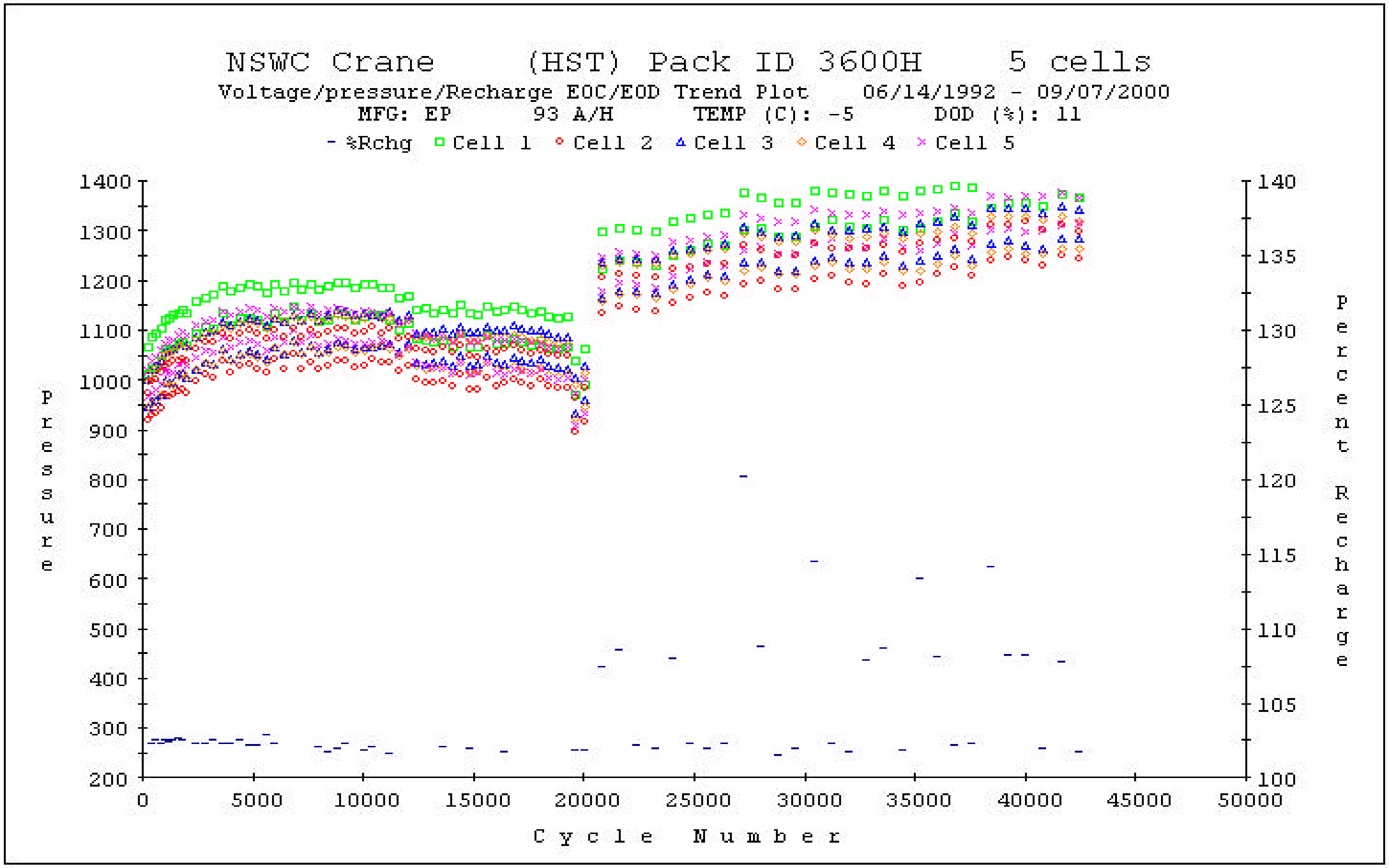
NSWC Crane Pack ID 3050S 7 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 01/14/2000 - 09/30/2000
MFG: EP IPV CELLS 50 A/H TEMP(C): 10 DEG
Vavg Vmax Vmin
1.60
1.50
1.40
1.30
1.20
1.10
1.00
Voltage
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Cycle Number


NSWC Crane Pack ID 3050S 7 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 01/14/2000 - 09/30/2000
MFG: EP IPV CELLS 50 A/H TEMP(C): 10 DEG
%Rchg
Cell 4
Pressure
Percent Recharge
Cycle Number
1000
900
800
700
600
500
400
300
200
120
118
116
114
112
110
108
106
104
102
100
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000

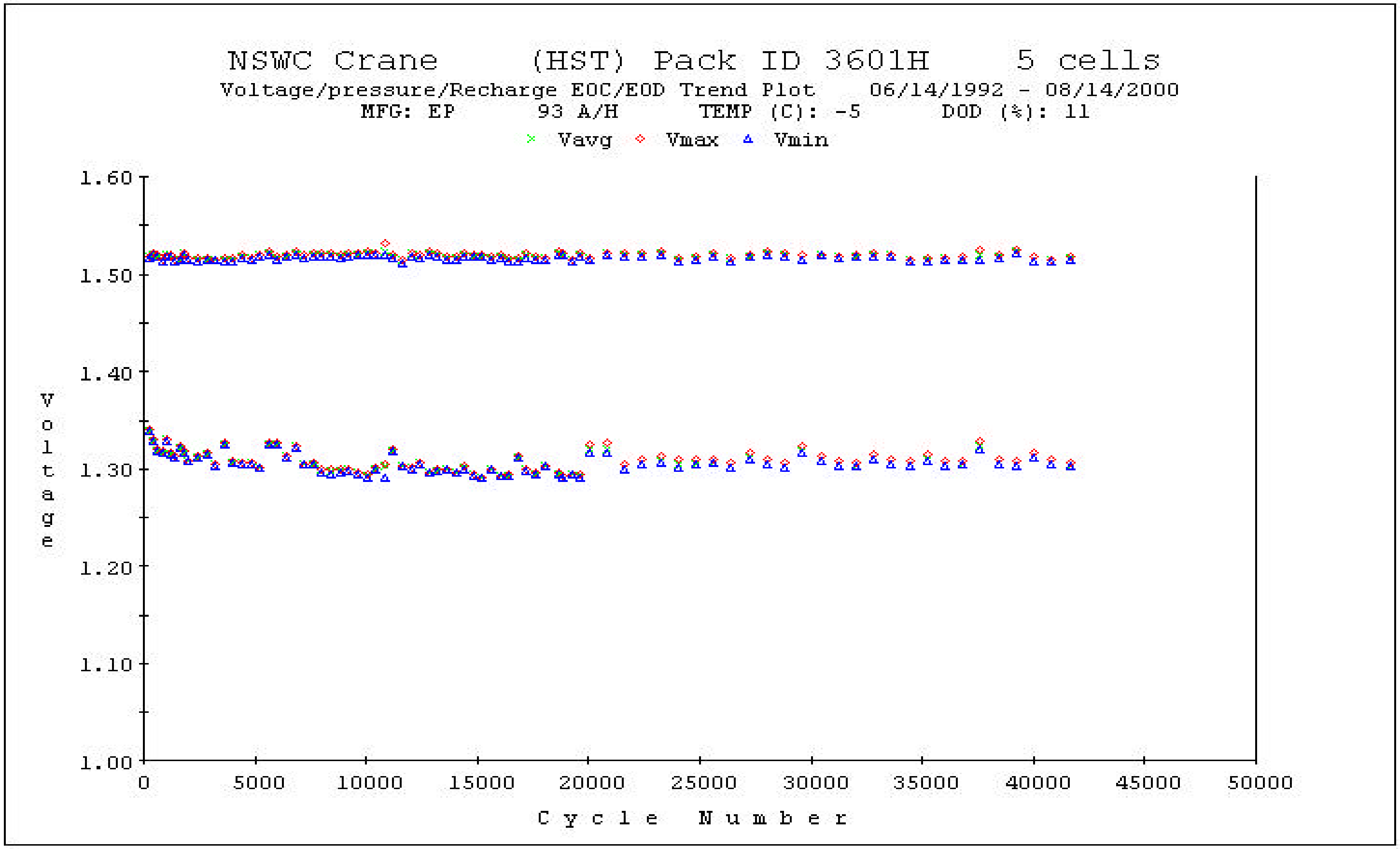

NSWC Crane Pack ID 3050H 6 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 10/12/1995 - 09/07/2000
MFG: EPI 50 A/H TEMP(C): 5 DOD(%): 20 FOR LANDSAT 7 SPACECRAFT
Vavg Vmax Vmin
Voltage
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0 3000 6000 9000 12000 15000 18000 21000 24000 27000 30000
Cycle Number


NSWC Crane Pack ID 3050H 6 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 10/12/1995 - 09/07/2000
MFG: EPI 50 A/H TEMP(C): 5 DOD(%): 20 FOR LANDSAT 7 SPACECRAFT
- %Rchg □ Cell 1 ° Cell 3
Pressure
Percent Recharge
Cycle Number
1000
900
800
700
600
500
400
300
200
120
118
116
114
112
110
108
106
104
102
100
0
3000
6000
9000
12000
15000
18000
21000
24000
27000
30000

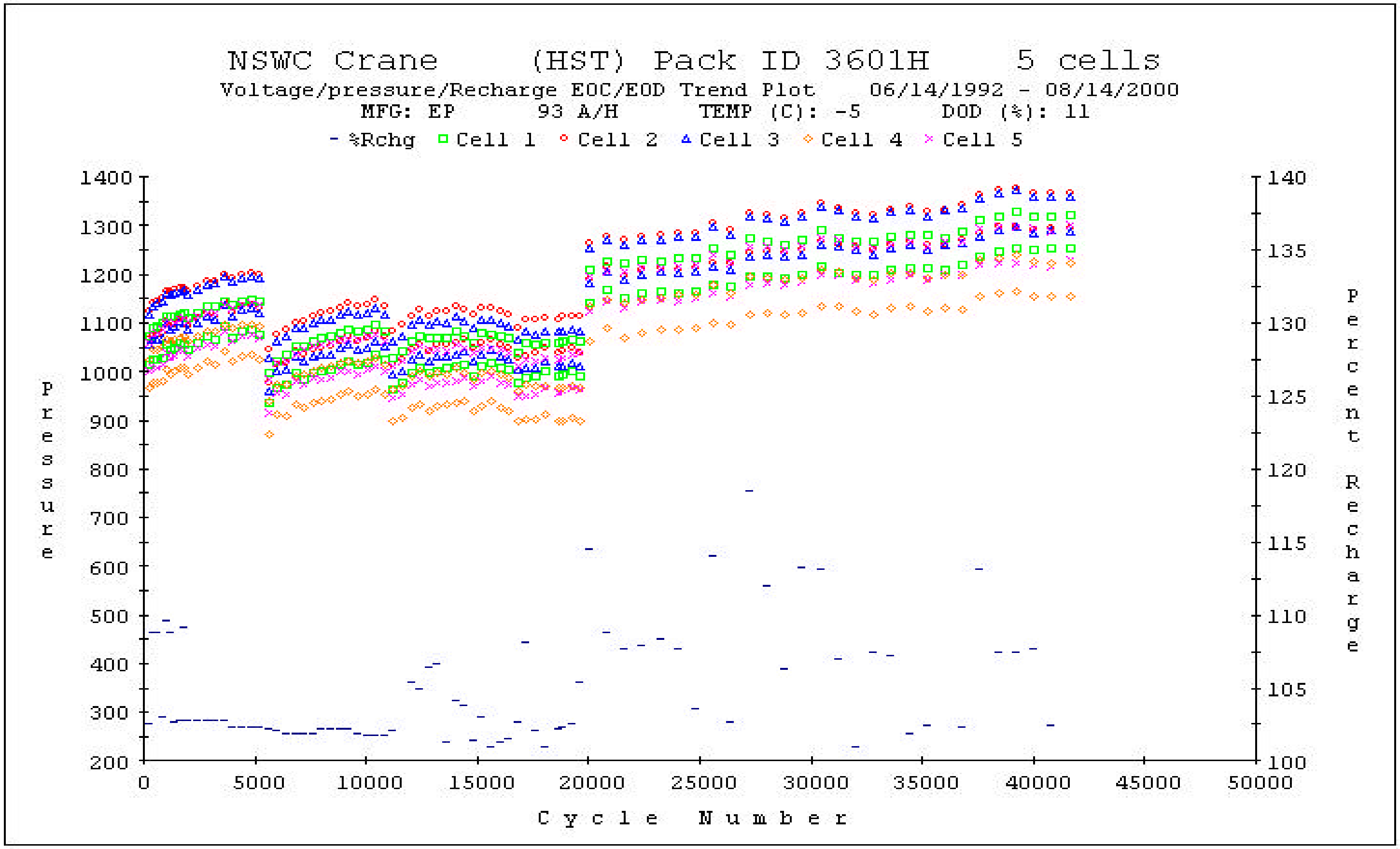

NSWC Crane (HST) Pack ID 3600H 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 06/14/1992 - 09/07/2000
MFG: EP 93 A/H TEMP (C): -5 DOD (%): 11
Vavg Vmax Vmin
1.60
1.50
1.40
1.30
1.20
1.10
1.00
Voltage
0 5000 10000 15000 20000 25000 30000 35000 40000 45000 50000
Cycle Number



NSWC Crane (HST) Pack ID 3600H 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 06/14/1992 - 09/07/2000
MFG: EP 93 A/H TEMP (C): -5 DOD (%): 11
- %Rchg □ Cell 1 ○ Cell 2 △ Cell 3 ◇ Cell 4 × Cell 5
Pressure
Percent Recharge
Cycle Number
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
140
135
130
125
120
115
110
105
100
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000



NSWC Crane (HST) Pack ID 3601H 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 06/14/1992 - 08/14/2000
MFG: EP 93 A/H TEMP (C): -5 DOD (%): 11
Vavg Vmax Vmin
Voltage
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Cycle Number


NSWC Crane (HST) Pack ID 3601H 5 cells
Voltage/pressure/Recharge EOC/EOD Trend Plot 06/14/1992 - 08/14/2000
MFG: EP 93 A/H TEMP (C): -5 DOD (%): 11
%Rchg Cell 1 Cell 2 Cell 3 Cell 4 Cell 5
Pressure
Percent Recharge
Cycle Number
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
140
135
130
125
120
115
110
105
100
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000

SUMMARY

- Quality EPT Ni-H2, EPT Super NiCd and SAFT NiCd cells have been demonstrated for Aerospace applications
- The data has been provided to NASA Centers and other Agencies for their use and application
  - Developed plan and used in NASA in-orbit battery management.
- Database on rechargeable cell/batteries is now available for customer use.

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Effect of Handling, Storage and Cycling on Ni-H_2 Cells: Second Plateau Phenomenon

Hari Vaidyanathan
Lockheed Martin Global Telecommunications
And
Gopalakrishna M. Rao
NASA/Goddard Space Flight Center

2000 NASA Aerospace Battery Workshop
Huntsville, Alabama
November 14-16, 2000

Background

- The discharge voltage profile for some Ni-H_2 cells exhibits a second plateau at about 0.8V
- The capacity at a lower voltage plateau results in loss of useful energy
- The proportion of capacity in the second plateau varies with handling, storage, use and cycling

Criteria for Cell Selection

- Cells received after ATP from the Vendor
- Cells stored cold in discharged open-circuit conditions
- Cells stored dry/cold and activated in later years
  - Room temperature exposure
- Cells removed from a workhorse battery
  - Room temperature exposure
  - Intermittent charging
  - Extensive use
  - Cell reversal

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Cell History

CELL I.D.	HISTORY
TERRA - 50 AH	
2-044	STORED AT LOW TEMP
1-005	STORED AT LOW TEMP
2-117	WORKHORSE BATTERY
2-146	WORKHORSE BATTERY
3-160	17317 LEO CYCLES (40%DOD AND 10°C)
3-205	STORED AT LOW TEMP
2-097	WORKHORSE BATTERY
2-048	WORKHORSE BATTERY
2-061	WORKHORSE BATTERY/500 LEO CYCLES (40%DOD AND 10°C)
HST - 93 AH	
10-515	ATP
10-511	DRY STORED (2 YRS), STORED UNCONTROLLED (1 YEAR) AFTER ATP
10-512	DRY STORED (2 YRS), STORED UNCONTROLLED (1 YEAR) AFTER ATP
11-754	DRY STORED (2 YRS), STORED UNCONTROLLED (1 YEAR) AFTER ATP
AQUA and AURA 160 AH	
1-041	ATP
2-102	ATP, SEAL REWORK, ATP

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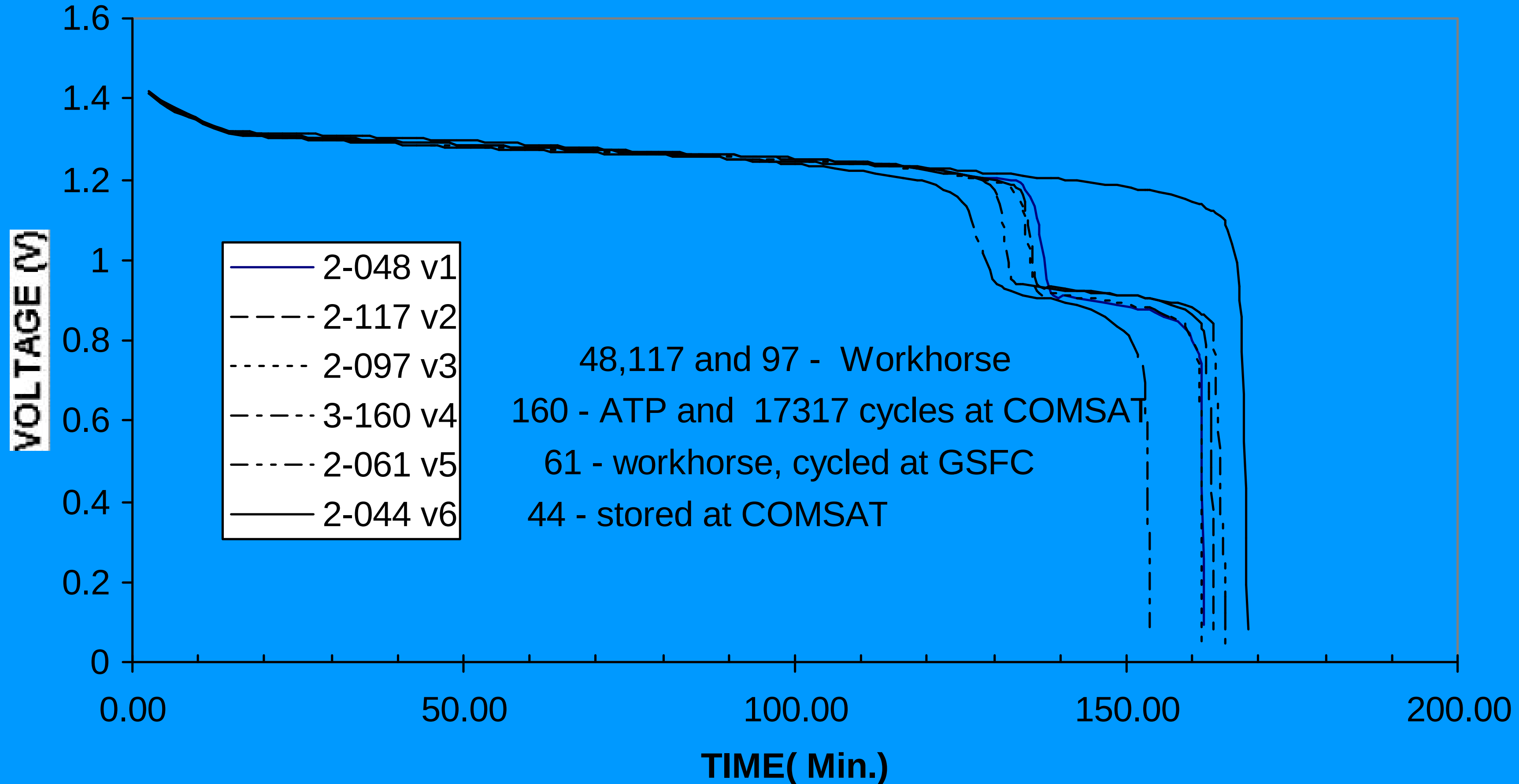
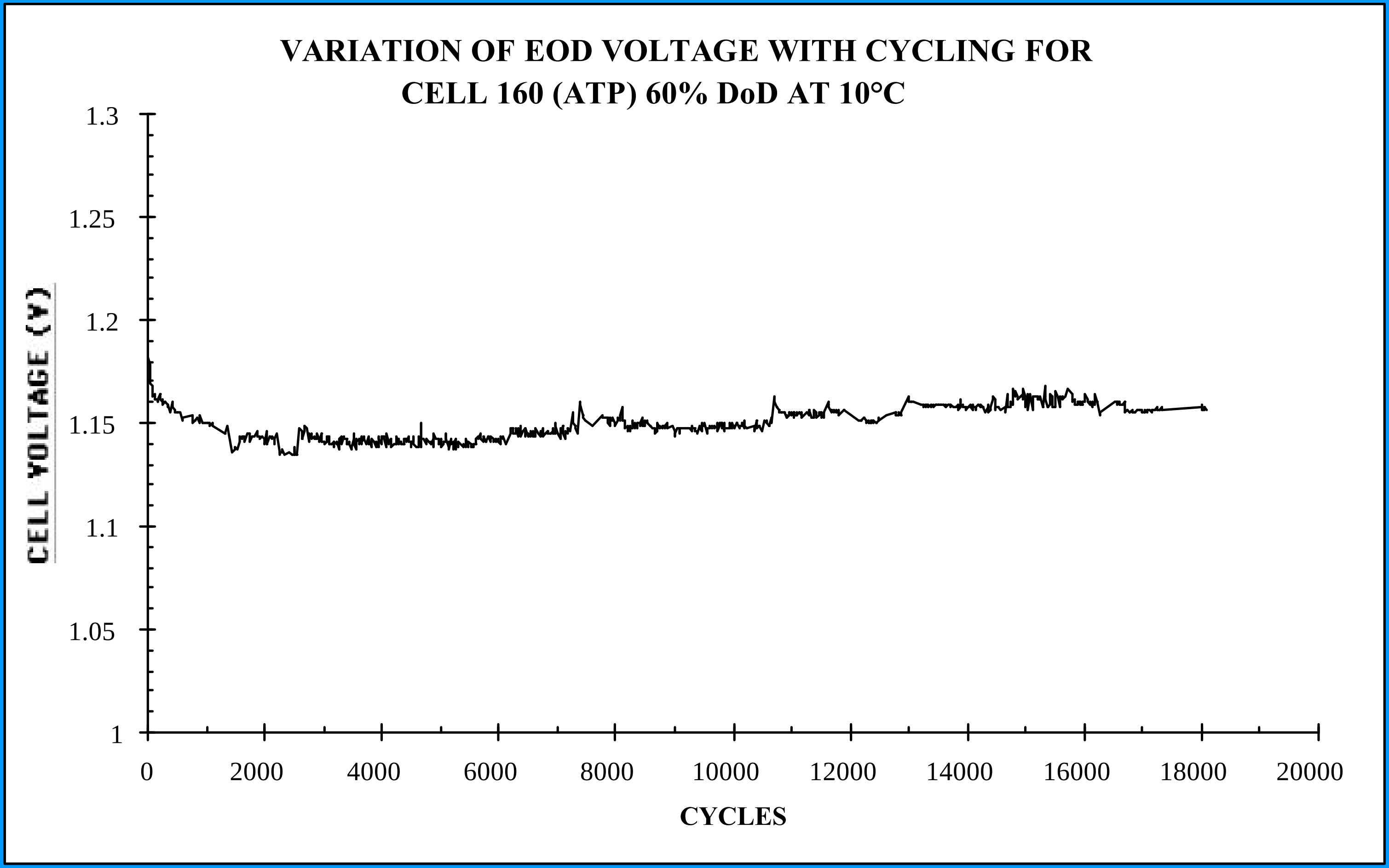
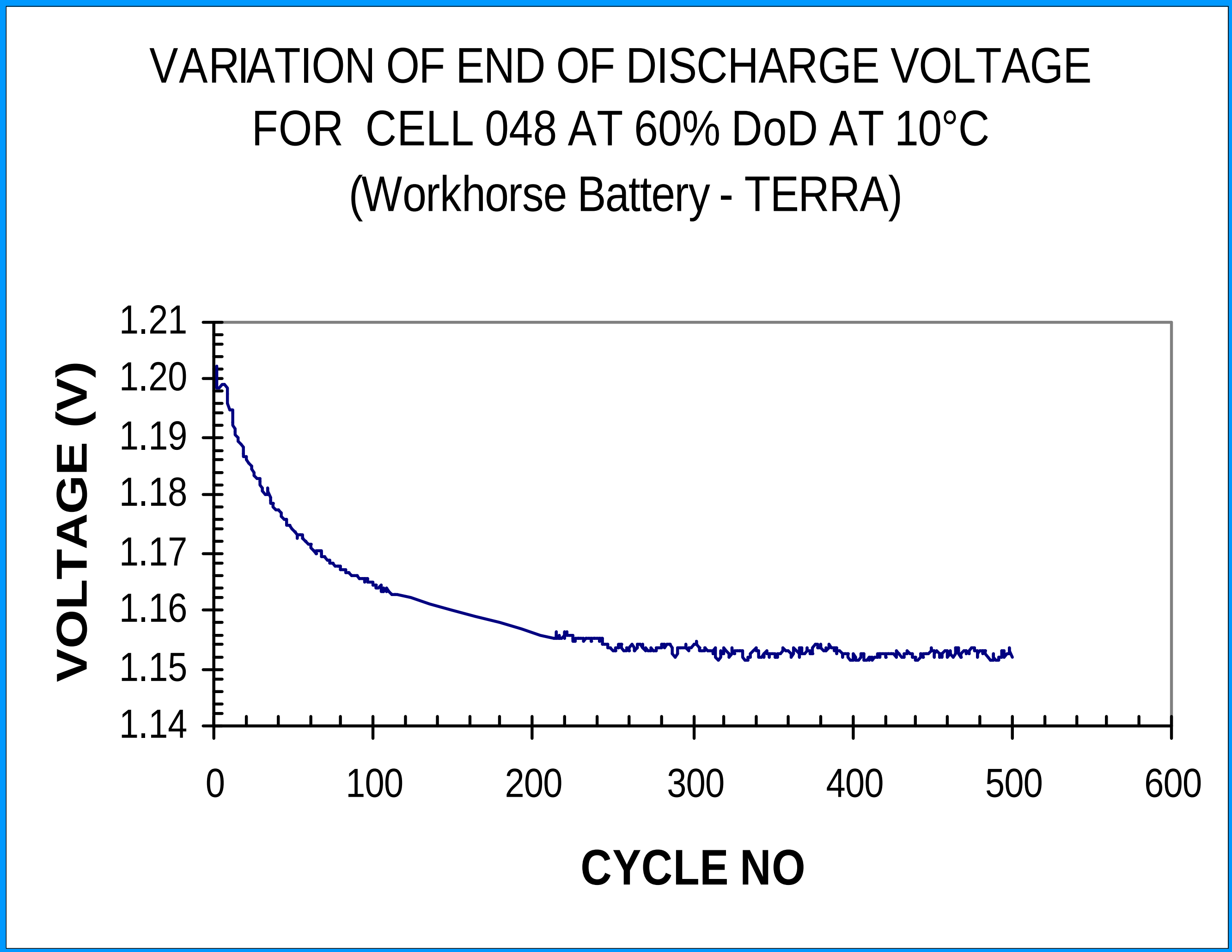
C/2 RATE DISCHARGE PROFILES AT10^{O}C

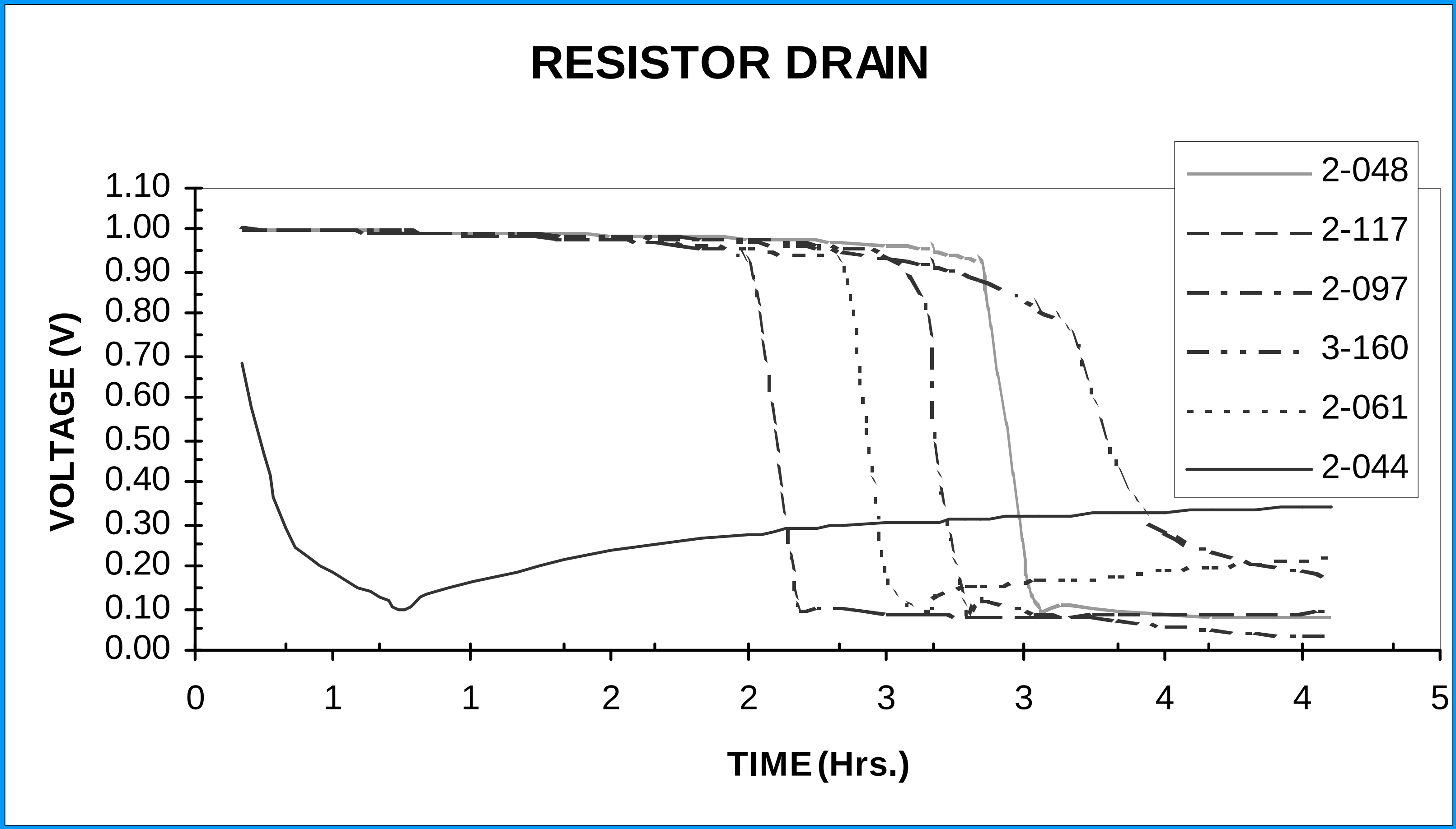


Second Plateau Capacity at C/2 Discharge

CELL I.D.	HISTORY	Capacity	AH,10°C	SECOND PLATEAU
		1V	0.1V	CAPACITY, %
	50 AH, TERRA			
2-044	Stored at low temp.	68.9	69.7	1.1
1-005	Stored at low temp.	63.6	64.3	1
2-117	Workhorse battery	56	63.8	12.2
2-146	Workhorse battery	62.5	63.9	2.2
3-160	17317 LEO cycles	53.4	64.5	17.2
3-205	Stored at low temp.	63.7	64.2	0.78
2-097	Workhorse battery	55.2	67.5	18.1
2-048	Workhorse battery	56	67.7	17.3
2-061	Workhorse battery, 500 LEO cycles	54.4	68.9	21
	93 AH, HST			
10-515	ATP	84.2	88.7	5
10-511	Dry storgae, Uncontrolled storage after ATP	93.4	98.3	5
10-512	Dry storgae, Uncontrolled storage after ATP	93	99.3	5.9
11-754	Dry storgae, Uncontrolled storage after ATP	91.8	97.5	5.8
	160 AH, AQUA and AURA			
1-041	ATP	184.7	185.1	0.3
2-102	ATP, Seal rework, ATP	192.2	192.9	0.2

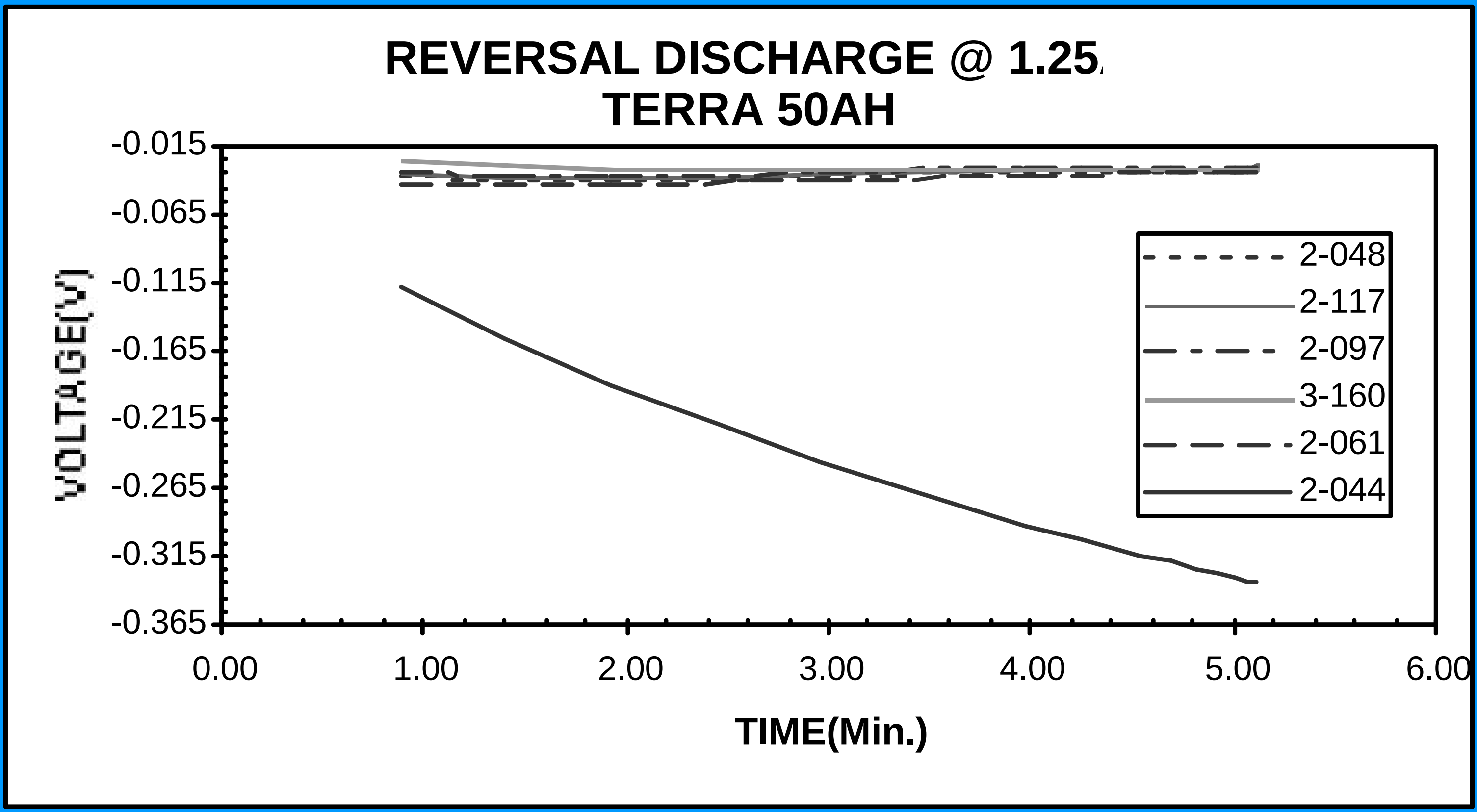

VARIATION OF EOD VOLTAGE WITH CYCLING FOR
CELL 160 (ATP) 60% DoD AT 10°C
CELL VOLTAGE (V)
1.3
1.25
1.2
1.15
1.1
1.05
1
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
CYCLES


VARIATION OF END OF DISCHARGE VOLTAGE
FOR CELL 048 AT 60% DoD AT 10°C
(Workhorse Battery - TERRA)
VOLTAGE (V)
1.21
1.20
1.19
1.18
1.17
1.16
1.15
1.14
0
100
200
300
400
500
600
CYCLE NO


RESISTOR DRAIN
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
VOLTAGE (V)
0
1
1
2
2
3
3
4
4
5
TIME (Hrs.)
2-048
2-117
2-097
3-160
2-061
2-044

Cell Reversal Test Condition

- Temperature = 20°C
- Charge at C/10 for 16 hrs followed by two discharges at C/2 to 1V and at C/20 to 0.01V and then resistive drain to 0.005V
- Reversal discharge at C/40 for 5 minutes


REVERSAL DISCHARGE @ 1.25
TERRA 50AH
VOLTAGE(V)
-0.015
-0.065
-0.115
-0.165
-0.215
-0.265
-0.315
-0.365
0.00
1.00
2.00
3.00
4.00
5.00
6.00
TIME(Min.)
2-048
2-117
2-097
3-160
2-061
2-044

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GAS ANALYSIS

CELL I.D.	GAS CONTENT
50 AH TERRA cell(2-044), stored at low temp.	No gas present
50 AH TERRA (2-061), workhorse, 500 cycles	vacuum
50 AH TERRA (2-097), workhorse	No gas present
50 AH TERRA (2-117), work horse	H2 less than 100mL
50 Ah TERRA (3-160), ATP, 17317 cycles	H2 3700 mL
50 AH TERRA (2-146), workhorse	vacuum
50 AH TERRA (3-205), stored at low temp.	vacuum
93 AH HST (11-754), stored uncontrolled 1 year	vacuum
93 AH HST (10-511), stored uncontrolled 1 year	vacuum
93 AH HST (10-512), stored uncontrolled 1 year	vacuum
93 AH HST (10-515), stored uncontrolled 1 year	vacuum
160 AH AQUA (1-041), ATP	vacuum
160 AH AURA (2-102), ATP, seal rework, ATP	vacuum

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NICKEL PRECHARGE

CELL ID	AH	ELECTRICAL	CHEMICAL	TOTAL	TOTAL, %
50 AH TERRA (2-044)	58.9	0.3	8.0	8.3	16.5
50 AH TERRA (2-117)	49.1	0.0	14.6	14.6	29.2
50 AH TERRA (3-160)	47.5	0.0	9.1	9.1	18.1
50 AH TERRA (2-146)	58.7	0.7	1.3	4.5	8.9
50AH TERRA (3-205)	57.3	1.0	8.7	9.7	19.4
93 AH HST (10-511)	89.3	0	7.9	7.9	8.8
93 AH HST (10-515)	78.6	1.4	12.8	13.2	14.7
160 AH AQUA Cell (1-41)	150	8	19.3	27.3	18.2
160 AH AURA Cell (2-102)	165	8.7	16.3	25	15.1

* Based on measured 20°C Capacity

Summary

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- Cell stored at low temperature did not exhibit a second plateau in the discharge profile
- Second plateau occurs in cells that are subjected to excessive use, high temperature exposure, intermittent charging, cell reversal, and cycling
- Cells exhibiting second plateau also have a large residual capacity at a lower voltage of about 0.8 V and a voltage plateau at 1V during resistive drain
- Gas analysis indicated the presence of large quantity of hydrogen in the cycled cell and relatively small quantity of hydrogen in ONLY one of the cells that exhibited second plateau
- Chemical analysis indicated the presence of Ni^{+3} in discharged positive plates

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Conclusions

- Proper handling of $Ni\text{-}H_2$ cells/batteries in storage, during I&T, and at launch site is very important to preserve the useful energy and to extend the mission life
- Cell reversal test is not a prudent test to verify or quantify the nickel pre-charge in $Ni\text{-}H_2$ cells/batteries
- The second plateau is due to the formation of Ni^{+3} that is electrochemically inactive
- Gas analysis of the cell, and Chemical analysis of the positive plate are confirmatory tests to determine the nature of pre-charge in $Ni\text{-}H_2$ cells

Large Lithium Ion Batteries for Aerospace and Aircraft Applications

Gregg C. Bruce and Lynn Marcoux
Eagle-Picher Energy Products
1155 West 15th Street, North Vancouver BC
Canada V7P 1M7

ABSTRACT

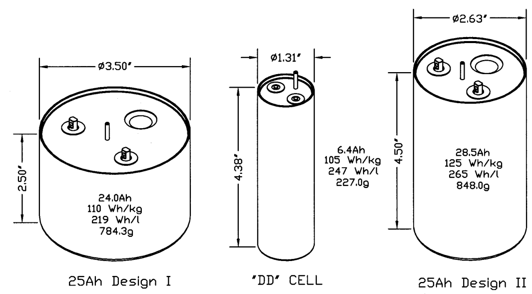
Eagle-Picher Energy Products (EPEP) has been manufacturing and testing large lithium ion cells (up to 100-Ah) for several years. Recently, work has focused on testing of different chemistries at variable temperatures and designing and fabricating 100-Ah cylindrical cells. For the aircraft application the largest concern is irreversible capacity loss at elevated temperatures (70°C). In contrast, for the aerospace application shelf-life and cycle life is critical. EPEP has found that the major contributor to the loss in low temperature performance due to high temperature testing was the positive electrode. Eagle-Picher Energy Products will discuss recent results of variable temperature cycling and 100-Ah cell performance.

INTRODUCTION

Eagle-Picher Energy Products has been developing large lithium ion cells for several years. The initial efforts were the result of a contract funded by the USAF and the Canadian Department of Defense. The program successfully demonstrated that lithium ion cells could be scaled up to sizes useful for spacecraft and aircraft applications. The program included the delivery of 10, 25-Ah Design I cells, 12, 25-Ah Design II cells and 12, DD (7-Ah) cells to the USAF and JPL. The three cells are shown in Figure 1. As a follow on EPEP is participating in the USAF/NASA Li Ion Battery Consortium with the development of a 25-Ah cell for Mars Lander applications and a 7-Ah cell for Mars Rover applications. In the initial stages of this contract 40, 25-Ah Design II cells were delivered to JPL and Lockheed Martin Astronautics (LMA).

One of the test requirements for the Mars missions is cell performance under variable temperature cycling. The cells were alternatively cycled at 40°C and –20°C. During the program the need for EP Energy Products to improve variable temperature performance became evident and work was initiated in this area.

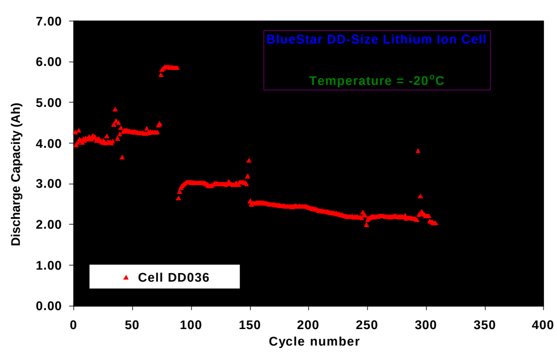
Figure 1. Eagle-Picher Energy Products 25-Ah, Design I, DD and 25-Ah Design II lithium ion cells.



RESULTS AND DISCUSSION - VARIABLE TEMPERATURE CYCLING

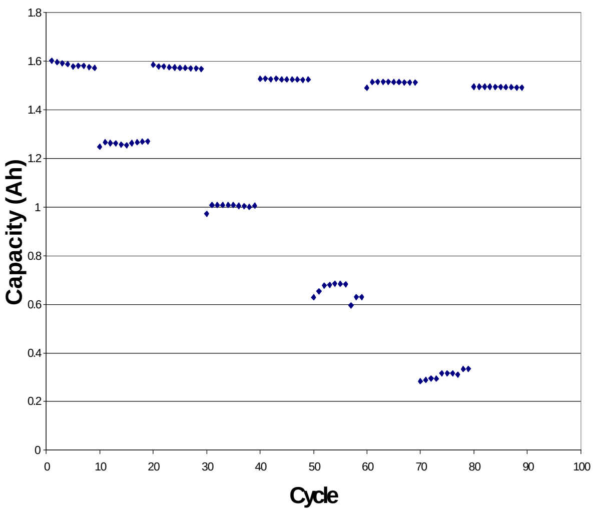
With planetary exploration missions performance under large temperature variations is required. One of the first tests completed at JPL on EPEP lithium ion cells was performance as a function of temperature. During the test program JPL noted that low temperature performance was adversely affected by high temperature cycling. Since the mission profile called for high temperature cycling followed by low temperature performance this could be mission limiting. The test results obtained by JPL are shown in Figure 2.

Figure 2. Variable temperature cycling for Eagle-Picher Energy Products DD cell performed at JPL.



Therefore, work focused on improving the variable temperature performance of EPEP cells. The first step was to repeat the JPL test results and then systematically change parameters to improve performance. EPEP decided to use C cells as a test bed due to materials required and the ease in manufacturing. The initial test results in this test format under variable temperature conditions are shown in Figure 3.

Figure 3. Variable temperature cycling for Eagle-Picher Energy Products baseline 1.6-Ah cells.



Of initial interest was that the cells tested by Eagle-Picher showed a far more rapid decline in capacity that the test results at JPL. This was found to be due to the difference in cell sizes. At –20°C the 25-Ah (tested by JPL) cell benefits more than the C cell (tested at EPEP) from self-heating. The first parameter tested was the binder used in the positive electrode. By consulting the manufacturer on solubility of PVDF binders in carbonate solvents the most insoluble binder was selected. Cells manufactured with this binder showed superior performance when compared to the baseline cells but further improvements were still required. The next parameter tested was positive electrode supplier. Samples of $LiCoO_2$ from two independent sources were obtained and tested. Surprisingly, the source of $LiCoO_2$ made a substranial difference in performance when compared to the baseline cells as shown in Figures 4 and 5.

The difference in performance was attributed to the physical characteristics of the positive electrode material. The main cause of the loss in low temperature performance due to high temperature cycling was attributed due to an increase in impedance on the positive electrode surface. This is thought to be the main driver since the performance at 40°C is not diminished as dramatically and cannot be attributed to $LiCoO_2$ dissolving in the electrolyte or to a structural change in the $LiCoO_2$.

Figure 4. Variable temperature cycling for Eagle-Picher Energy Products 1.6-Ah cells, $LiCoO_2$ from supplier A.

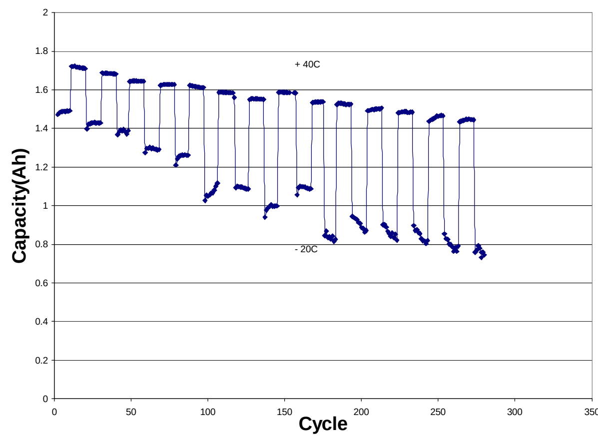
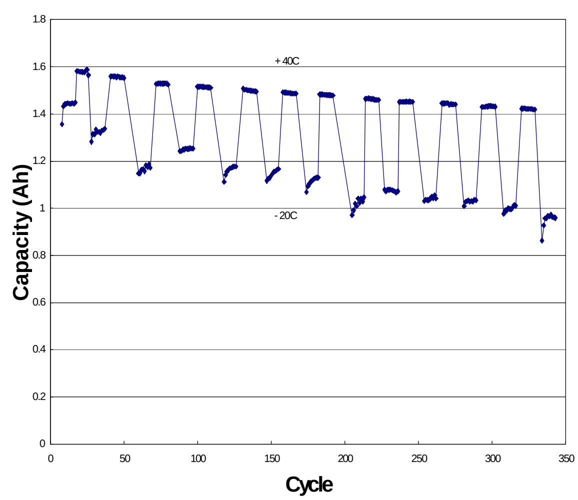


Figure 5. Variable temperature cycling for Eagle-Picher Energy Products 1.6-Ah cells, $LiCoO_2$ from supplier B.



Since it became quite obvious that the major factor in low temperature performance was the active material two other metal oxide positive electrode materials were tested. The materials tested were $LiNi_{0.82}Co_{0.18}O_2$ and $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$. The results for the mixed metal oxide positive electrodes are shown in Figures 6 and 7.

Figure 6. Variable temperature cycling for Eagle-Picher Energy Products 1.6-Ah cells, $LiNi_{0.82}Co_{0.18}O_2$.

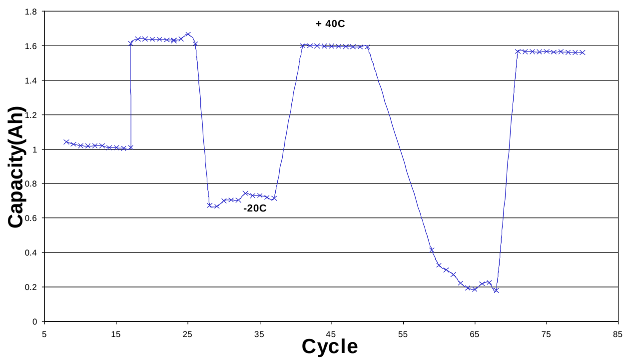
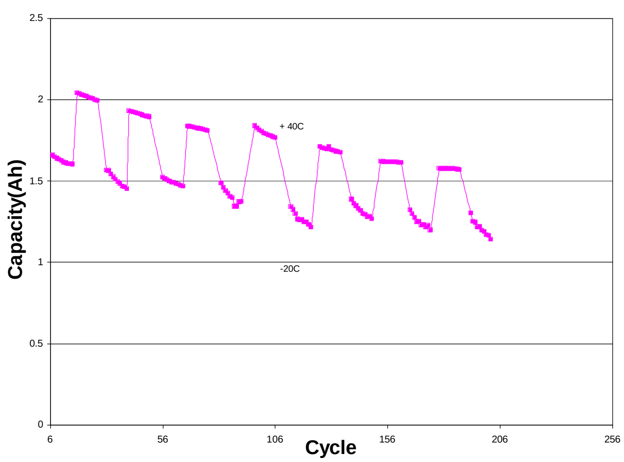


Figure 7. Variable temperature cycling for Eagle-Picher Energy Products 1.6-Ah cells, $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$.



As can be seen from all the data presented two factors play in the loss in capacity at low temperature due to high temperature cycling. The first and primary factor is the positive electrode active material and the second is the binder. Work will continue to further enhance cell performance under these conditions.

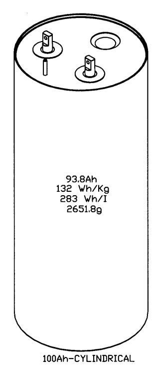
CELL PERFORMANCE – 100-Ah CYLINDRICAL CELL

Recently, Eagle-Picher Energy Products has been working with very large lithium ion cells for use in spacecraft or aircraft applications. The latest cell developed is a 90 to 100-Ah cylindrical cell. The physical characteristics of the cell are given in Table 1. A general drawing of the cell is shown in Figure 8.

Table 1. Physical characteristics of 100-Ah, 86211 lithium ion cell.

Parameter	100-Ah, 86211
Cell height	8.30”
Cell diameter	3.406”
Positive electrode length	1112 cm
Positive electrode width	17.7 cm
Inter tab distance	93 cm
Negative electrode length	1142 cm
Negative electrode width	18.0 cm
Inter tab distance	95 cm

Figure 8. General drawing of the 86211 lithium ion cell.



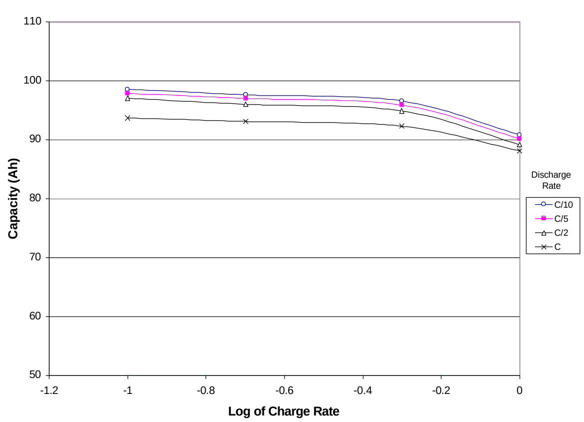
The cell utilizes a $LiCoO_2$ positive electrode and a graphite negative electrode. The electrodes have six tabs which are fusion welded to a 0.250” diameter molybdenum pin in at glass-to-metal feed-through. The cell has a rupture disc and shut-down separator for safety and uses a standard fill tube for cell activation. The physical characteristics accompanied with the performance characteristics for the 86211 cell are given in Table 2.

Table 2. Performance and physical characteristics of 86211 cell.

	Cell Weight g	Capacity Ah	Specific Energy Wh/kg	Energy Density Wh/l
Ave.	2651.8	93.8	132.0	282.6
Std. Dev.	23.1	2.1	2.3	6.5

As with all cylindrical cells when compared to a plate cell design the often cited drawbacks are rate capability and thermal management. The cell was tested for rate capability with various charge and discharge rates from C/10 (10A) to C (100A). In all cases the cell was charged to a voltage limit of 4.1V and then held at constant potential for 2.5 hours and then discharged to 3.0V. The results of these tests are shown in Figure 9.

Figure 9. Rate capability of the 86211 lithium ion cell at various charge and discharge rates.



The data shows that the cell is starting to see rate limitations at the C rate.

The mass analysis of the 86211 cell is shown in Table 3. The relatively low values for the cap and can is related to the inherent tube strength of the cylindrical design.

Table 3. Mass analysis of 86211 Cell.

Component	Mass, g	% of Total
Can	213.0	8.0
Cap Assembly	54.0	2.0
Electrolyte	688.5	25.2
Positive electrode	1074.5	40.5
Negative electrode	517.5	19.5
Miscellaneous	124.3	4.7
Total	2651.8	100

The cells were tested for cycle life at the C/5 and the C/2 charge and discharge rates. The C/5 test was carried out at 20A to a 4.1V cut-off with a voltage clamp for a further 1.5 hours. The C/2 rate was tested at 45A with a voltage clamp of 4.1V for a total charge time of 6 hours. The C/5 results are shown in Figure 10 and the C/2 results are given in Figure 11.

Figure 10. Cycle life of 86211, 100-Ah cell at 20°C, 100% depth of discharge at C/5.

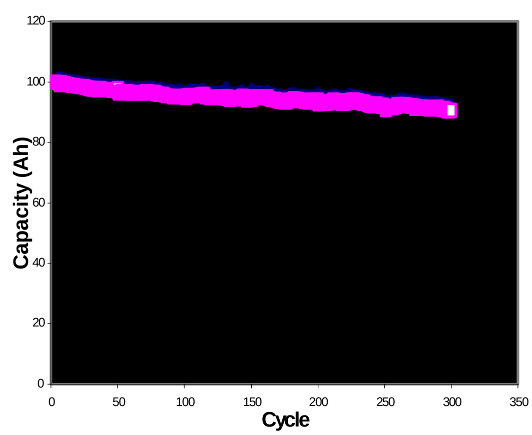
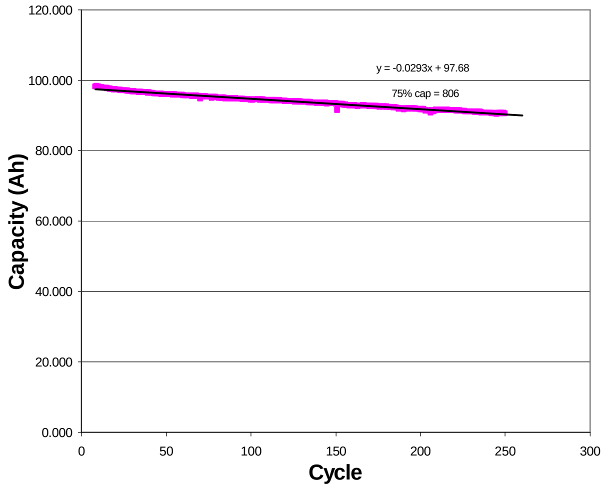


Figure 11. Cycle life of 896211 100-Ah cell at $20^{o}C$, 100% depth of discharge at C/2.



The cycle life projections for the two cells tested at the C/5 rate indicate that 75% of initial capacity will not be reached until 940 and 998 cycles. For the C/2 rate test the projection is for greater than 800 cycles to 75% of initial capacity.

CONCLUSION

The reduced capacity at low temperature due to high temperature cycling is attributed primarily to the positive electrode. The performance for the 86211 cell is quite impressive for a $LiCoO_2$ cathode with good specific energy and energy density and excellent cycle life.

ACKNOWLEDGMENTS

The continuing support, technical assistance and test data supplied by Marshall Smart and Kumar Bugga of JPL and Richard Mash and Steve Vukson of Wright-Patterson AFB is gratefully acknowledged.

PERFORMANCE AND ABUSE TESTING OF 5 YEAR OLD LOW RATE AND MEDIUM RATE LITHIUM THIONYL CHLORIDE CELLS

2000 NASA AEROSPACE BATTERY WORKSHOP

Rick Frerker
Wenlin Zhang, PhD
Schlumberger

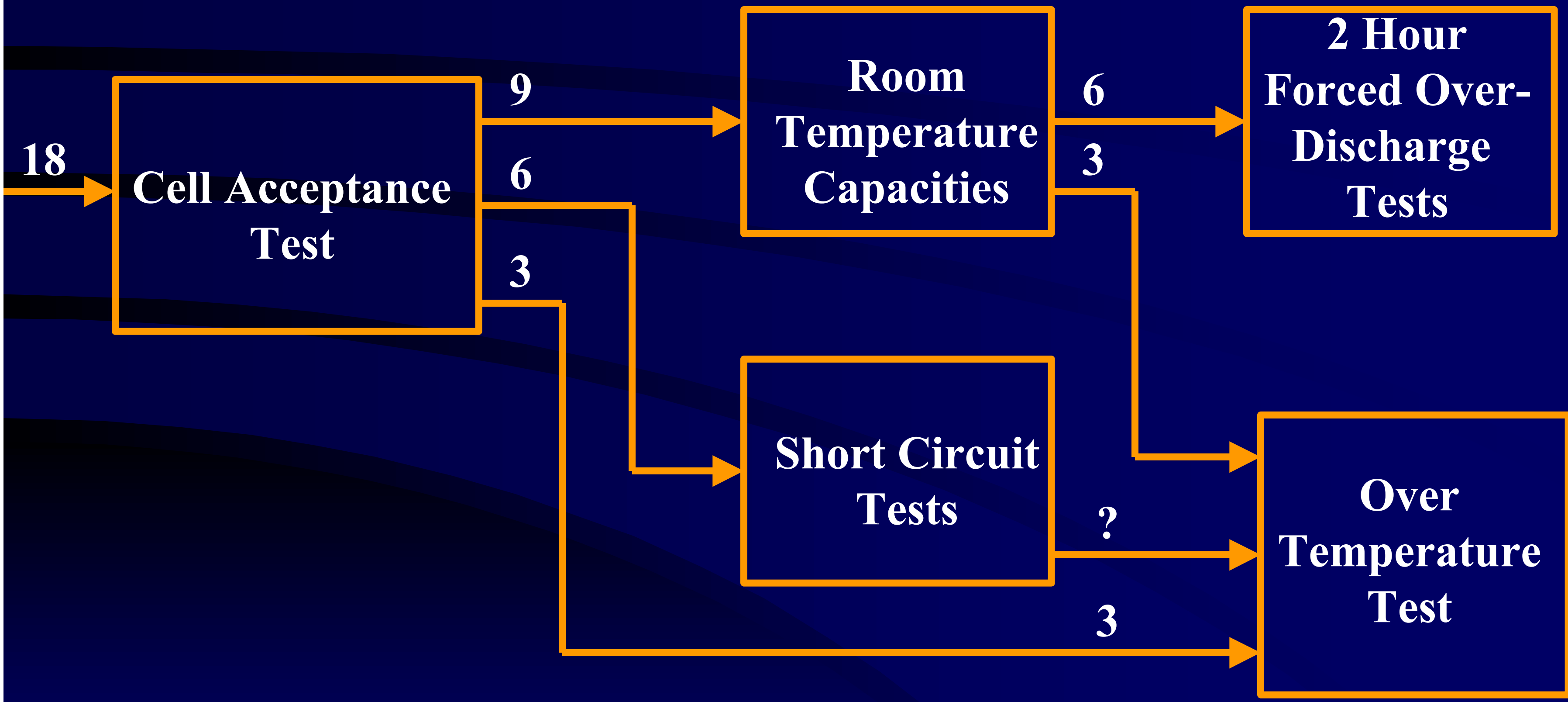
Judith Jeevarajan
Lockheed Martin / NASA-JSC

Bobby J. Bragg
NASA-JSC

5 Year Old Lithium Thionyl Chloride Cells Used In The Test (18 each type)

- Low Rate 'D' Part No. LTC-114
  - 14 Ahr (@50 ohms and 3.0V cutoff)
  - Sandia Design
- Medium Rate 'D' Part No. LTC-111
  - 12 Ahr (90 mA and 2.5V cutoff at 25 ^{o}C
- Medium Rate 'sub D' Part No. LTC-115
  - 11 Ahr (100 mA and 2.0 V cutoff at 25 ^{o}C
  - Sandia Design, Military Aviation qualified cell

Test Plan (Overview)



Cell Acceptance Test

Measure OCV
Voc > 3.6 Volts

→

5 Ohm Load for 90 s
Vcc ≥ 3.5 Volts

→

160 ^{o}F - 2 hours
No Leaks

→

Cell Acceptance Test Results
All 54 Cells

Measure OCV
Voc > 3.6 Volts

→ **PASS** **3.65 V** →

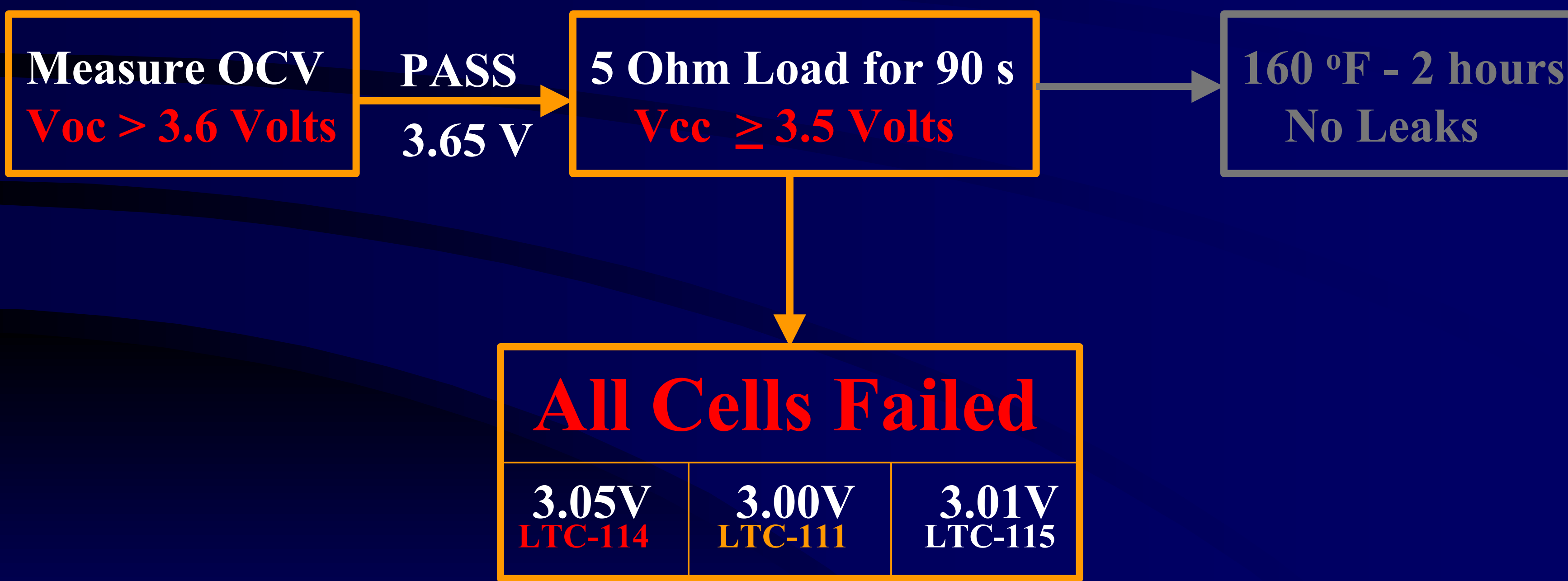
5 Ohm Load for 90 s
Vcc ≥ 3.5 Volts

→

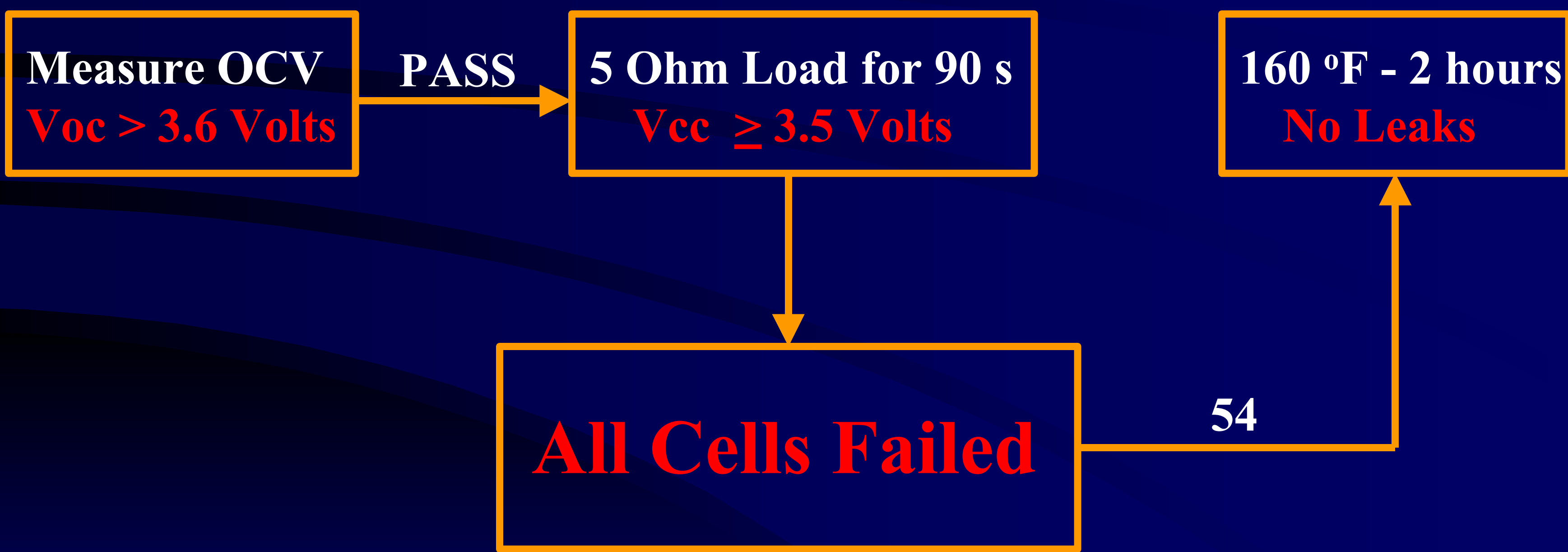
160 °F - 2 hours
No Leaks

→

Cell Acceptance Test Results
All 54 Cells



Cell Acceptance Test (Revised)

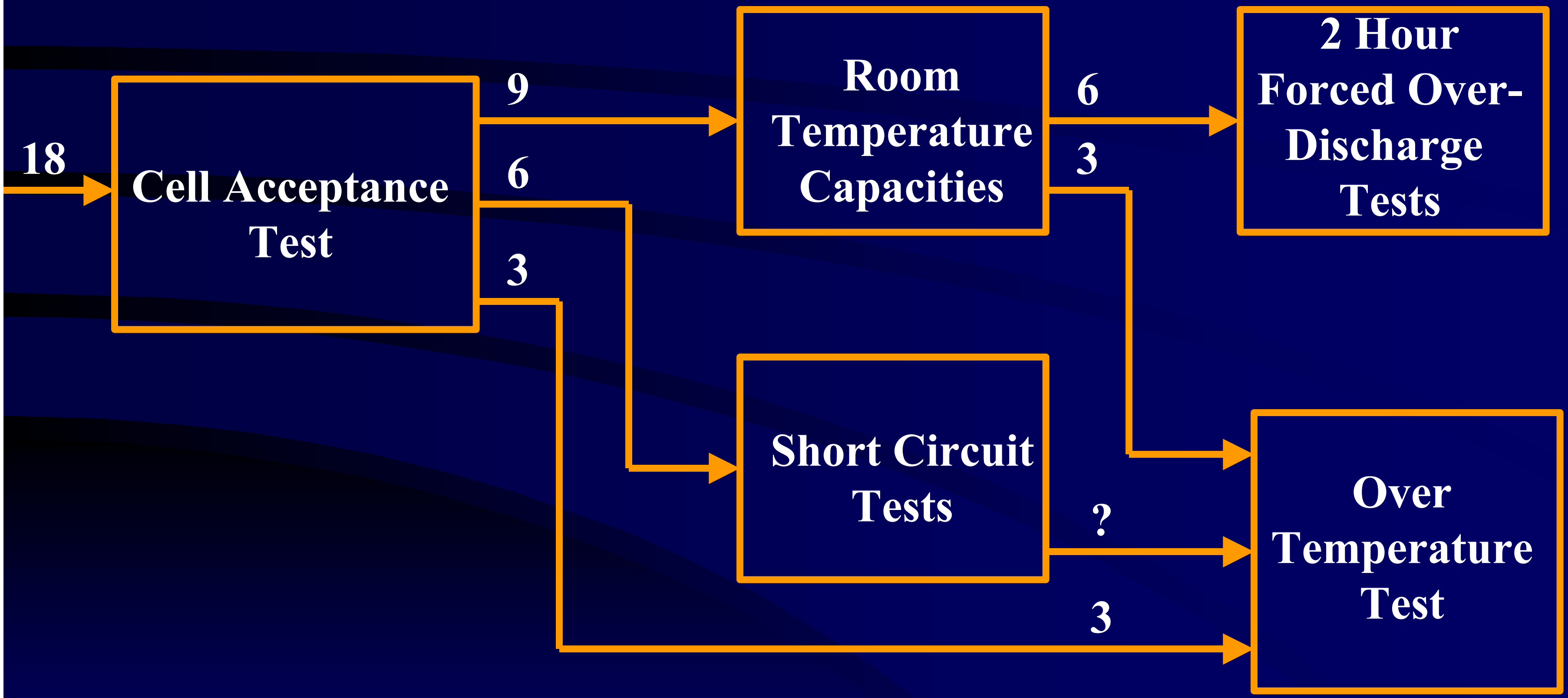


Test Plan - Part 1
Cell Acceptance Test Results

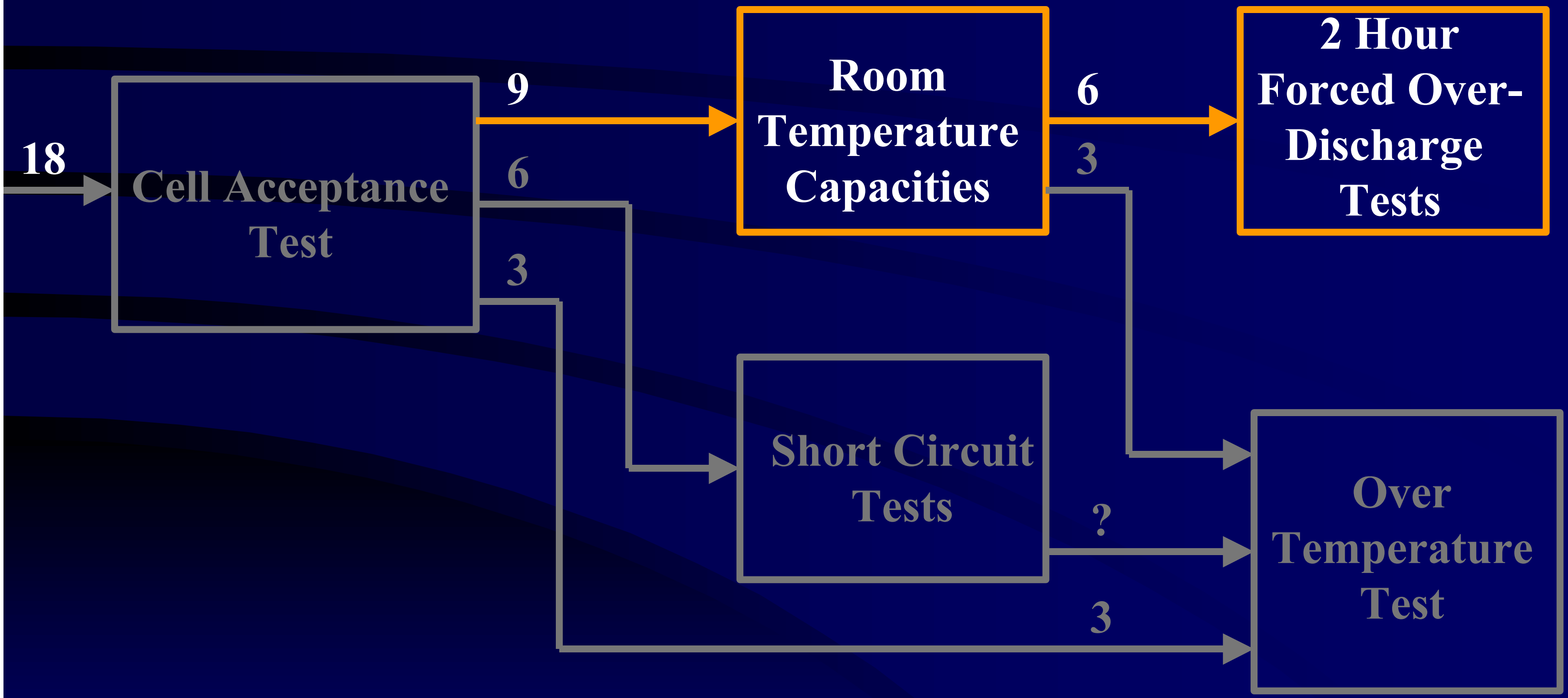
160 °F - 2 hours
No Leaks

→ **54 PASS**

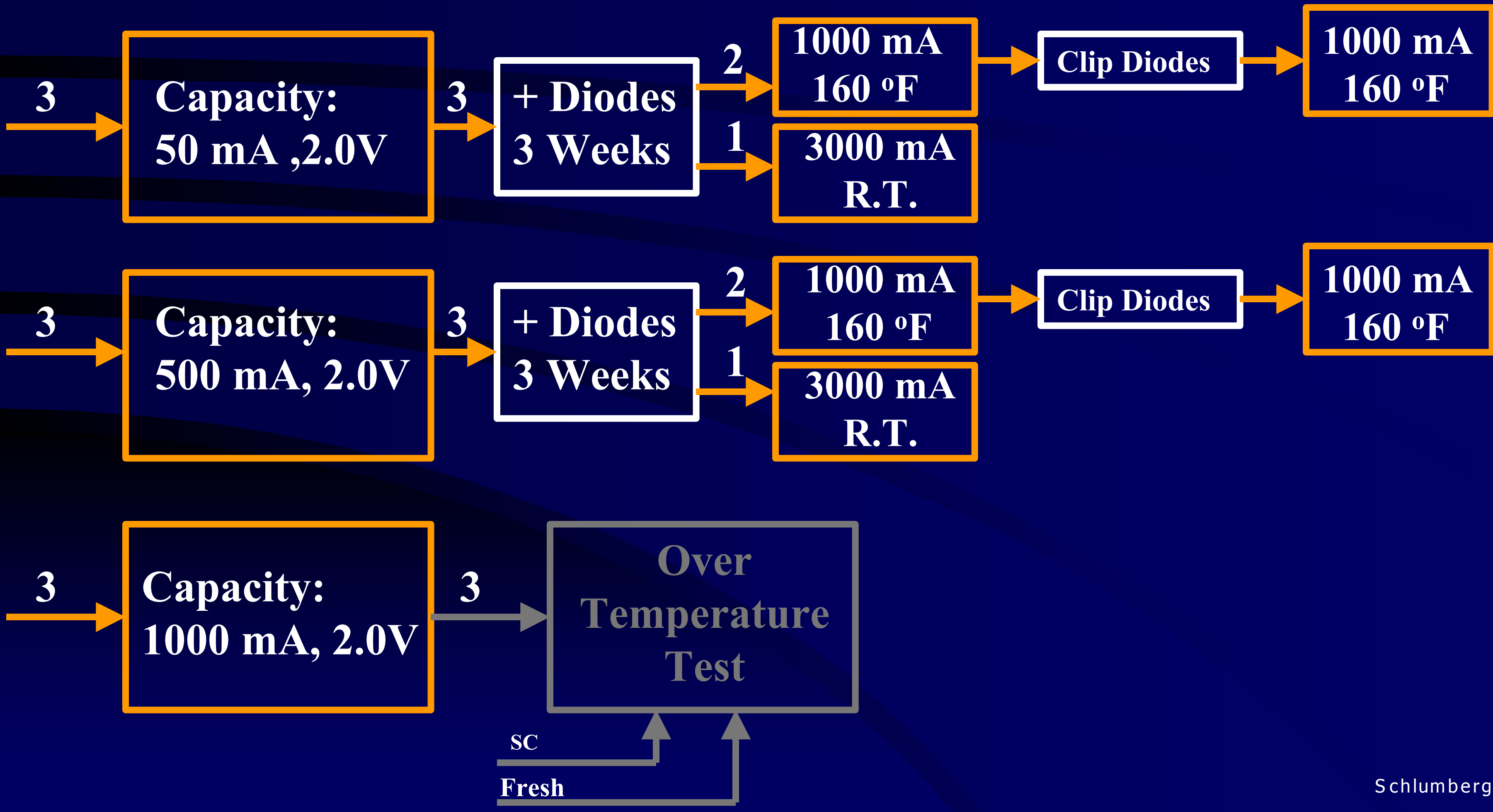
Test Plan (Overview)



Test Plan (Overview)



Room Temperature Capacity and Forced Overdischarge Test



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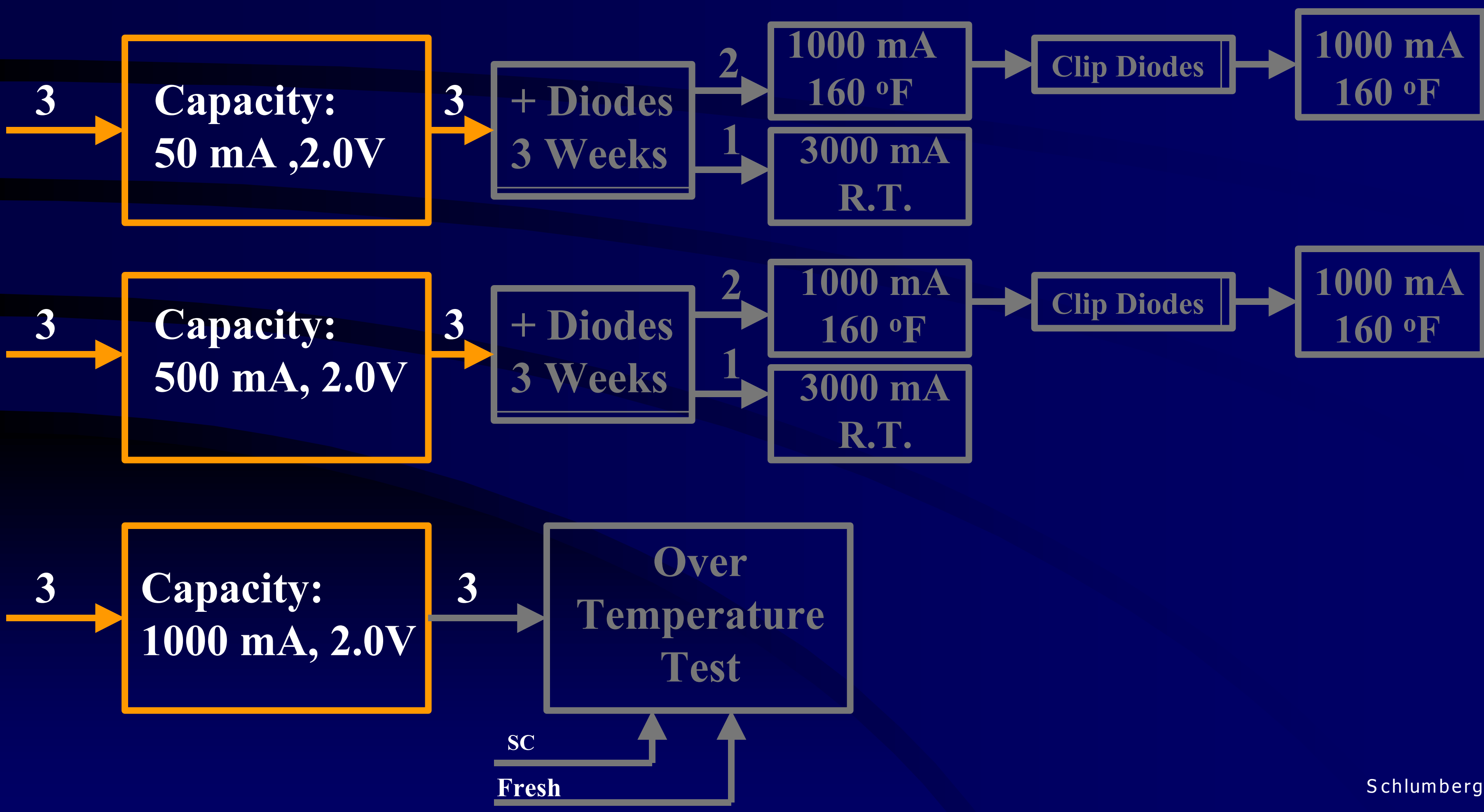
Room Temperature Capacity and Forced Overdischarge Test



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Capacity Test Results

Capacity (Ah)								
50 mA			500 mA			1000 mA		
LTC-114	LTC-111	LTC-115	LTC-114	LTC-111	LTC-115	LTC-114	LTC-111	LTC-115
15.7	15.0	11.8	8.6	13.7	5.3	4.4	12.2	3.3
15.6	14.9	12.7	8.9	13.8	5.6	4.9	12.8	3.1
15.7	14.9	13.0	8.7	13.3	5.2	4.8	12.7	Note

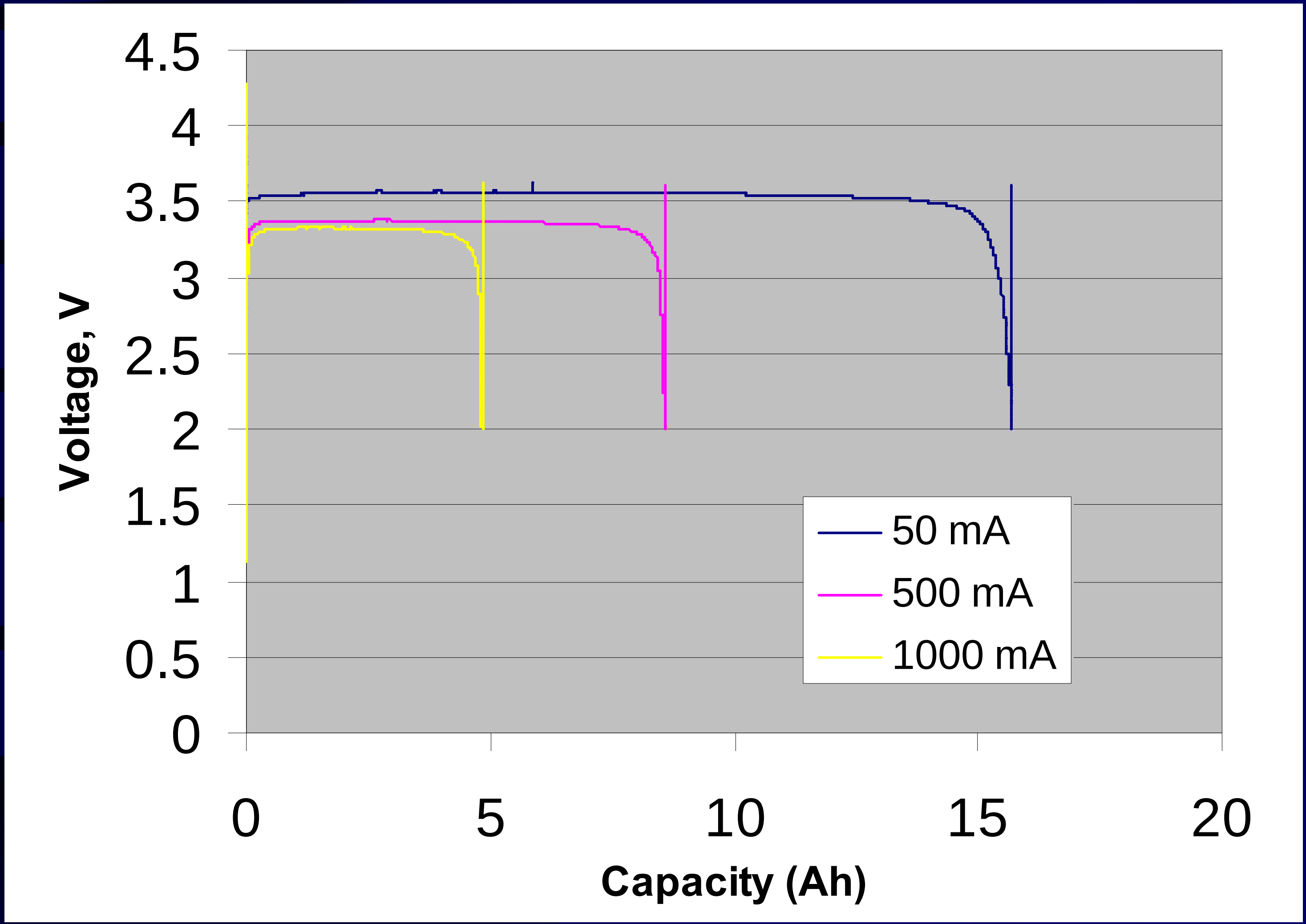
	LTC-114	LTC- 111	LTC 115
Rated Capacities:	14 Ah	12 Ah	11 Ah

Note: One LTC-115 cell had tab break off and repair was not possible

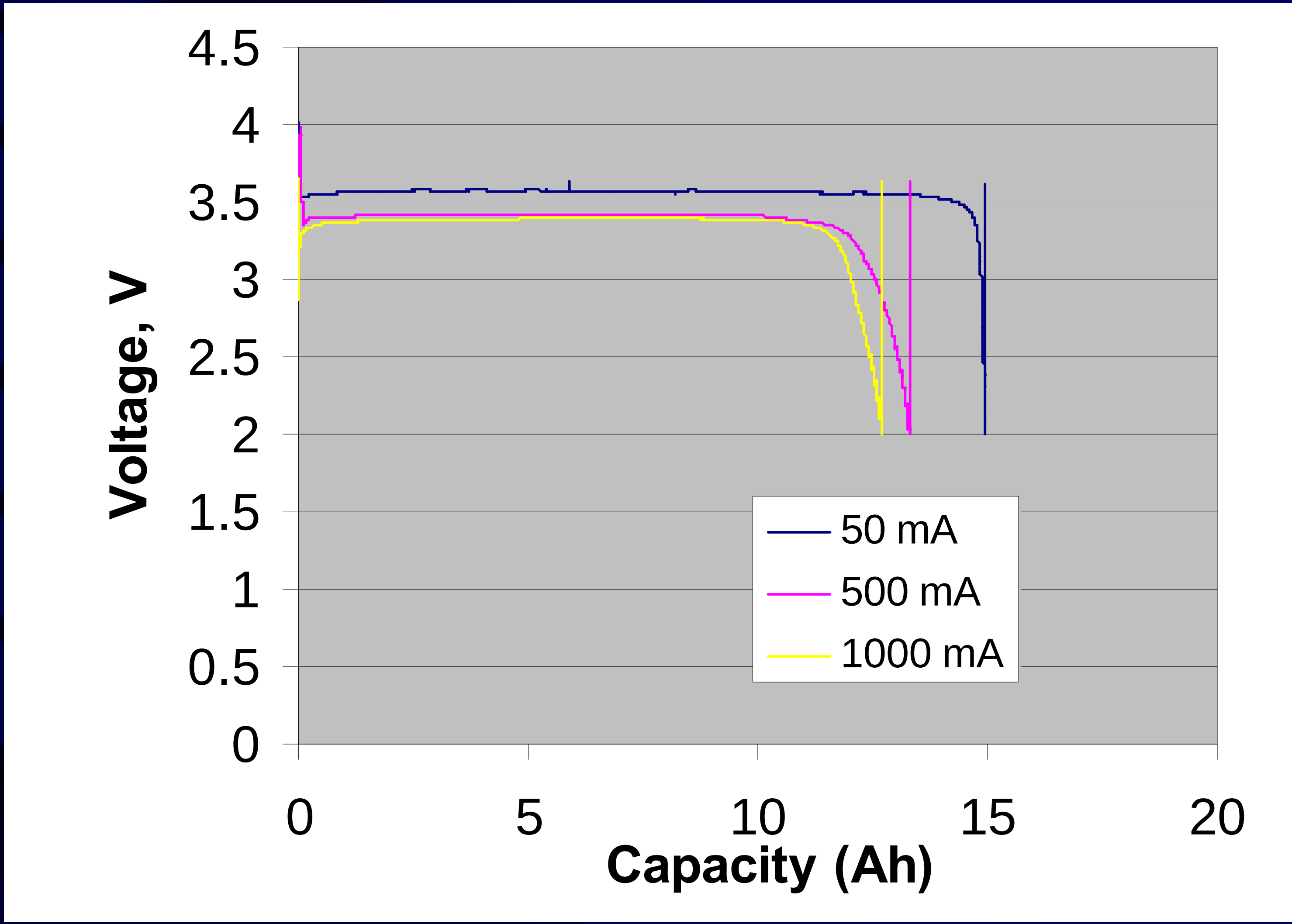
Average Cell Capacity

	LTC-114	LTC- 111	LTC 115
Rated Capacity (Ah)	14	12	11
50 mA Capacity (Ah)	15.7	14.9	12.5
500 mA Capacity (Ah)	8.7	13.6	5.4
1000 mA Capacity (Ah)	4.7	12.6	3.2

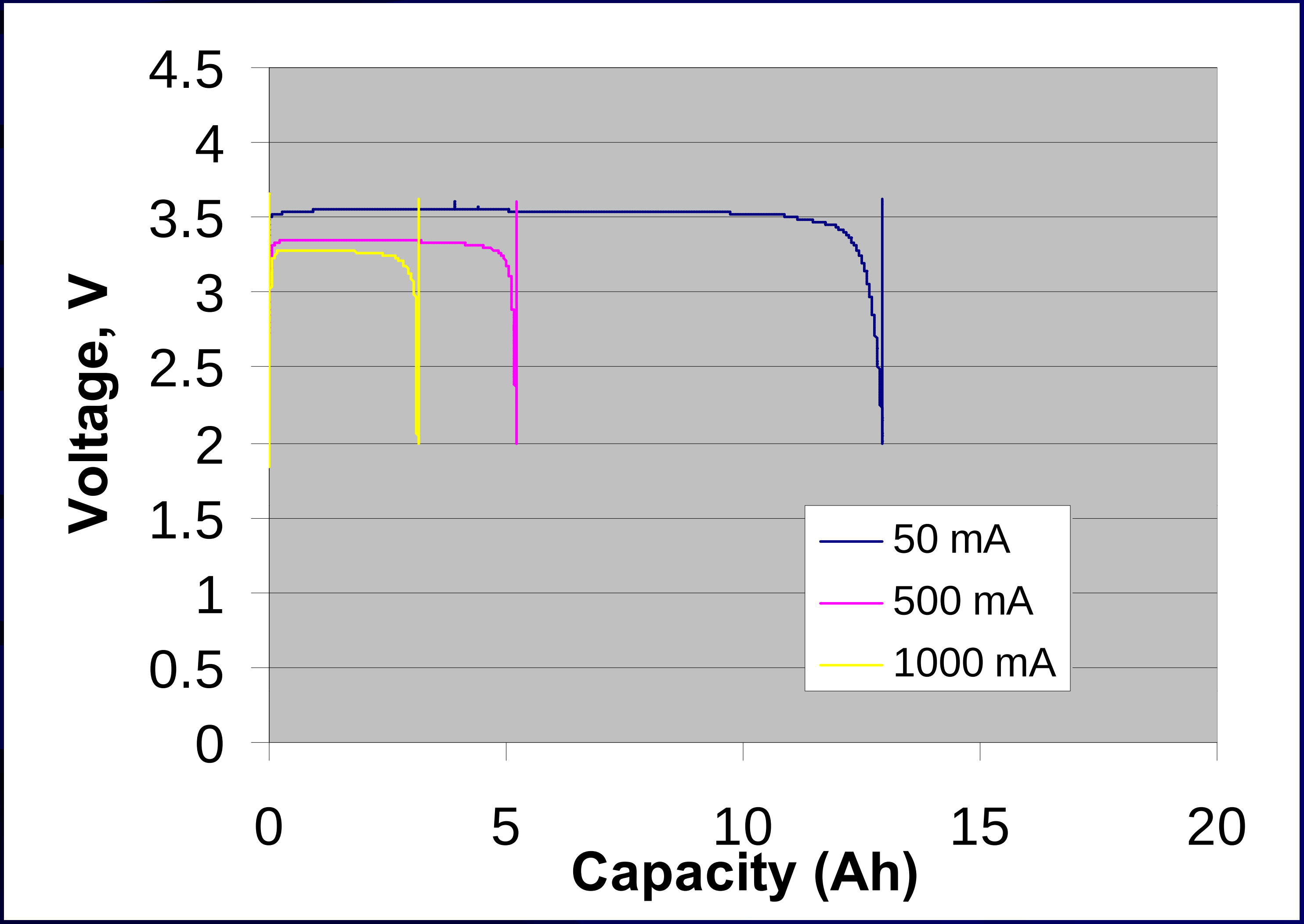
	LTC-114	LTC- 111	LTC 115
Rated Capacities:	14 Ah	12 Ah	11 Ah



Typical Discharge Curves - LTC-114



Typical Discharge Curves - LTC-111



Typical Discharge Curves - LTC-115

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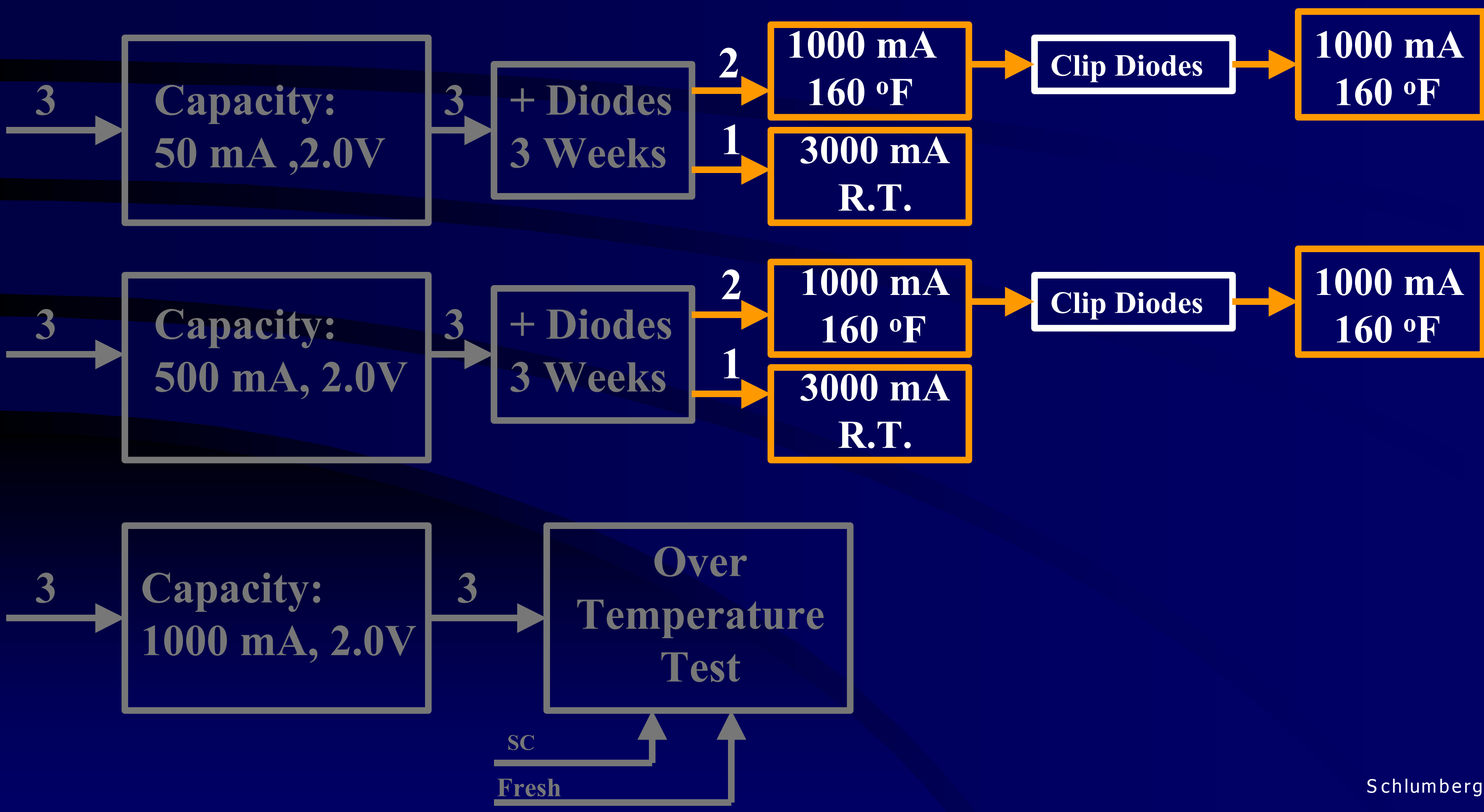
Room Temperature Capacity and Forced Overdischarge Test



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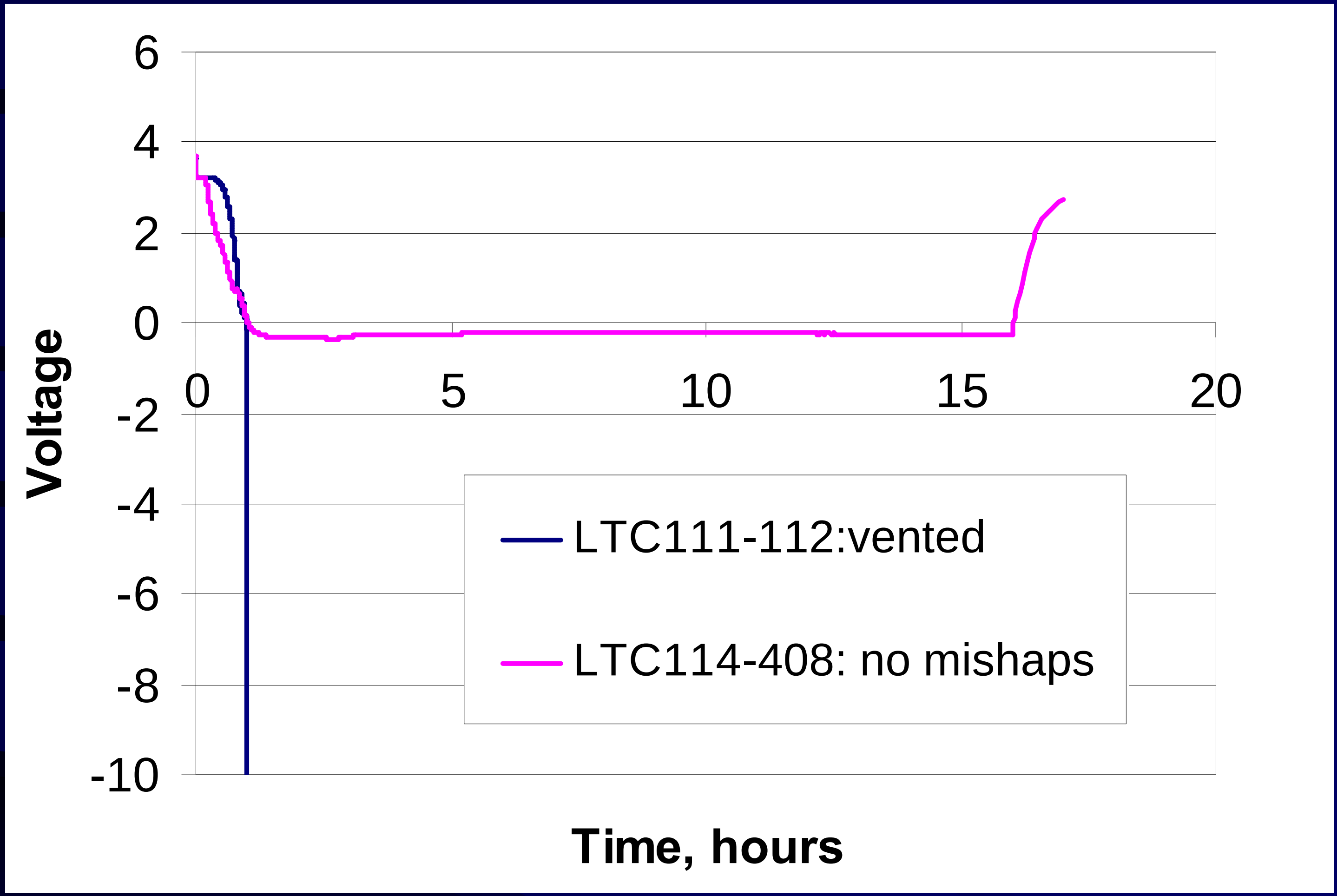
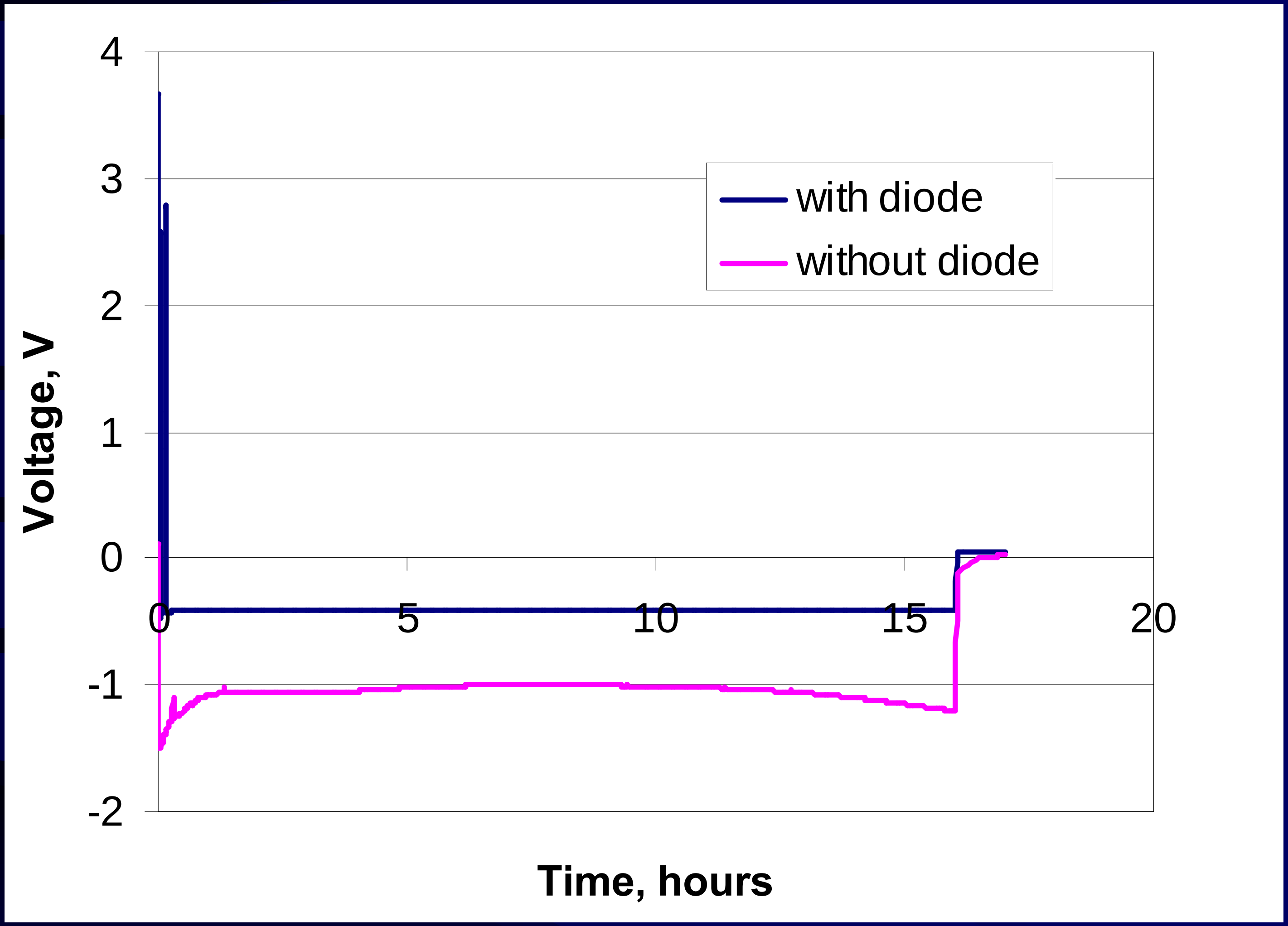
1 Amp at 160F Over-Discharge Test Results

Cell Type	With Diodes	Without Diodes
After 50 mA discharge capacity test		
LTC-114	ok	ok
	ok	ok
LTC-111	ok	ok
	ok	ok
LTC-115	ok	ok
	ok	ok
After 500 mA discharge capacity test		
LTC-114	ok	ok
	ok	ok
LTC-111	vented	not available
	vented	not available
LTC-115	ok	ok
	ok	ok

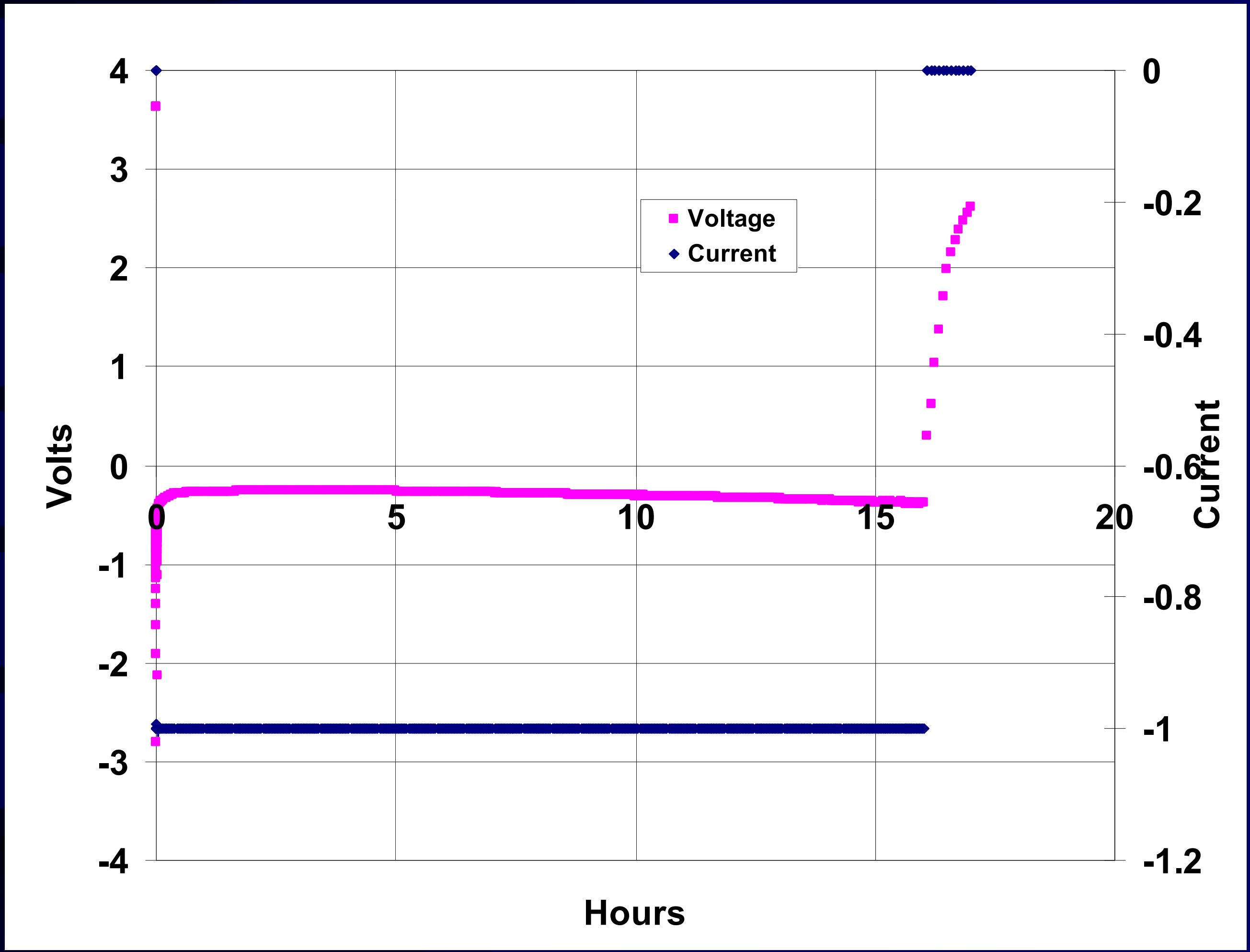


Voltage behavior during 1 A over-discharge with diode at 160ºF - LTC-111 (vented) and LTC-114 (no mishaps)

Schlumberger



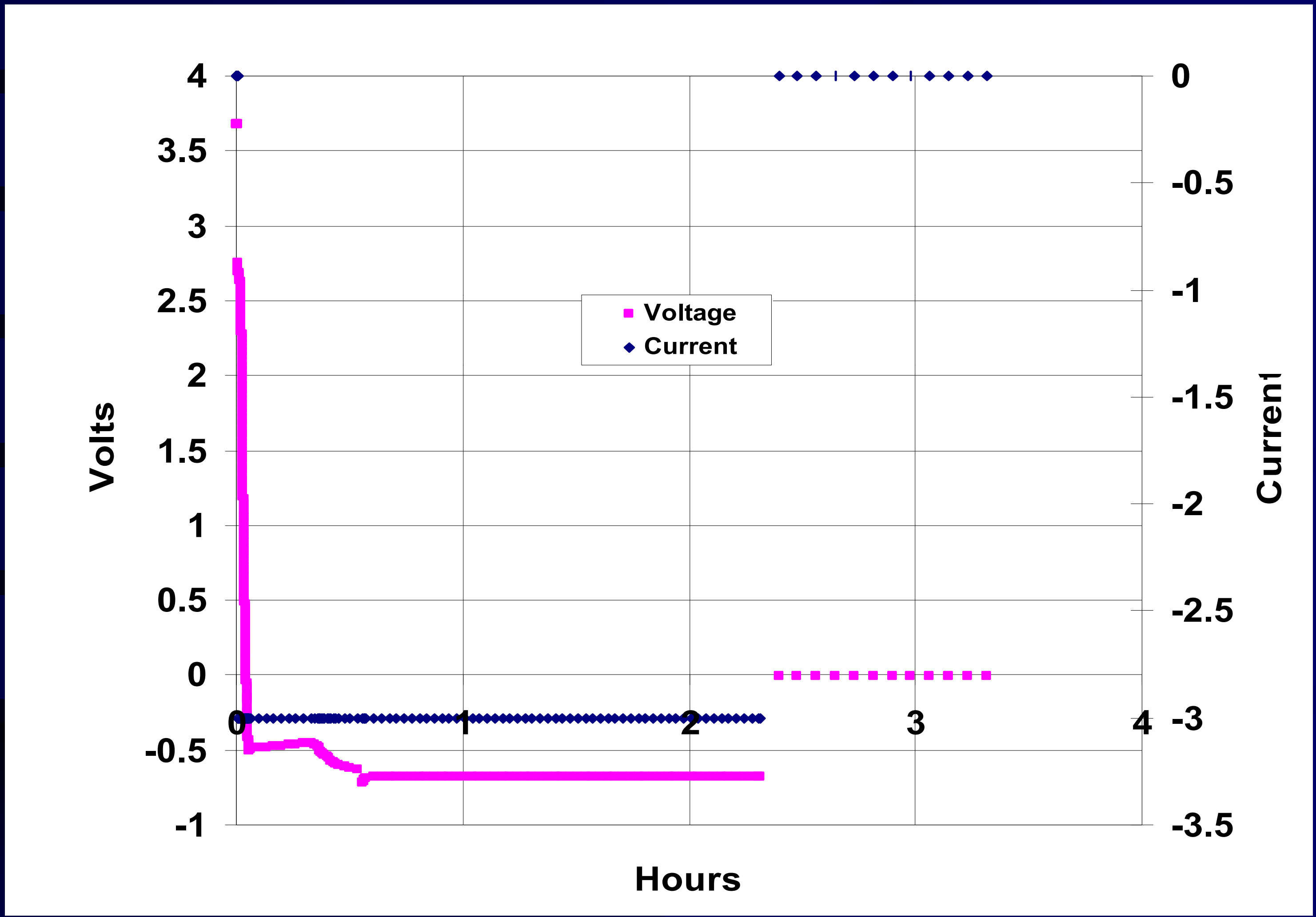
Voltage behavior during 1 A over-discharge with diode at 160 ºF and afterwards without diode at 160 ºF - LTC-111



Voltage behavior during 1 A over-discharge without diode at 160 °F - LTC-114

3 Amps at R.T. Over-Discharge Test Results

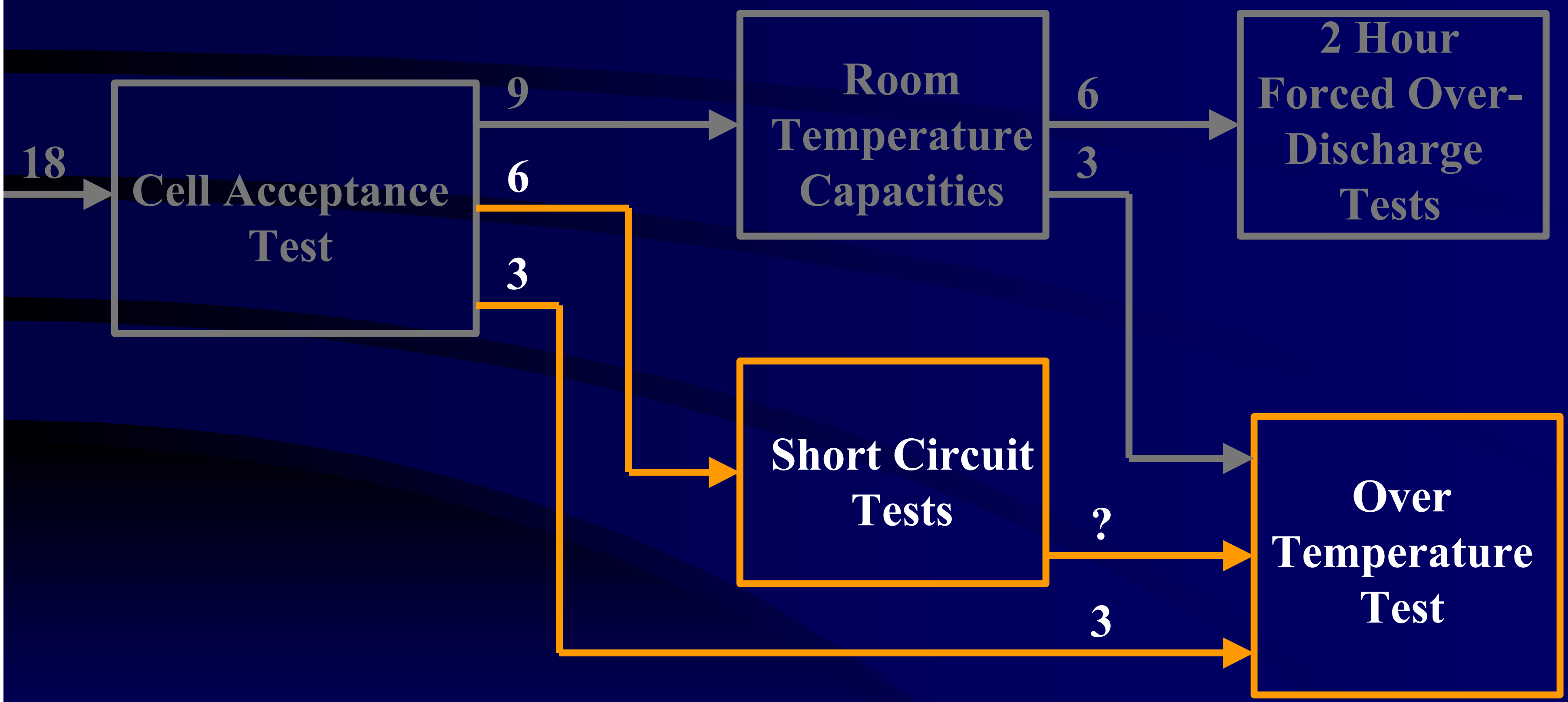
Cell Type	With Diodes
After 50 mA discharge capacity test	
LTC-114	ok
	ok
LTC-111	ok
	ok
LTC-115	ok
	ok
After 500 mA discharge capacity test	
LTC-114	ok
	vented
LTC-111	ok
	ok
LTC-115	ok
	ok



3 Amp Over Discharge Curve (Vented) - LTC-114

LTC-114 Cell Vented during 3A Over-Discharge

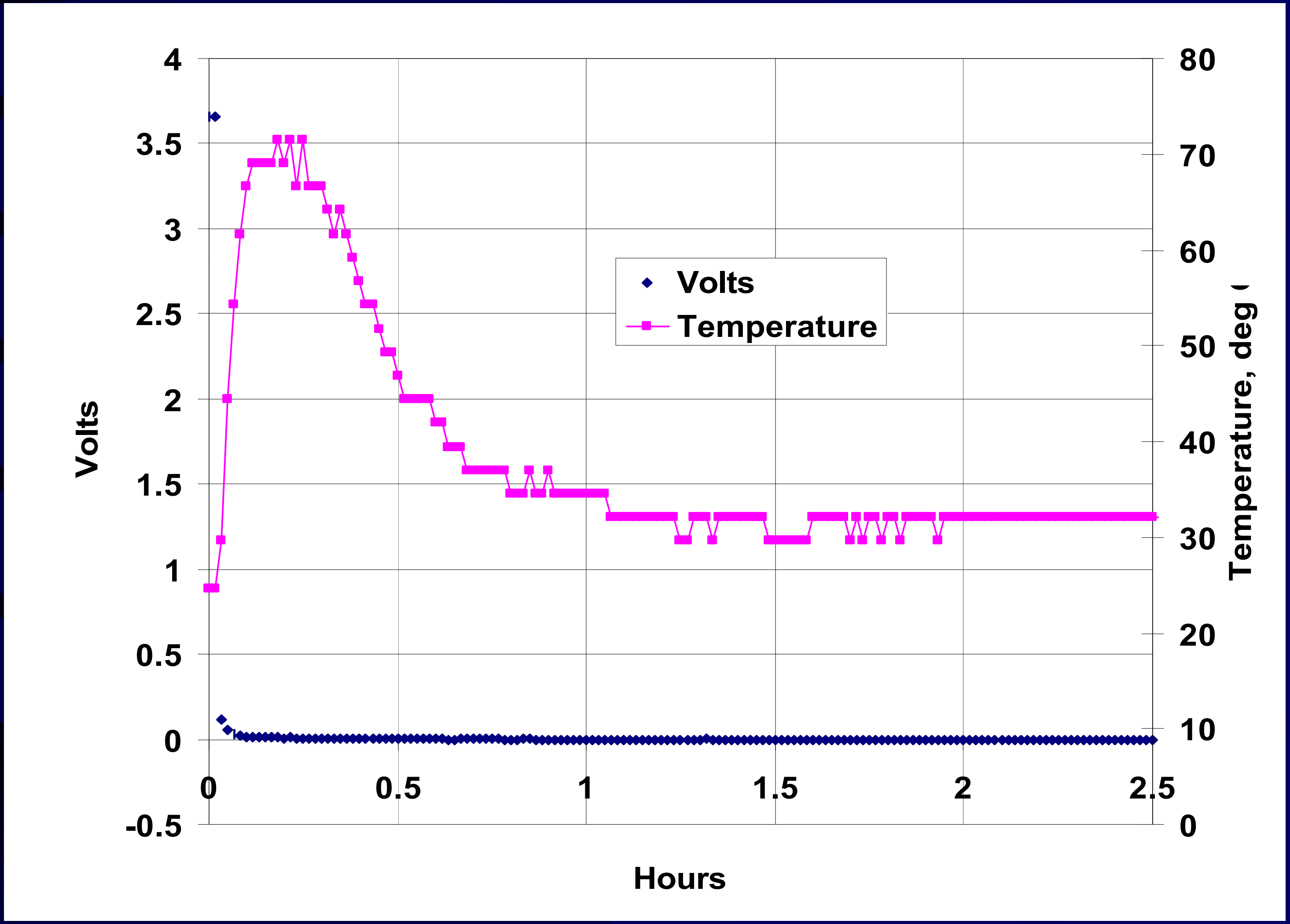
Test Plan (Overview)



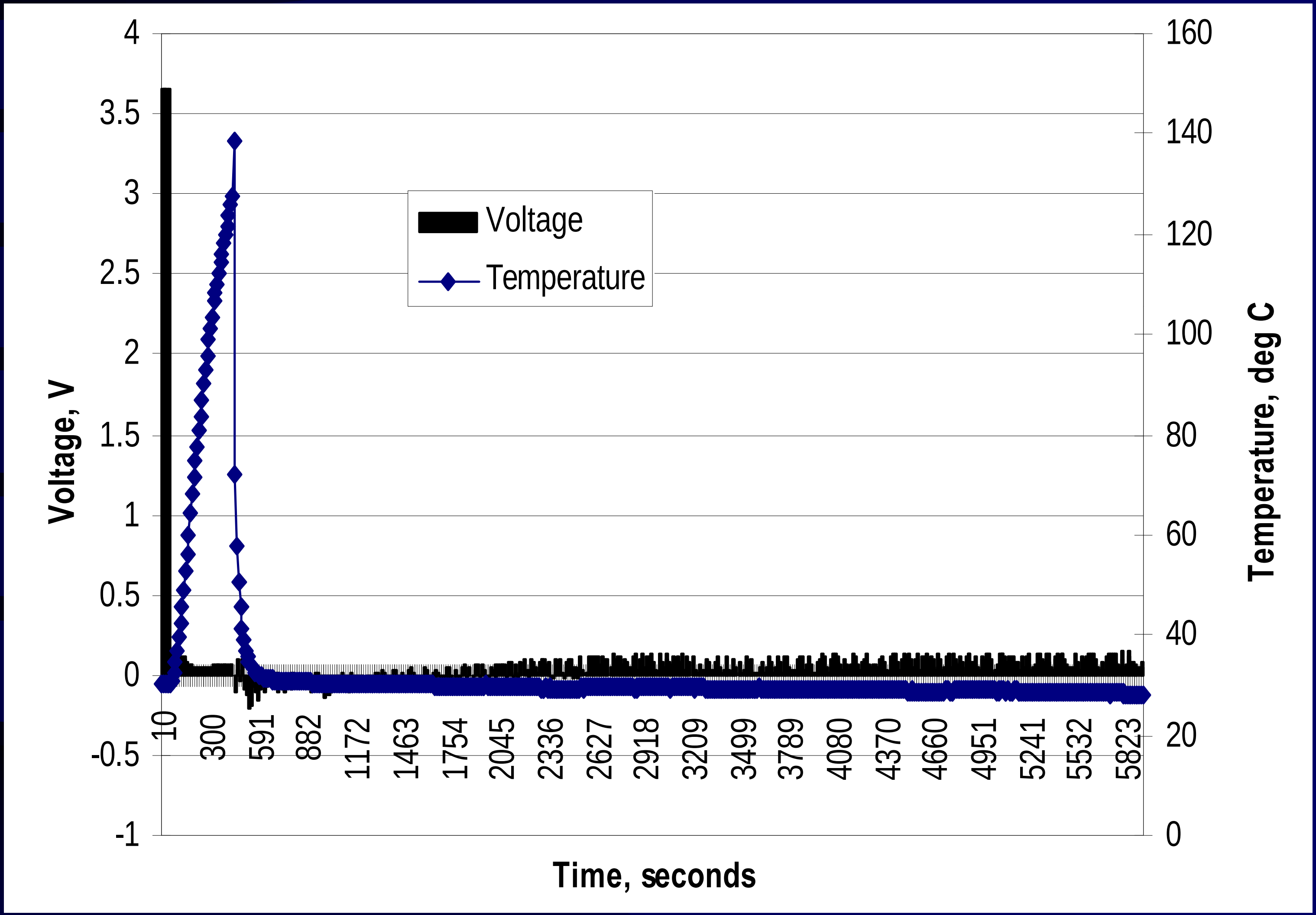
Room Temperature Short Circuit Test Results

Cell Type	0.050 Ohm short	1 Ohm short
LTC-114	Ok - Cell open in 20 min.	Cell open in 1 hour
	Ok - Cell open in 15 min.	Cell open in 1 hour
	Ok - Cell open in 20 min.	Cell open in 1 hour
LTC-111	Exploded	Ok - No Mishaps
	Leaked	Ok - No Mishaps
	Exploded	Ok - No Mishaps
LTC-115	Cell open immediately	Cell open in 1 hour
	Cell open immediately	Cell open in 1 hour
	Cell open immediately	Cell open in 1 hour

Note: Cells with 'Ok' went on to the Over Temperature Test



Typical Short Circuit (50 mΩ) Curve - LTC-114



Typical Short Circuit (50 mΩ) Curve - LTC-111

Over Temperature Test Results

Condition	Samples	Status
After 1 A Discharge Capacity Test	LTC-114	Ok up to 120 ºC
		Ok up to 120 ºC
		Ok up to 120 ºC
	LTC-111	Vented at ~115 ºC
		Vented at ~116 ºC
		Vented at ~120 ºC
	LTC-115	Ok up to 120 ºC
		Ok up to 120 ºC
Short Circuit Test Survivors	LTC-114	Ok up to 120 ºC
		Ok up to 120 ºC
		Ok up to 120 ºC
	LTC-111	Vented at ~100 ºC
		Vented at ~100 ºC
		Vented at ~100 ºC
	LTC-115	Not tested - All Cells Open Circuit
Fresh Cells	LTC-114	Vented at ~170 ºC
		Vented at ~170 ºC
	LTC-111	Ok up to 170 ºC
		Ok up to 170 ºC
		Ok up to 170 ºC
	LTC-115	Vented at ~120 ºC

Conclusions

- Cells passed most of the acceptance test including consistent Voc of 3.65V and no mishaps during 2 hour 160 ^{o}F thermal exposure. However, all cells failed minimum loaded voltage under the 5 Ohm load test probably due to their 5 year storage conditions.
- The medium rate LTC-111 demonstrated very good discharge rate capability. The low rate LTC114 'D' and the medium rate LTC-115 'sub D' both showed significant capacity loss at high discharge rates of 500 mA and greater.
- The medium rate LTC-115 'sub D' had 5% capacity dispersion at 50 mA discharge, while the LTC-111 had 0.2% and the LTC-114 had 0.4% capacity dispersion.
- The medium rate LTC-111 tend to explode or leak when force over-discharged at 160 ^{o}F following high rate discharge of 500 mA. The LTC-114 and LTC115 both survived 1 Amp over-discharge with and without diodes for 16 hours.

Conclusions

- Most cells survived the 3 A over-discharge at room temperature for 2 hours. The cell that failed was the LTC-114 after high rate discharge of 500 mA similar to the results of the 1 A over-discharge test.
- Most cells opened during 0.05 Ohm short circuit test without incident but three LTC-111cells exploded apparently due to a lack of a thermal cutoff switch. The LTC-114 cells exposed to a hard short of 0.05 Ohms recovered but the LTC-114 cells exposed to a soft short of 1 Ohm did not. This is probably due to the activation of a resetable fuse during a hard short.
- Fresh cells tend to survive exposure to higher temperatures than cells previously discharged at high rate (1 Amp). LTC-111 cells tend to vent at lower temperatures than the all LTC-114 cells and the LTC-115 cells that were previously discharged at rates exceeding 1 Amp.

Acknowledgements

NASA Johnson Space Center - Funding for this investigation under Program NASA/T-4551 W

Simulated LEO Cycling of AEA-STRV Lithium-Ion Battery Modules

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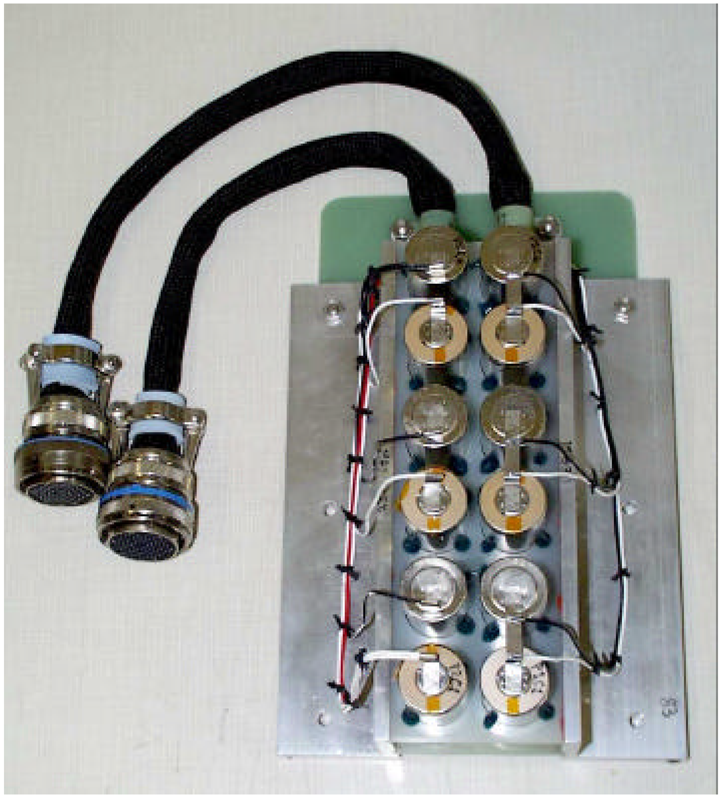
The 2000 NASA Aerospace Battery Workshop
Holiday Inn -- Research Park
Huntsville, Alabama
November 14 - 16, 2000

Scope

- Lithium-ion battery modules, similar to the modules to be flown on the STRV spacecraft, have been on test for almost two years.
- The modules, designed and assembled by AEA Technology plc, each contain twelve Sony 26650 cells.
- Characterization testing and LEO cycling through 2700 25% DOD cycles were reported at this workshop last year.
- This presentation summarizes the results of the simulated LEO cycling to date.

Test Articles



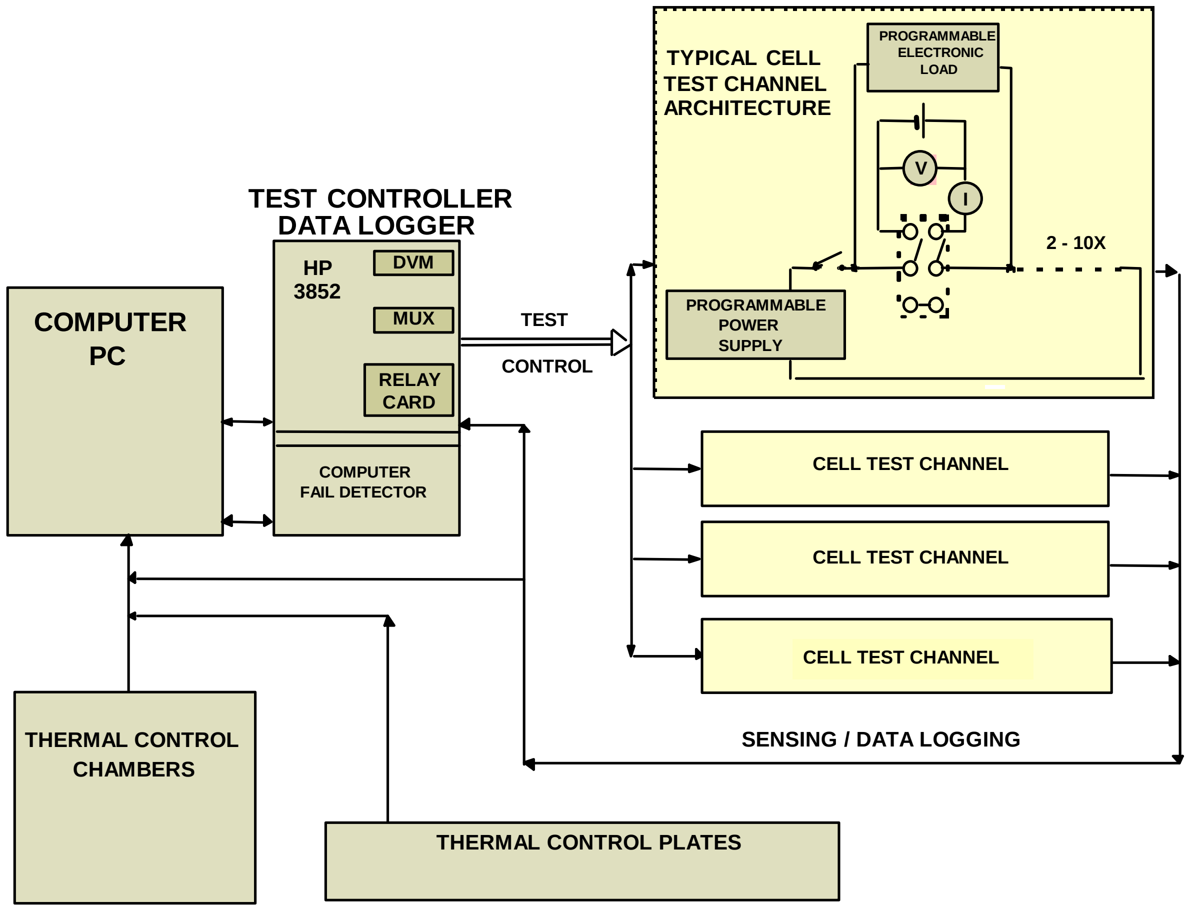
- **STRV modules consist of two 6-cell strings of Sony 26650 cells.**
- **Test modules were reconfigured**
  – **one 6-cell string**
  – **two 2-cell strings**
  – **two individual cells**
- **Each cell is equipped with a thermocouple at its midpoint.**

Test Plan

Simulated Leo Cycling

- Depth of Discharge: 25% (basis 2.7 Ah nameplate capacity)
- Orbit: 100 minutes with 36 minute eclipse periods
- Charge regime: 0.5C to CVL; taper until eclipse discharge
- Charge management: Pack level, e.g.,
  - 6-cell average voltage for the 6-cell packs
  - 2-cell average voltage for the 2-cell packs
  - individual cell control for the single cells
- Discharge: 0.42C (36 minutes)
- Two modules were tested; one at 25°C and one at 15°C

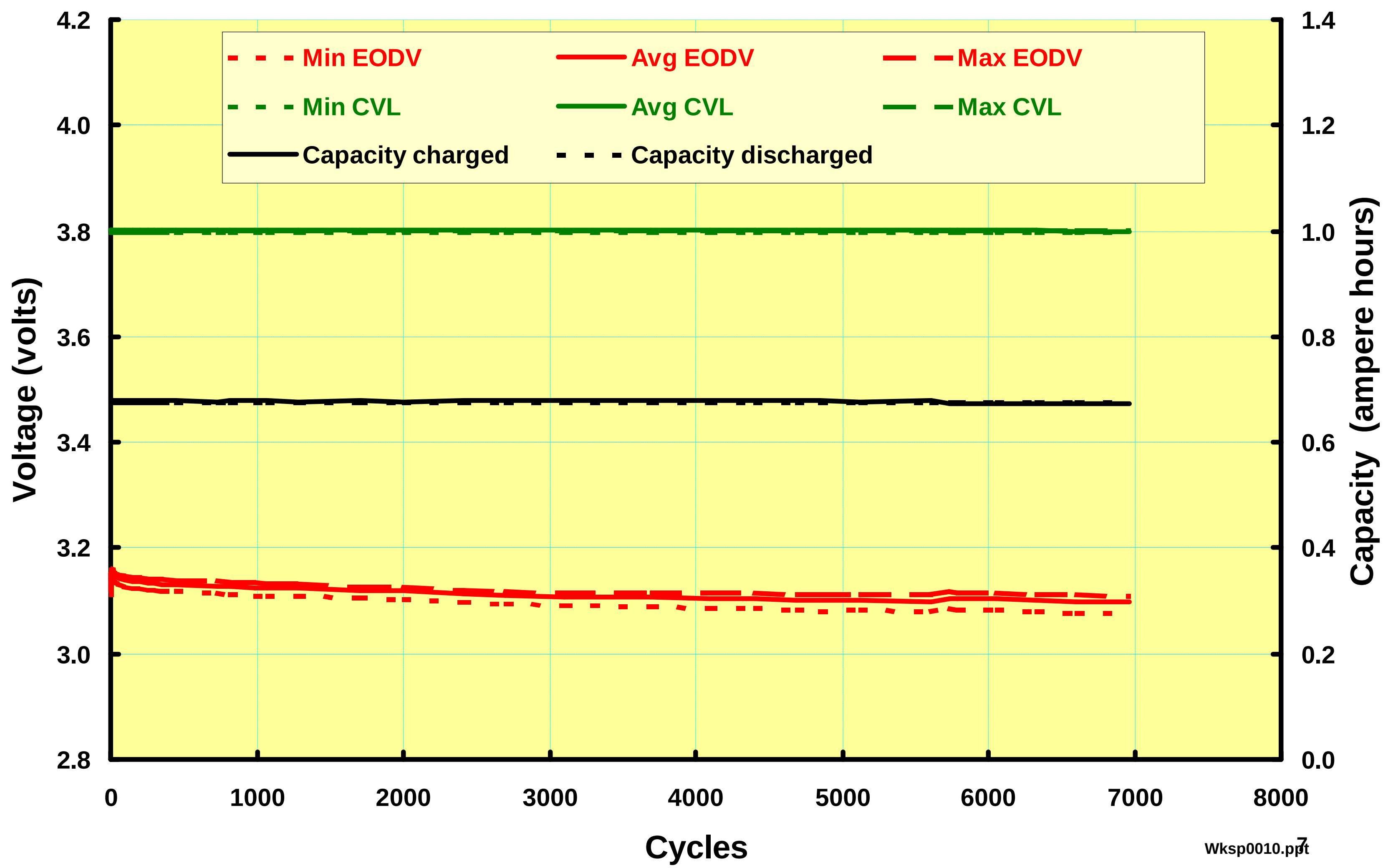
Test Setup


TYPICAL CELL TEST CHANNEL ARCHITECTURE
PROGRAMMABLE ELECTRONIC LOAD
V
I
2 - 10X
PROGRAMMABLE POWER SUPPLY
TEST CONTROLLER DATA LOGGER
HP 3852
DVM
MUX
RELAY CARD
COMPUTER FAIL DETECTOR
COMPUTER PC
TEST
CONTROL
CELL TEST CHANNEL
CELL TEST CHANNEL
CELL TEST CHANNEL
SENSING / DATA LOGGING
THERMAL CONTROL CHAMBERS
THERMAL CONTROL PLATES

Simulated LEO Cycling Results

- 25°C End of Discharge Voltage trend charts
  - 6-cell Pack
  - 2-cell pack (typical of two)
  - single cells (both cells on one plot)
- 15°C End of Discharge Voltage trend charts
  - 6-cell Pack
  - 2-cell pack (typical of two)
  - single cells (both cells on one plot)
- 6-cell pack dispersion analysis
  - EODV Trending
  - Rate of Change of EODV
  - EOCV Trending

25% DOD LEO Cycling at 25 Deg C -- 6-Cell Pack



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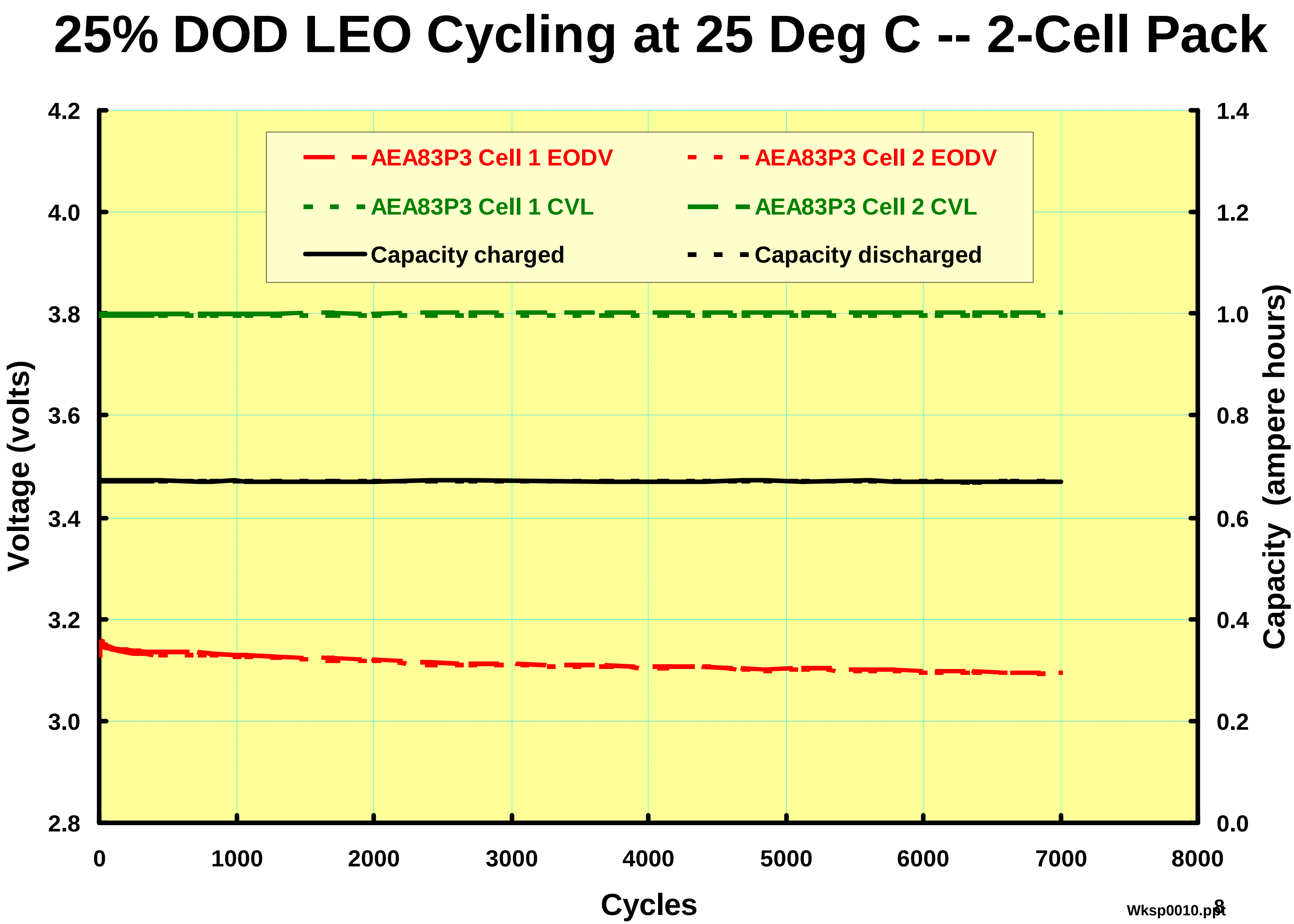
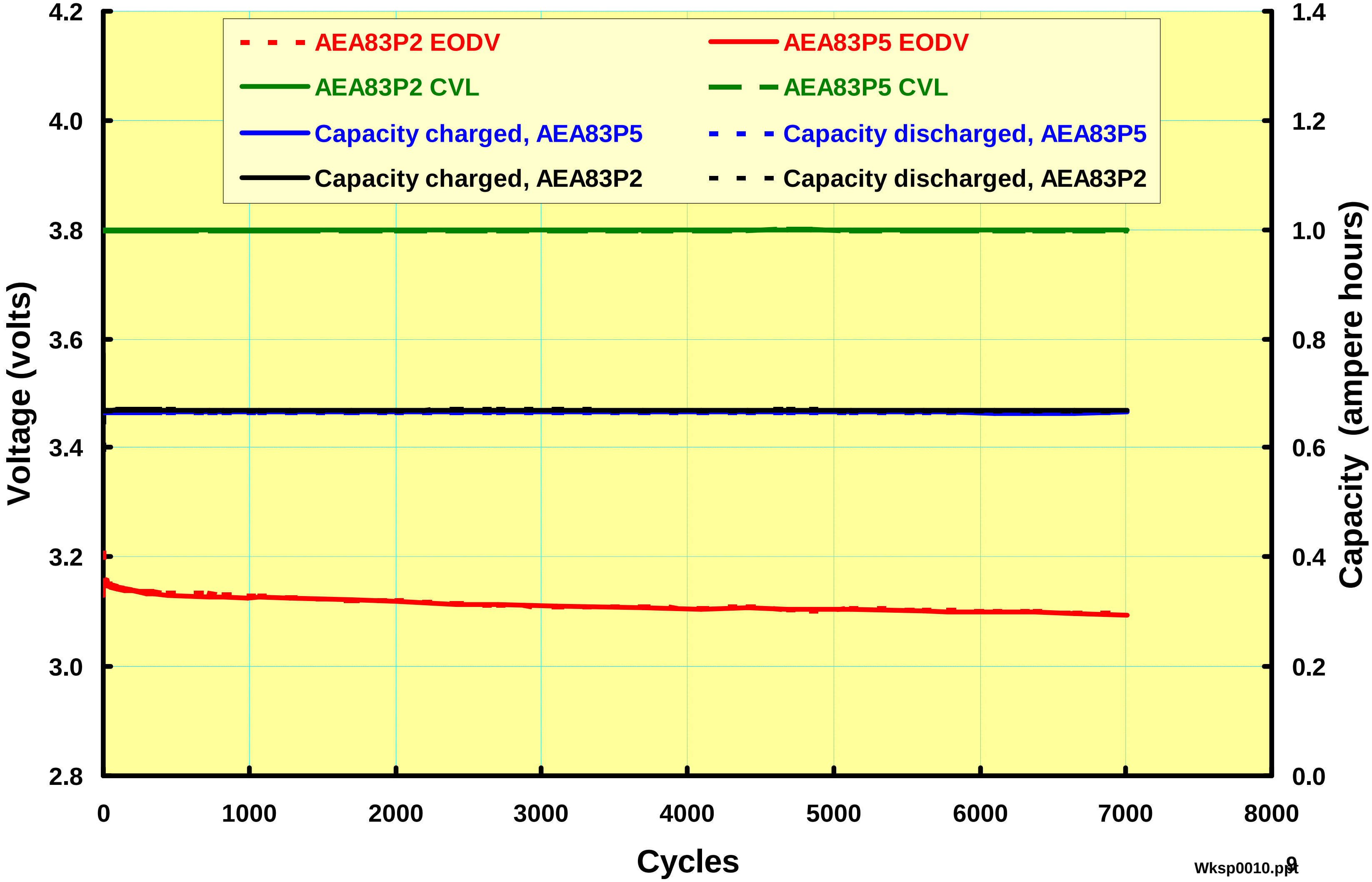

25% DOD LEO Cycling at 25 Deg C -- 2-Cell Pack
AEA83P3 Cell 1 EODV
AEA83P3 Cell 2 EODV
AEA83P3 Cell 1 CVL
AEA83P3 Cell 2 CVL
Capacity charged
Capacity discharged
Voltage (volts)
Capacity (ampere hours)
Cycles
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
6000
7000
8000

25% DOD LEO Cycling at 25 Deg C -- Single Cells



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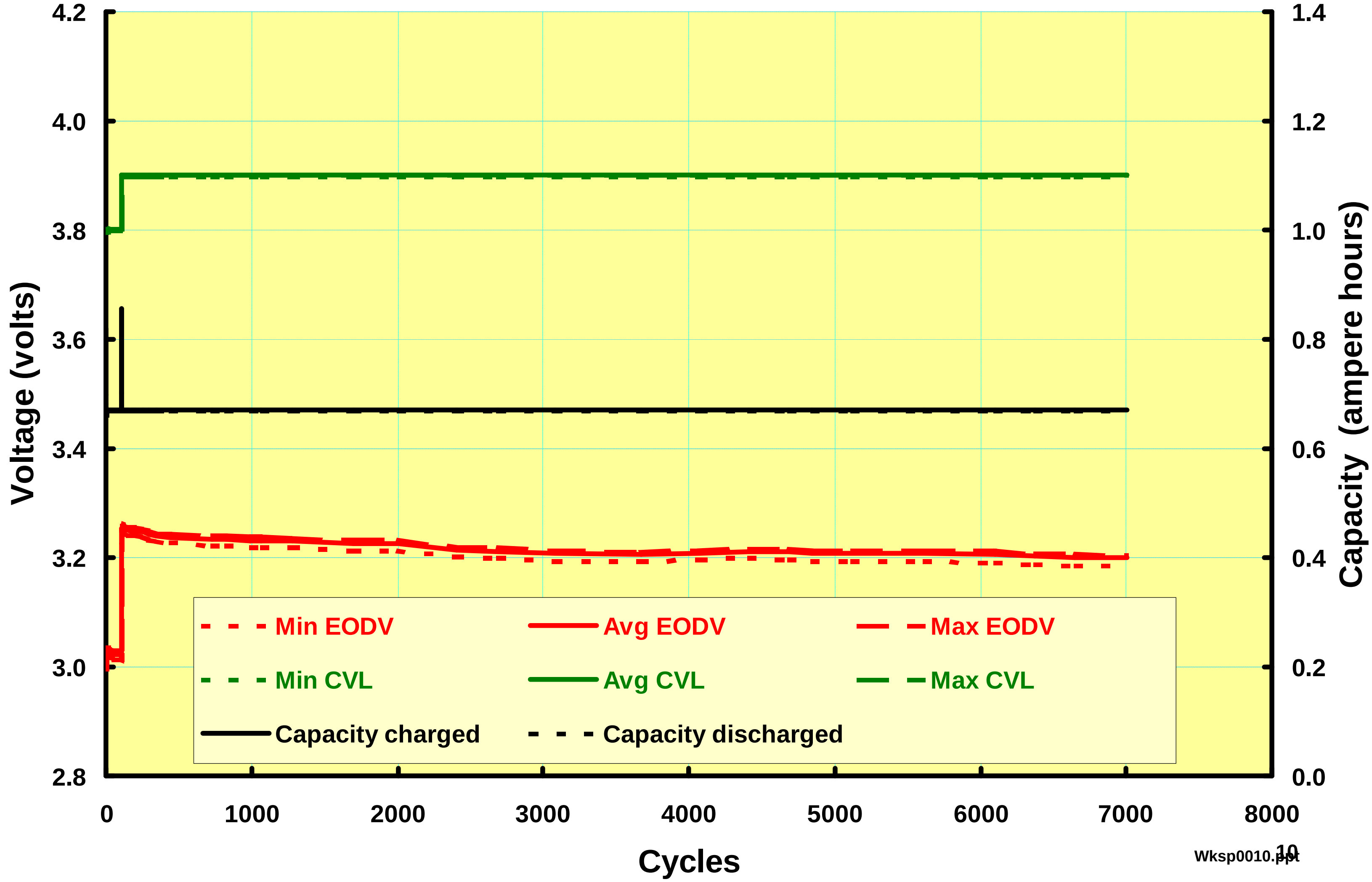
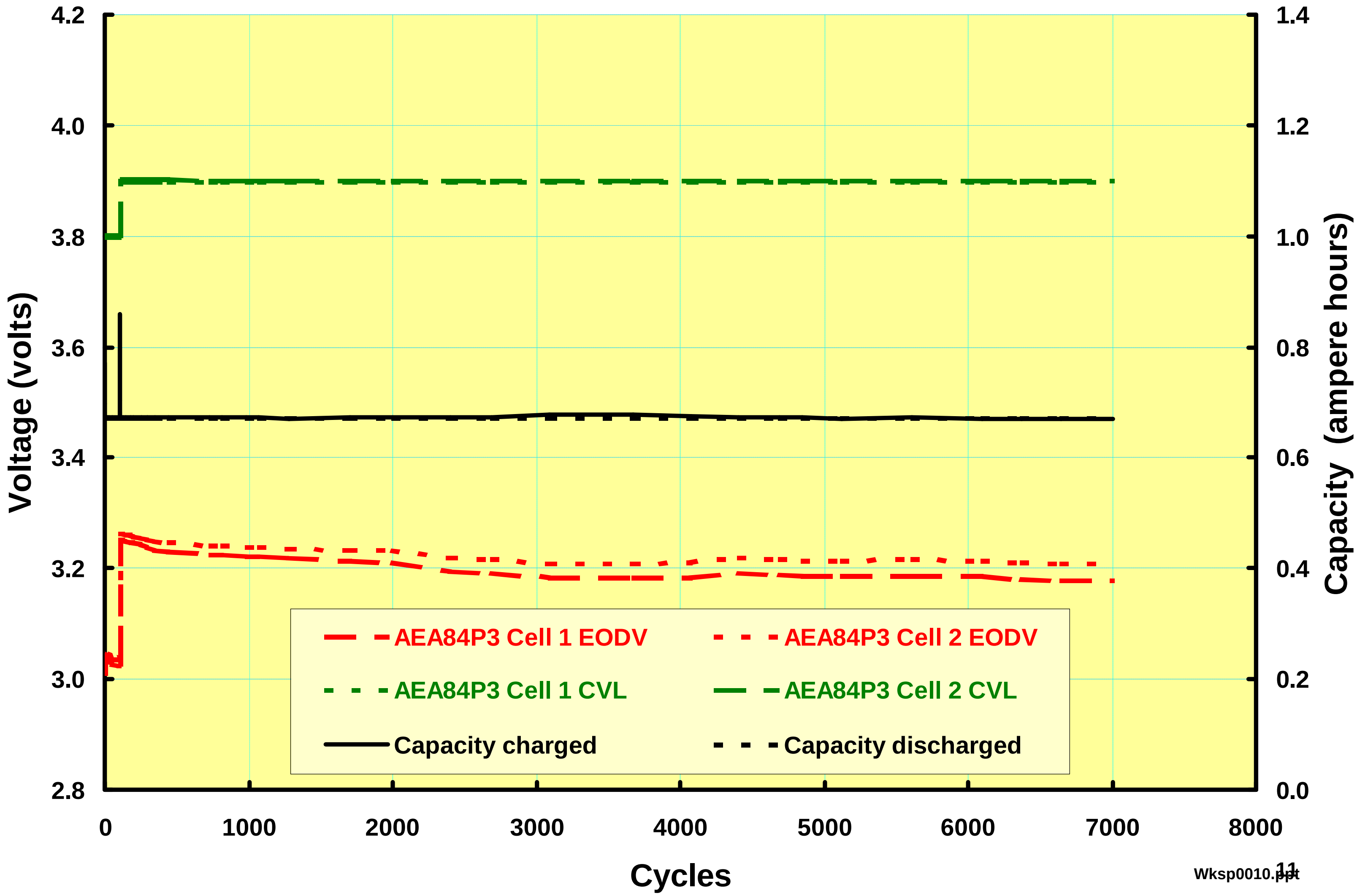
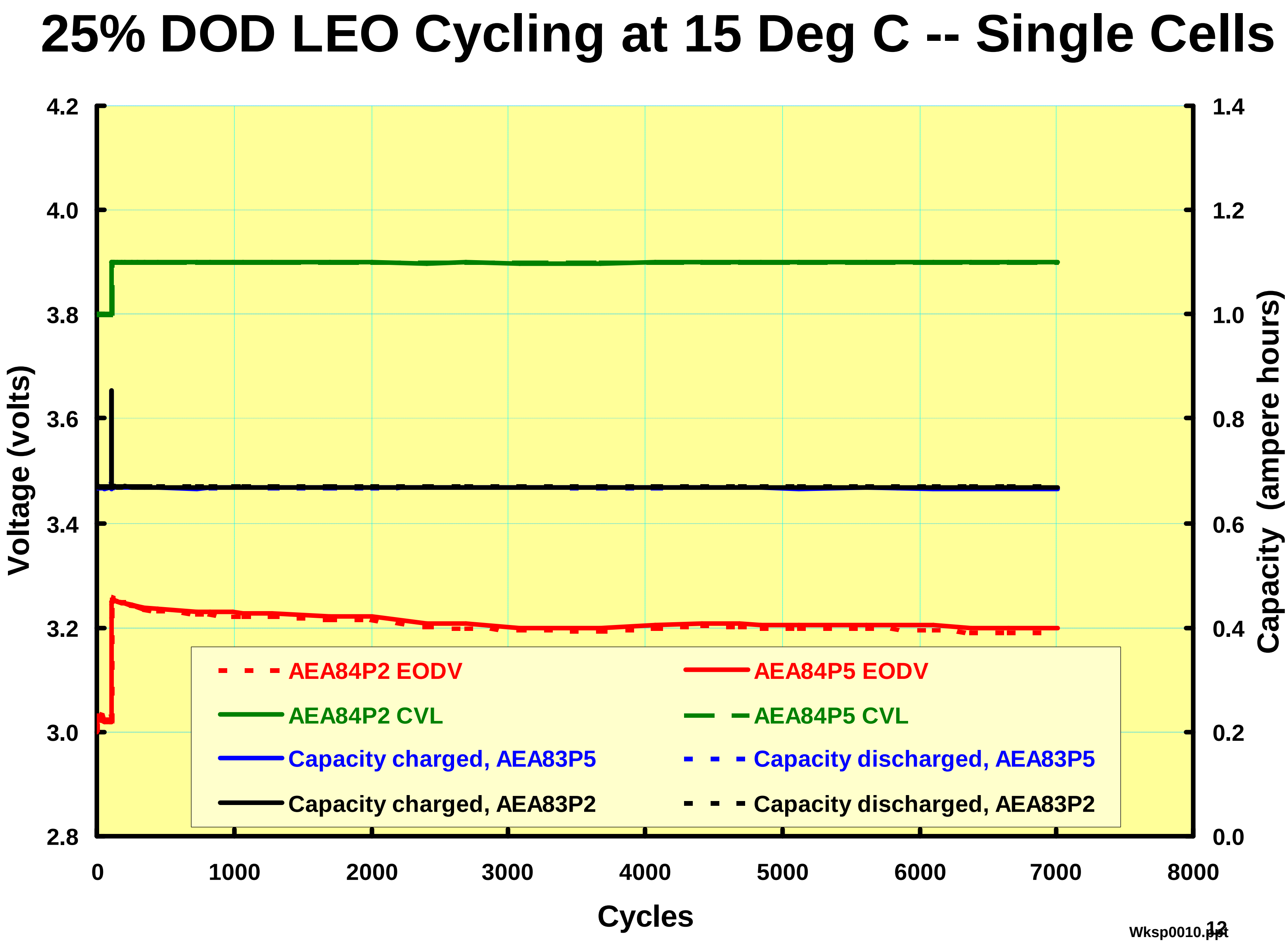
25% DOD LEO Cycling at 15 Deg C -- 6-Cell Pack



Wksp0010.ppt

25% DOD LEO Cycling at 15 Deg C -- 2-Cell Pack





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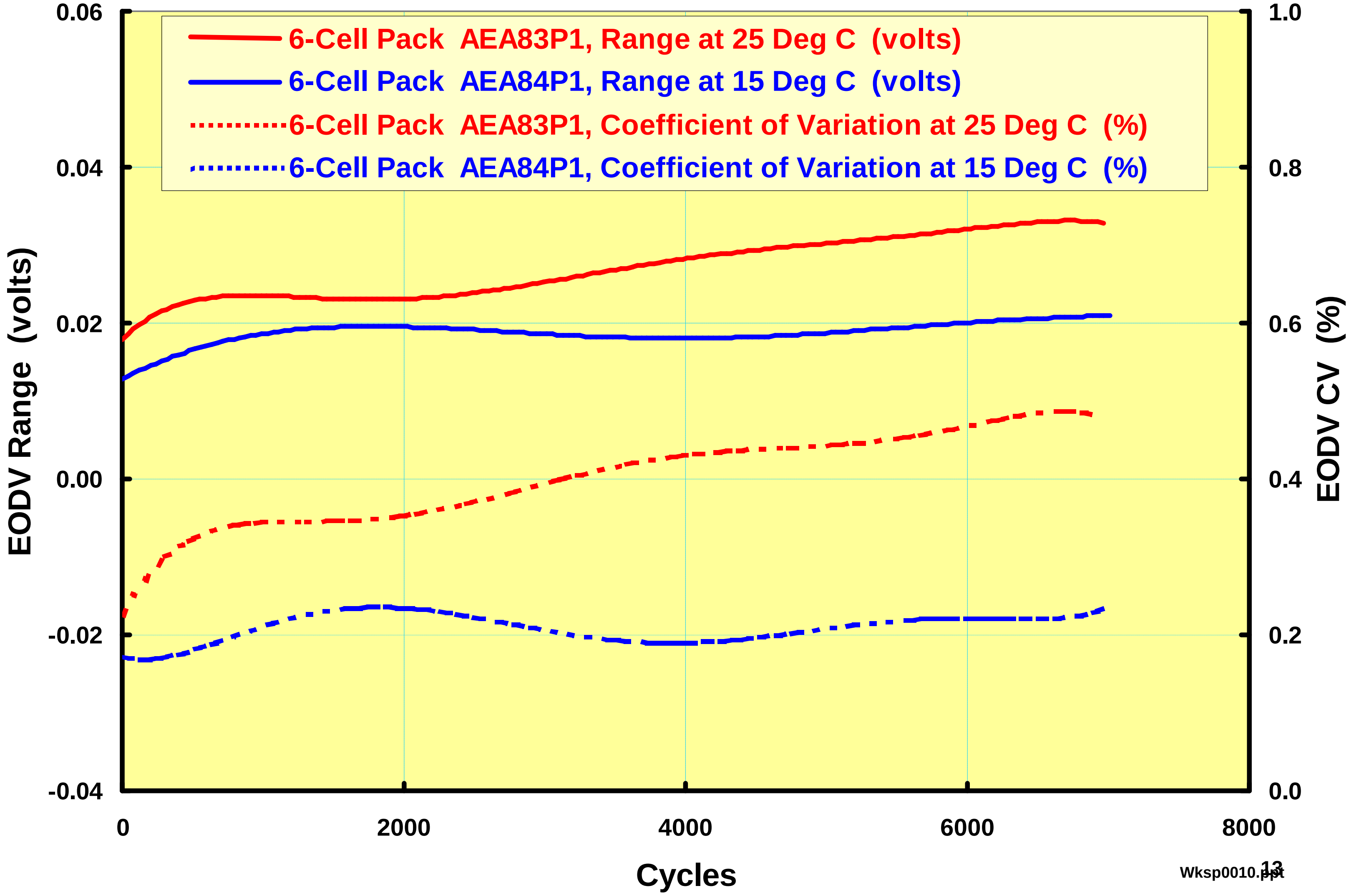
EODV Dispersion Trending

AEA STRV 6-Cell Packs at 15ºC and 25ºC



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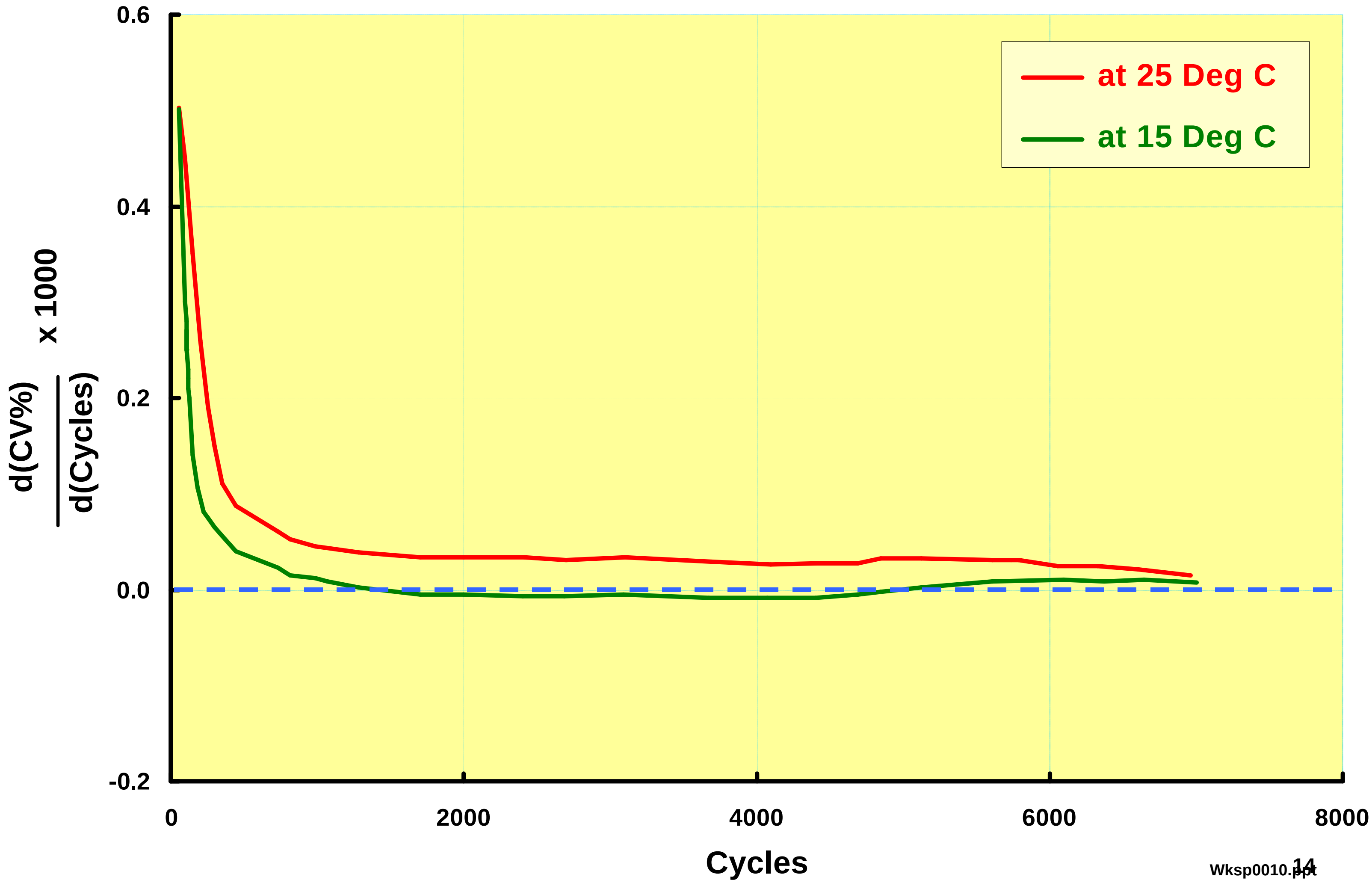
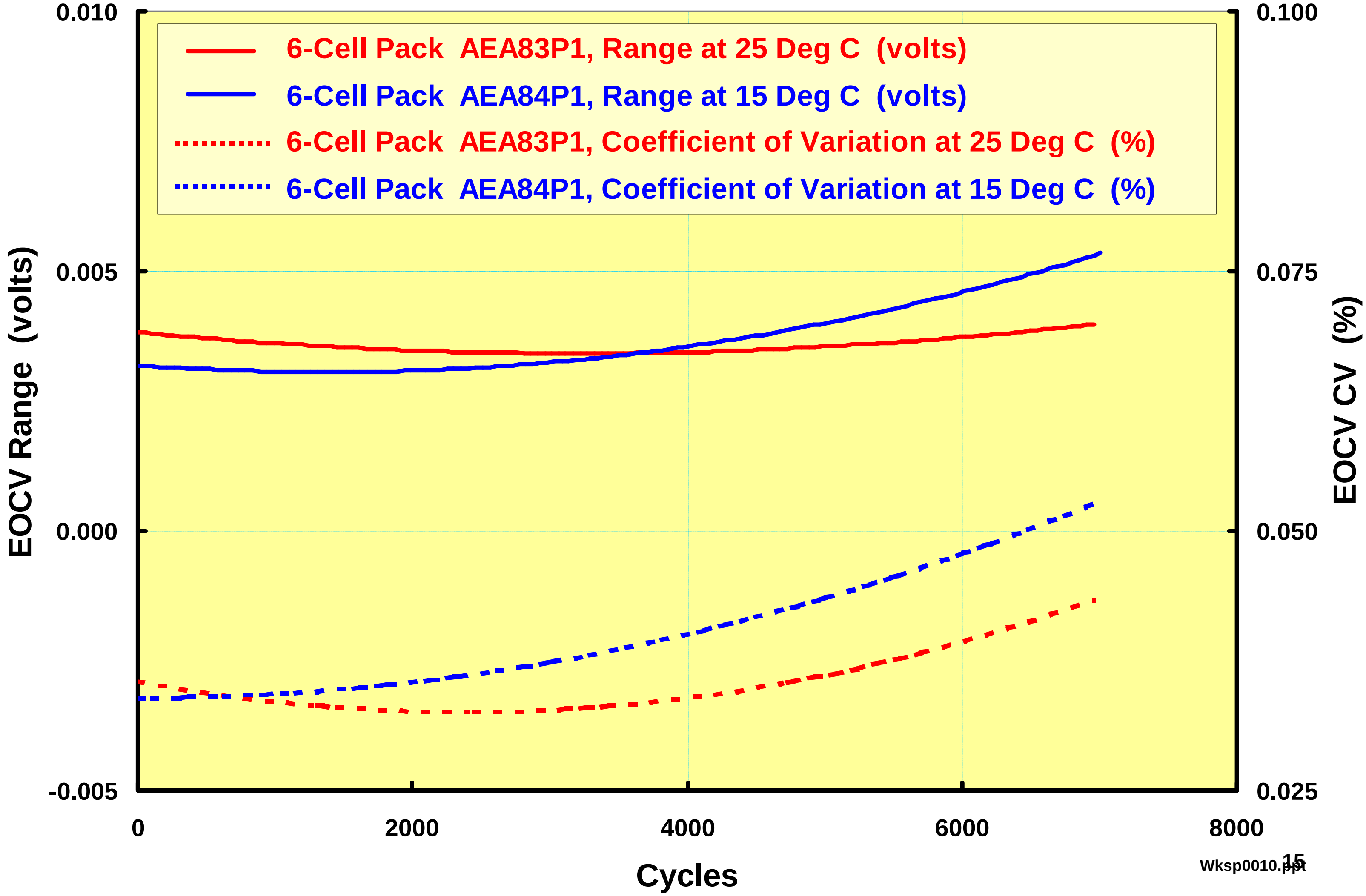
Rate of Change of EODV Dispersion as a Function of Cycling

AEA STRV 6-Cell Packs



EOCV Dispersion Trending

AEA STRV 6-Cell Packs at 15ºC and 25ºC



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Summary

- Simulated 25% DOD LEO cycling of AEA STRV battery modules is continuing at 15ºC and 25ºC
  - The STRV "two 6-cell strings" configuration was modified to provide 6-cell strings, 2-cell strings and individual cells.
  - Charge control is at the pack level.
- 7700 cycles have been completed without incident.
- EODV voltage dispersion (in the absence of cell level balancing) is stable at 15ºC and increasing slightly at 25ºC.
- The test is continuing.

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Technologies, LLC

Progress Toward a Li-ion Spacecraft Battery

CHAD KELLY & JAMES DeGRUSON

15 NOVEMBER 2000

NASA AEROSPACE BATTERY WORKSHOP

EAGLE PICHER Technologies, LLC

PROGRESS Late 99'

✦**Specific Energy**

- 100 Wh/Kg in 1999

✦**Energy Density**

- 300 Wh/L in 1999

✦**Impedance (SLC-16002)**

- 3.5 milliohms in 1999

✦**Temperature Capability**

- 10% @ C/5 @ -30^{o}C in 1999

✦**Cycle Life**

✦**LEO 25% from 100%SOC**

- 2700 completed 1999

✦**GEO Battery**

- 36 Abb. GEO in 1999

✦**Rate Capability**

- C Max in 1999

PROGRESS
Late 99' and 2000'

EAGLE PICHER Technologies, LLC

✦**Specific Energy**

- 100 Wh/Kg in 1999
- >150 Wh/Kg in 2000

✦**Energy Density**

- 300 Wh/L in 1999
- >380 Wh/L in 2000

✦**Impedance (SLC-16002)**

- 3.5 milliohms in 1999
- 1.4 milliohms in 2000

✦**Temperature Capability**

- 10% @ C/5 @ -30^{o}C in 1999
- >75% @ 0.6C -30^{o}C in 2000

✦**Cycle Life**

✦**LEO 25% from 100%SOC**

- 2700 completed 1999
- 13000 projected 2000

✦**GEO Battery**

- 36 Abb. GEO in 1999
- 101 Abb. GEO in 2000
- >808 Battery Cycles W/o Electronics

✦**Rate Capability**

- C Max in 1999
- 3.3C Tested in 2000

EAGLE PICHER Technologies, LLC

Characteristics of the SLC-16002 Cell Design

	98/99’
Size	3”x7.15”x0.94”
Mass	840g
Ah	20Ah@10A 24Ah BOL
Wh/Kg	>100Wh/Kg
Rate Capability	20A Max 12Ah Delivered

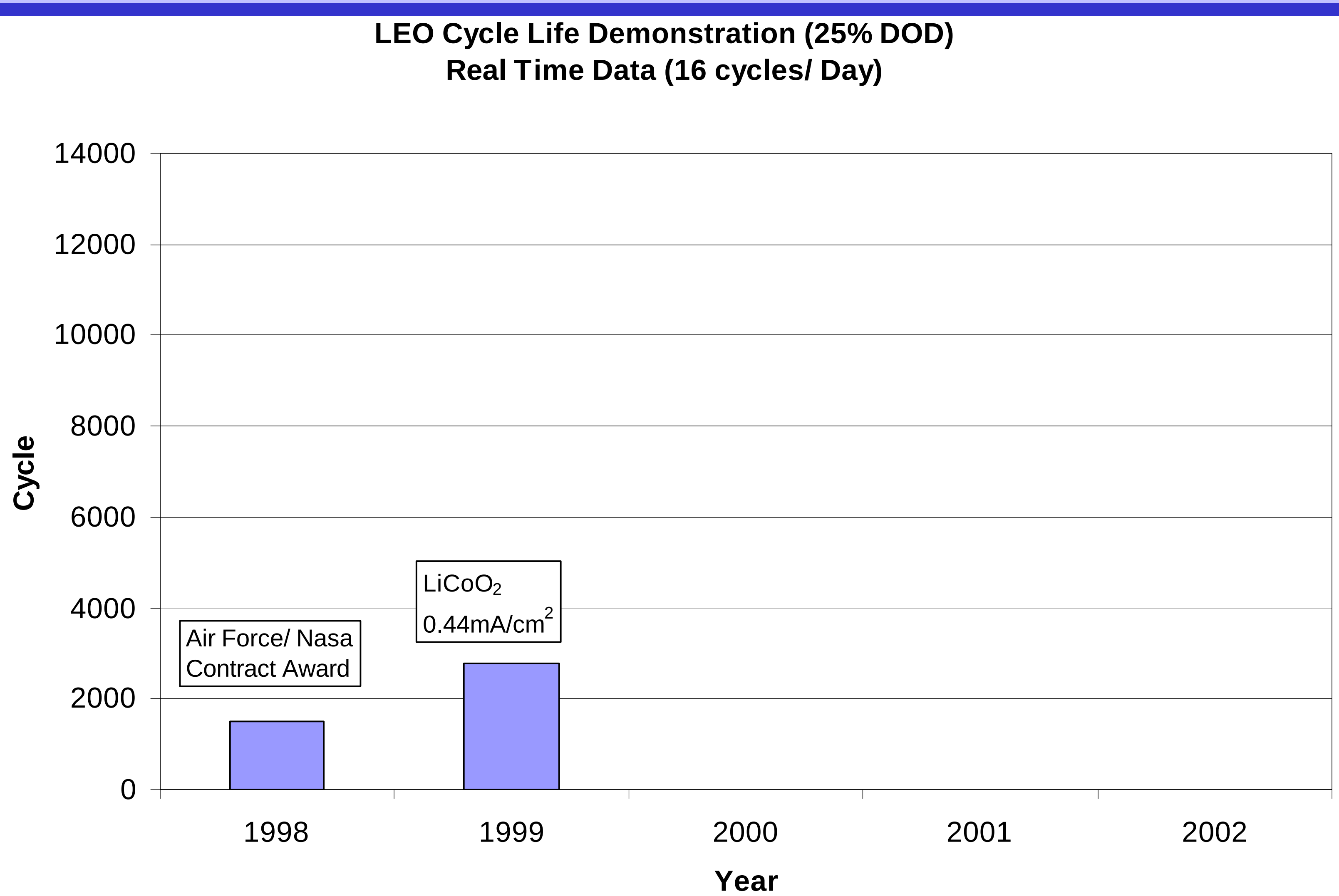
EAGLE PICHER Technologies, LLC

Characteristics of the SLC-16002 Cell Design

	98/99’	2000’
Size	3”x7.15”x0.94”	3”x7.15”x0.94”
Mass	840g	815g
Ah	20Ah@10A 24Ah BOL	35Ah@35A 38Ah BOL
Wh/Kg	>100Wh/Kg	>150Wh/Kg
Rate Capability	20A Max 12Ah Delivered	117A Tested 12Ah Delivered

EAGLE PICHER Technologies, LLC

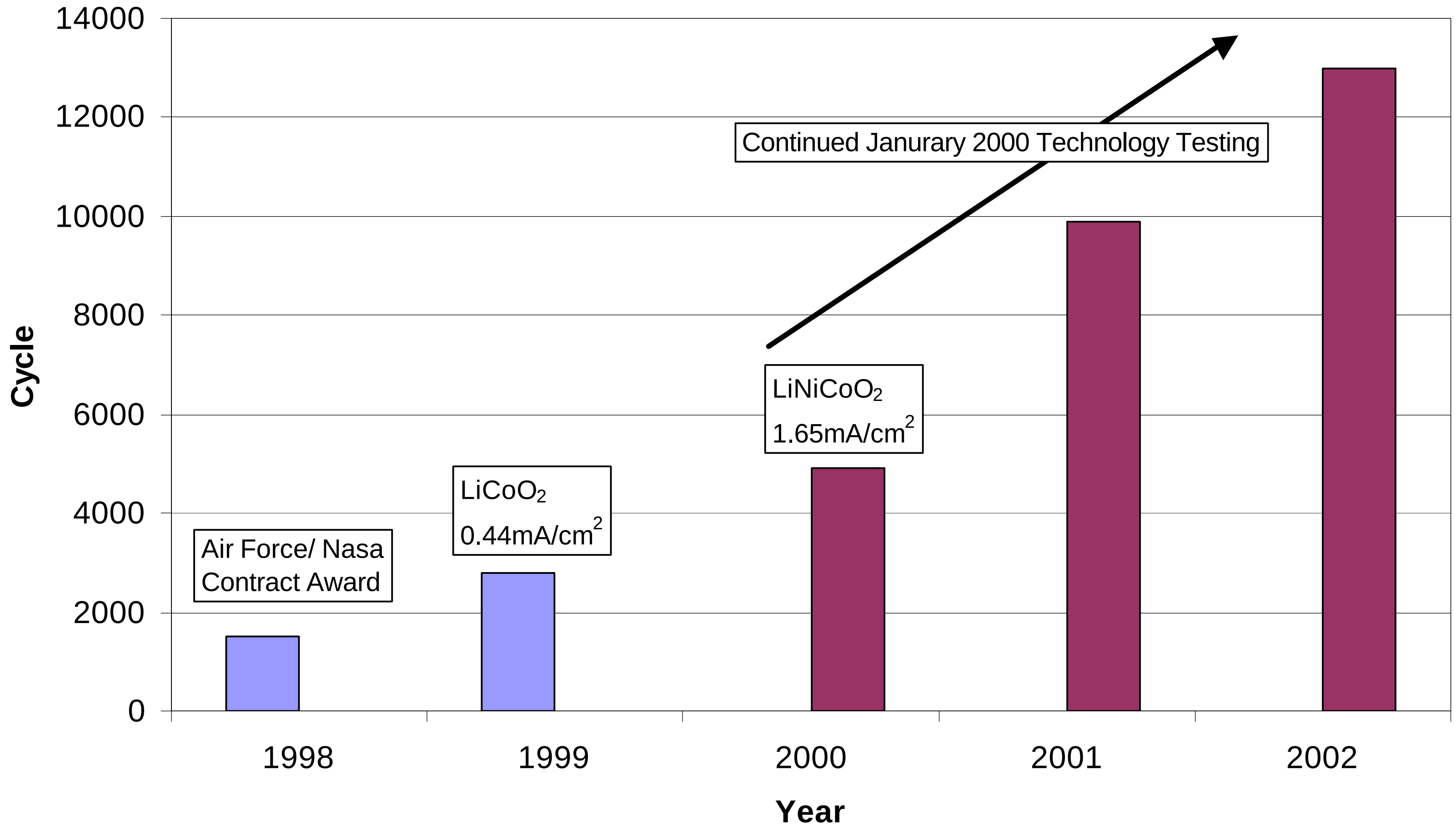
PROGRESS SINCE INCEPTION OF USG CONTRACT



Technologies, LLC

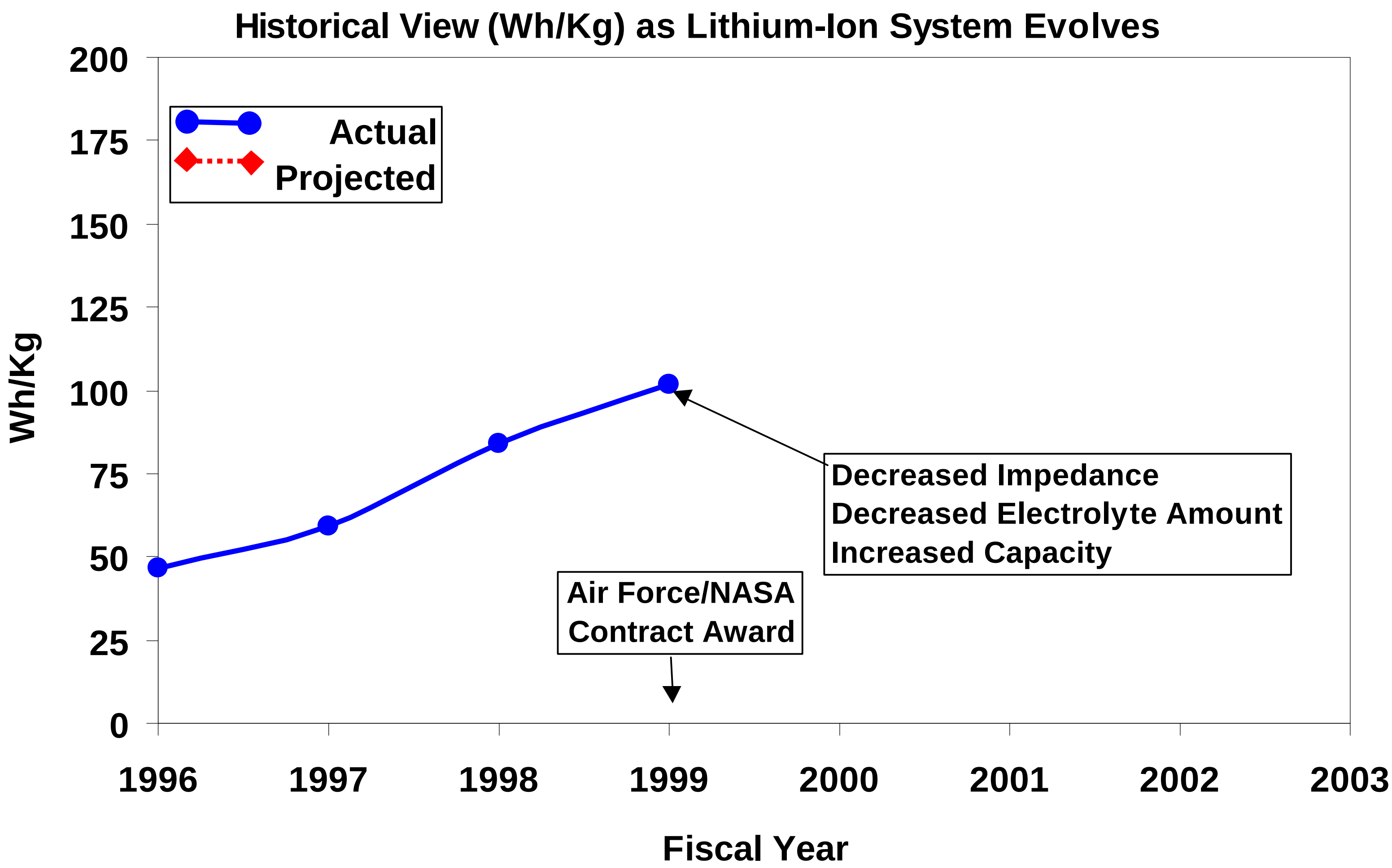
PROGRESS SINCE INCEPTION OF USG CONTRACT

LEO Cycle Life Demonstration (25% DOD)
Real Time Data (16 cycles/ Day)



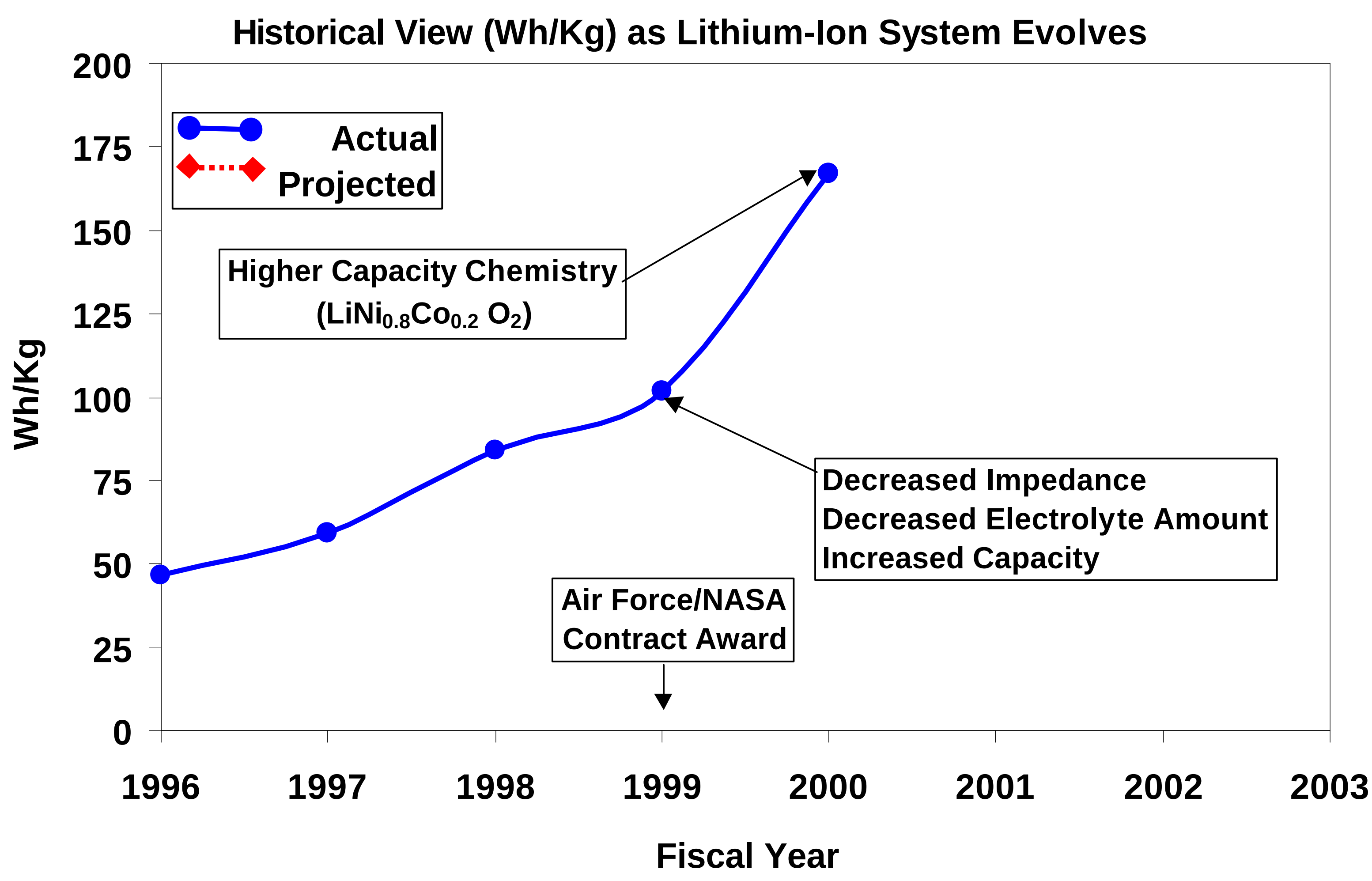
Eagle Picher Technologies, LLC

PROGRESS SINCE INCEPTION OF CONTRACT



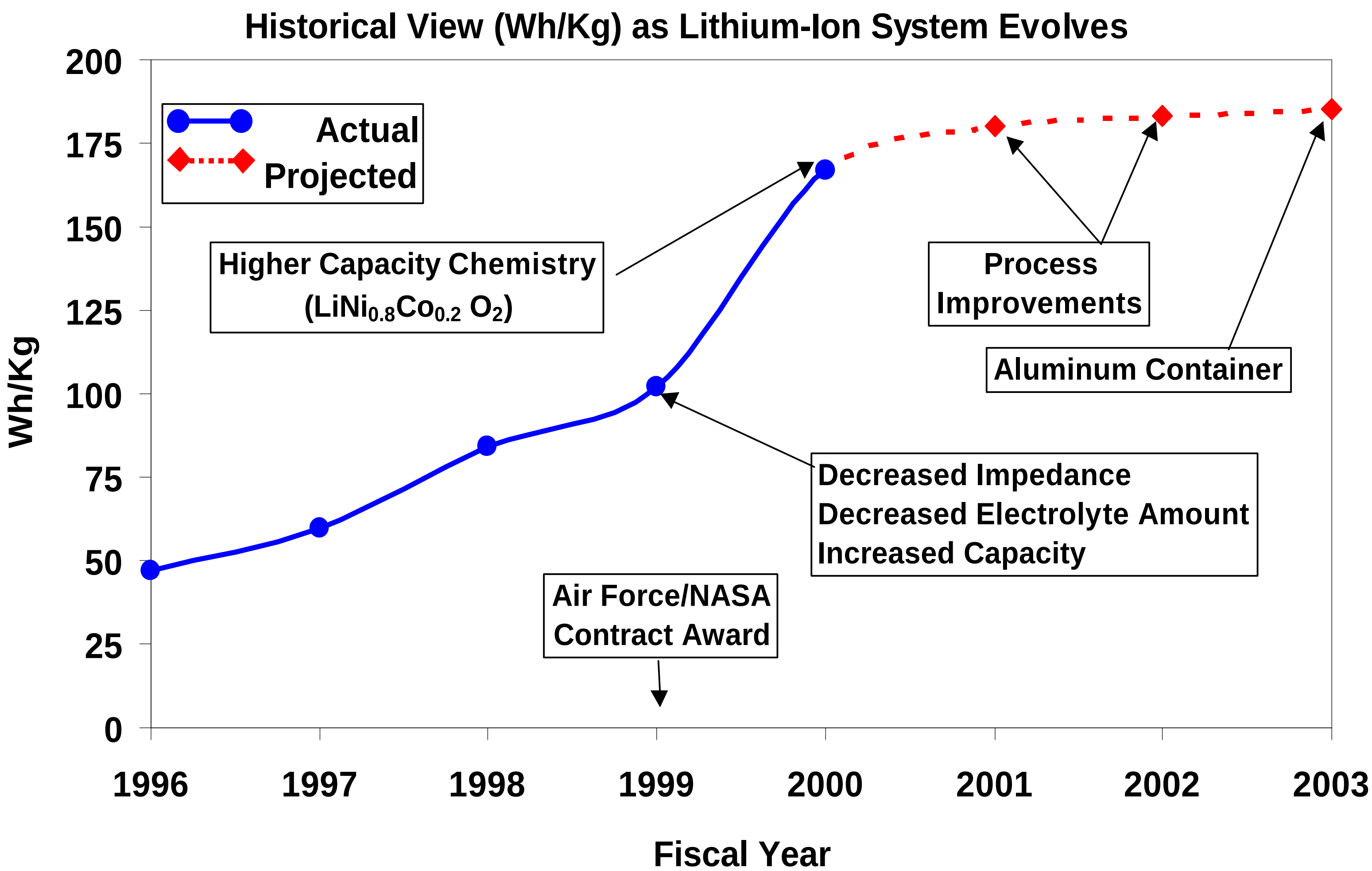
EAGLE PICHER Technologies, LLC

PROGRESS SINCE INCEPTION OF CONTRACT



Eagle Picher Technologies, LLC

PROGRESS SINCE INCEPTION OF CONTRACT



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CELL EVALUATION

Rate/Temperature Tests

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **PURPOSE: DETERMINE DISCHARGE CHARACTERISTICS OF "NEW" CHEMISTRY**
  - **CHARGE RATE EFFECTS**
  - **DISCHARGE RATE EFFECTS**
  - **TEMPERATURE EFFECTS**
    - CELL DISCHARGE CAPACITY (AHRS)
    - CELL DISCHARGE ENERGY (WHRS)
    - CELL ENERGY DENSITY (WHRS/KG)

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **PURPOSE: DETERMINE DISCHARGE CHARACTERISTICS OF "NEW" CHEMISTRY**
  - **CHARGE RATE EFFECTS**
  - **DISCHARGE RATE EFFECTS**
  - **TEMPERATURE EFFECTS**
    - CELL DISCHARGE CAPACITY (AHRS)
    - CELL DISCHARGE ENERGY (WHRS)
    - CELL ENERGY DENSITY (WHRS/KG)
  - **TEST RATES EXPRESSED IN mA/cm^2 OF CATHODE SURFACE AREA**
    - ALLOWS RESULTS TO BE "SCALED" FOR OTHER PRISMATIC CELL DESIGNS

EAGLE PICHER Technologies, LLC

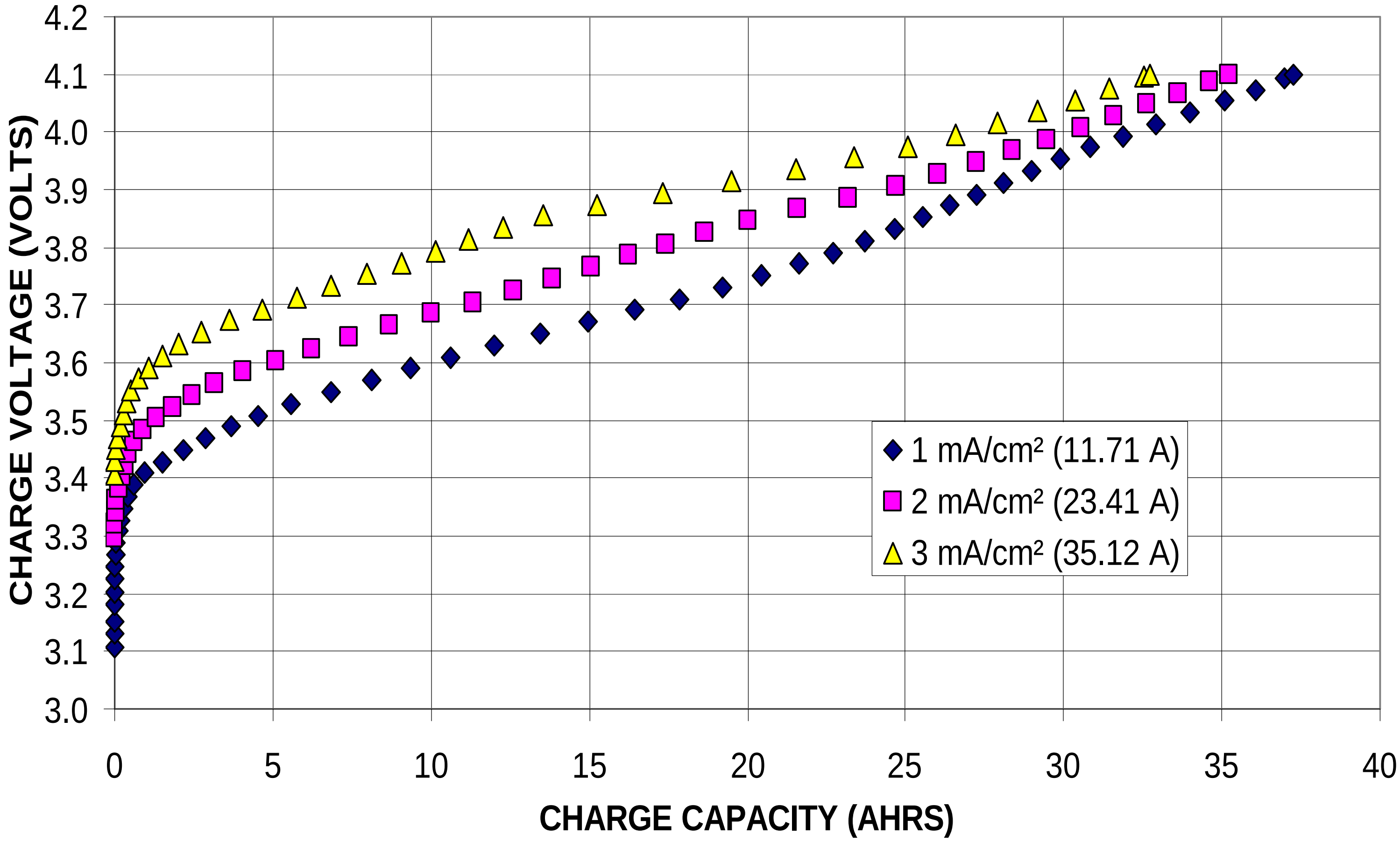
SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **PURPOSE: DETERMINE DISCHARGE CHARACTERISTICS OF "NEW" CHEMISTRY**
  - **CHARGE RATE EFFECTS**
  - **DISCHARGE RATE EFFECTS**
  - **TEMPERATURE EFFECTS**
    - CELL DISCHARGE CAPACITY (AHRS)
    - CELL DISCHARGE ENERGY (WHRS)
    - CELL ENERGY DENSITY (WHRS/KG)
  - **TEST RATES EXPRESSED IN mA/cm^2 OF CATHODE SURFACE AREA**
    - ALLOWS RESULTS TO BE "SCALED" FOR OTHER PRISMATIC CELL DESIGNS

- **STANDARD SLC-16002 (35 AHR NAMEPLATE) CELL DESIGN CHOSEN AS TEST VEHICLE**

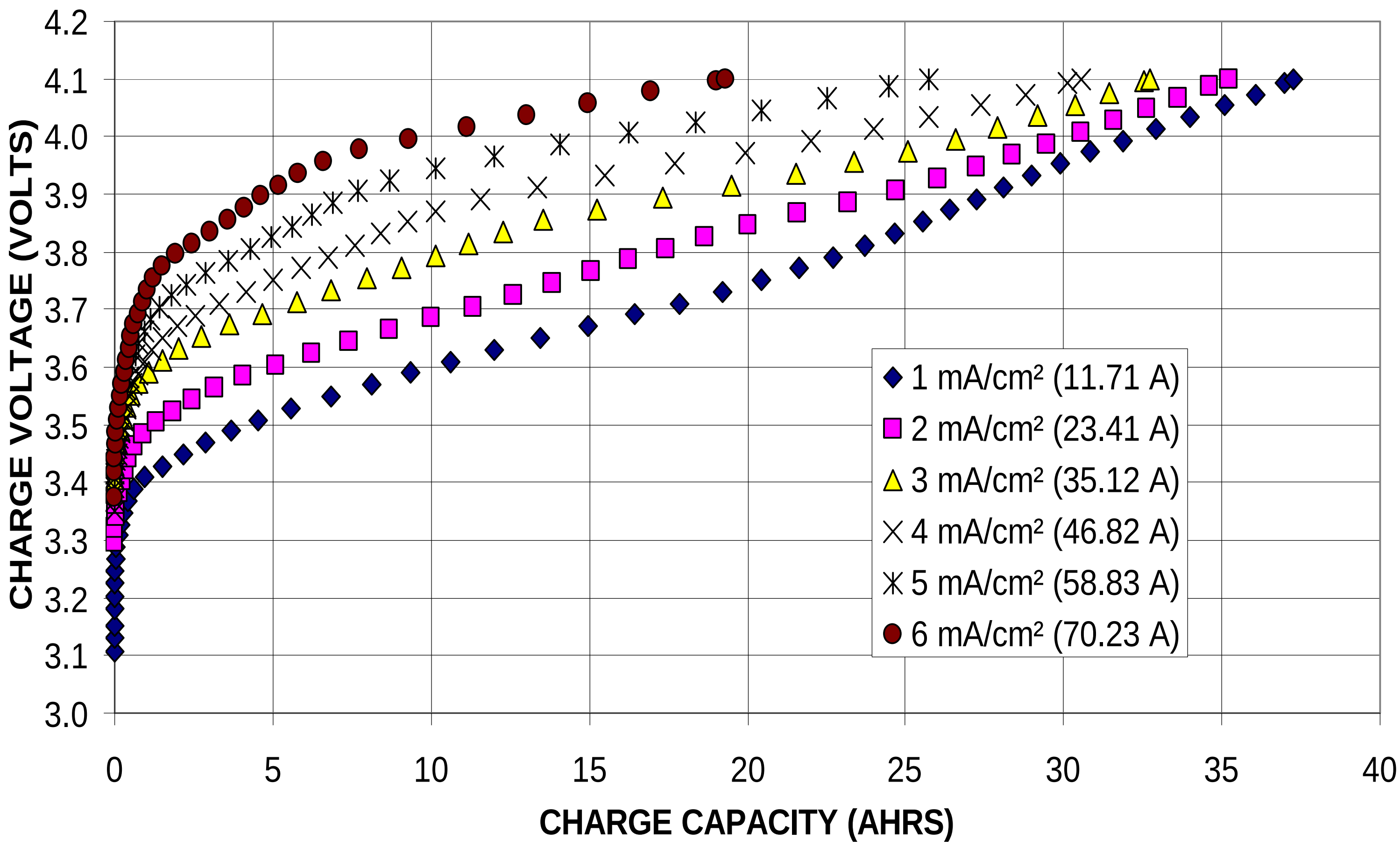
EAGLE EP PICHER
Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL CHARGE VOLTAGE @ 23°C



EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL CHARGE VOLTAGE @ 23°C



SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **CHARACTERIZE STANDARD SLC-16002 (35 AHR NAMEPLATE) CELL DESIGN**
  - **AMBIENT TEMPERATURE (23°C) CHARGE VS:**
    - 70°C DISCHARGE
    - 60°C DISCHARGE
    - 50°C DISCHARGE
    - 40°C DISCHARGE
    - 23°C DISCHARGE
    - 10°C DISCHARGE
    - 0°C DISCHARGE
    - -10°C DISCHARGE

Eagle Picher Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- CHARACTERIZE STANDARD SLC-16002 (35 AHR NAMEPLATE) CELL DESIGN
  - AMBIENT TEMPERATURE (23°C) CHARGE VS:
    - 70°C DISCHARGE
    - 60°C DISCHARGE
    - 50°C DISCHARGE
    - 40°C DISCHARGE
    - 23°C DISCHARGE
    - 10°C DISCHARGE
    - 0°C DISCHARGE
    - -10°C DISCHARGE
  - SAME TEMPERATURE CHARGE & DISCHARGE
    - 23°C
    - 10°C
    - 0°C

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- CHARACTERIZE STANDARD SLC-16002 (35 AHR NAMEPLATE) CELL DESIGN
  - **AMBIENT TEMPERATURE (23°C) CHARGE VS:**
    - 70°C DISCHARGE
    - 60°C DISCHARGE
    - 50°C DISCHARGE
    - 40°C DISCHARGE
    - 23°C DISCHARGE
    - 10°C DISCHARGE
    - 0°C DISCHARGE
    - -10°C DISCHARGE
  - **SAME TEMPERATURE CHARGE & DISCHARGE**
    - 23°C
    - 10°C
    - 0°C
  - **DISCHARGE RATES FROM 1 mA/cm² (C/3 AMPS) thru 10 mA/cm² (3.3C AMPS)**

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

✦ TEST PROFILE

- **CHARGE CELL AT 2.34 AMPS (0.2 mA/cm²) TO 4.1 VOLTS**
- **DISCHARGE CELL PER THE FOLLOWING STEP RATE SEQUENCE:**
  - 117.06 AMPS (10 mA/cm²)
  - 105.35 AMPS (9 mA/cm²)
  - 93.65 AMPS (8 mA/cm²)
  - 81.94 AMPS (7 mA/cm²)
  - 70.23 AMPS (6 mA/cm²)
  - 58.53 AMPS (5 mA/cm²)
  - 46.82 AMPS (4 mA/cm²)
  - 35.12 AMPS (3 mA/cm2)
  - 23.41 AMPS (2 mA/cm²)
  - 11.71 AMPS (1 mA/cm²)

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

✦ TEST PROFILE

- **CHARGE CELL AT 2.34 AMPS (0.2 mA/cm²) TO 4.1 VOLTS**
- **DISCHARGE CELL PER THE FOLLOWING STEP RATE SEQUENCE:**
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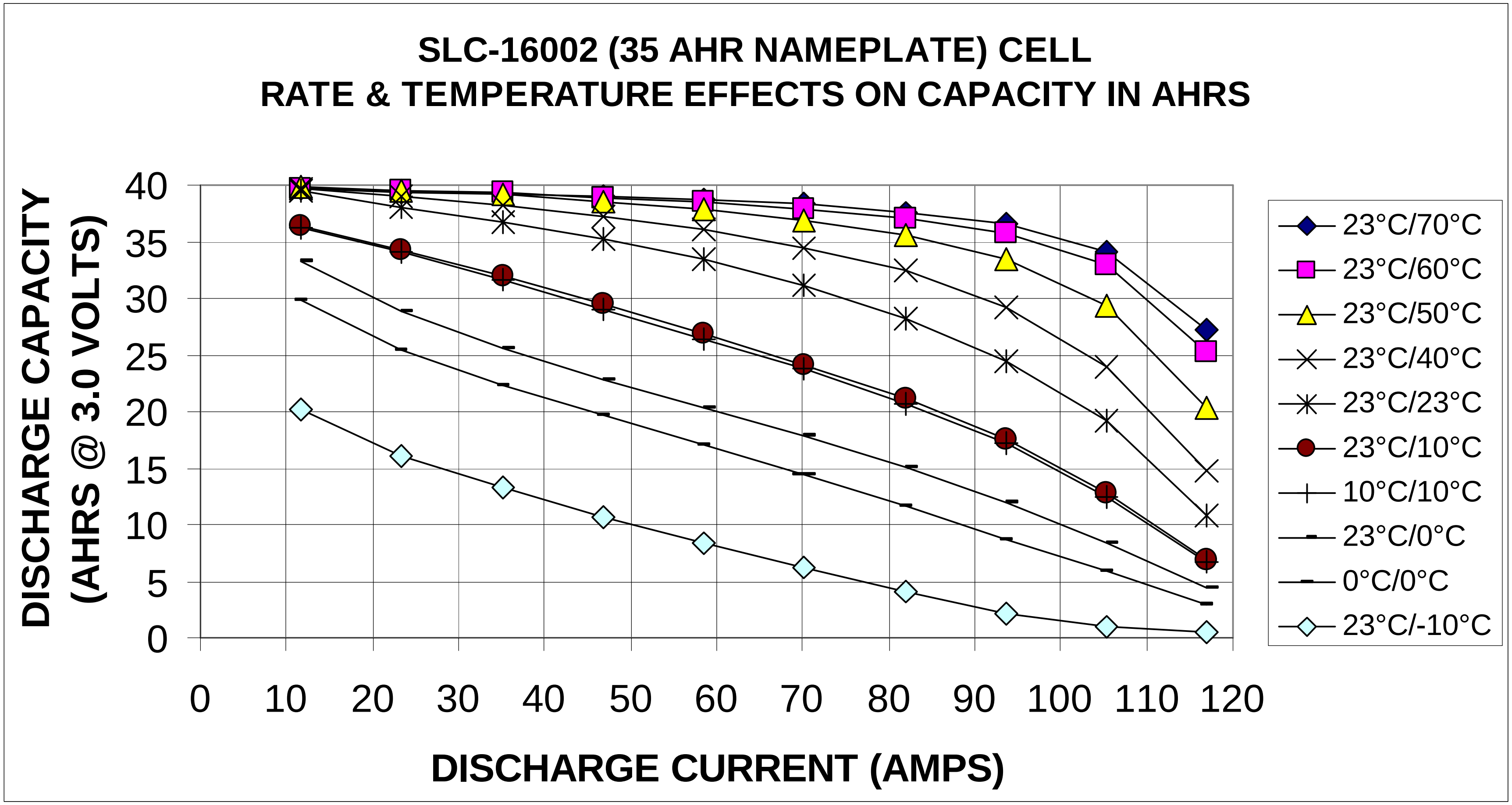
  - ➢ 105.35 AMPS (9 mA/cm²)
  - ➢ 93.65 AMPS (8 mA/cm²)
  - ➢ 81.94 AMPS (7 mA/cm²)
  - ➢ 70.23 AMPS (6 mA/cm²)
  - ➢ 58.53 AMPS (5 mA/cm²)
  - ➢ 46.82 AMPS (4 mA/cm²)
  - ➢ 35.12 AMPS (3 mA/cm2)
  - ➢ 23.41 AMPS (2 mA/cm²)
  - ➢ 11.71 AMPS (1 mA/cm²)
- **ALL DISCHARGE STEPS TO 3.0 VOLT CUT-OFF**
- **15 MINUTE OPEN CIRCUIT BETWEEN DISCHARGE STEPS FOR VOLTAGE RECOVERY & TEMPERATURE RESTABILIZATION**
- **TOTAL CAPACITY IS CUMULATIVE AS RATE STEPS DOWN**

EAGLE EP PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS



SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

✦ AMBIENT TEMPERATURE (23°C) CHARGE TEST SUMMARY

- **SIGNIFICANT CELL CAPACITY AVAILABLE AT ELEVATED DISCHARGE RATES**
  - **3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
    - 32 SECOND PULSE @ -10°C
    - 54% OF NAMEPLATE CAPACITY @ 23°C
    - 97% OF NAMEPLATE CAPACITY @ 70°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- AMBIENT TEMPERATURE (23°C) CHARGE TEST SUMMARY
  - SIGNIFICANT CELL CAPACITY AVAILABLE AT ELEVATED DISCHARGE RATES
    - 3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF
      - 32 SECOND PULSE @ -10°C
      - 54% OF NAMEPLATE CAPACITY @ 23°C
      - 97% OF NAMEPLATE CAPACITY @ 70°C
    - 2C AMPS (6 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF
      - 18% OF NAMEPLATE CAPACITY @ -10°C
      - 89% OF NAMEPLATE CAPACITY @ 23°C
      - 109% OF NAMEPLATE CAPACITY @ 70°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **AMBIENT TEMPERATURE (23°C) CHARGE TEST SUMMARY**
  - **SIGNIFICANT CELL CAPACITY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 32 SECOND PULSE @ -10°C
      - 54% OF NAMEPLATE CAPACITY @ 23°C
      - 97% OF NAMEPLATE CAPACITY @ 70°C
    - **2C AMPS (6 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 18% OF NAMEPLATE CAPACITY @ -10°C
      - 89% OF NAMEPLATE CAPACITY @ 23°C
      - 109% OF NAMEPLATE CAPACITY @ 70°C
    - **C AMPS (3 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 38% OF NAMEPLATE CAPACITY @ -10°C
      - 105% OF NAMEPLATE CAPACITY @ 23°C
      - 112% OF NAMEPLATE CAPACITY @ 70°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- ***SAME TEMPERATURE*** **CHARGE/DISCHARGE TEST SUMMARY**
  - **SIGNIFICANT CELL CAPACITY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 17% OF NAMEPLATE CAPACITY @ 0°C
      - 36% OF NAMEPLATE CAPACITY @ 10°C
      - 54% OF NAMEPLATE CAPACITY @ 23°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

✦ ***SAME TEMPERATURE*** **CHARGE/DISCHARGE TEST SUMMARY**

- **SIGNIFICANT CELL CAPACITY AVAILABLE AT ELEVATED DISCHARGE RATES**

  ➢ **3C AMPS (9 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
  - 17% OF NAMEPLATE CAPACITY @ 0°C
  - 36% OF NAMEPLATE CAPACITY @ 10°C
  - 54% OF NAMEPLATE CAPACITY @ 23°C

  ➢ **2C AMPS (6 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
  - 41% OF NAMEPLATE CAPACITY @ 0°C
  - 67% OF NAMEPLATE CAPACITY @ 10°C
  - 89% OF NAMEPLATE CAPACITY @ 23°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- ***SAME TEMPERATURE*** **CHARGE/DISCHARGE TEST SUMMARY**
  - **SIGNIFICANT CELL CAPACITY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 17% OF NAMEPLATE CAPACITY @ 0°C
      - 36% OF NAMEPLATE CAPACITY @ 10°C
      - 54% OF NAMEPLATE CAPACITY @ 23°C
    - **2C AMPS (6 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 41% OF NAMEPLATE CAPACITY @ 0°C
      - 67% OF NAMEPLATE CAPACITY @ 10°C
      - 89% OF NAMEPLATE CAPACITY @ 23°C
    - **C AMPS (3 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 64% OF NAMEPLATE CAPACITY @ 0°C
      - 90% OF NAMEPLATE CAPACITY @ 10°C
      - 105% OF NAMEPLATE CAPACITY @ 23°C

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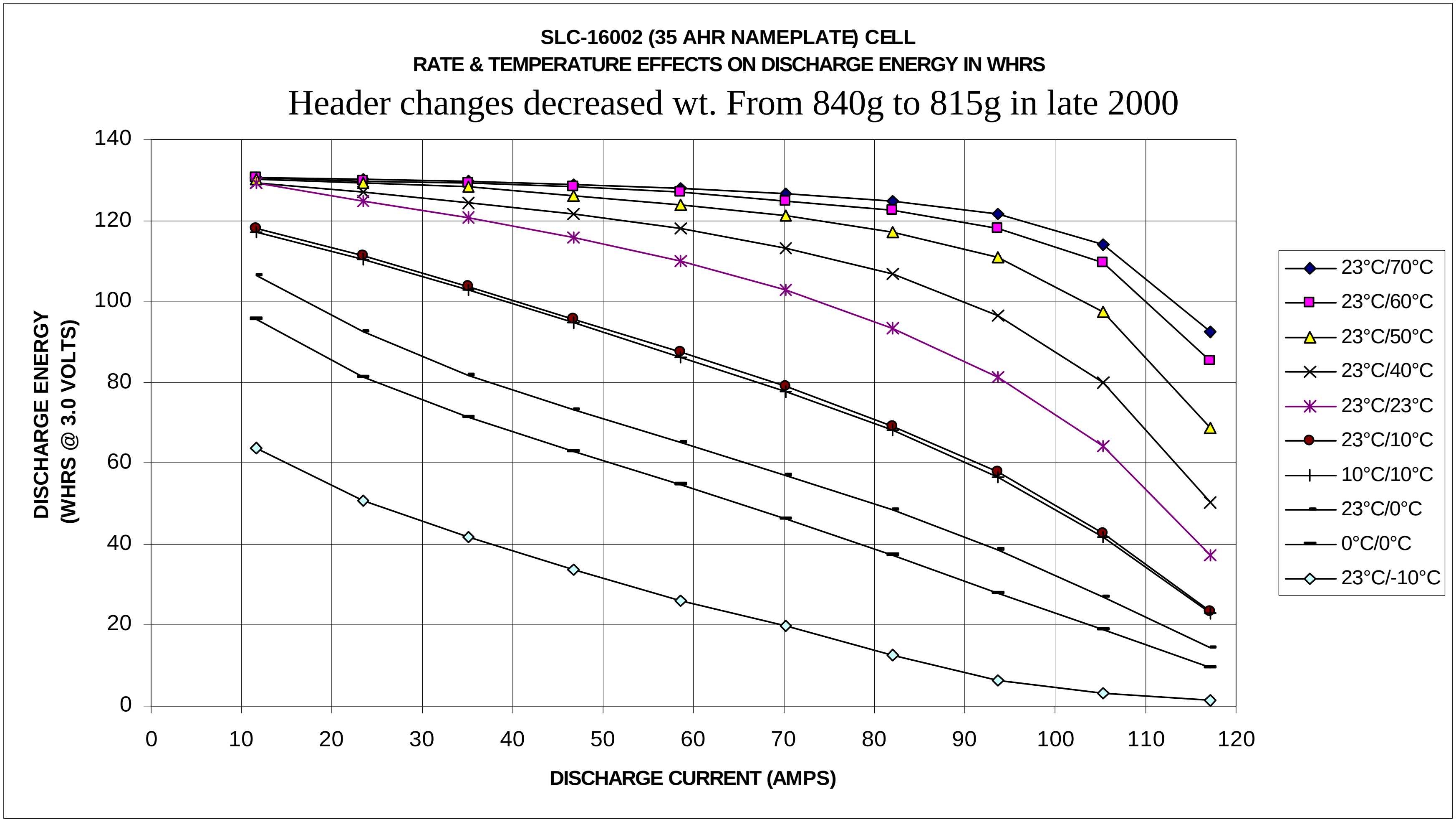
SLC-16002 (35 AHR NAMEPLATE) CELL TESTS



Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **AMBIENT TEMPERATURE (23°C) CHARGE TEST SUMMARY**
  - **CELL DISCHARGE ENERGY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 3.25 WHRS @ -10°C
      - 64.38 WHRS @ 23°C
      - 113.96 WHRS @ 70°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- **AMBIENT TEMPERATURE (23°C) CHARGE TEST SUMMARY**
  - **CELL DISCHARGE ENERGY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 3.25 WHRS @ -10°C
      - 64.38 WHRS @ 23°C
      - 113.96 WHRS @ 70°C
    - **2C AMPS (6 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 19.64 WHRS @ -10°C
      - 102.80 WHRS @ 23°C
      - 126.75 WHRS @ 70°C

EAGLE PICHER Technologies, LLC

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- AMBIENT TEMPERATURE (23°C) CHARGE TEST SUMMARY
  - CELL DISCHARGE ENERGY AVAILABLE AT ELEVATED DISCHARGE RATES
    - 3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF
      - 3.25 WHRS @ -10°C
      - 64.38 WHRS @ 23°C
      - 113.96 WHRS @ 70°C
    - 2C AMPS (6 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF
      - 19.64 WHRS @ -10°C
      - 102.80 WHRS @ 23°C
      - 126.75 WHRS @ 70°C
    - C AMPS (3 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF
      - 41.72 WHRS @ -10°C
      - 120.57 WHRS @ 23°C
      - 129.58 WHRS @ 70°C

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SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- ***SAME TEMPERATURE*** **CHARGE/DISCHARGE TEST SUMMARY**
  - **CELL DISCHARGE ENERGY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 18.67 WHRS @ 0°C
      - 41.57 WHRS @ 10°C
      - 64.38 WHRS @ 23°C

SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- ***SAME TEMPERATURE*** **CHARGE/DISCHARGE TEST SUMMARY**
  - **CELL DISCHARGE ENERGY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 18.67 WHRS @ 0°C
      - 41.57 WHRS @ 10°C
      - 64.38 WHRS @ 23°C
    - **2C AMPS (6 mA/cm^2) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 46.40 WHRS @ 0°C
      - 77.54 WHRS @ 10°C
      - 102.80 WHRS @ 23°C

EAGLE PICHER Technologies, LLC

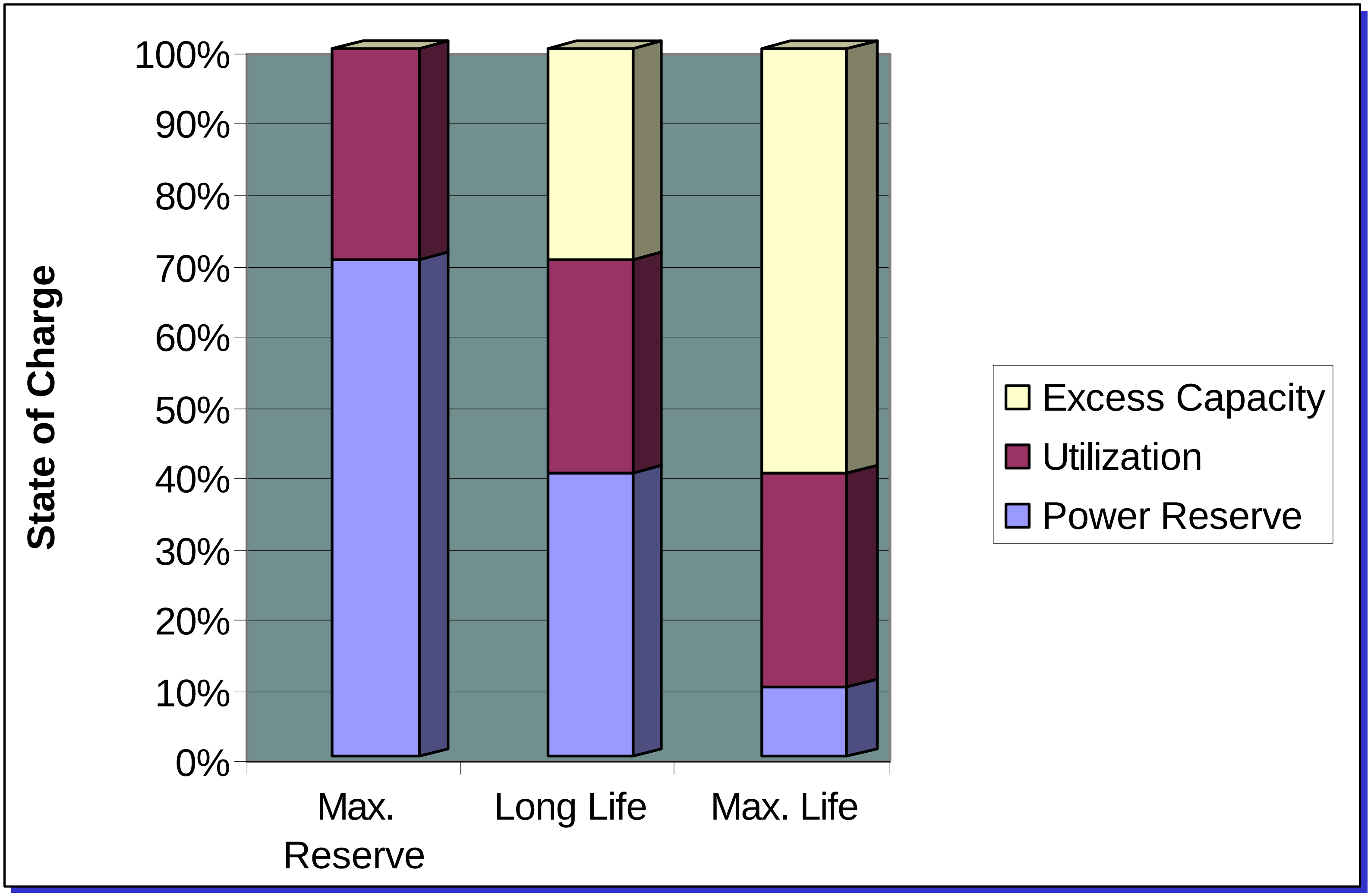
SLC-16002 (35 AHR NAMEPLATE) CELL TESTS

- ***SAME TEMPERATURE*** **CHARGE/DISCHARGE TEST SUMMARY**
  - **CELL DISCHARGE ENERGY AVAILABLE AT ELEVATED DISCHARGE RATES**
    - **3C AMPS (9 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 18.67 WHRS @ 0°C
      - 41.57 WHRS @ 10°C
      - 64.38 WHRS @ 23°C
    - **2C AMPS (6 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 46.40 WHRS @ 0°C
      - 77.54 WHRS @ 10°C
      - 102.80 WHRS @ 23°C
    - **C AMPS (3 mA/cm²) DISCHARGE RATE TO 3.0 VOLT CUT-OFF**
      - 71.50 WHRS @ 0°C
      - 102.55 WHRS @ 10°C
      - 120.57 WHRS @ 23°C

LEO/GEO Tests

EAGLE PICHER Technologies, LLC

Utilization Levels for EPT Li-ion



EAGLE PICHER
Technologies, LLC

LEO Testing

- 25% DOD
- 100% SOC

- C/4 Charge
- C/2 Discharge

EAGLE PICHER Technologies, LLC

LEO Testing

- 25% DOD
- 100% SOC

- C/4 Charge
- C/2 Discharge

- 4850 Cycles Accumulated

- Projected to 13000 Cycles

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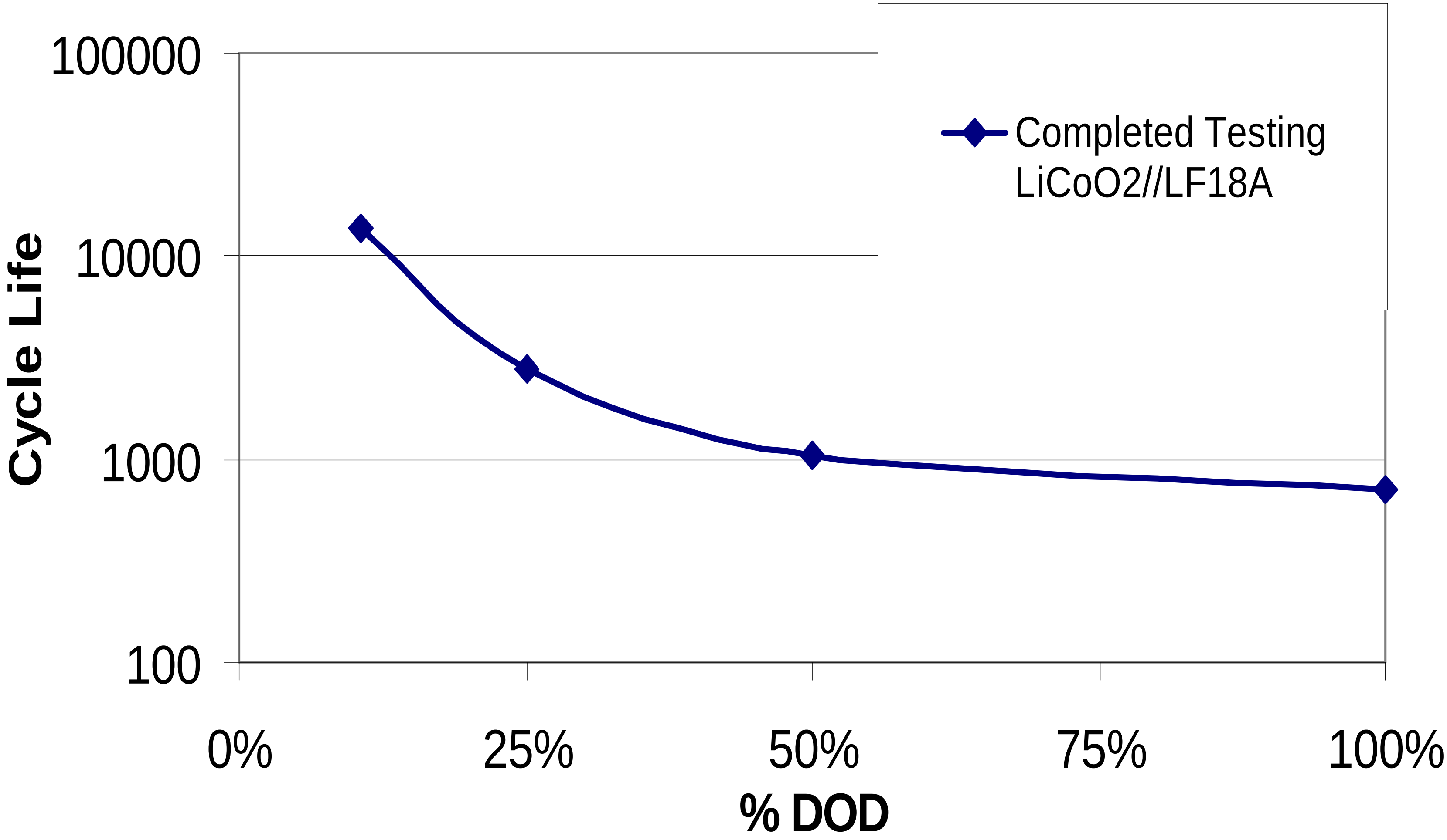
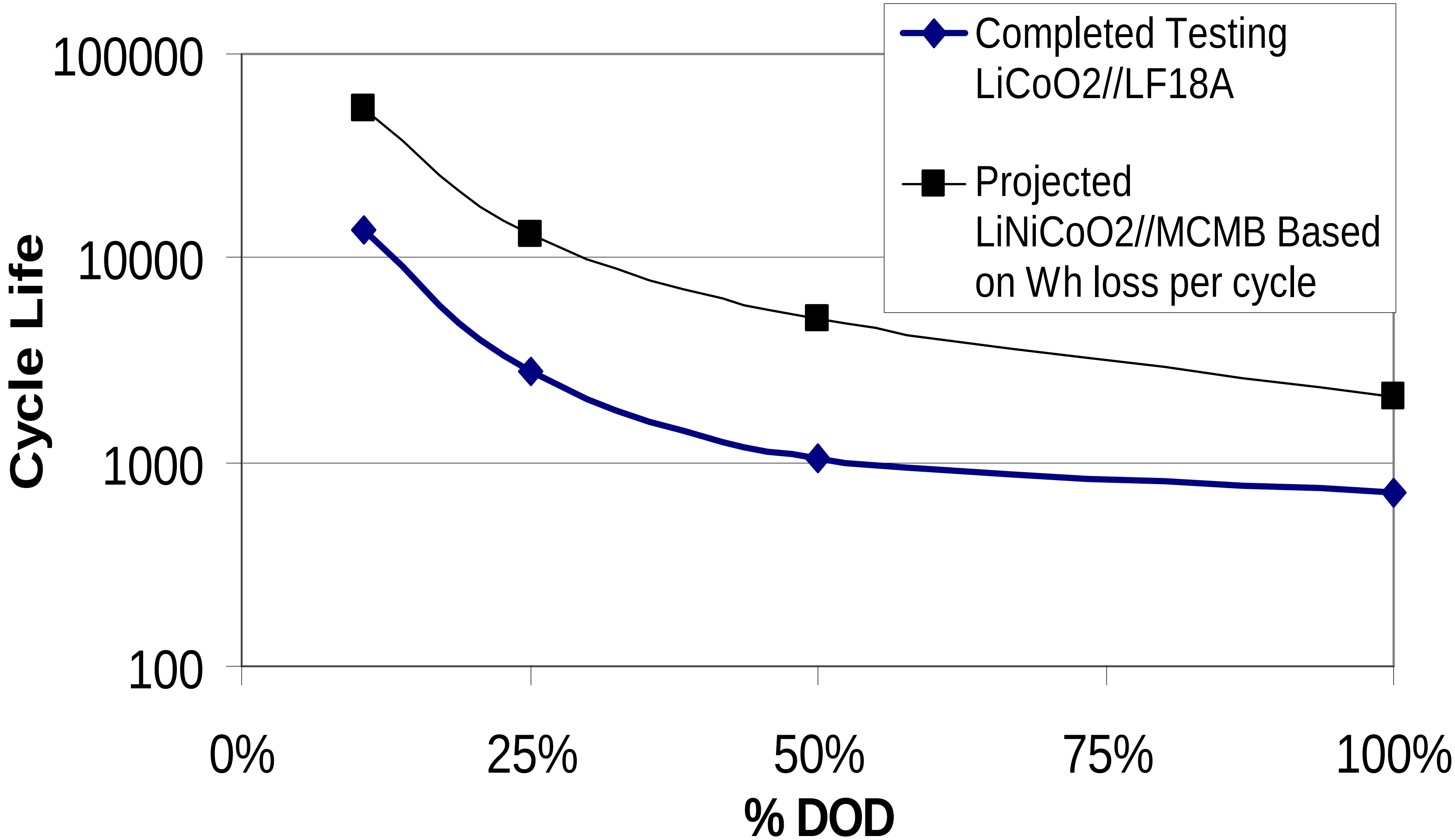
Completed an Projected Cycle Life



Completed an Projected Cycle Life

EAGLE PICHER Technologies, LLC



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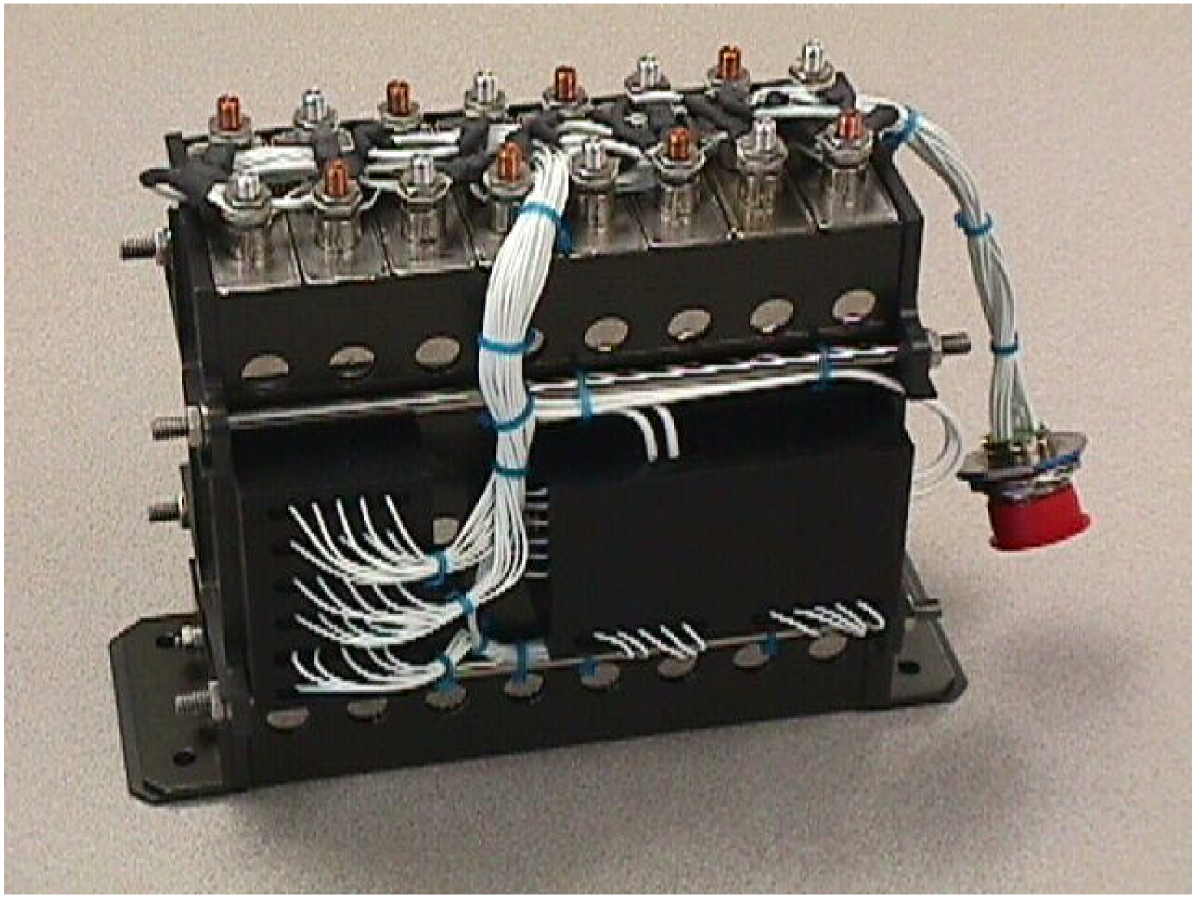
IRAD GEO Battery Development

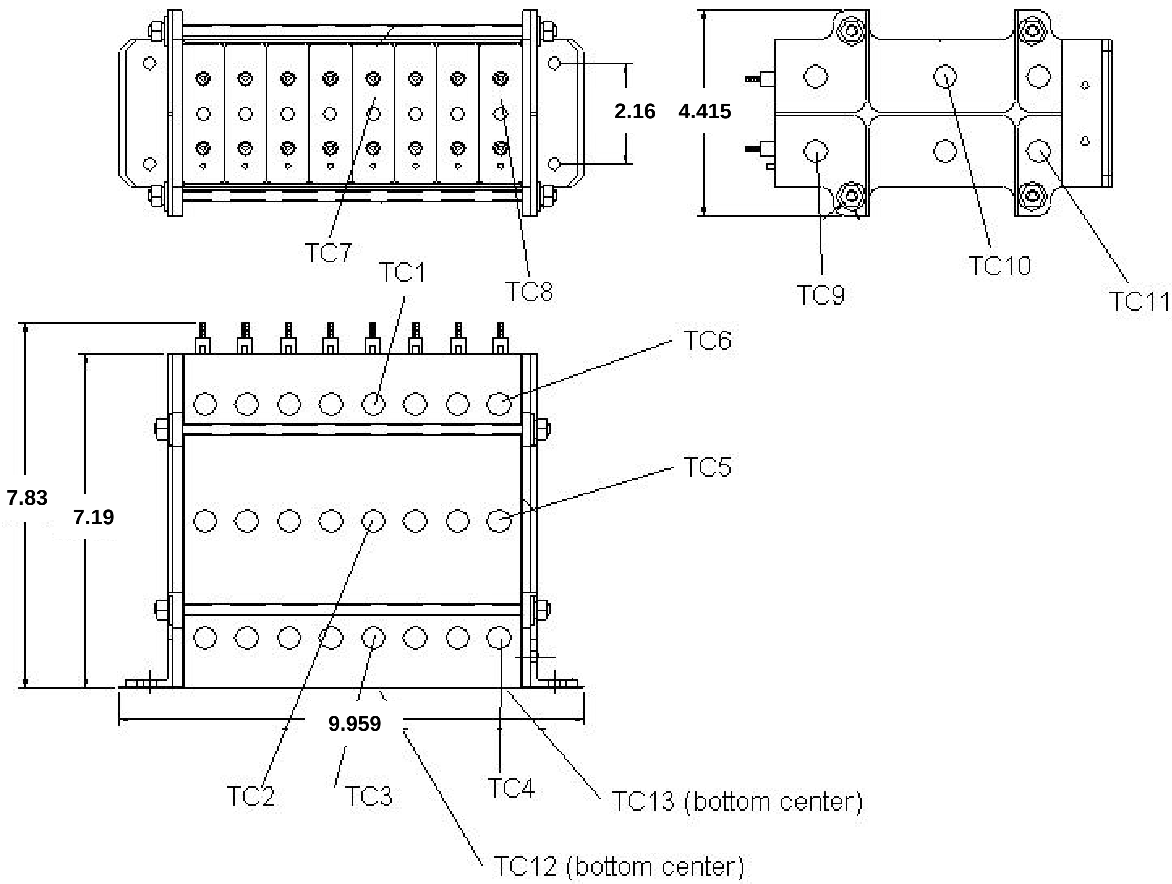
- Battery Design
- Thermal Characteristics
- Battery Life Data



Battery Structure & Design

EAGLE PICHER Technologies, LLC

- **SLB-16001 battery**
- **Comprised of eight SLC-16002 cells**
- **Structural & thermal hardware includes:**
  - Aluminum alloys
  - RTV's
  - Thermal transfer enhancement materials
  - High strength fastening systems
  - Electrically neutral architecture

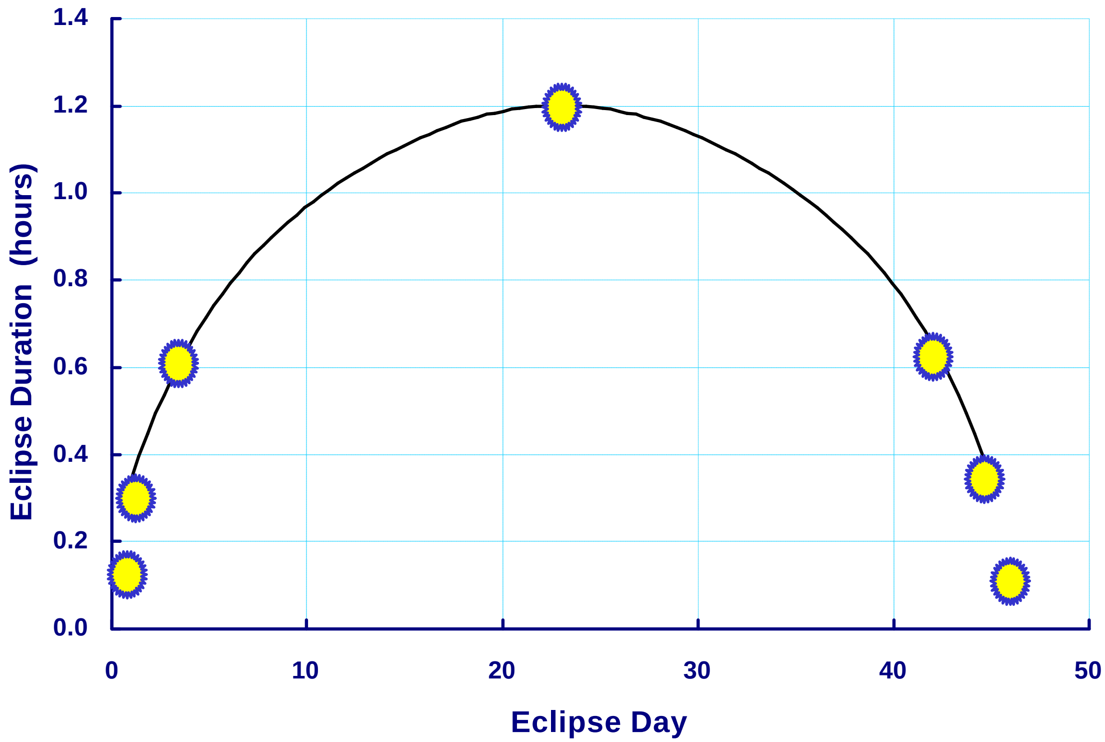


Series String Battery Testing

EAGLE PICHER Technologies, LLC

- **Abbreviated GEO Season for initial series battery testing**
  - 7.5%DOD
  - 15%DOD
  - 30%DOD
  - 60%DOD
  - 30%DOD
  - 15%DOD
  - 7.5%DOD

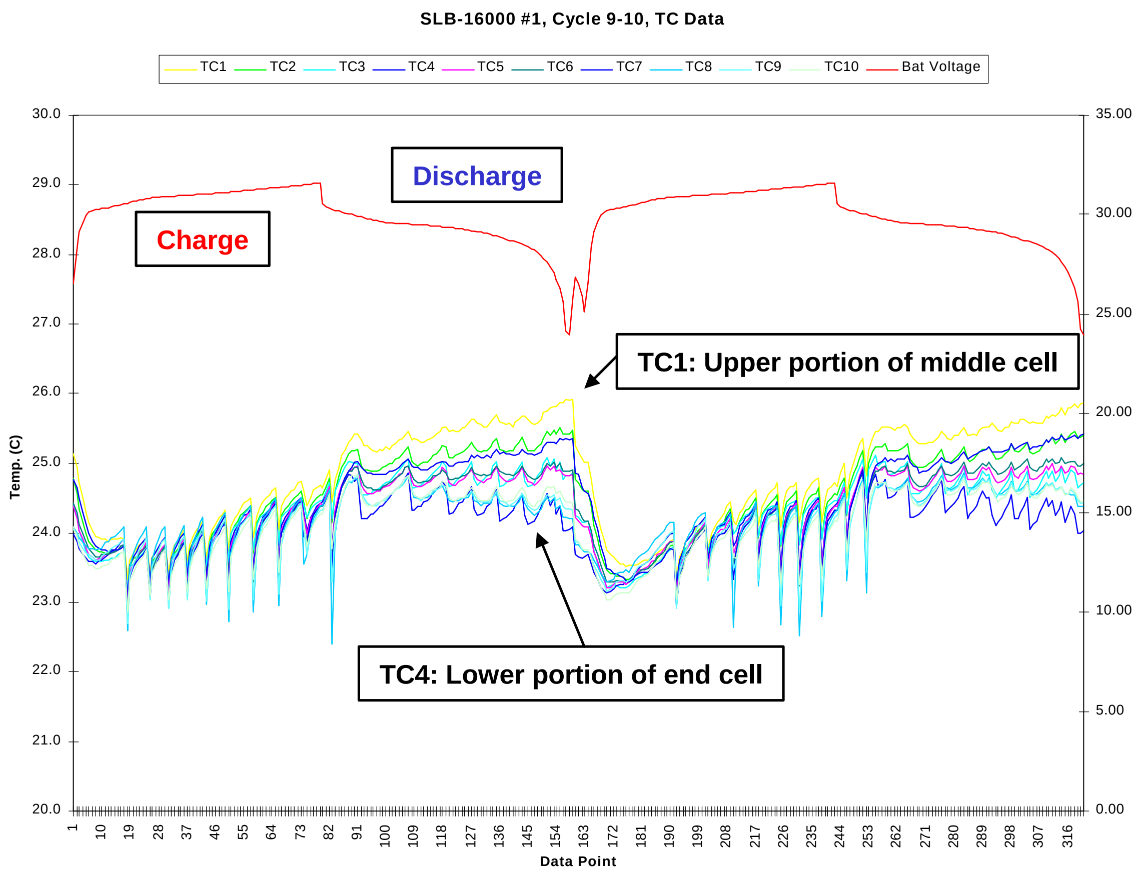
- **30 minute rest between cycles**



Thermal Characteristics of Battery

EAGLE EP PICHER Technologies, LLC

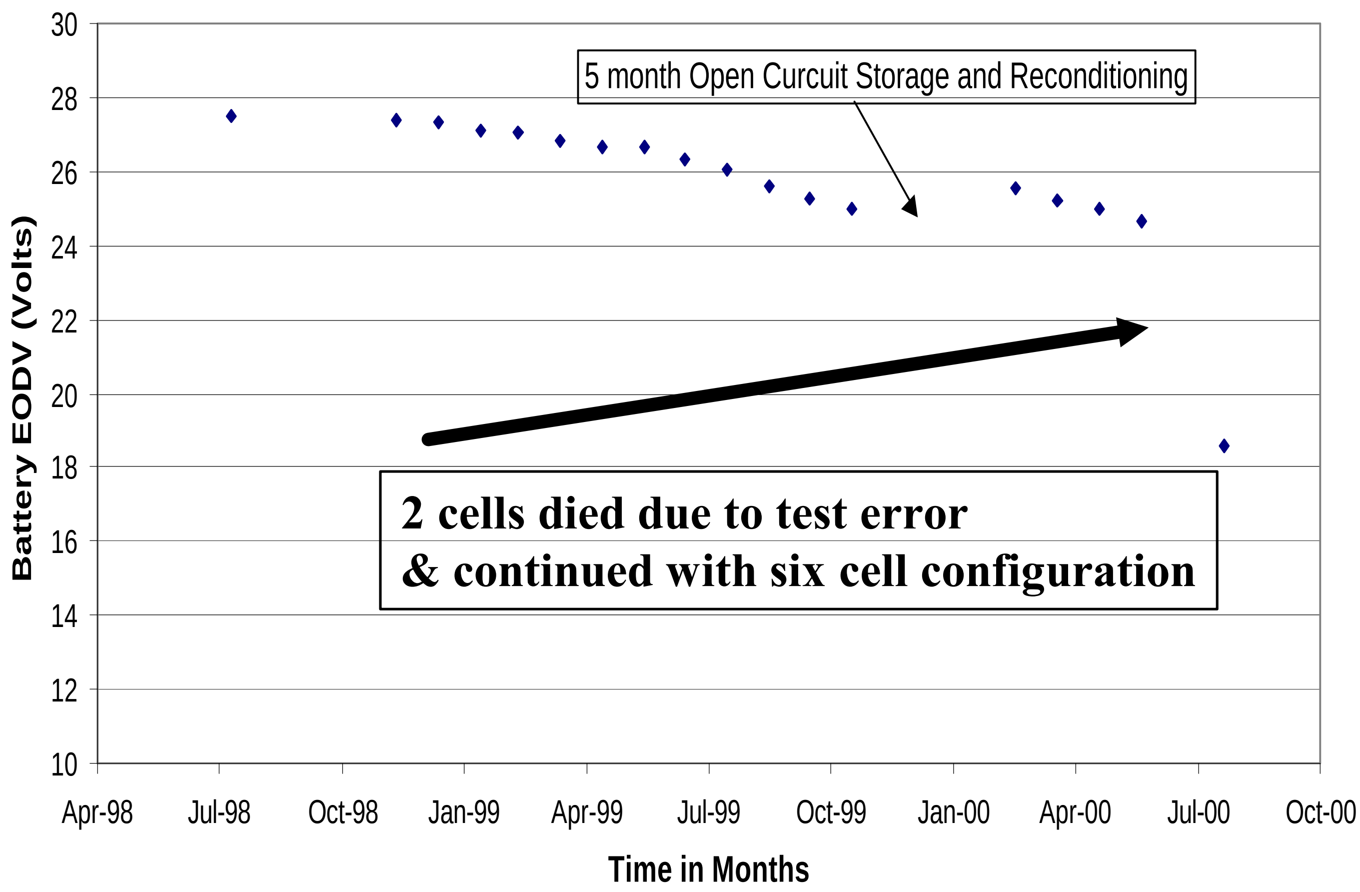
- Low variance in DT leads to longer life
- High rate and High Cycle Life applications Higher Importance
- 2°C maximum temperature variance throughout entire battery during full cycle



EAGLE EP PICHER Technologies, LLC

End of Discharge Voltage 60% DOD Operation

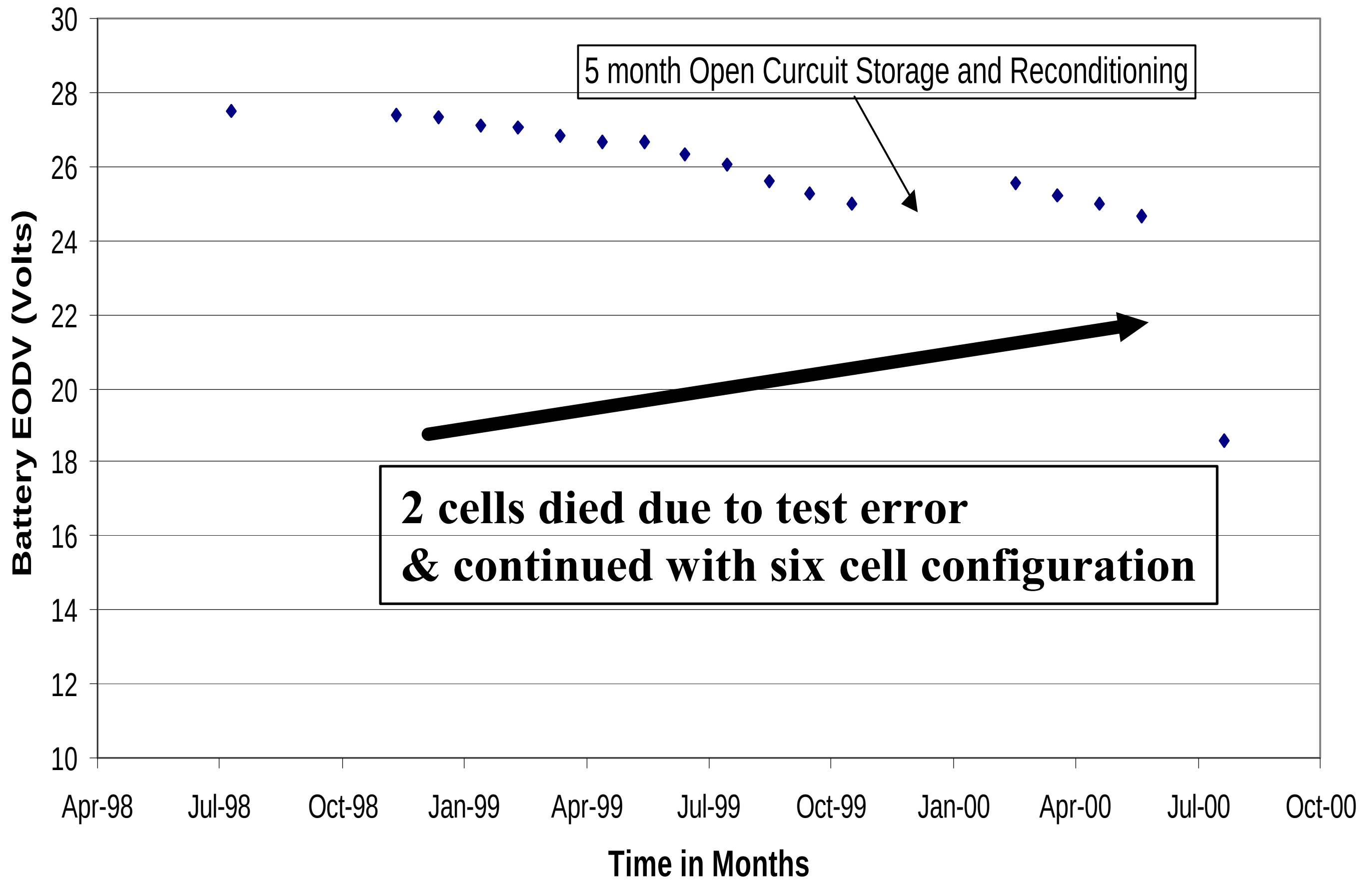
- Historical data has shown End of discharge voltage linear until approximately 3.2 volts/cell



EAGLE PICHER Technologies, LLC

End of Discharge Voltage 60% DOD Operation

- **Historical data has shown End of discharge voltage linear until approximately 3.2 volts/cell**
- **Results**
  - 101 Abb. GEO Seasons (>808 Cycles w/o electronics)
  - Represents 18 seasons in GEO
  - 9 years in orbit



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Conclusions

- ✦Chemistry changes have shown significant increases in
  - ✦Energy Density/ Specific Energy
  - ✦Rate / Temperature Capability
  - ✦Life

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Conclusions

- ✦Chemistry changes have shown significant increases in
  - ✦Energy Density/ Specific Energy
  - ✦Rate / Temperature Capability
  - ✦Life

- ✦GEO Battery Cycled over 2.5 years w/o individual cell control or bypass electronics

EAGLE PICHER Technologies, LLC

Conclusions

- ✦Chemistry changes have shown significant increases in
  - ✦Energy Density/ Specific Energy
  - ✦Rate / Temperature Capability
  - ✦Life
- ✦GEO Battery Cycled over 2.5 years w/o individual cell control or bypass electronics
- ✦Acceptable performance demonstrated during safety testing (Jim DeGruson 0830 Thursday)

Lithium-Ion Satellite Batteries Using Small Cells

By

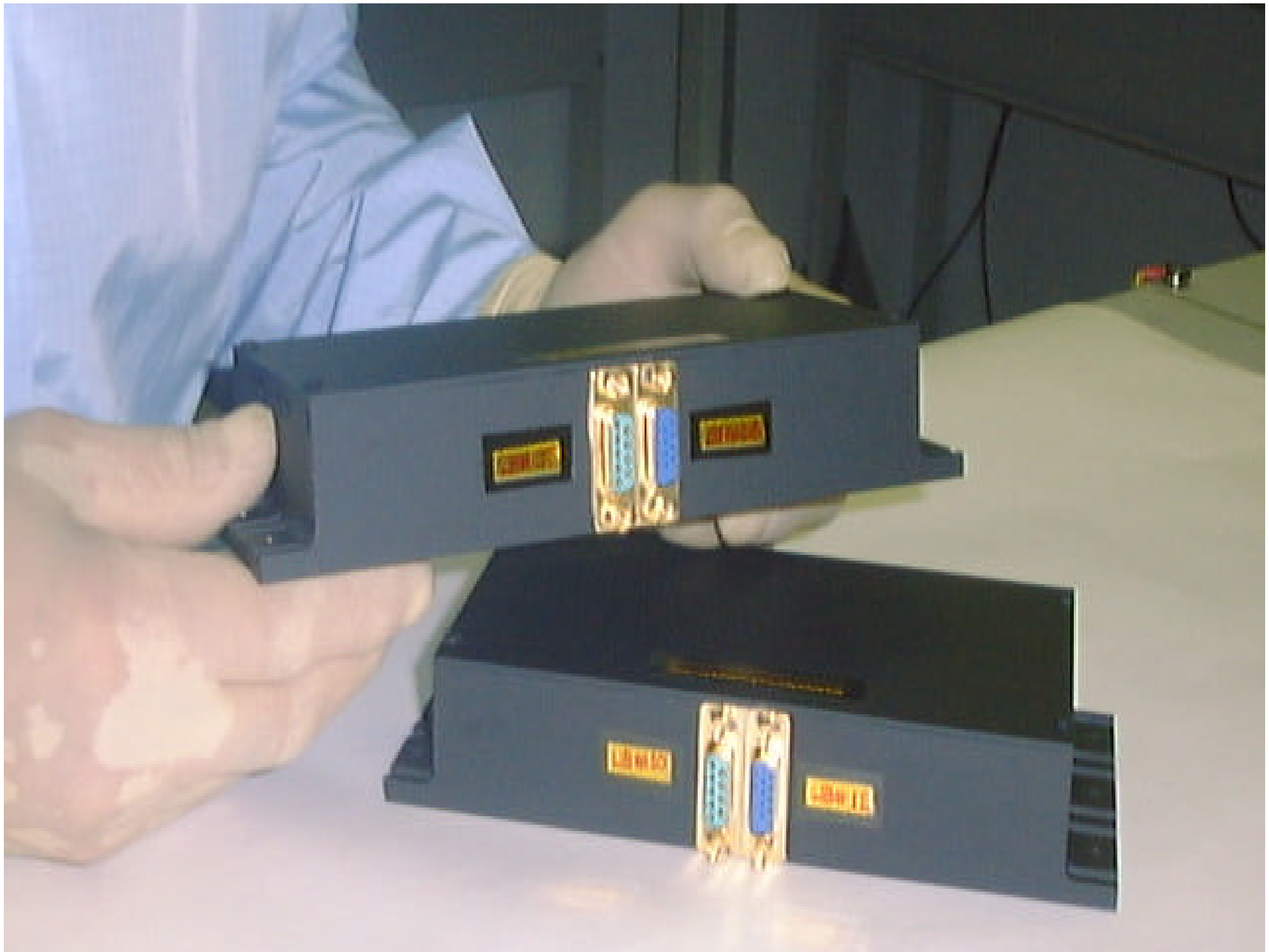
David Lizius & Phil Cowles, COM DEV

Rob Spurrett & Carl Thwaite, AEA Technology

NASA Aerospace Battery Workshop, Huntsville

November 2000

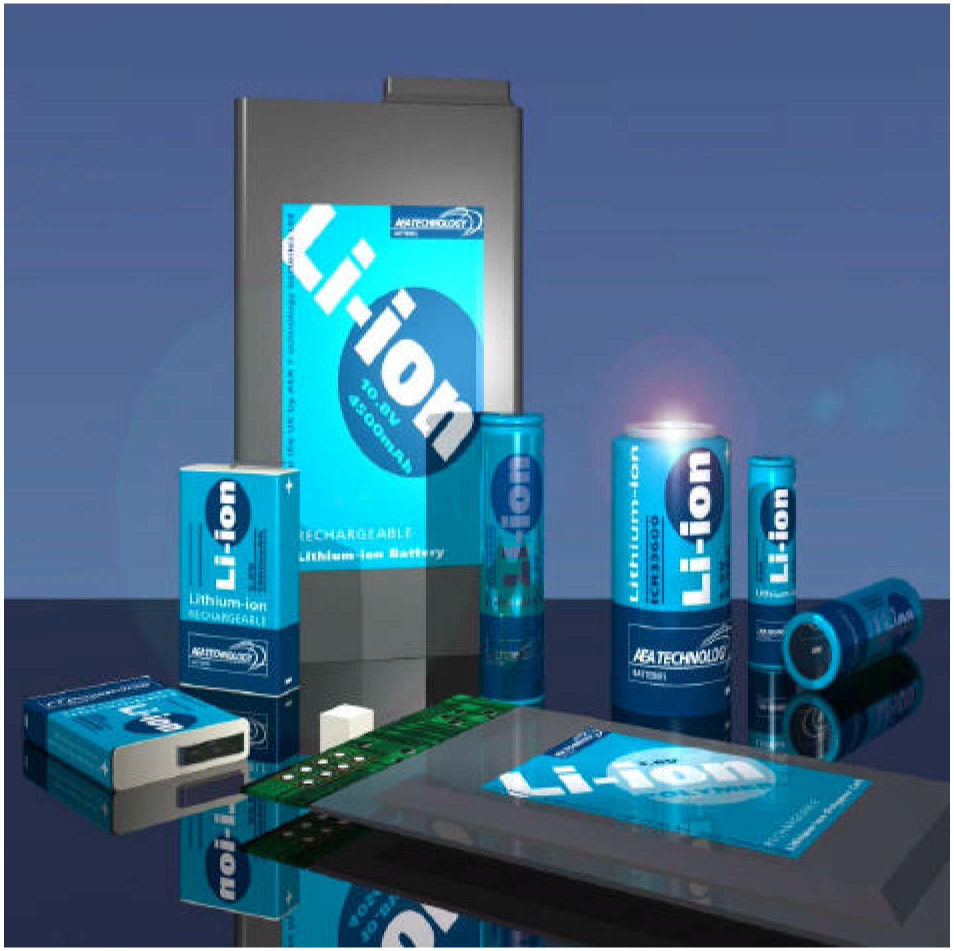
STRV 1d: Launched 16 November 2000



Contents

- Why small cells ?
- Using Sony cells in flight applications
- Battery Design
- Life Tests

Small Lithium-Ion Cells



Small Beginnings

- Early Lithium-ion cells were generally small cells
  - Small means <5Ah
  - Sony 18650 gained early commercial success
- Tests on small cells showed potential benefits for space
  - Weight, volume, thermal advantages widely recognized
- The space industry requires many sizes of battery
  - Voltages from ~8V to ~125V
  - Capacity from 3Ah to several 100Ah
- Different paths to adopting Lithium-ion technology for space
  - 'Large batteries need large cells' approaches
  - 'Small cell' approaches

Small Cell Approach

- Use a single design of small cell in all applications
- Implies the use of an array of cells
  - Use a larger array for a large battery – not a larger cell
  - Similar philosophy to solar array
- Initial motivation for a small cell approach
  - Design & qualify a single cell design
  - Small cells are easier to design and manufacture
  - Negligible thermal gradient within cell
  - Scalability, redundancy & reliability
  - Experience with early small batteries is directly applicable to later large batteries
- Small cell approach is rapidly gaining acceptance

Flight Programs

Mission	Customer	Mission Type	Launch Date	Status
STRV-1c	UK MOD	GTO	Nov 2000	In Orbit
PROBA	ESA	LEO	Q1 2001	FM in test
ROSETTA	Astrium, UK	Interplanetary platform	2003	FM in test
MARS-EXPRESS	Astrium, Fr	Interplanetary platform	2003	PFM in manufacture
RoLand	CNES, Fr	Lander	2003	FM delivered
Beagle2	Astrium, UK	Lander	2003	BDR complete
SciSat	CSA	LEO	2002	Program KO

Sony 18650 Hard Carbon

- Mature technology - in mass production since 1992
- Production standard frozen since 1995
- Good performance and lifetime characteristics
- 5.4Wh @ 40.5g =>133Wh /kg when battery delivered
- Highly uniform production
- Tested by many organizations
- Sony now manufacture several 18650 Lithium-ion cells: only the hard carbon type is considered here

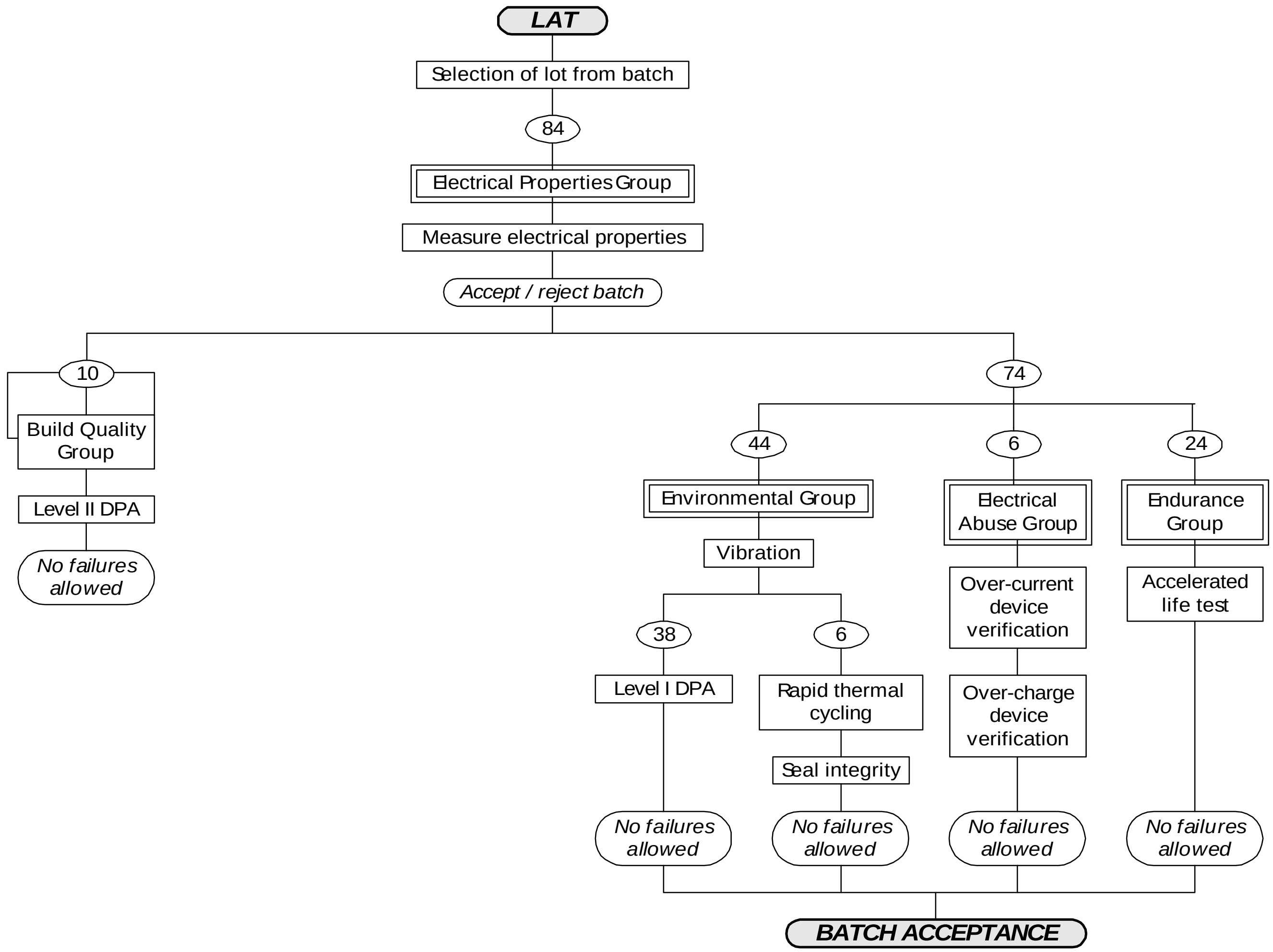
Cell Qualification Tests

CELL QUALIFICATION PARAMETER	VALUE
Non-Operating TVAC	-50°C to +70°C
Operating TVAC	Charge –25 to 60°C Discharge –25 to 60°C
Short term (emergency) temperature excursion limits	Charge and discharge at 80°C Charge and discharge at -60°C
Random Vibration	Three axis, 240 seconds per axis In-plane: 30.4g_{rms} (peak PSD 2g^2/Hz) Out of plane: 30.4g_{rms} (peak PSD 2g^2/Hz)
Shock	100 g, 0.5 ms half-sine (2000g qual at module level)
Radiation Tolerance	100krad and 20krad at 0%, 50% and 100% SOC
Fuse Blowing	10*C* for >250 ms @ 100% SoC 4*C* for >250 ms @ 70% SoC

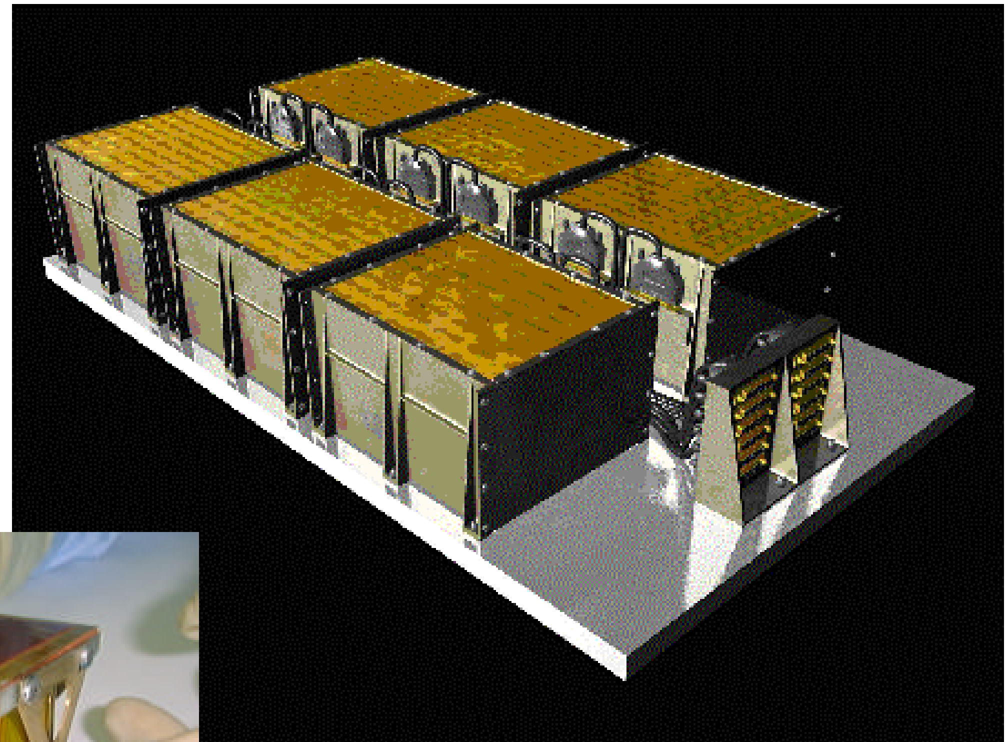
Cell Quality Control

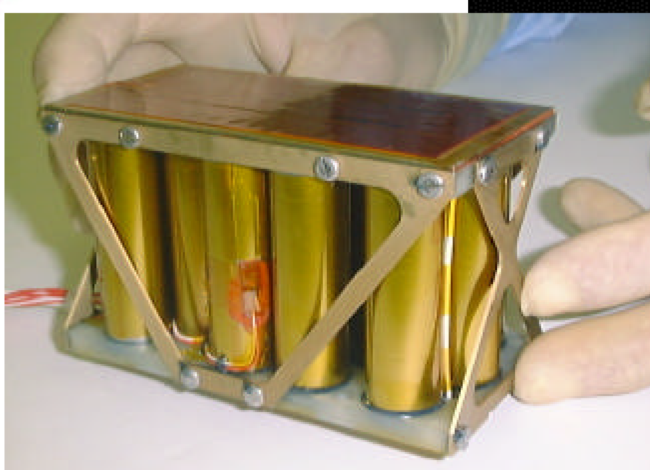
- Sony implement high level of material & process control
  - High volume production
  - 5000 cells per hour
- Long term, close relationship with Sony
- Long term supply agreement with Sony
  - Regularly procure batches > 10,000
- Lot Acceptance Test on each batch procured for space use
- Screening tests on every cell

Lot Acceptance Test



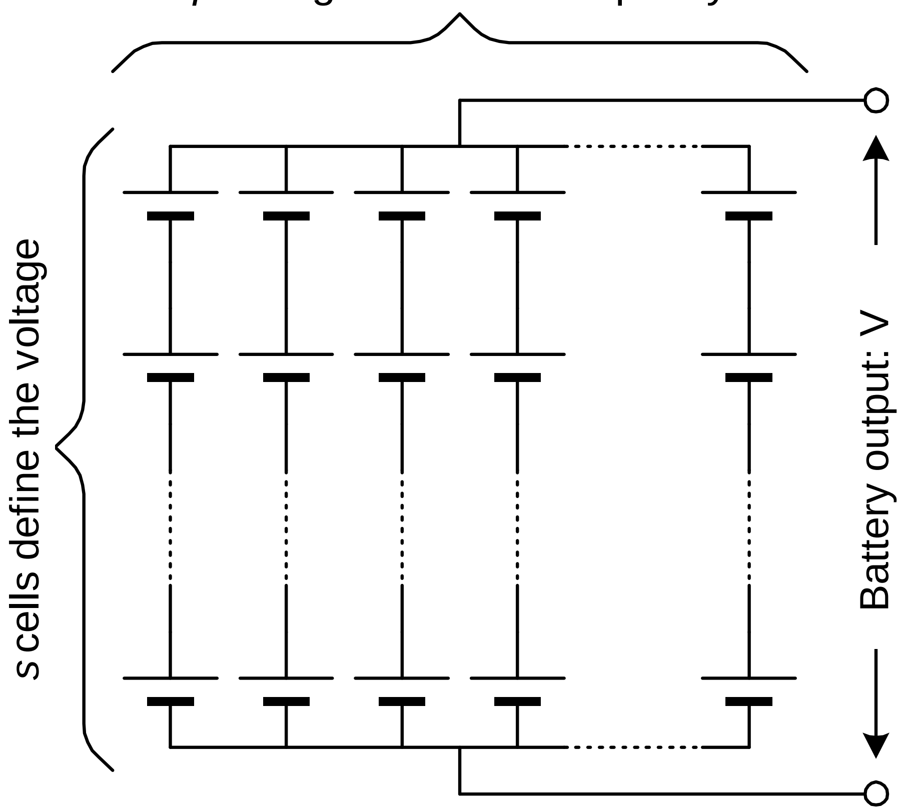
Small Cell – Small & Large Batteries





Battery Electrical Design

- Connect cells in series to provide the required voltage
- Connect strings in parallel to provide the required capacity
- Battery is a two terminal device- charge management is at battery level only
- Packaged into modules. Each module contains complete strings

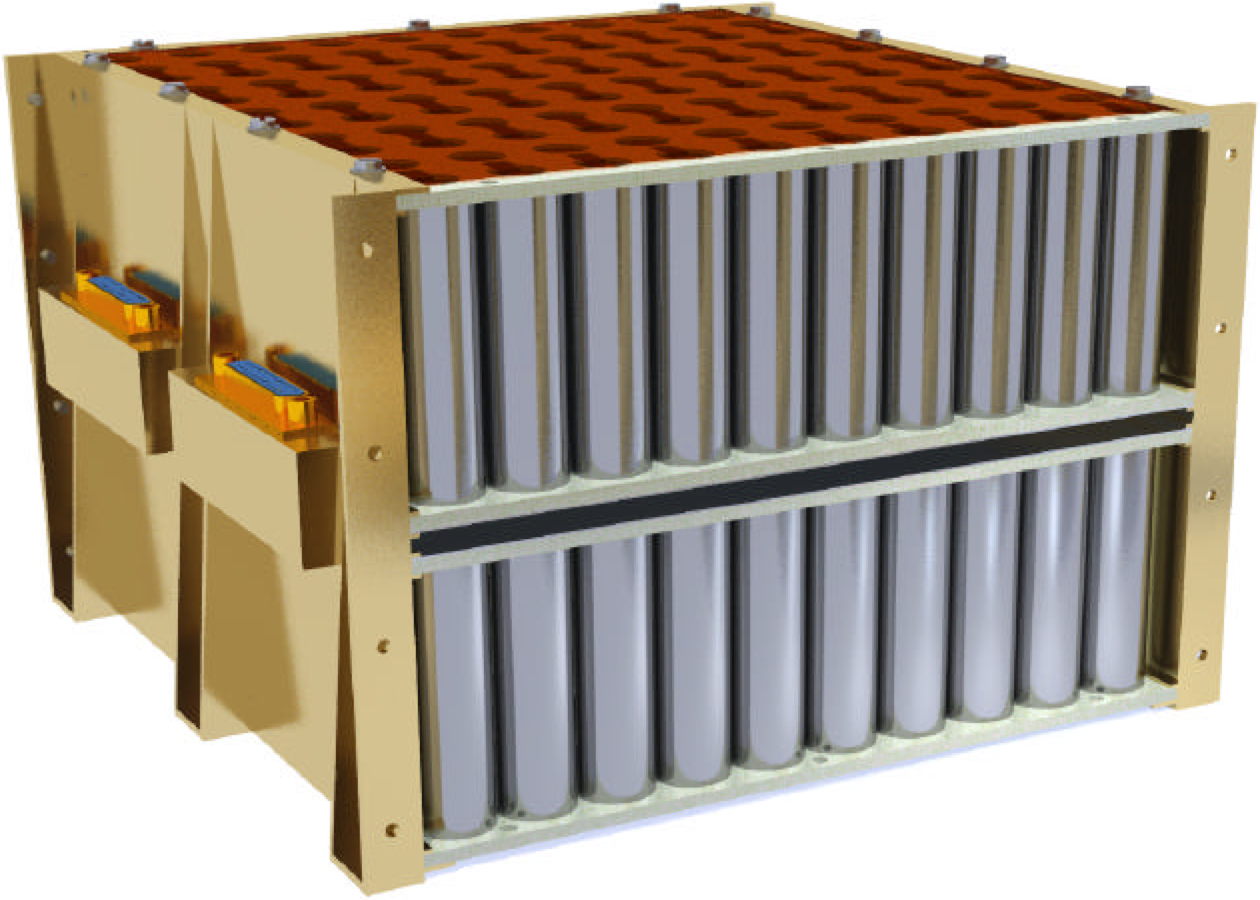


s-p topology

Reliability

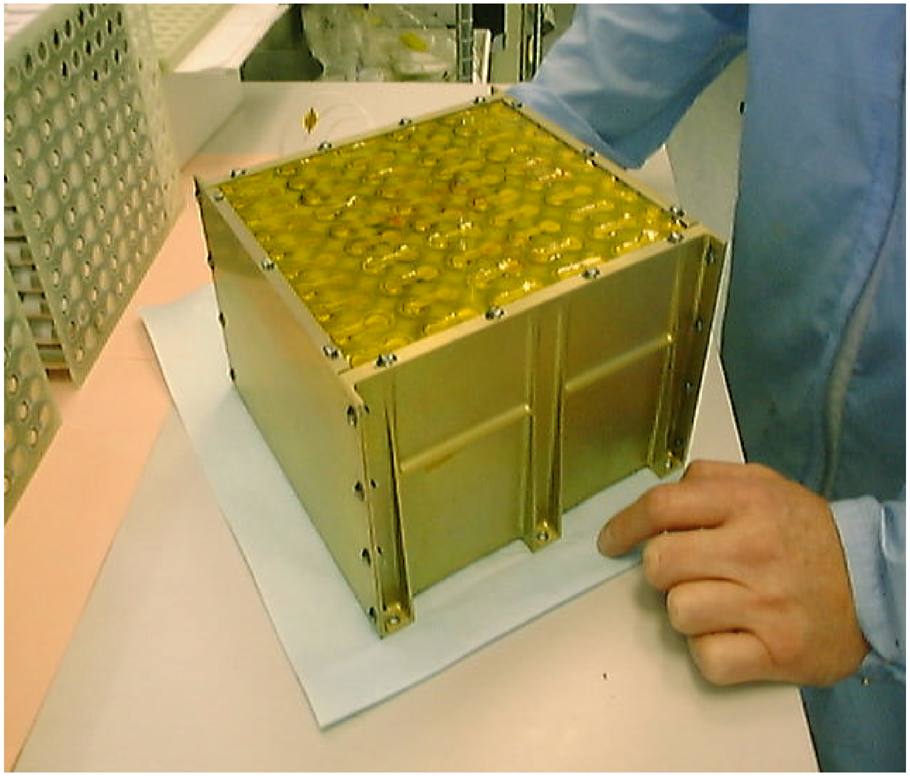
- Found the Sony cells to be robust & reliable
- Assessment using MIL HBK has been performed
- Small cell approach allows redundant strings to be included at very low mass penalty
- Provision of modest levels of redundancy allows high reliability to be easily achieved and reduces stress on cells
- (Try getting a solar array manufacturer to use a small number of very large solar cells !)

Cell Packaging Concept



Qualified Battery Module

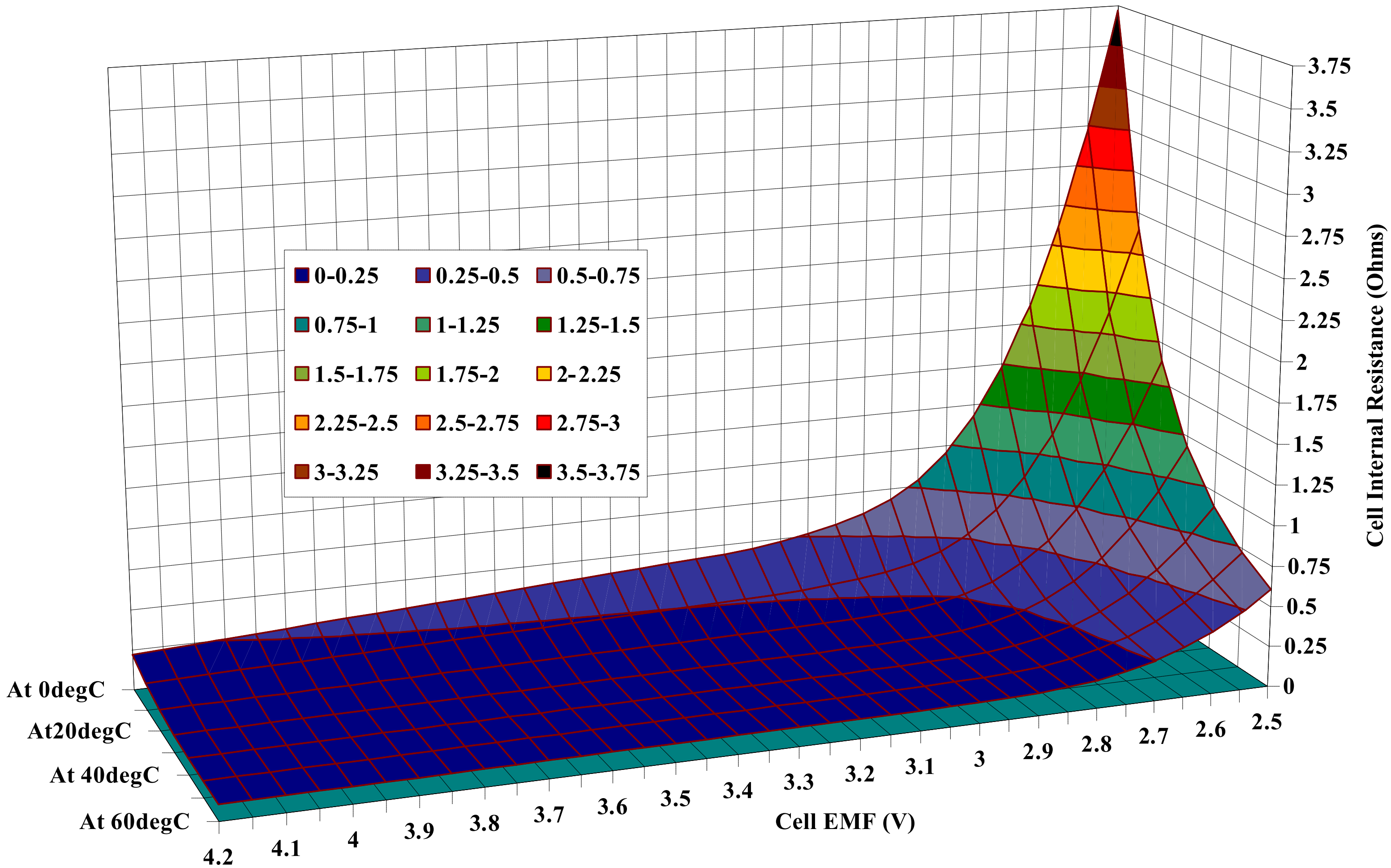
- Qualification of a point design of a highly scalable concept
- Each string has 11 cells for 50V operation
- Module contains 20 strings for 30Ah capacity
- Testing completed Jan 1999
- Measured battery energy density is 117 Wh/kg



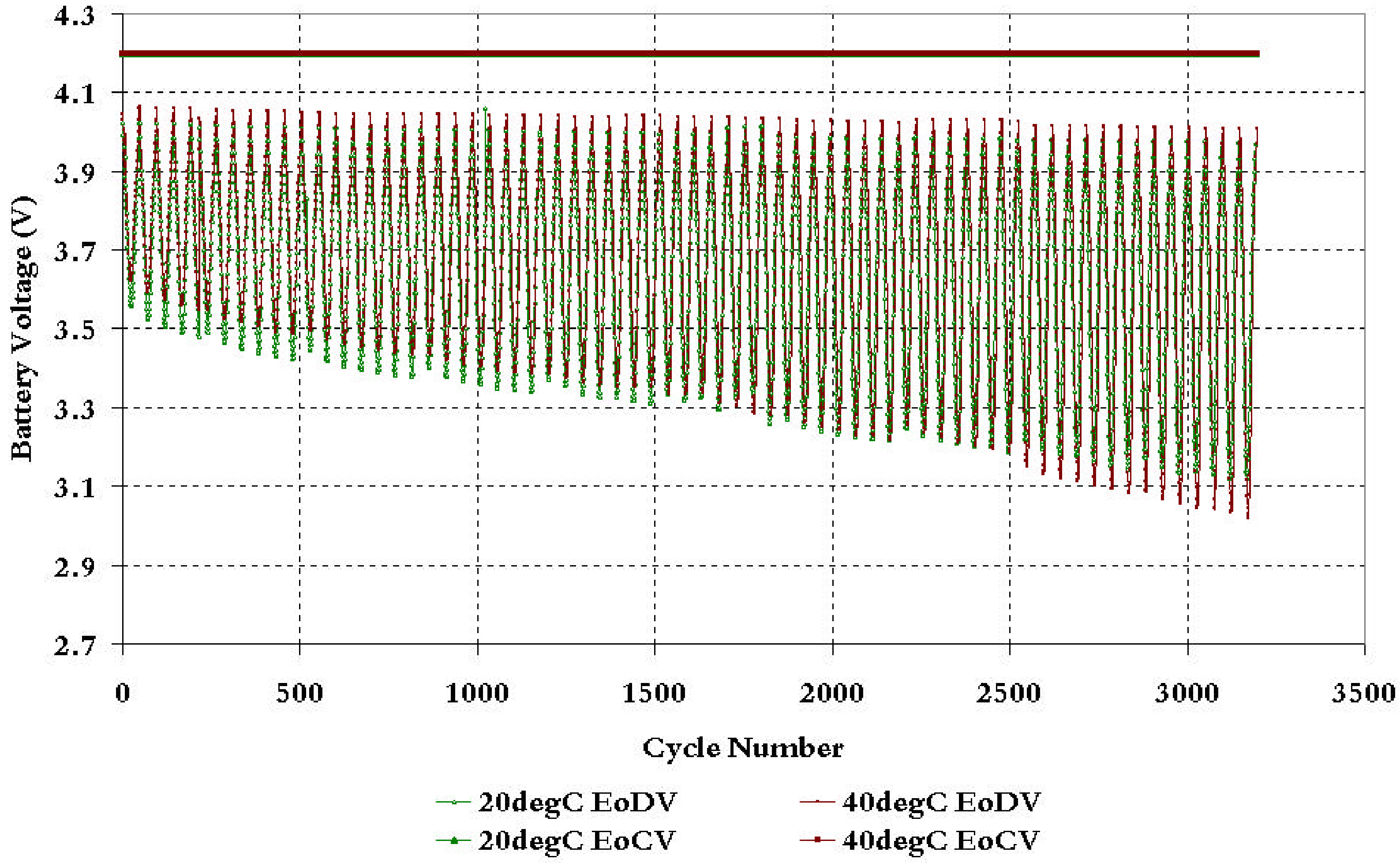
Characterization & Life Test

- Extensive testing for space applications
  - 2 million cell-hours
- Most tests performed on small 6s 2p modules
- All generic life tests performed at 4.2V per cell EOCV
- Temperature sensitivity
  - 0°C, 10°C, 20°C, 40°
- Depth of discharge (relative to BOL 4.2V capacity)
  - 10% to 100%
- Rate
  - C/2 to 1.8C in discharge, C/20 to 1.8C in charge
- Real time tests

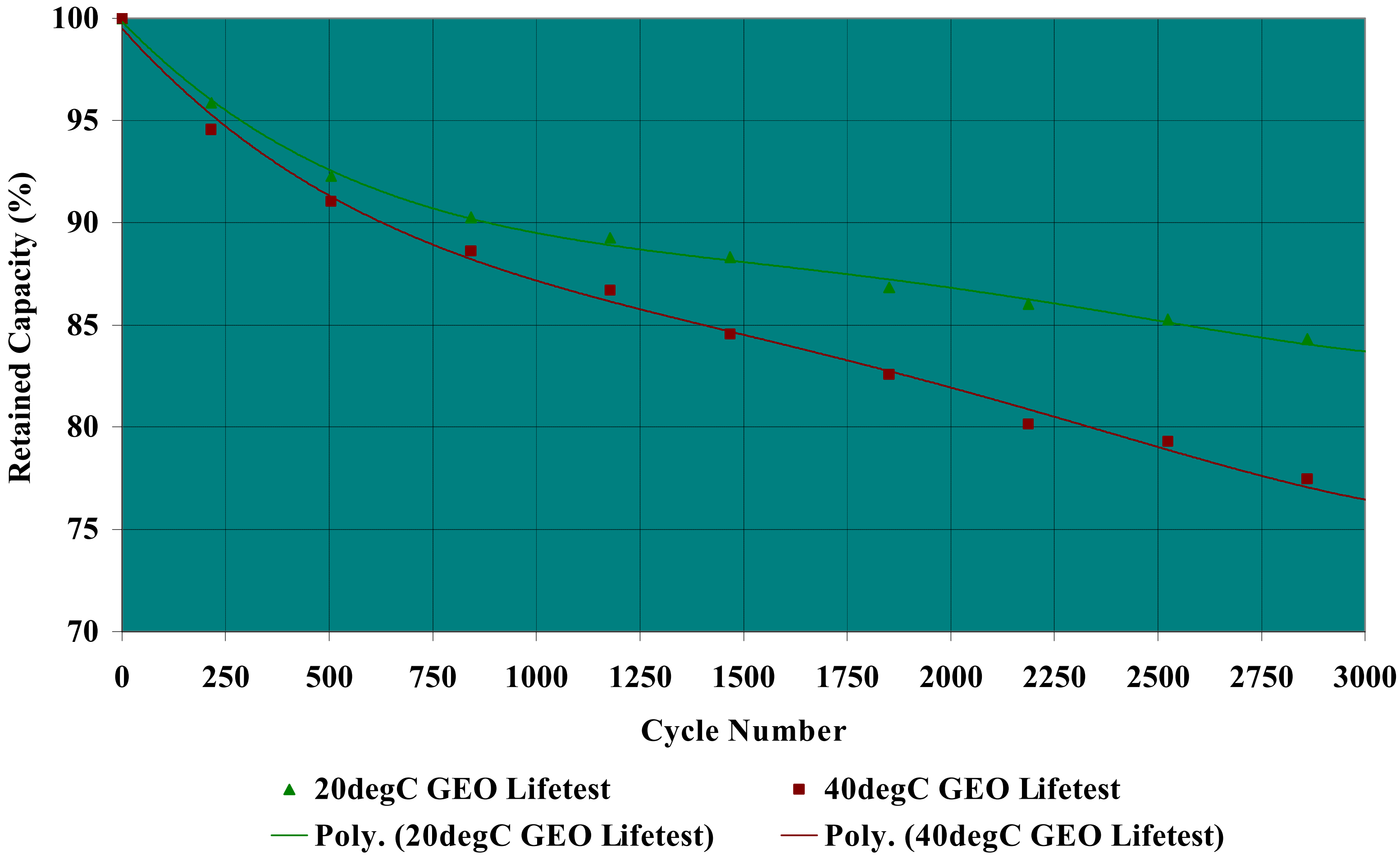
Internal Resistance



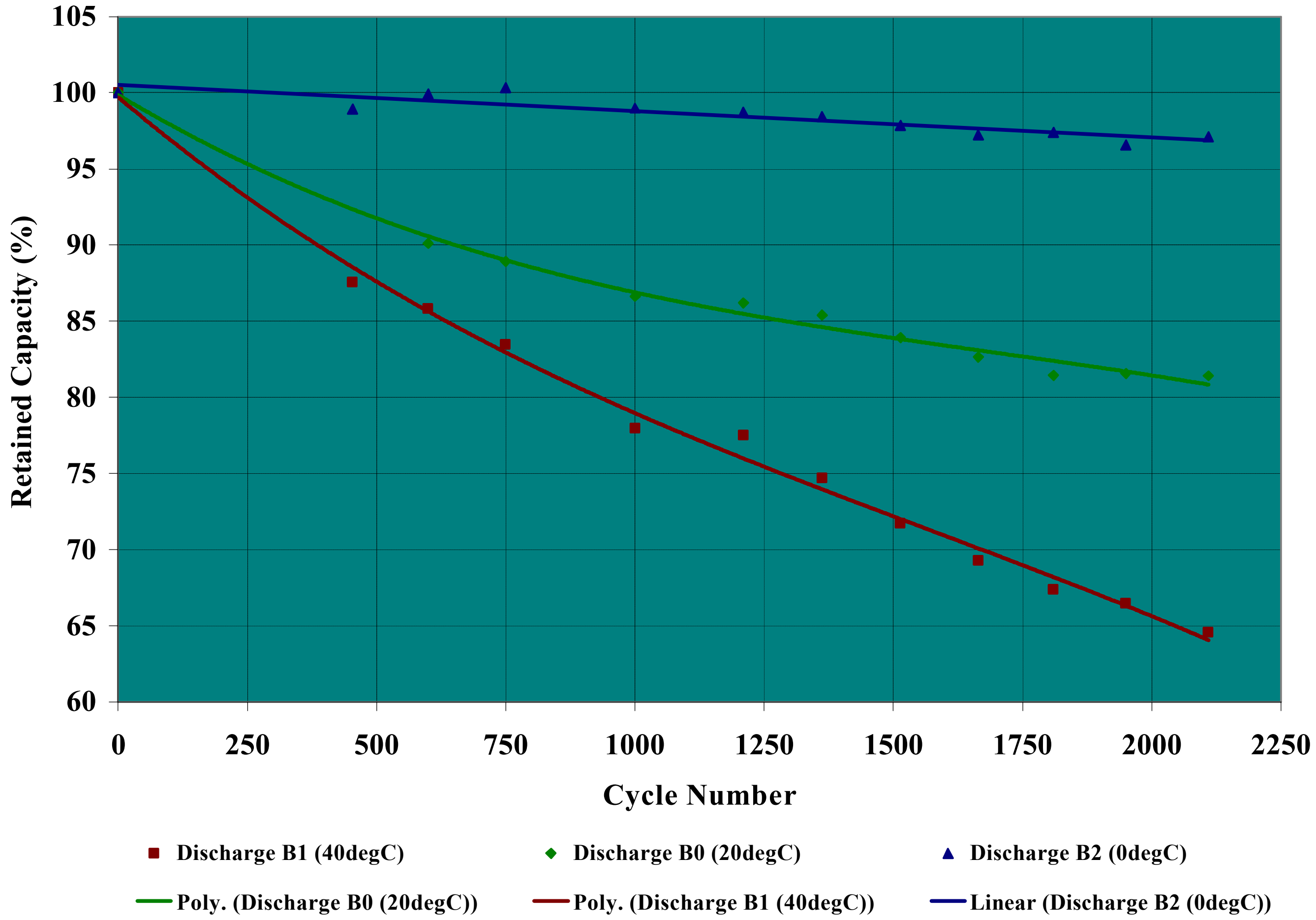
72 Simulated GEO Eclipse Seasons



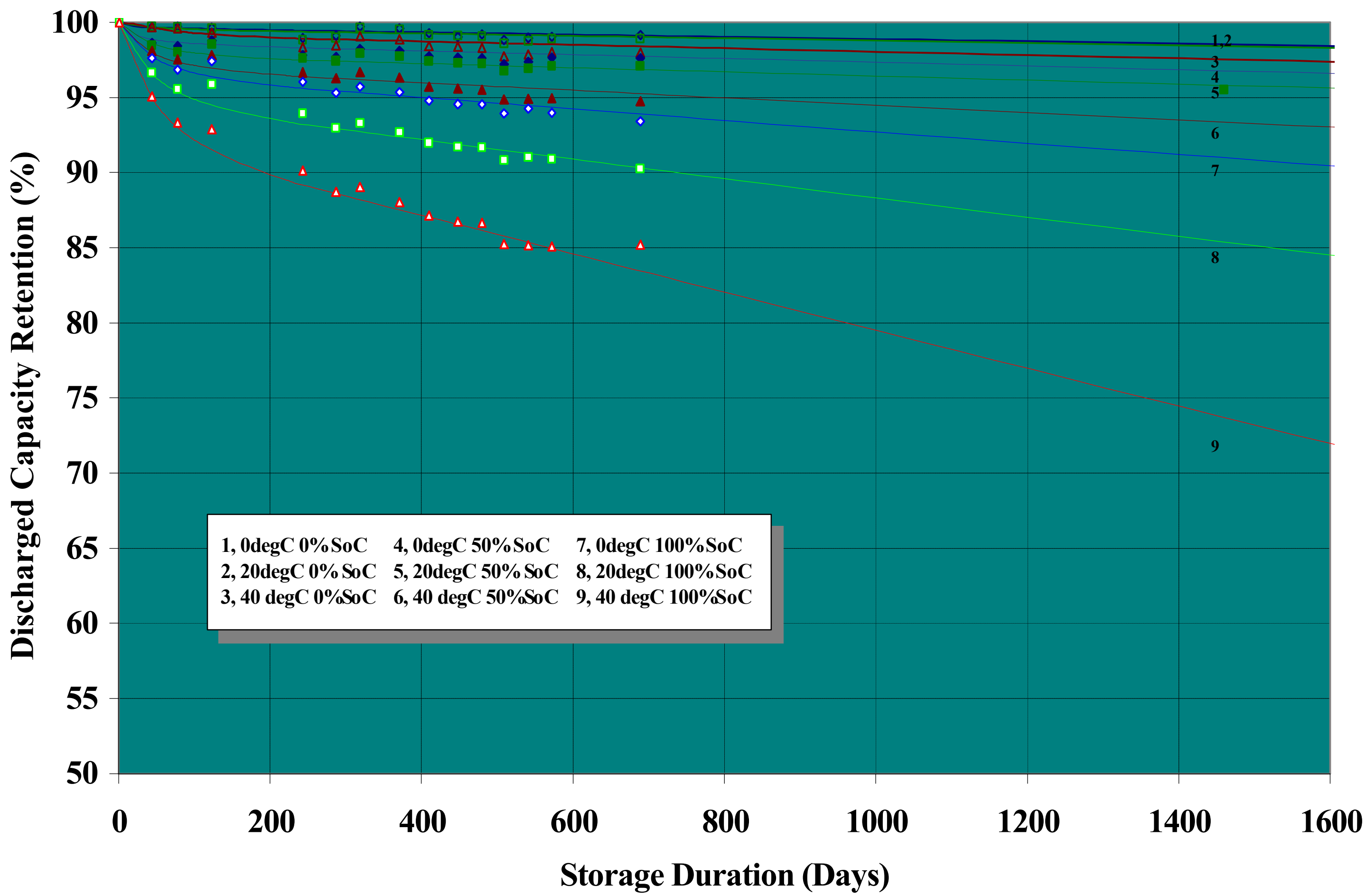
Capacity After Variable DOD Cycling



Constant DOD GEO cycling



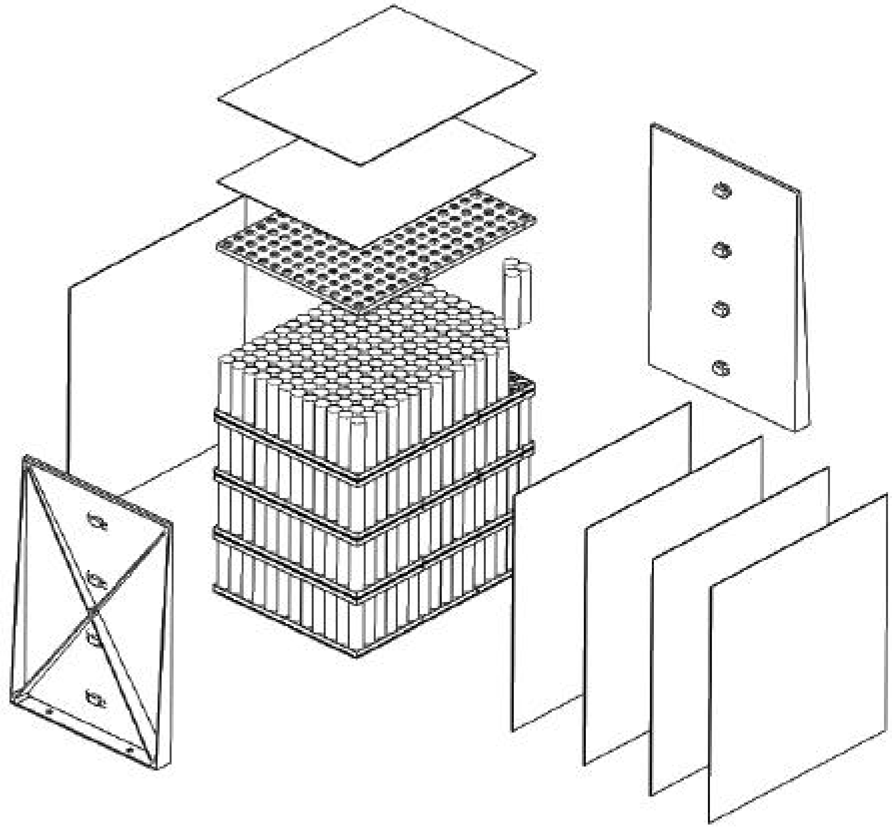
Calendar Aging



AEA TECHNOLOGY SPACE

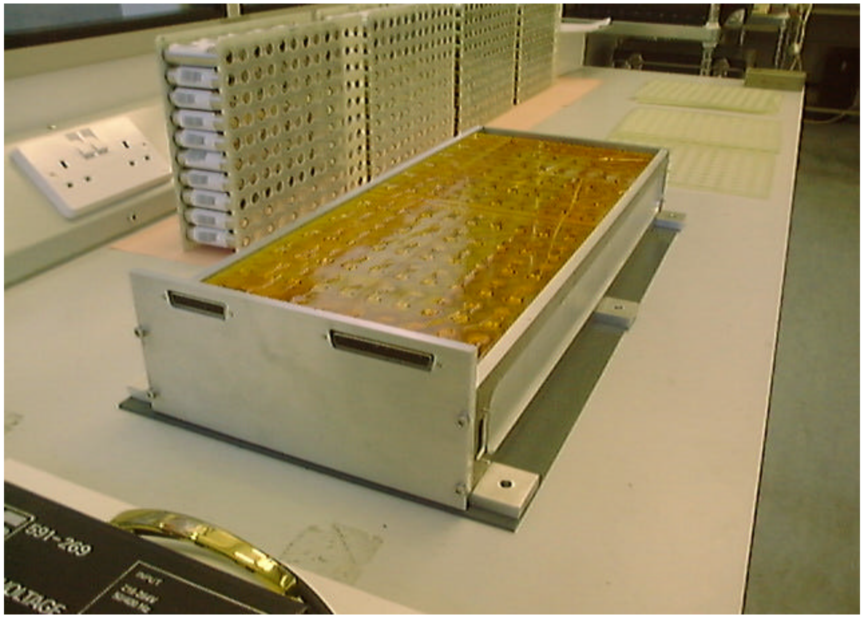
COM DEV SPACE GROUP

Larger Modules



Scale – Up Tests

- Series of planned ground tests
- Voltages between 50V and 100V
- Single & multiple module tests
- Several different test locations



Conclusions

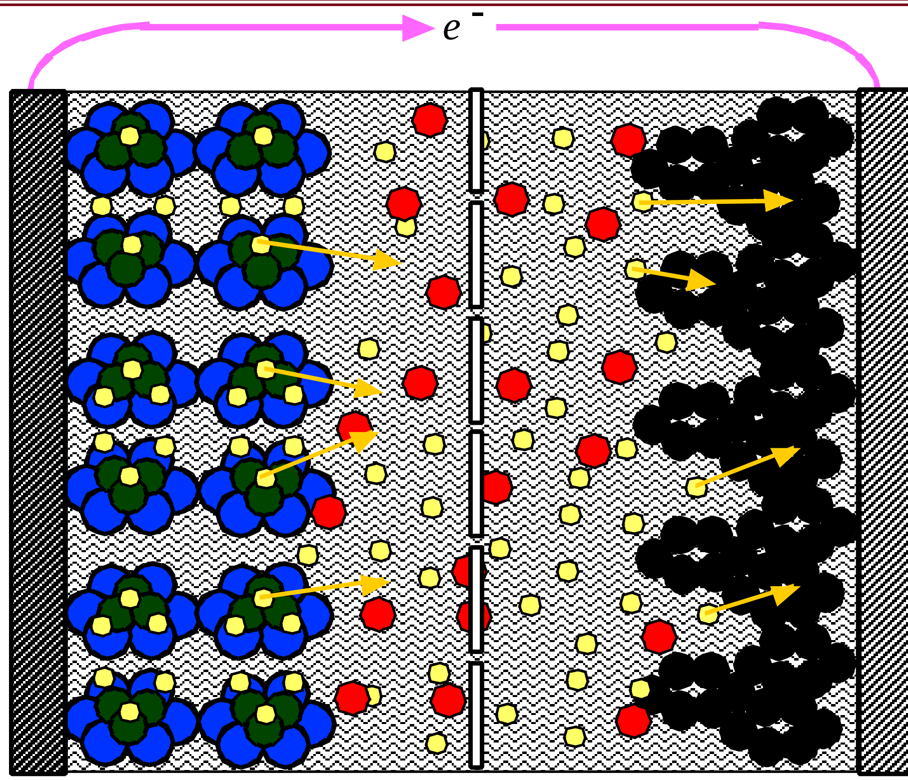
- Small cell approach to satellite Lithium-ion batteries is both viable and attractive
- Small cells can be used to build large batteries
- Use of Sony 18650 HC cells maximizes maturity and delivers excellent performance
- Excellent possibilities for delivering much higher performance in the future

Characterization of Electrolytes by Computer Modeling

Brandy Moore,
Richard Whiteley,
James Currie and
Kevin Johnson

Pacific University
Forest Grove, Oregon

Background of Lithium Battery Technology



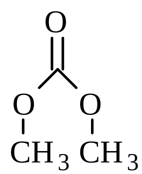
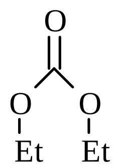
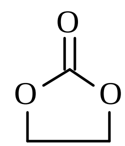
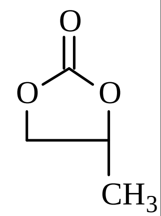
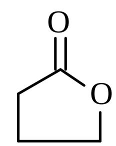
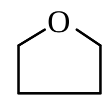
$LiNiO_2 \longrightarrow xLi^+ + Li_{1-x}NiO_2 + xe^-$

$C_6 + yLi^+ + ye^- \longrightarrow Li_yC_6$

Electrolyte Requirements

- The Ideal Solvent
  - Large liquid range
  - Low viscosity
  - Ability to solvate ions
  - Minimal toxicity
  - Large working voltage

Status Quo for Solvents

						
M.P.	**4.6°C**	**-43**	**+39**	**-49**	**-43**	**-109**
B.P.	**91°C**	**126**	**248**	**240**	**203**	**66**
Viscosity	**0.59cP**	**0.75**	**1.86 ***	**2.5**	**1.75**	**0.48**
Dielectric Constant e	**3.12**	**2.82**	**89.6 ***	**64.4**	**39**	**7.75**
****Solution Conductivity**	**11.00 mS/cm**	**5.00**	**6.97**	**5.28**	**10.62**	**12.87**

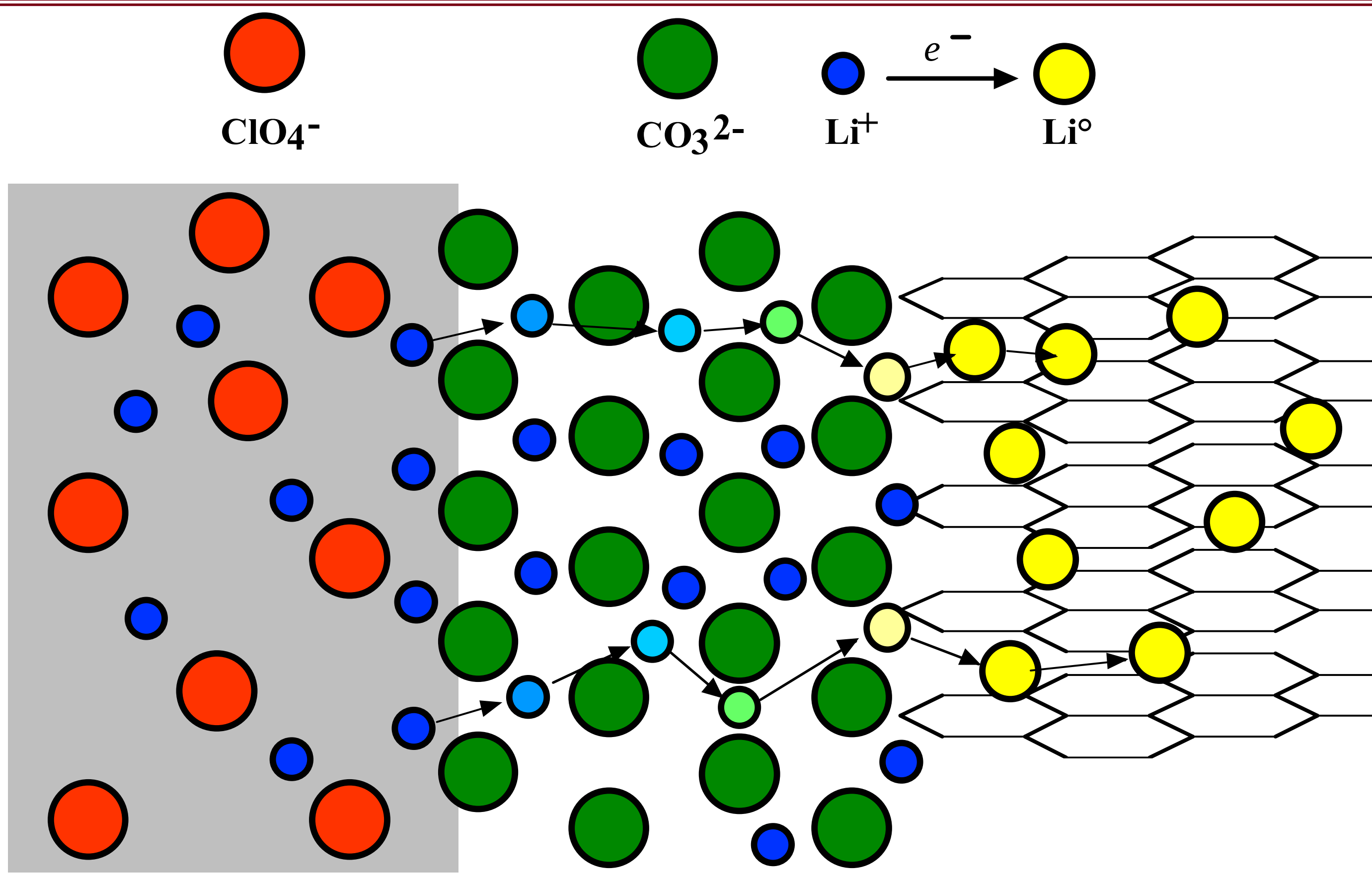
* At 40°C

** 1 M LiAsF

The Problem

- The electrolyte (solvent) can be reduced in lieu of Li^+ ion reduction / intercalation.
- This causes significant, irreversible capacity loss on the first charge cycle.
- It can also lead to considerably more capacity loss over long periods.
- The S.E.I. or P.E.I. that forms with electrolyte decomposition mitigates further decomposition of the electrolyte, but this S.E.I. or P.E.I. also inhibits charge transfer at the anode and this limits the *power* of the Li Ion cell.

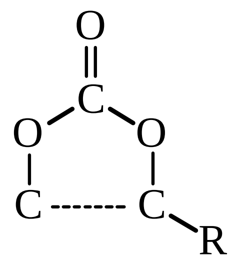
How the SEI works



Questions

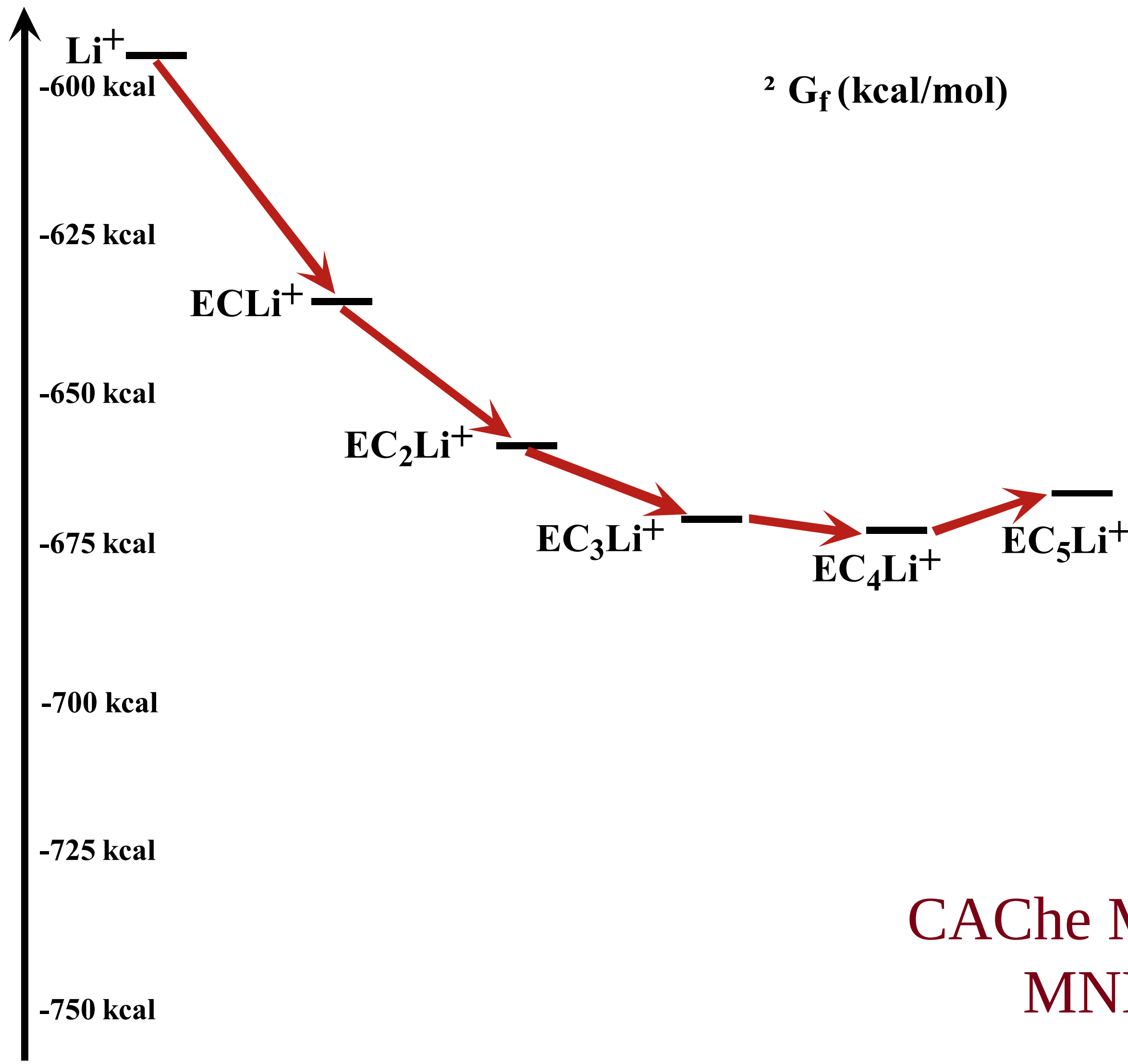
- Can the behavior of electrolyte solvent be predicted through computer modeling?
  - What *molecular* properties of a solvent make it susceptible to electrochemical degradation?
  - What properties of a solvent make it form a S.E.I. or P.E.I.?
  - Can a solvent be designed that will not be oxidized or reduced under charge or discharge conditions?
  - If not, can a solvent be designed that will form a thin, robust S.E.I.?

Generally Accepted Behavior of Alkyl Carbonates



- They strongly coordinate Li^+ ions, probably 4:1[1,2]
- There is an electron transfer to the electrolyte well anodic of Li^+ ion reduction[3]
- Subsequent electron transfers are likely[4,5]
- *After* the reduction process, these Alkyl Carbonates decompose to:[4,6,7] polymerization products, $CH_2{=}CHR_{(g)}$, $CO_{2(g)}$, $(CHROCO_2Li)_{2(s)}$, and $Li_2CO_{3(s)}$
- Chloroethylene Carbonate *also* easily loses Cl^- [8]

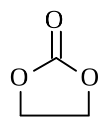
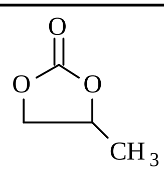
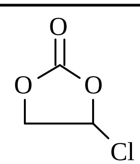
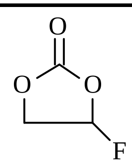
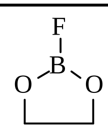
Free Energy Map 1



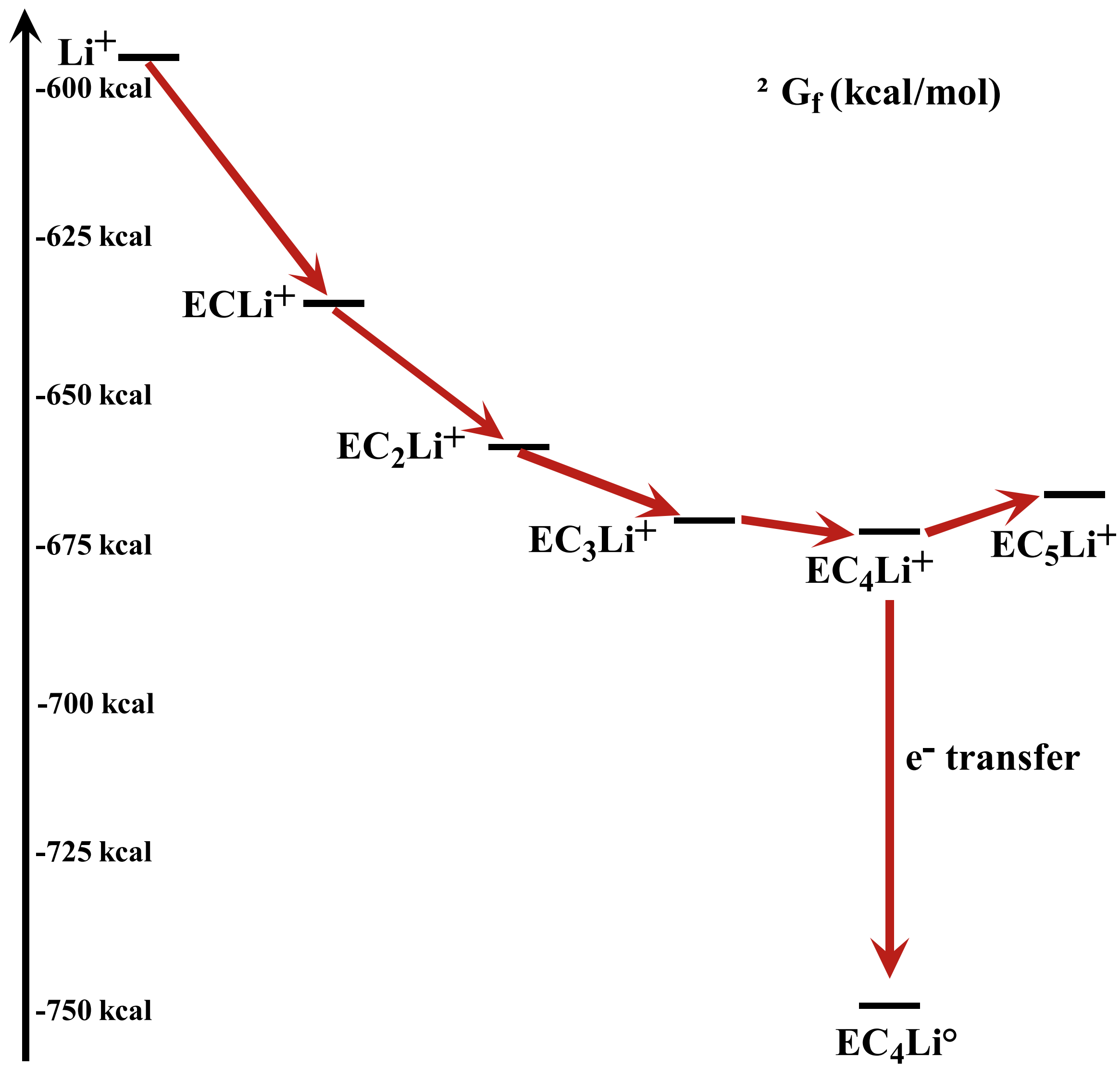
CAChe MOPAC
MNDO

Li^+ Ion Solvation

$$Li^{+} + nS \longrightarrow LiS_n^{+}$$

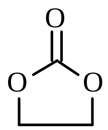
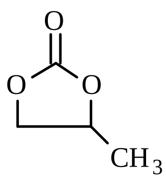
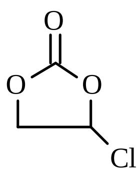
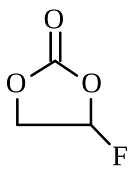
Solvent	Ave. n	$\alpha_{LiS_{n(mode)}^{+}}$	^{2}G° form. kcal/mole
	3.97	0.97	-78
	3.98	0.98	-87
	4.00	1.00	-72
	4.00	1.00	-71
	5.92	0.93	-140

Free Energy Map 2

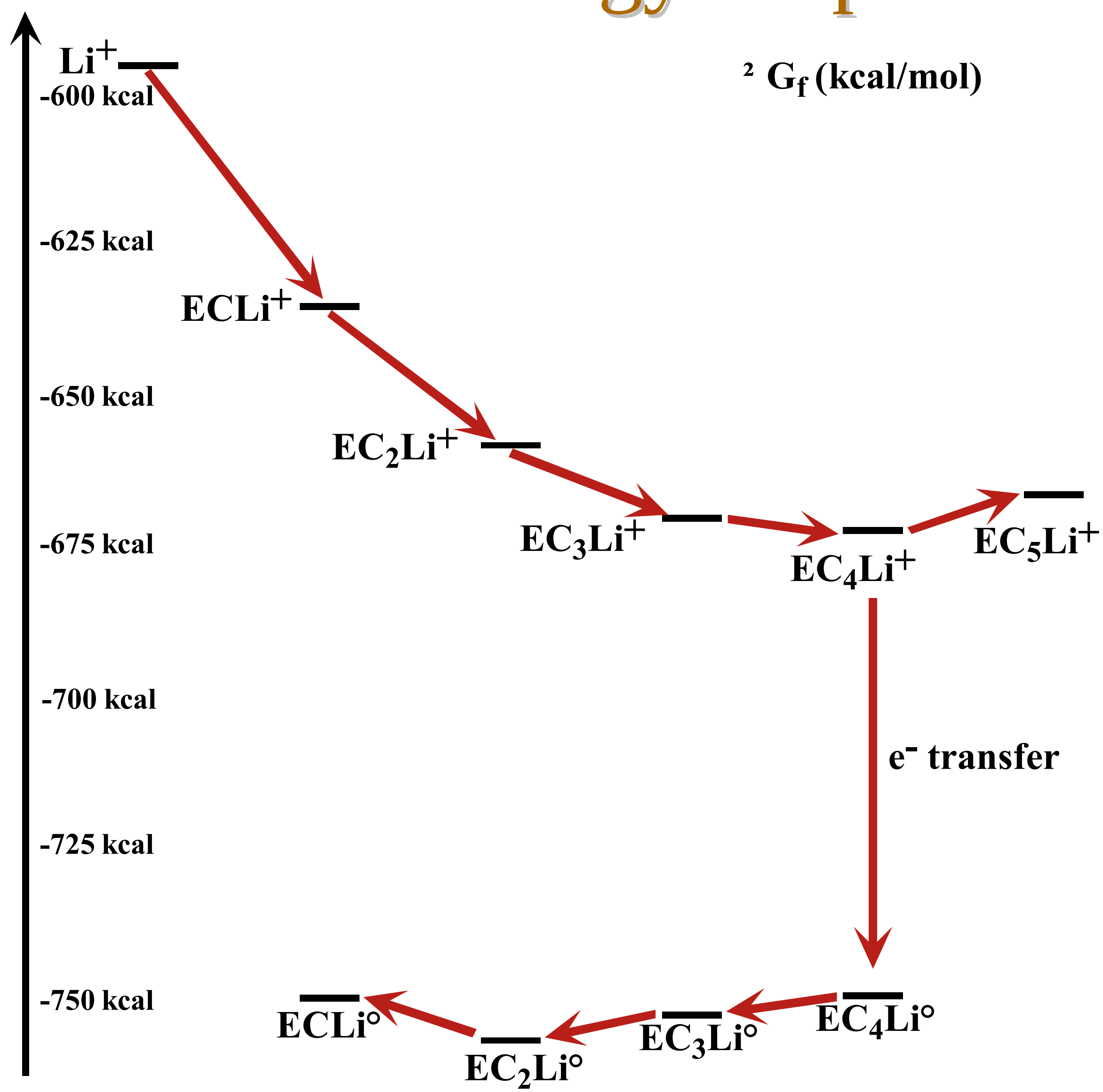


First Reduction Process

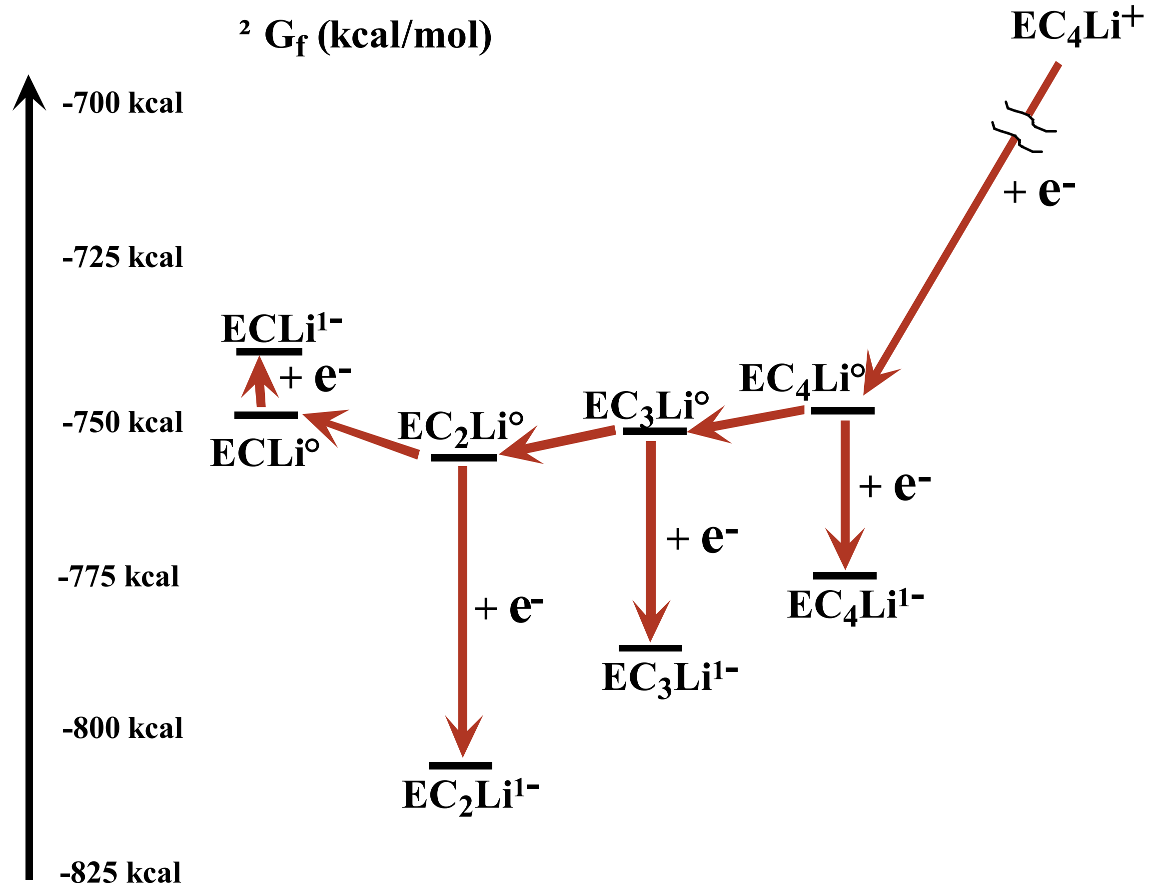
$S + e^- \longrightarrow S^-$ $\quad$ $LiS_4^+ + e^- \longrightarrow LiS_n^0$

Solvent	E.A. (S) (eV)	$^2G°_{red}$ (kcal/mole)	E.A. (LiS_4^+)	$^2G°_{red}$
	-0.97	-1.5	1.9	-77
	-1.02	-1.1	1.8	-70
	0.30	-12.5	2.7	-88
	-0.68	-9.3	2.3	-80

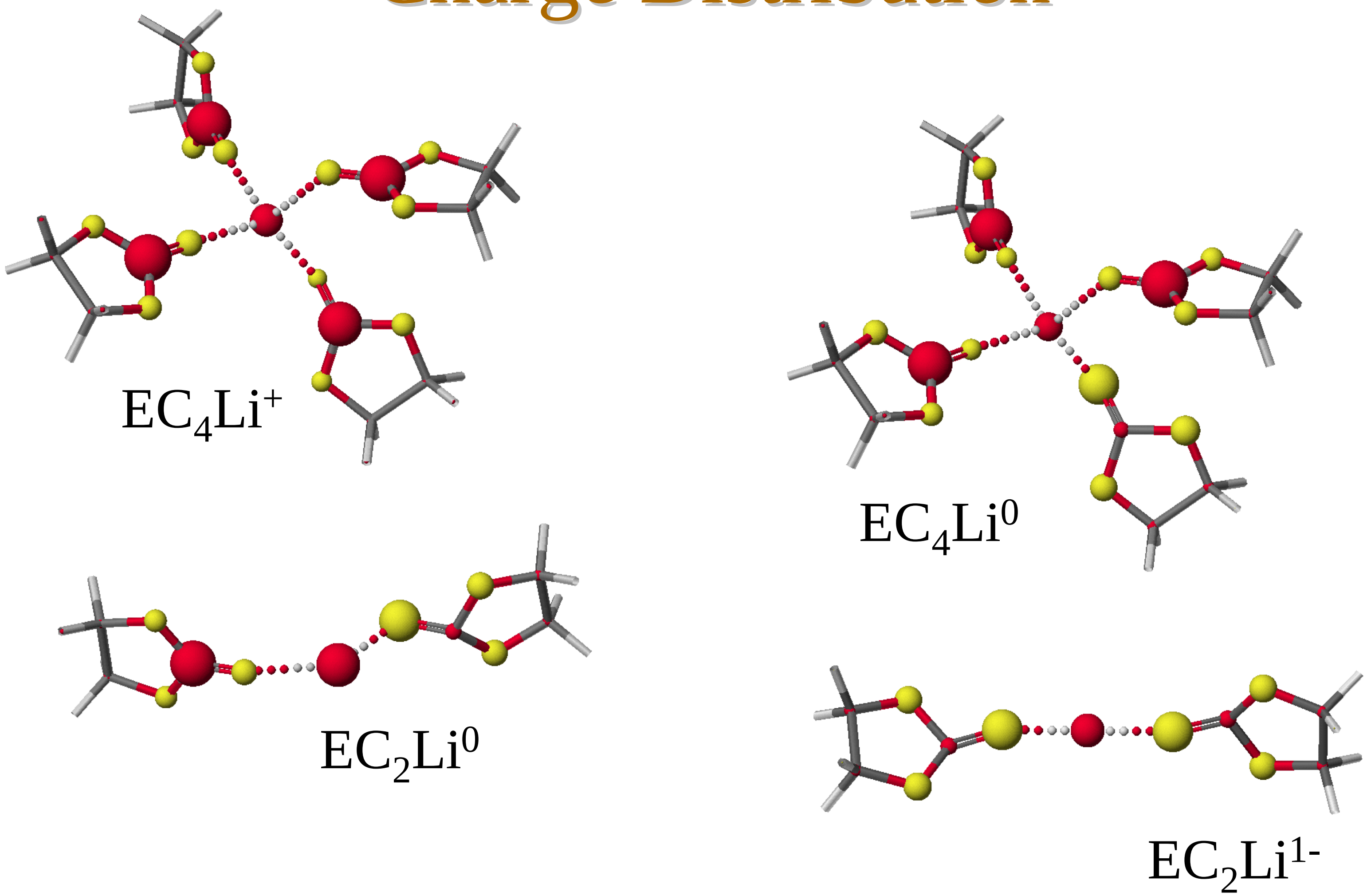
Free Energy Map 3

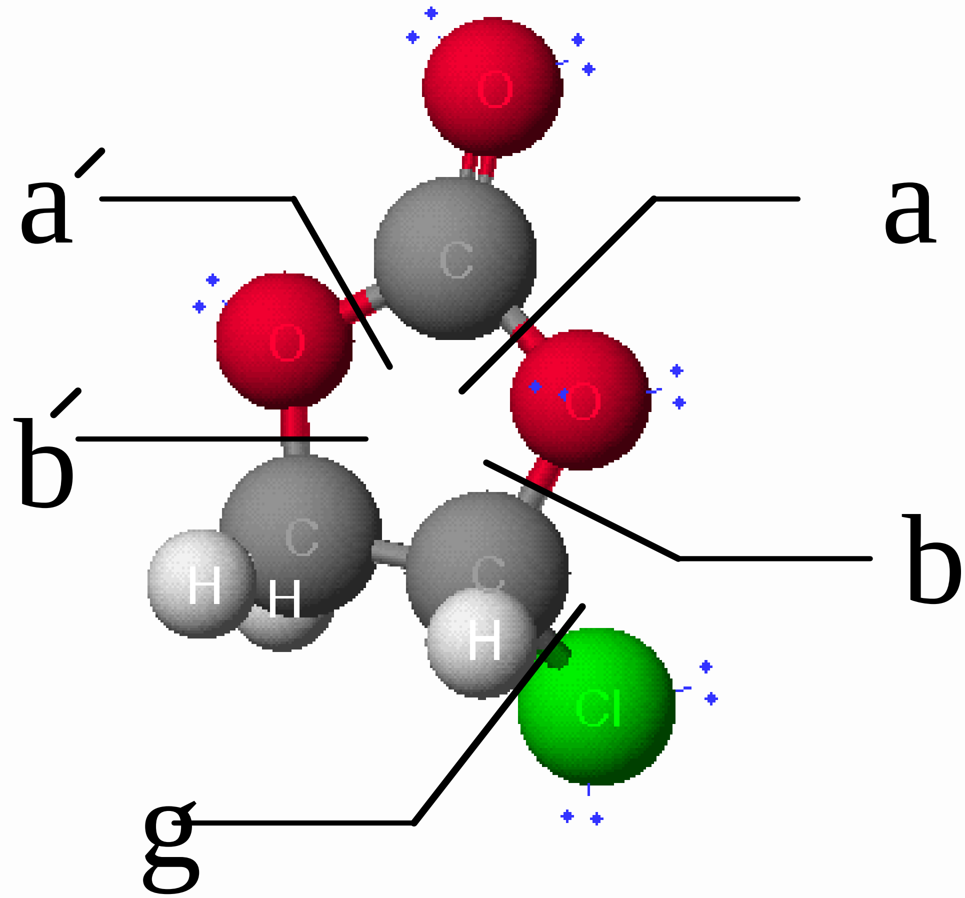


Free Energy Map 4



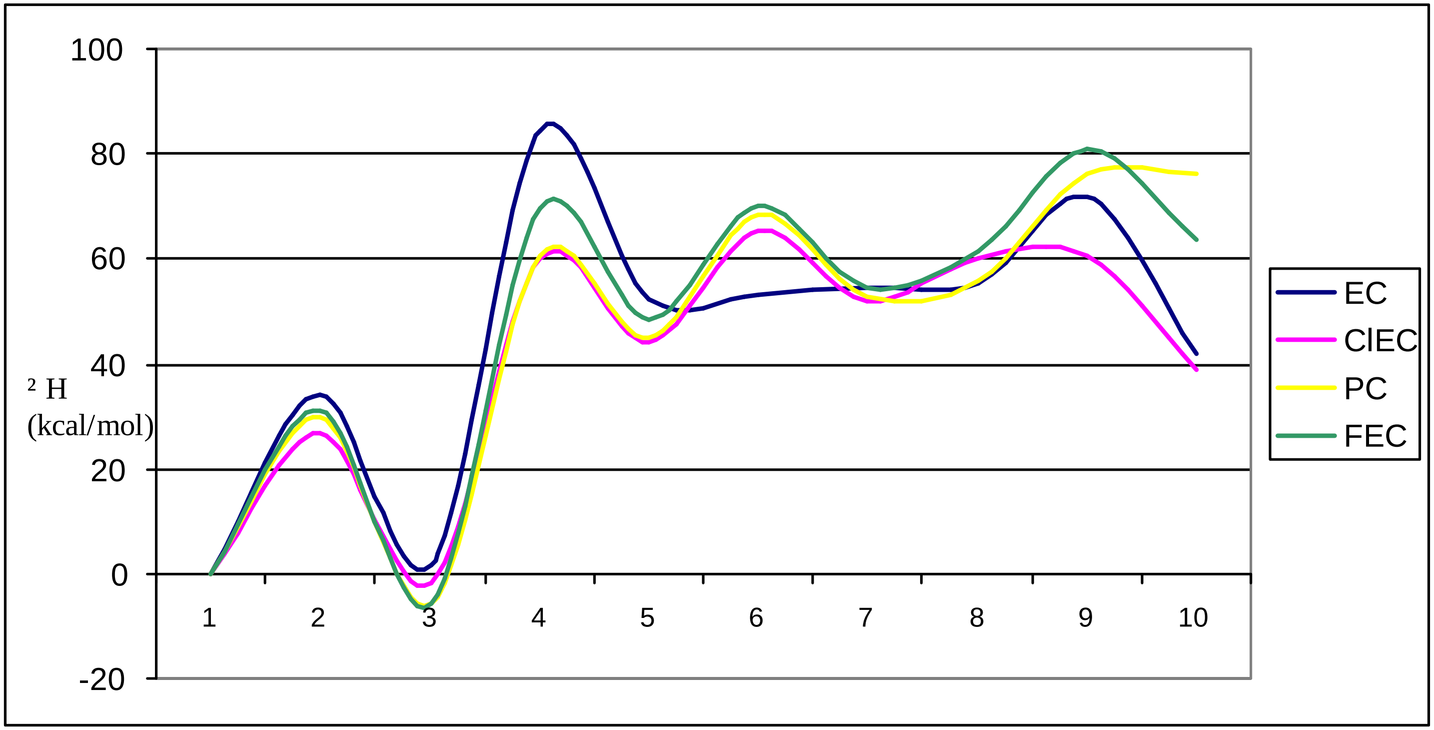
Charge Distribution





a´
a
b´
b
g
O
C
O
O
C
C
H
H
H
Cl

? H Normalized Reaction Pathway



1 doubly reduced w/ 2 solvent molec

2 breaking beta bond (transition state)

3 broken beta bond (opt)

4 addition of 3rd electron

5 optimized structure w/ 3e-

6 breaking other beta bond (transition state)

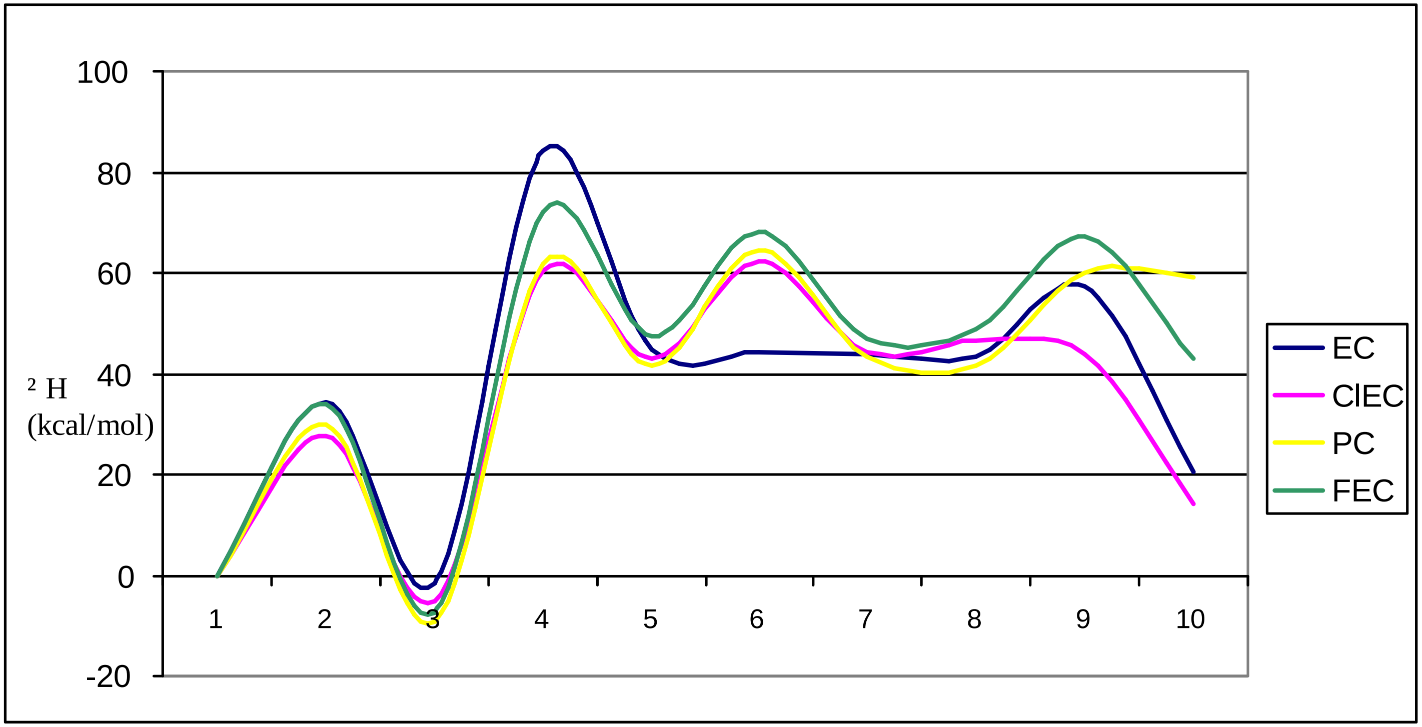
7 optimized, carbonate formed

8 CH_2=CH-R lost

9 losing solvent molecule (transition state)

10 isolated lithium carbonate

? G Normalized Reaction Pathway



1 doubly reduced w/ 2 solvent molec

2 breaking beta bond (transition state)

3 broken beta bond (opt)

4 addition of 3rd electron

5 optimized structure w/ 3e-

6 breaking other beta bond (transition state)

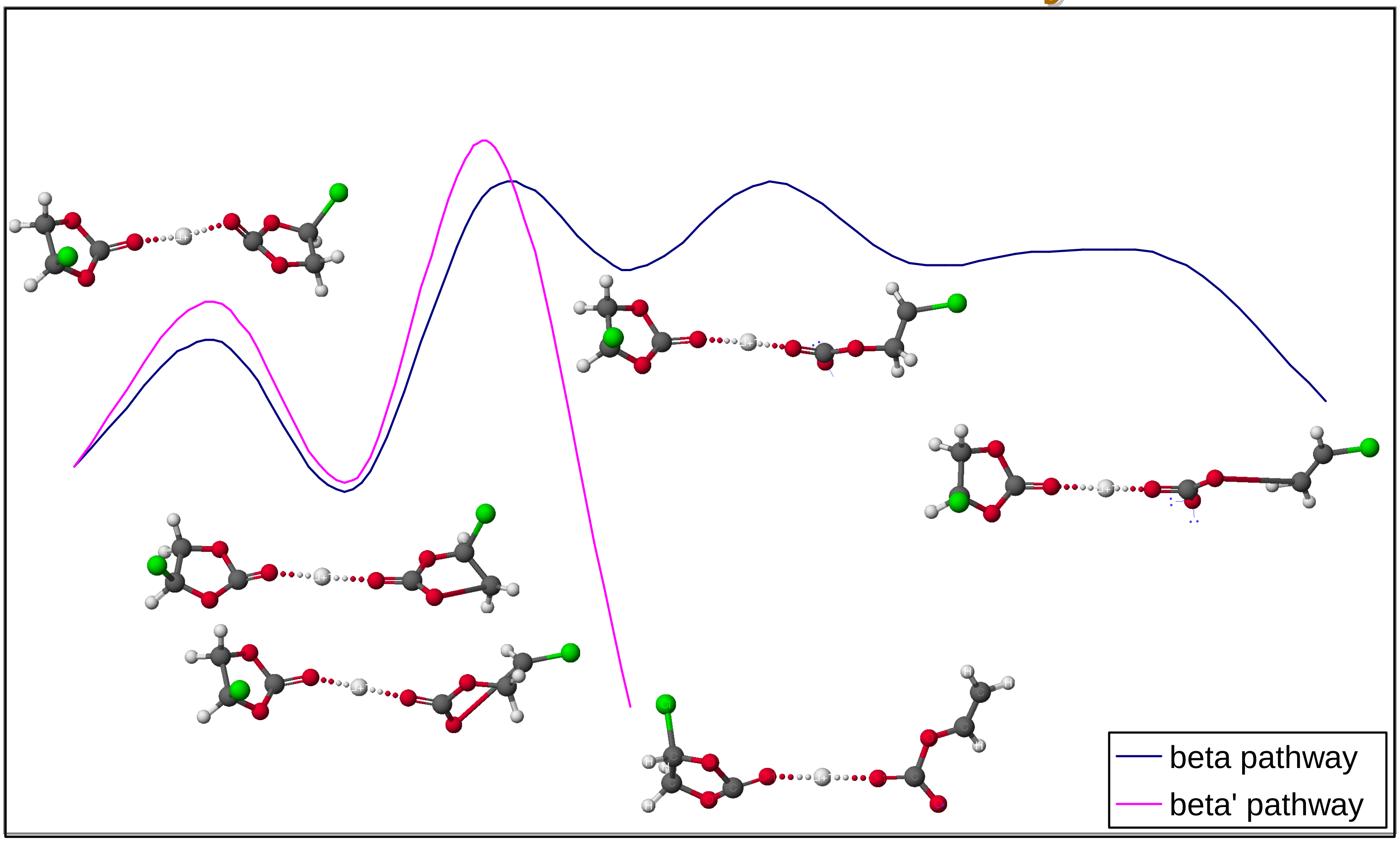
7 optimized, carbonate formed

8 CH_2=CH-R lost

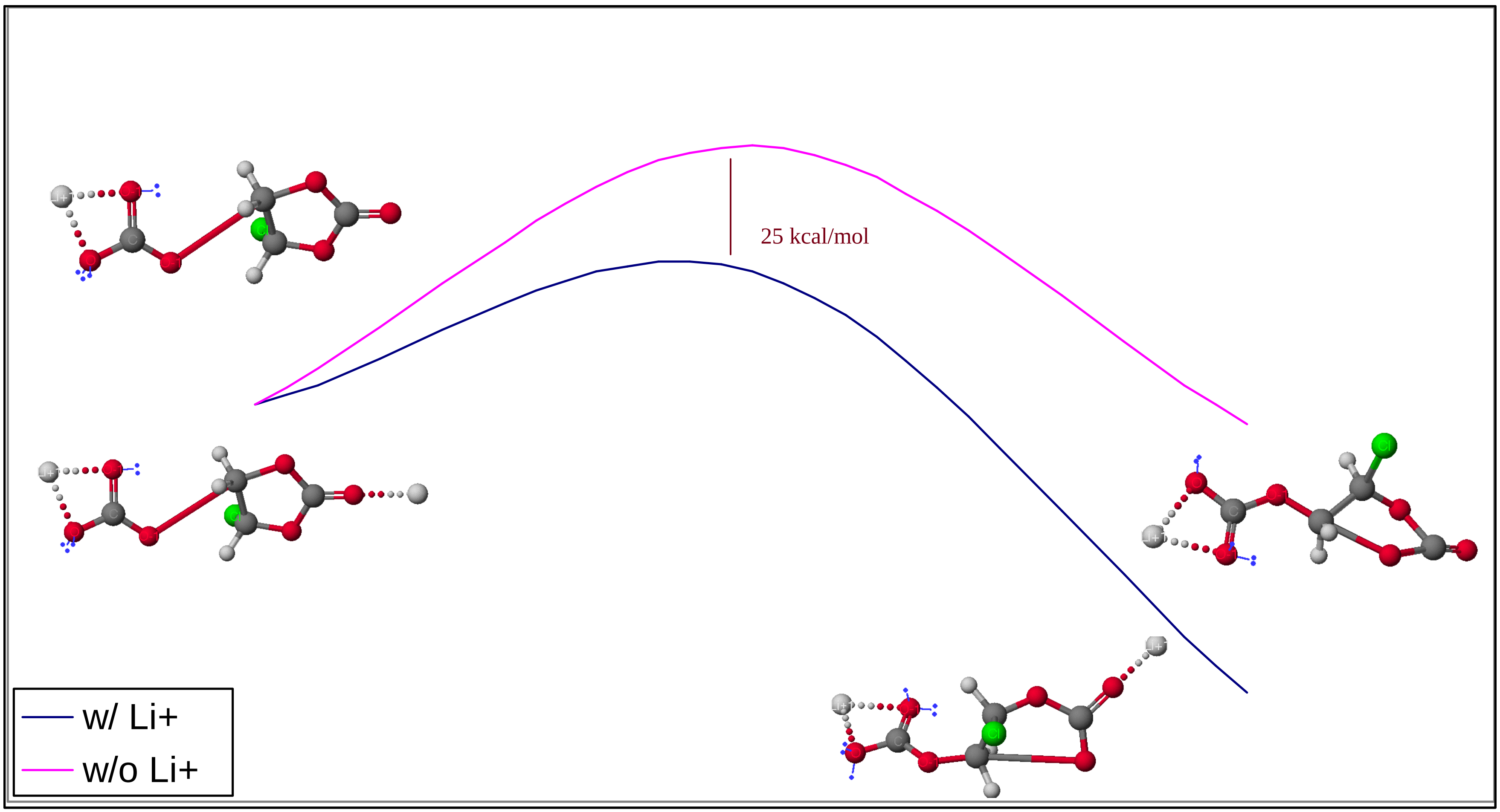
9 losing solvent molecule (transition state)

10 isolated lithium carbonate

ClEC Reactions Pathways



ClEC Reactions Pathways



Future Work

- Further analysis of the pathways obtained from this research using *ab initio* calculations and updated parameters in MOPAC.
- Investigate oxidation processes.
- Design and characterize new solvents based on this work.

References

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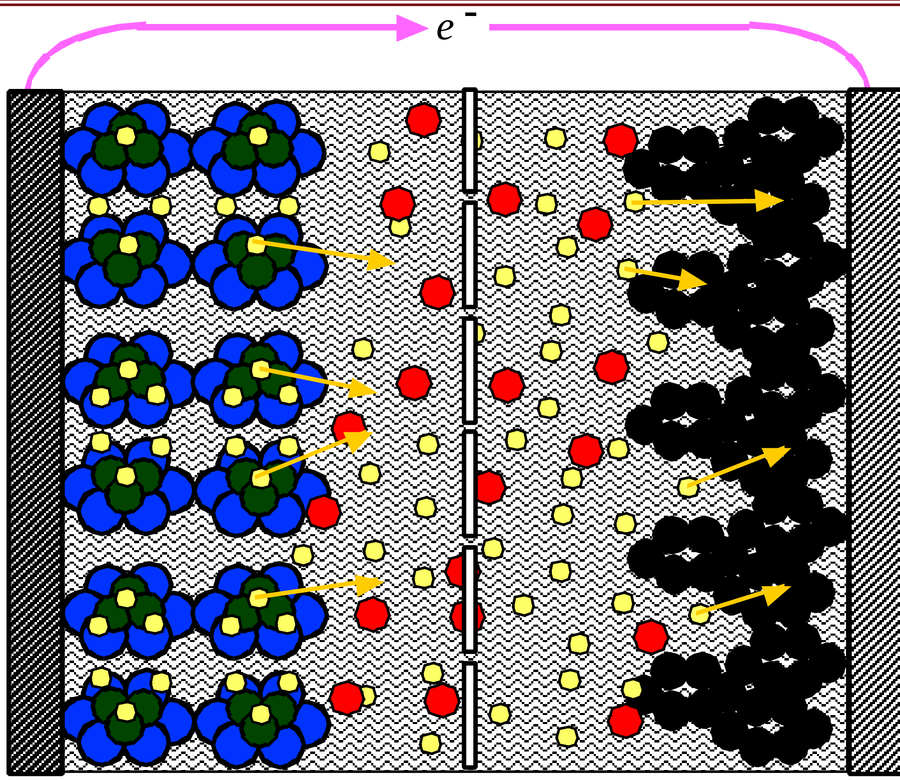
8. Z.X. Shu, R.S. McMillan, J.J. Murray and I.J. Davidson, *ibid*, 143, 2230-2235 (1996).

Acknowledgements

- Murdock Charitable Trust
- Pacific University

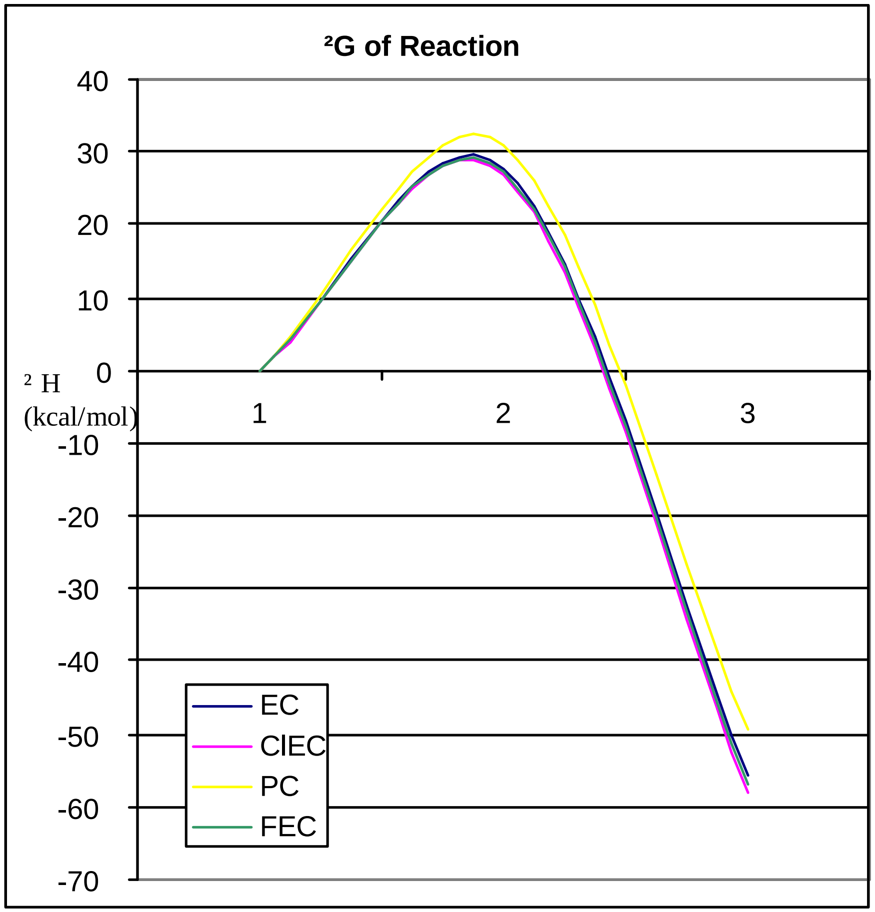
The Lithium Ion Cell

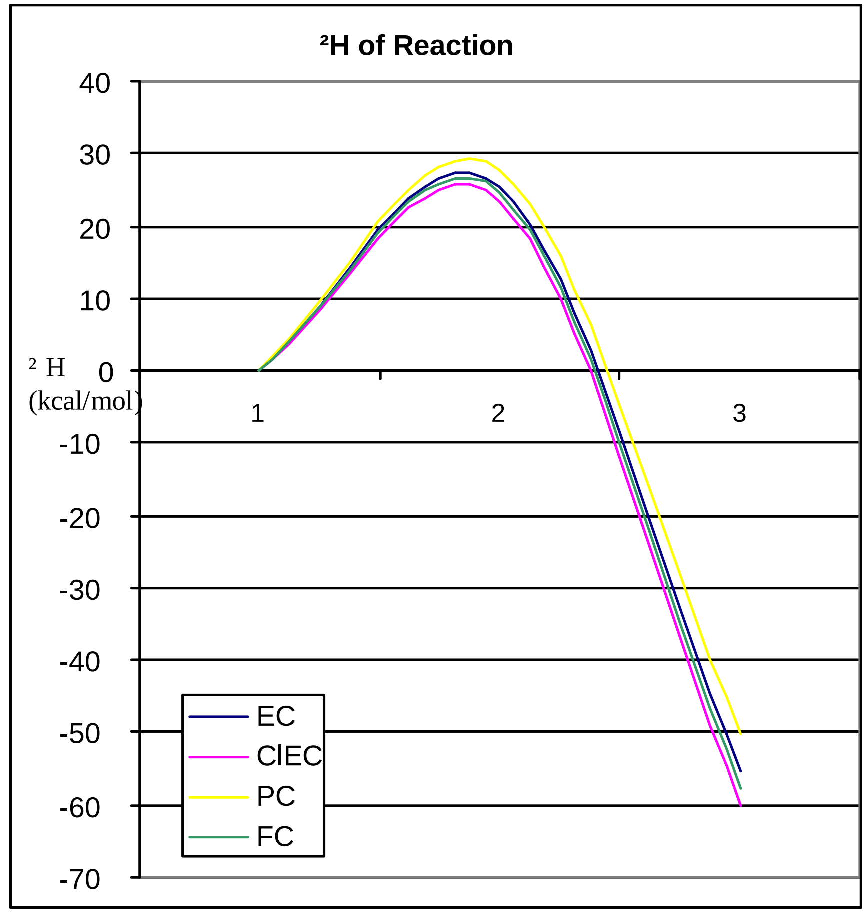


$$LiNiO_2 \longrightarrow xLi^+ + Li_{1-x}NiO_2 + xe^-$$

$$C_6 + yLi^+ + ye^- \longrightarrow Li_yC_6$$

Carbonate Reaction Pathways





LOCKHEED MARTIN

Li-ion EMU Battery Testing

Raymond Rehm

Lockheed Martin Space Operations

Bobby Bragg

NASA Johnson Space Center

Brad Strangways

Symmetry Resources

EMU BATTERY LIFE TESTING OBJECTIVES

- A 45Ah Li-ion battery comprised of five (5) Yardney prismatic cells is being evaluated to replace the silver-zinc cells in the Extra-vehicular Mobility Unit (EMU).
- The tests being conducted at Symmetry Resources are to determine if the 5 cell battery can meet the mission objective of 500 duty cycles and maintain a minimum voltage of 16.0 V without an individual cell voltage dropping below 3.0V.
- 40 Real Time cycles were conducted to develop BOL trend data (This accomplishment would exceed the current silver-zinc capability).
- Decision to switch to accelerated cycling for the remaining 460 cycles was made since "Real Time" cycling requires 1 day/cycle.

This presentation covers the initial test data

WHY CHANGE THE EMU BATTERY?

<u>Silver Zinc Design</u>

11 Zn/AgO Cells in Series

Cell Compliment Wt = 11.6 lbs

Cell Compliment Cost = $10K

45Ah Capacity BOL (Full Cap)

425 Day Wet Life, 32 Cycle Life

237.6 Wh/L BOL

141.0 Wh/Kg BOL

<u>Li-ion Design</u>

5 $LiNi_{1-X}Co_xO_2$ Cells in Series

Cell Compliment Wt = 12.2 lbs

Cell Compliment Cost = $20K

45Ah Capacity BOL (Full Cap)

Goal of 5 yr Wet Life, 500+ Cycle Life

262.8 Wh/L BOL

148.8 Wh/Kg BOL

EMU BATTERY LIFE TESTING

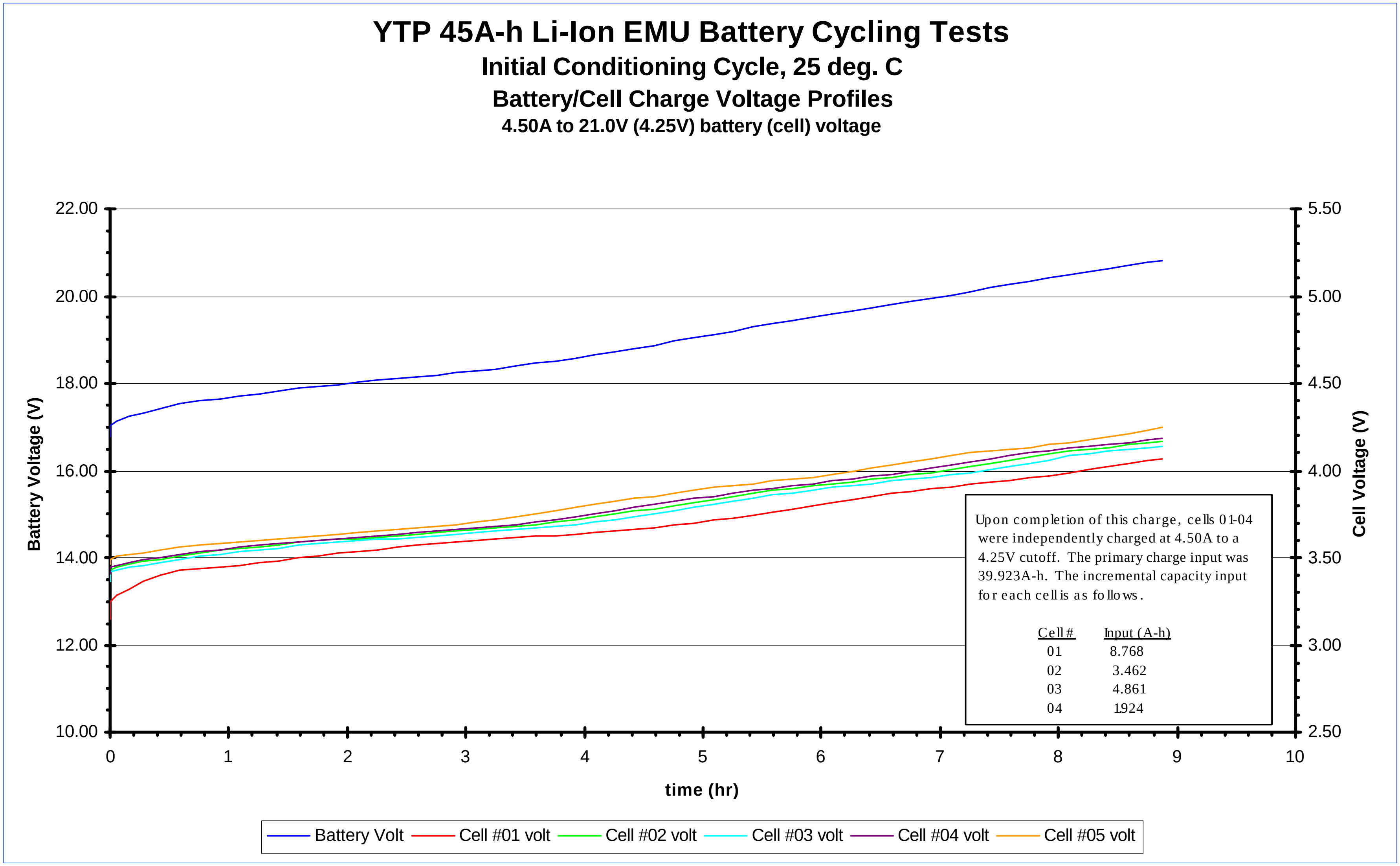
Characterization Testing at 50°C, 25°C, -10°C

40 Real Time Cycles at 25°C

460 Accelerated Cycles at 25°C

Characterization Testing at 50°C, 25°C, -10°C

LOCKHEED MARTIN



CHARACTERIZATION TESTING

Stabilize at Temperature

Charge at 4.5 amps to Battery Voltage of 21.0V or Cell Voltage 4.2V

Discharge at 10.0 amps to Battery Voltage of 14.5V or Cell Voltage of 2.7V

50°C Capacity = 48.09Ah (107.0% of 25°C)

25°C Capacity = 44.96Ah

-10°C Capacity = 31.31Ah (69.6% of 25°C)

REAL TIME CYCLING

Discharge at 3.8 amps for 7 hours or Battery Voltage of 16.0V, Cell Voltage of 3.0V

Charge at 1.55 amps for 20 hours or Battery Voltage of 20.5V, Cell Voltage of 4.1V

Every 20th Cycle, Continue Discharge to Battery Voltage of 16.0V, Cell Voltage of 3.0V

40 CYCLES COMPLETED

ACCELERATED CYCLING

Discharge at 11.0 amps for 2 hours 25 minutes or Battery Voltage of 16.0V, Cell Voltage of 3.0V

Charge at 11.0 amps to a Battery Voltage of 20.5V, Cell Voltage of 4.1V.

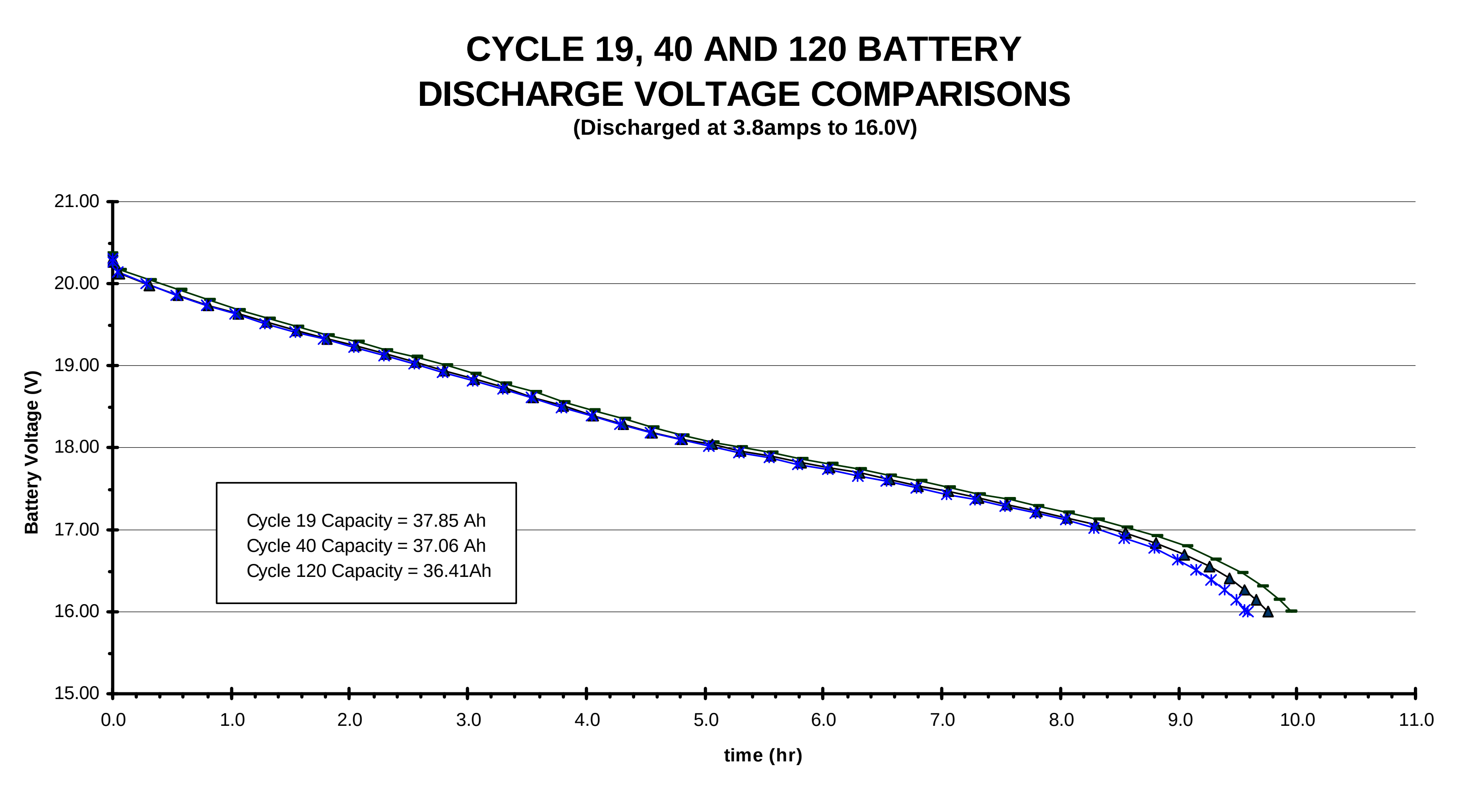
Then charge at 5.0 amps to a Battery Voltage of 20.5V, Cell Voltage of 4.1V.

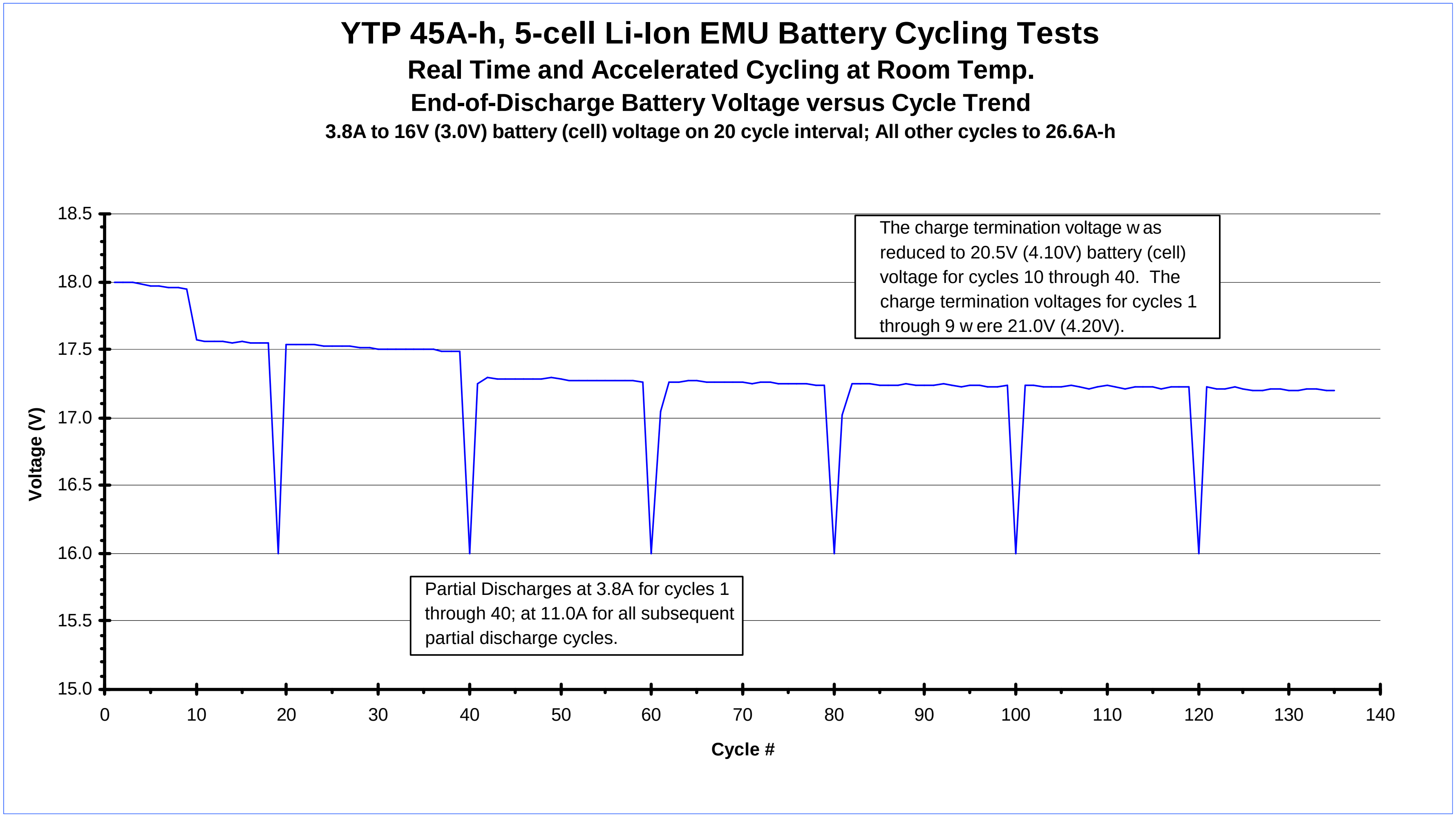
Then charge at 2.0 amps to a Battery Voltage of 20.5V, Cell Voltage of 4.1V.

Then charge at 1.0 amp to a Battery Voltage of 20.5V, Cell Voltage of 4.1V.

Every 20 Cycles Discharge Battery at 3.8 amps to 16.0V (Cell Voltage of 3.0V)

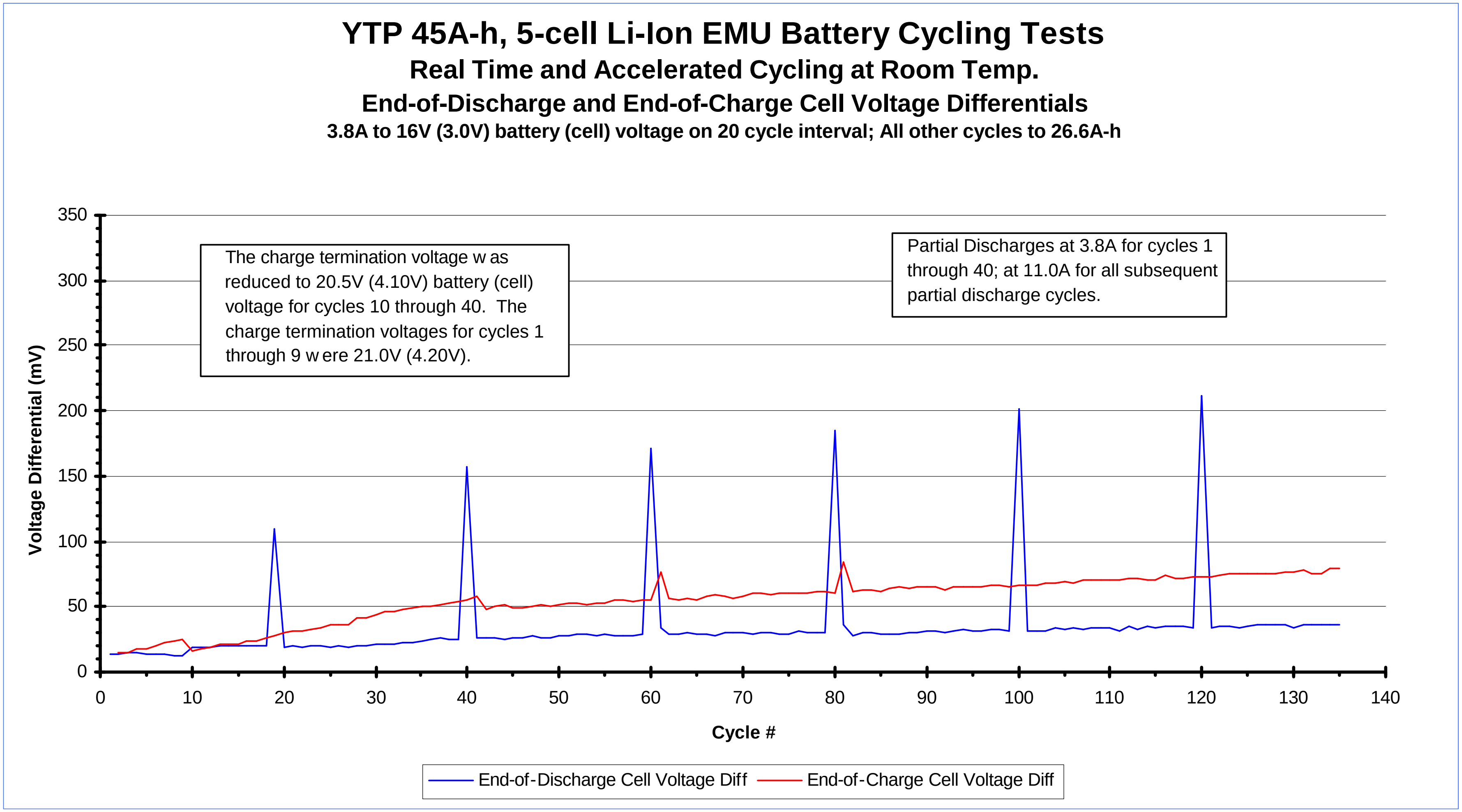
CYCLING IN PROGRESS


CYCLE 19, 40 AND 120 BATTERY
DISCHARGE VOLTAGE COMPARISONS
(Discharged at 3.8amps to 16.0V)
Battery Voltage (V)
21.00
20.00
19.00
18.00
17.00
16.00
15.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
time (hr)
Cycle 19 Capacity = 37.85 Ah
Cycle 40 Capacity = 37.06 Ah
Cycle 120 Capacity = 36.41Ah



FORM SEAT 076 (08/26/1997)

LOCKHEED MARTIN



SUMMARY

- The Data Indicates the Potential to Meet the 500 Cycle Objective Within the EMU Mission Requirements.

- Capacity to 16.0 Volts at 120 Cycles (36.41Ah) Exceeds Requirement by 36.9 %.

- Battery Charge Method and Cell Protective Circuitry Need to be Addressed.

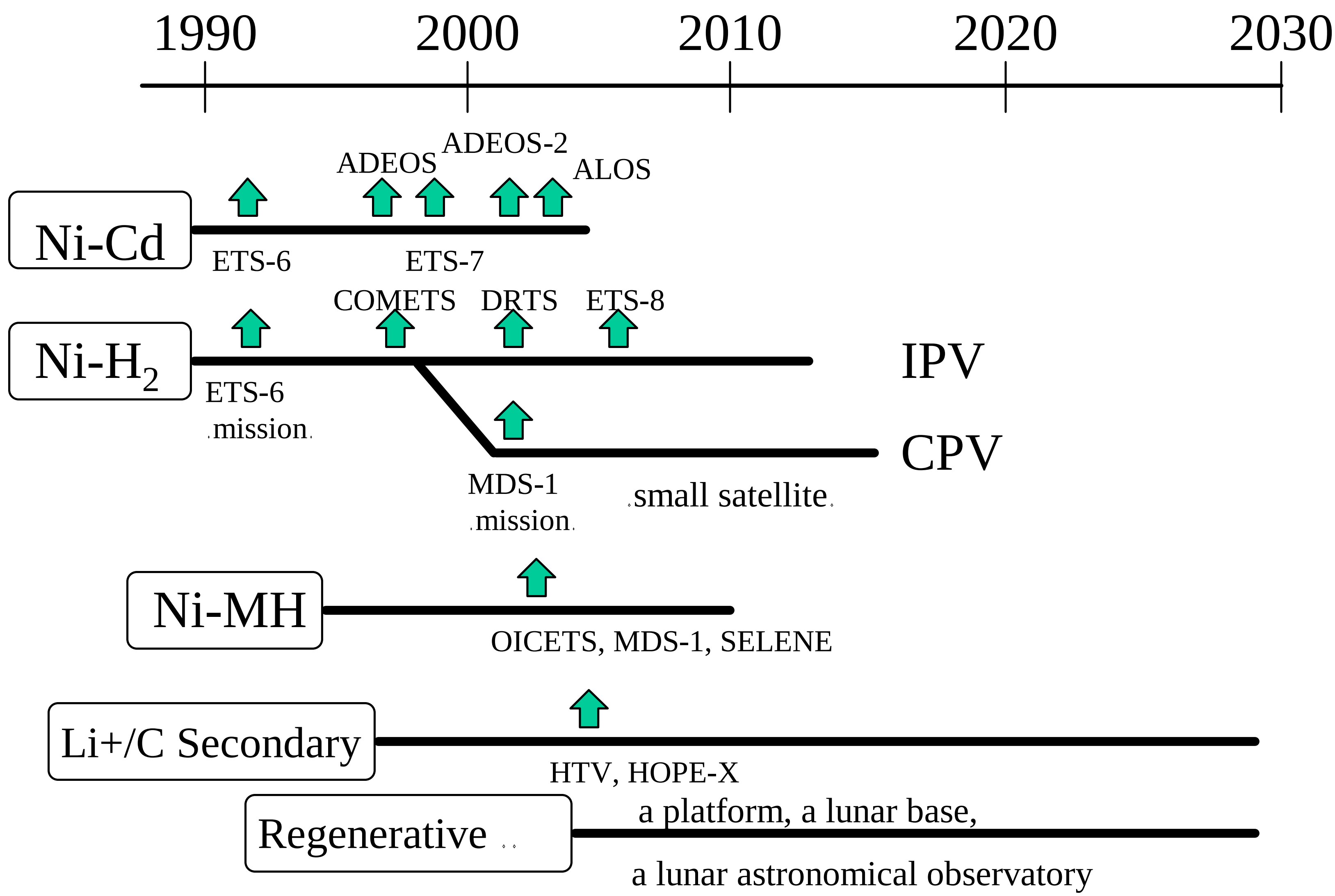
- 40 Additional Cells Have Been Ordered for Additional Performance and Safety/Abuse Testing for This Cell Design.

R&D Status of Li-Ion Secondary Cells at Tsukuba Space Center, NASDA

Y. Sone, X. Liu, H. Kusawake, K. Kanno, and S. Kuwajima

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

Development of Space Batteries at NASDA



NASDA

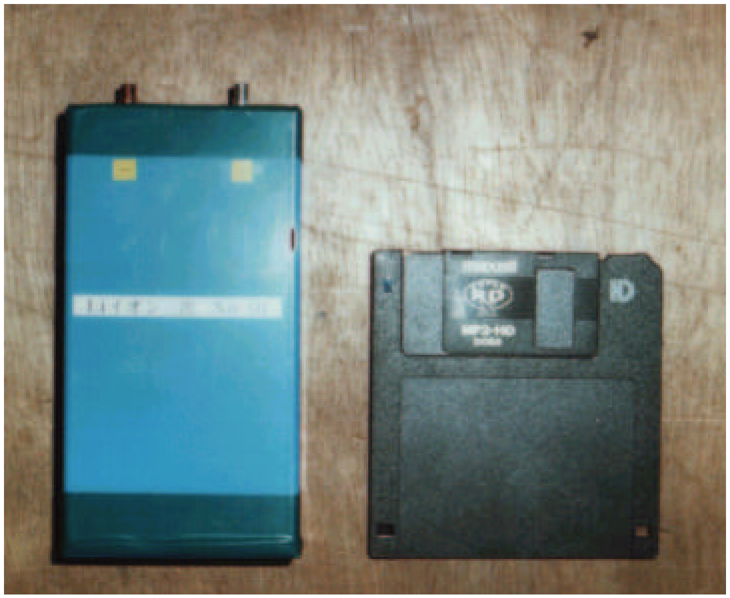
List of Li-Ion Secondary Cells

Data Update
October 2000

Phase	Capacity /Ah	Package	Mode	Temp /?	DOD /%	Charge(CC-CV)		Discharge	C/D Ratio	Sample Number		Date Started	Cycle Number	
						CC/A	CV/V(/cell)	Current/A		Initial	Present		Ended	Present
Feasibility Study using Commercial Cells	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	2	May-95	--	22,000
	1.0	CELL	LEO	20	25	0.3	4.1	0.5	1.01	2	2	May-95	--	22,000
	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	2	May-95	--	22,000
	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	2	Sept-96	--	15,000
	1.0	CELL	LEO	20	18	0.21	4.1	0.35	1.01	2	2	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	1	Sept-96	3,203	15,000
	1.0	CELL	LEO	20	30	0.36	4.2	0.6	1.01	2	2	Sept-96	--	15,000
	1.0	CELL	LEO	20	30	0.36	4.1	0.6	1.01	2	1	Sept-96	3,003	15,000
	1.2	CELL	LEO	20	18	0.36	4.1	0.6	1.01	2	1	Sept-96	14,143	15,000
	1.2	CELL	LEO	20	18	0.36	4.0	0.6	1.01	2	2	Sept-96	--	15,000
Simulation Tests for Satellite Applications	30	CELL	LEO	20	25	9	4.05	15	1.005	5	5	Sept-98	--	9,600
	30	CELL	LEO	20	40	15	4.05	24	1.005	5	4[1)]	Sept-98	--	9,200
	10	CELL	LEO	20	25	3	4.05	5	1.005	2	2	June-99	--	6,000
	10	CELL	LEO	20	40	5	4.05	8	1.005	3	3	June-99	--	6,000
	100	CELL	LEO	15	25	25	3.95	50	1.005	5	5	May-99	--	5,200
	100	CELL	LEO	15	40	50	3.95	80	1.005	5	5	July-99	--	4,800
	100	CELL	GEO	15	80	10	3.95	67	1.005	5	5	Aug-99	--	320
	90	CELL	LEO	10	40	45	4.2	72	1.000	5	5	June-00	--	1,100
	90	CELL	GEO	10	80	9	4.2	60	1.000	5	5	July-00	--	45

NASDA

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 / Higher Limited 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 originality of the cell design is the negative electrode. Instead of Cu sheet, porous Ni is used as a current collector. Graphite covers the surface of porous Ni, thus it performs as a negative electrode.

Trend Data of 10 Ah $LiCoO_2$/Graphite Cells

Data Update

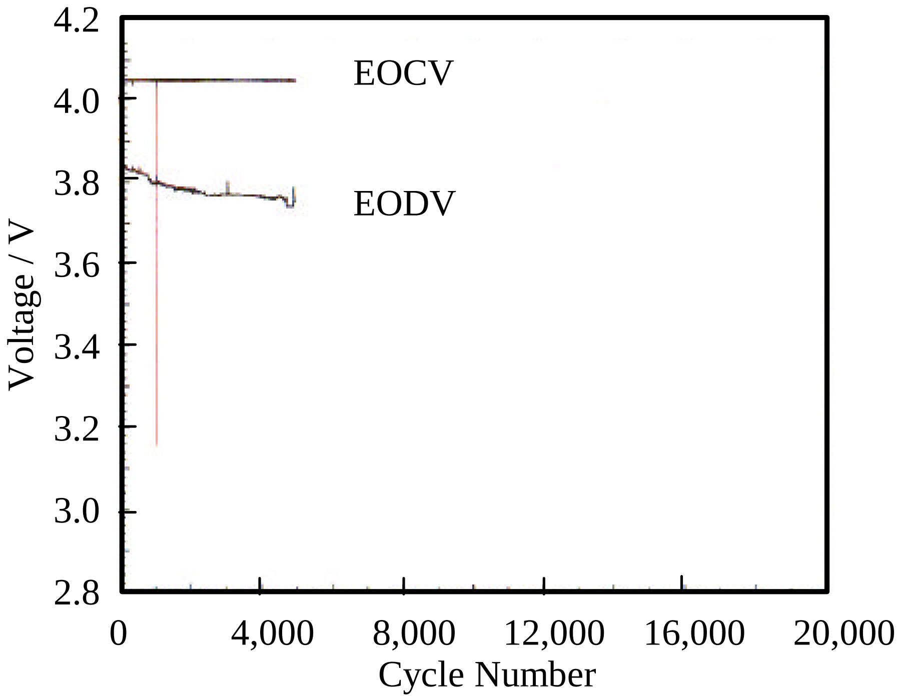


Fig. Life Cycle Trend of DOD=25% LEO Test
Two cells are connected in series.

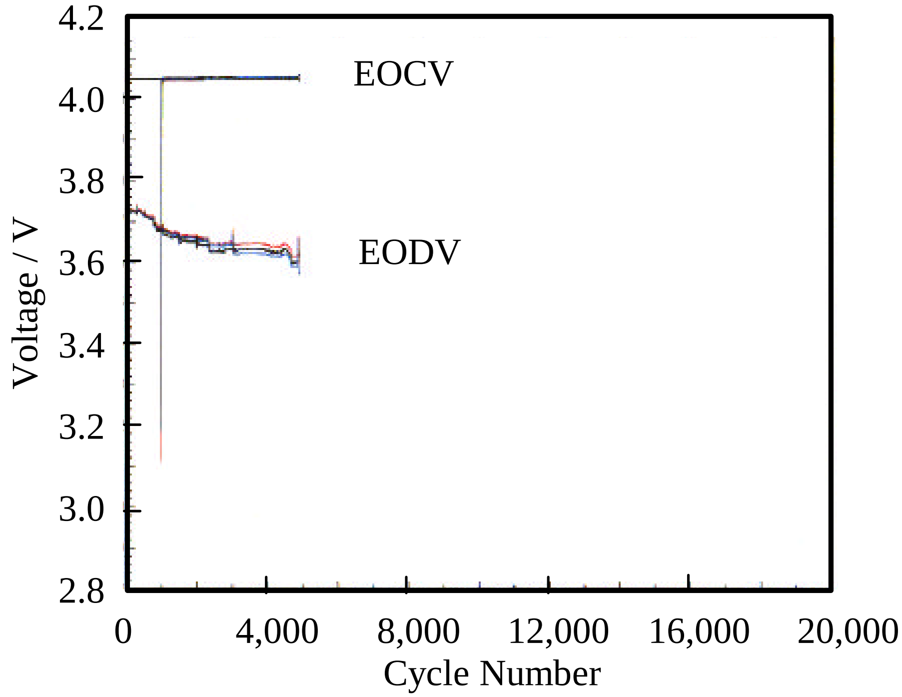


Fig. Life Cycle Trend of DOD=40% LEO Test
Three cells are connected in series.

Above figures show the trends of LEO tests using 10 Ah prismatic cells. We are testing the performance of the cells under two different DOD conditions. We have not observed any variety of EOCV or EODV of the cells with a series connection.

Trend Data of 10 Ah $LiCoO_2$/Graphite Cells

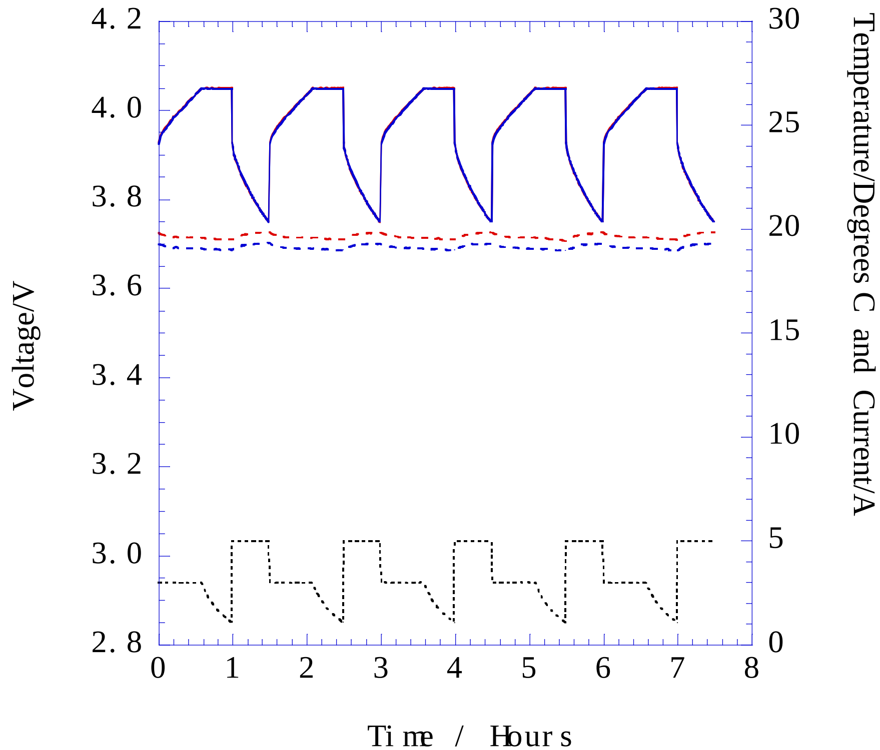


Fig. Recent Cycle Performance of DOD=25% LEO Test

Two cells are connected in series.

—— Voltage —— Temperature · Current

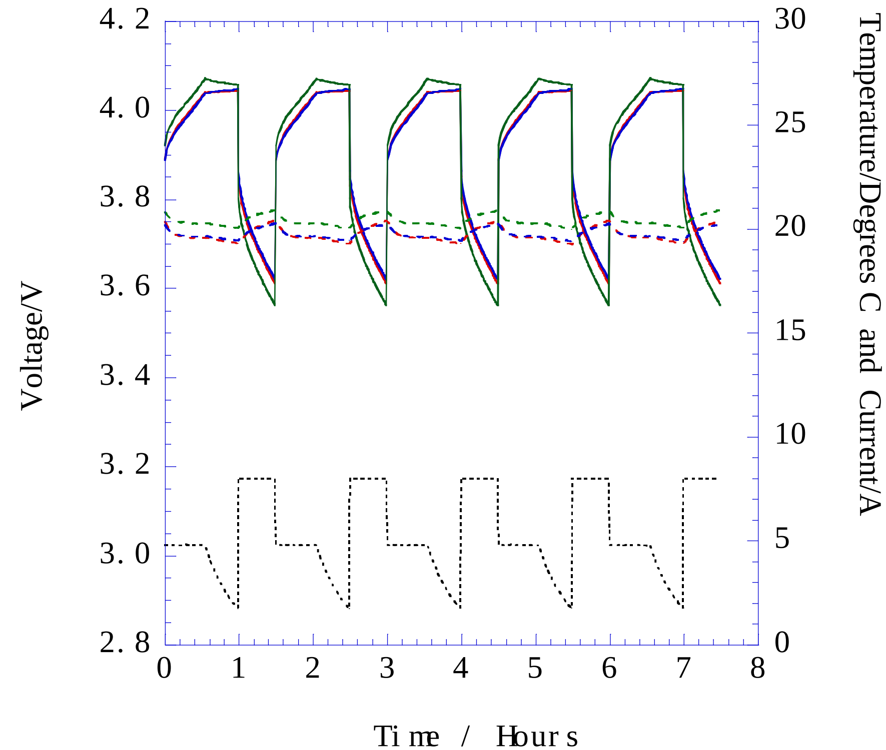


Fig. Recent Cycle Performance of DOD=40% LEO Test

Three cells are connected in series.

—— Voltage —— Temperature · Current

Above figures are charge and discharge curves for recent five cycles. The charge and discharge curves of two cells are almost identical in the case of DOD=25% LEO test, while one of the three cells shows a higher charge voltage and lower discharge voltage in the case of DOD40% LEO test. We believe that the impedance of the cell is increasing, now.

Trend Data of 10 Ah $LiCoO_2$/Graphite Cells

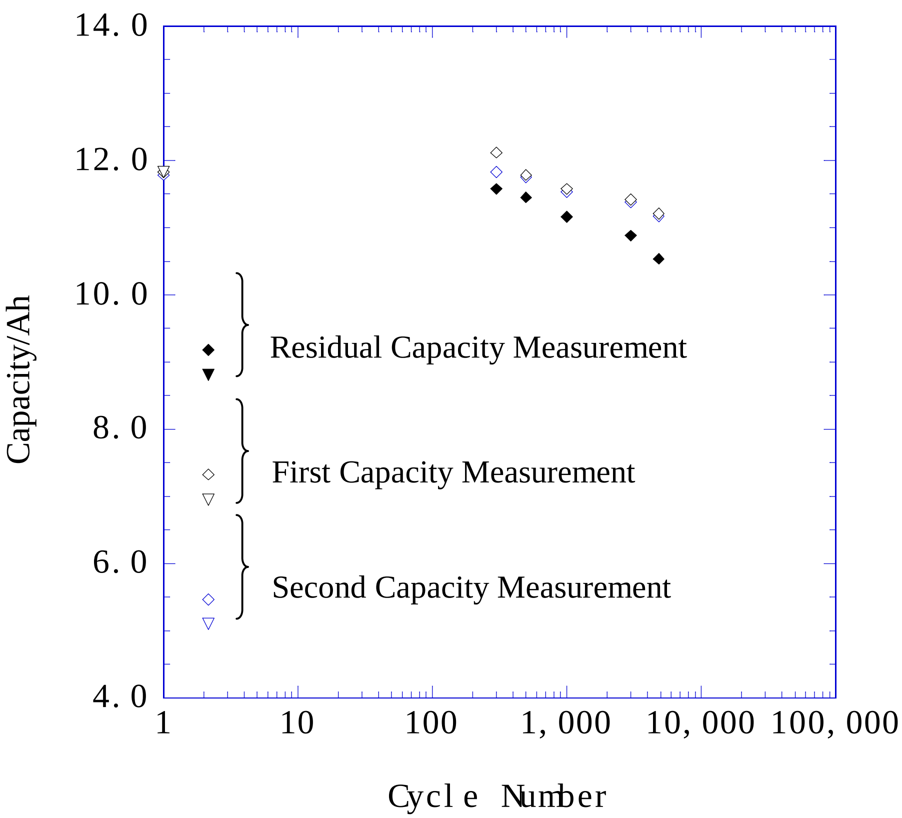


Fig. Capacity Trend by Cycles, LEO Test/DOD25%

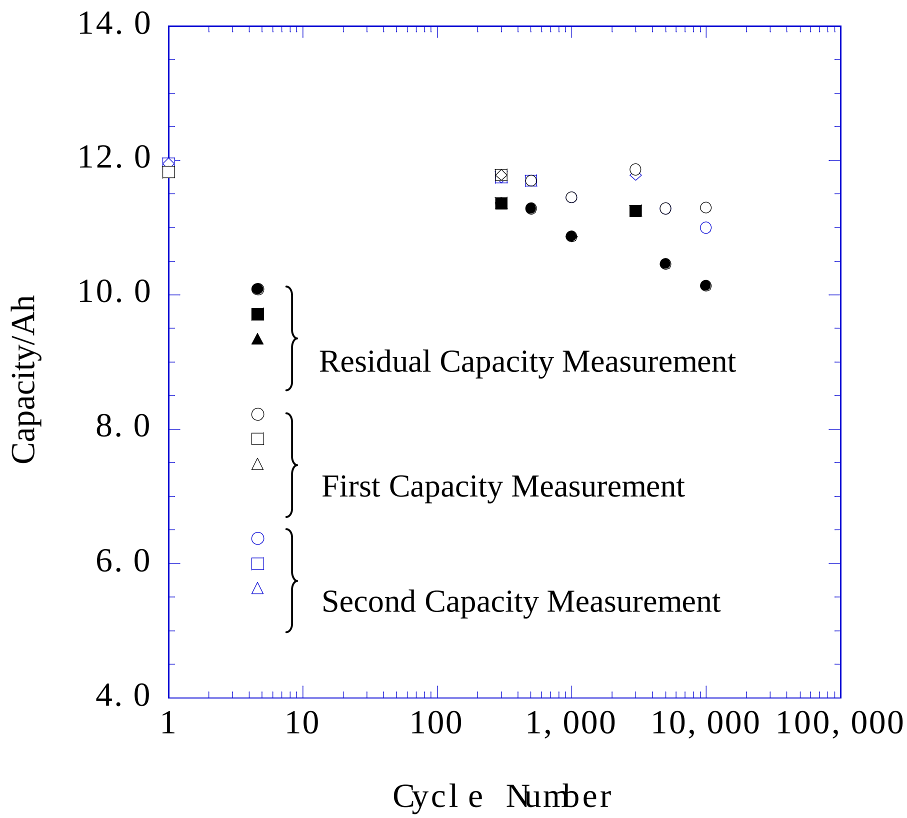


Fig. Capacity Trend by Cycles, LEO Test/DOD40%

Capacities of samples are slightly decreasing. However, in the both case, all samples still keep their nominal capacity.

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 / Higher Limited Voltage		4.1 V
Discharge Voltage	Nominal Voltage	3.6 V
	Lower Limited Voltage	3.0 V

30 Ah prismatic cells were prepared by Japan Storage Battery Co. (denoted as JSB) in 1998. Our request to JSB was to fabricate a ‘Prismatic Cell’ using popular electrode materials. Positive and Negative electrodes were $LiCoO_2$ and C (graphite), respectively. They prepared square sheets of electrodes on the basis of their conventional Li-Ion cells for ground applications that requested 7 hours for the ideal full charge.

Trend Data of $LiCoO_2$/Graphite Cells

Data Update

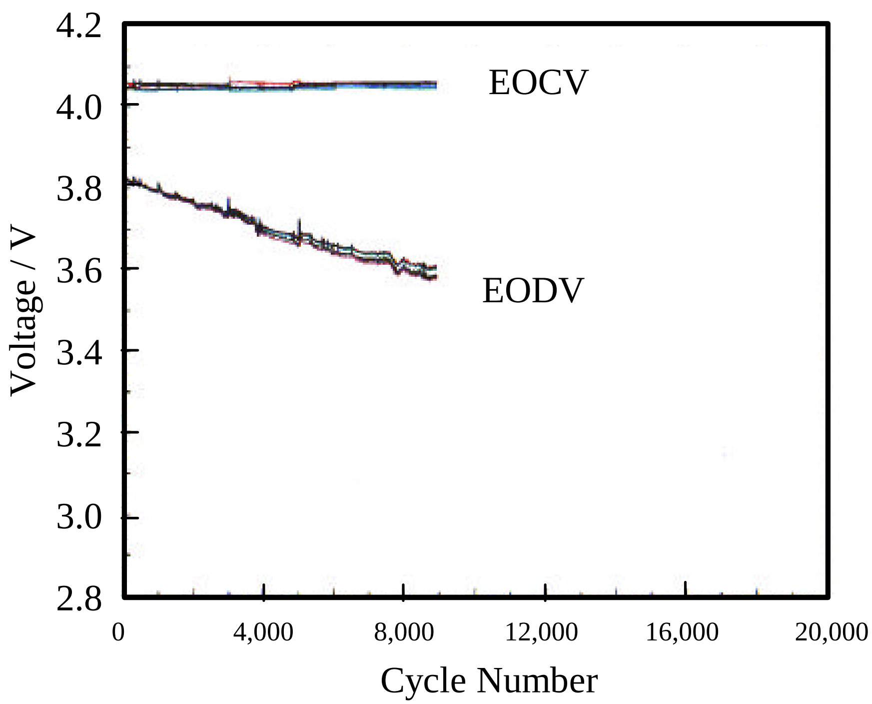


Fig. Life Cycle Trend of DOD=25% LEO Test
Five cells are connected in series.

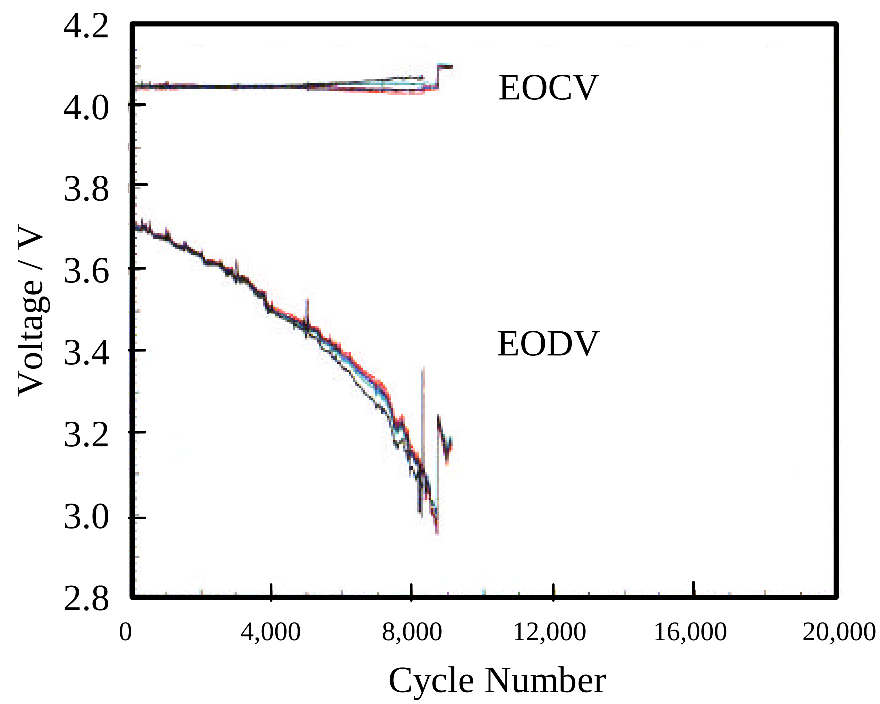


Fig. Life Cycle Trend of DOD=40% LEO Test
Five cells used to be connected in series. At 8,269 cycle, one of the cells was removed for DPA.

Five cells were connected in series for the above measurements. The performance of cells have been very stable in the case of DOD=25%, while a considerable decrease in EODV was observed in the case of DOD=40%.

Trend Data of 30 Ah $LiCoO_2$/Graphite Cells

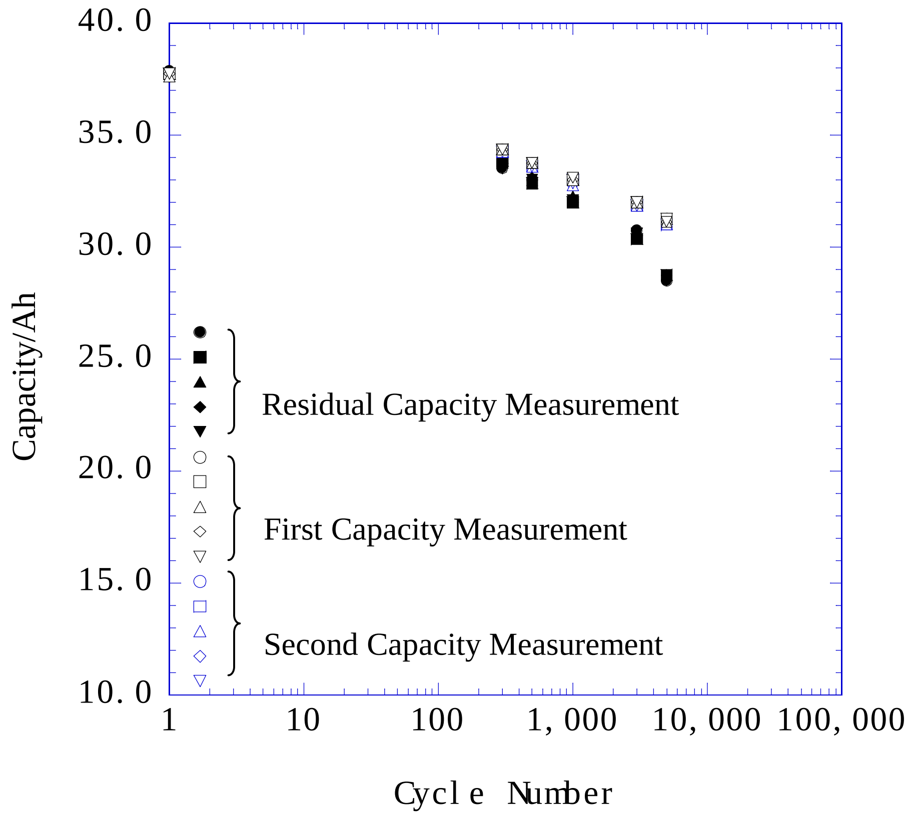


Fig. Capacity Trend by Cycles, LEO Test/DOD25%

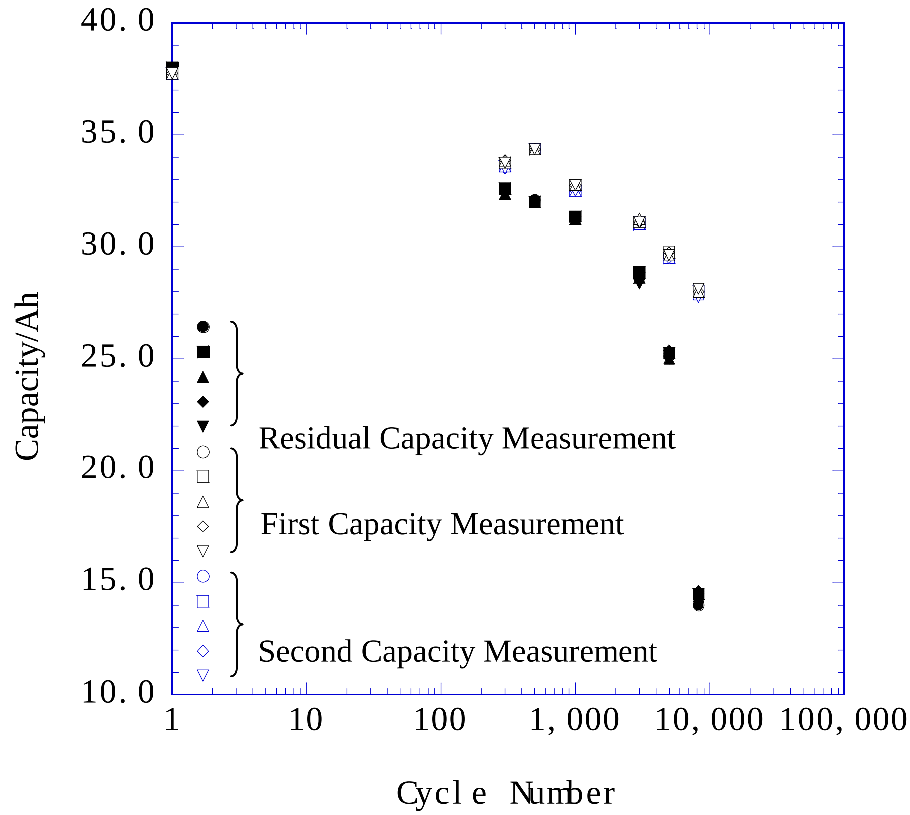


Fig. Capacity Trend by Cycles, LEO Test/DOD40%

In the test with DOD=25%, we observed a constant decrease in capacity. The residual capacity during cycle test was almost the same as the capacity obtained after full charge. In test with DOD=40%, high decrement of residual capacity was observed, which resulted in the considerable decrease in EODV. It is notable that we obtained high capacity after full charge, which means that the charge amount during DOD=40% cycles was too small due to the lack of charge duration (60 min.) for '98 models to maintain its cycle performance.

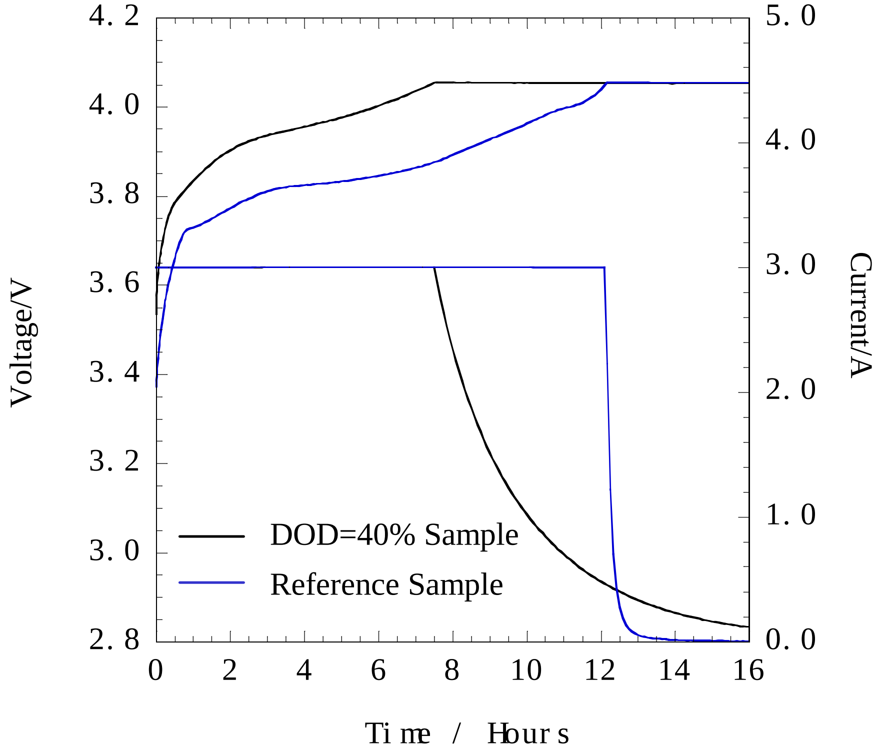


Fig. Charge curves of 30Ah cells
Charge Condition : CC(3A)-CV(4.05V), at 20.

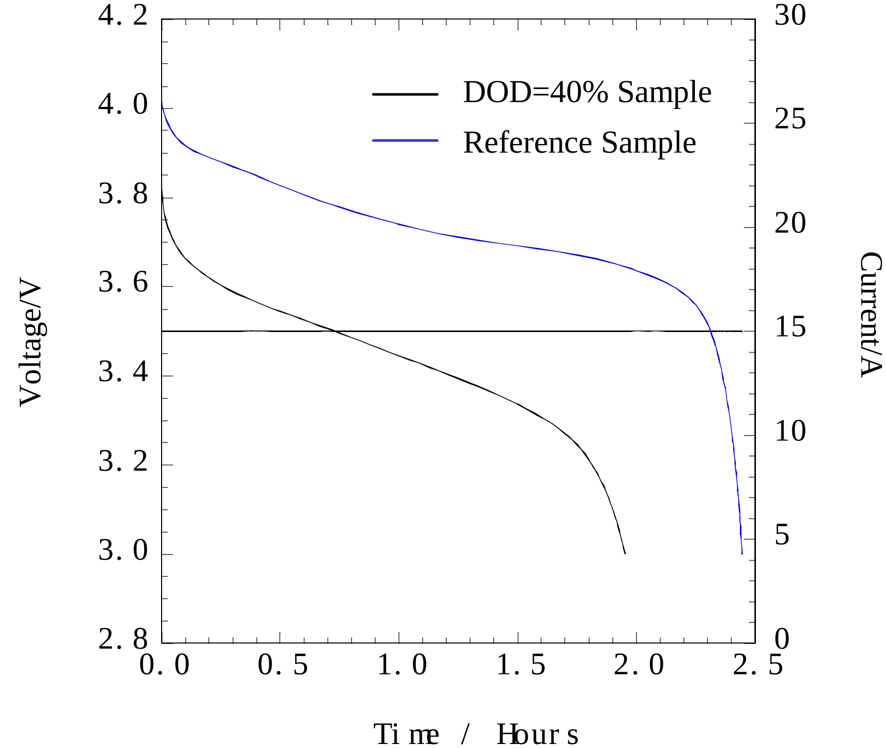


Fig. Discharge curves of 30Ah cells
Discharge Condition : CC(15A), at 20.

Fig. Capacity Measurement before DPA.

In order to understand the reason of the high decrease in EODV and residual capacity, we decided to perform destructive physical analysis (DPA) using a sample of DOD=40% cycle test. As a reference, we used an as-prepared cell which had been stored at room temperature by JSB. The charge and discharge curves of the sample after life cycle test suggested an increase in impedance. The capacity of DOD=40% sample was ca. 20% smaller than that of the reference.

Fig. Positive Electrode

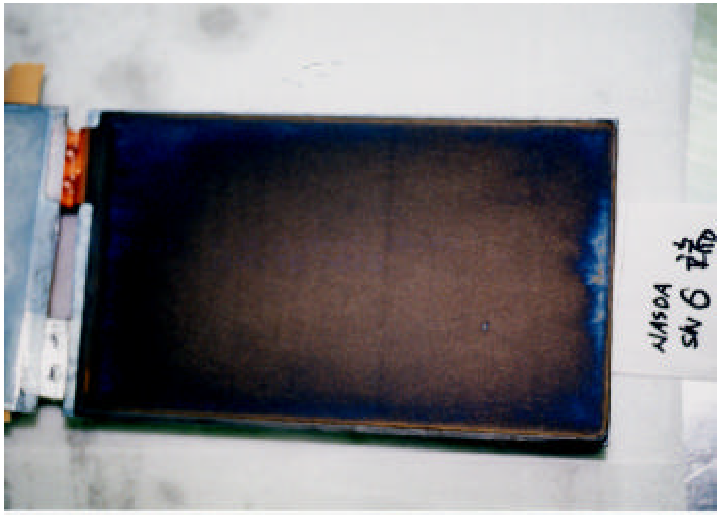


Fig. Negative Electrode

Fig. Pictures of electrodes after destruction.

These are photographs of electrodes after DPA. These appearances and SEM images revealed that the electrodes still kept a smooth surface condition. Separators and electrodes seemed to be enough wet for electrochemical conduction.
The significant increase in water content in the solvent and the composition change in the electrolyte were not detected by means of Karl Fischer Titration and LC-FTIR.
Electrochemical measurements were carried out using a glass cell with three electrodes configuration. Both reference and counter electrodes were lithium metal foils. Samples for working electrodes were taken out from an inner (central side) and an outer (case side) sheet of a stack.

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DPA of 30 Ah $LiCoO_2$/Graphite Cells

Contract research with JSB

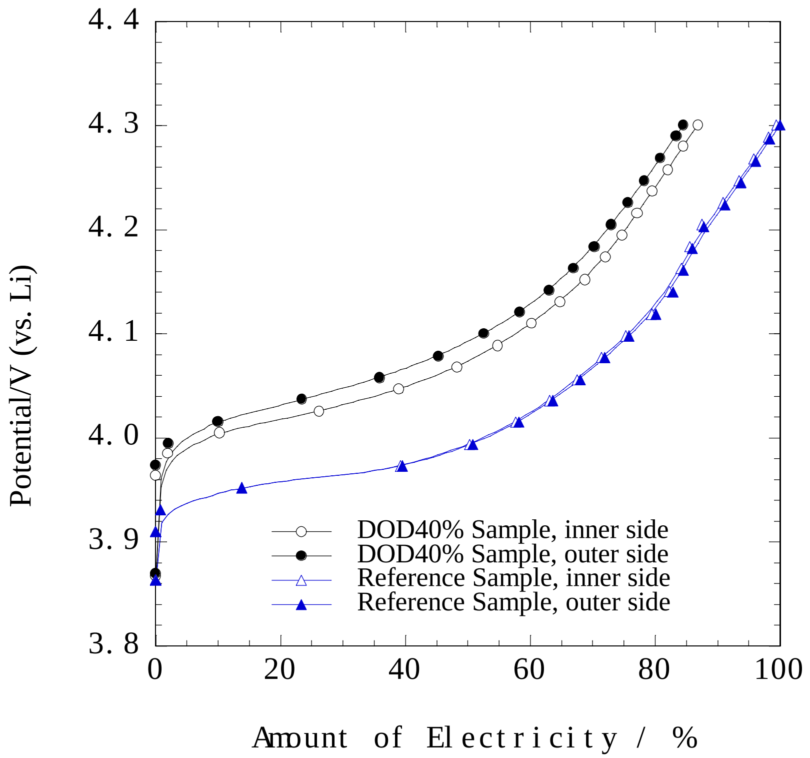

Fig. Charge curves of Positive Electrodes

Charge Condition : CC(0.5mA/cm²) to 4.3V, at 25.

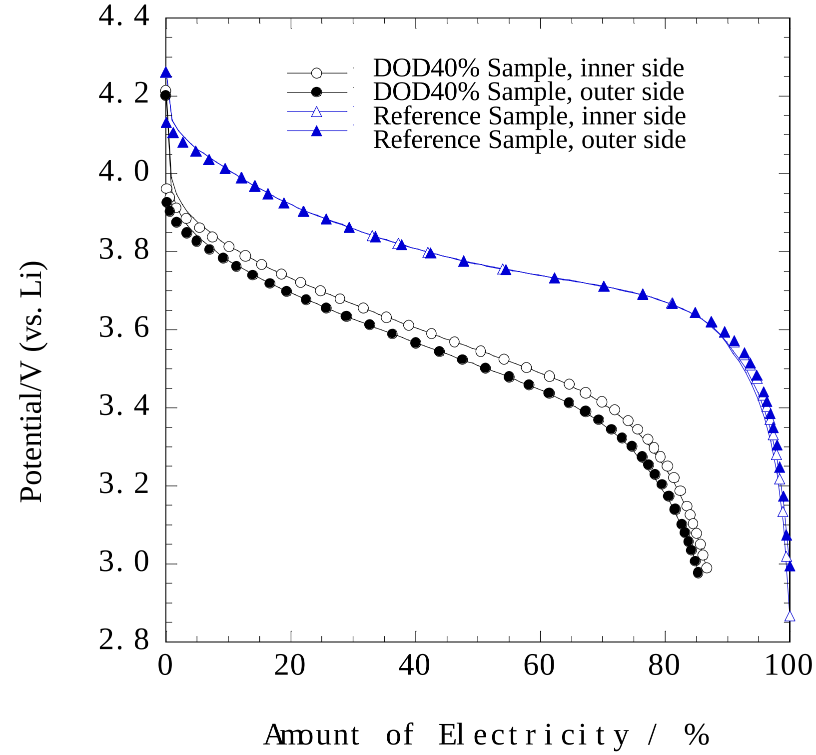

Fig. Discharge curves of Positive Electrodes

Discharge Condition : CC(2.0mA/cm²) to 3.0V, at 25.

Fig. Capacity Measurement of Positive Electrodes.

Capacities of positive electrodes were measured. The samples from DOD=40% test cell showed a lower capacity than that from the as-prepared reference cell, while the samples coming from the common cell stack showed almost the same curves and capacities.

DPA of 30 Ah $LiCoO_2$/Graphite Cells

Contract research with JSB

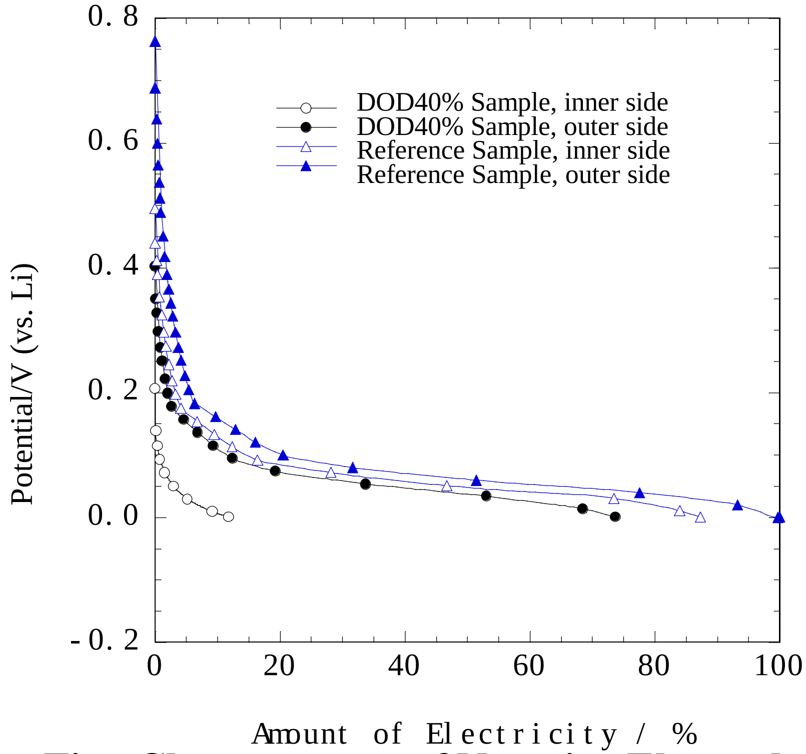

Fig. Charge curves of Negative Electrodes

Charge Condition : CC(0.5mA/cm²) to 0.0V, at 25.

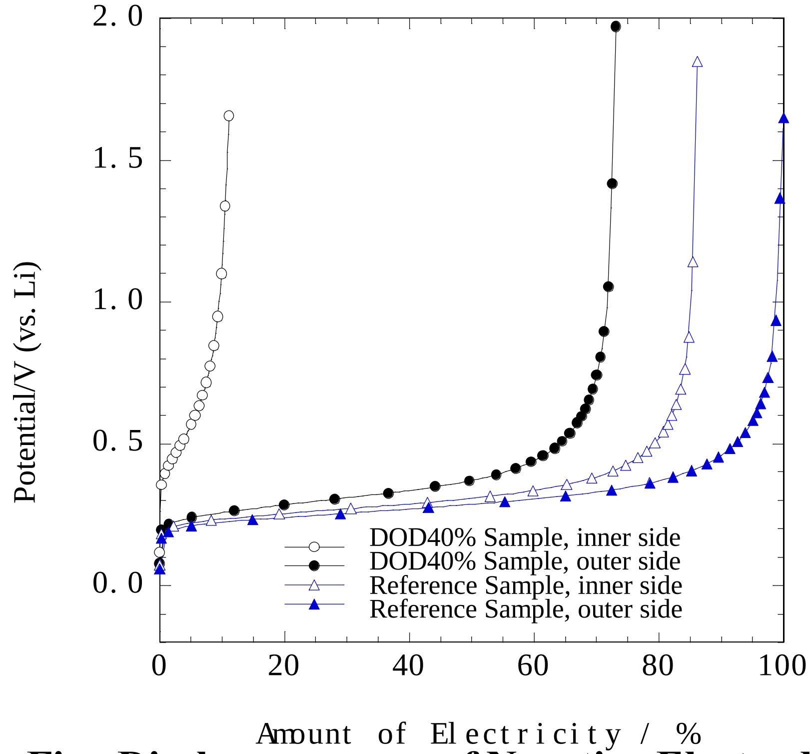

Fig. Discharge curves of Negative Electrodes

Discharge Condition : CC(2.0mA/cm²) to 1.5V, at 25.

Fig. Capacity Measurement of Negative Electrodes.

Capacities of negative electrodes were also measured. A fairly degradation of performance was observed in the case of DOD=40% test cell. The degradation of the inner sheet of a stack was more considerable than that of the outer sheet. An increase in thickness and impedance was also observed in the negative electrode. We believe that the degradation of negative electrodes played an important role in the decreasing residual capacity of DOD=40% test cells.

Based on these results, accompanied with the experience of 100Ah elliptic cylinder cells, we have started the discussion of the new trial cell which might enable high rate charge targeting LEO applications.

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Trend Data of 30 Ah $LiCoO_2$/Graphite Cells

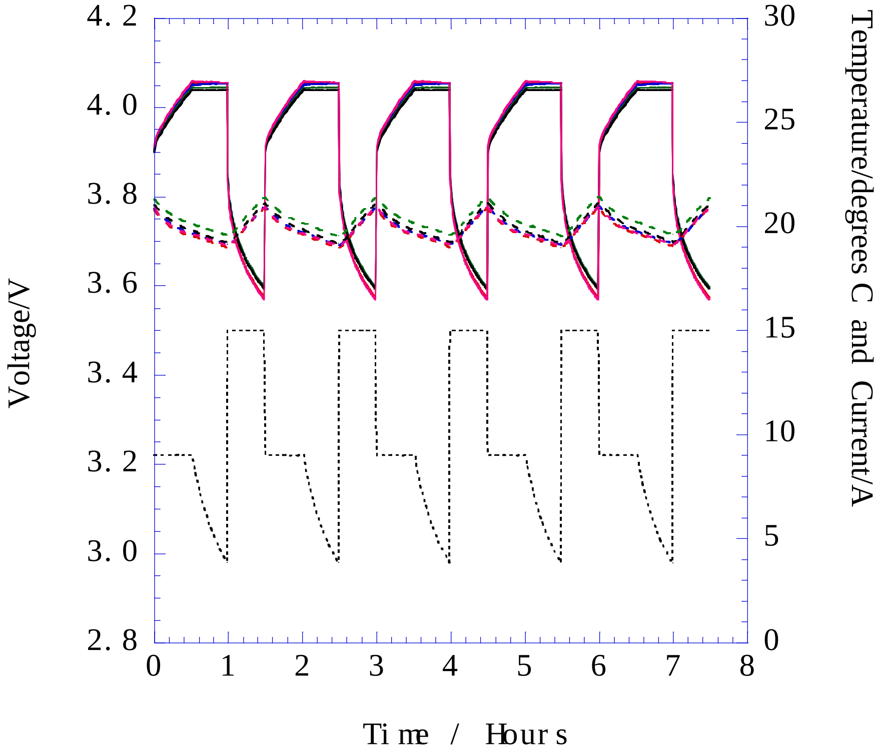

Fig. Recent Cycle Performance of DOD=25% LEO Test

Five cells are connected in series.

Voltage Temperature Current

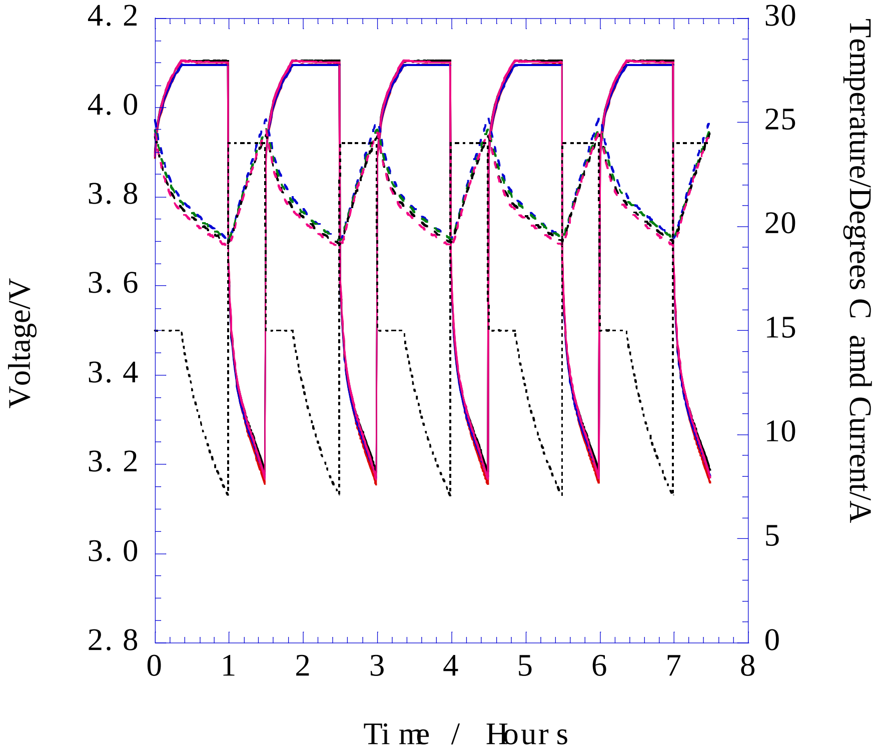

Fig. Recent Cycle Performance of DOD=40% LEO Test

Four cells are connected in series.

Voltage Temperature Current

Above figures are charge and discharge curves for recent five cycles. When we restarted the cycle test with DOD=40% after the replacement of a cell for DPA, we raised the CV condition up to 4.1V to continue the cycles. As shown above, very stable performance is observed currently.

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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 / Higher Limited Voltage		3.98 V
Discharge Voltage	Nominal Voltage	3.6 V
	Lower Limited Voltage	2.75 V

Mitsubishi Electric Co. (MELCO) and Japan Storage Battery Co. (JSB) have been cooperating for the development of lithium ion secondary battery for space applications. In 1998, we decided to collaborate with these companies to accelerate our R&D of lithium ion secondary battery for the NASDA future satellites.

- MELCO is going to establish the battery system including the charge method. For example, MELCO studies the electric circuits, safety unit, and others to maintain and evaluate the safety of the whole battery system.
- JSB performs the cell design, manufacturing, and checking the single cell performance. Life cycle test, safety test of cells, storage effects are included in its study. JSB has improved the cell design for this 100Ah cell to reduce the increase in impedance during cycles.
- NASDA focuses the evaluation on the long-term performance as a battery.

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

Data Update

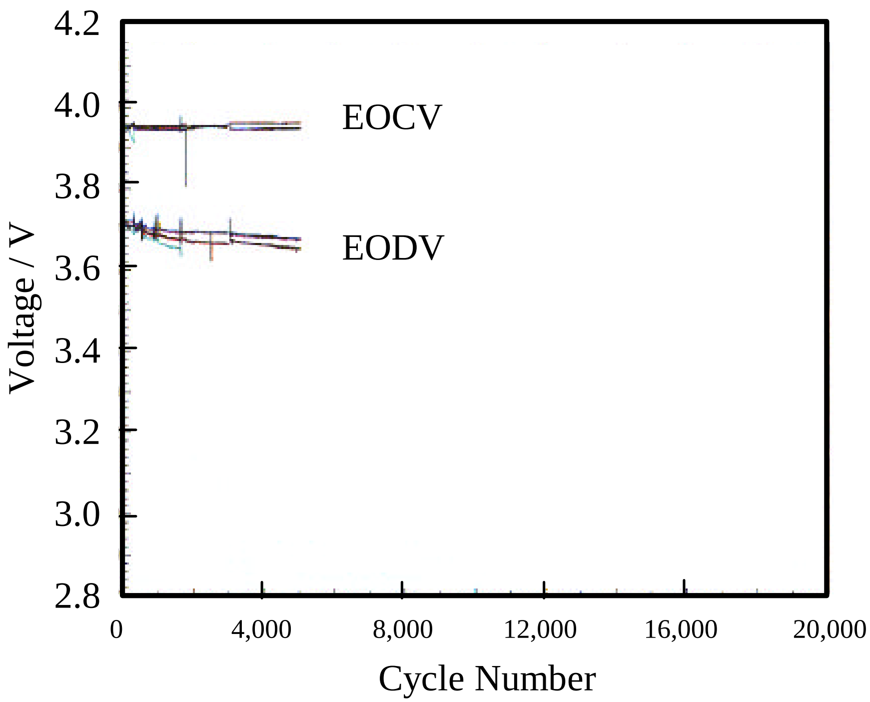

Fig. Life Cycle Trend of DOD=25% LEO Test
Five cells are connected in series.

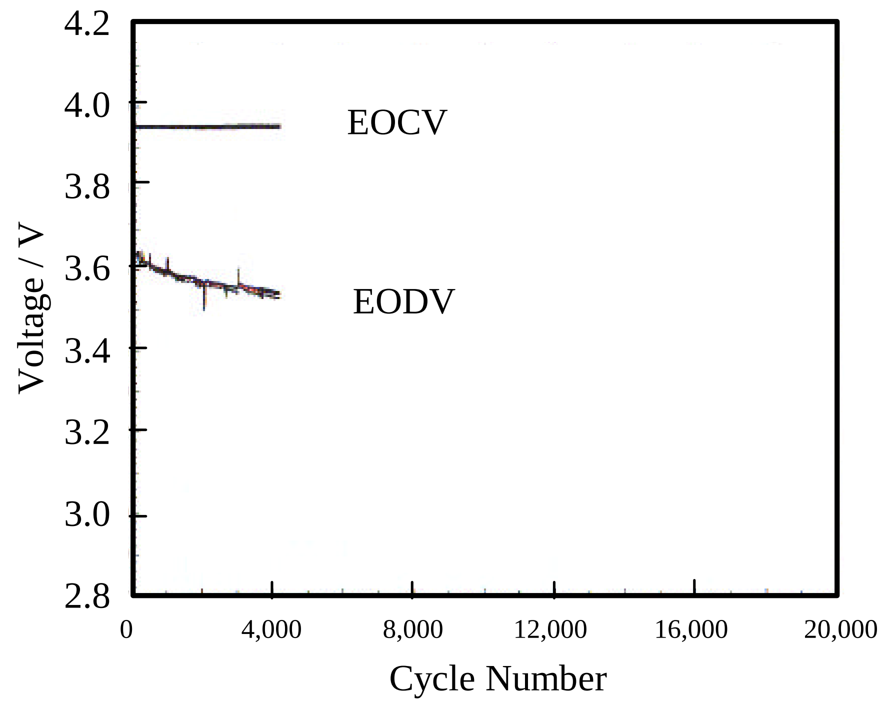

Fig. Life Cycle Trend of DOD=40% LEO Test
Five cells are connected in series.

In the case of DOD=25% test, we observed lower EODV of a cell until ca. 1,600 cycles. It was because of the loose contact between the terminal of the cell and the external lead from the instruments. Today, though both EOCV and EODV sprit into different levels, we have almost the same cycle trends of the cells connected together in series.
In the case of DOD=40%, we observed nearly no difference in the performance of five cells connected in series.

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

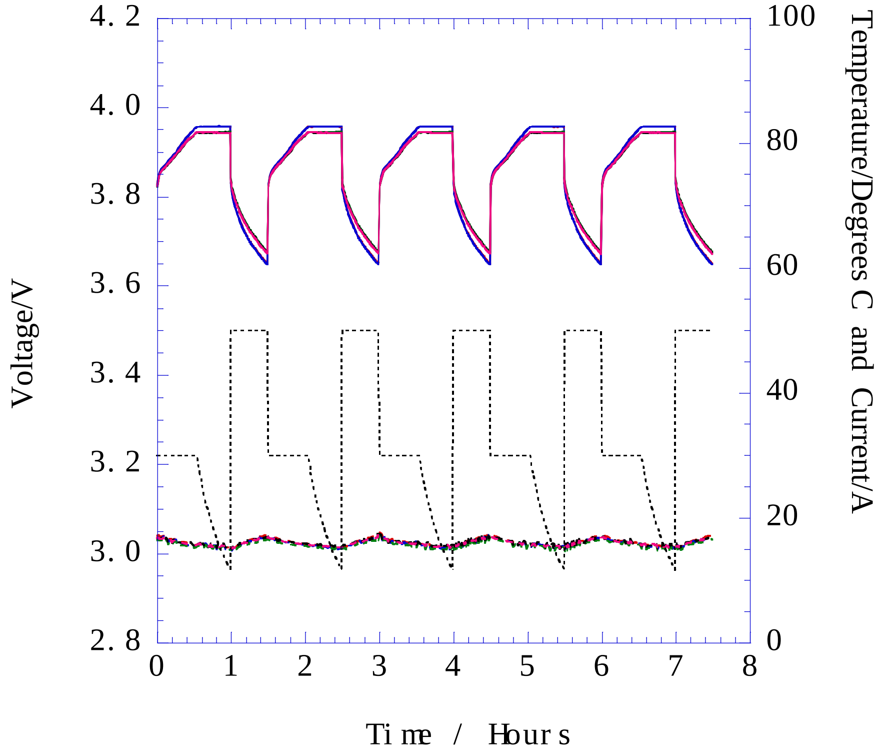

Fig. Recent Cycle Performance of DOD=25% LEO Test

Five cells are connected in series.

Voltage Temperature Current

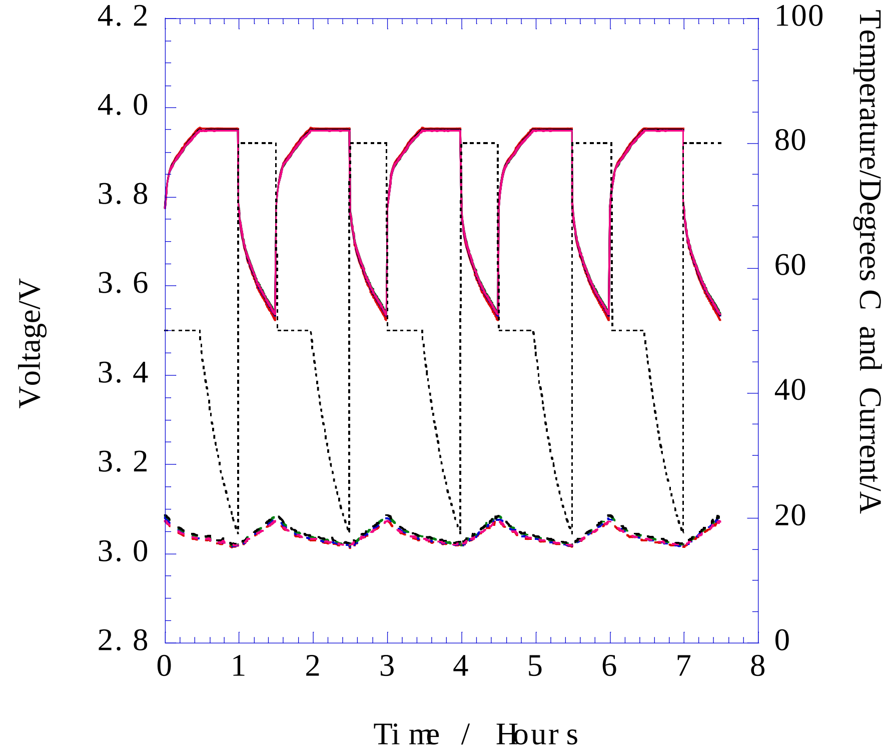

Fig. Recent Cycle Performance of DOD=40% LEO Test

Five cells are connected in series.

Voltage Temperature Current

Above figures are charge and discharge curves for recent five cycles. Very stable performance is still observed.

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

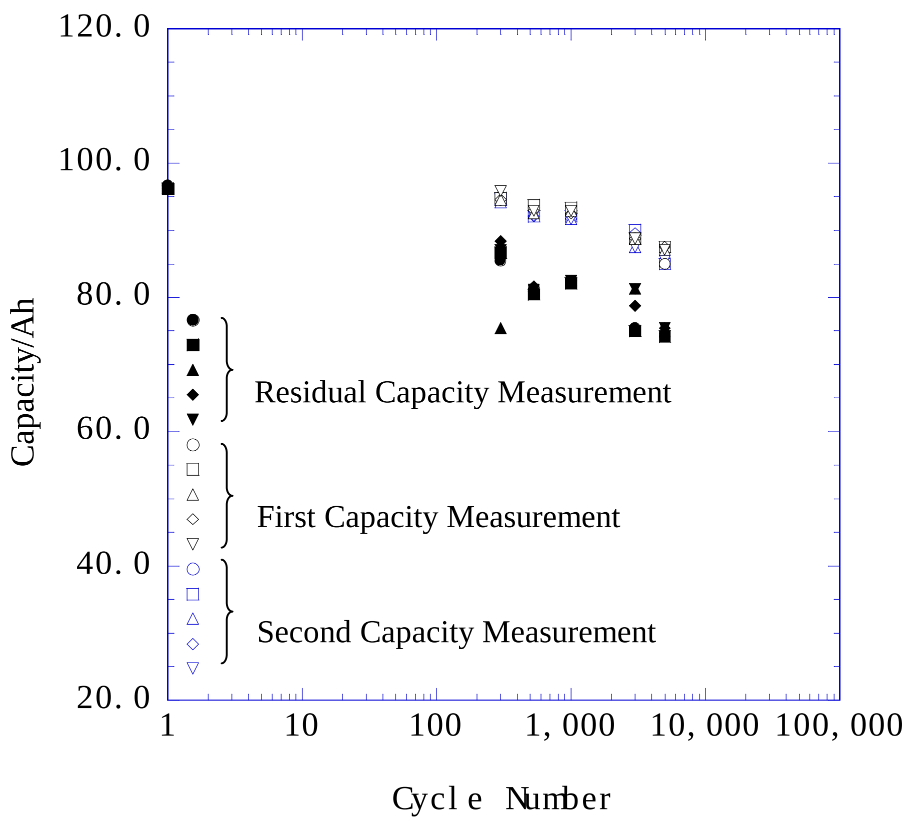

Fig. Capacity Trend by Cycles, LEO Test/DOD25%

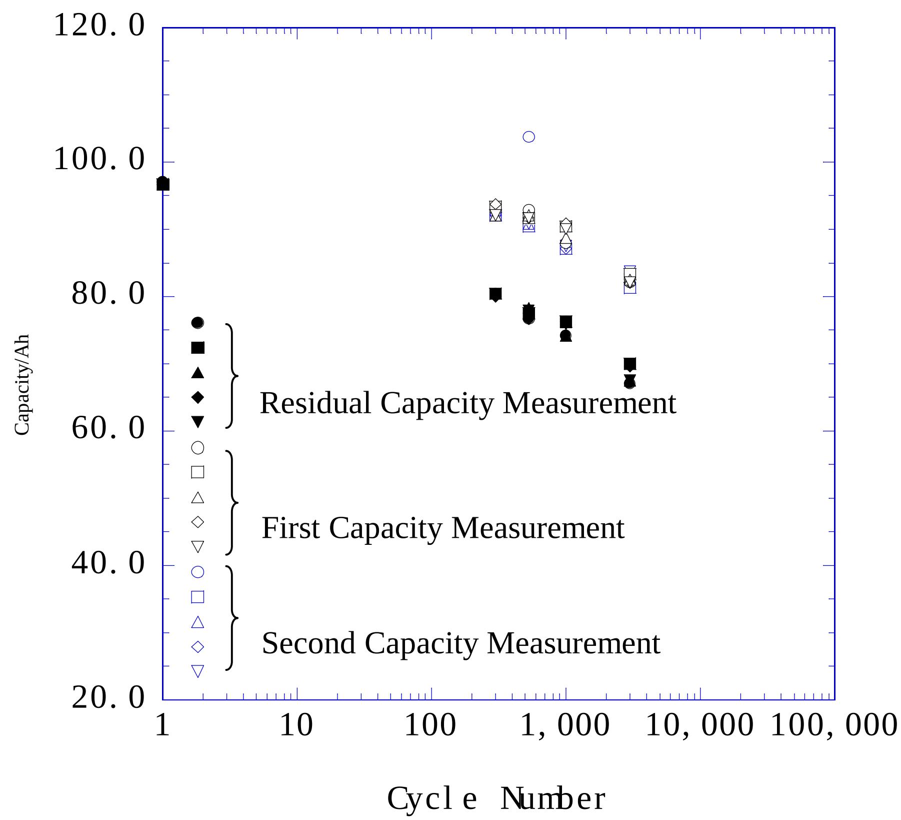

Fig. Capacity Trend by Cycles, LEO Test/DOD40%

Capacities of samples are decreasing slightly. Significant degradation has not been observed, yet.

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Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

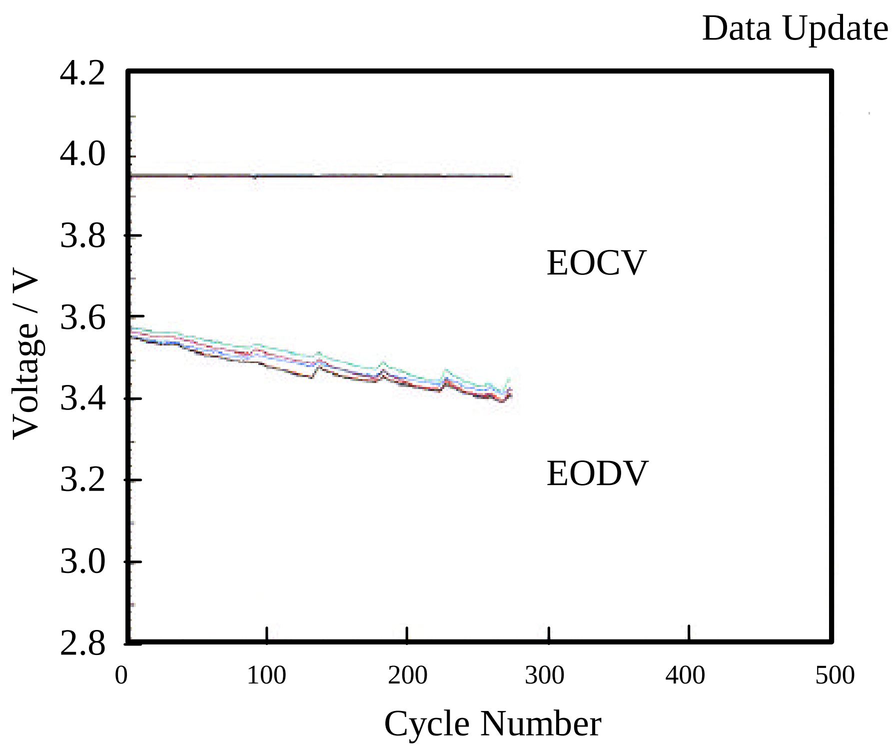

Fig. Life Cycle Trend of DOD=80% GEO Test
Five cells are connected in series.

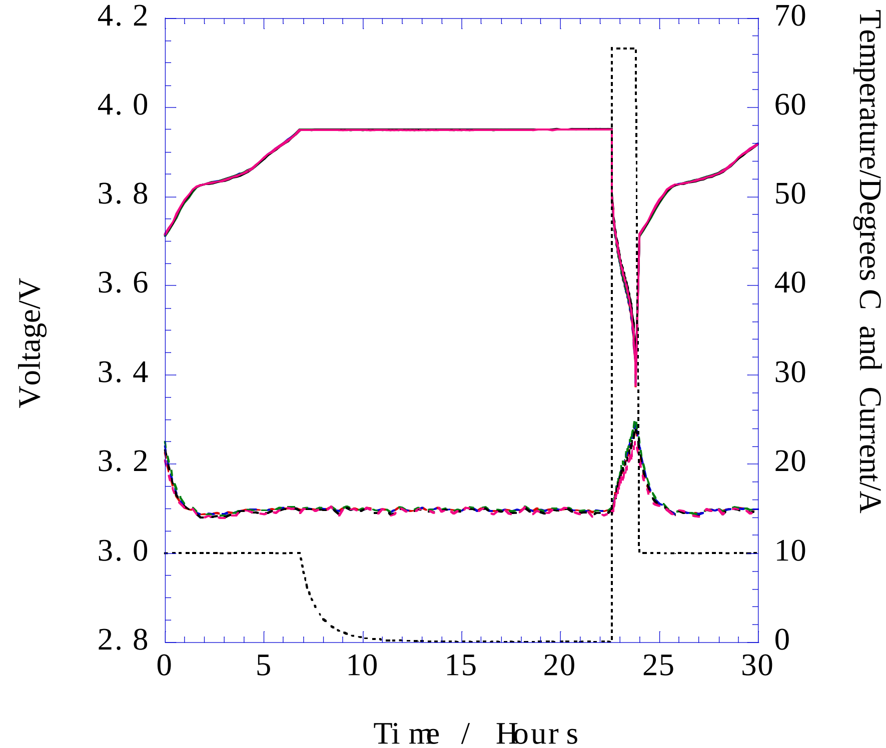

Fig. Cycle Curve of DOD=80% GEO Test
Five cells are connected in series.
Voltage Temperature Current

After 300 cycles, the end of discharge voltage decreased to 3.4 V. A constant decrease in the end of discharge voltage is still observed.

Trend Data of 100 Ah $LiCoO_2$/Graphite Cells

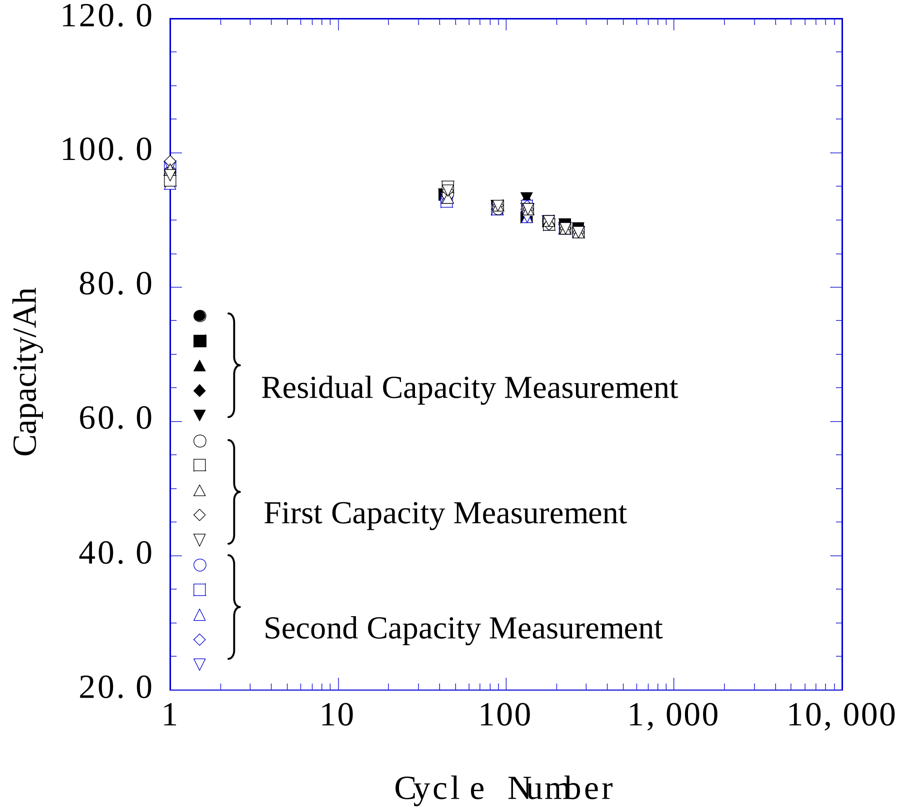

Fig. Capacity Trend by Cycles, GEO Test/DOD80%

Capacity of samples is decreasing slightly. Significant degradation has not been observed, yet.

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Temperature Dependence of Capacity, 100 Ah $LiCoO_2$/Graphite Cells

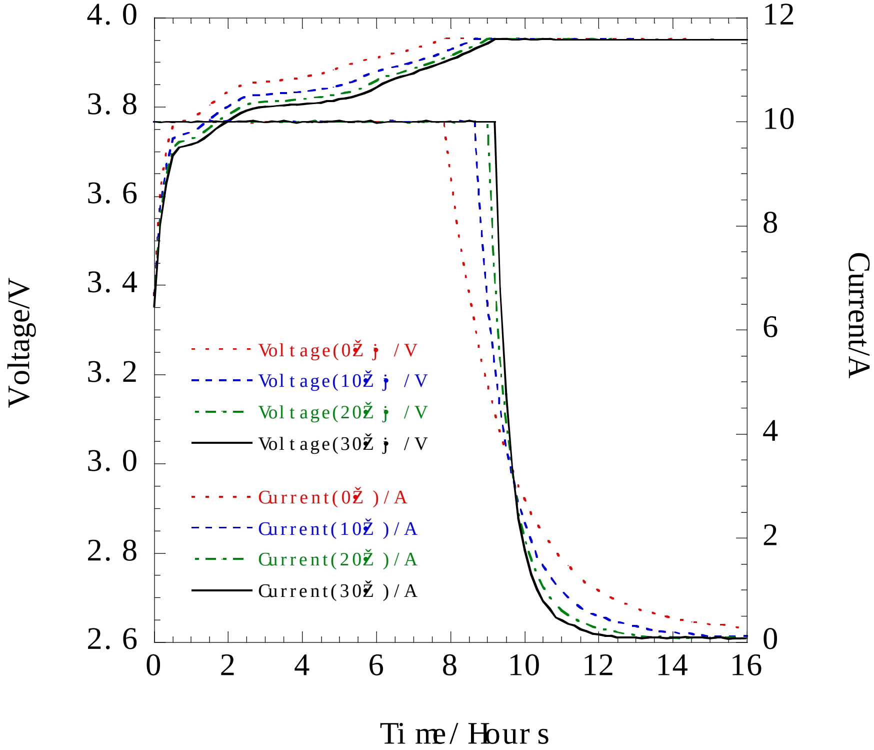

Fig. Charge curves

Charge Condition : CC(10 A)-CV(3.95 V)

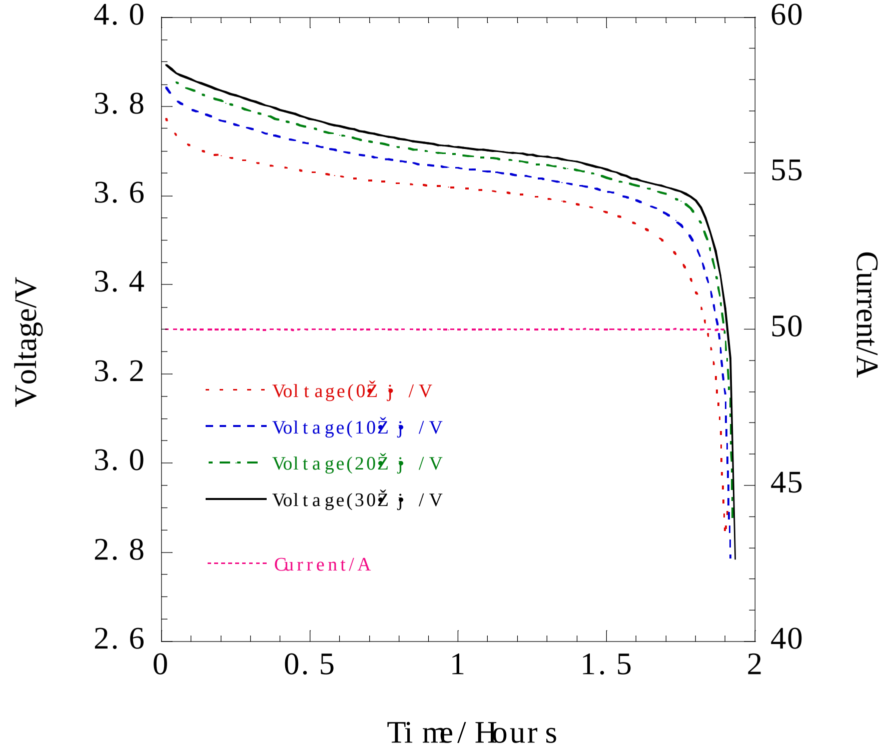

Fig. Discharge curves

Discharge Condition : CC(50 A) to 2.8 V

Fig. Capacity Measurement at different temperatures, measured before we started life cycle test.

We measured capacities of a cell at different temperatures. There was an increase in charge voltage and a decrease in discharge voltage with decreasing temperature, while we could obtain almost the same capacity in every measurement.

Temperature Dependence of Capacity, 100 Ah $LiCoO_2$/Graphite Cells

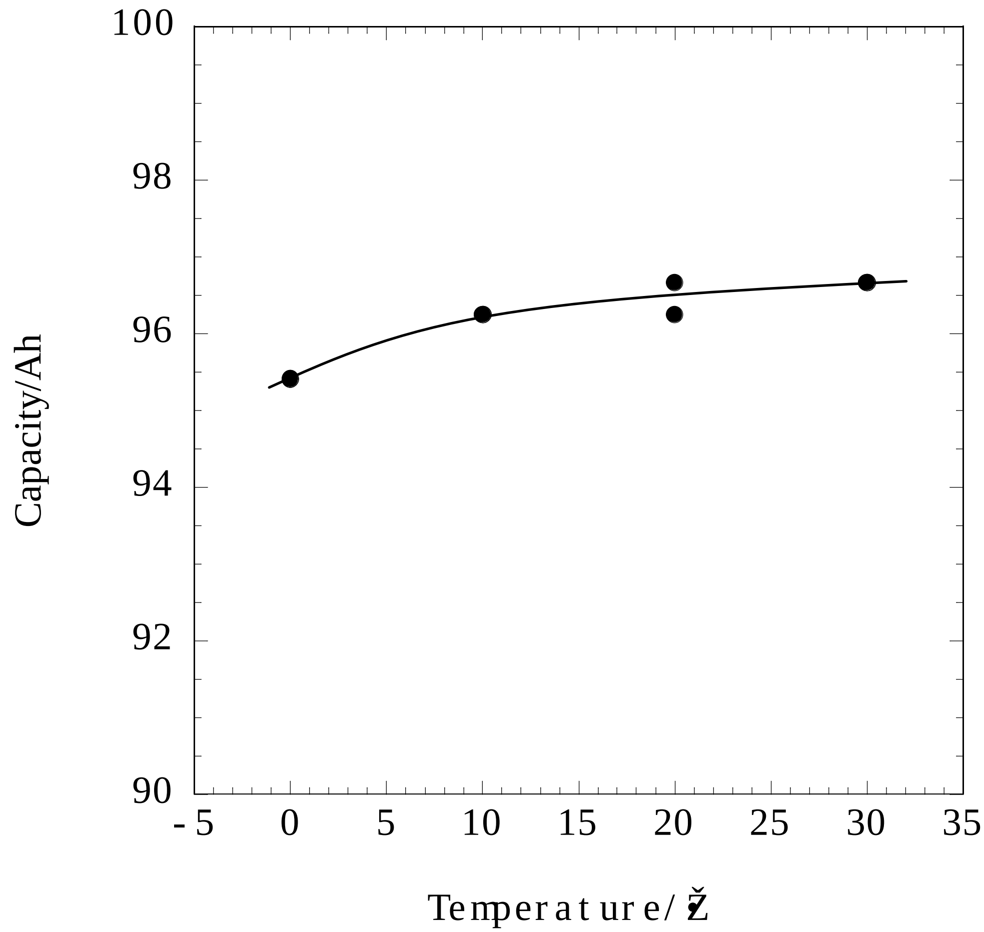

Fig. Temperature dependence of capacity
100 Ah Elliptic Cylindrical Cell from JSB.

We obtained a smaller capacity at 0., though the decrement was almost negligible.

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90Ah $LiMn_2O_4$/Non-Graphite Cells

Cell Style		Cylinder
Electrode	positive electrode	LiMn2O4
	negative electrode	C (non-graphite)
Capacity		90 Ah
Weight		3.3 kg
Dimensions		φ67mm x 410 mm
Energy Density	per weight	104 Wh/kg
	per volume	237 Wh/L
Charge Voltage / Higher Limited Voltage		4.2 V
Discharge Voltage	Nominal Voltage	3.8 V
	Lower Limited Voltage	2.5 V

Above battery and cell are under development by the cooperation of IHI Aerospace Co. (IAC) and Shinkobe Electric Machinery Co. We started the collaboration with these companies, too, in 1999. They used $LiMn_2O_4$ and C (non-graphite) for the positive and negative electrode, respectively.

Trend Data of 90 Ah $LiMn_2O_4$/Non-Graphite Cells

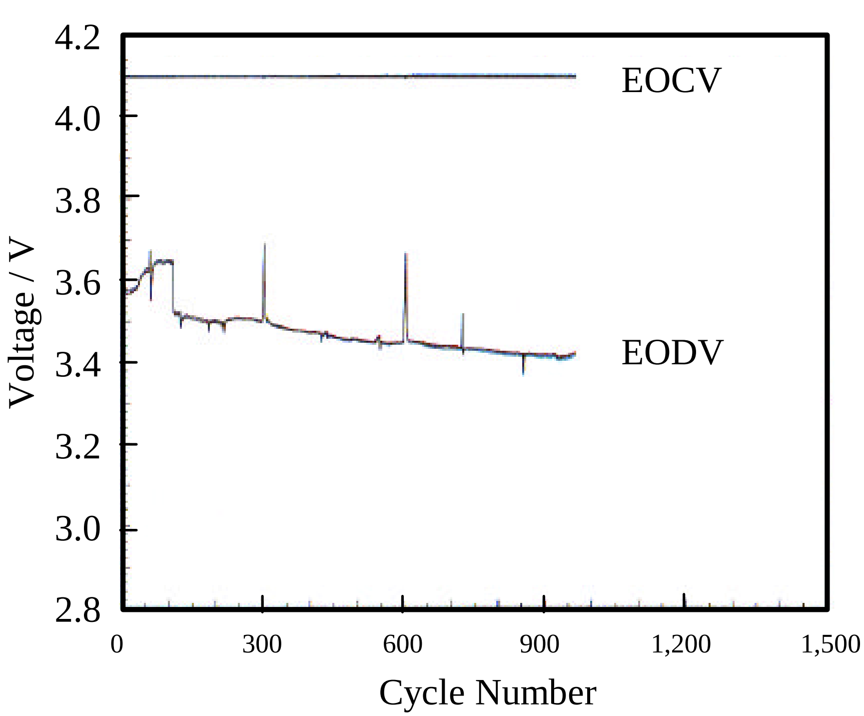

Fig. Life Cycle Trend of DOD=40% LEO Test
Five cells are connected in series.

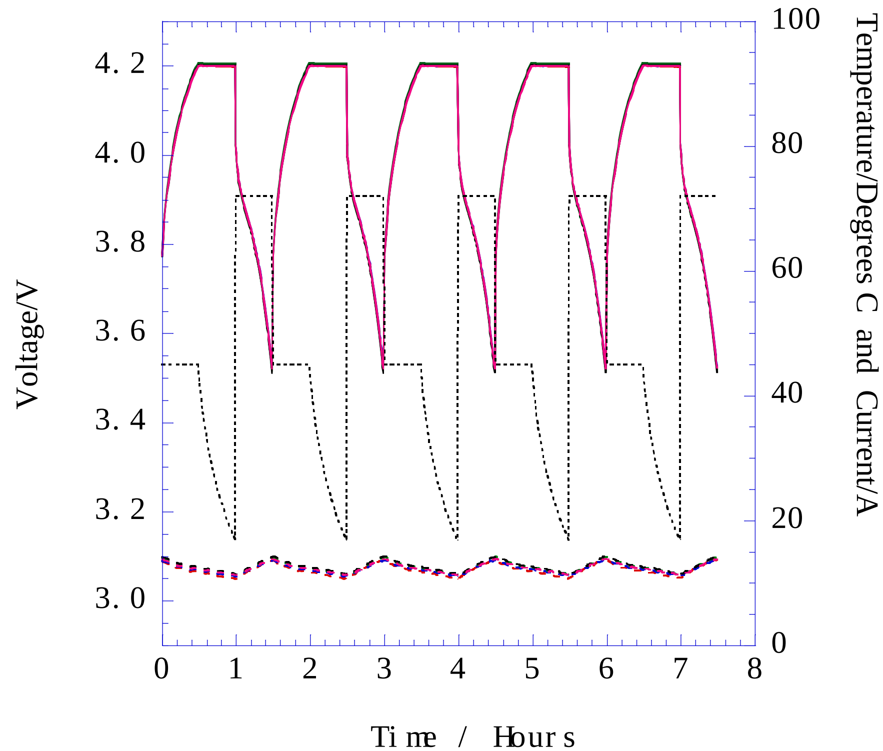

Fig. Recent Cycle Performance of DOD=40% LEO Test
Five cells are connected in series.
Voltage Temperature Current

Above figures show the trends of the performance during DOD=40% life cycle test. The charge and discharge curves of five cells in series have been almost identical through the test.

Trend Data of 90 Ah $LiMn_2O_4$/Non-Graphite Cells

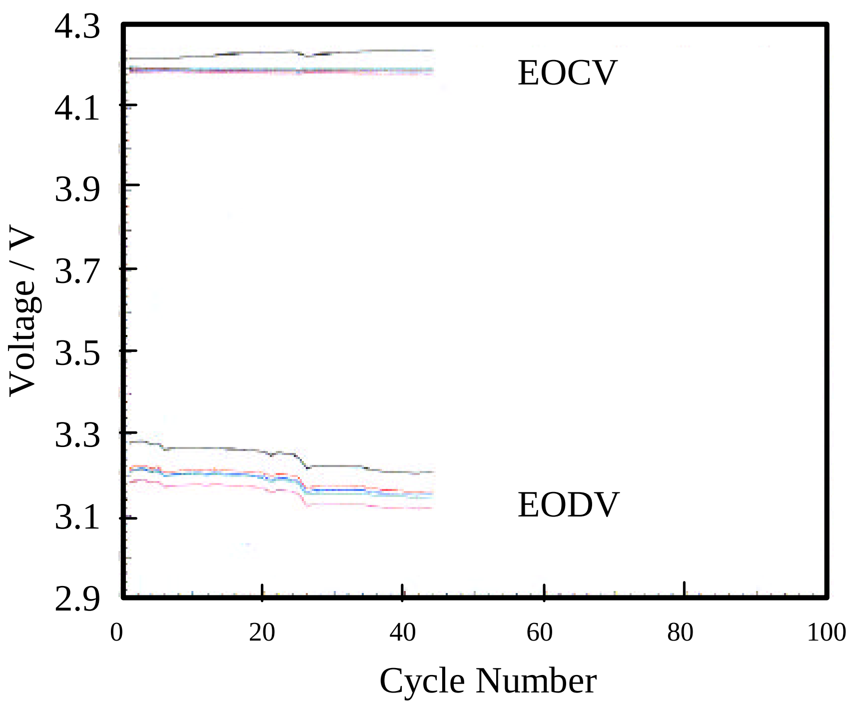

Fig. Life Cycle Trend of DOD=80% GEO Test
Five cells are connected in series.

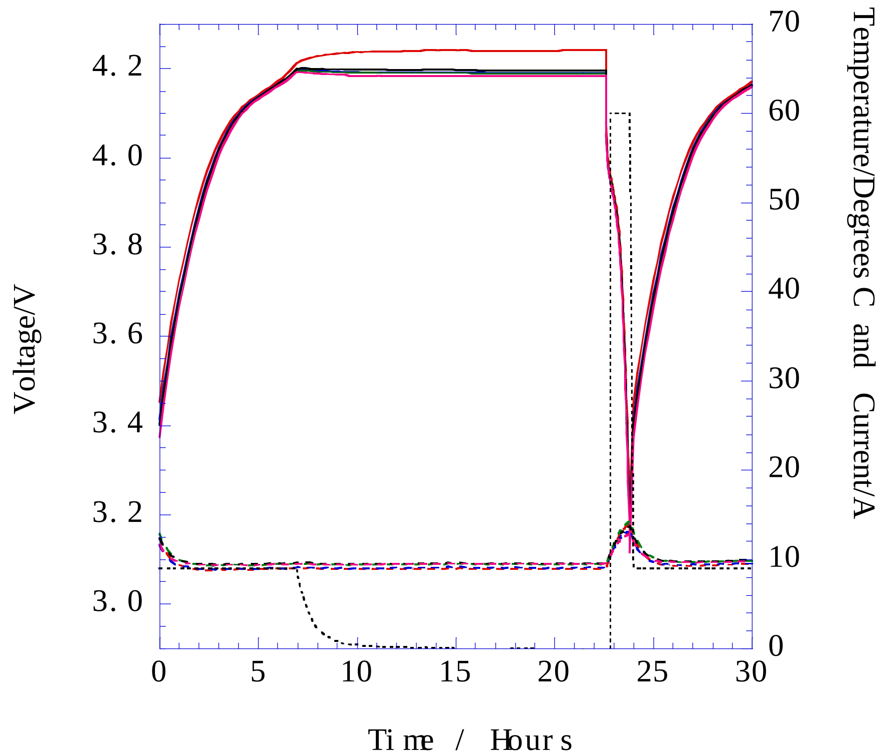

Fig. Recent Cycle Performance of DOD=80% GEO Test
Five cells are connected in series.
Voltage Temperature Current

One of the cells showed higher voltage in the both case of charge and discharge. When we checked the capacity after 45 cycles, we discharged each cell down to 2.5V. We expected the same state of charge among these five cells by this treatment.

Trend Data of 90 Ah $LiMn_2O_4$/Non-Graphite Cells

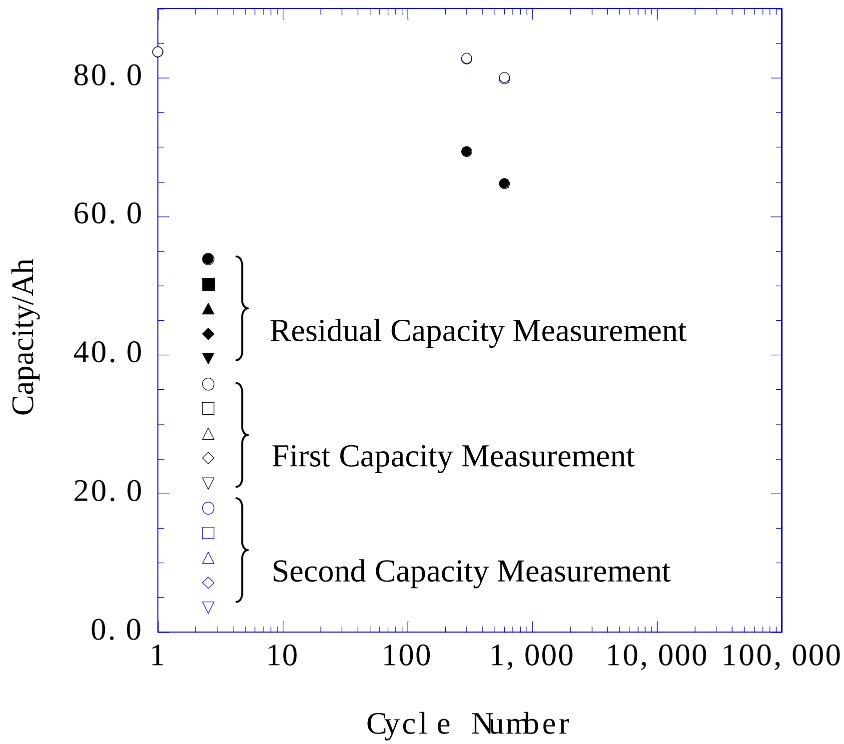

Fig. Capacity Trend by Cycles, LEO Test/DOD40%

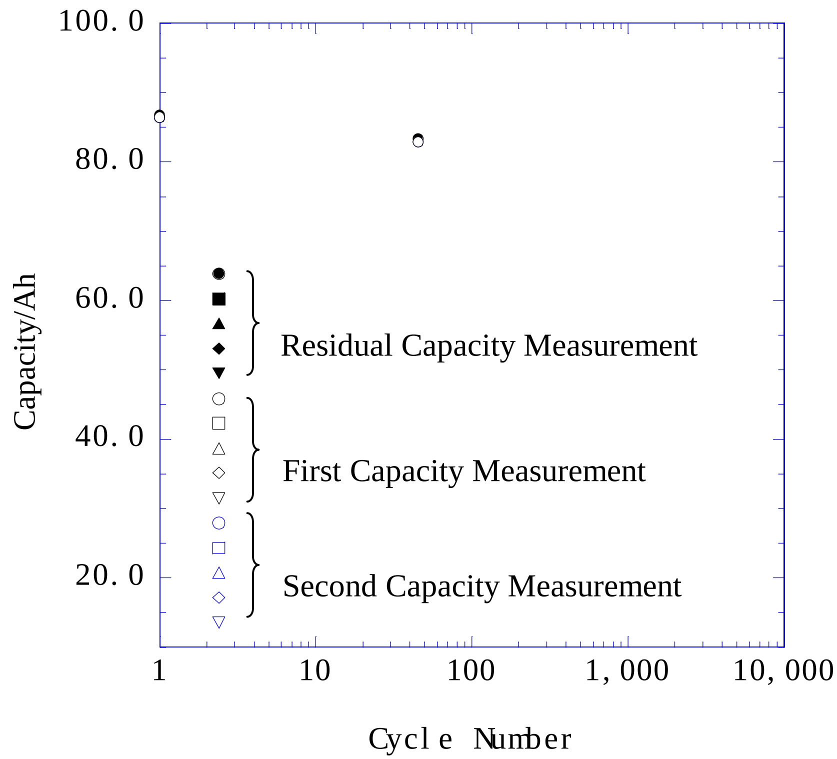

Fig. Capacity Trend by Cycles, GEO Test/DOD80%

Temperature Dependence of Capacity, 90 Ah $LiMn_2O_4$/Non-Graphite Cells

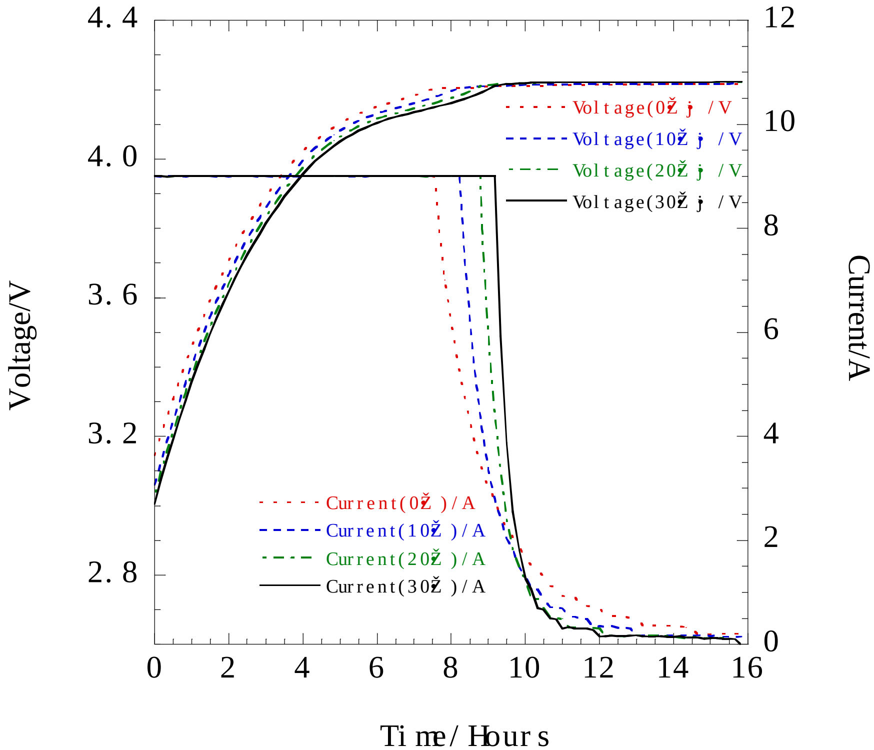

Fig. Charge curves

Charge Condition : CC(9 A)-CV(4.2 V)

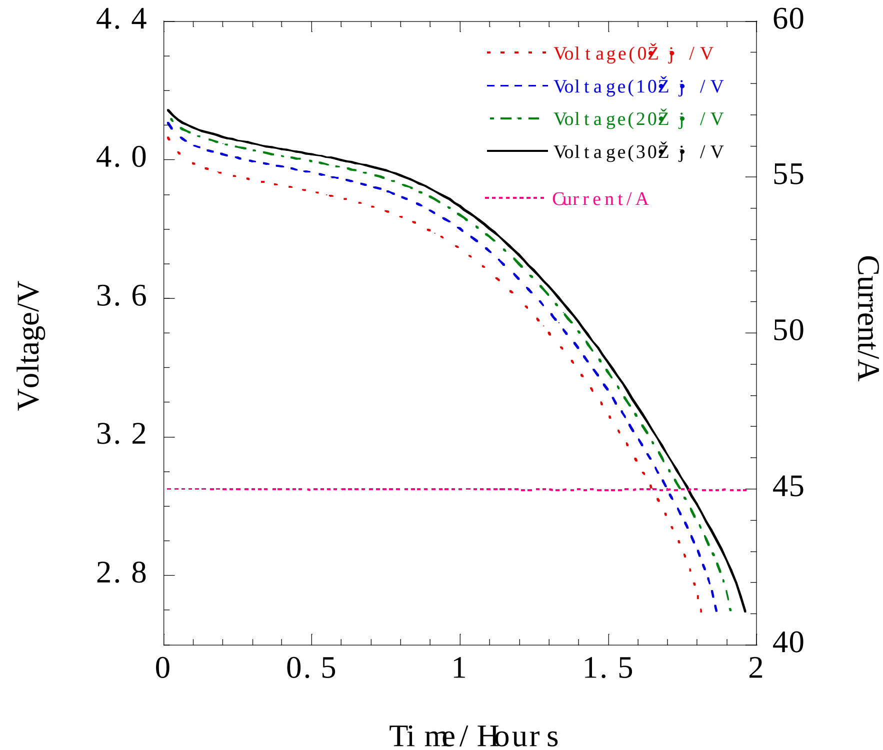

Fig. Discharge curves

Discharge Condition : CC(45 A) to 2.7 V

Fig. Capacity Measurement at different temperatures, measured at 45 cycle of GEO test.

We measured capacities of a cell at different temperatures. The typical curves of the cell using C (non-graphite) were observed. Because of this discharge curve, at lower temperature, we observed the decrease in capacity.

Temperature Dependence of Capacity, 90 Ah $LiMn_2O_4$/Non-Graphite Cells

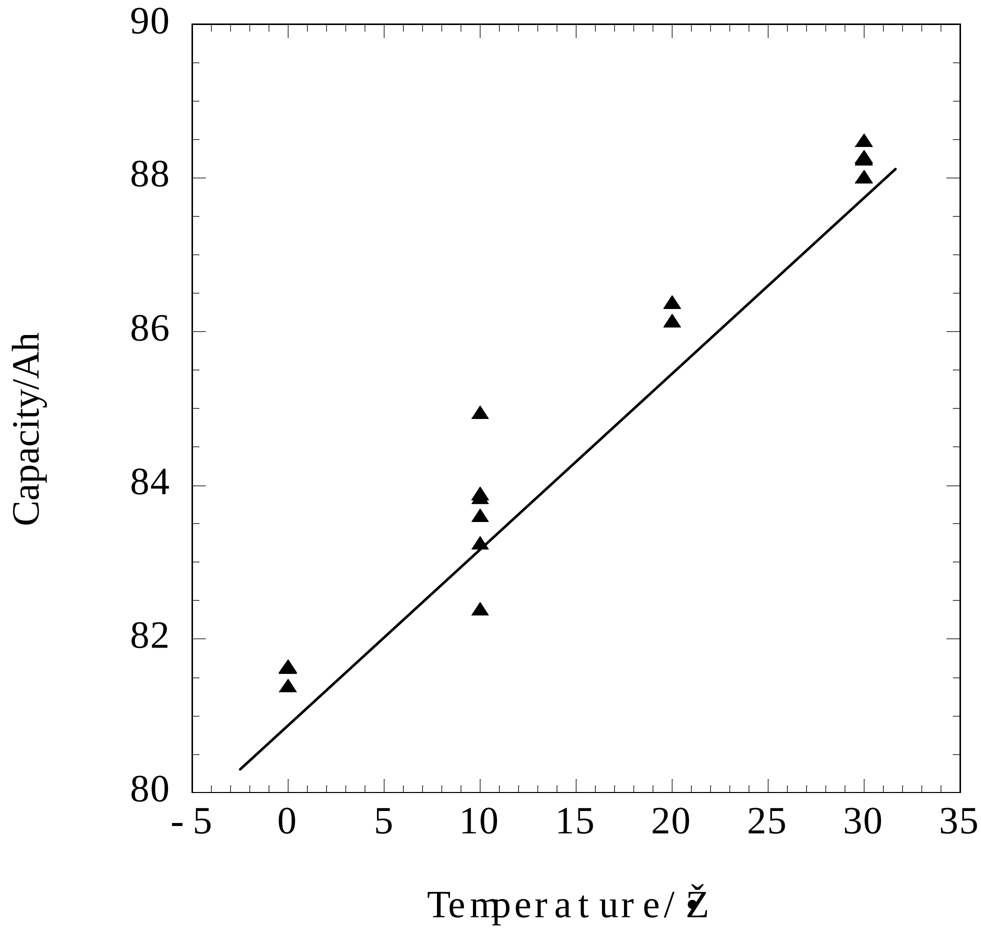

Fig. Temperature dependence of capacity
90 Ah Cylinder Cell from IAC.

Capacity of 90Ah cells linearly increased with temperature. The capacity at 0 was almost 8% smaller than that obtained at 30.

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Summary

Life cycle performance of large size Li-Ion secondary cells is studied at Tsukuba Space Center, NASDA.

. 10 Ah $LiCoO_2$/Graphite Cell

LEO simulating test reveals stable cycle performance of the cells with series connection. We have already tested more than 6,000 life cycles in DOD=25/40% test.

. 30 Ah $LiCoO_2$/Graphite Cell

More than 9,000 cycles have passed in DOD=25 /40% LEO cycle test.

The performance of cells have been very stable in the case of DOD=25%, while a considerable decrease in EODV and residual capacity was observed in the case of DOD=40%. In order to understand the degradation of DOD=40% samples, we performed destructive physical analysis. The analysis suggested us that the degradation of negative electrode played an important role in the degradation of cell performance.

Based on these results, accompanied with the experience of 100Ah elliptic cylinder cells, we have started the discussion of the new trial cell which might enable high rate charge targeting LEO applications.

. 100 Ah $LiCoO_2$/Graphite Cell

More or less than 5,000 cycles have passed in DOD=25/40% LEO cycle test, and more than 300 cycles have passed in DOD=80% GEO cycle test. No significant degradation of the performance has been observed, yet. Thermal effect on capacity was also presented.

. 90 Ah $LiMn_2O_4$/Non-Graphite Cell

The study of this type of cells has just started. More than 1,000 cycles in DOD=40% LEO test and 45 cycles in DOD=80% GEO test have passed. Thermal effect on capacity was also presented.

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NASA/GSFC Testing of Li-Ion Cells: Update

Hari Vaidyanathan
Lockheed Martin Global Telecommunications
Clarksburg, Maryland
And
Gopalakrishna M. Rao
NASA-Goddard Space Flight Center
Greenbelt, Maryland

2000 NASA Aerospace Battery Workshop
Huntsville, Alabama
November 14-16, 2000

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Objective

- Cell Characterization
  - Capacity
  - Self-discharge
  - Mid-discharge voltage
- Determination of Cycling Performance as a Battery Pack under LEO regime
  - Number of cycles
  - Charge voltage
  - Temperature

Cells Under Study

- Prismatic Cells
  - 20 AH Yardney
  - 1.5 AH Wilson Greatbatch
- Cylindrical Cells
  - 12 AH, 4 AH and 1.25 AH SAFT
- Polymer cells
  - 3 AH Alliant Tech.
  - 8 AH Lithium Technology, Inc.

Characterization Data

- Self-discharge - 72 hours charged open-circuit stand
  - Yardney = 1.4%
  - SAFT =1.4%
  - Alliant Tech (ATK) = 2%
  - Wilson Greatbatch (WG) =1.4%
- Capacity Decrease when the discharge rate is increased to C/2 from C/5
  - Yardney - 2%
  - SAFT - 0.9%
  - ATK - 2%
  - WG - 25%

Characterization Data -Contd.

- Mid-discharge voltages at C/2 discharge rate
  - Yardney = 3.51V
  - SAFT = 3.56V
  - ATK = 3.54 V
  - WG = 3.65V
- Cell impedance (mohms) at 50% SOC
  - SAFT = 1.74
  - Yardney = 10.2
  - ATK = 51
  - WG = 68

Characterization Data -Contd.

- Capacity at 0^{o}C in percentage of capacity at 25^{o}C

  - Yardney = 92%
  - SAFT = 91%
  - WG = 91%
  - ATK = 51%

LEO Cycling: Conditions

- Continuous cycling in a regime consisting of 30 min. discharge and 60 min. charge at the rate of 16 cycles/day
- Temperature = -20°C to 40°C
- Depth of discharge = 40%
- Charge voltage clamped at a Battery/Pack voltage at C/2 rate with current taper
- Recharge ratio = 1-1.01

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LEO Cycling: Data

Number of cells and cell type	CAP, AH AT 25°C	Charge Vlimit	CYCLES	STATUS
8 - SAFT 12AH	11.4	3.85	2745	Continuing
8 - Yardney 20AH*	24.9	4	2739	Continuing
5 - Alliant Tech 3AH	2.06	4	2359	Discontd
8 - WG 1.5AH	1.43	4.1	10	Discontd
8 - Li-Tech 8AH	7.1	4.1	2	Discontd
2 - SAFT 4AH	4	3.85	7472	Continuing
2 - SAFT 1.25AH	1.3	3.85	11323	Continuing

* Cells 192,194,195 and 196 have previously completed 2966 cycles.

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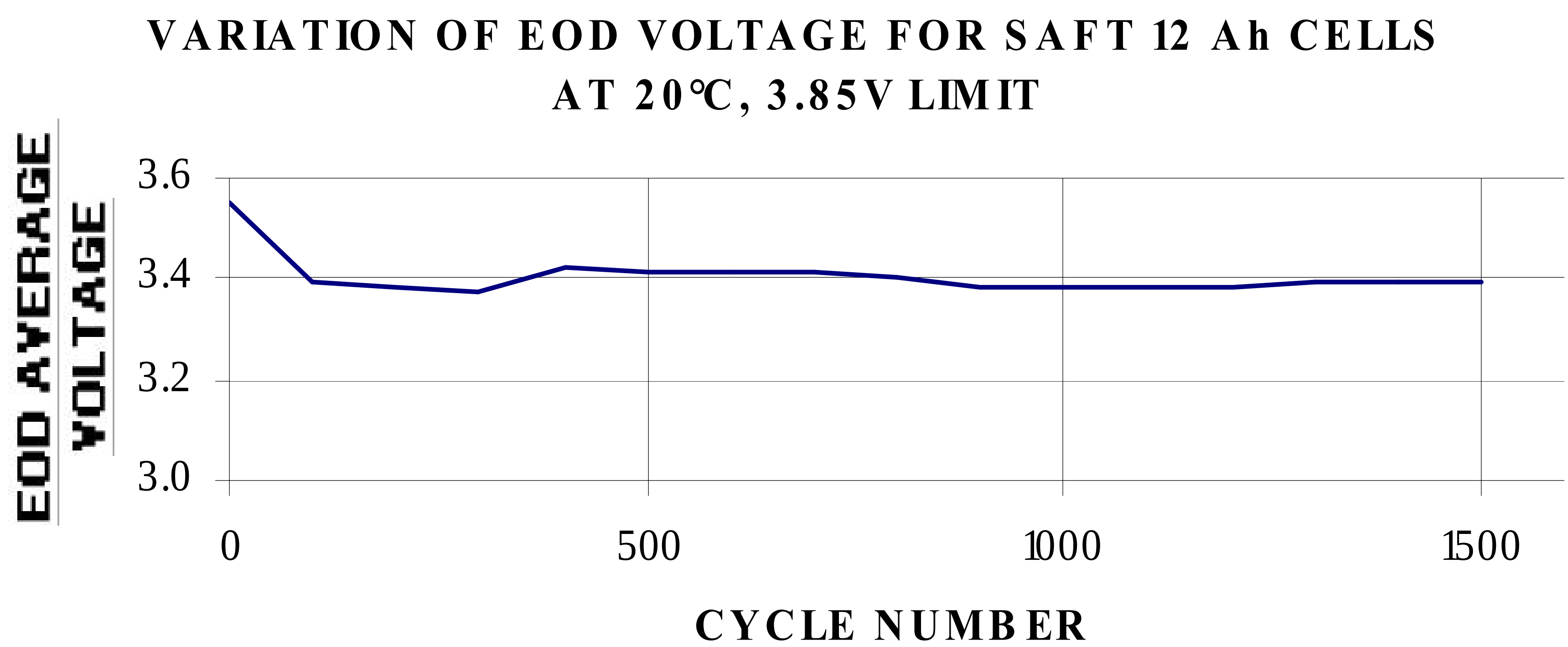

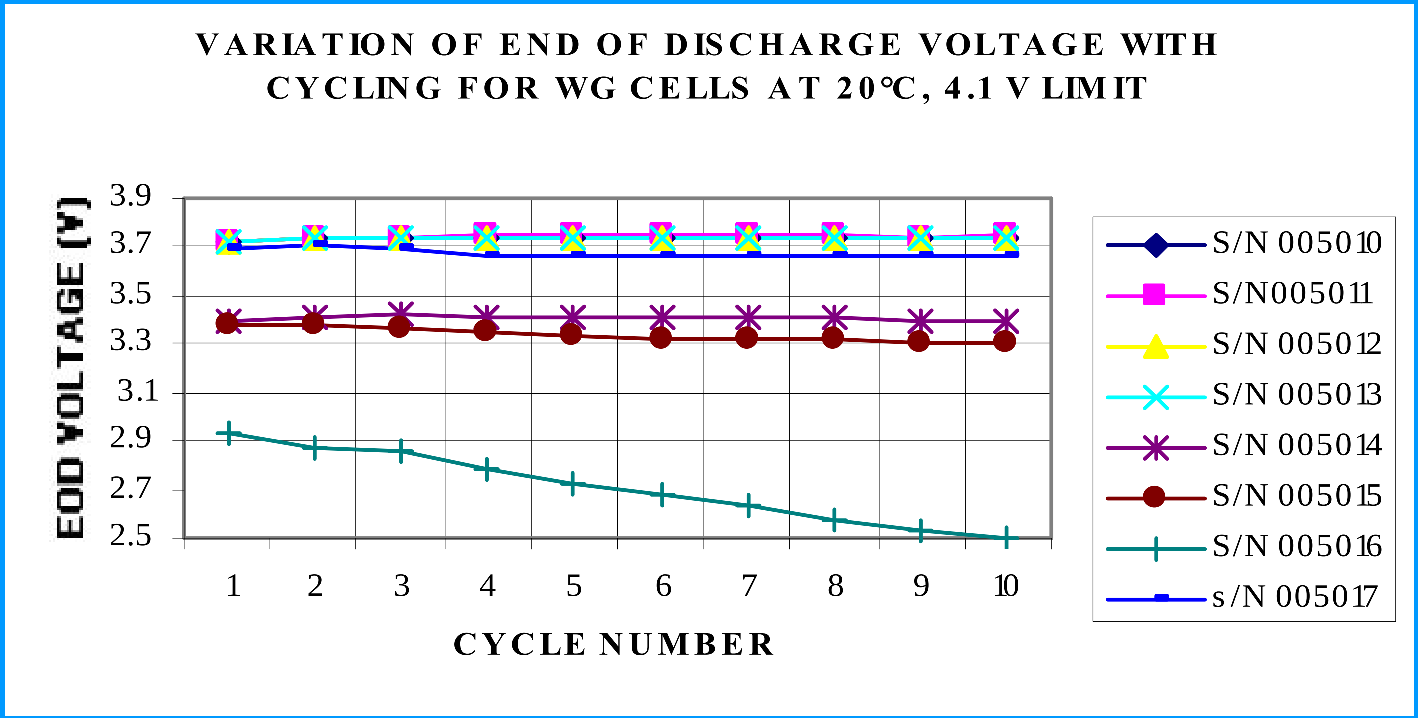
VARIATION OF END OF DISCHARGE VOLTAGE WITH
CYCLING FOR WG CELLS AT 20°C, 4.1 V LIMIT
EOD VOLTAGE (V)
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
1
2
3
4
5
6
7
8
9
10
CYCLE NUMBER
S/N 005010
S/N005011
S/N 005012
S/N 005013
S/N 005014
S/N 005015
S/N 005016
s/N 005017

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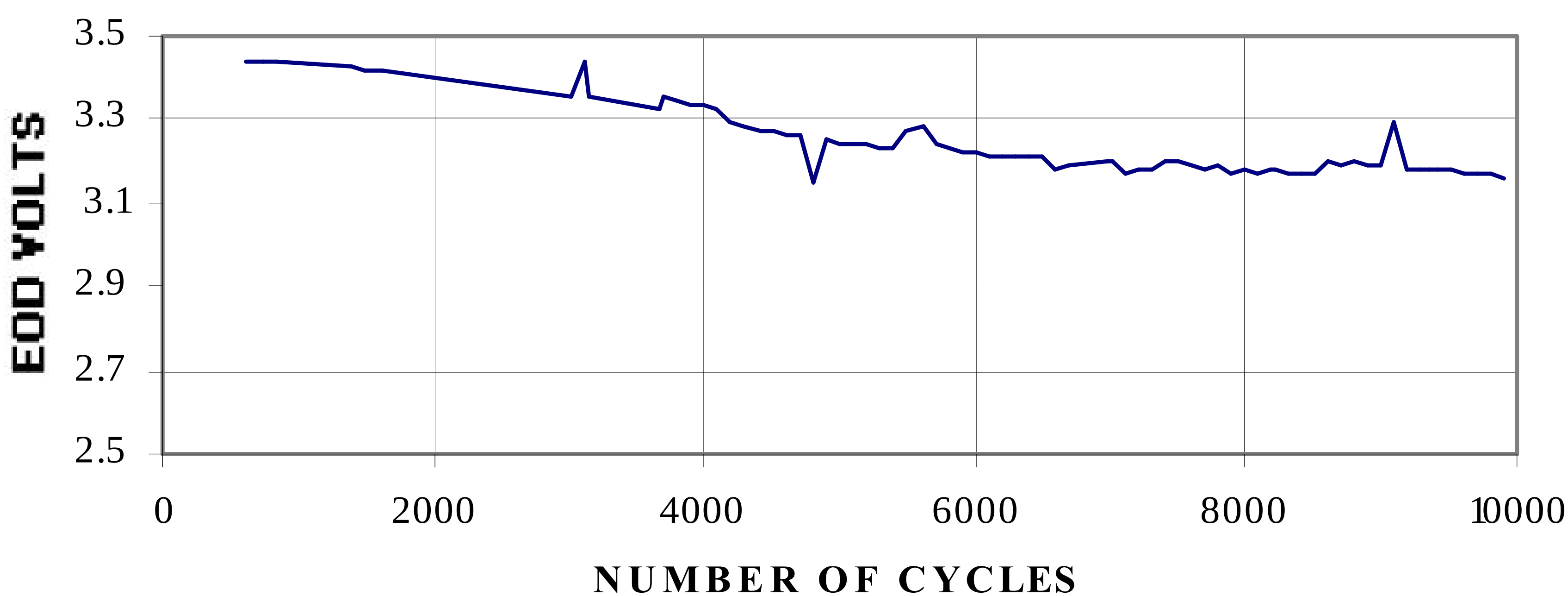
VARIATION OF EOD WITH CYCLING FOR SAFT 1.25 AH CELL AT 30°C, 3.85V LIMIT



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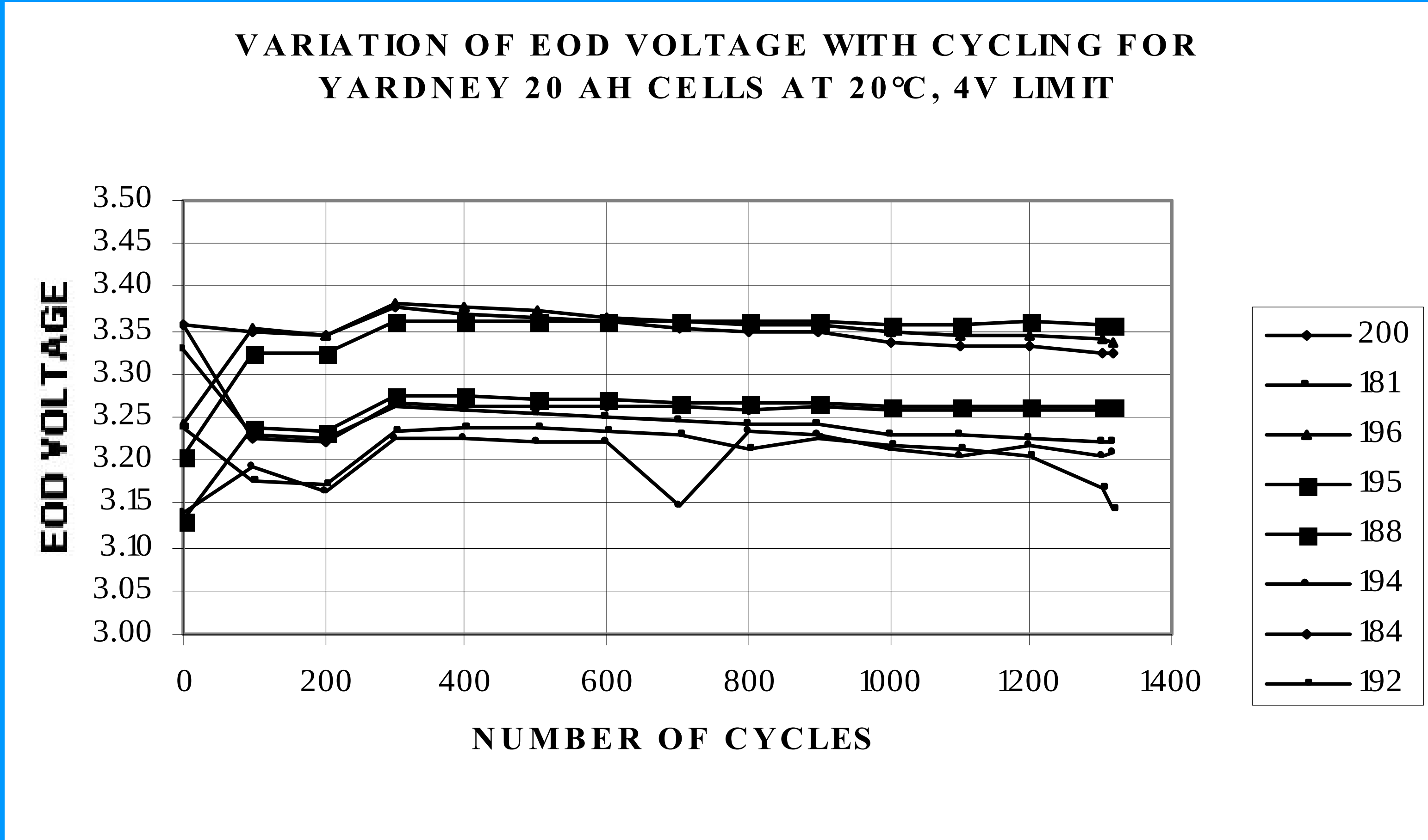

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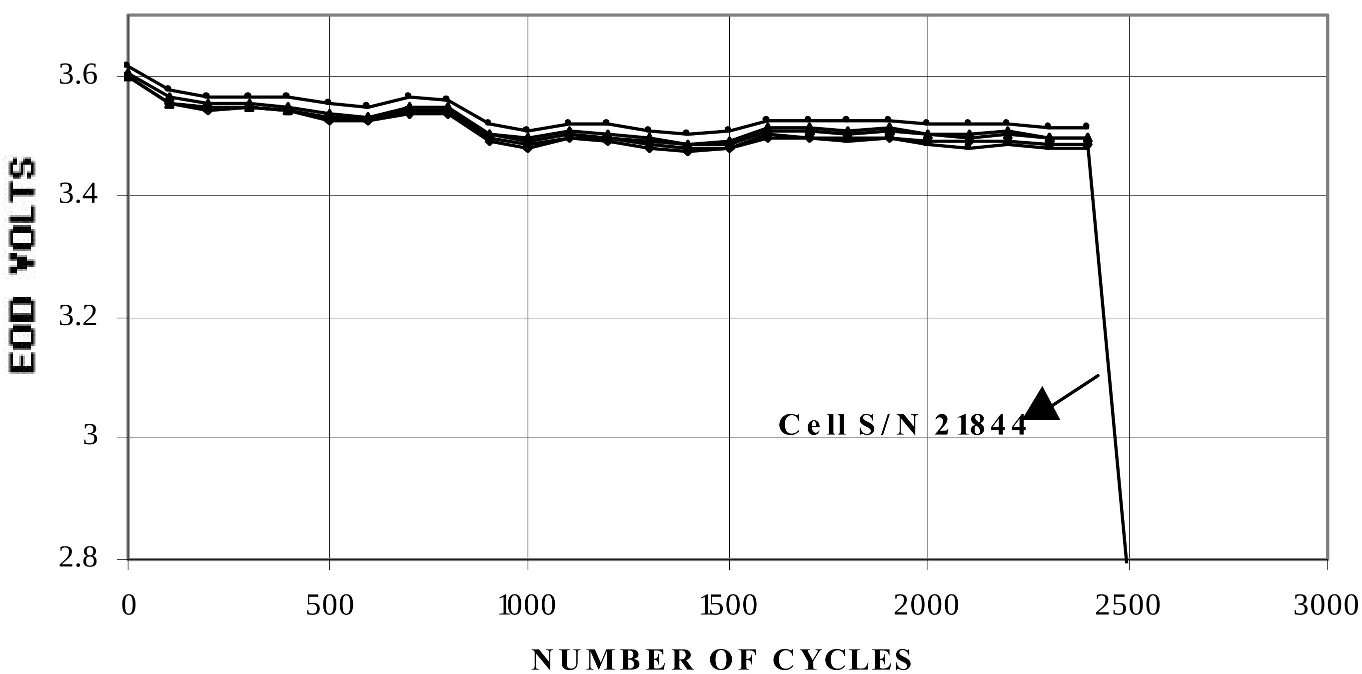
VARIATION OF EOD VOLTAGE WITH CYCLING FOR ALLIANT TECH 3 AH CELLS AT 20°C, 4V LIMIT



PERFORMANCE TWO 2-CELL SAFT 4 AH BATTERIES

Temp °C	Number of cycles		End of dischg voltage		Comments
30	4289		3.217		cell charged to 3.85V
40	550		3.266		cell charged to 3.85V
0	560		2.816		cell charged to 4.1V
-20	2		2		cell charged to 4.3V
-10	39		2.755		cell charged to 4.48V
10	442		3.039		cell charged to 4.1V
20	6157		3.17		cell charged to 3.85V

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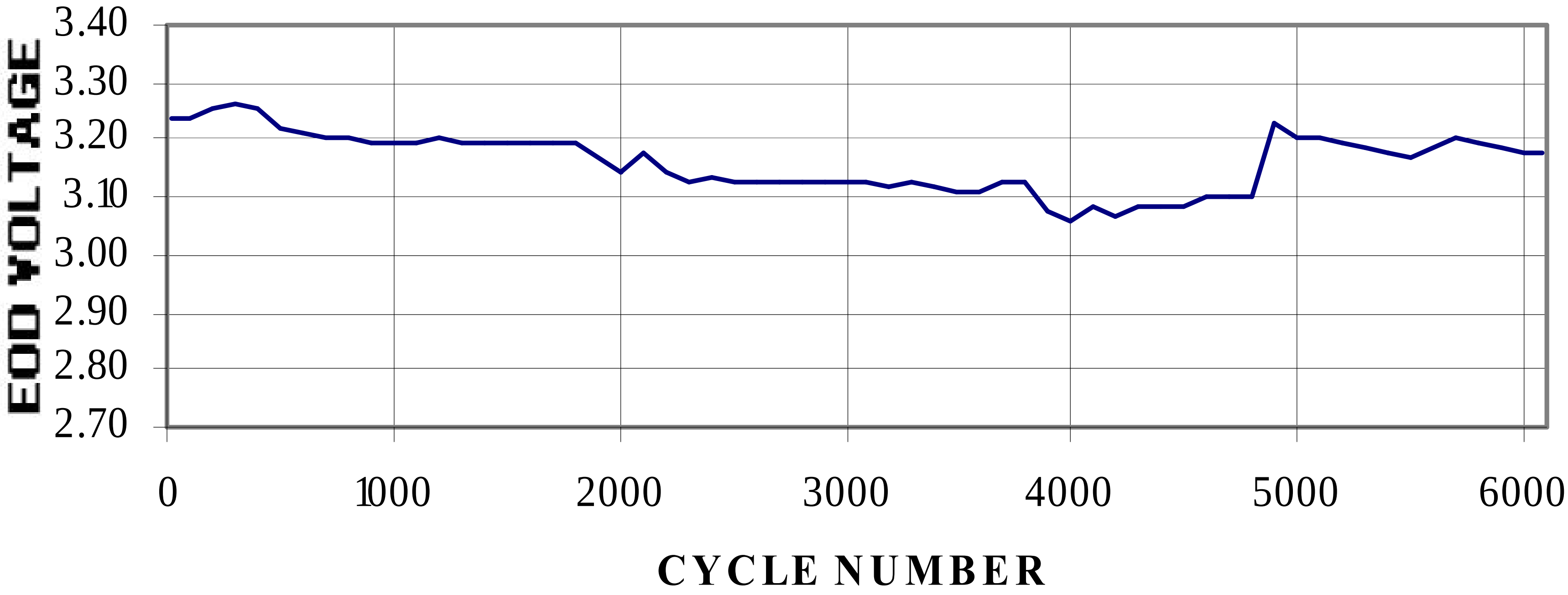
VOLTAGE BEHAVIOR DURING CYCLING FOR SAFT 4AH CELLS 20°C, 3.85 V LIMIT



Conclusions

- The self-discharge rate of Li-ion cells is 1.4% in the 72-hr charged open-circuit stand test that is superior to NiCd and NiH_2 Batteries
- Charge acceptance of the cells decreases with temperature
- Cells cannot be cycled in a 90-minute orbit and 40% DoD at minus 10°C unless the voltage limit on charge is increased to 4.5V
- Limited cycling excursion to minus 20°C (low temperatures) does not appear to impair the cycling behavior at 20°C
- The solid electrolyte and gel electrolyte cells' performance is inferior to the liquid electrolyte cells under our LEO test conditions
- The data suggests the potential use of a battery level charging by monitoring and managing the cell parameters

Lithium Ion Battery Design and Safety

The NASA Aerospace Battery Workshop, Marshall Space Flight Center, and the NASA Aerospace Flight Battery Systems Program at Huntsville AL.

George Au and Laura Locke

Presented by George Au

US Army CECOM RDEC

AMSEL-RD-C2-AP-BA

Fort Monmouth, NJ 07703

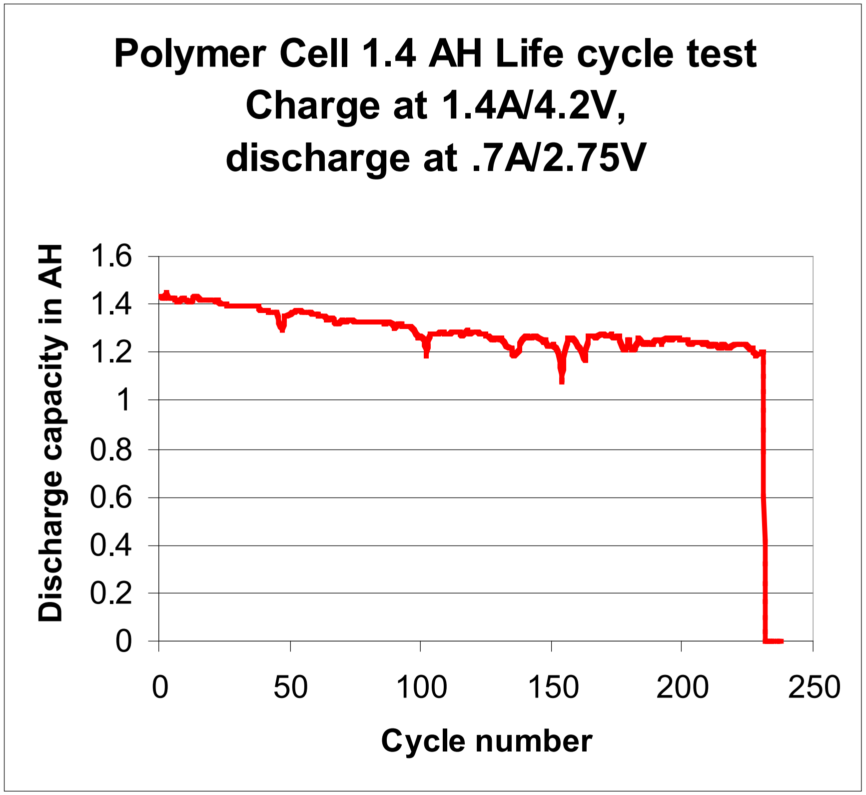
732-427-4886

George.Au@mail1.monmouth.army.mil

14-16 Nov. 2000

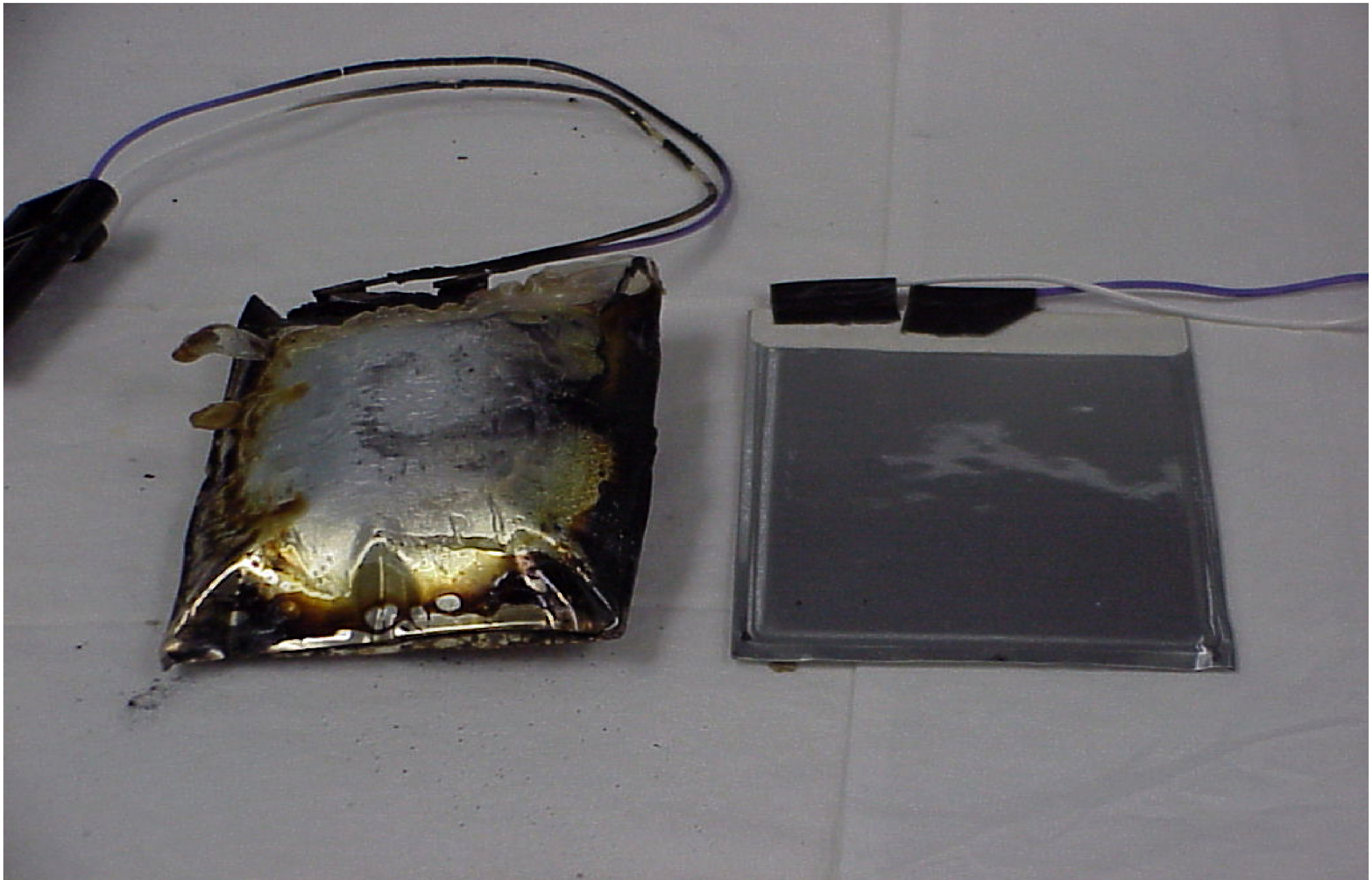
CECOM Bottom Line: THE SOLDIER

Life Cycle Test for commercial 1.4 AH Polymer Cell



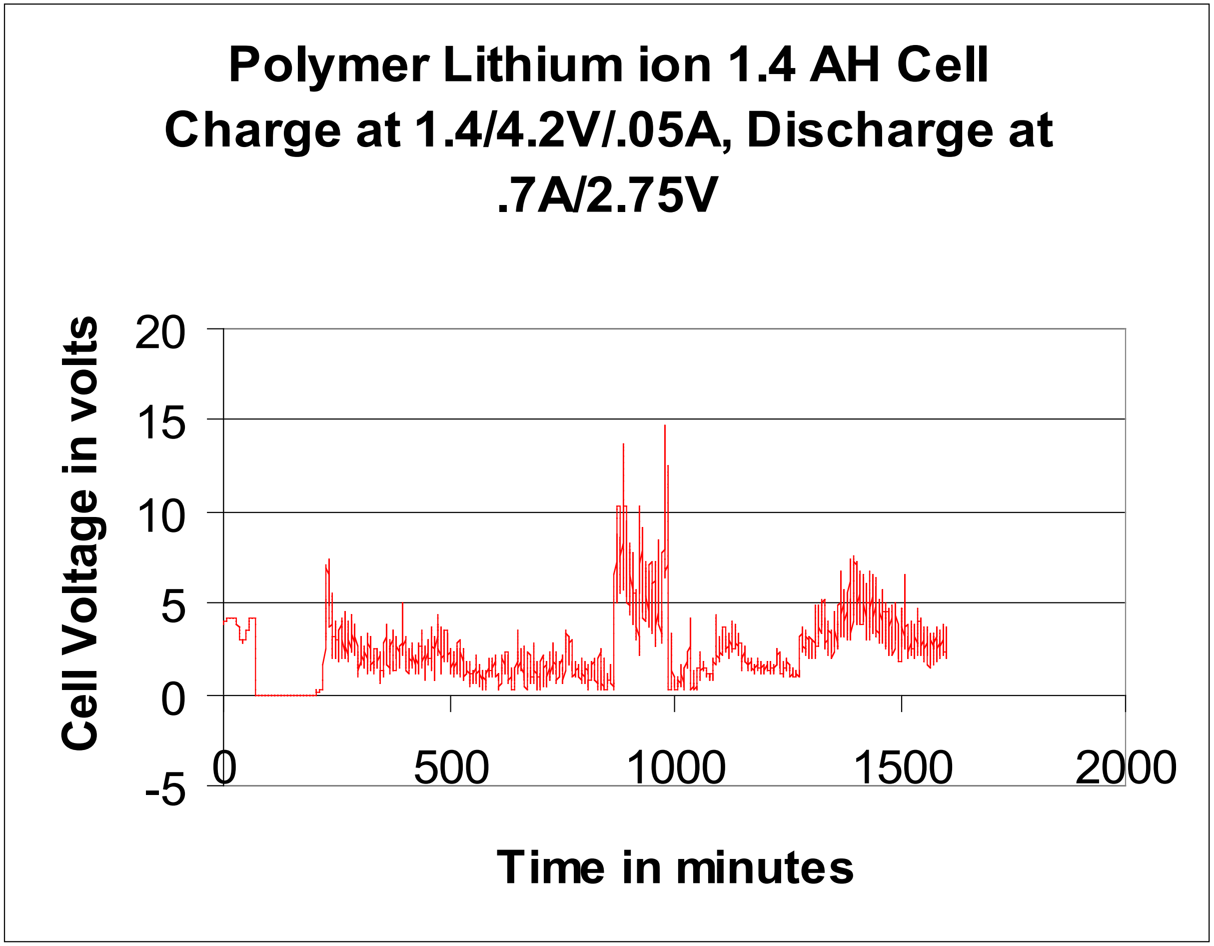
CECOM Bottom Line: THE SOLDIER

Burned 1.4 AH Polymer Lithium ion Cell During Cycling



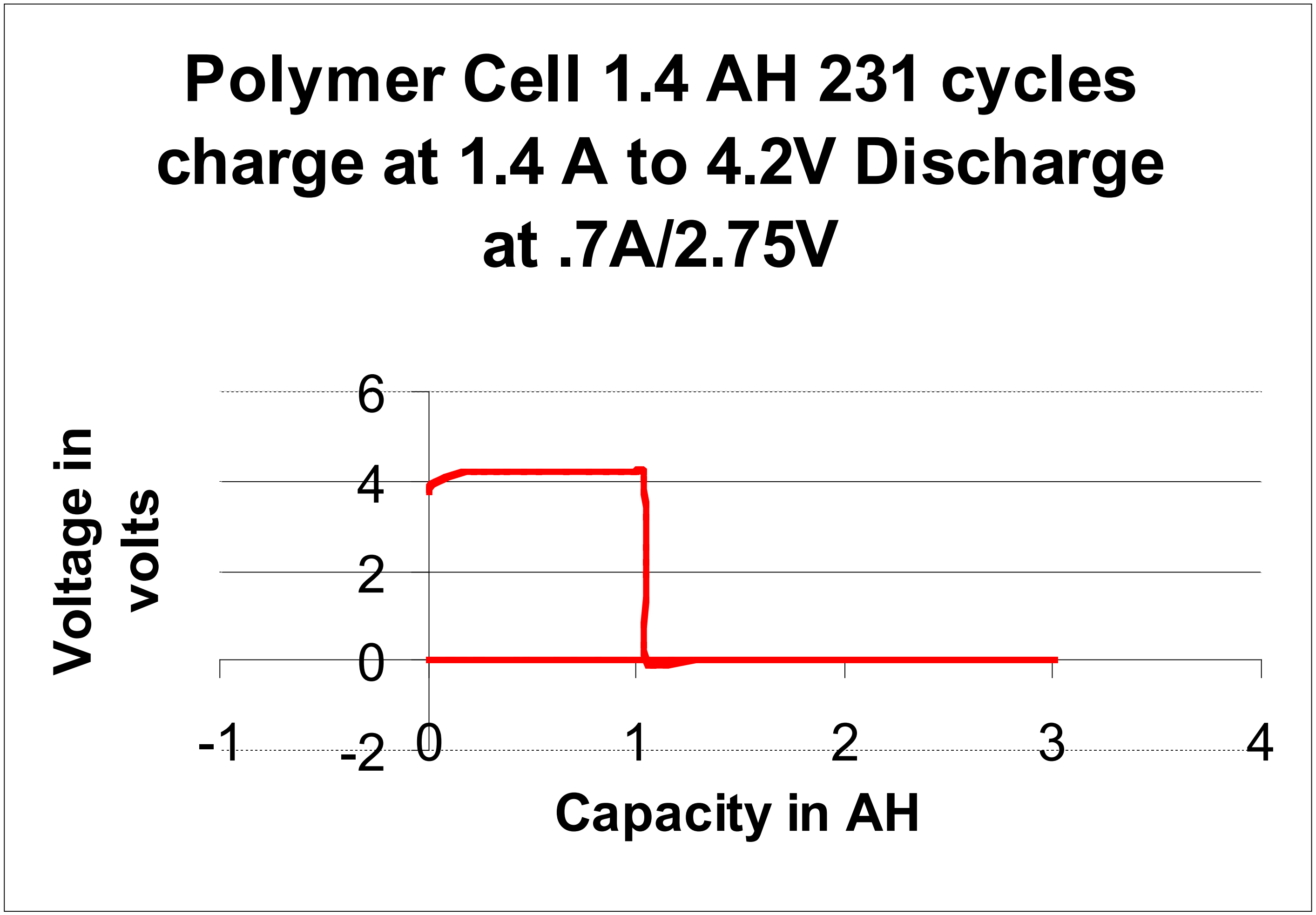
CECOM Bottom Line: THE SOLDIER

Shorted Polymer Lithium ion Cell During Cycling From 231 to 238



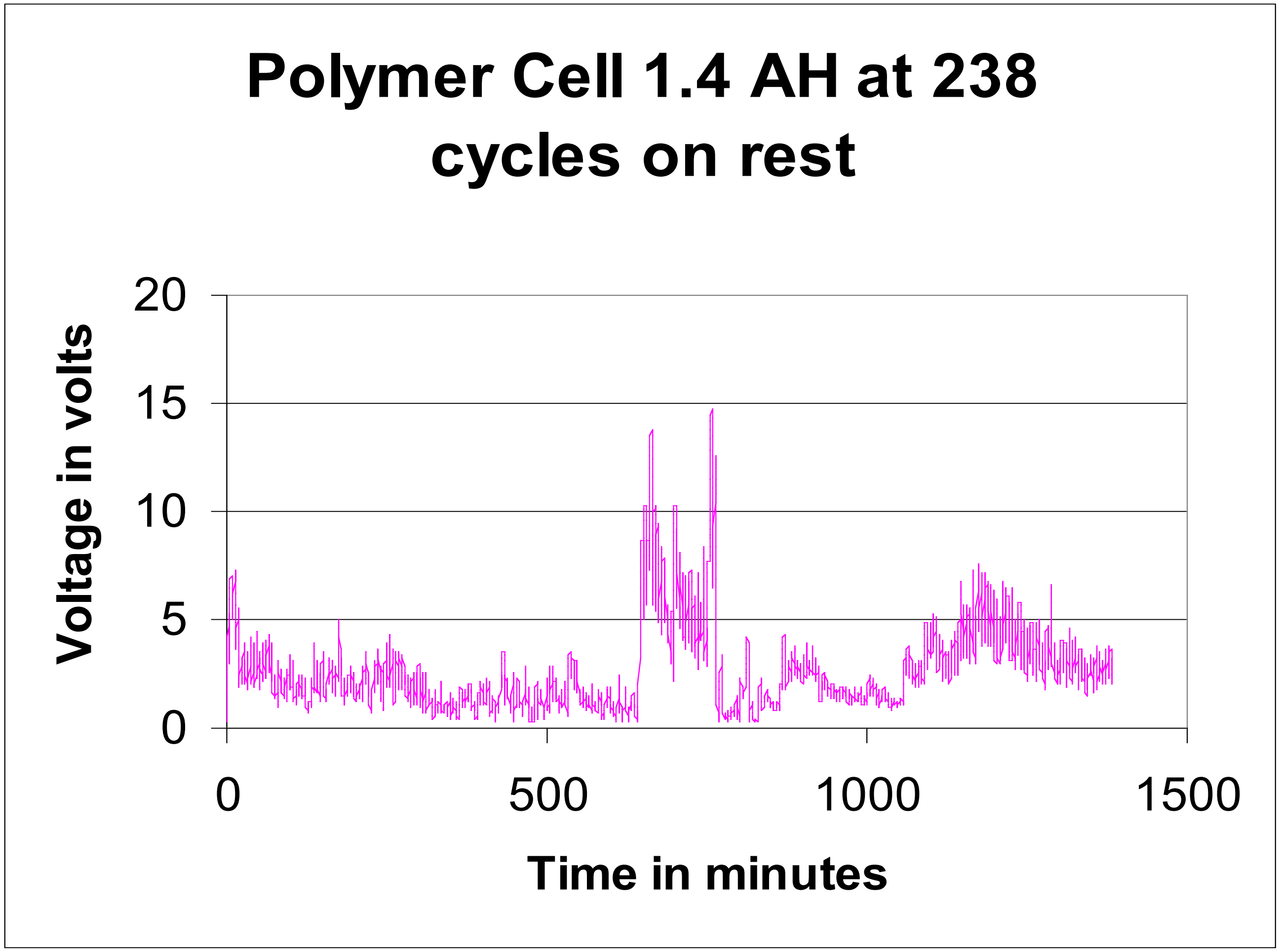
CECOM Bottom Line: THE SOLDIER

Shorted 1.4 AH Polymer Lithium ion Cell During Cycling



CECOM Bottom Line: THE SOLDIER

Shorted Polymer Lithium ion Cell During Cycling



CECOM Bottom Line: THE SOLDIER

Polymer Lithium ion Cell Cycle Data

					AH	WH	A	V	
12318	231	4	62d 16:46	0d 01:00	0	0	0	3.57116	R
12319	231	5	62d 16:46	0d 00:00	6.23E-05	0.000233	1.399863	3.78265	C
12320	231	5	62d 16:47	0d 00:00	0.007572	0.029184	1.400015	3.882628	C
12321	231	5	62d 16:48	0d 00:01	0.034713	0.136102	1.400015	3.983154	C
12322	231	5	62d 16:50	0d 00:03	0.088652	0.353757	1.399939	4.083131	C
12323	231	5	62d 16:54	0d 00:07	0.170985	0.694314	1.399939	4.183108	C
12324	231	5	62d 17:04	0d 00:17	0.373095	1.542775	1.067292	4.199588	C
12325	231	5	62d 17:14	0d 00:27	0.532285	2.21114	0.872969	4.200137	C
12326	231	5	62d 17:24	0d 00:37	0.664404	2.765814	0.701534	4.200137	C
12327	231	5	62d 17:34	0d 00:47	0.771445	3.215159	0.588388	4.200137	C
12328	231	5	62d 17:44	0d 00:57	0.858548	3.580753	0.468299	4.199588	C
12329	231	5	62d 17:54	0d 01:07	0.929777	3.879686	0.379568	4.200137	C
12330	231	5	62d 18:04	0d 01:17	0.986491	4.117654	0.310979	4.200137	C
12331	231	5	62d 18:14	0d 01:27	1.032339	4.309986	0.243534	4.199588	C
12332	231	5	62d 18:16	0d 01:29	1.042173	4.351228	0.268788	1.900114	C
12333	231	5	62d 18:16	0d 01:29	1.042175	4.351228	0.391012	0	C
12334	231	5	62d 18:26	0d 01:39	1.27551	4.351228	1.400015	0	C
12335	231	5	62d 18:36	0d 01:49	1.508846	4.351228	1.400015	0	C
12336	231	5	62d 18:46	0d 01:59	1.742182	4.351228	1.399939	0	C
12337	231	5	62d 18:56	0d 02:09	1.975518	4.351228	1.400015	0	C
12338	231	5	62d 19:06	0d 02:19	2.208854	4.351228	1.399939	0	C
12339	231	5	62d 19:16	0d 02:29	2.44219	4.351228	1.400015	0	C
12340	231	5	62d 19:26	0d 02:39	2.675526	4.351228	1.400015	0	C

CECOM Bottom Line: THE SOLDIER

Polymer Lithium ion Cell Cycle Data

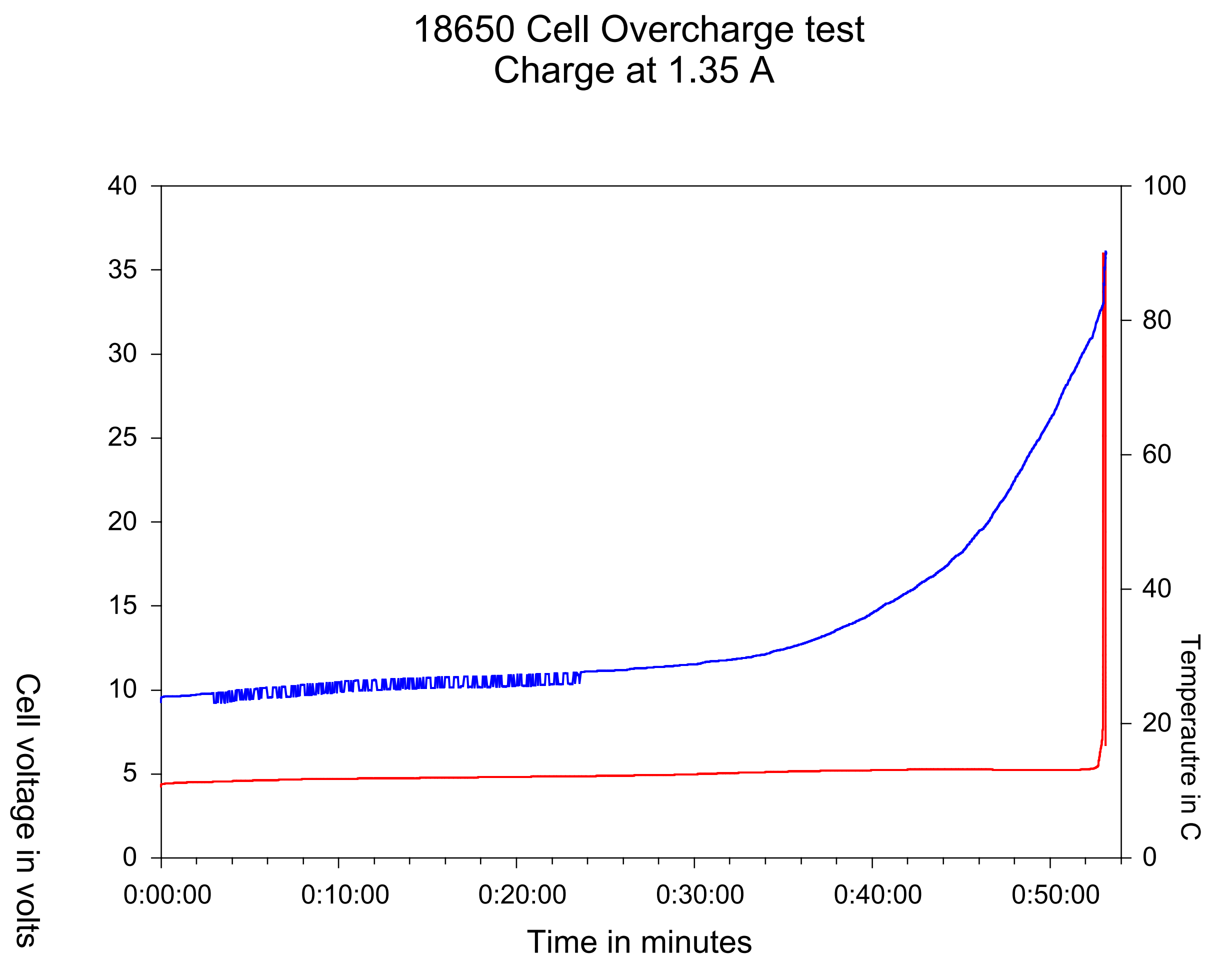
					AH	WH	A	V
12245	230	3	62d 08:36	0d 01:14	0.873924	3.171562	0.700008	3.356374
12261	230	4	62d 09:35	0d 00:31	0	0	0	3.535454
12262	230	4	62d 09:55	0d 00:51	0	0	0	3.560174
12269	230	5	62d 10:21	0d 00:17	0.375898	1.554214	1.038605	4.200137
12270	230	5	62d 10:31	0d 00:27	0.53513	2.222758	0.87686	4.200137
12271	230	5	62d 10:41	0d 00:37	0.666299	2.773442	0.701839	4.200137
12272	230	5	62d 10:51	0d 00:47	0.773657	3.224118	0.587701	4.200137
12273	230	5	62d 11:01	0d 00:57	0.860612	3.589092	0.467994	4.199588
12274	230	5	62d 11:11	0d 01:07	0.931791	3.887816	0.385214	4.200137
12275	230	5	62d 11:21	0d 01:17	0.988114	4.124145	0.305257	4.200137
12276	230	5	62d 11:31	0d 01:27	1.034228	4.3176	0.244984	4.200137
12277	230	5	62d 11:41	0d 01:37	1.070484	4.469645	0.19791	4.200137
12278	230	5	62d 11:51	0d 01:47	1.100572	4.595777	0.159075	4.199588
12279	230	5	62d 12:01	0d 01:57	1.124518	4.696127	0.13344	4.199588
12280	230	5	62d 12:11	0d 02:07	1.144839	4.781248	0.105058	4.199588
12281	230	5	62d 12:21	0d 02:17	1.16137	4.85045	0.093462	4.199588
12282	230	5	62d 12:31	0d 02:27	1.175664	4.910261	0.072938	4.199588
12283	230	5	62d 12:41	0d 02:37	1.187588	4.960122	0.06836	4.200137
12284	230	5	62d 12:51	0d 02:47	1.197909	5.003245	0.052949	4.200137
12285	230	5	62d 13:01	0d 02:57	1.206755	5.040179	0.051499	4.200137
12288	230	6	62d 13:23	0d 00:20	0	0	0	4.171572
12289	230	6	62d 13:43	0d 00:40	0	0	0	4.16553
12295	231	3	62d 14:28	0d 00:24	0.289628	1.10583	0.700008	3.693111
12296	231	3	62d 14:38	0d 00:34	0.406296	1.532536	0.699931	3.62884
12297	231	3	62d 14:48	0d 00:44	0.522964	1.952393	0.699931	3.573358
12298	231	3	62d 14:58	0d 00:54	0.639632	2.366408	0.700008	3.527214
12299	231	3	62d 15:08	0d 01:04	0.7563	2.774047	0.700008	3.456901
12300	231	3	62d 15:18	0d 01:14	0.872968	3.172226	0.700008	3.371206
12316	231	4	62d 16:17	0d 00:30	0	0	0	3.539849
12317	231	4	62d 16:37	0d 00:50	0	0	0	3.564569
12324	231	5	62d 17:04	0d 00:17	0.373095	1.542775	1.067292	4.199588

CECOM Bottom Line: THE SOLDIER

12374	233	4	63d 01:49	0d 01:00	0	0	0	0	R
12375	233	5	63d 01:49	0d 00:00	6.23E-05	0	1.400015	0	C
12376	233	5	63d 01:59	0d 00:10	0.233398	0	1.399939	0	C
12377	233	5	63d 02:09	0d 00:20	0.466734	0	1.400015	0	C
12378	233	5	63d 02:19	0d 00:30	0.70007	0	1.400015	0	C
12379	233	5	63d 02:29	0d 00:40	0.933406	0	1.399939	0	C
12380	233	5	63d 02:39	0d 00:50	1.166742	0	1.400015	0	C
12381	233	5	63d 02:49	0d 01:00	1.400078	0	1.399939	0	C
12382	233	5	63d 02:59	0d 01:10	1.633413	0	1.400015	0	C
12383	233	5	63d 03:09	0d 01:20	1.866749	0	1.400015	0	C
12384	233	5	63d 03:19	0d 01:30	2.100085	0	1.399939	0	C
12385	233	5	63d 03:29	0d 01:40	2.333421	0	1.399939	0	C
12386	233	5	63d 03:39	0d 01:50	2.566757	0	1.400015	0	C
12387	233	5	63d 03:49	0d 02:00	2.800093	0	1.399939	0	C
12388	233	5	63d 03:57	0d 02:08	3.000003	0	1.399939	0	C
12389	233	6	63d 03:57	0d 00:00	0	0	0	0	R
12390	233	6	63d 04:17	0d 00:20	0	0	0	0	R
12391	233	6	63d 04:37	0d 00:40	0	0	0	0	R
12392	233	6	63d 04:57	0d 01:00	0	0	0	0	R
12393	234	3	63d 04:57	0d 00:00	0	0	0	0	D
12394	234	4	63d 04:57	0d 00:00	0	0	0	0	R
12395	234	4	63d 05:17	0d 00:20	0	0	0	0	R
12396	234	4	63d 05:37	0d 00:40	0	0	0	0	R
12397	234	4	63d 05:57	0d 01:00	0	0	0	0	R
12398	234	5	63d 05:57	0d 00:00	6.23E-05	0	1.399939	0	C
12399	234	5	63d 06:07	0d 00:10	0.233398	0	1.400015	0	C
12400	234	5	63d 06:17	0d 00:20	0.466734	0	1.399939	0	C
12401	234	5	63d 06:27	0d 00:30	0.70007	0	1.399939	0	C
12402	234	5	63d 06:37	0d 00:40	0.933406	0	1.399939	0	C
12403	234	5	63d 06:47	0d 00:50	1.166742	0	1.399939	0	C
12404	234	5	63d 06:57	0d 01:00	1.400078	0	1.400015	0	C
12405	234	5	63d 07:07	0d 01:10	1.633413	0	1.399939	0	C
12406	234	5	63d 07:17	0d 01:20	1.866749	0	1.399939	0	C
12407	234	5	63d 07:27	0d 01:30	2.100085	0	1.400015	0	C
12408	234	5	63d 07:37	0d 01:40	2.333421	0	1.400015	0	C
12409	234	5	63d 07:47	0d 01:50	2.566757	0	1.399939	0	C
12410	234	5	63d 07:57	0d 02:00	2.800093	0	1.400015	0	C
12411	234	5	63d 08:06	0d 02:08	3.000003	0	1.400015	0	C
12412	234	6	63d 08:06	0d 00:00	0	0	0	0	R

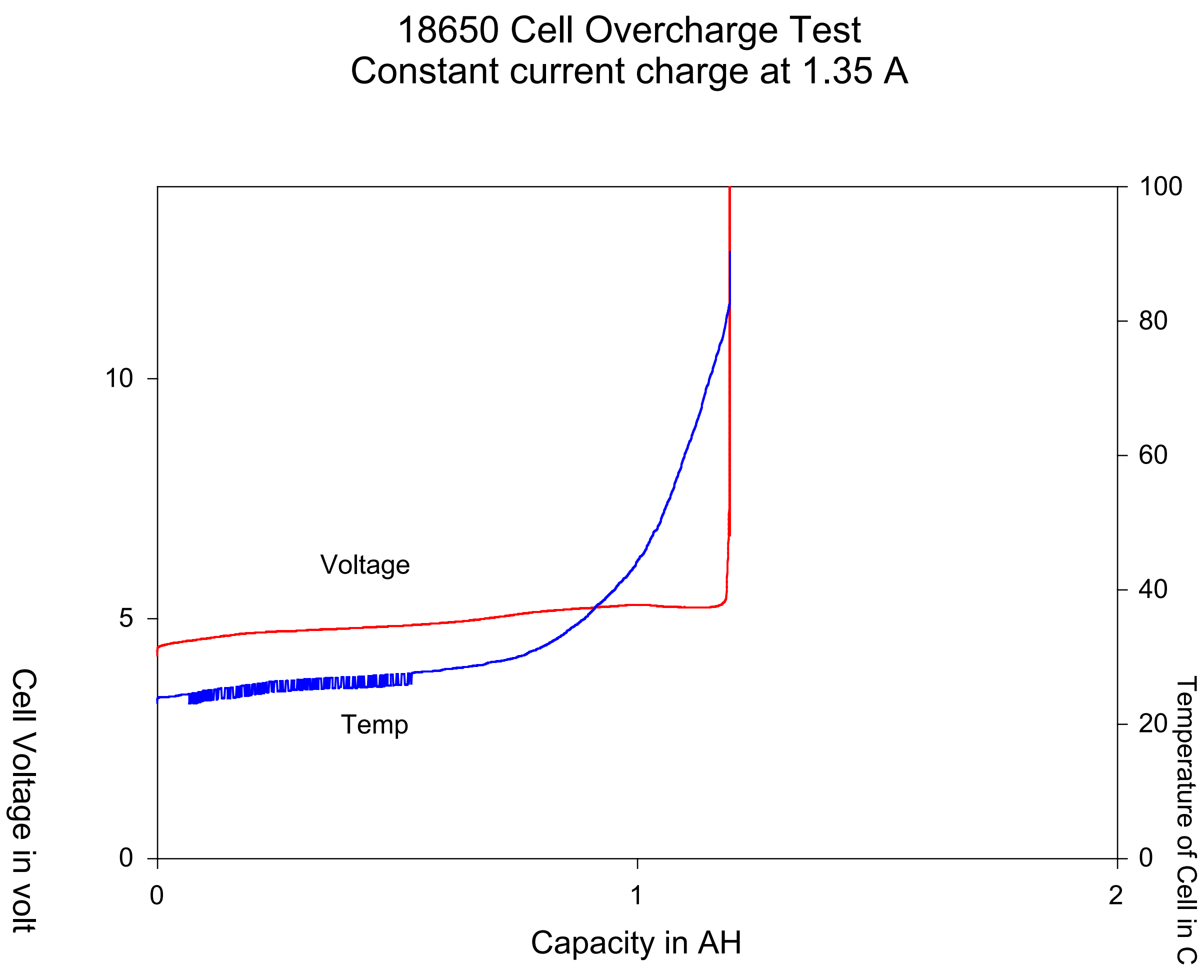
CECOM Bottom Line: THE SOLDIER

Overcharge Tests for Commercial 18650



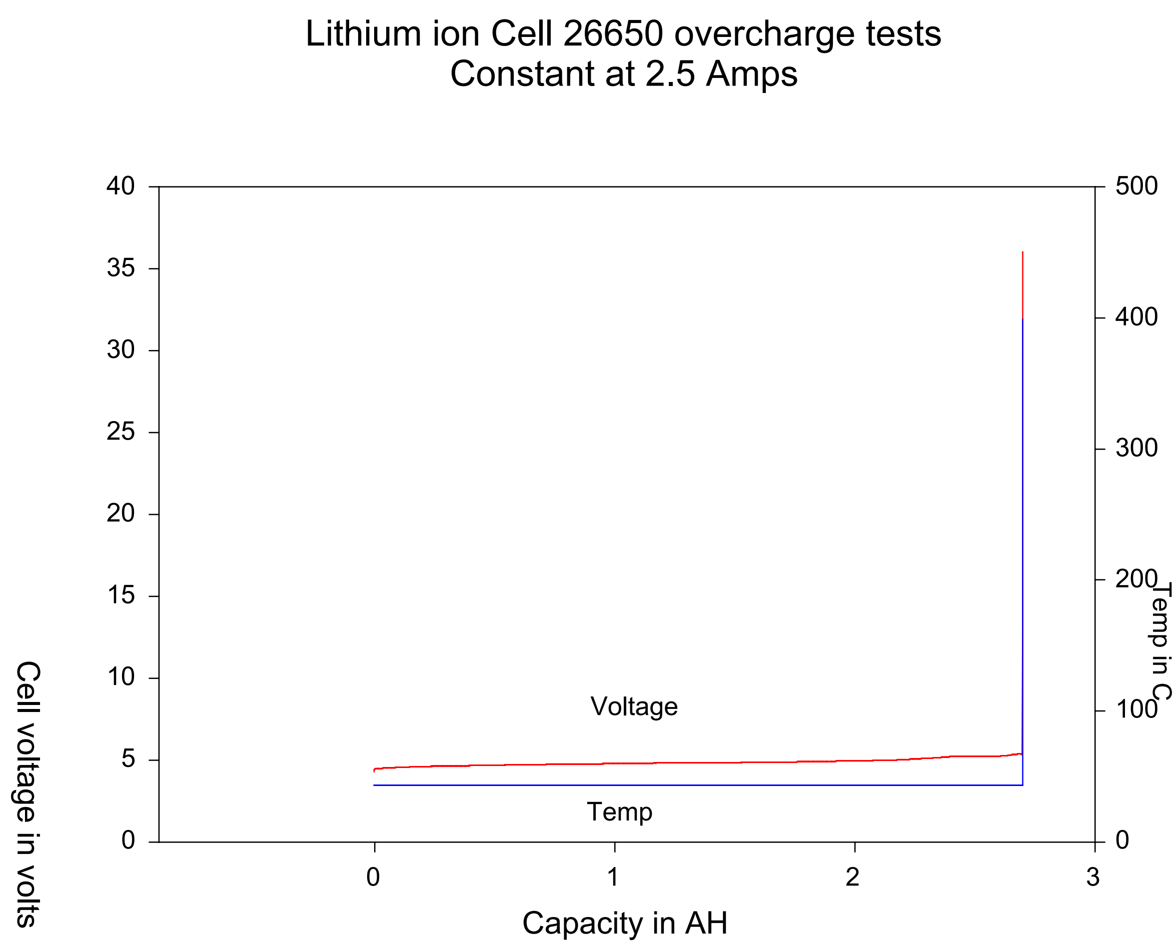
CECOM Bottom Line: THE SOLDIER

Overcharge Tests for Commercial 18650



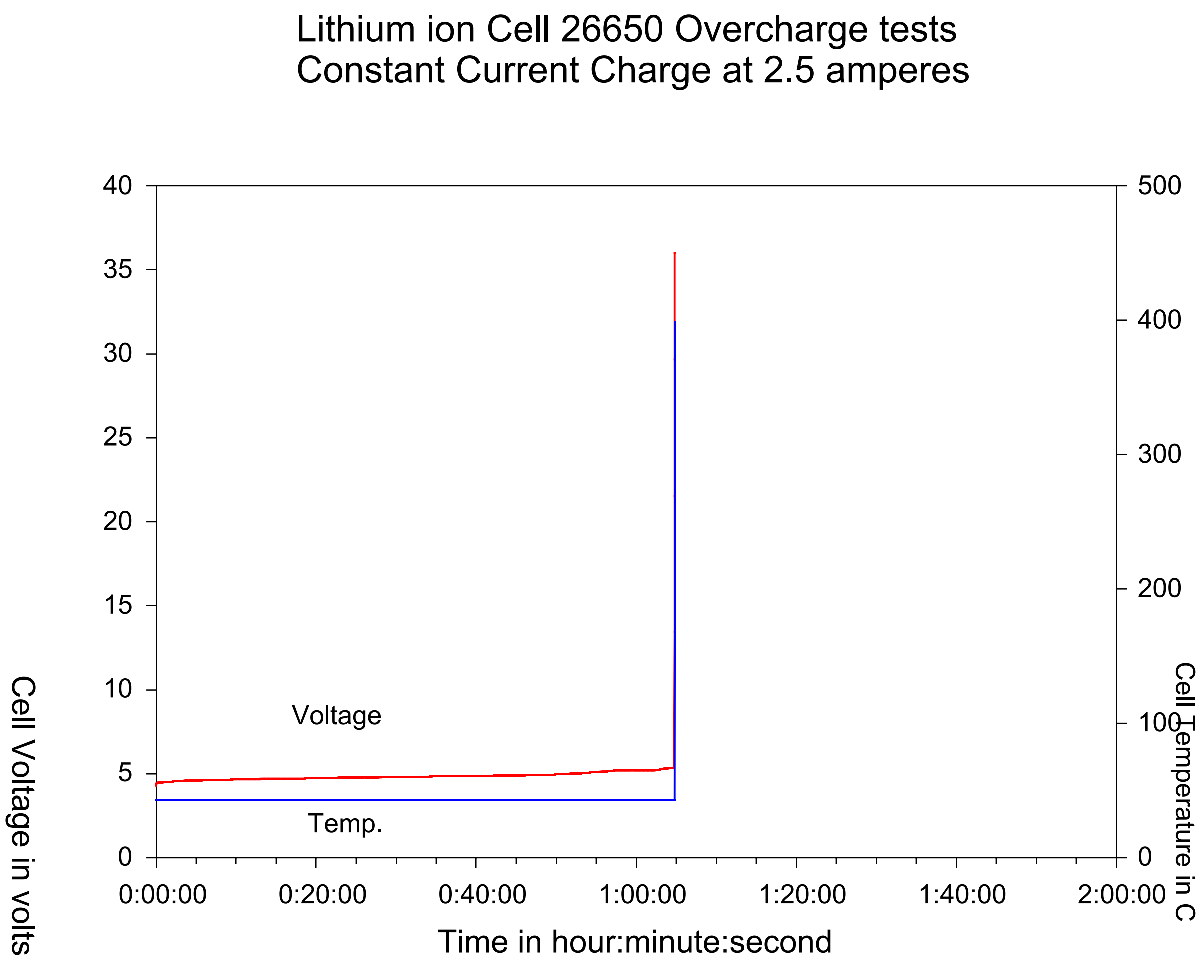
CECOM Bottom Line: THE SOLDIER

Overcharge Test for Commercial 26650



CECOM Bottom Line: THE SOLDIER

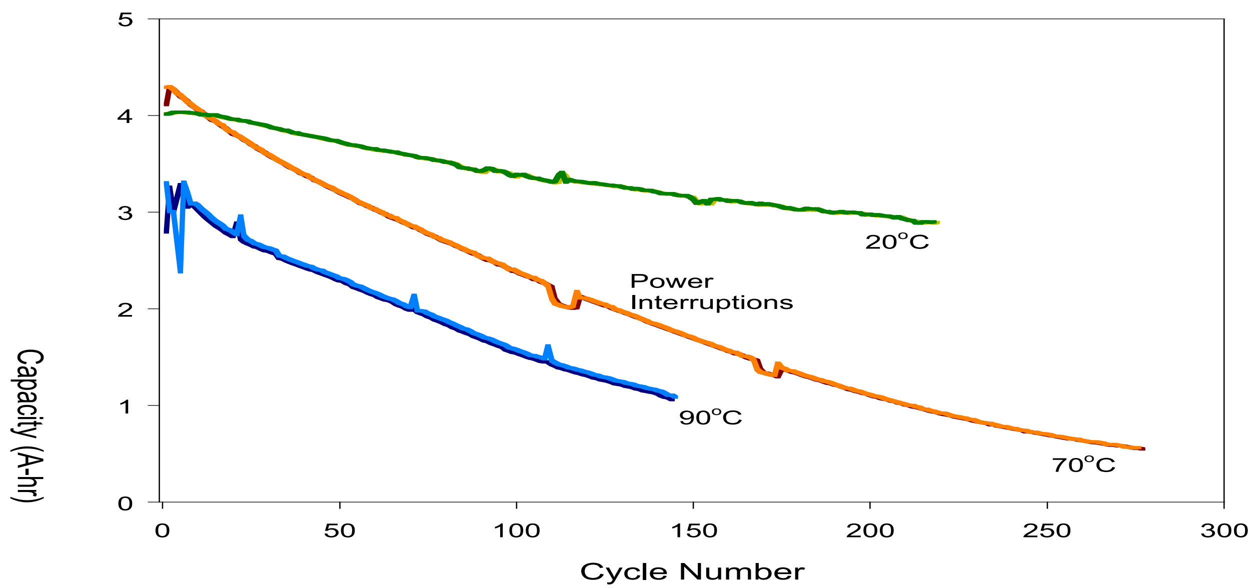
Overcharge Test for Commercial 26650



CECOM Bottom Line: THE SOLDIER

Lithium ion D cell cycling at 20 C, 70 C, and 90 C

Fig 9: 34570 (D) cell #20, #18, and #21 w/1.0M $LiPF_6$ 1EC:1DMC:1EMC
Discharge 2A / Charge 4A
#20 at 70°C, #18 at 20°C, #21 at 90°C
Lifecycle Test



Discharge capacity fade rate:
20°C: 0.147% for 1st 127 cycles; 0.128% for 1st 219 cycles
70°C: 0.416% for 1st 136 cycles; 0.313% for 1st 277 cycles
90°C: 1.547% for 1st 144 cycles

Overcharge Test Lithium ion D Cell with Rupture disk and Electrolyte Started to Leak out

CECOM Bottom Line: THE SOLDIER

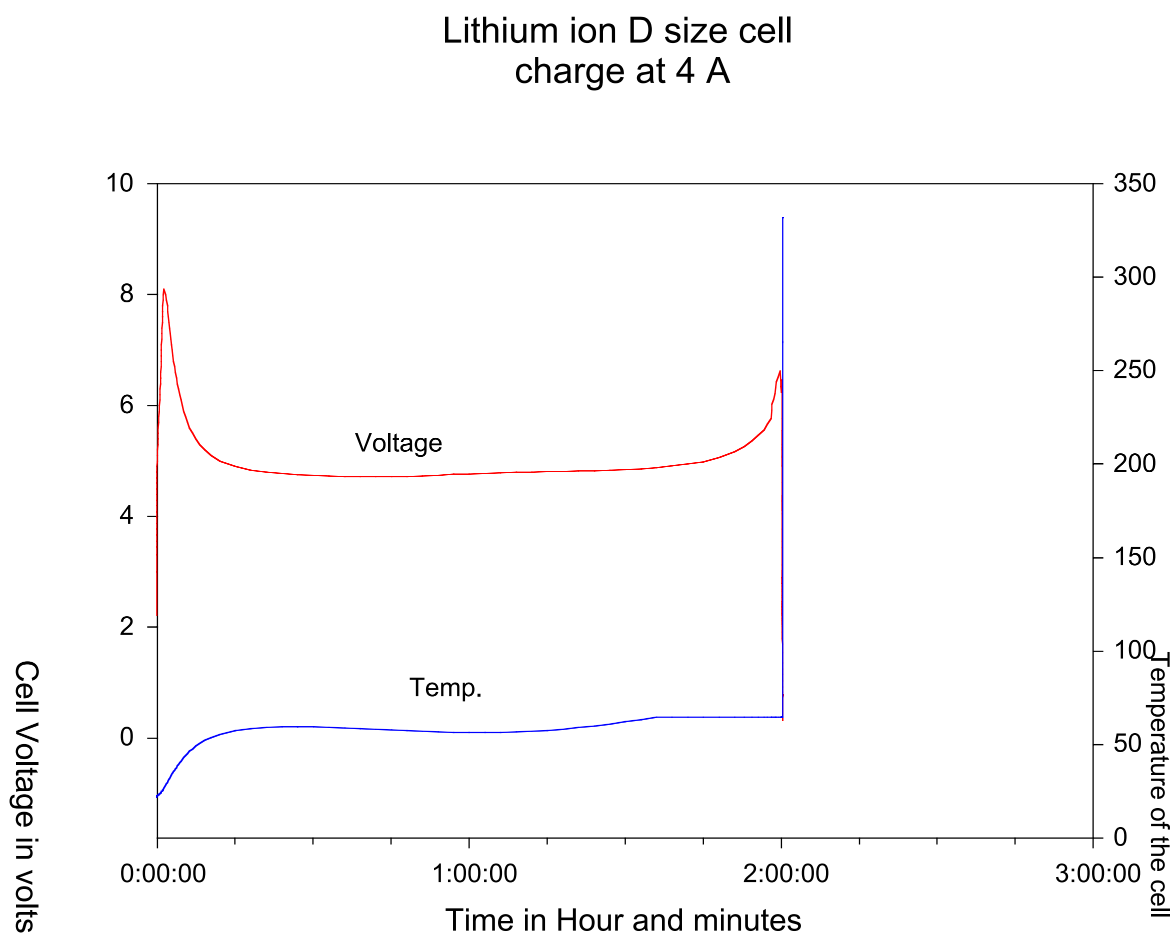
Overcharge Test D cell Spark Come out of Rupture vent

CECOM Bottom Line: THE SOLDIER

Overcharge Test D cell, Voltage went to Zero and Temperature rise to 256 C

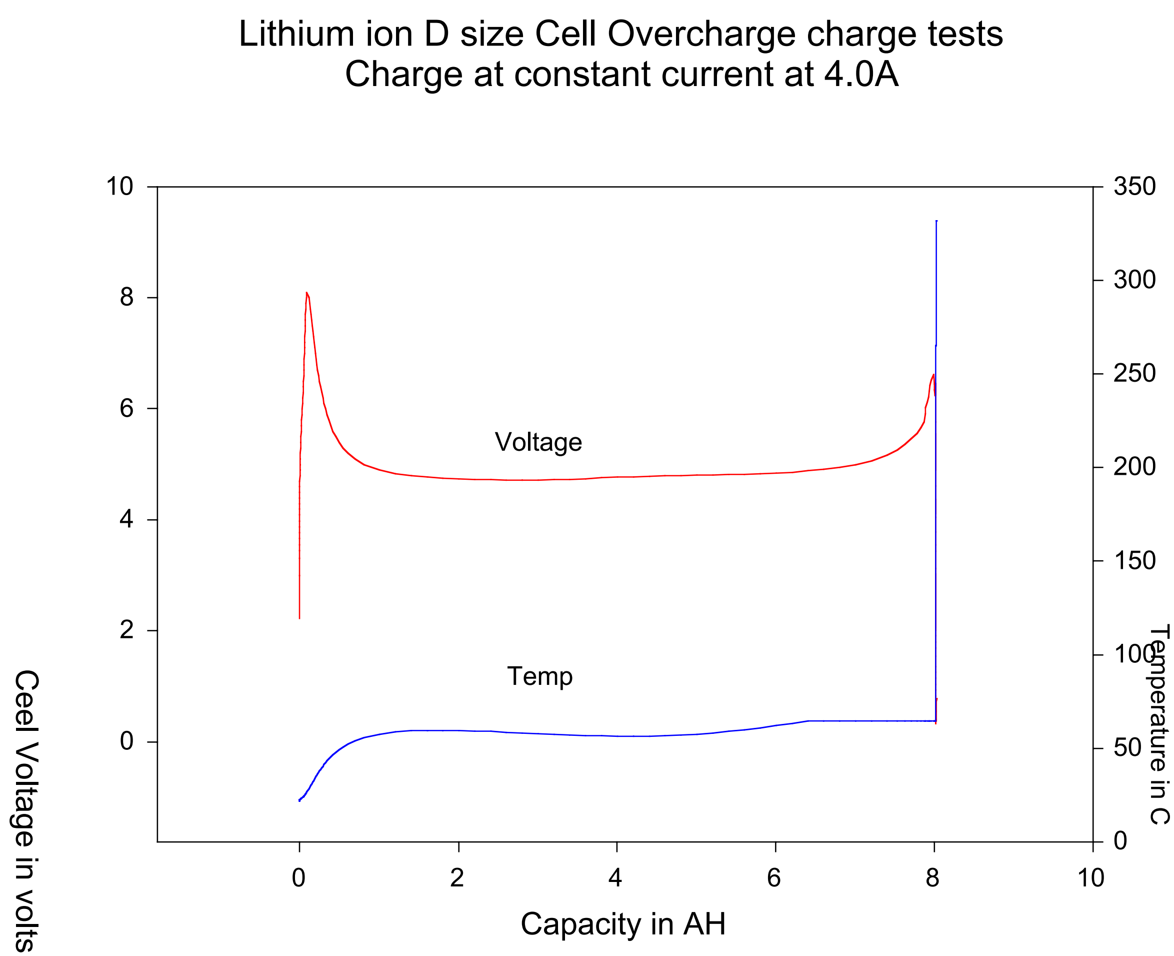
CECOM Bottom Line: THE SOLDIER

Overcharge Test Lithium ion "D" Size



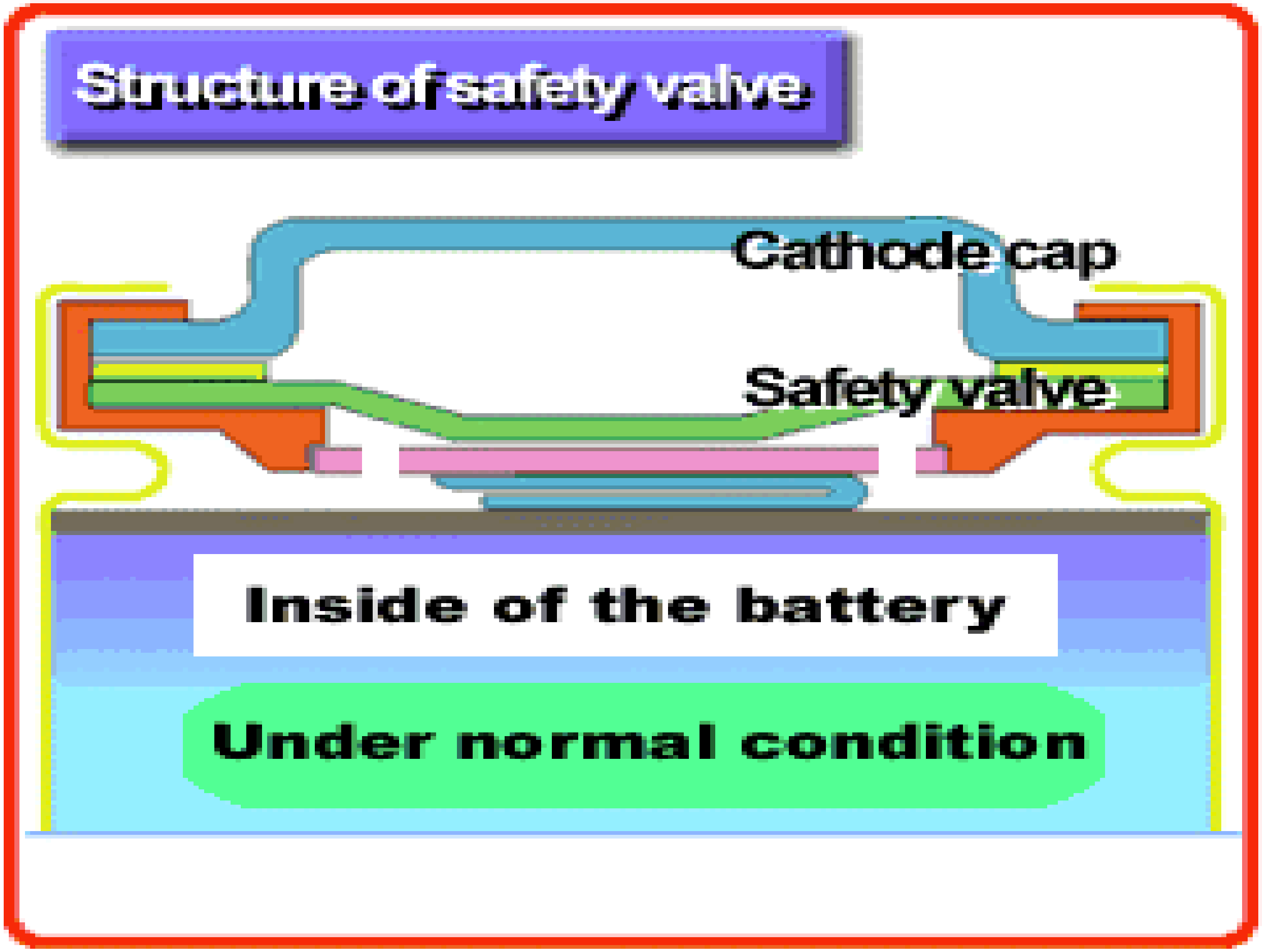
CECOM Bottom Line: THE SOLDIER

Overcharge Test Lithium ion "D" Size



CECOM Bottom Line: THE SOLDIER

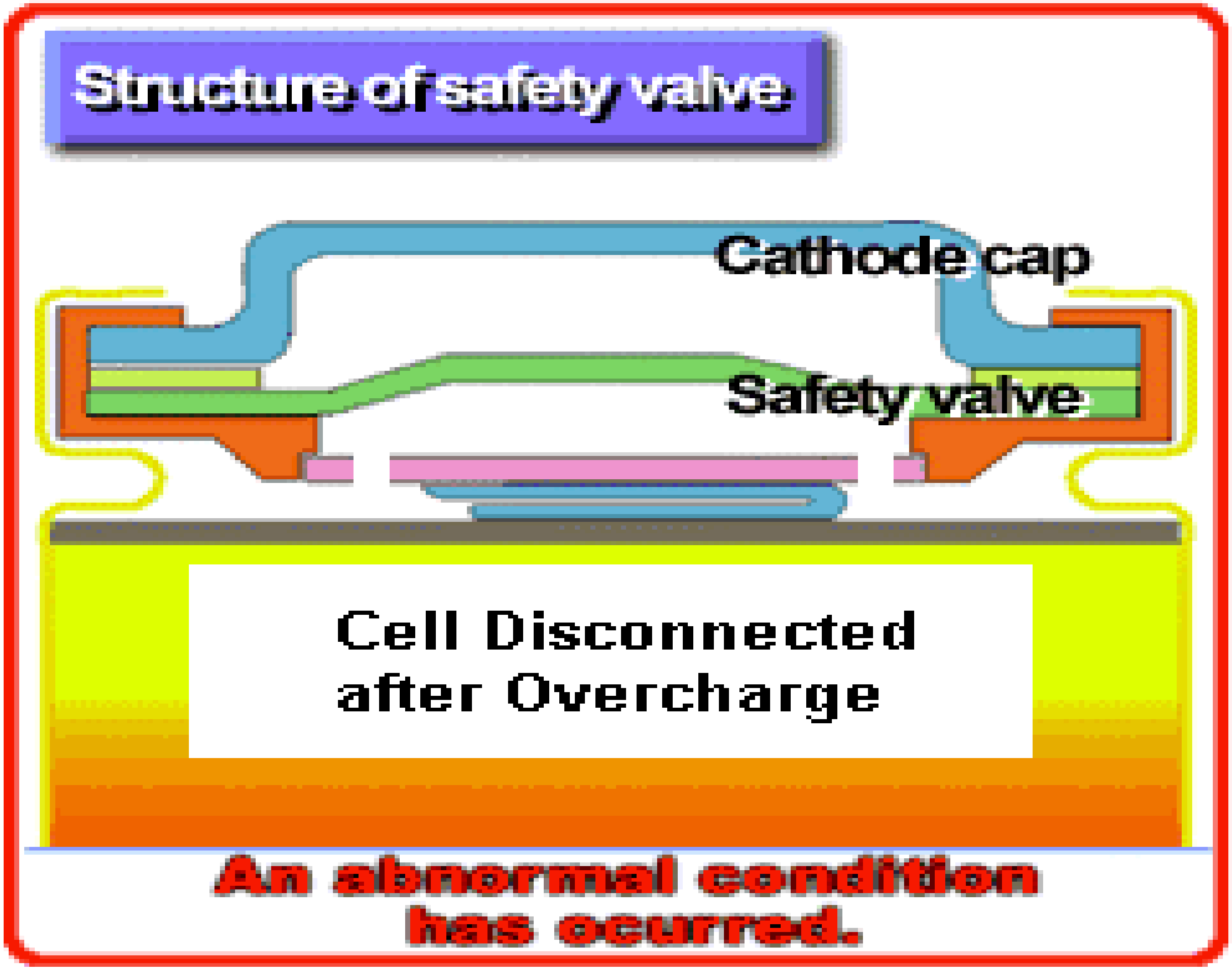
Commercial 18650 Pressure Disconnect Vent



From M.Reid, E-One Moli Energy Limited

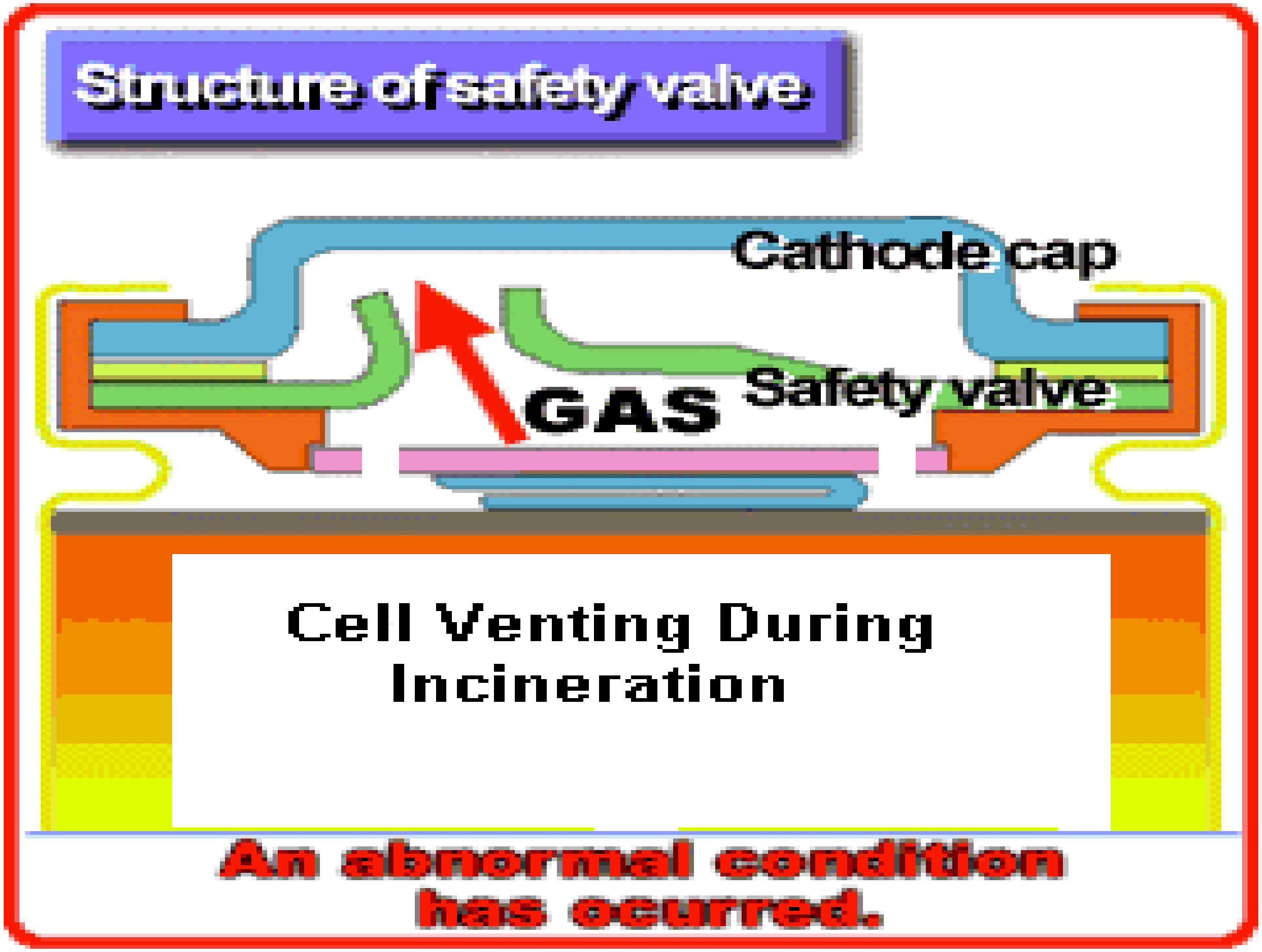
CECOM Bottom Line: THE SOLDIER

Commercial 18650 Pressure Disconnect Vent



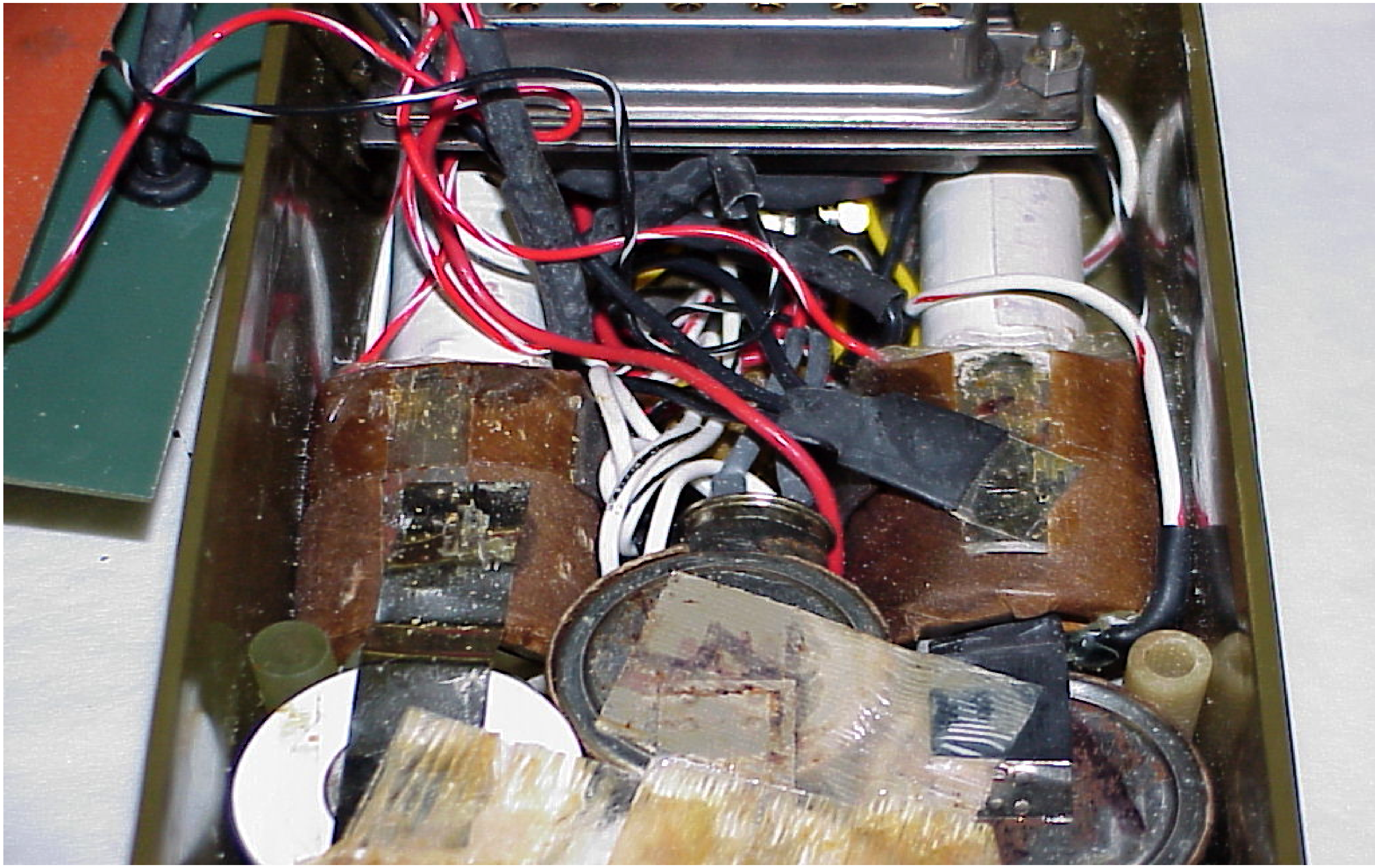
From M.Reid, E-One Moli Energy Limited

Commercial 18650 Pressure Disconnect Vent



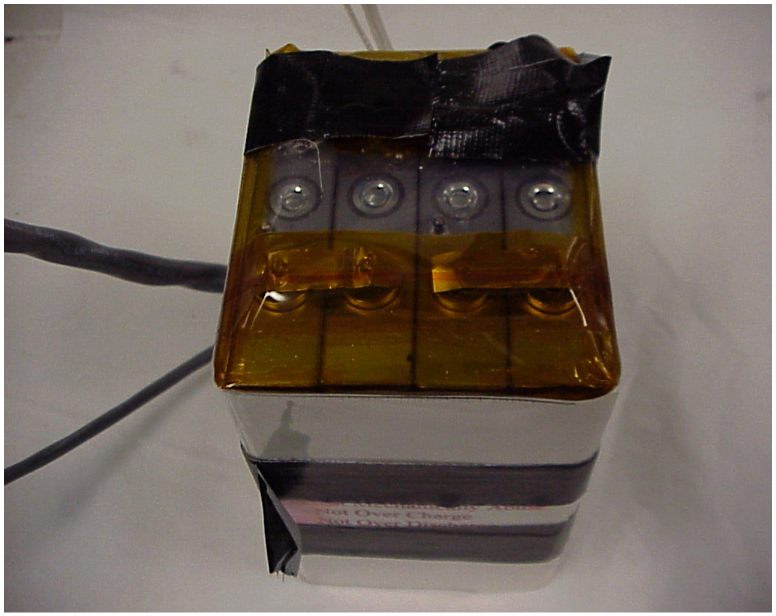
From M.Reid, E-One Moli Energy Limited

Nicad BB-542/U using Pressure Switch for Fast Charge Termination or Cutoff



CECOM Bottom Line: THE SOLDIER

Large Lithium ion Cell and Batteries using the rupture disk



20 AH, 14.4 V Battery

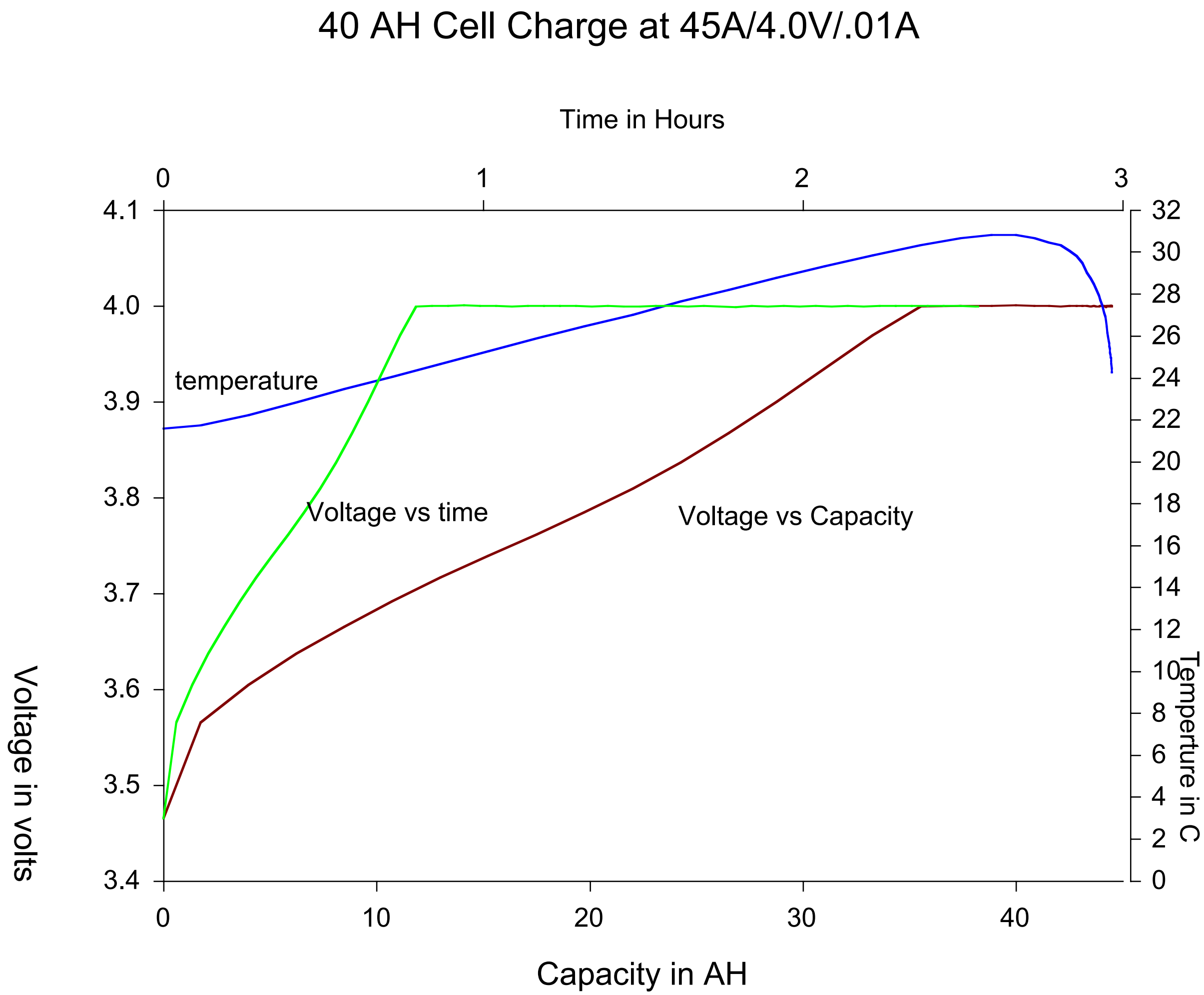
40 AH, Single Cell

CECOM Bottom Line: THE SOLDIER

Propose Mechanical Pressure Switch for a large Lithium ion Cell

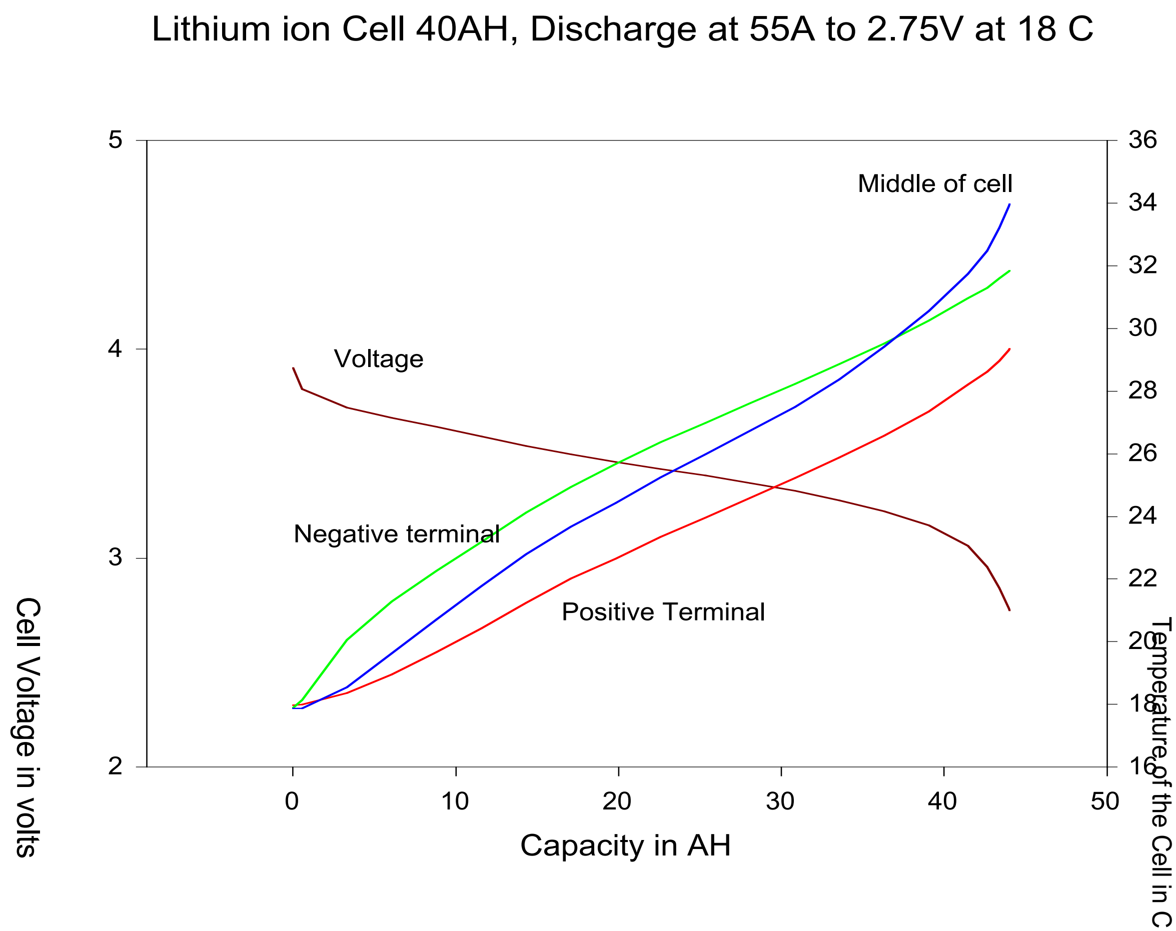
CECOM Bottom Line: THE SOLDIER

40 AH Cell Charge at C rate to 4.0V



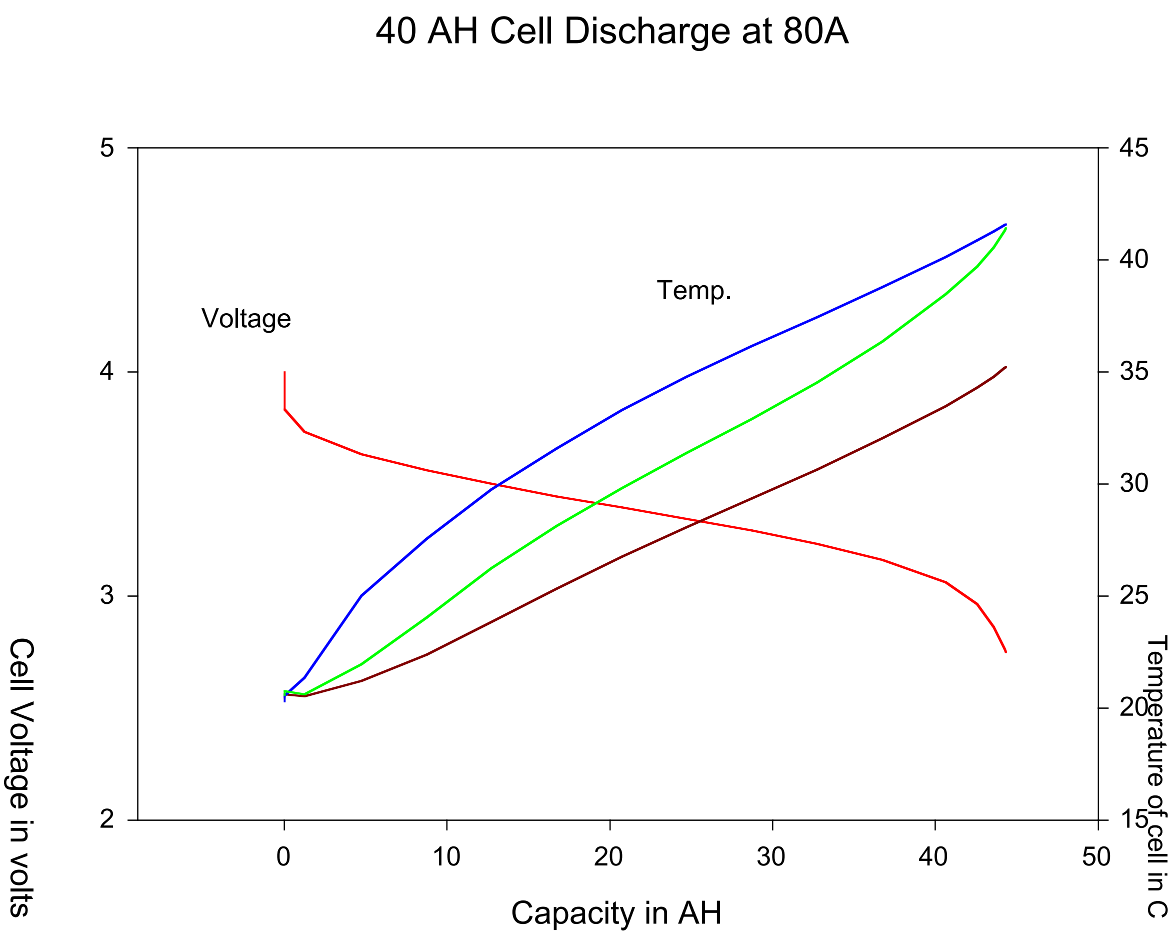
CECOM Bottom Line: THE SOLDIER

40 AH Lithium ion Cylindrical Cell Discharge at 55 Amperes to 2.75V Cutoff



CECOM Bottom Line: THE SOLDIER

40 AH Cell Discharge at 2C



CECOM Bottom Line: THE SOLDIER

Propose Cell Specification For a Large Lithium ion Cell

3.5.3 Cell safety A single cell that does not contain any electronics shall meet all the safety requirement listed below:

3.5.3.1 Cell overcharge . After being subjected to the test as specified in 4.4.2.3.1 the cell shall not explode or catch fire or spark. No electrodes or separator material of the cell shall be outside of the cell case.

3.5.3.2 Cell short circuit. After being subjected to the test as specified in 4.4.2.3.2 the cell shall not explode or catch fire.

3.5.3.3 Cell Forced-Discharge. After a single cell in the string has been subjected to the test as specified in paragraph 4.4.2.3.3 , there shall be no leaking, venting, fire or explosion.

4.4.2.3.1 Cell overcharge. A single cell shall be placed in a temperature chamber set at $25^{o}C$. A thermocouple shall attach to the side of the cell, and current carrying and voltage monitoring leads shall be attached to the terminals. A constant C/2 current charging rate shall be applied for 8 hours continuously. Cell temperature, voltage, and current shall be recorded. A single cell shall meet the requirement for 3.5.3.1.

4.4.2.3.2 Cell short circuit. A single cell shall be shorted by connecting the positive and negative terminals of the cell with a less than 8 inch in length of No. 0 AWG or equivalent copper wire. The cell shall be completely discharged and the battery case temperature has returned to near ambient temperature. The cell shall meet the requirement of 3.5.3.2.

4.4.2.3.3 Cell forced-discharge. A completely discharged single cell (less than 0.2 volts) is to be forced-discharge in accordance with method 2 of the forced-discharge test of UL-1642. One cell for each cell string shall be discharged at the rate specified (see 3.1) to a test end voltage of two-thirds of its open circuit voltage. It shall then be connected in series with the appropriate number of charged cells which shall then be discharged at the rate specified (see 3.1) to a test end voltage of the applicable specification sheet. All cells shall comply with requirements (see 3.5.3.3).

CECOM Bottom Line: THE SOLDIER

Conclusion and Recommendation for Lithium ion Cell & Battery Safety Design

Cell Level

• Shall have Pressure Switch for large Lithium ion Cell and Pressure Disconnect and /or PTC device for small lithium ion Cell. These Devices must capable to disrupt of current flow.

Battery Level

• Charge controller – Overvoltage and undervoltage, Temperature devices.

Charger Level

• Overvoltage, Undervoltage, overcharge, temperature termination.

Acknowledgements

DARPA, Technology Reinvestment Program

Saft America, Inc.

Yardney (Lithion) Inc.

E-One Moli Energy Limited

Maxell Inc.

NASA, Mars Exploration Program

JPL, California Institute of Technology

US Army, CECOM, Ft. Monmouth

US Airforce, Wright Paterson AFB

CECOM Bottom Line: THE SOLDIER

EAGLE PICHER
Technologies, LLC

SAFETY & ABUSIVE TESTS on DIFFERENT Li-ION SYSTEMS

JAMES DeGRUSON & CHAD KELLY

16 NOVEMBER 2000

NASA AEROSPACE BATTERY WORKSHOP

EAGLE EP PICHER
Technologies, LLC

SLC-16002 CELL DESCRIPTION

- ~ SIZE: 3 IN. X 7 IN. X 1 IN.
- WEIGHT: 815 GRAMS
- CAPACITY: 35 Ah
- IMPEDANCE: .0014 W
- ENERGY DENSITY: >380 Wh/L
- SPECIFIC ENERGY: >150 Wh/Kg

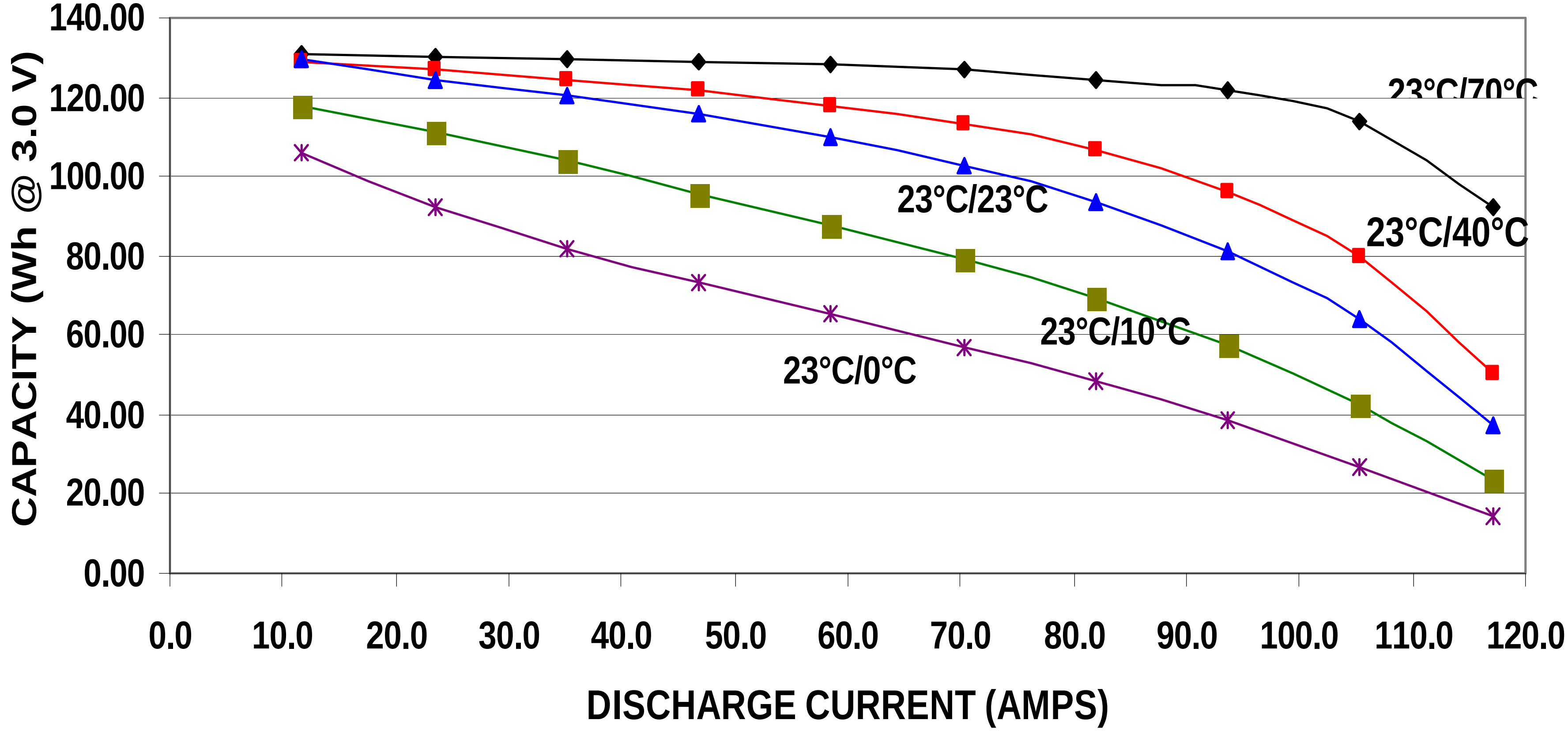
EAGLE PICHER
Technologies, LLC

SLC-16002 CELL DESIGN FEATURES

- ✦ **STAINLESS STEEL CONTAINMENT**
- ✦ **BURST DISC DIAPHRAM**
  - .25 INCH DIAMETER
  - OPENS AT 125 PSI
- ✦ **POLYMERIC TERMINAL SEALS**
- ✦ **ELECTROLYTE: $LiPF_6$ in EC/DEC**
- ✦ **SEPARATOR: CELGARD 2300**
- ✦ **$LiNiCoO_2$ AND $LiCoO_2$**

EAGLE PICHER
Technologies, LLC

SLC-16002 DISCHARGE RATE CHARACTERISTICS



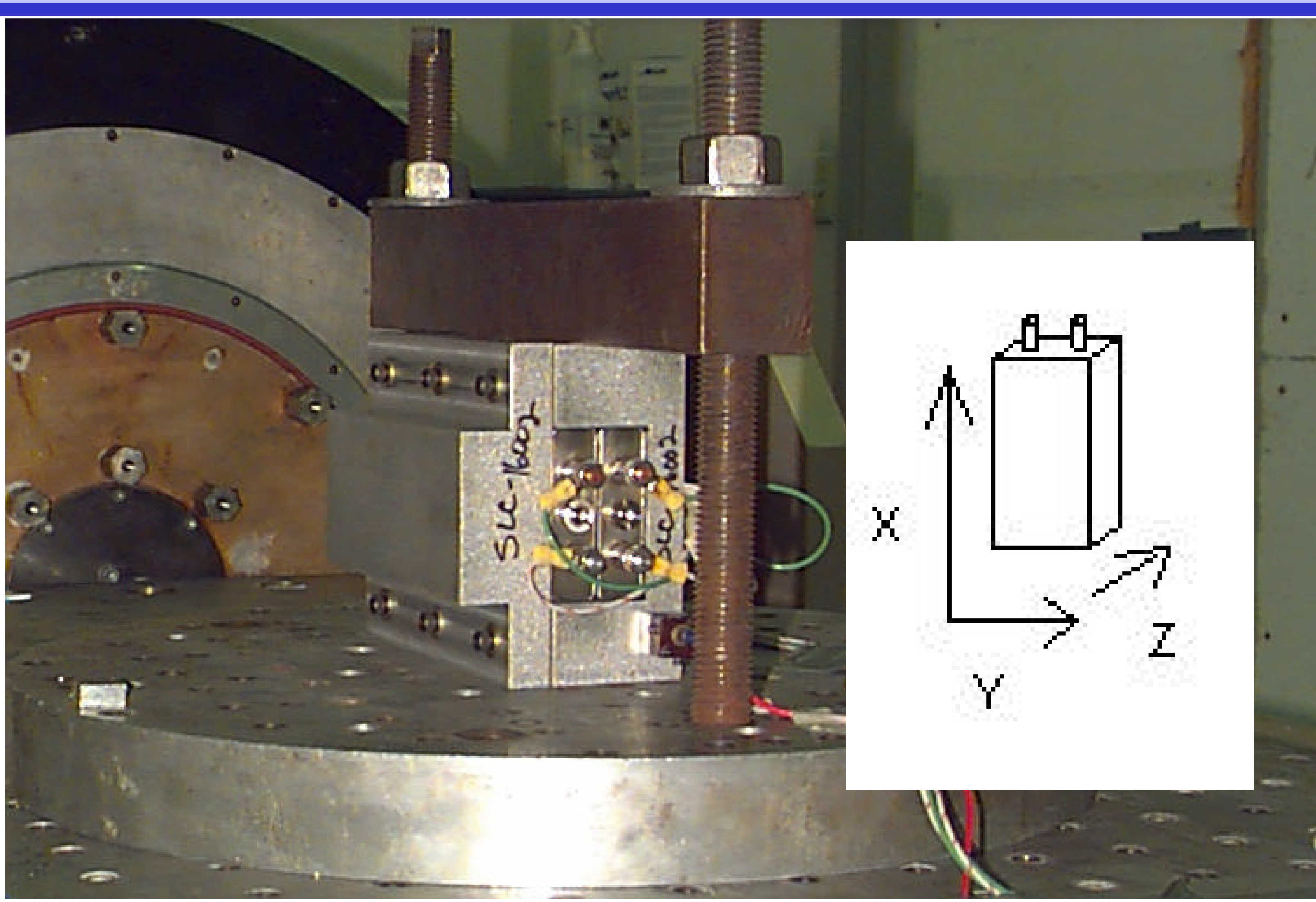
Eagle Picher Technologies, LLC

SAFETY & ABUSE TEST PLAN

- RANDOM VIBRATION
- SHOCK
- TEMPERATURE SHOCK
- HIGH TEMPERATURE EXPOSURE
- ALTITUDE SIMULATION
- EXTERNAL SHORT CIRCUIT
- OVER-DISCHARGE
- OVER-CHARGE
- CRUSH
- PUNCTURE

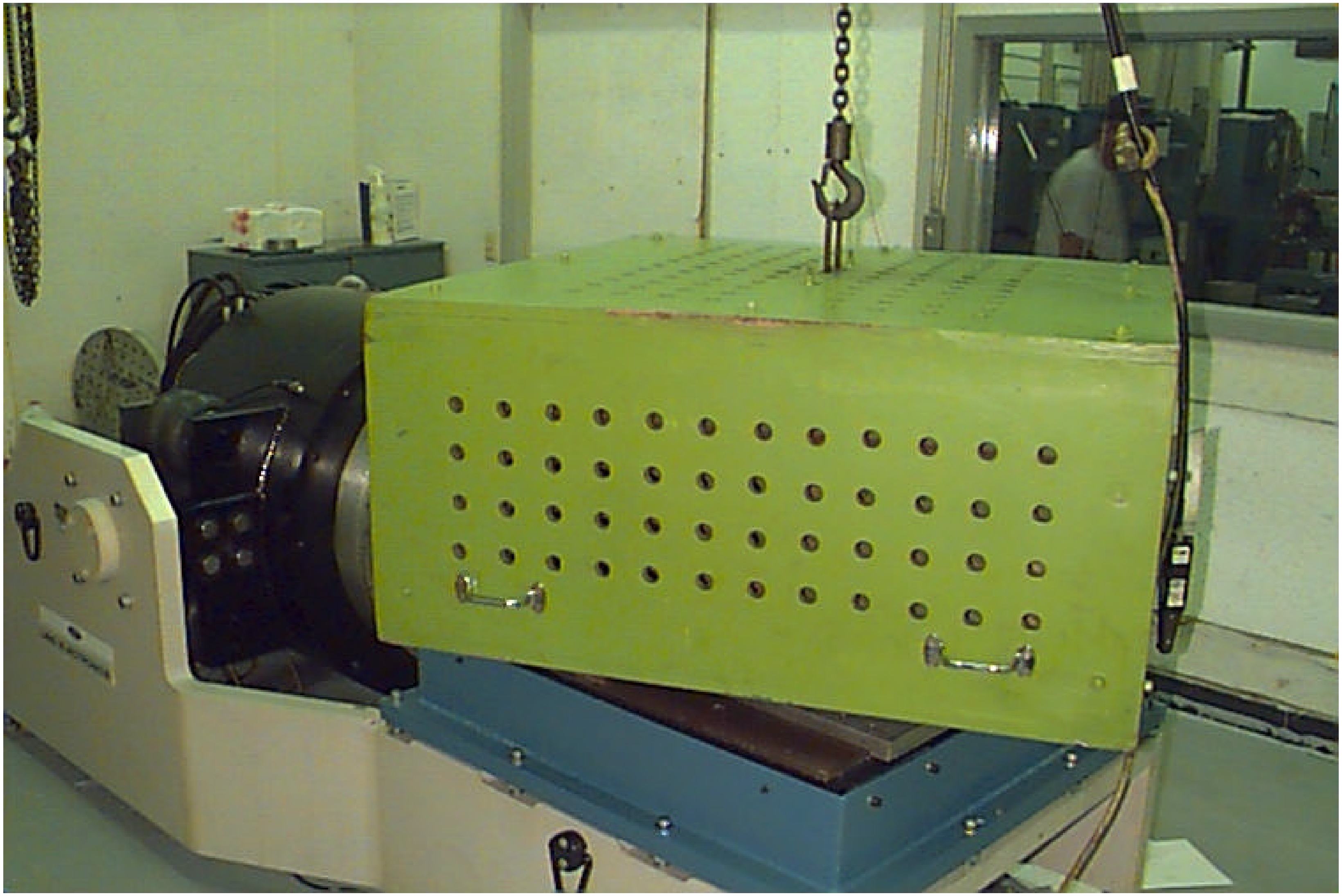
EAGLE PICHER
Technologies, LLC

VIBRATION SET-UP



Eagle Picher Technologies, LLC

VIBRATION SAFETY SHROUD



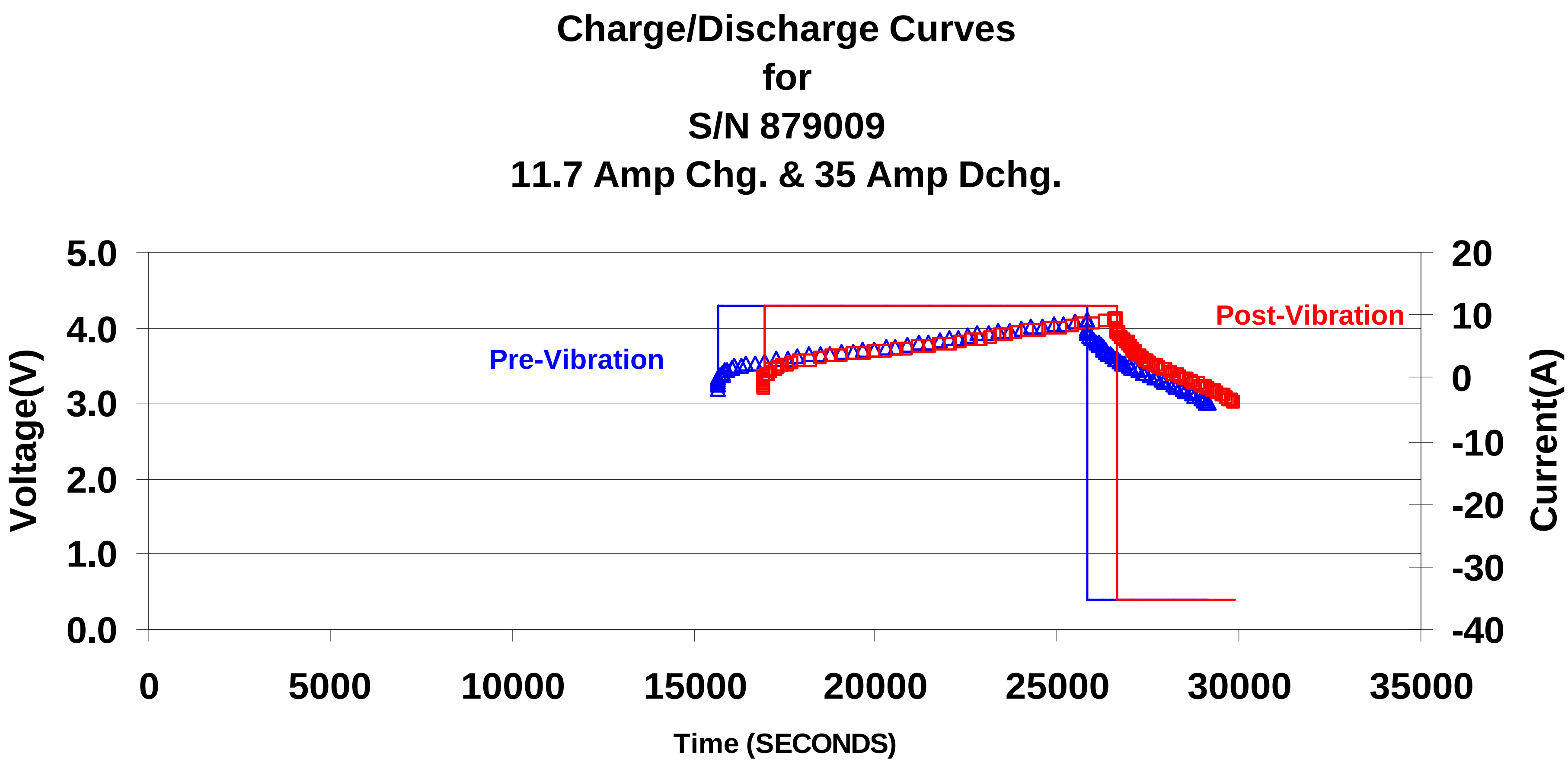
EAGLE PICHER
Technologies, LLC

VIBRATION TEST DESCRIPTION

- **RANDOM VIBRATION**
- **CELLS AT 100% SOC & 50% SOC**
- **OCV MONITORED DURING TEST**
- **DURATION: 4 HRS/AXIS FOR TOTAL OF 12 HOURS**
- **31.4 Grms**
- **FREQUENCY: 60 to 2000 Hz**
- **PSD: .03 to .20 G^2/Hz**

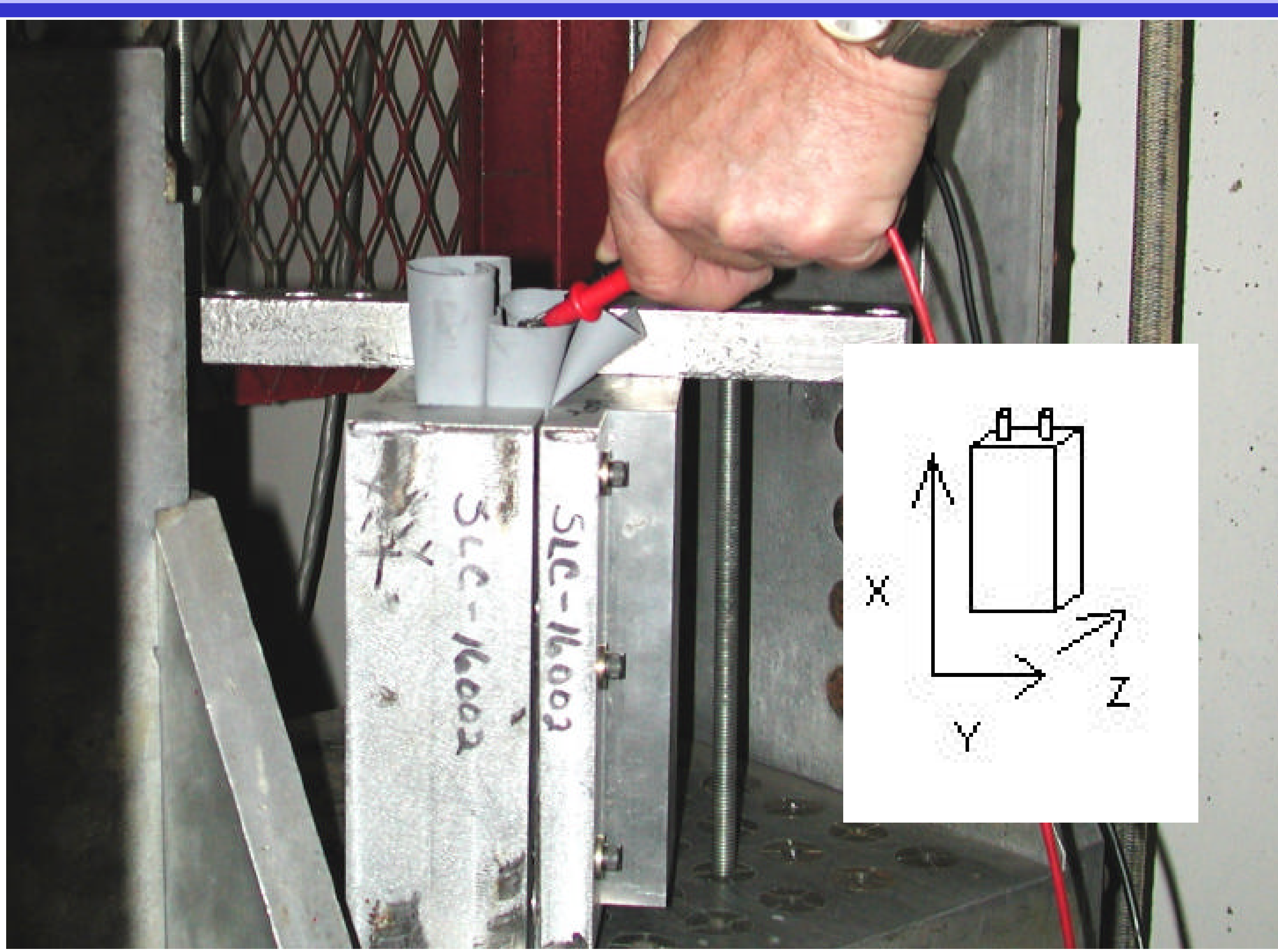
EAGLE PICHER
Technologies, LLC

NO ADVERSE EFFECTS FROM RANDOM VIBRATION



EAGLE PICHER Technologies, LLC

SHOCK TEST SET-UP



EAGLE PICHER Technologies, LLC

SHOCK TEST DESCRIPTION

- AFTER VIBRATION, SAME TWO CELLS WERE SHOCK TESTED
- CELLS WERE AT 100% SOC & 50% SOC
- ONE SHOCK/AXIS for a TOTAL OF 3 SHOCKS
- MINIMUM ACCELERATION: 75 Gs DURING 1st THREE MS
- PEAK ACCELERATION: 165 Gs
- TEST REFLECTS TRANSPORTATION REQUIREMENTS
- CELLS WERE UNPACKAGED
- AIRCRAFT REQUIREMENTS NOT AS SEVERE

EAGLE PICHER Technologies, LLC

SHOCK TEST RESULTS

- ✦ X-RAY PRIOR & AFTER SHOCK
- ✦ SHOCK HAD NO EFFECT ON CELLS
- ✦ CELL VOLTAGE UNCHANGED
- ✦ ELECTRICAL PERFORMANCE UNCHANGED

EAGLE PICHER Technologies, LLC

HIGH-TEMPERATURE EXPOSURE TEST

✦ TEST DESCRIPTION

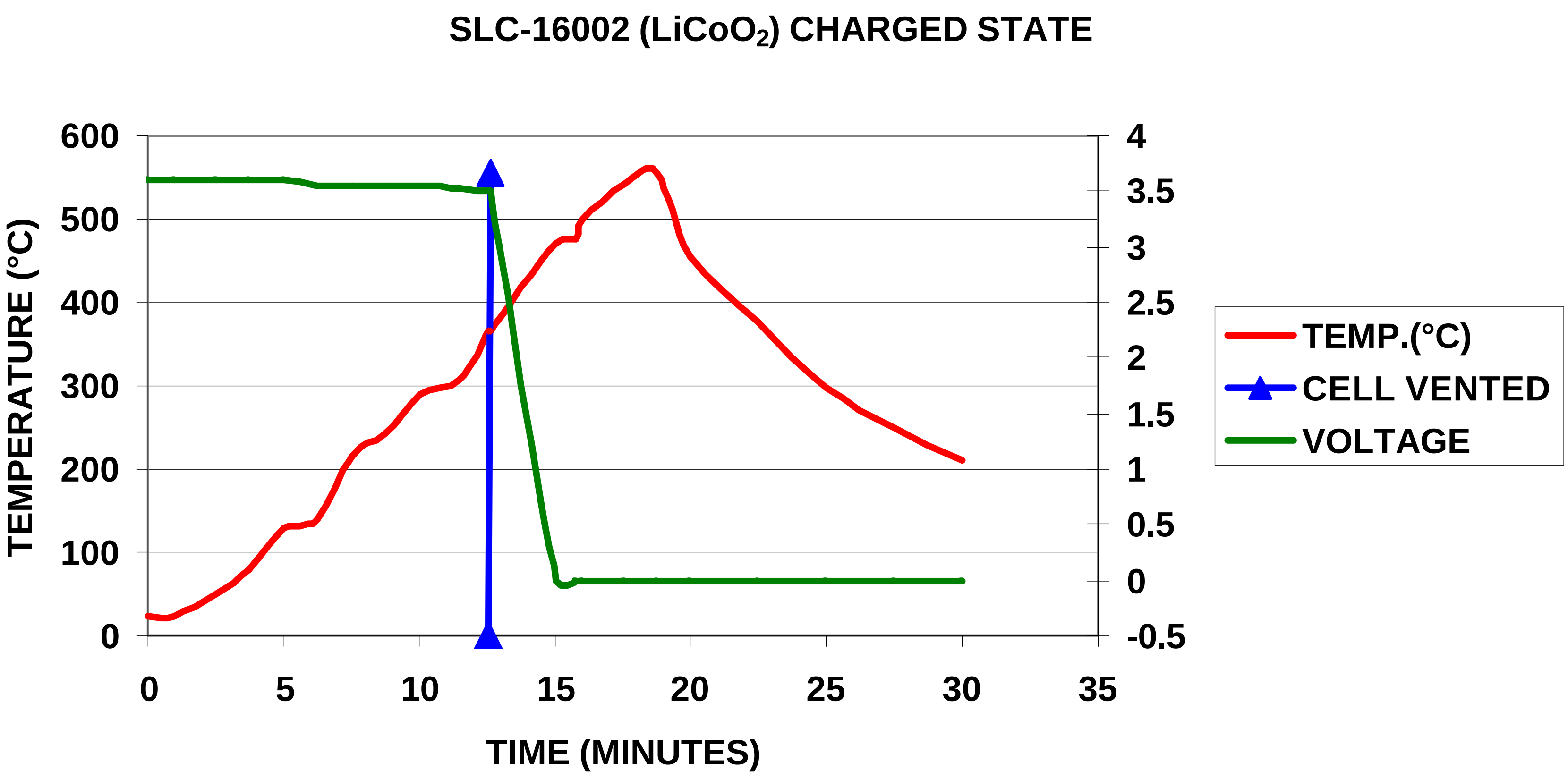
- $LiCoO_2$ CHEMISTRY
- TEST PERFORMED ON CELL IN 100% SOC
- HEAT BLANKET WRAPPED AROUND CELL
- CELL HEATED TO @550°C

✦ TEST RESULTS

- CELL VENT OPENED AT 360°C
- SMOKE BUT NO FLAME OR FIRE
- NO RUPTURE OF CELL CONTAINER

EAGLE EP PICHER Technologies, LLC

HIGH TEMPERATURE EXPOSURE TEST



EAGLE PICHER
Technologies, LLC

ALTITUDE SIMULATION TESTING

✦ TEST DESCRIPTION

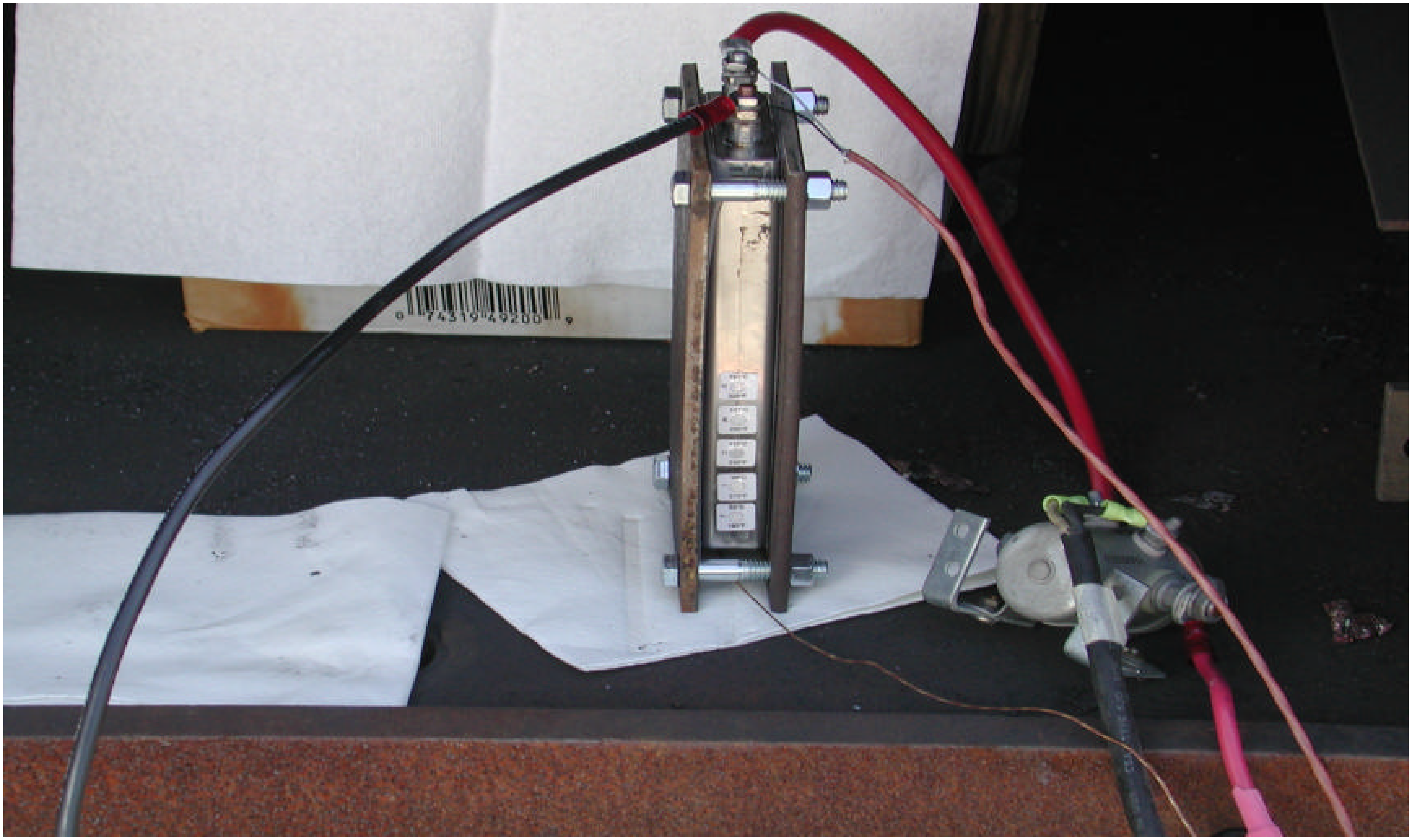
- THREE CELL CONTAINERS COMPLETE WITH VENTS/TERMINALS
- TABLE 1 of MIL-E-5400 for CLASS 2 EQUIPMENT
- SIMULATION OF 70,000 FEET, AMBIENT TEMPERATURE

✦ TEST RESULTS

- NO EFFECT ON CONTAINER OR VENT
- ALL REQUIREMENTS MET

EAGLE PICHER Technologies, LLC

SHORT-CIRCUIT TEST



EAGLE PICHER Technologies, LLC

SHORT-CIRCUIT TEST DESCRIPTION

- ✦ $LiNiCoO_2$ CELL IN 100% SOC
- ✦ .09 OHM RESISTOR APPLIED ACROSS TERMINALS
- ✦ VOLTAGE, CURRENT, TIME & TEMPERATURE MONITORED
- ✦ TEST TIME: APPROXIMATELY 20 HOURS

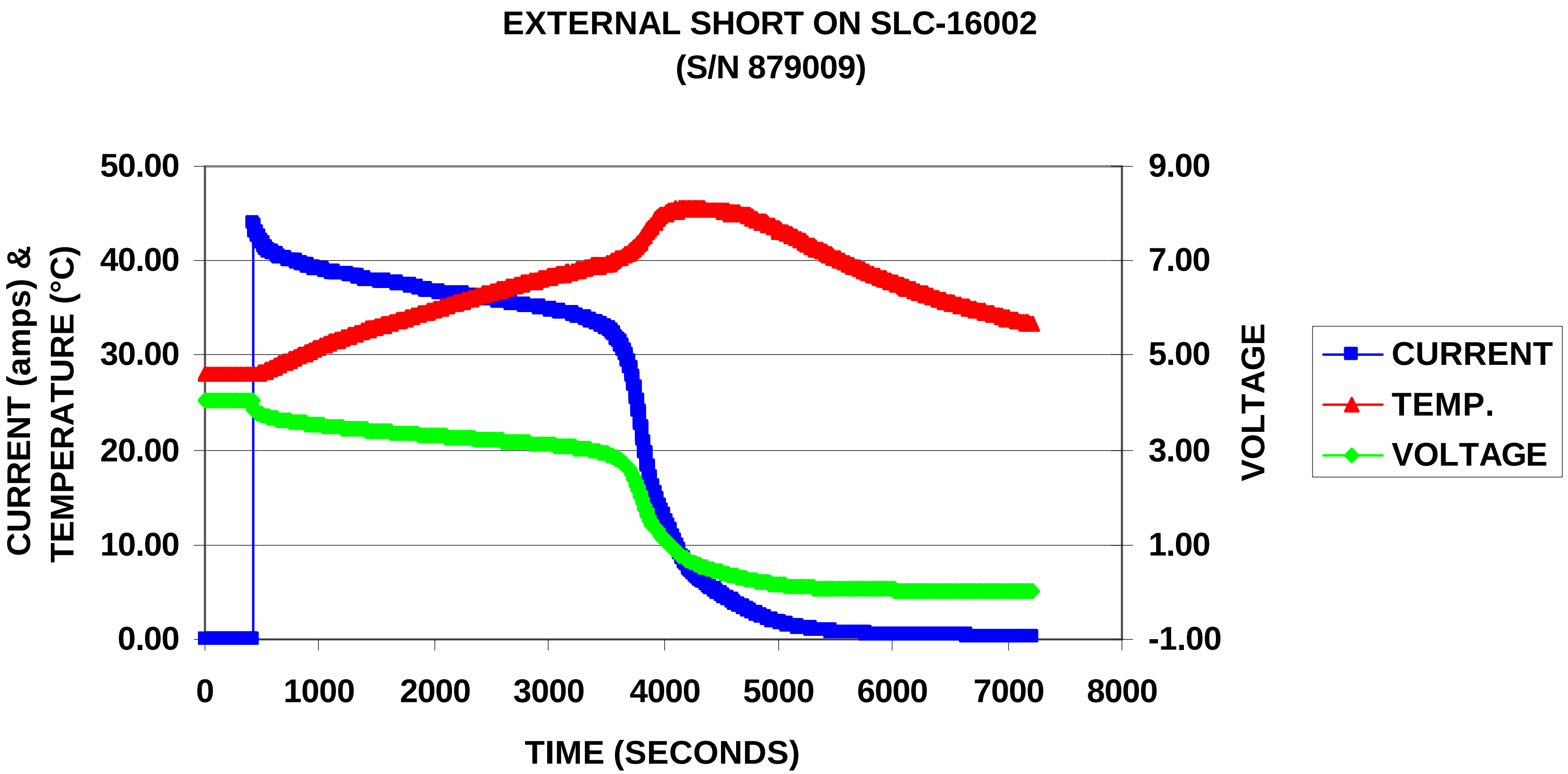
EAGLE PICHER Technologies, LLC

SHORT-CIRCUIT TEST RESULTS

- ✦ INITIALLY CELL PEAKED AT 3.87 VOLTS @ 44.1 AMPS
- ✦ INITIAL TEMPERATURE 26°C
- ✦ PEAK TEMPERATURE: 45°C AT 1 Hr & 3 MINUTES
- ✦ AFTER 2 HOURS: VOLTAGE <.02 VOLTS & TEMP. 33°C
- ✦ NO VENTING OR RUPTURE

EAGLE PICHER Technologies, LLC

SHORT-CIRCUIT TEST



EAGLE PICHER Technologies, LLC

OVER-DISCHARGE TEST

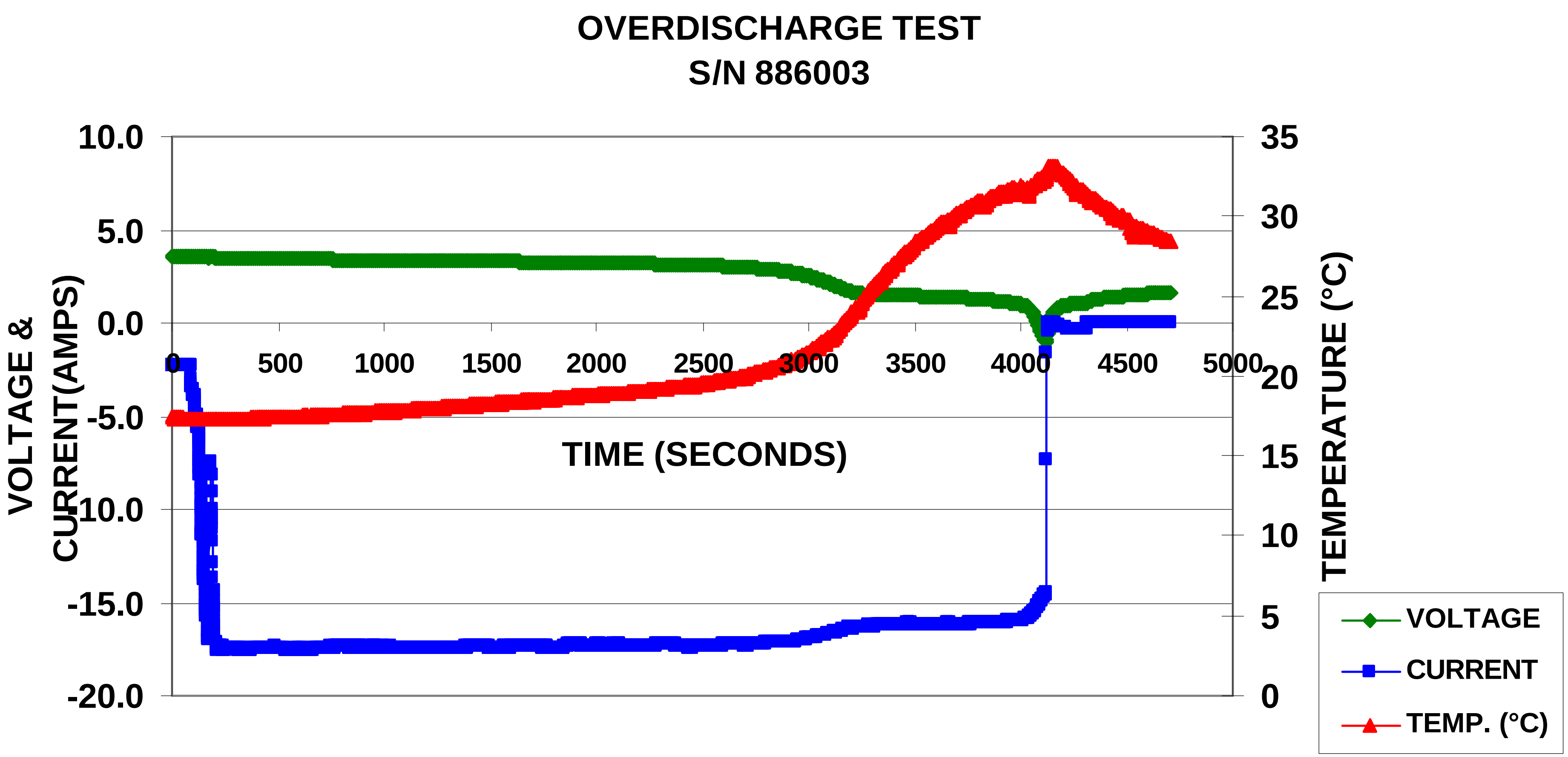
✦ TEST DESCRIPTION:

- SLC-16002 CELL – $LiNiCoO_2$ CHEMISTRY
- CELL IN 50% SOC
- DISCHARGE CELL AT "C/2" RATE TO NEGATIVE ONE VOLT
- MONITOR VOLTAGE, CURRENT, TIME, & TEMPERATURE

✦ TEST RESULTS:

- NO VENT
- ALL REQUIREMENTS MET

OVER-DISCHARGE TEST



EAGLE PICHER
Technologies, LLC

POST-TEST OVER-DISCHARGE RESULTS

- VENT DIAPHRAGM INTACT
- NO COLOR CHANGE IN THERMAL SENSITIVE DOTS
- NO PHYSICAL CHANGE IN CELL

EAGLE PICHER Technologies, LLC

OVER-CHARGE TEST

✦ TEST DESCRIPTION

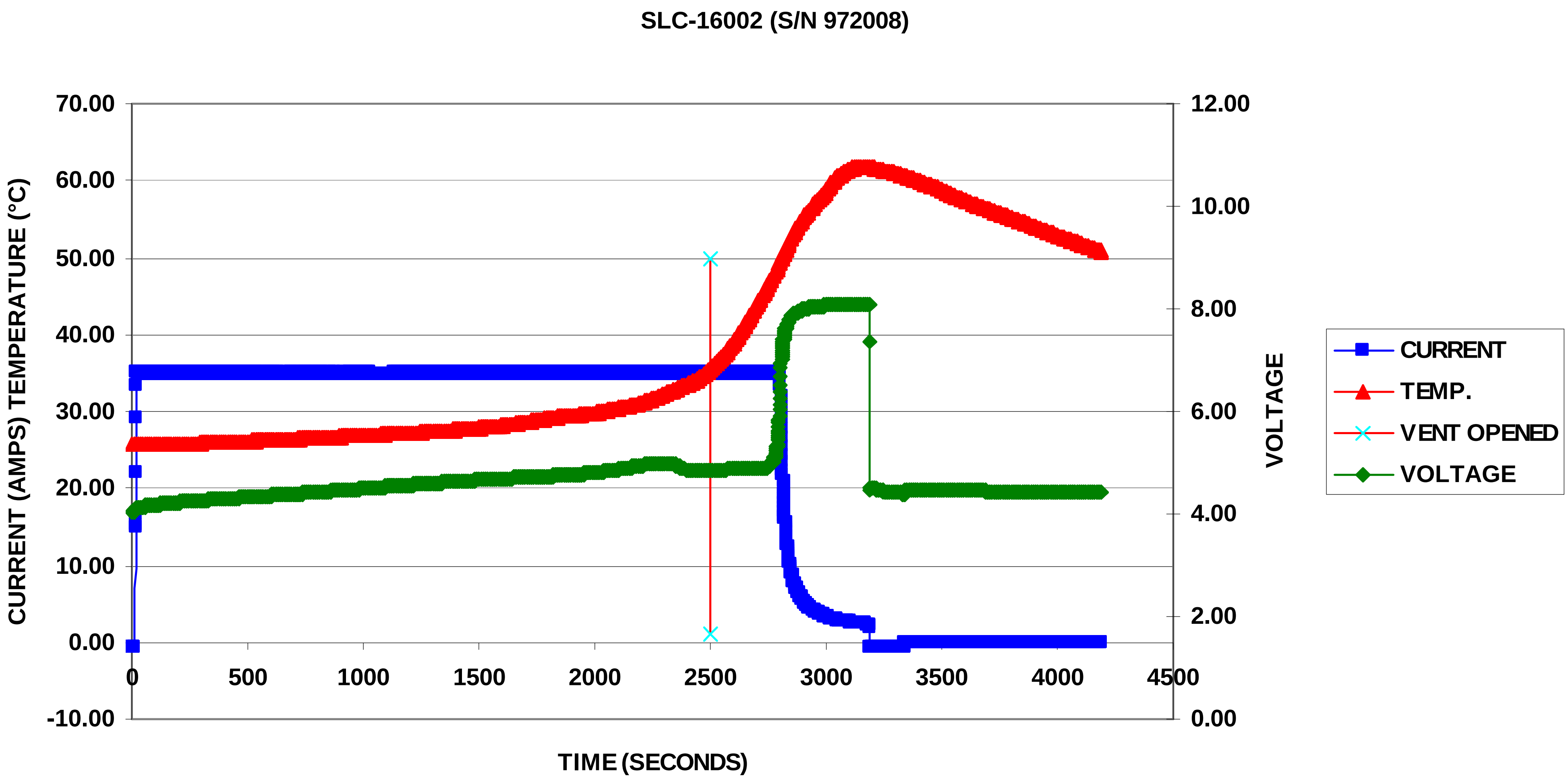
- SLC-16002 ($LiNiCoO_2$)
- CELL IN 100% SOC
- AMBIENT TEMPERATURE
- CHARGE RATE: "C" RATE to 200% of RATED CAPACITY (70 Ah)

✦ TEST RESULTS

- CELL DID VENT AT VENT DIAPHRAGM
- NO FLAME OR RUPTURE
- ALL REQUIREMENTS MET

OVER-CHARGE TEST

EAGLE PICHER Technologies, LLC



Eagle Picher Technologies, LLC

POST-TEST OVER-CHARGE RESULTS

- VENT DIAPHRAGM OPEN
- TERMINAL SEALS UNAFFECTED
- NO DISTORTION OF CELL

EAGLE PICHER Technologies, LLC

CONCLUSIONS

- ✦ NO EXPLOSIONS OR CELL CASE RUPTURES
- ✦ PRESSURE VENT WORKS AS INTENDED
  - SHORT CIRCUIT & OVER-DISCHARGE DID NOT VENT
- ✦ POLYMERIC TERMINAL SEALS PRESENT NO PROBLEMS
- ✦ PRISMATIC CELL DESIGN RESULTS IN RUGGED CONSTRUCTION WHICH WITHSTANDS EXTREME ENVIRONMENTS

FUTURE SAFETY WORK

- ADDITIONAL TESTING BEING CONDUCTED ON $LiNiCoO_2$
- LARGE QUANTITY OF CELLS FOR EACH TEST
- DOT TESTING BEING ADDRESSED
- CRUSH, PUNCTURE, & TEMP. SHOCK BEING CONDUCTED

LiTech LLC

Lithium-ion Battery Technology Configured to Tolerate Overcharge and Overdischarge

S. Hossain, Y. Saleh, R. Loutfy
LiTech, LLC
7960 S. Kolb Road
Tucson, AZ 85706

NASA Aerospace Battery Workshop
Holiday Inn-Research Park
Huntsville, Alabama
November 13-16, 2000

LiTech LLC

Limitations of Present Lithium-ion Battery Technology

$$LiMO_2 + C \rightleftharpoons Li_{0.5}MO_2 + Li_{0.5}C$$

Overdischarge

↓

Copper Dissolution

↓

Cell Fails

Overcharge

↓

Lithium Deposition

+

Solvent Decomposition

↓

Explosion/Fire

LiTech LLC

There are Shortfalls of Present Lithium-ion Battery Technology for the Production of High Capacity, High Voltage Batteries

- Almost Zero Tolerance
- Huge Capital Investment
- Complicated Electronic Circuits
- High Cost
- Safety Concerns

LiTech LLC

LiTech Lithium-ion Cell Components

Cathode or Positive Electrode	**: $LiCoO_2$, $LiNiCoO_2$, $LiMn_2O_4$**
Anode or Negative Electrode	**: C-C Composite**
Electrolyte	**: $LiPF_6$ in Carbonate-based Organic Solvent**
Separator	**: Poly-olefin**
Cell Design	**: Prismatic, Cylindrical**

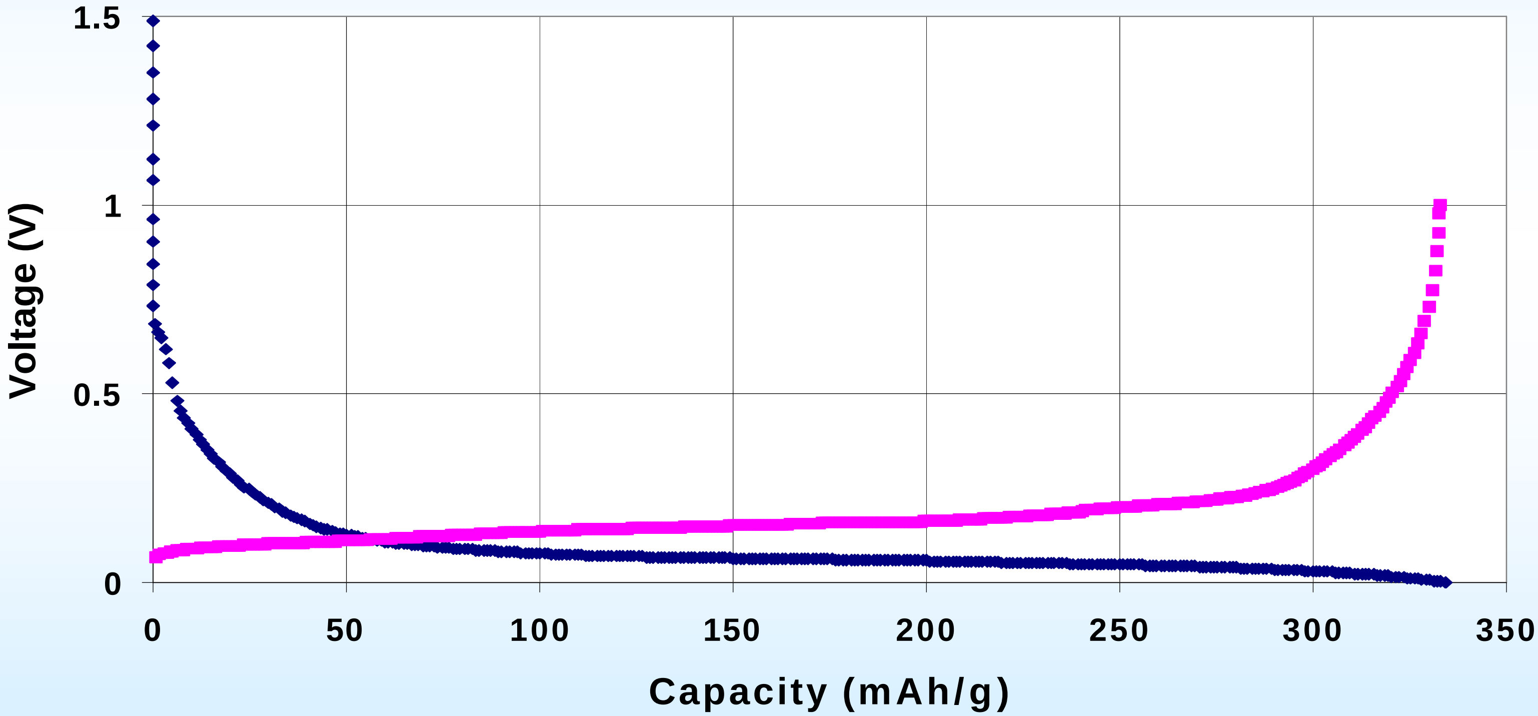
LiTech LLC

Why C-C Composite as Anode for Lithium-ion Batteries?

- Substrate is Carbon - no Dissolution of Substrate during Overdischarge
- Substrate can act as Li^+ Sink - can accept lithium ion during Overcharge
- Strong Mechanical Integrity - High Cycle Life
- No Binder, no Carbon Black, high Compression - High Thermal Conductivity, Flame Retardant and Low Self Discharge
- C-C Composite Anodes are Reusable

LiTech LLC

C-C Composite Exhibits High Reversible Capacity and almost Zero Irreversible capacity Loss



First Discharge-Charge Behavior of C-C Composite at 0.5 mA/cm2 in 1M LiPF6 Electrolyte (EC:DMC 1:1 v/v). Counter Electrode: Li.

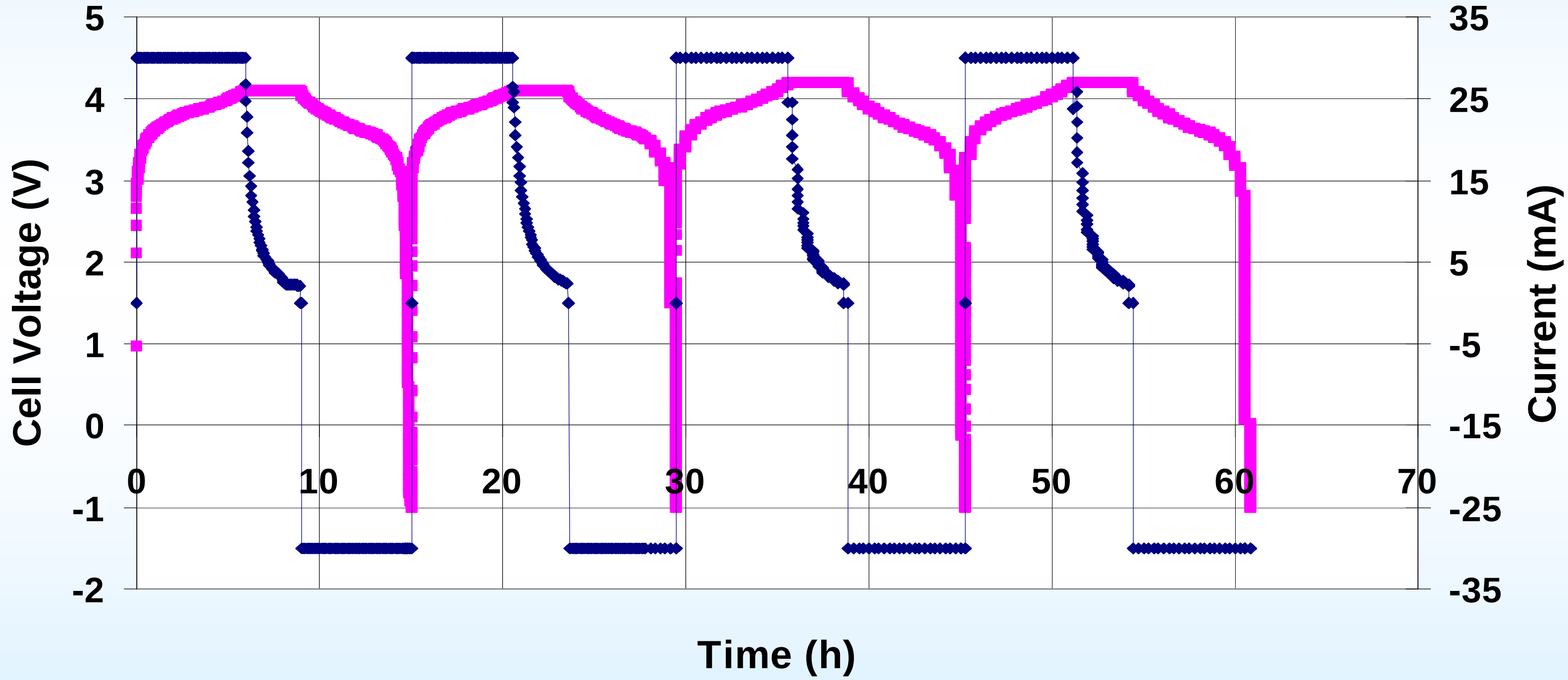
LiTech LLC

Specifications and Characteristics of LiTech's Lithium-ion Cells

Cell Type	T (mm)	W (mm)	L (mm)	Nominal Capacity (mAh)	Cell Weight (g)	Energy Density (Wh/l)	Specific Energy (Wh/kg)
ICP-015674	0.7	56	74	215	6.8	274	117
ICP-033555	2.3	35	55	350	10.0	292	130
ICP-025674	1.9	56	74	650	16.5	305	145
ICP-035674	2.6	56	74	1,000	23.0	343	160

LiTech LLC

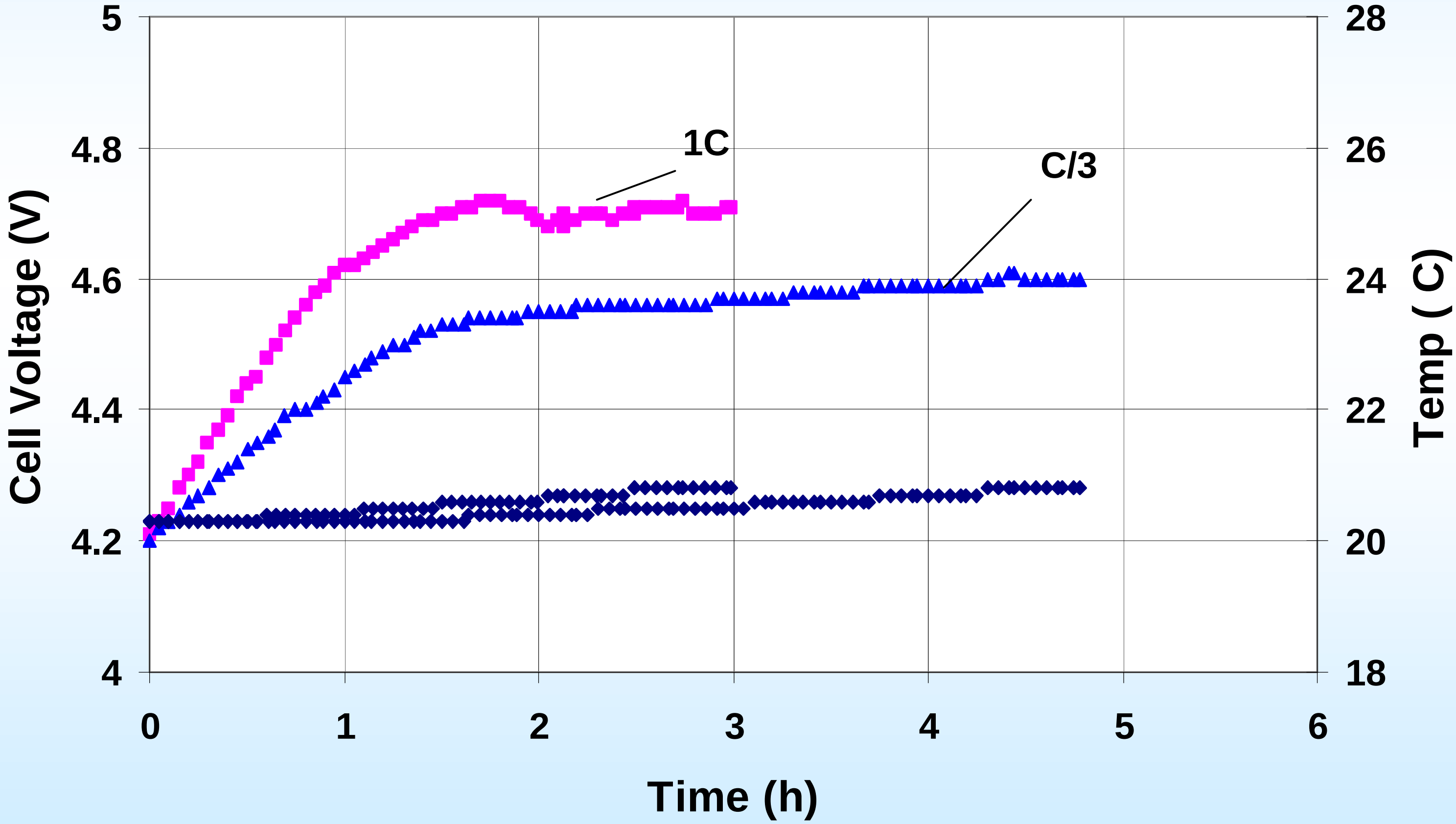
LiTech's Lithium-ion Cell can Accept Repeated Overdischarge



Charge-Overdischarge Behavior of a LiTech Lithium-ion Cell. Cathode: LiCoO2. Electrolyte: 1M LiPF6 in EC/DMC (1:1 v/v).

LiTech LLC

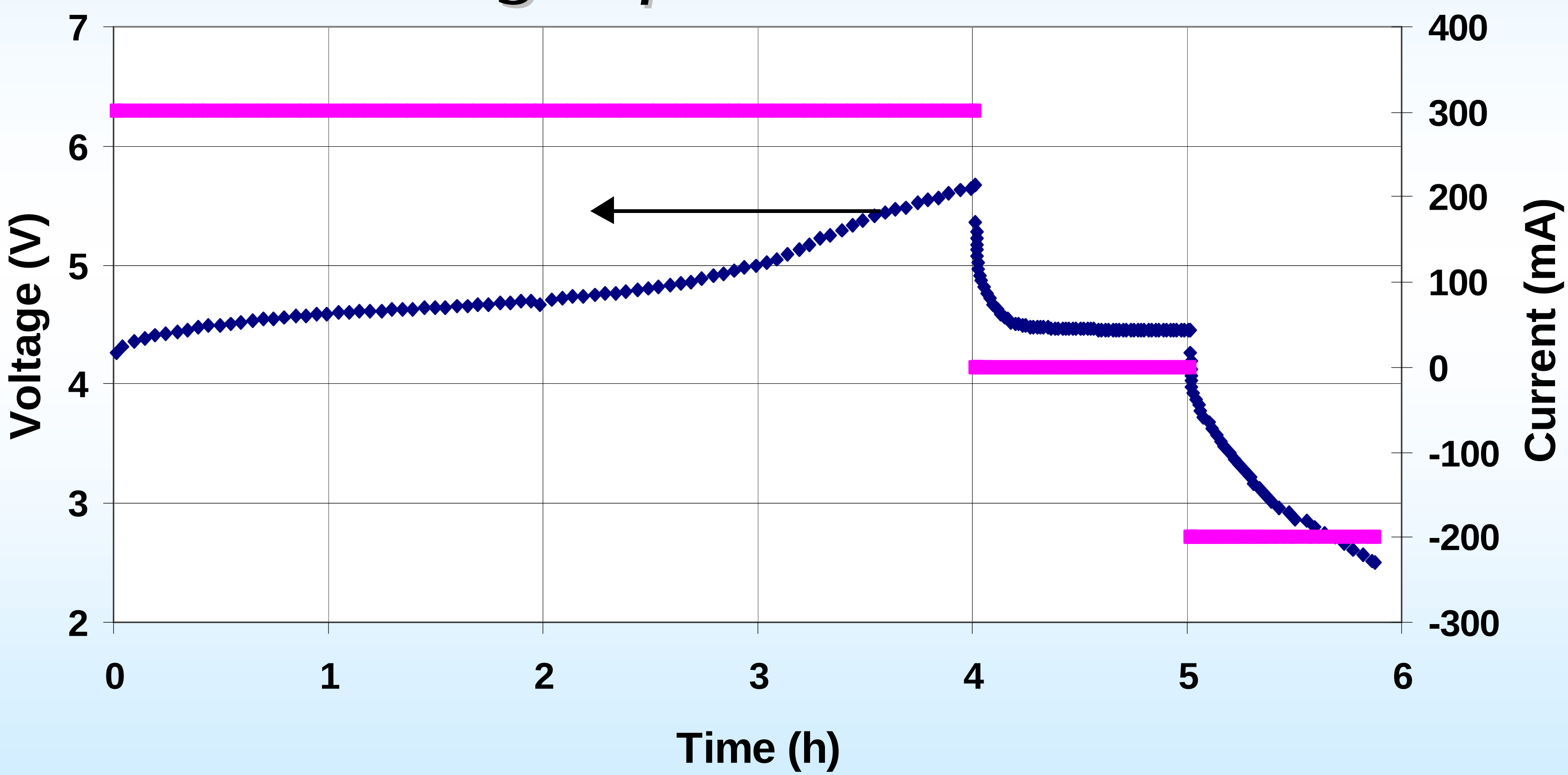
No Significant increase in Cell Temperature on Overcharge



Voltage-Temperature Response of LiTech's Lithium-ion Cell during Overcharge at two Different Rates.

LiTech LLC

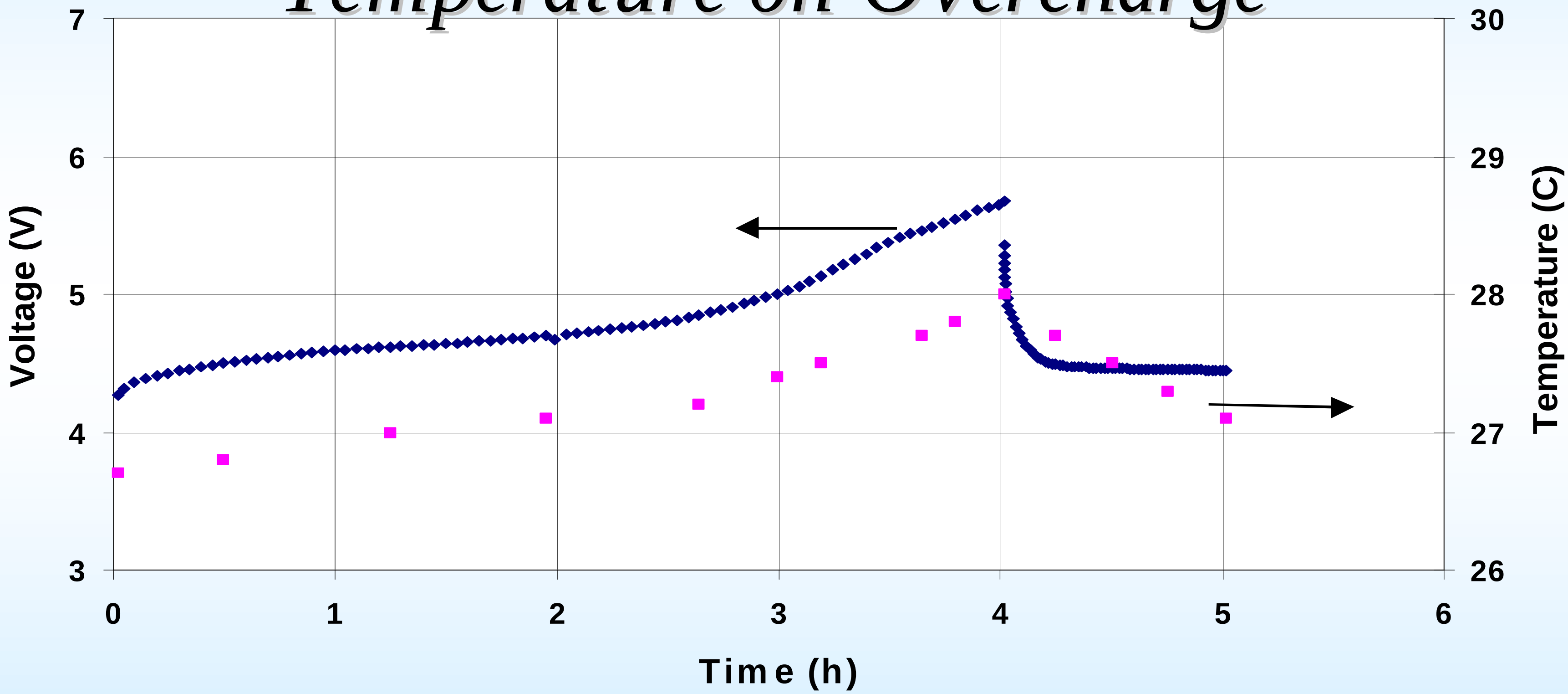
No Smoke, Fire, or Explosion during Overcharge of a 1Ah Cell



Voltage Response during Overcharge followed by Rest and Discharge of a 1Ah Lithium-ion Cell.

LiTech LLC

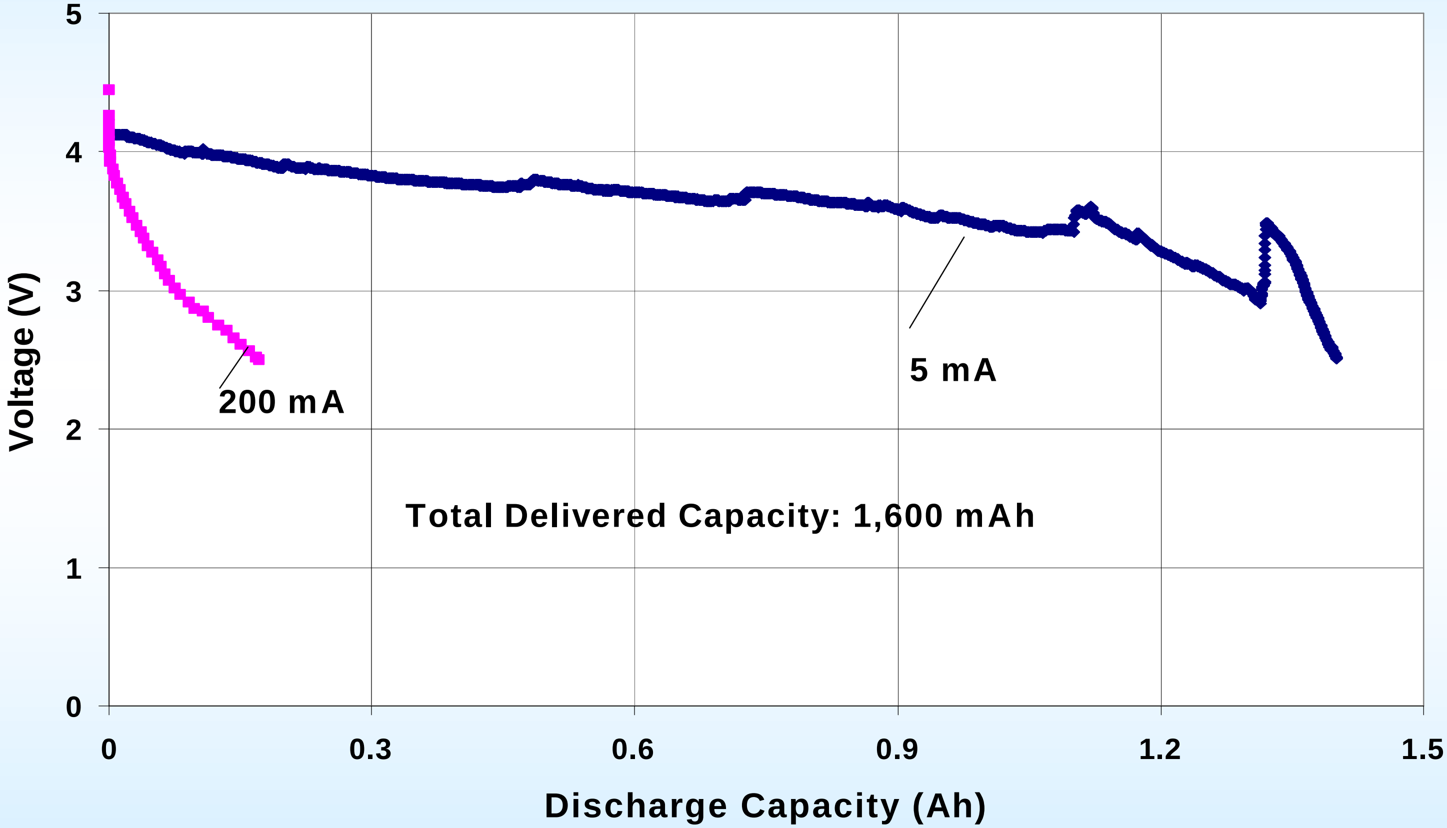
No Significant increase in Cell Temperature on Overcharge



Voltage-Temperature Responses during Overcharge followed by Rest of a 1Ah Lithium-ion Cell.

LiTech LLC

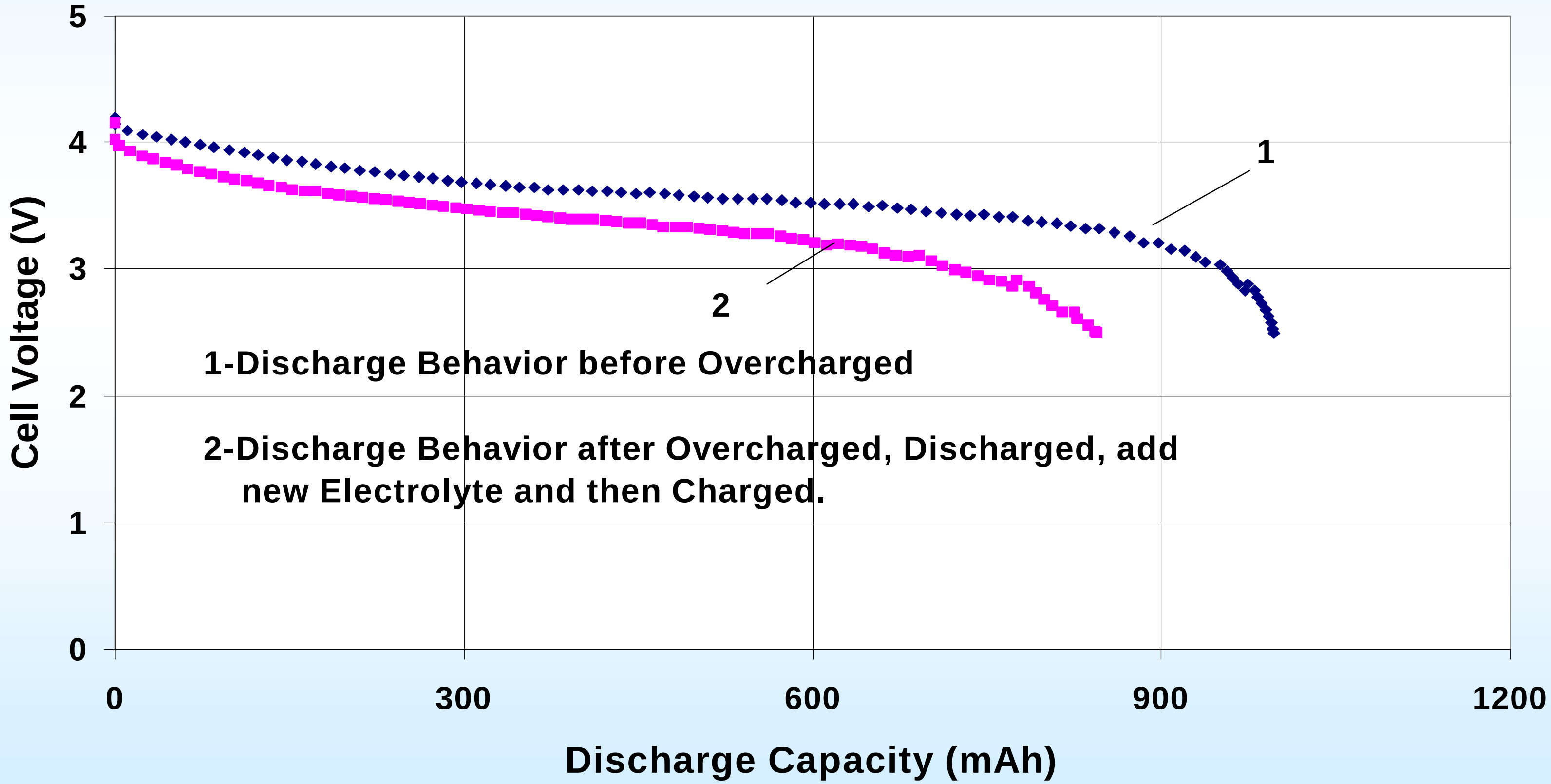
Overcharged Cell can be Discharged



Discharge Behavior of an Overcharged Lithium-ion Cell first at 200 mA and then at 5 mA Current Drains.

LiTech LLC

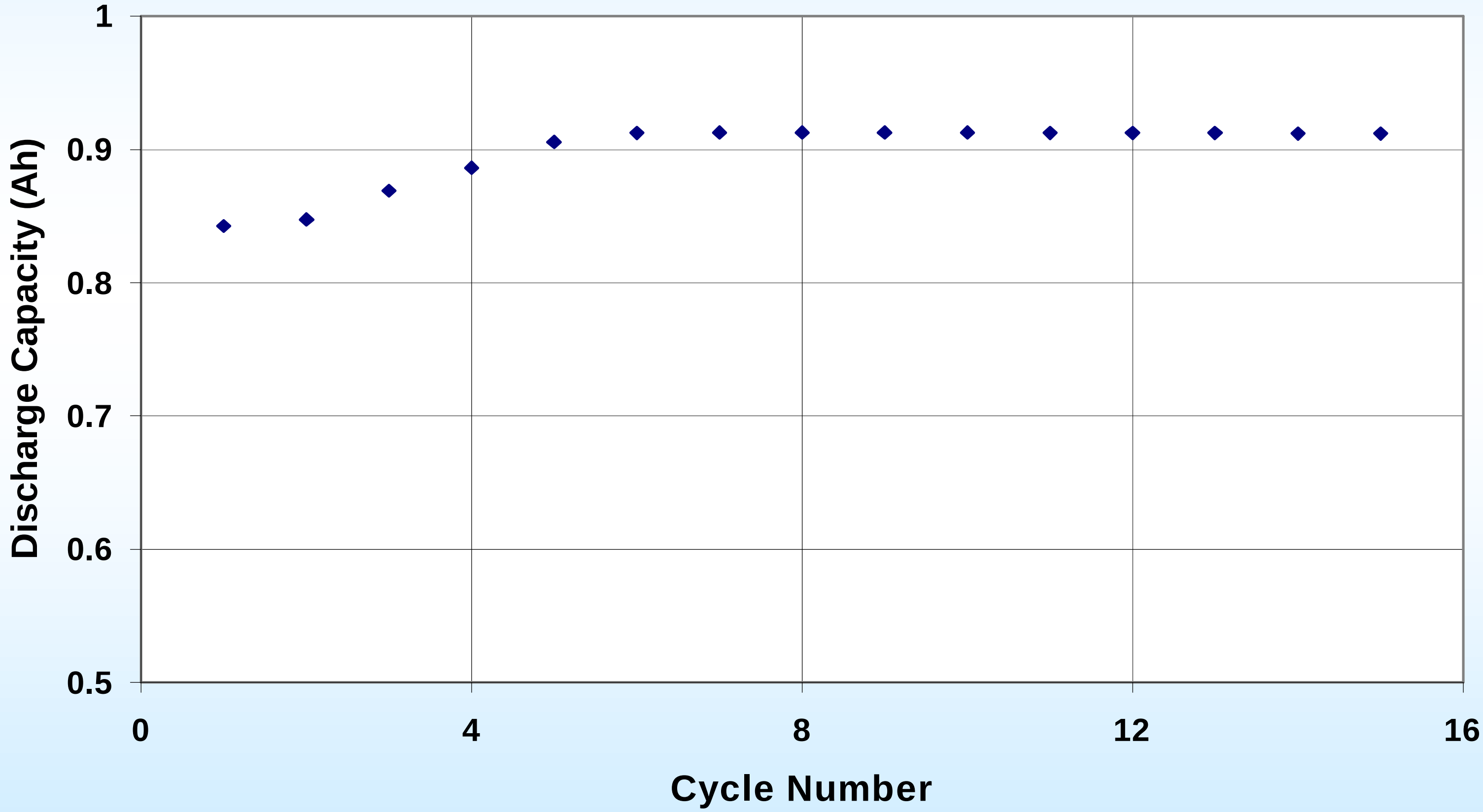
Lithium-ion Cells Exposed to Overcharge can Deliver over 85% Capacity



Discharge Behavior of a Lithium-ion Cell before and after Exposed to Overcharge.

LiTech LLC

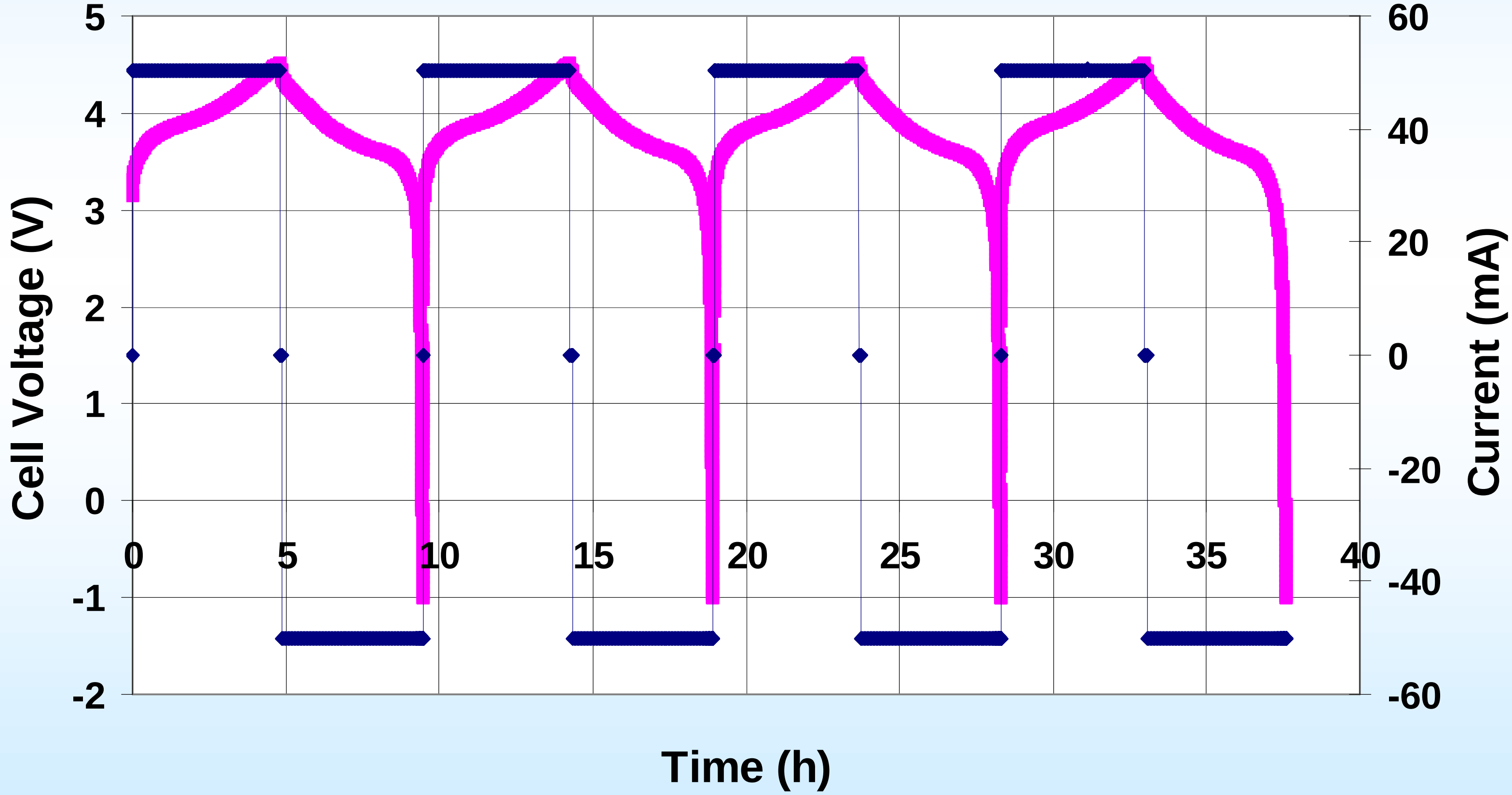
Overcharged Cell, after fully Discharged and Adding fresh Electrolyte, can also be Cycled



Cycling Behavior of an Overcharged Cell. Rated Cell Capacity was 1 Ah.

LiTech LLC

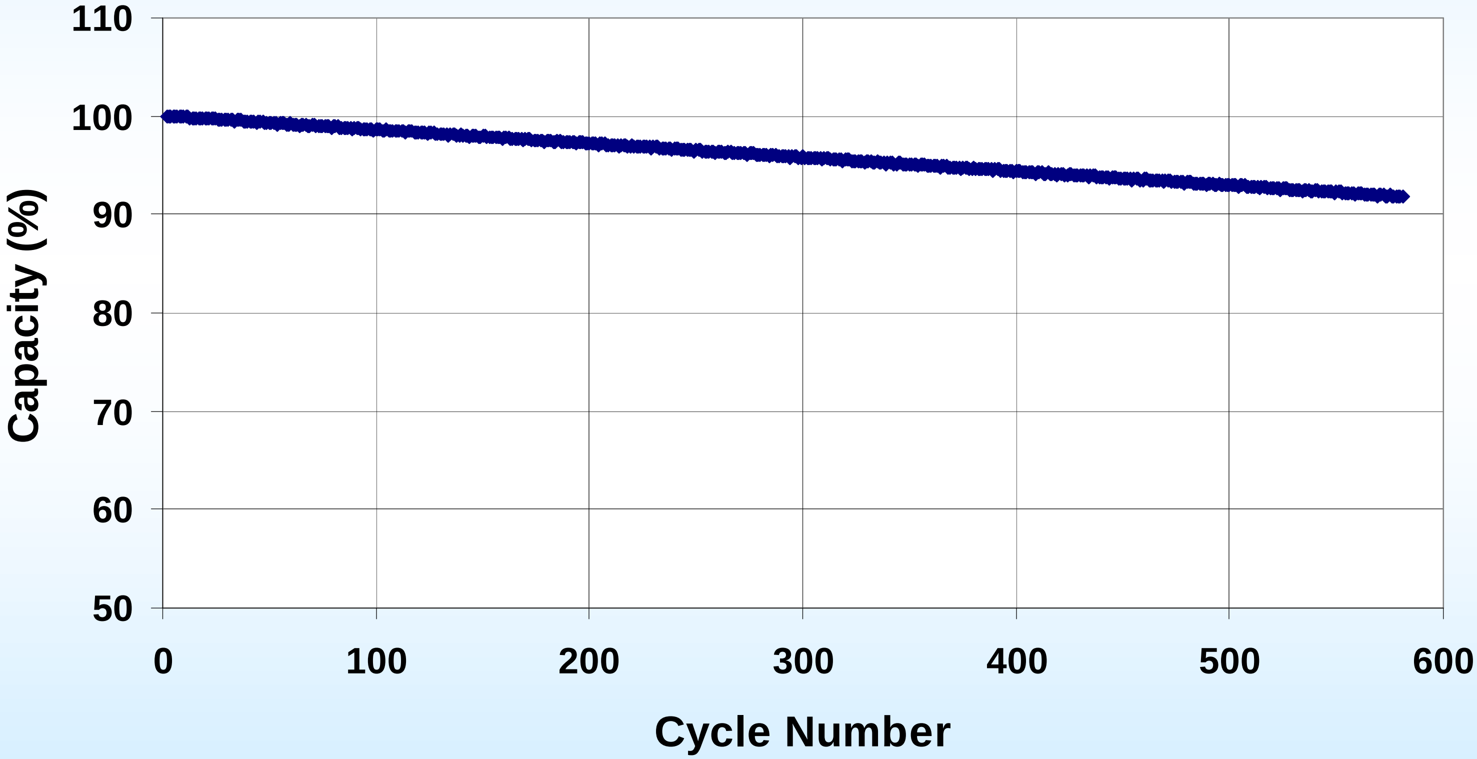
LiTech Lithium-ion Cells can Accept Repeated Overcharge/Overdischarge



Repeated Overcharge/Overdischarge Behavior of a LiTech Lithium-ion Cell.

LiTech LLC

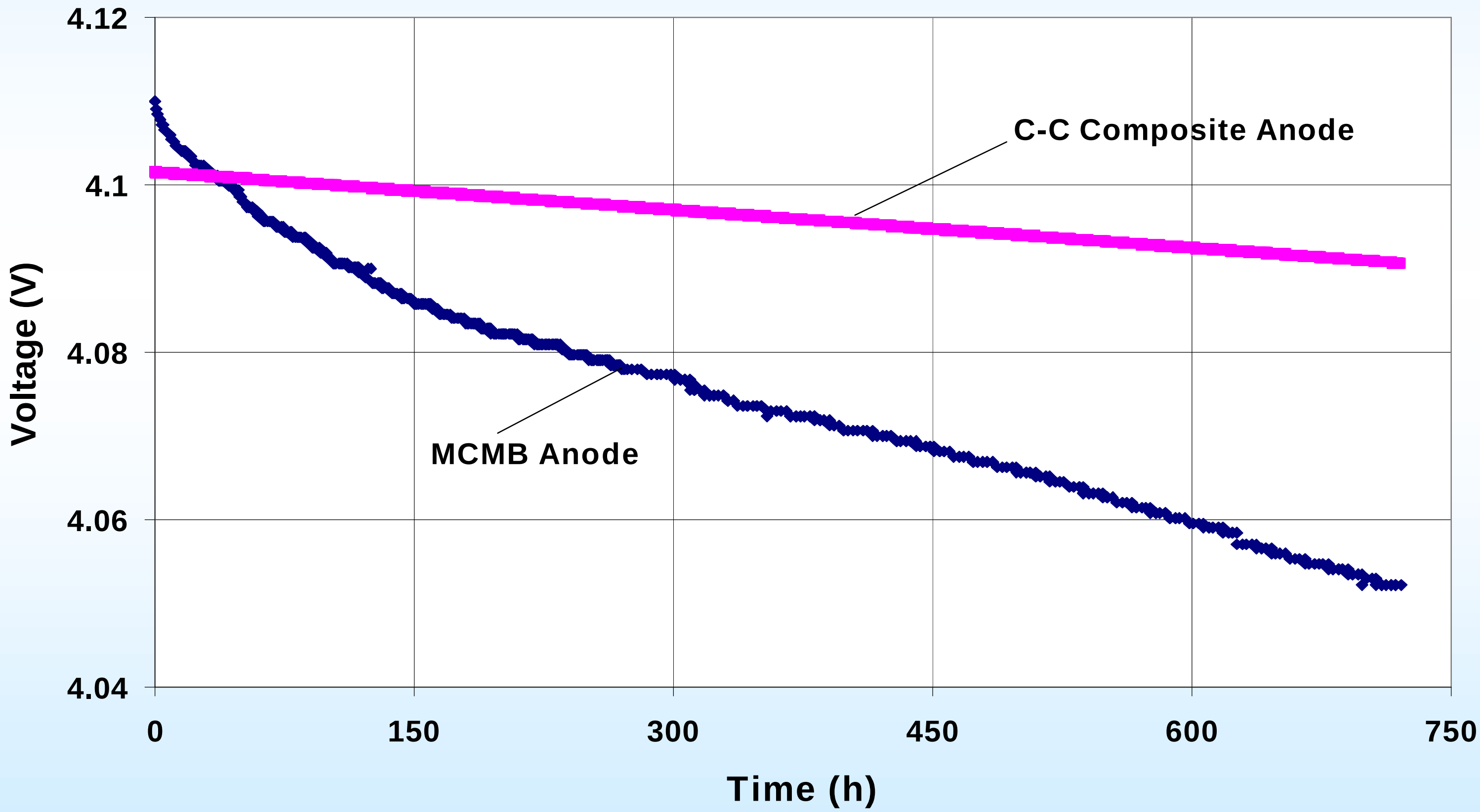
Delivers 550 cycles with over 90% Capacity Retention



Cycling Behavior of a LiTech Lithium-ion Cell at C/5 Rate. Cathode: $LiCoO_2$. Electrolyte: 1M $LiPF_6$ in EC/DMC (1:1 v/v).

LiTech LLC

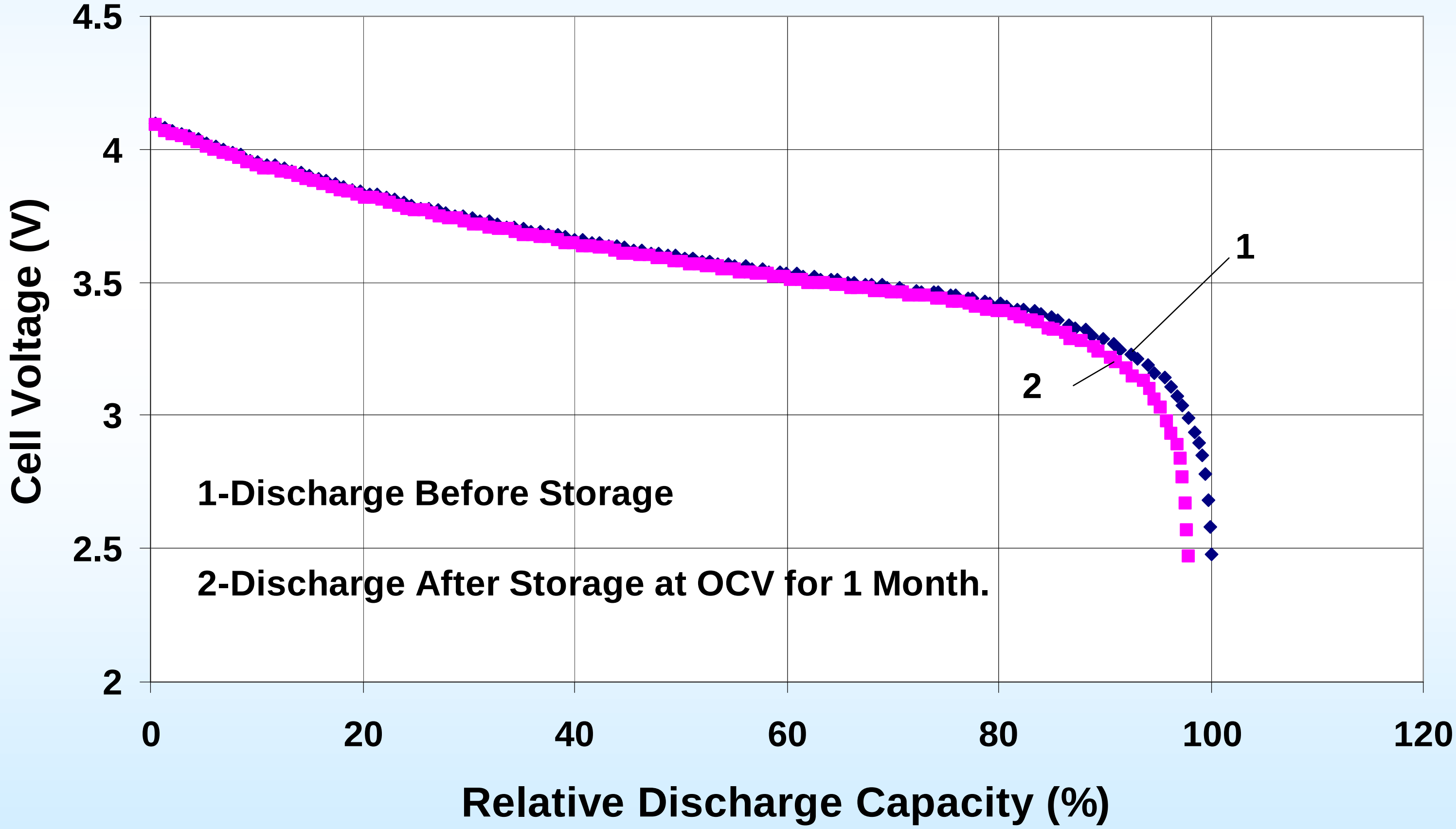
Only 10 mV Voltage Decay after Storage for 1 Month at Ambient Temperatures



Voltage Decay of Lithium-ion Cells at OCV stored at Ambient Temperatures.

LiTech LLC

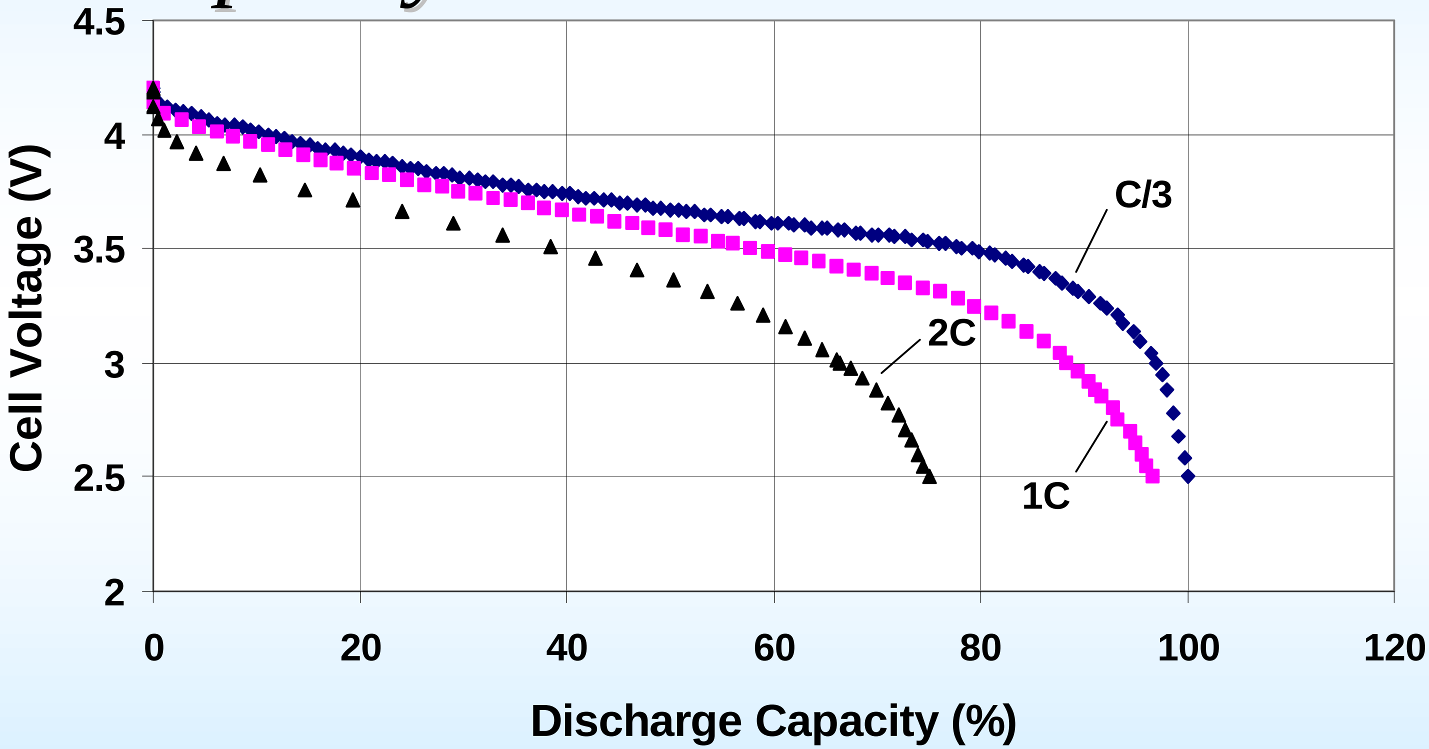
Only 2% Capacity Loss After 1 Month of Storage at Ambient Temperatures.



Discharge Behavior (Before and After Storage) of a LiTech Lithium-ion Cell at C/4 Rate.

LiTech LLC

At 1C Rate, the Cell Delivers 95% Capacity



Discharge Behavior of LiTech's Lithium-ion Cell at Different Current Drains. Cathode: LiCoO2. Electrolyte: 1M LiPF6 in EC/DMC (1:1 v/v).

LiTech LLC

Safety and Abuse Test Results

Tests	Results
Overdischarge	No Performance Degradation.
Overcharge	No Fumes, No Fire, No Explosion.
External Short-circuit	No Fumes, No Fire, No Explosion.
Internal Short-circuit (Nail Penetration)	No Fumes, No Fire, No Explosion.

LiTech LLC

LiTech Lithium-ion Battery Technology offers:

- **Low Cost**
- **Enhanced Safety**
- **High Energy Density**
- **Long Life, and**
- **Low Self-Discharge**

The Technology is the Right Choice for the Production of High Capacity, High Voltage Batteries.

On the Behavior of Lithium Ion Batteries During Short Circuit and Extended Overcharge

Randolph A. Leising,[a] Marcus J. Palazzo,[a]
David M. Spillman,[a] Esther S. Takeuchi,[a]
and Kenneth J. Takeuchi[b]

[a]Wilson Greatbatch Ltd., Clarence, NY
[b]SUNY at Buffalo, Department of Chemistry, Buffalo, NY

Introduction

- The safety of lithium ion batteries under abusive conditions is a primary concern of battery manufacturers and their customers.
- Placement of thermocouples within a battery will provide more accurate information on the internal temperature during these reactions.
- Short circuit conditions or extreme overcharge of lithium ion batteries may result in high temperatures, and can lead to violent reactions under some circumstances.

Introduction

- External short circuit tests were conducted on medium sized prismatic batteries while the voltage, current, case temperature, and internal temperature were monitored and recorded.
- The rate of overcharge was systematically varied for batteries having the same cell balance.
- Extended overcharge tests were conducted on medium size prismatic batteries which contained thermocouples that were positioned within the wound electrode stack.

Introduction

- The effects of cell balance, i.e. ratio of lithiated cobalt oxide to carbon weight, on the overcharge reaction was investigated.
- Partially delithiated cathodes were placed into batteries containing non-lithiated anodes and subjected to an extended overcharge test.
- Several mechanisms may contribute to lithium ion battery instability during abusive conditions.

Experimental

- Battery Materials:
  - Cathode: $LiCoO_2$
  - Anode: Graphite
  - Electrolyte: 1.0 M $LiPF_6$ in alkyl carbonates
  - Separator: Polyethylene
- Battery Design:
  - Nominal capacity: 1.5 Ah
  - Stainless steel case
  - Hermetically sealed
  - Internal (sealed with epoxy) and external Type-K thermocouples

External Short Circuit Test

- Conducted on medium size prismatic batteries at room temperature in still air within an explosion proof chamber.
- Electrode weight ratio was 2.8, and batteries were charged to 4.10 volts prior to test.
- External circuit resistance was approximately six milliohms. The battery voltage, current, case temperature, and internal temperature were recorded.

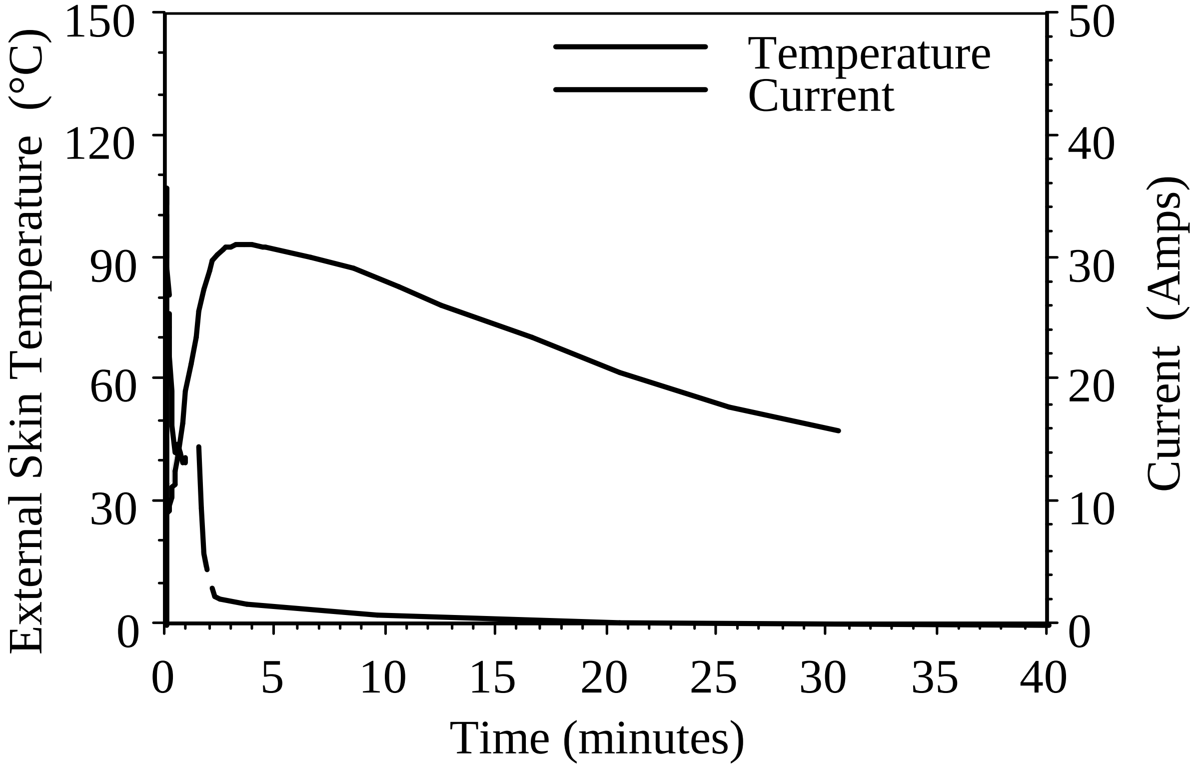


Figure 1: External case skin temperature
during 10 mž short circuit test.

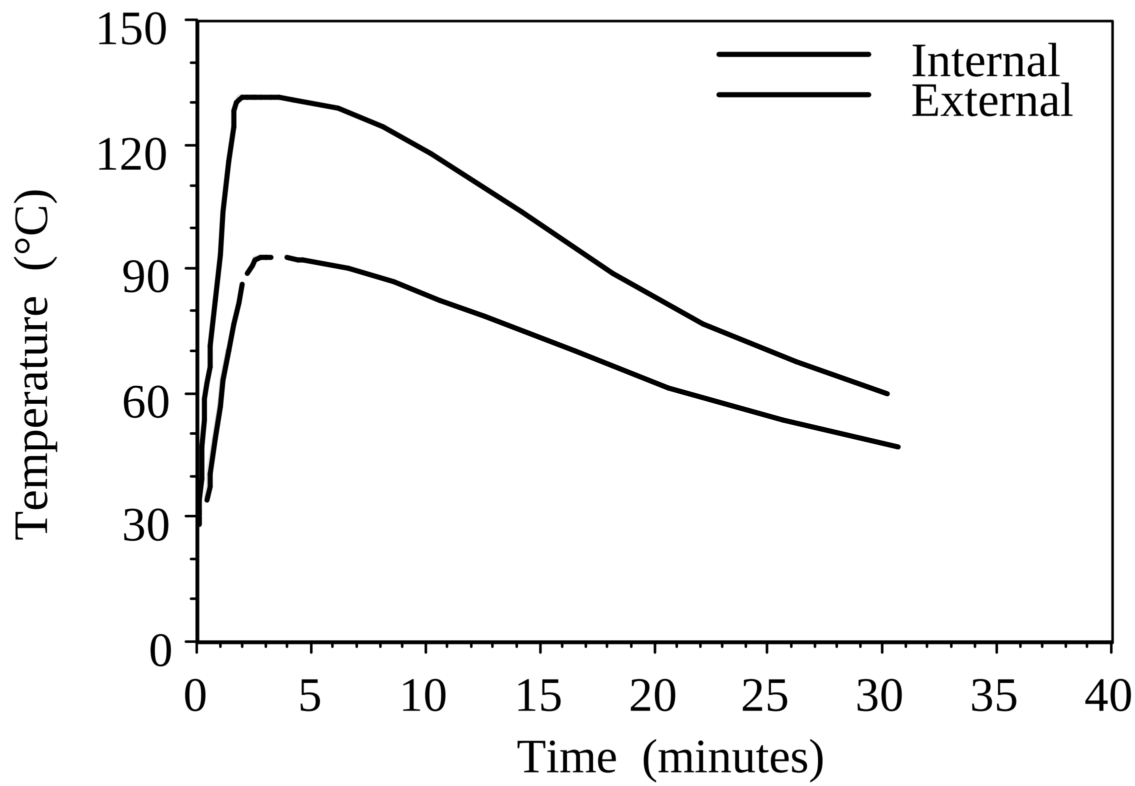


Figure 2: Cell temperature during 10 mž short circuit test.

Short Circuit Test Summary

- The current peaked at about 36 amps (24C rate) within 0.2 seconds when the external short circuit was applied. The battery voltage simultaneously decreased from 4.10 volts to less than 0.25 volts.
- The current stabilized at 14 to 15 amps during the first 1.5 minutes, sharply decreased to about two amps, and then slowly decayed thereafter.

Short Circuit Test Summary

- The external case temperature increased to between 94 and 109°C within two minutes, while the internal temperature of the battery increased to about 132°C at a faster rate.
- The polyethylene separator fused, and greatly reduced the short circuit current.
- The batteries remained hermetic, and swelled only slightly.
- Placing thermocouples within the battery provided important temperature data.

Effect of Charge Rate on Overcharge Reaction

- Medium size prismatic batteries having a cell balance of 2.8 were outfitted with external thermocouples, charged to 4.10 volts, and subjected to an extended overcharge test in an explosion-proof chamber.
- Batteries were tested at rates of 150 mA, 300 mA, 525 mA, and 1.5 amps, i.e. C-rates of about 0.10, 0.2, 0.35, and 1.0, respectively.

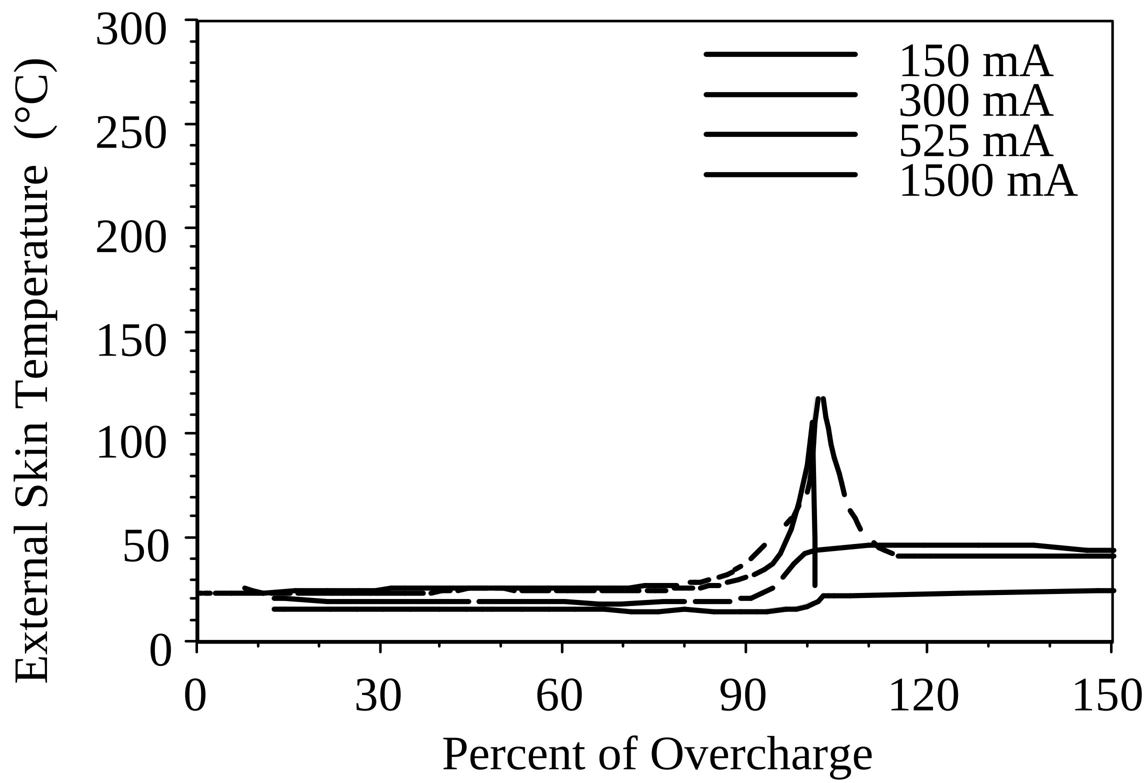


Figure 3: External case skin temperature at various overcharge rates.

Summary of Charge Rate Effect on Overcharge Reaction

- External case temperature remained constant until >75% overcharge.
- At higher charge rates, the external case temperature was observed to increase at lower states of overcharge. The highest temperature was observed after full delithiation of the cathode.
- Under lower charge rates, batteries swelled but remained hermetic. Under a 1.5 amp charge rate, the battery ruptured.

Thermal Profile during Overcharge Reaction

- Medium size prismatic batteries having a cell balance of 2.8 were outfitted with internal and external thermocouples, and tested within an explosion proof chamber.
- Batteries were initially charged to 4.10 volts, and then subjected to an extended overcharge test at room temperature in still air. The overcharge rates were 525 mA, i.e. about C/3 rate, and 1.5 amps, i.e. 1C rate.

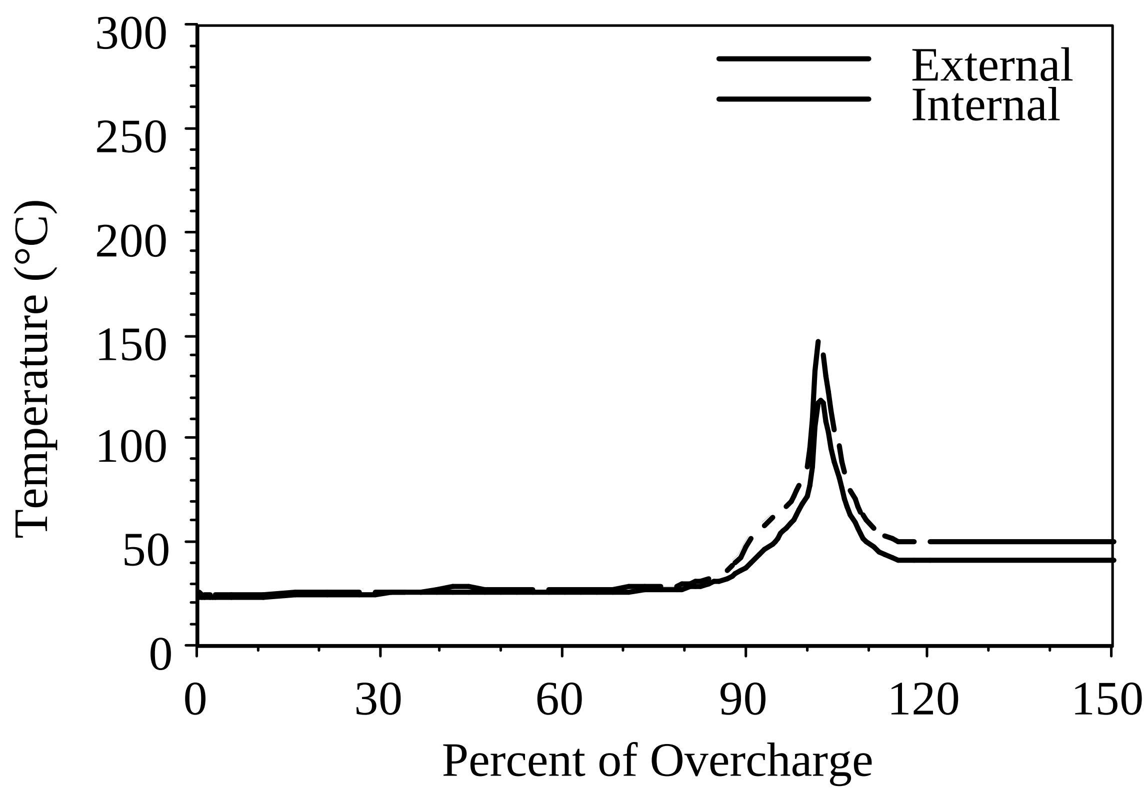


Figure 4: Cell temperature during 525 mA overcharge test.

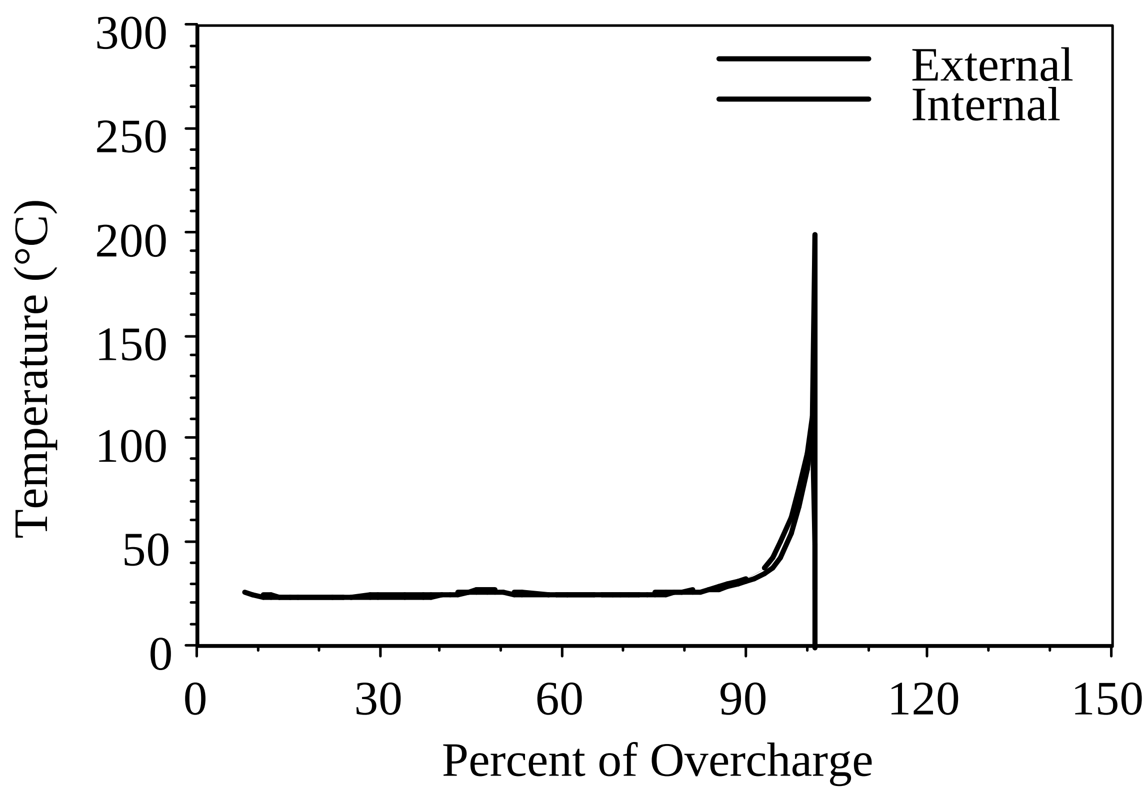


Figure 5: Cell temperature during 1.5 amp overcharge test.

Summary of Thermal Profile during Overcharge Reaction

- Batteries overcharged at 525 mA did not vent, exhibited a case temperature of about 120°C, and an internal temperature of about 148°C.
- Batteries overcharged at 1.5 amps ruptured, exhibited a case temperature of about 107°C, and an internal temperature of about 199°C.

Effect of Cell Balance on Overcharge Reaction

- Medium size prismatic batteries having a nominal capacity of 1.5 Ah were built with the following modifications in order to achieve an overall balance of about 2.3, 2.8, and 3.3:
  - Fixed cathode weight combined with varying anode weight.
  - Fixed anode weight combined with varying cathode weight.

Effect of Cell Balance on Overcharge Reaction

- Batteries were initially charged to 4.10 volts, and then subjected to an extended overcharge test at room temperature in still air. The test was conducted in an explosion proof chamber.
- The overcharge rate was 1.0 amp, i.e. C/1.5 rate, and the battery voltage and external case temperature were monitored throughout test.

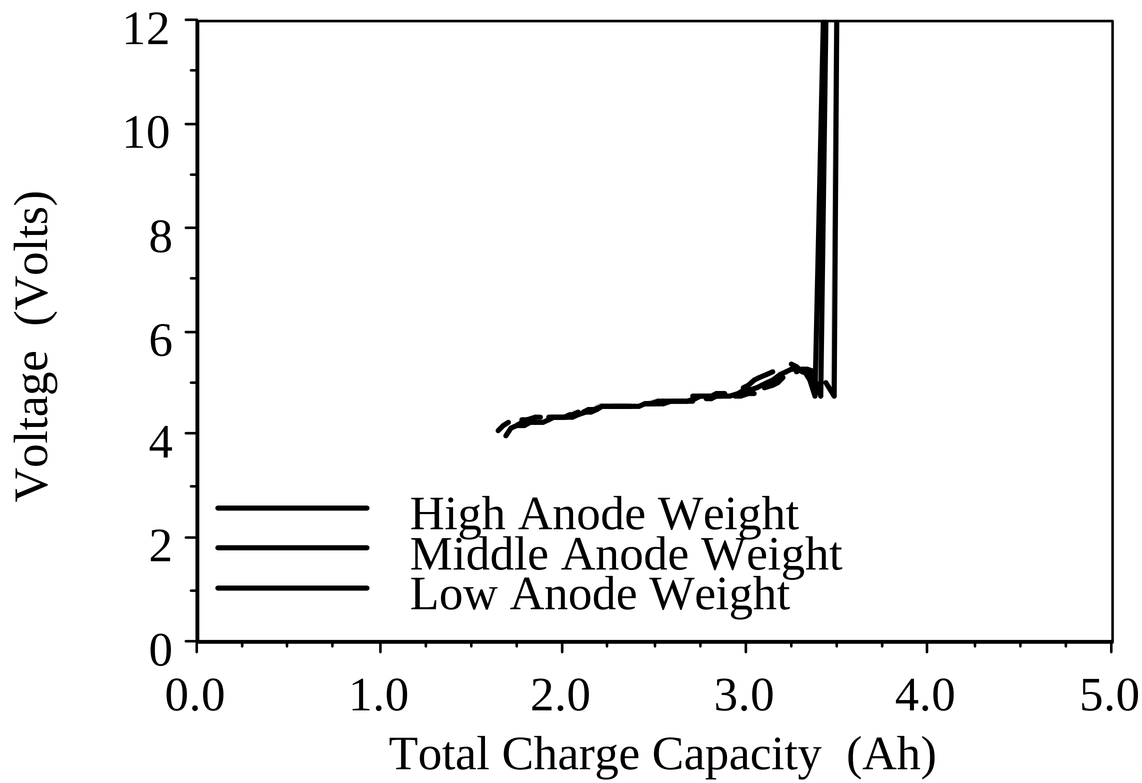


Figure 6: Overcharge test at 1 amp with anode weight varied.

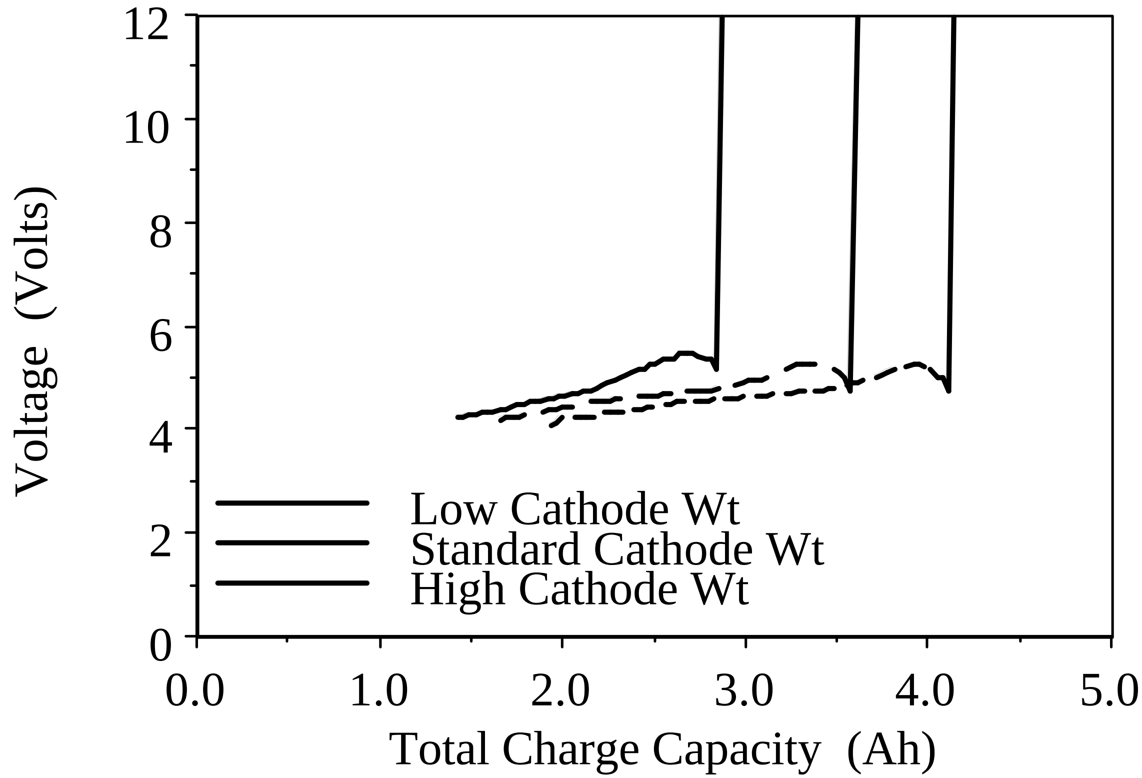


Figure 7: Overcharge test at 1 amp with cathode weight varied.

Summary for Effect of Cell Balance on Overcharge Reaction

- All batteries ruptured as a result of extended overcharge at 1.0 amp, i.e. C/1.5 rate.
- Batteries containing a fixed cathode weight exhibited an external case temperature of up to 105°C, and the rupture point was independent of the amount of anode material.
- Batteries containing a fixed anode weight exhibited an external case temperature of up to 112°C, and the rupture point tracked the amount of cathode material.

Evaluation of Partially Delithiated Cathodes

- Partially delithiated cathodes were removed from batteries that were subjected to formation and discharge, i.e. the nominal formula was $Li_{0.9}CoO_2$, or that were charged to 4.10 volts following formation, i.e. the nominal formula was $Li_{0.5}CoO_2$.
- Batteries containing partially delithiated cathodes and non-lithiated anodes were then assembled. They contained both internal and external thermocouples.

Evaluation of Partially Delithiated Cathodes

- Batteries were charged to 4.10 volts, and then subjected to an extended overcharge test at room temperature in still air. The test was conducted in an explosion proof chamber.
- The overcharge rate was 0.75 amps, i.e. C/2 rate, and the battery voltage, external case temperature, and internal temperature were monitored throughout test.

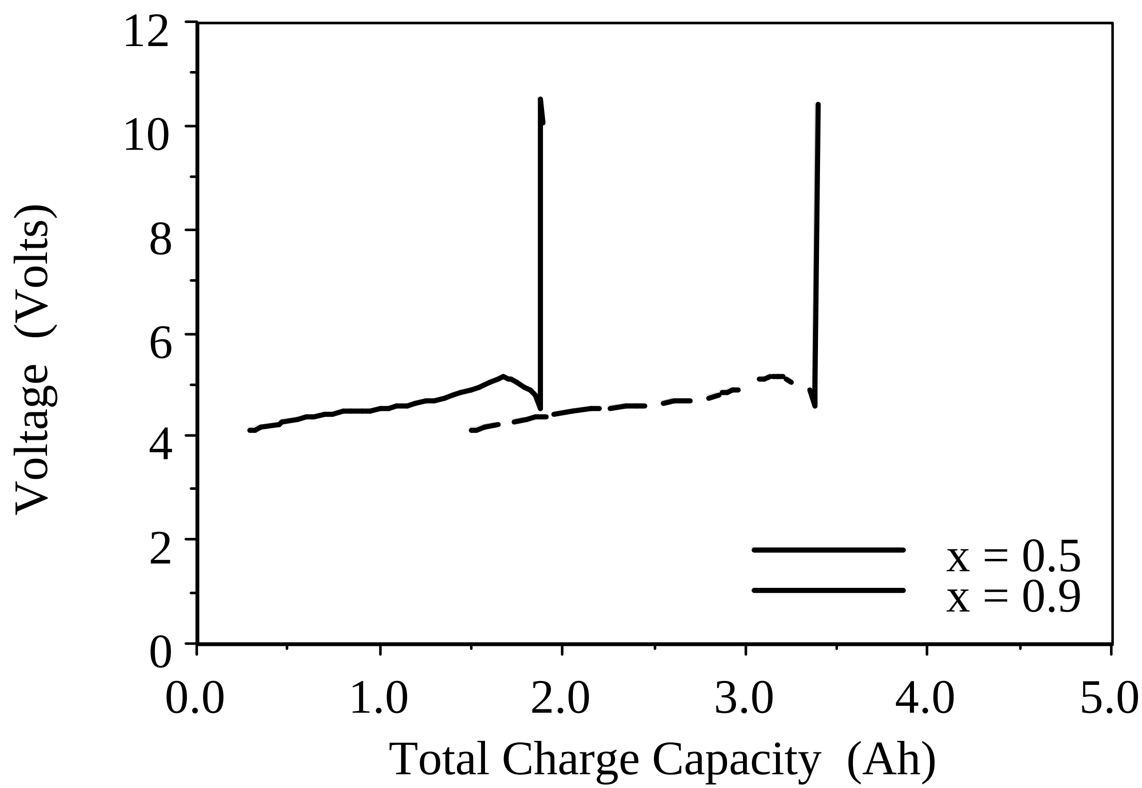


Figure 8: Voltage on 750 mA overcharge test for cells containing LixCoO2.

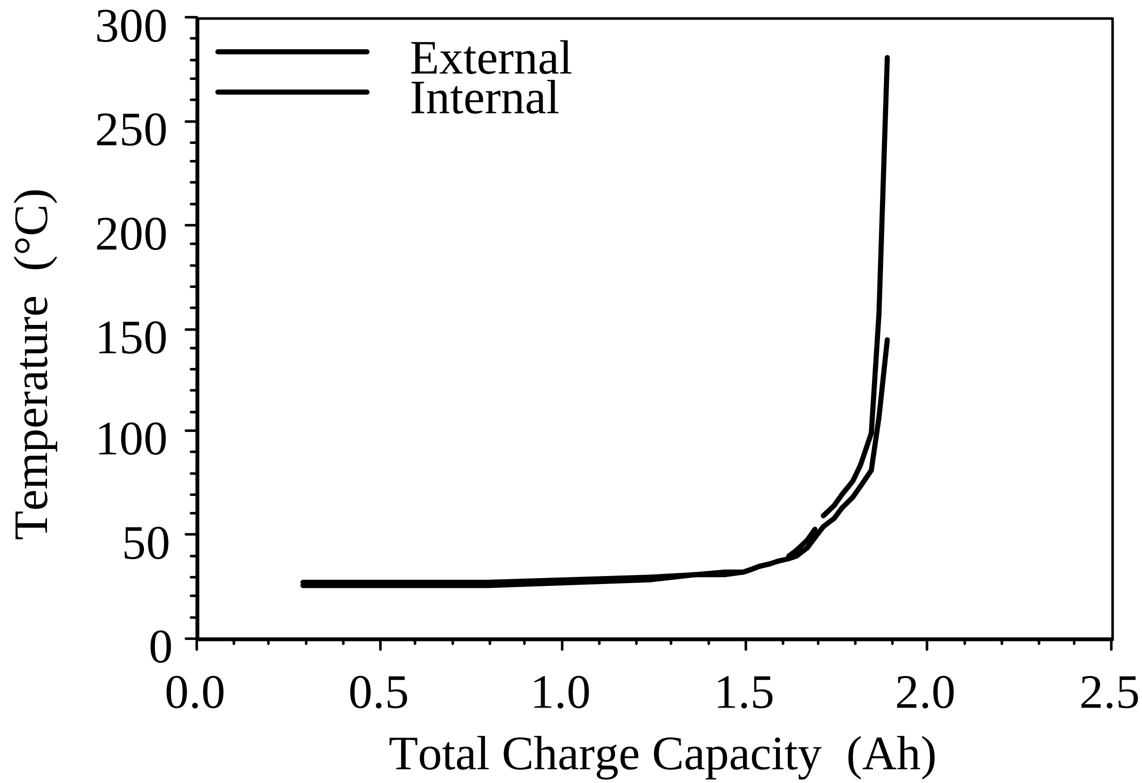


Figure 9: Temperature on 750 mA overcharge test for cells containing Li0.5CoO2.

Summary for Evaluation of Partially Delithiated Cathodes

- Both batteries ruptured during overcharge test.
- The shape of both voltage curves was similar, with the noticeable difference being the time, i.e. charge capacity, until the batteries reached full overcharge.
- Batteries containing the slightly delithiated cathode material, $Li_{0.9}CoO_2$, exhibited an external case temperature of 116°C, and an internal temperature of 215°C.

Summary for Evaluation of Partially Delithiated Cathodes

- Batteries containing the more highly delithiated cathode material, $Li_{0.5}CoO_2$, exhibited an external case temperature of 145°C, and an internal temperature of 281°C.
- Melting of lithium may be a cause of cell rupture on extended overcharge in standard batteries.
- Batteries that are unlikely to contain deposited lithium metal on the anode still ruptured on extended overcharge, although at a higher temperature.

Mechanisms Contributing to Battery Instability during Abuse

- Reaction of lithiated carbon and electrolyte.
- Reaction of lithiated carbon with PVDF binder.
- Melting of lithium.
- Autocatalytic exothermic reaction of Li_xCoO_2 above 150°C.

Mechanisms Contributing to Battery Instability during Abuse

- Oxidation of electrolyte due to high potential of cathode following complete removal of lithium.
- Reaction of highly delithiated Li_xCoO_2 and electrolyte near 250°C.
  - Evolution of oxygen near 230°C.
  - Decomposition of CoO_2 to Co_3O_4 at 245 °C.

Conclusions

- Short circuit and extended overcharge reactions were studied in medium size prismatic lithium ion batteries containing graphite anodes and lithiated cobalt oxide cathodes.
- Placement of thermocouples within batteries can provide more detailed information of battery temperature during abusive tests.
- During short circuit tests, batteries swelled slightly, and the shutdown separator was capable of limiting the internal temperature to 132°C.

Conclusions

- The overall response of a battery during extended overcharge is dependent, among other things, upon the charge rate, indicating that the ability of the battery to adequately dissipate heat is an important design consideration.
- While reduction of lithium plating during overcharge via the use of a low cell balance may improve the safety tolerance of the battery, it alone is not likely to be sufficient to prevent rupture during abuse.

Conclusions

- The overall reactivity of lithium ion batteries is due to a combination of chemical reactions that can occur on the anode and the cathode, and that may also involve the electrolyte and binder.

Performance and Safety Of Lithium Ion Cells

B. V. Ratnakumar, M. C. Smart, L. Whitcanack and S. Surampudi
Jet propulsion Laboratory, Pasadena, California
and
R. Marsh
Wright-Patterson Air Force Base, Dayton, OH

JPL

Supported by Mars Program Office and NASA Code S Battery Programs

NASA Battery Workshop, Nov. 14-16, 2000, Huntsville, AL

Evaluation of Lithium-Ion Cells at JPL

- **Cycle life performance at room temperature (25^{o}C)**
- **Cycle life performance at low temperature (-20^{o}C)**
- **Cycle life at alternating temperatures (40 and -20^{o}C)**
- **Discharge rate characterization (at 40, 25, 0, and -20^{o}C)**
- **Charge rate characterization (at 40, 25, 0, and -20^{o}C)**
- **Capacity retention tests**
- **Accelerated LEO Tests**
- **Storage characterization tests (cruise conditions)**
- **VT charge characterization tests**
- **Electrical characterization by a.c. impedance**
- **Thermal characterization**

NASA-DOD Interagency Li Ion Program

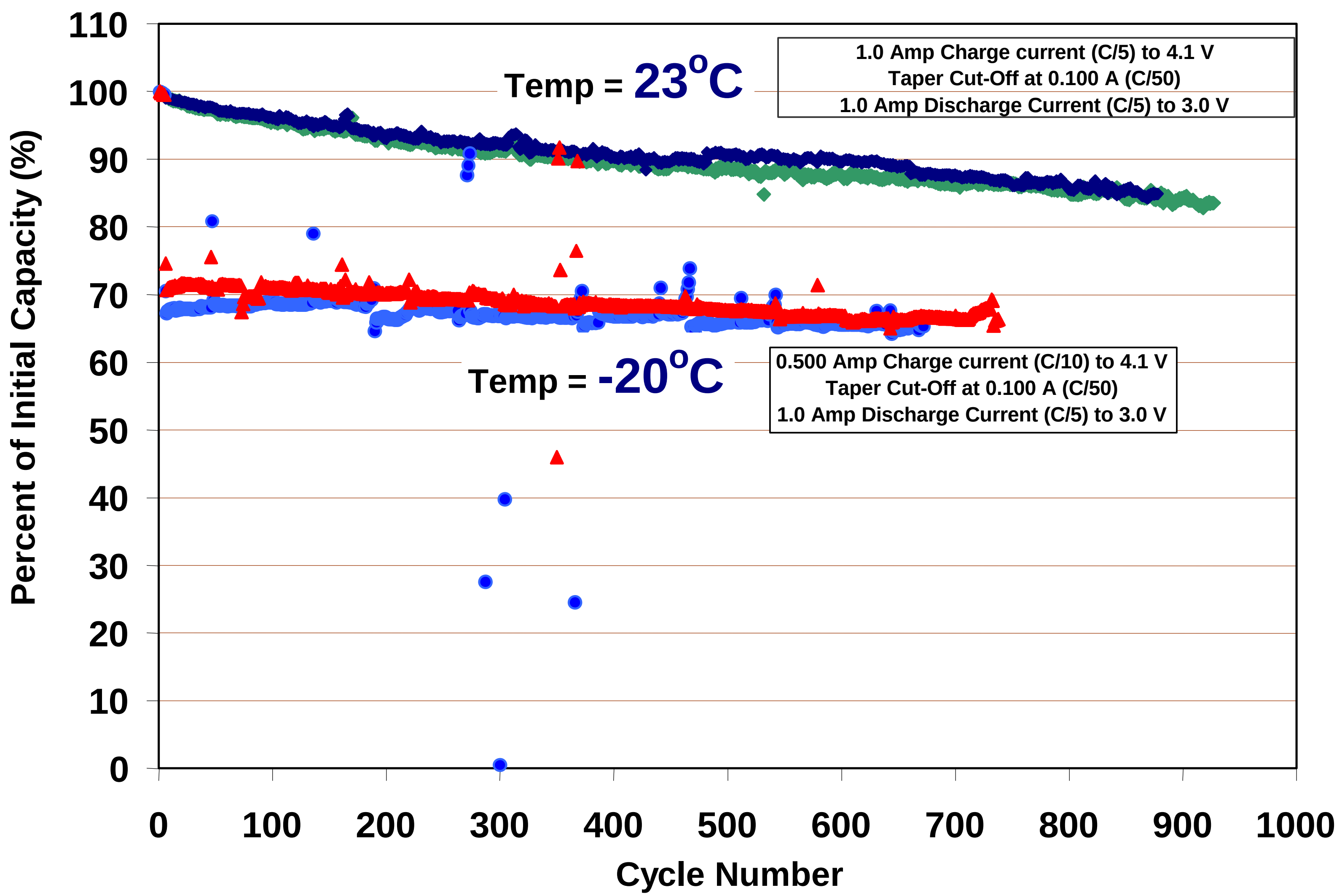
Objectives

- DEVELOP HIGH SPECIFIC ENERGY AND LONG CYCLE LIFE Li -ION BATTERIES
- ESTABLISH U.S. PRODUCTION SOURCES
- DEMONSTRATE TECHNOLOGY READINESS
  - LANDERS BY 2001
  - ROVERS BY2003
  - GEO MISSIONS BY 2003
  - AVIATION/UAV's BY 2001
  - MILITARY TERRESTRIAL APPLNS's BY 2001
  - LEO MISSIONS BY 2003

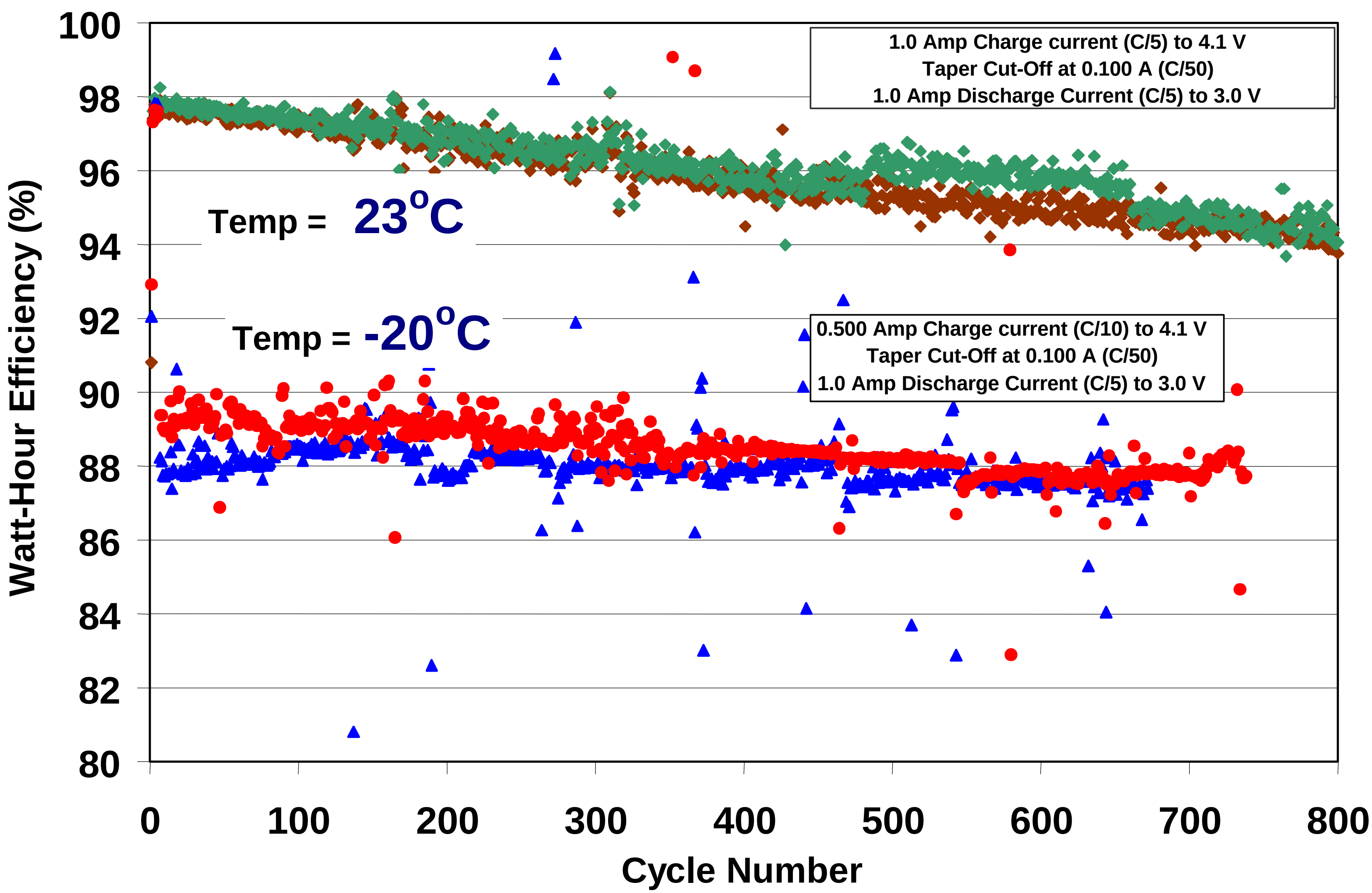
Technology Drivers

Mission	Technology Driver
Lander Rover	Low Temperature Operation High rate Pulse Capability
GEO S/C	10-20 Year Operating life Large Capacity cells (50-200 Ah)
LEO PlanetaryS/C	Long Cycle life(30,000) Medium Capacity Cells (50 Ah)
Aircraft	Low temperature Operation High Voltage Batteries (270 V)
UAV	Large Capacity cells (200 Ah) High Voltage Batteries (100V)

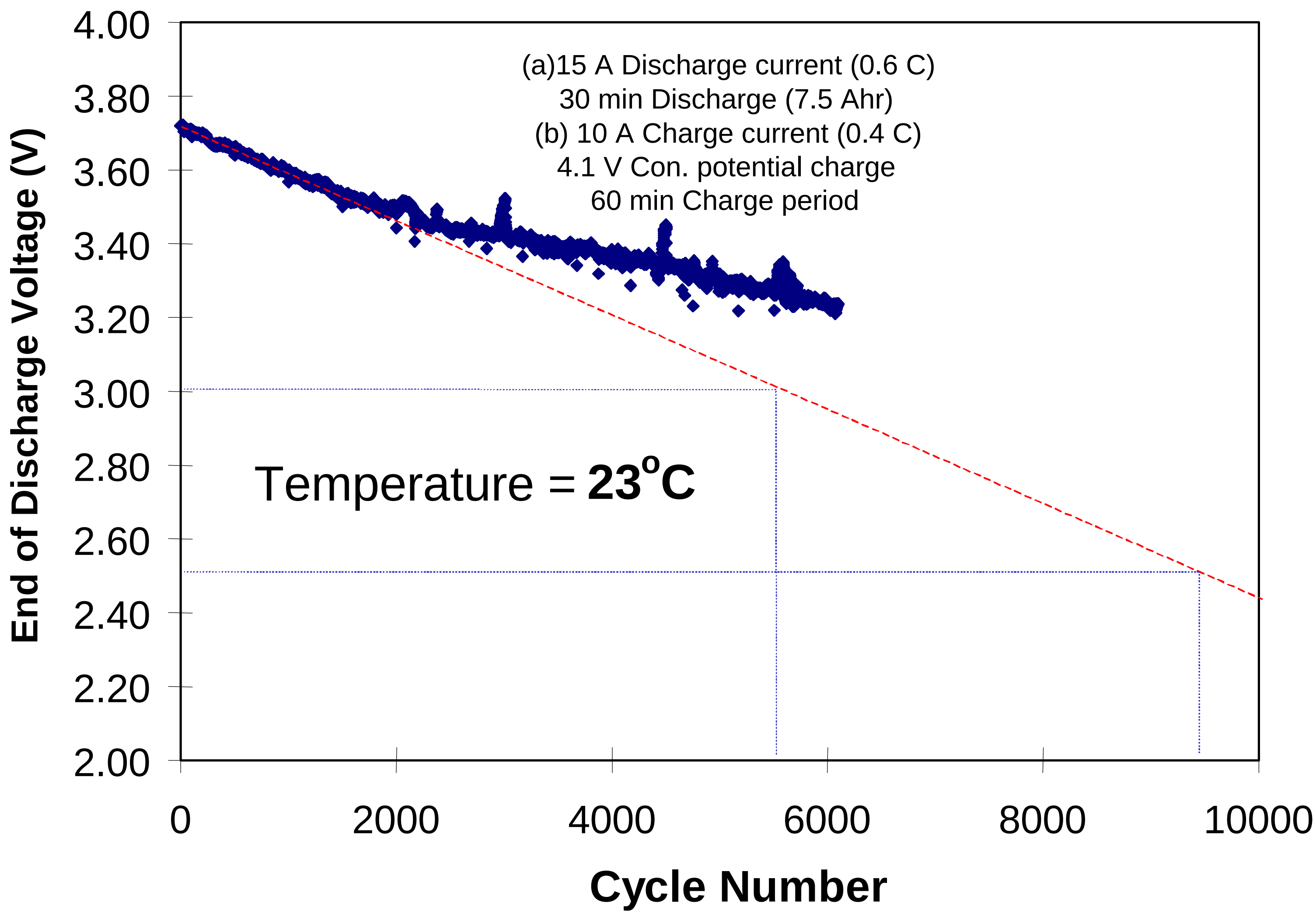
Cycle Life of Li Ion Cells



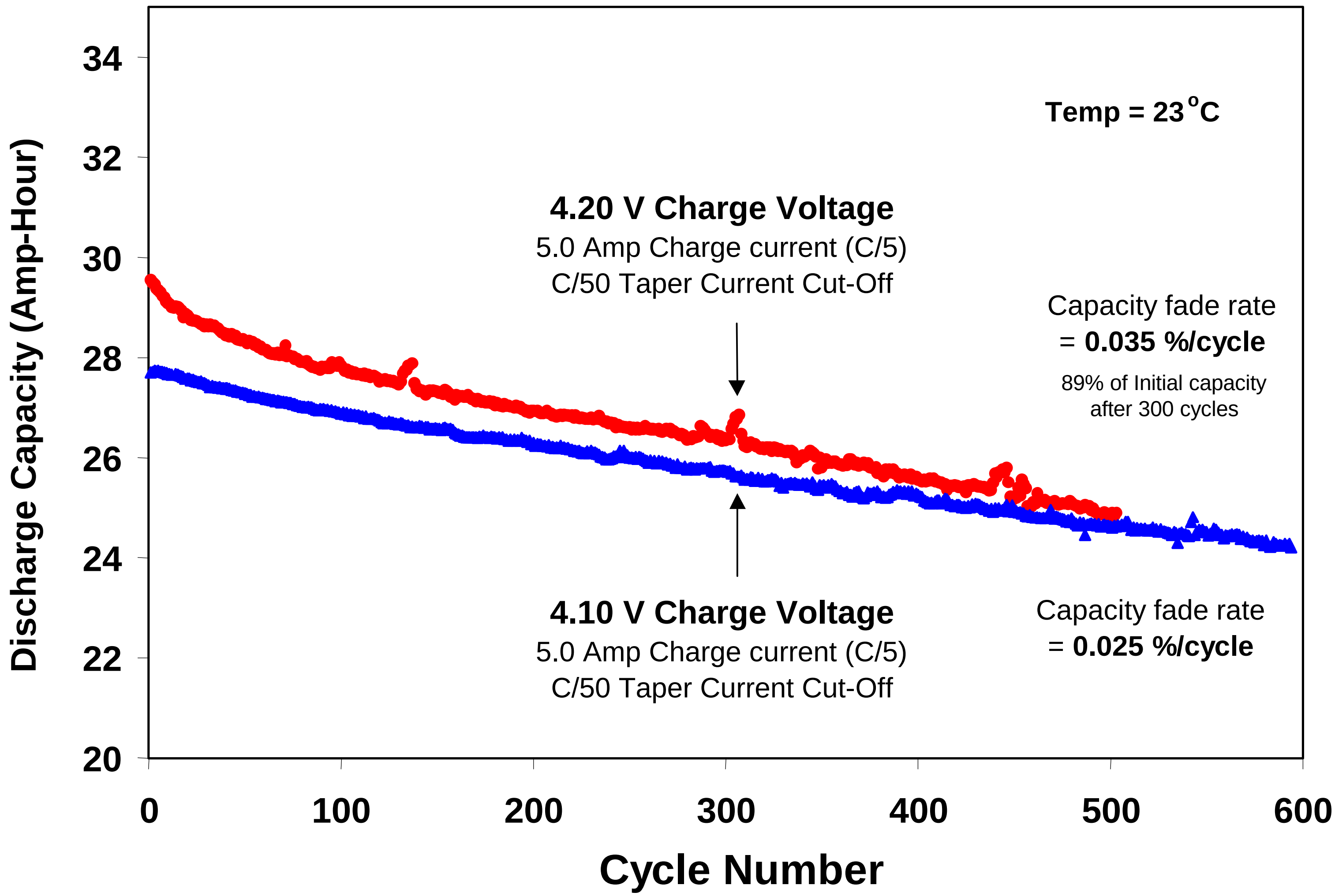
Cycle Life of Li Ion Cells-Energy efficiency



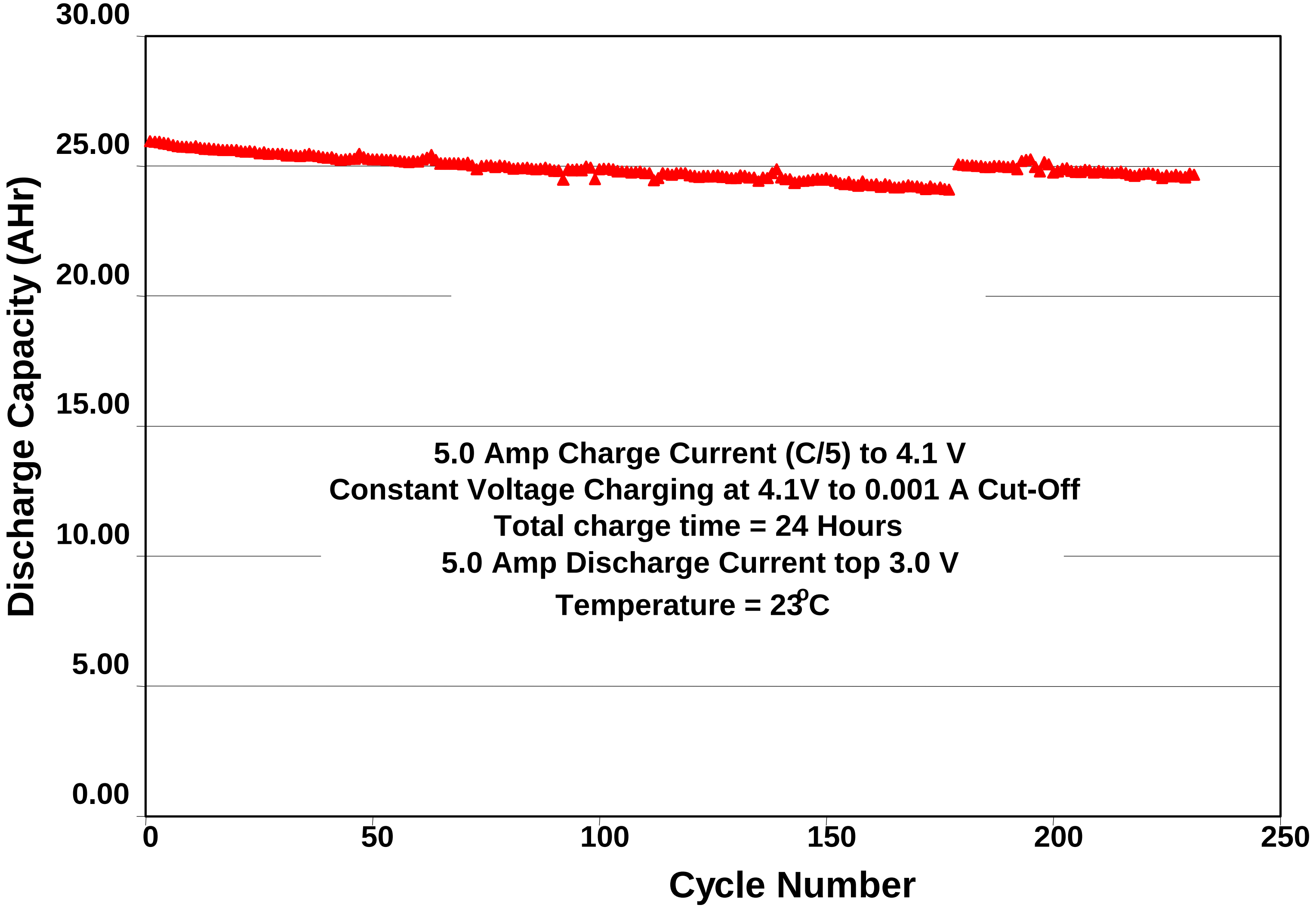
Cycle Life of Li Ion Cells to Partial DOD Accelerated LEO



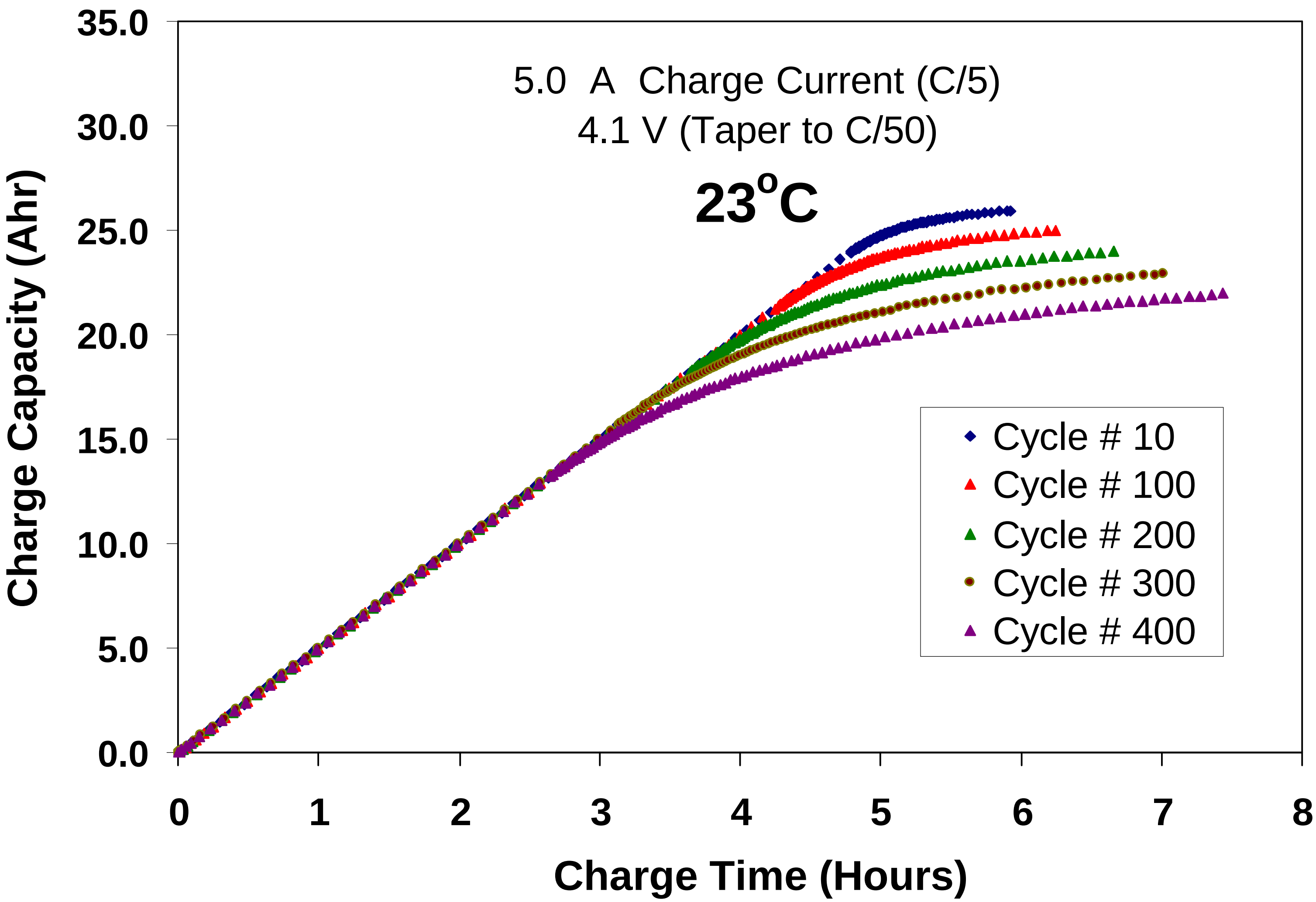
Tolerance to Higher Charge Voltage



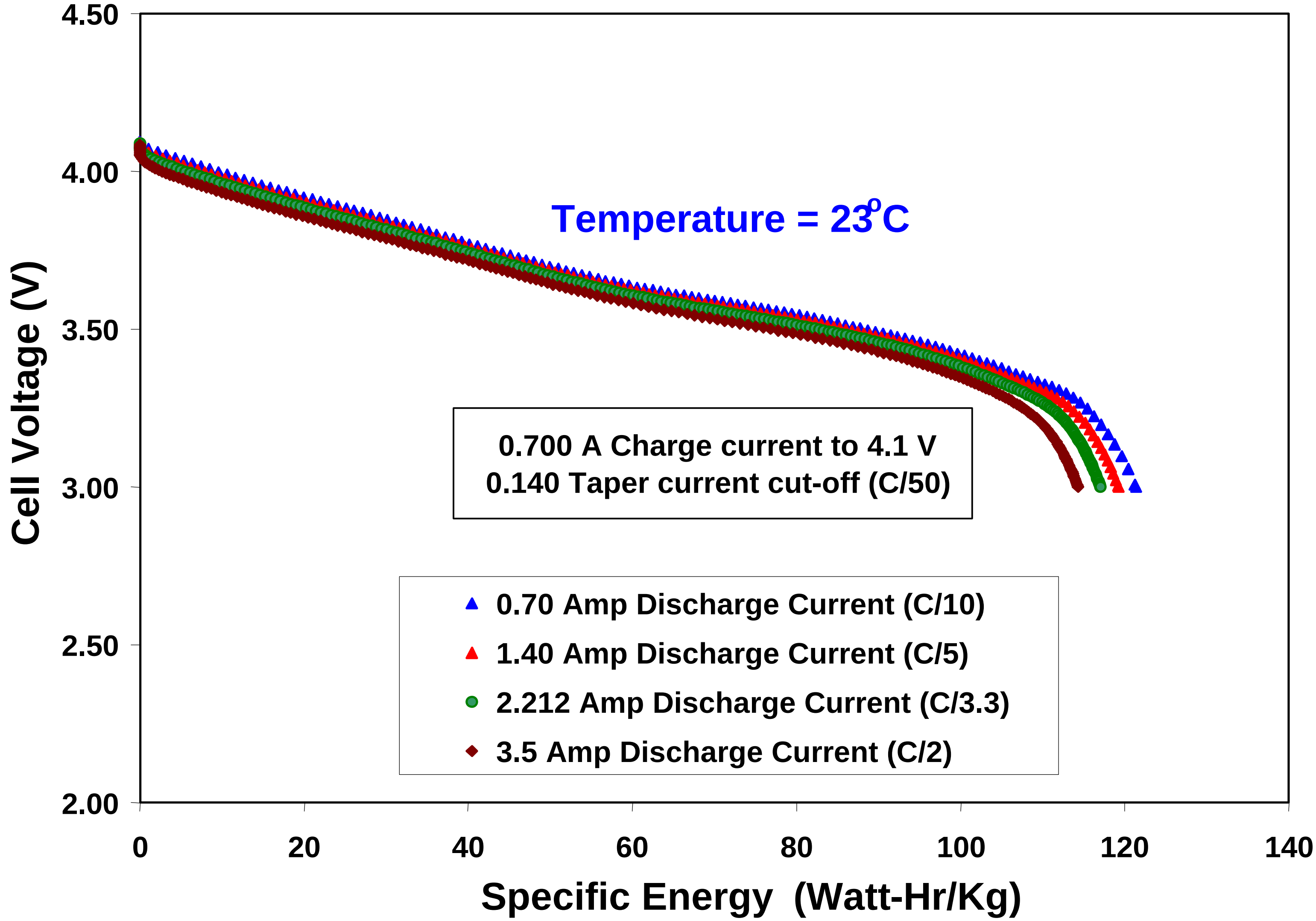
Tolerance to Extended Tapered Charge



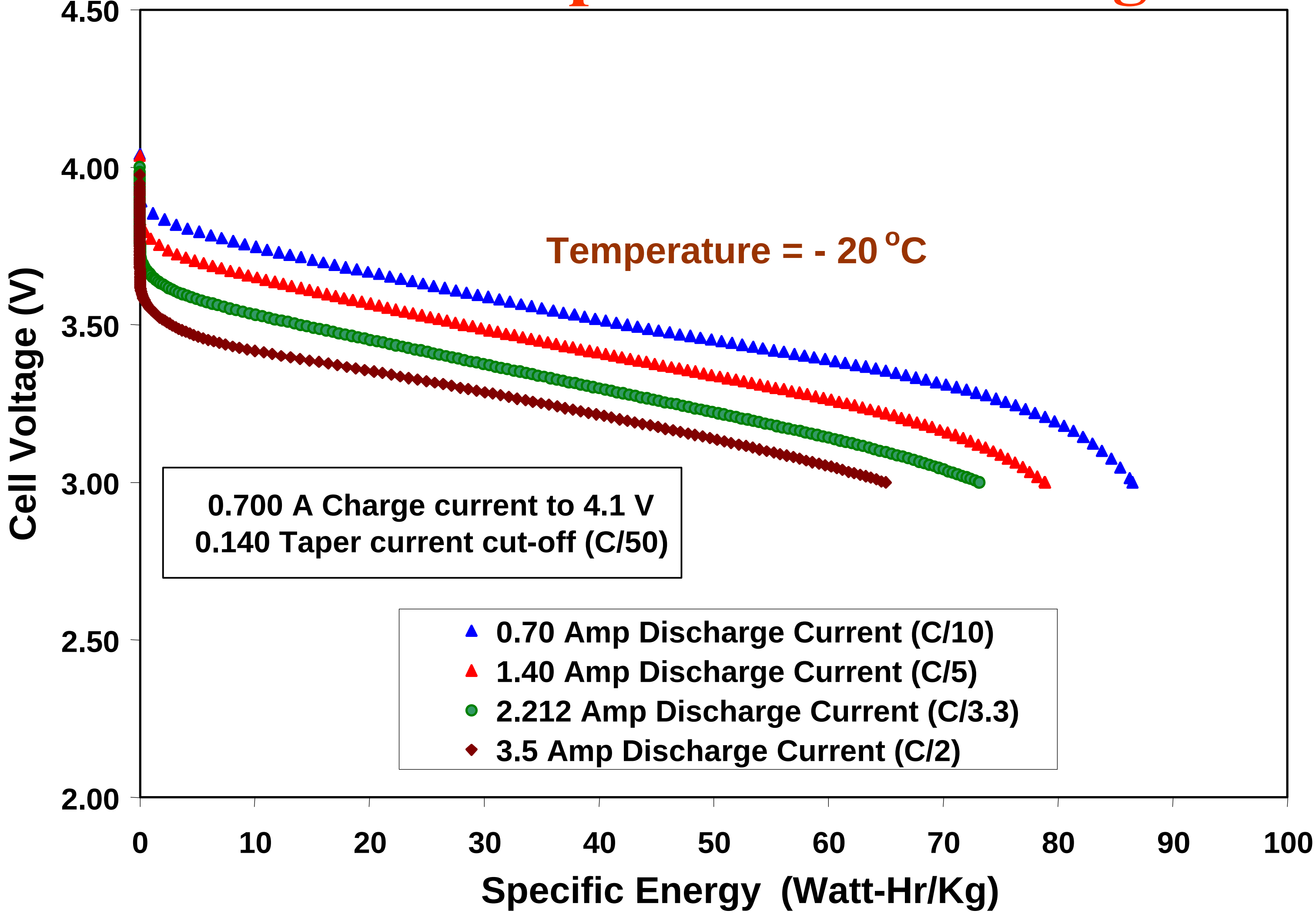
Charge on Cycling



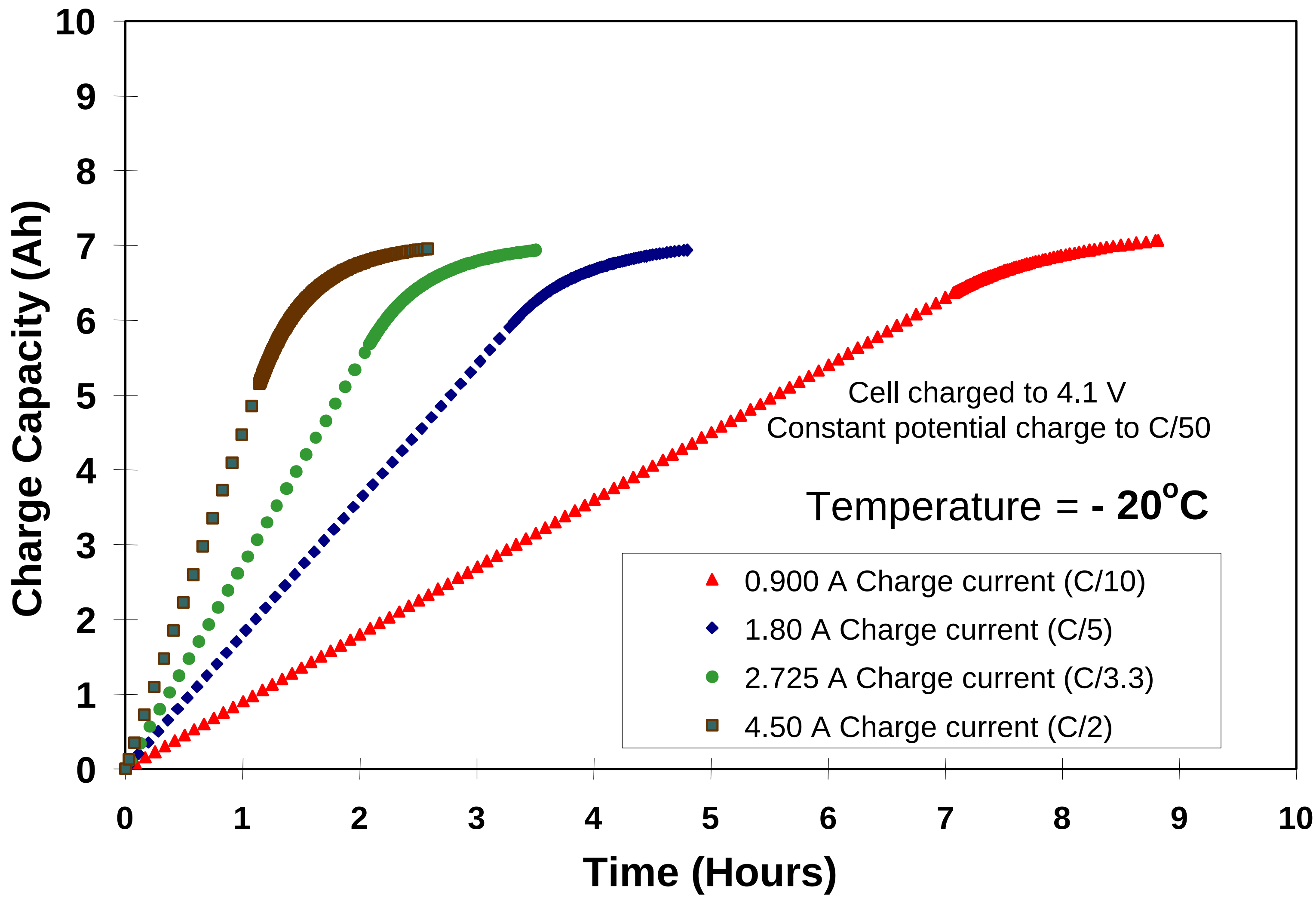
Specific Energy



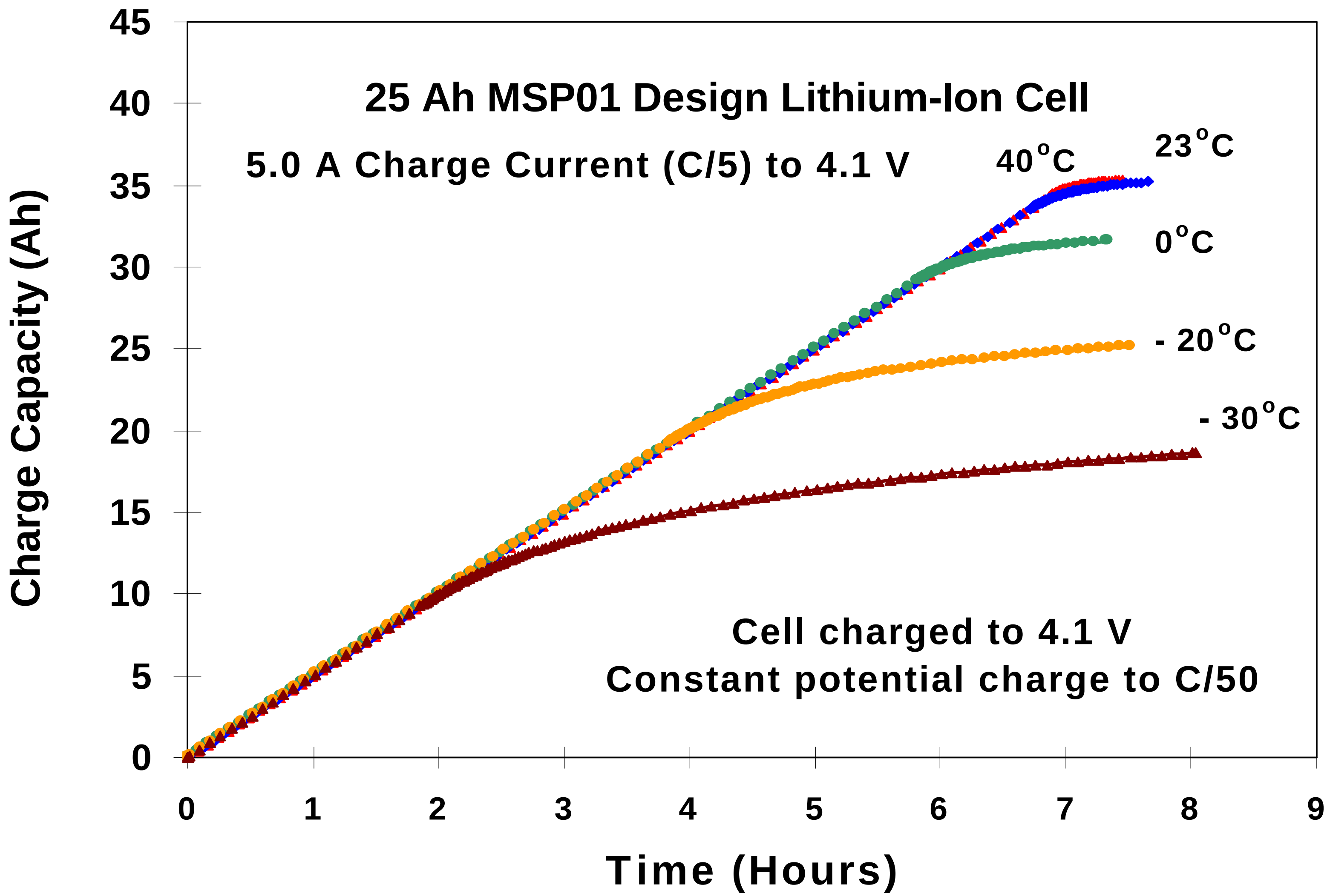
Low Temperature Discharge



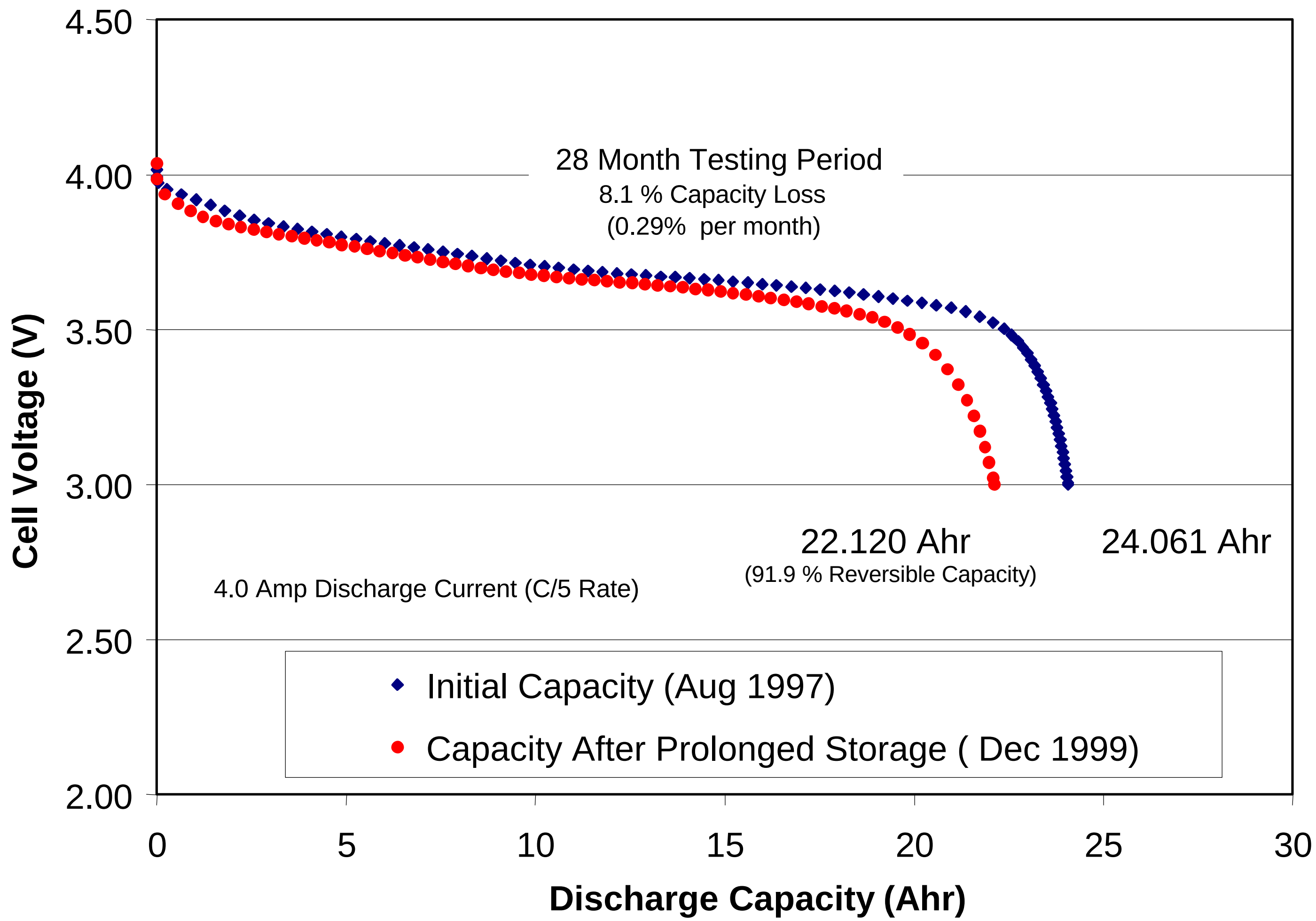
Low Temperature Charge



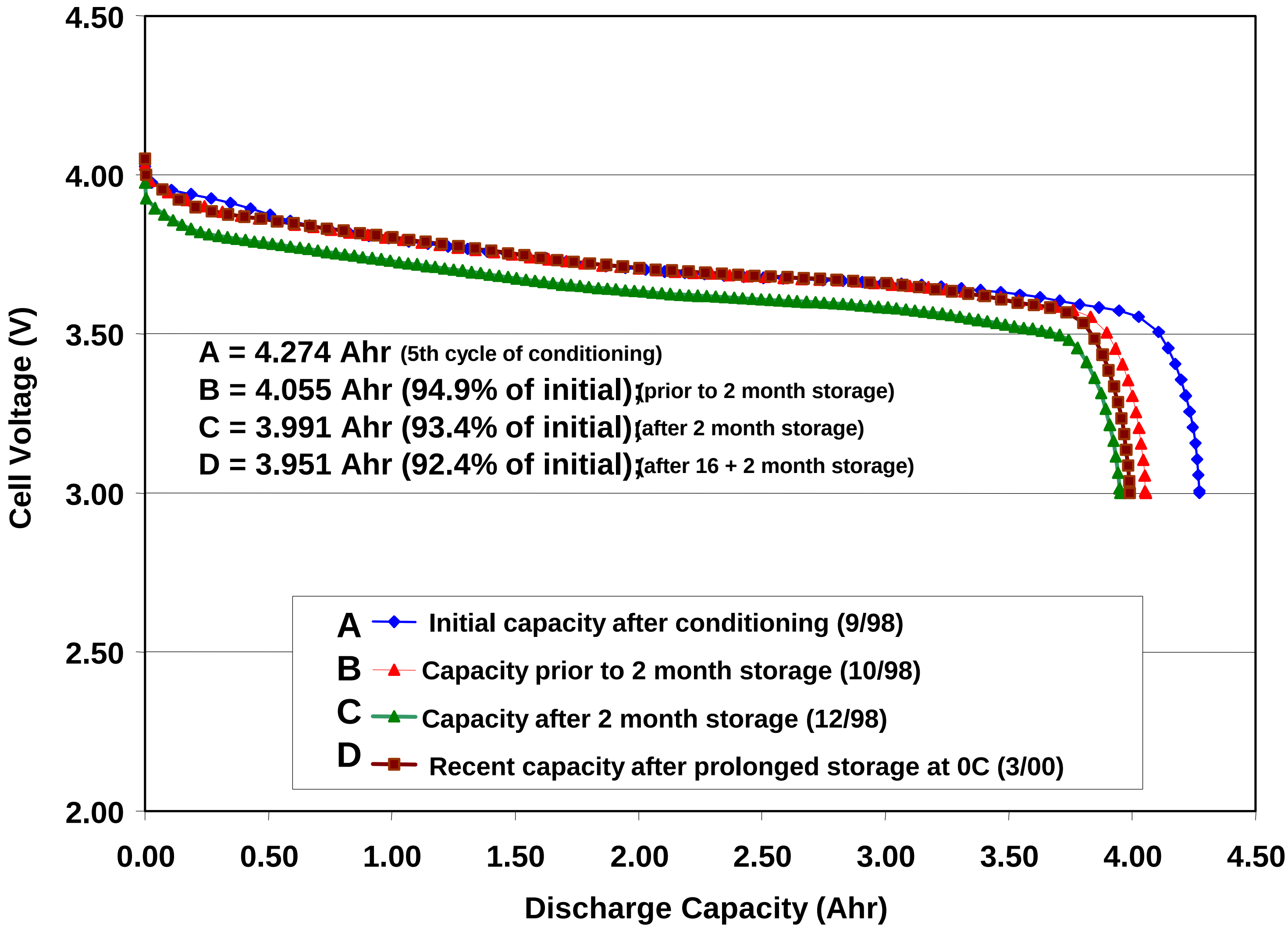
Charge Characteristics of a 25 Ah cell



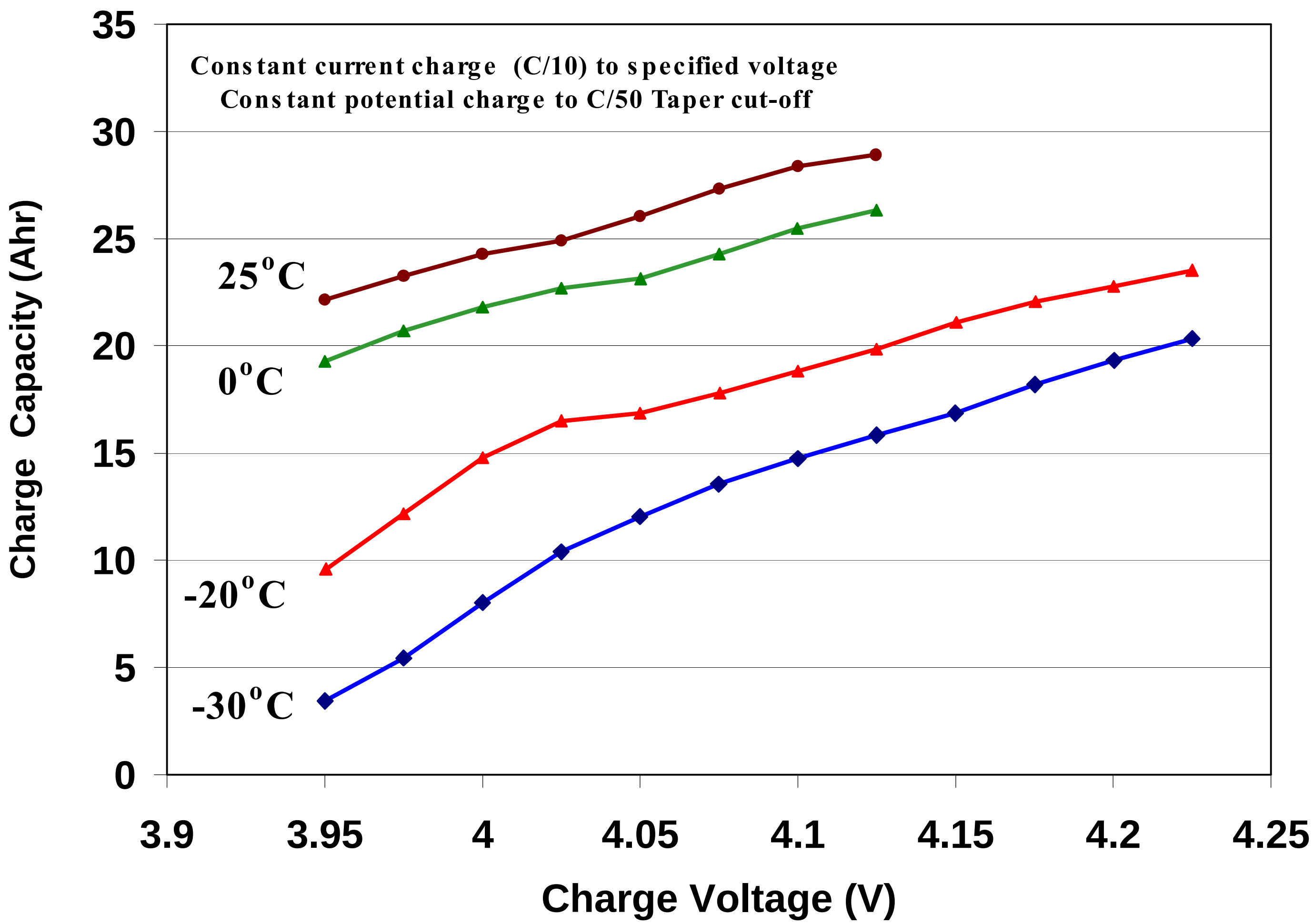
Storage Characteristics



Storage Characteristics



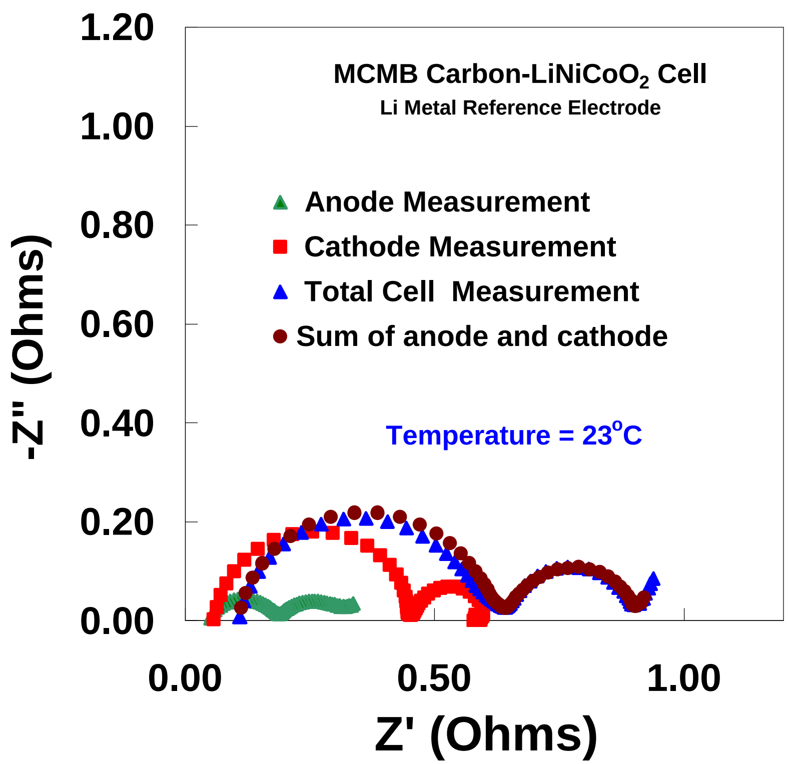
V/T Curves of Li Ion Cells



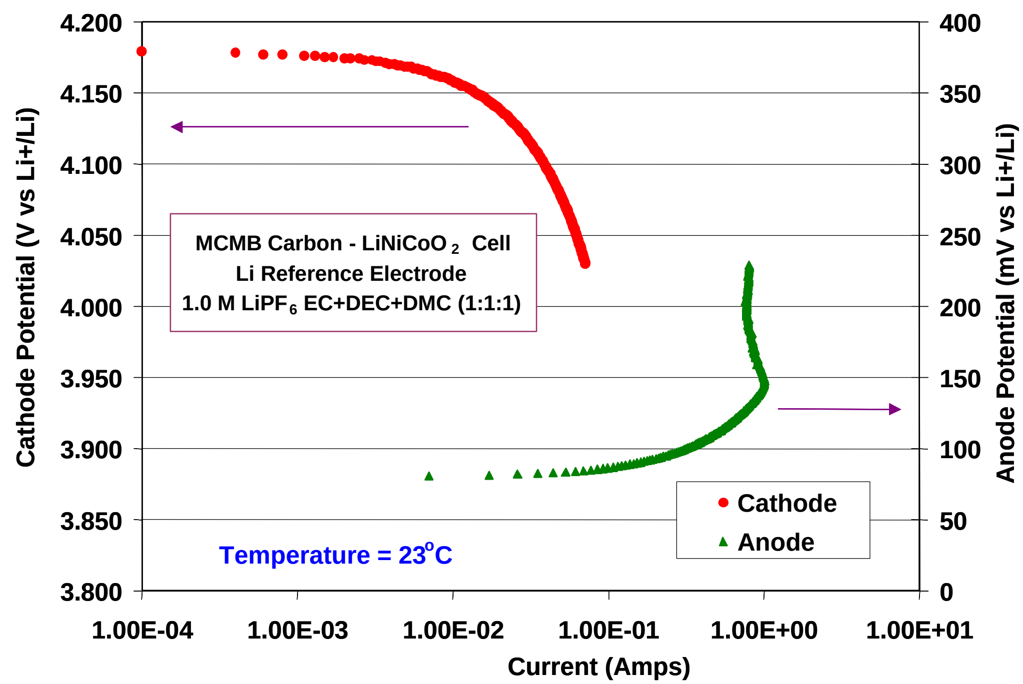
- Are higher charge voltages justified at lower temperature ?
- Need to define specific conditions under which lithium plating can occur (rate and system dependent).

Impedances in a Li Ion Cell

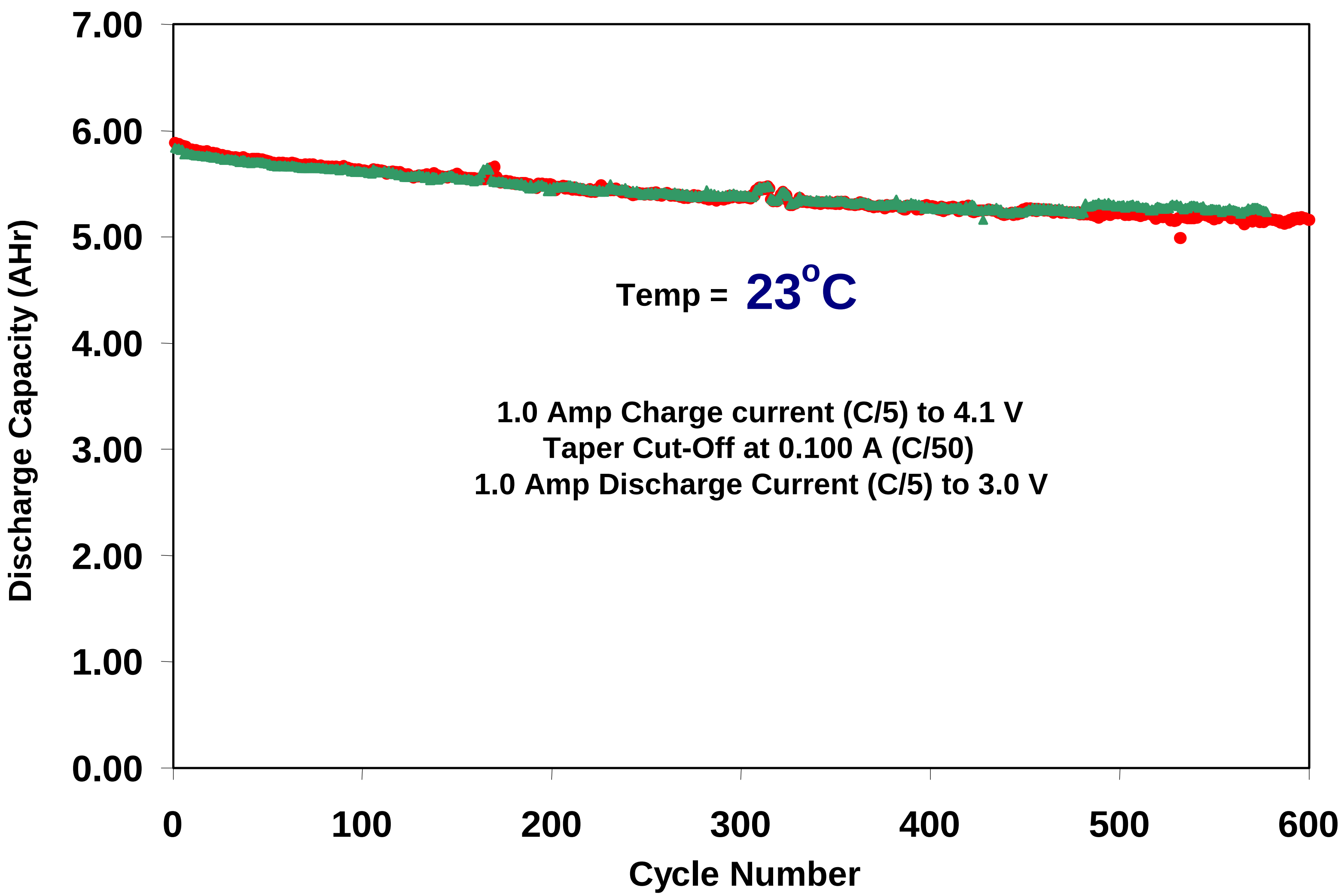
EIS of a Li Ion Cell



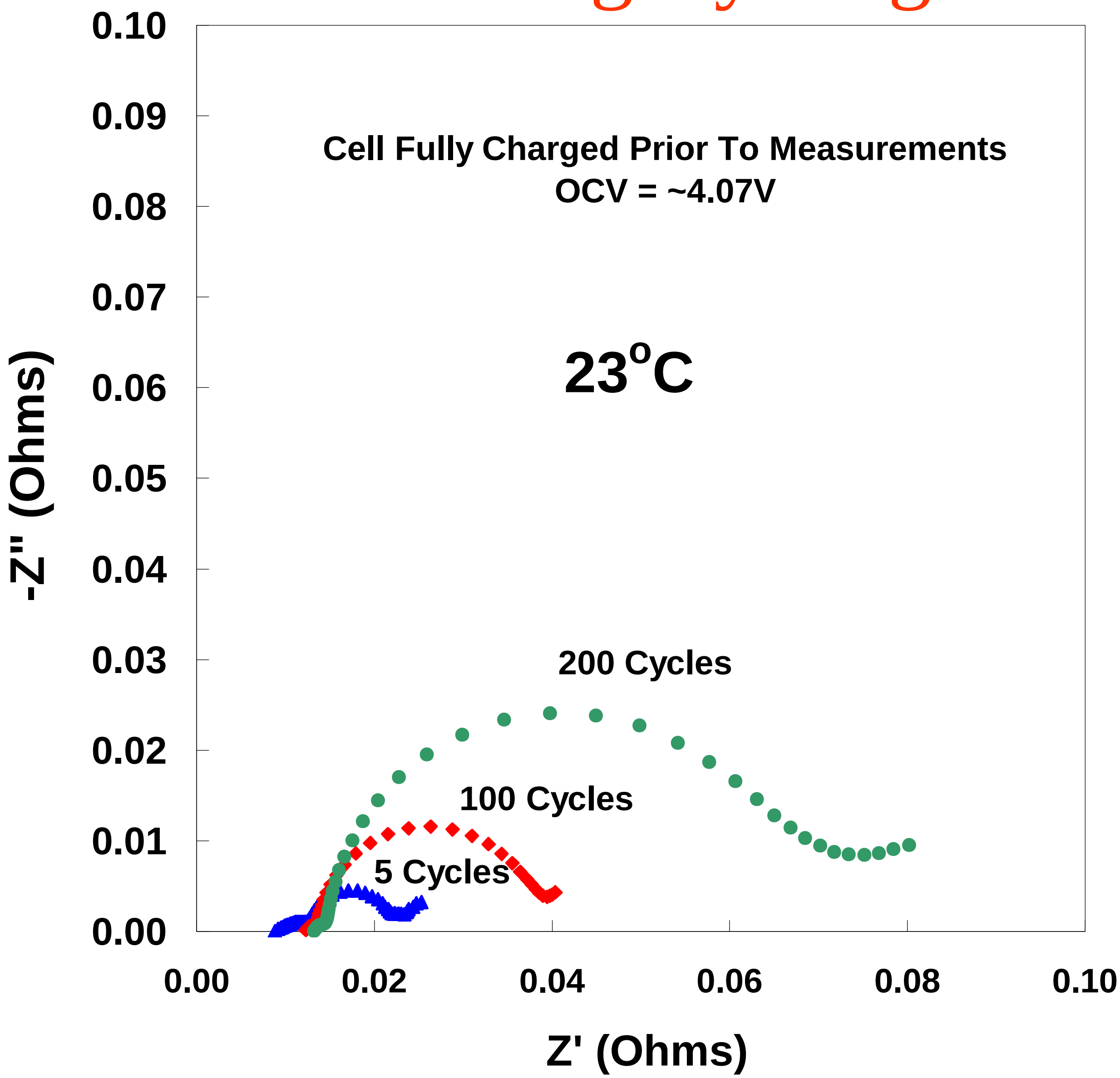
DC Polarizations in Li Ion Cell



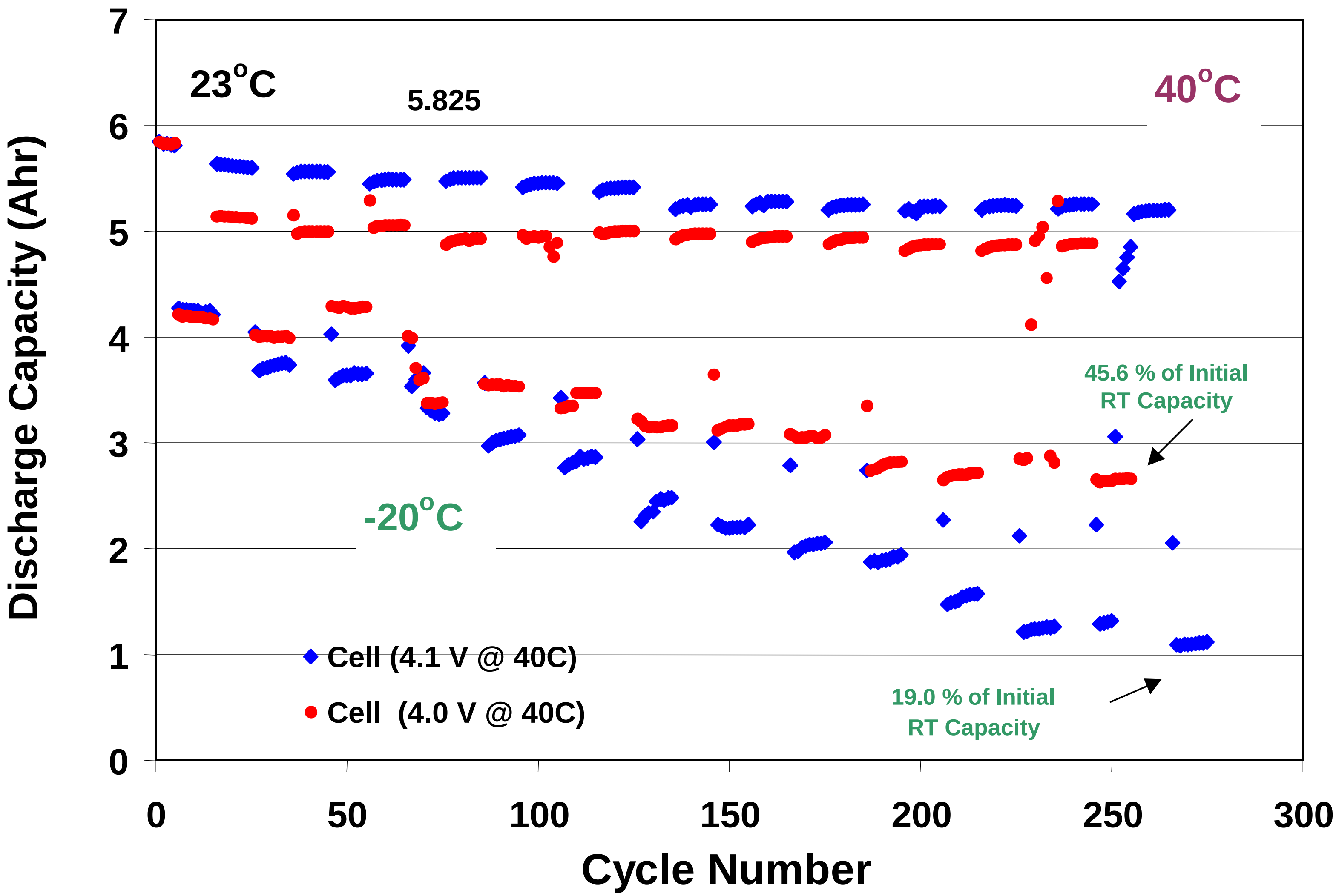
Cycling (100%DOD) at 25°C



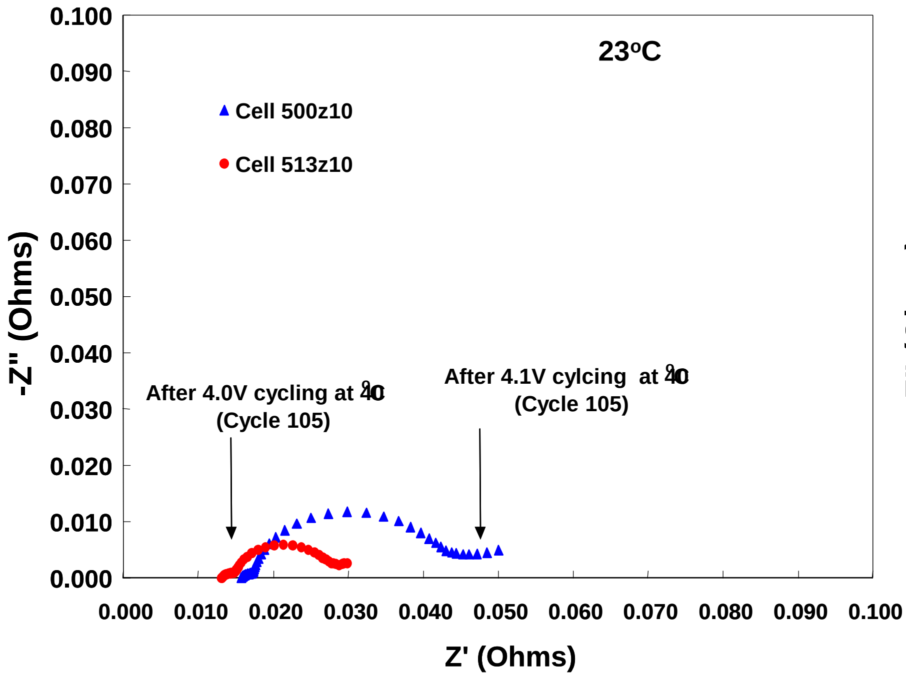
EIS During Cycling

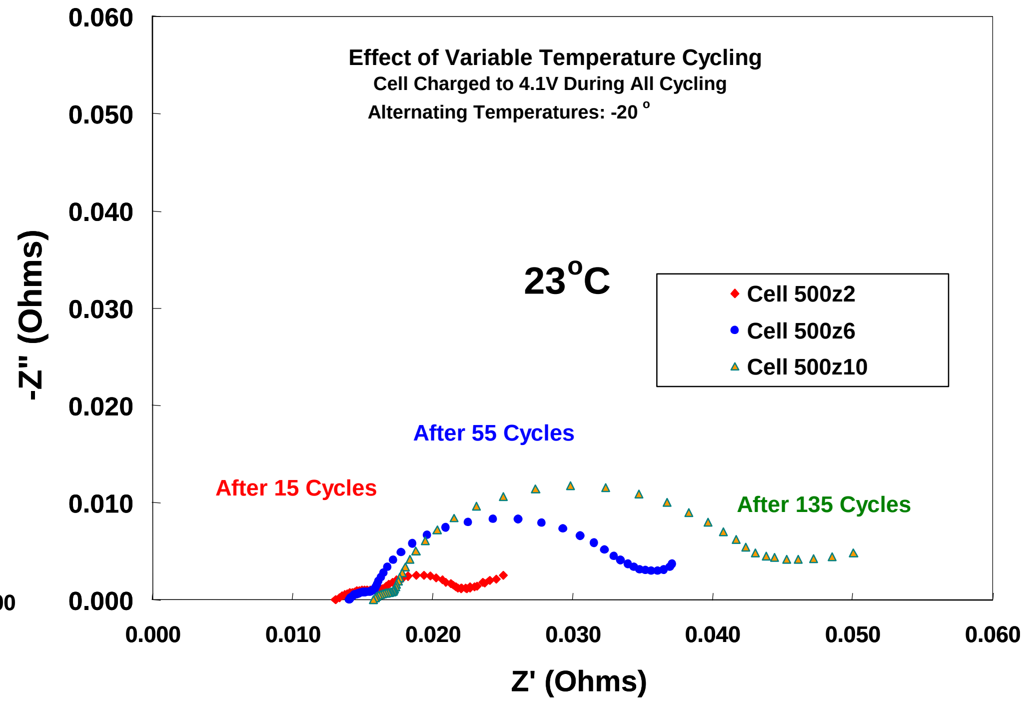


Variable Temperature Cycling

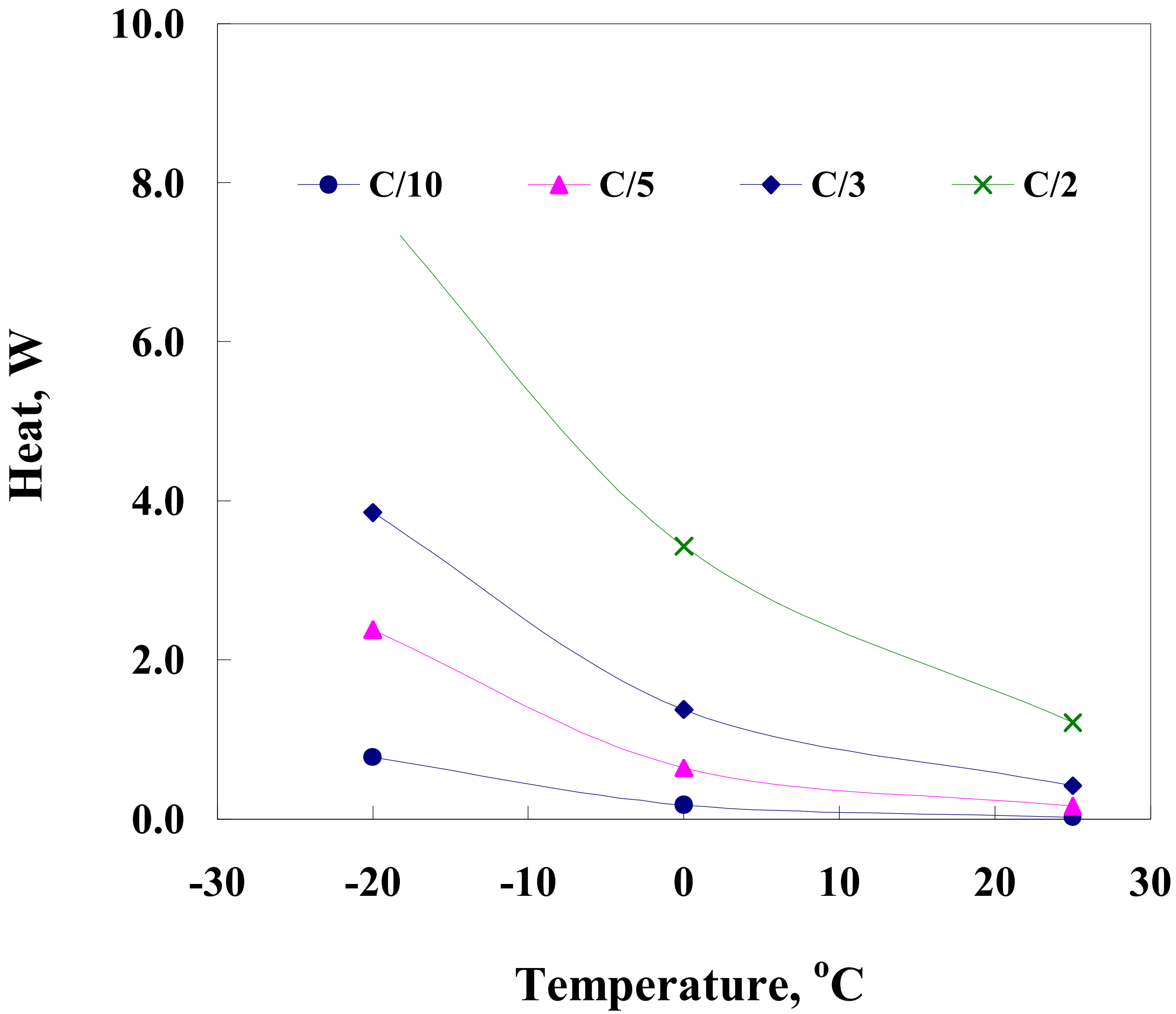


EIS During Variable Temperature Cycling





Heat Generation Rates on Discharge



Safety Events at JPL

- Li Ion Cell Venting upon Inadvertent External short (20-35Ah)
  - No injuries to personnel
  - No damage to equipment
- Li Ion Cell Venting on Extended LT Cycling (5-10 Ah)
  - No injuries to personnel
  - No damage to equipment
- Venting of a pouch (Polymer) cell
  - No damage to equipment

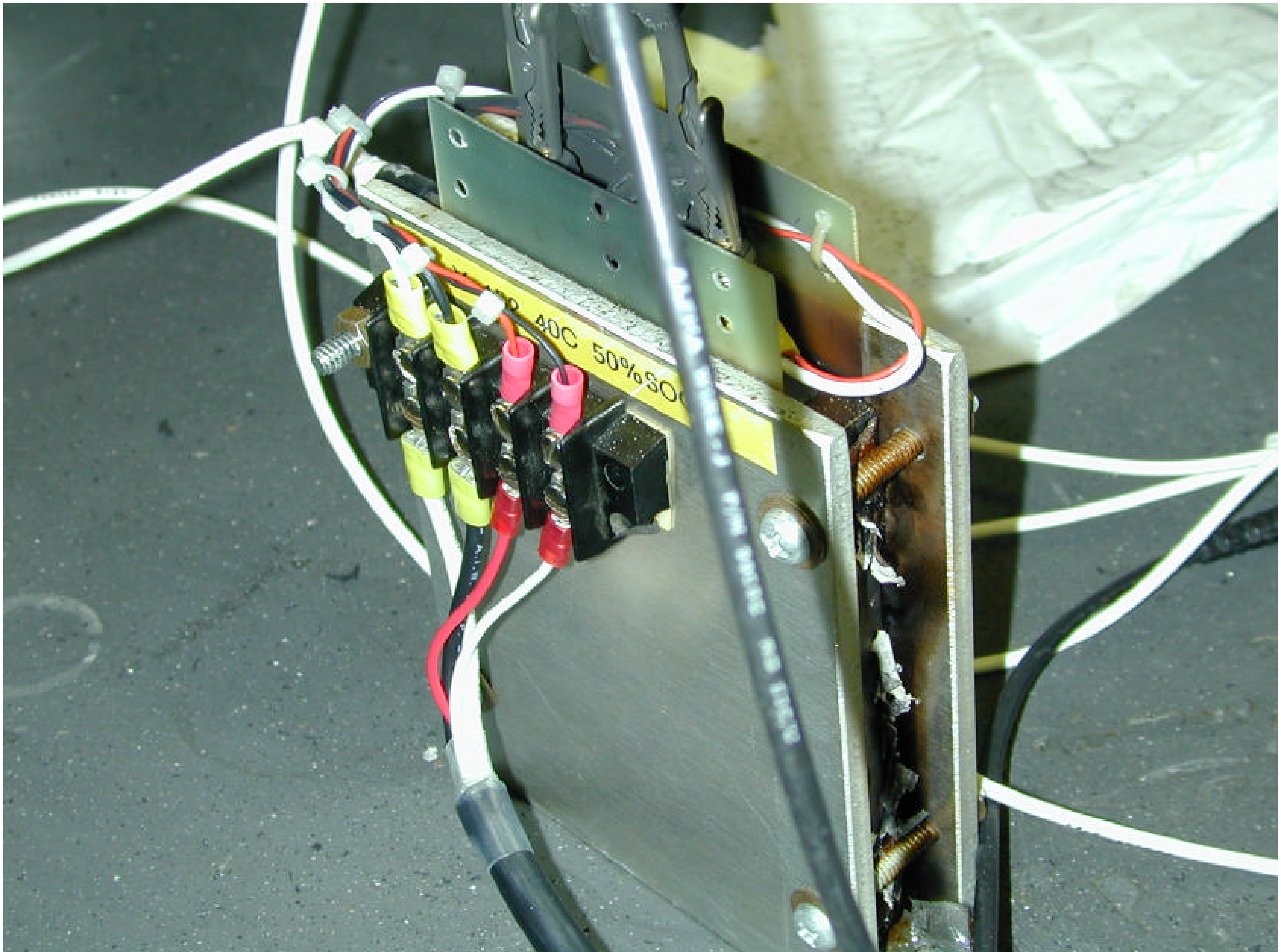
Short Circuit Incident
History of the Cell

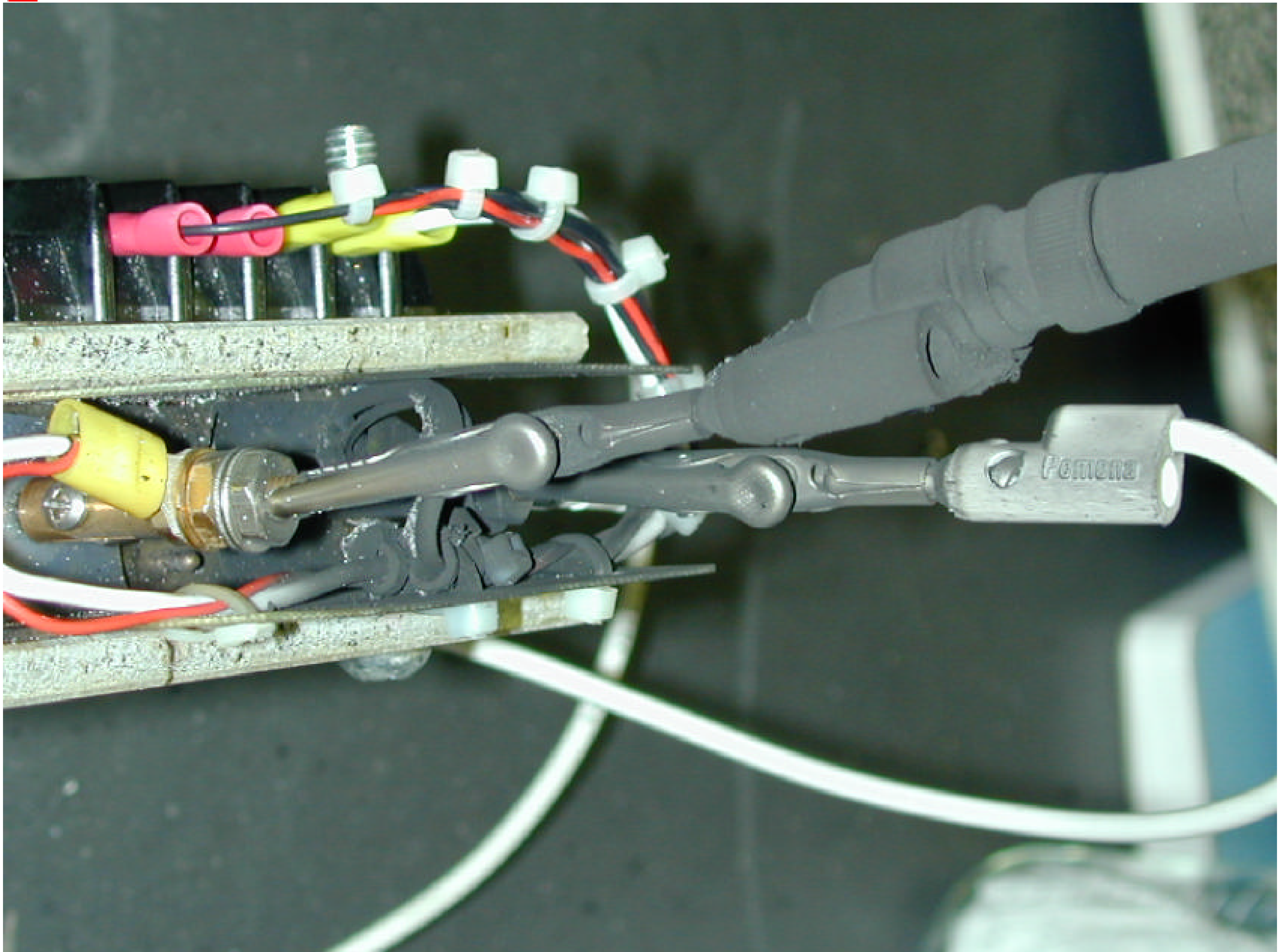
- **2 Month storage in Open Circuit.**
- **10 Month on OCV stand.**
- **Extended storage at 0^{o}C**
- **Mars Mission Profile**
- **AC impedance ***

Storage

25 Ahr Generation I Lithium-Ion Cells

Cell Number and Storage Mode	Initial: Initial Capacity (After Cond.)	Two Month Storage: Capacity Prior To Storage (Ah)	Two Month Storage: Stored Capacity	Two Month Storage: Cell Voltage after 10 Month Storage	Two Month Storage: Capacity After Storage (Ah) 1st Disch.	Two Month Storage: Capacity After Storage (Ah) 5th Disch.	Two Month Storage: Capacity Loss (% of stored capacity)	Two Month Storage: Rever. Capacity (%)	Ten Month Storage: Capacity Prior To Storage (Ah)	Ten Month Storage: Stored Capacity	Ten Month Storage: Cell Voltage after 10 Month Storage	Ten Month Storage: Capacity After Storage (Ah) 1st Disch.	Ten Month Storage: Capacity After Storage (Ah) 5th Disch.	Ten Month Storage: Capacity Loss (% of stored capacity)	Ten Month Storage: Rever. Capacity (%)	Total Reversible Capacity After 12 Months (% from Initial)
151 (0°C and 50 % SOC)	27.879	27.609	14.000	2.565 V	0.000	27.327	100	98.976	26.972	14.000	0.578 V	0.000	27.602	100	102.337	99.006
152 (40°C and 50 % SOC)	28.749	28.021	14.000	3.308 V	1.968	27.479	85.943	98.065	27.918	14.000	0.482 V	0.000	27.675	100	99.129	96.263
178 (0°C and 100 % SOC)	25.475	25.471	25.487	3.982 V	23.114	24.781	9.310	97.289	24.607	24.623	3.762 V	16.996	25.279	30.975	102.731	99.227
201 (40°C and 100 % SOC)	25.674	25.670	25.584	3.834 V	19.611	25.156	23.349	97.998	23.912	23.807	3.608 V	10.309	23.789	56.699	99.486	92.659


40C 50%SOC


Pomona

Summary

- Lithium ion cells developed under the DOD/NASA consortium were found to exhibit:
  - High specific energy (>120 Wh/kg) and High energy density (300 Wh/l)
  - Long cycle life (over 1000 Cycles)
  - Excellent low temperature performance(-20 C Operation)
  - Good storage characteristics

- Three minor safety incidents occurred over a period of three years of testing more than five hundred lithium ion cells of 1-35 Ah sizes.

- Further improvements in cell design will minimize such safety events.

Secondary Lithium-ion Cell and Battery Safety

NASA Battery Workshop 2000

Rob Spurrett & Carl Thwaite, AEA Technology plc, UK

Philip Cowles, COM DEV Ltd, Canada

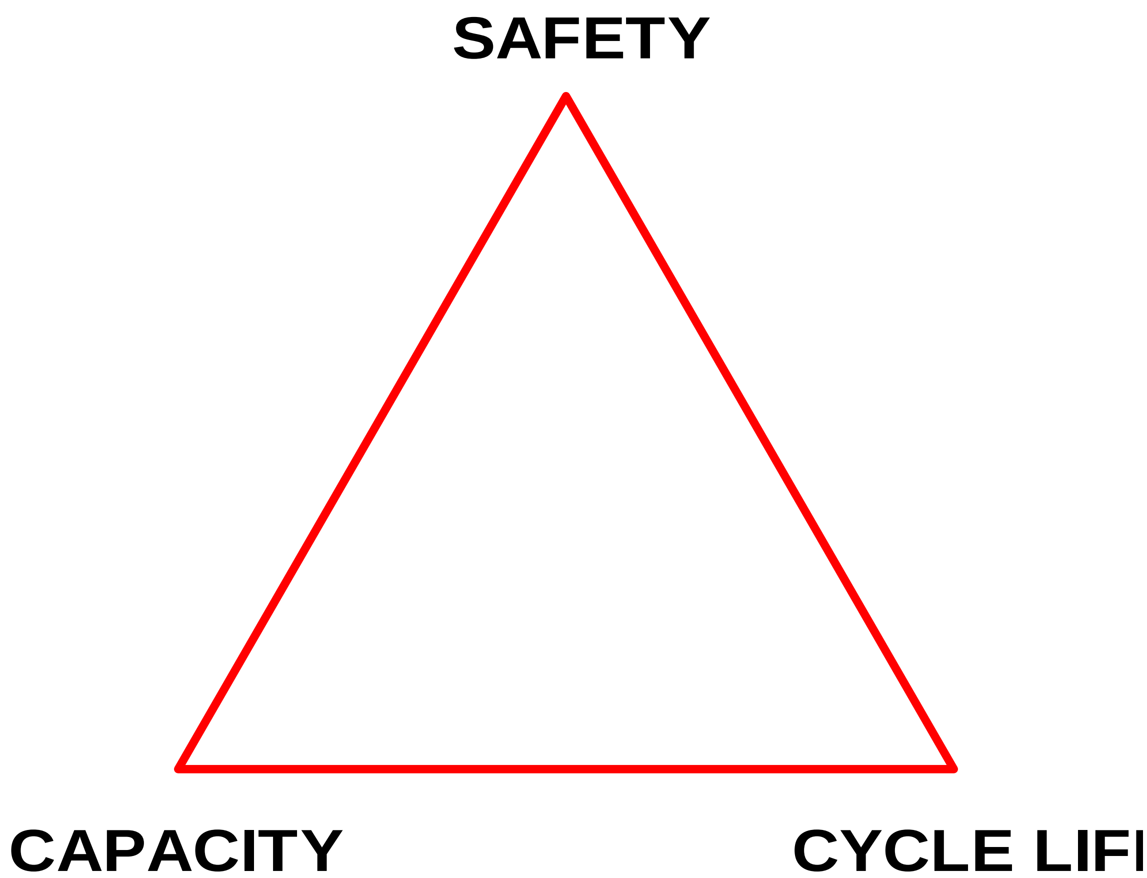
AEA TECHNOLOGY SPACE

COM DEV SPACE GROUP

Introduction

- AEA Technology and COM DEV teamed to build Lithium-ion batteries currently based on the Sony 18650HC (hard-carbon), widely regarded as the safest cell.
- This paper describes
  - the safety features built into Sony 18650HC cell.
  - the formal safety approval tests performed on the cell.
  - safety tests performed as part of the LAT test.
  - supplementary test data from on-going programmes.
- Briefly discusses safety with respect to battery level safety.

Cell Safety Trades - 1

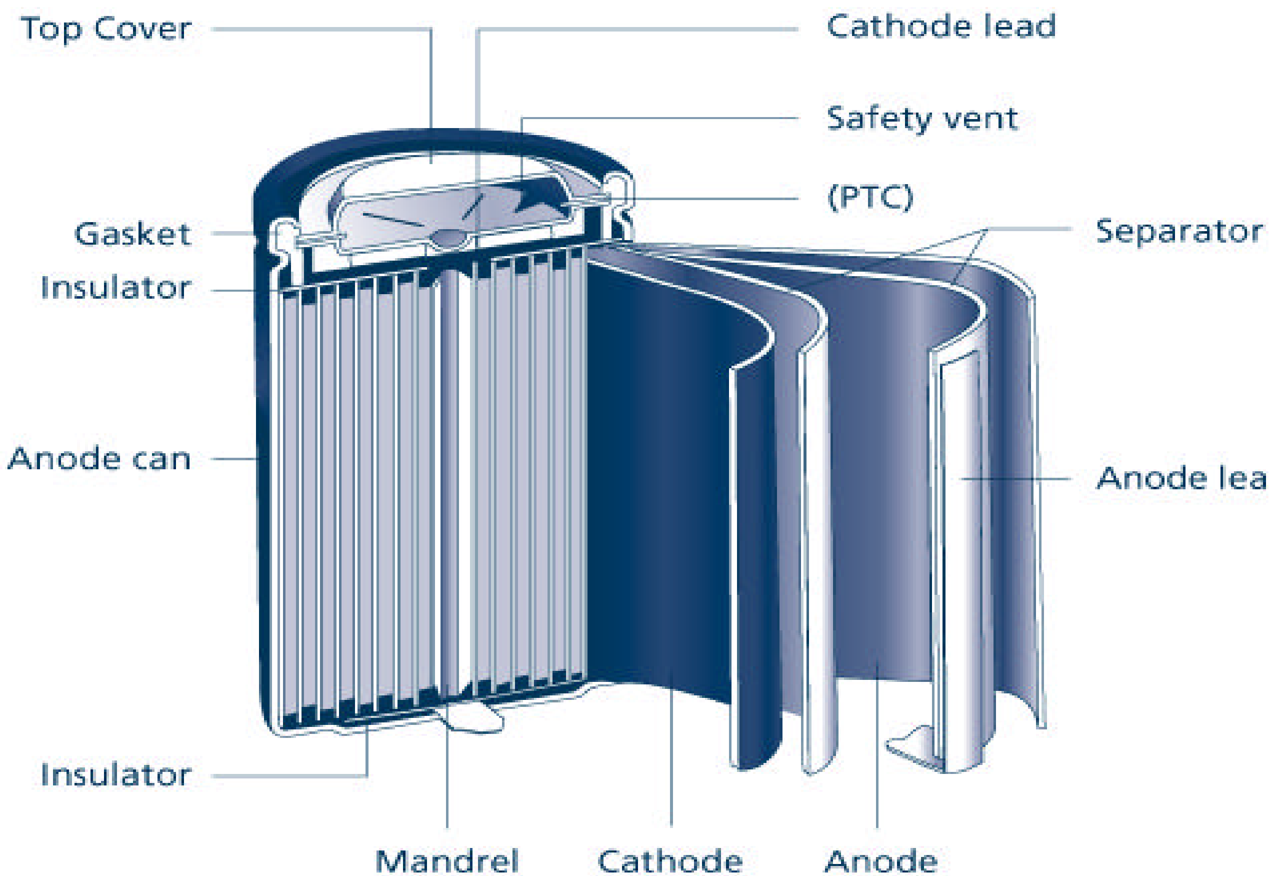


Cell Safety Trades - 2

- AEA Technology provides contract R&D to every major Japanese cell producer.
- Secondary Lithium-ion cell design is a trade of safety, capacity and cycle-life.
- Optimise any two from three, but optimising all three is tough.
- Sony 18650HC, the first generation commercial cell, was principally optimised for cycle-life and safety.
- Most commercial cells are optimised for capacity and cycle-life, leaning very strongly towards capacity.
- For most new producers, safety is always a secondary concern, until the required capacity/cycle-life has been achieved. This is a BIG MISTAKE!

Sony 18650HC Cell

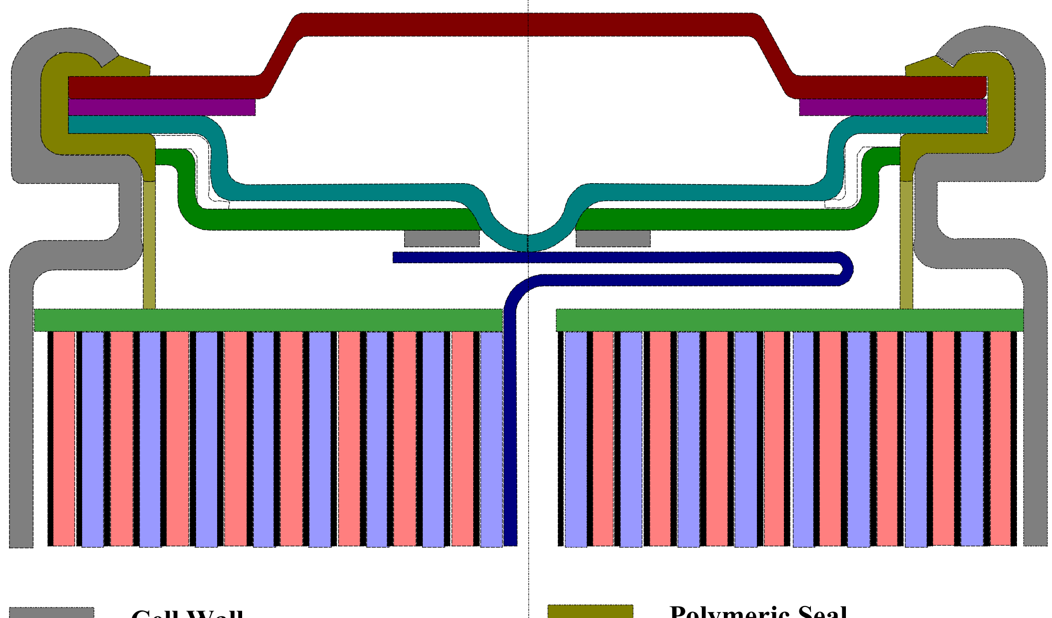
- ∅18mm, 65mm long
- 1.5 Ah capacity
- 5.4 Wh energy
- 133 Wh/kg
- Hard carbon anode with PVDF binder
- $LiCo_2$ with PVDF binder
- DEC/PC electrolyte, 1M $LiPF_6$



Safety Features - 1

- Over-charge Protection
  - Non-reversible, triggered on over 100% overcharge
  - Internal pressure rises to ~10 bar and breaks an internal connection
  - Ensures that the cell fails open circuit
- Shut-down Separator
  - Non-reversible
  - Microporous, melts at T>120degC to shut down reaction
- Over-current (short-circuit) Protection
  - Reversible Positive Temperature Coefficient (PTC)
  - Thermally operated in seconds - does not impact fuse blowing capability
- Cell vent
  - Operates to release internal pressure if safety mechanisms described above fail

Safety Features - 2



Cell Wall

Top Cover

PTC Annular Ring

Pressure Disk

Cathode Tag Support

Cathode Tag Mounting Disk

Cathode Tag

Polymeric Seal

Possible Seal Extent (SONY Diag)

White Polymer Collar

Polymer Electrode Roll Isolator Disk

Cathode

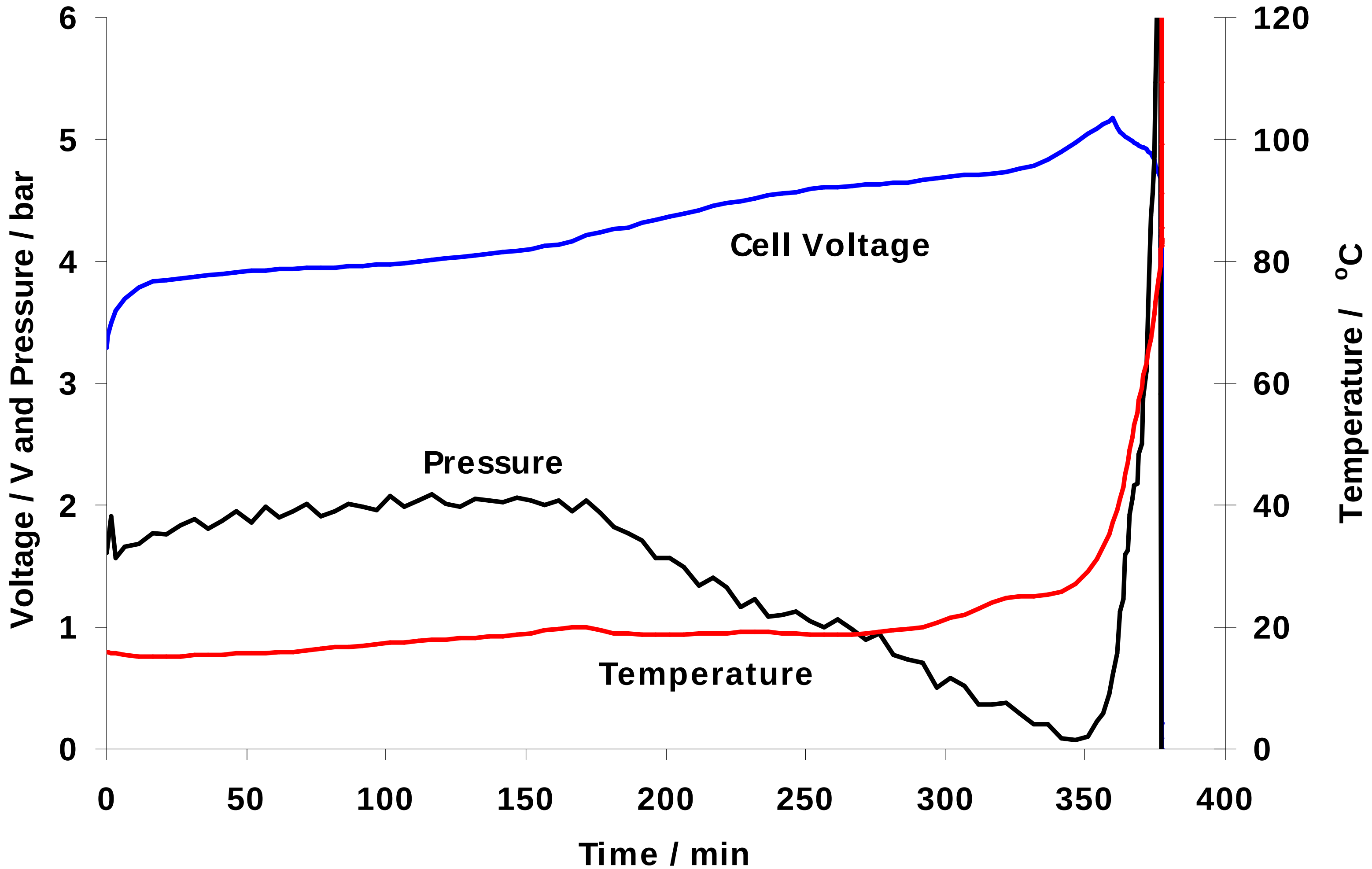
Anode

Electrode Separator

Overcharge Design - 1

- Cell overcharge protection is **essential** for safe battery operation
- For complete safety, we think the device should be - autonomous, highly repeatable, non-electronic, safe against inadvertent operation
- Typical properties from a constant current charge on a Lithium-ion cell are shown on next slide
- A protection mechanism can trigger on: temperature, pressure, chemical, or over-voltage
- Sony picked pressure (on the grounds of inadvertent operation)
- Downside is that to trigger on pressure, a gassing agent must be added, Sony add $LiCo_2O_3$
- Gassing agents have an impact on capacity/cycle-life

Overcharge Design - 2



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PROPRIETARY INFORMATION

Overcharge Design - 3

- For the Sony 18650HC cell recommended EOCV is 4.2V +/- 50mV
- Hard-carbon + DEC/PC electrolyte, tolerant to high charge voltage
- High margin on overcharge
- Up to 4.3V little impact on cycle-life - data later
- Typically need 100% overcharge to trigger the device
- Device operates at 4.7V to 5V
- Despite many ‘incidents’ over eight years of making batteries for space and terrestrial applications, we have **never** had an explosion or fire with Sony cells .

SAFETY TESTS

Safety Tests - 1

- Tests to standard IEC requirements performed by Sony and some tests repeated by AEA Technology
- All tests repeated for accreditation by Underwriters Laboratory in US - http://www.ul.com
- Conform to standards
  - UL-1642 Lithium-ion cells
  - see http://ulstandardsinfonet.ul.com/scopes/1642.html
  - SU-2054 Lithium-ion battery packs
  - see http://ulstandardsinfonet.ul.com/scopes/2054.html
- Following table summarises the tests and pass/fail criteria
- All cells passed

Safety Tests - 2

	Condition	Results
Spike Penetration	Five Inch Spike	No Gas
Crush I	13 kg Iron	No Fire
Crush II	ϕ 16 Bar	No Fire
Drop I	1.5m Height	No Leakage
Drop II	1.0 m Height	No Difference
Drop III	10 m Height	No Gas
Abnormal Voltage I	+35V 46A	No Gas
Abnormal Voltage II	-35V 46A	No Gas
Abnormal Voltage III	-13V 46A	No Gas
Over Charge	2A 5V	No Gas
Salt Water	5% Salt, 24H	No Fire
Burn	Gas Burner	No Explosion
Heat	Hot Plate	No Explosion

Safety Tests - 3

	Condition	Results
Micro Wave	Micro Wave Oven	No Fire
Hot Water	100°C	No Gas
Heated Oil	180°C	No Fire
Melted Solder	230°C	No Explosion
Internal Short Circuit	Pin Holed Separator	No Gas
Short Circuit	$< 15\ m\Omega$	No Fire
AC Input	100 V	No Explosion
Drilling	ϕ 4	No Fire
Weak Welding		No Difference
Low Pressure	1mm Hg 1 min	No Difference
Weather	-20°C, 1H - 25°C, 1 Day	No Leakage
Hot Temperature	85°C, 72 H	No Difference
Low Temperature	-40°C, 3 Days	No Difference

LAT SAFETY TESTS

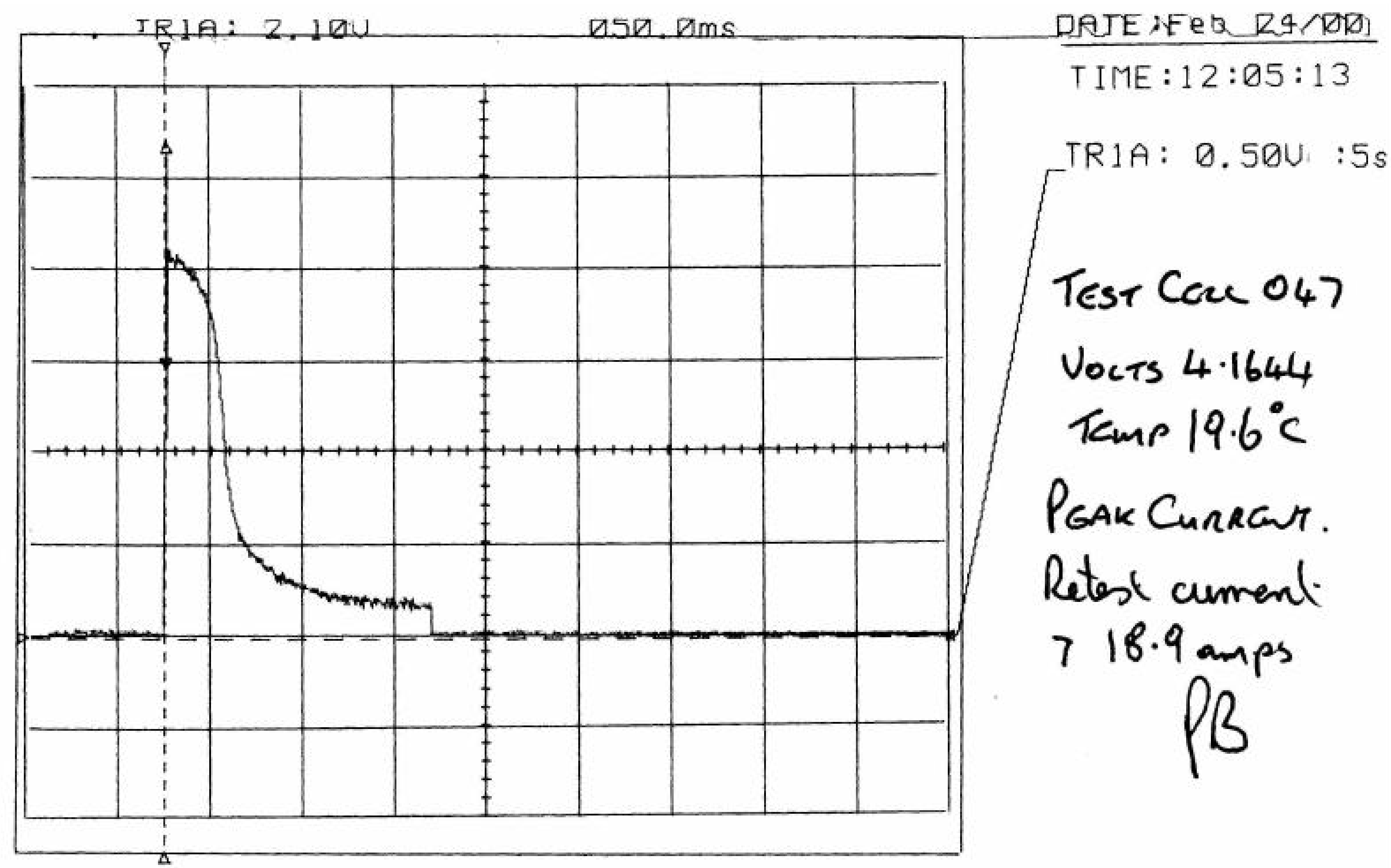
LAT Safety Tests

- Lot Acceptance Test (LAT) performed by AEA Technology/COM DEV on samples of 84 cells taken from every batch
- LAT is adapted from ESA SCC hi-rel component specifications
- LAT includes relevant abuse testing and verification of cell safety features

Overcurrent Protection - 1

- Purpose: to validate operation of the overcurrent protection
- Performed on six fully charged cells from each 84 cell sample
- Cells shorted with a 100mΩ resistor at ambient temperature
- Pass/fail is for peak current > 15 A (10C)
- Falling to < 2C in 10 seconds
- Allowed to stabilised for 1 hour
- Repeatability tested - deliver same peak current within 10%
- Following slide shows typical current history - time base 5 sec per division and volts 0.5V per division measured across 100mΩ
- Typical spacecraft fuse blowing requirements are easily met

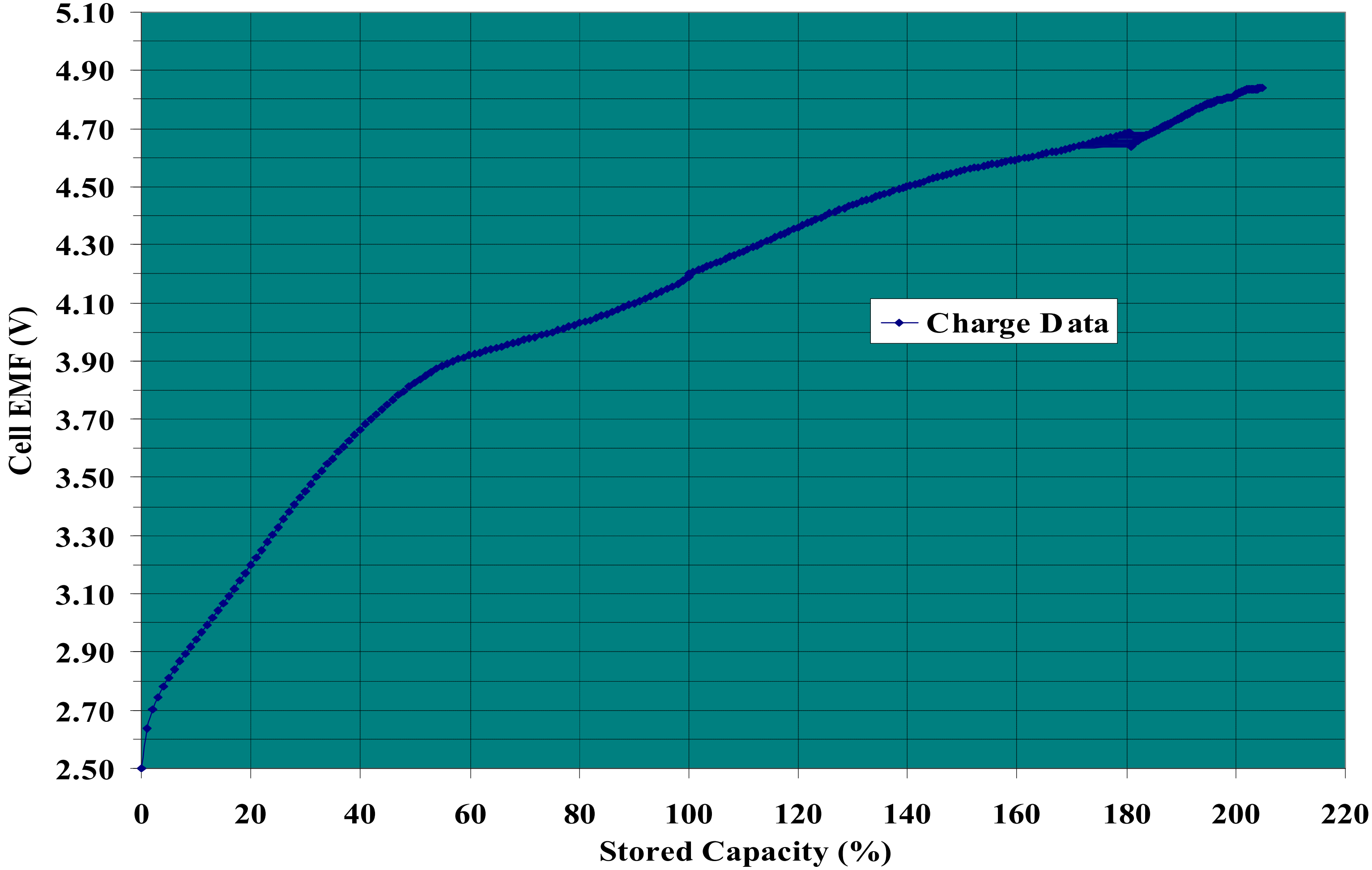
Overcurrent Protection - 2



Overcharge Protection - 1

- Performed on the same 6 cells subjected to overcurrent test
- Cells charged at C/10 until failure (overcharge operates)
- Typically takes 10 - 11 hours from fully charged to operate the disconnect, i.e. an overcharge of at least 100%
- Voltage and temperature monitored
- No significant temperature rise (<3 degrees)
- Disconnect operates between 4.7V and 5.0V
- Current drops to 0mA - high impedance tested
- Test followed by Destructive Physical Analysis to verify correct operation of the device.

Overcharge Protection - 2



Thermal Shock/High Temperature

- More demanding than *IEC 5.3.2 Thermal Shock Test*
- Also performed at higher temperature than *IEC High Temperature Storage Test*
- Before cycling cells are subjected to qualification level vibration (LLS, HLS, random at $30g_{rms}$ 4 minutes per axis, plus 100g 0.5msec shock)
- Cycle up to $80^{o}C$ then down to $-20^{o}C$
- Repeated three times
- Dwell time at each temperature 2hours
- Time for temperature transition < 1 hour
- Performed on six cells from each 84 cell sample
- Full electrical performance required for a 'pass'

Burst Pressure Tests

- Really a test of the cell seal rather than the cell can
- Lower end of cylindrical can removed
- Active contents of cell removed
- Pressure applied hydraulically to limit of test set-up
- 450 p.s.i. (31 bar)
- No detectable leakage or fall in pressure
- (Additionally, as part of the LAT, the leak-rate of the seal is measured in a vacuum with a helium leak detector.)

AEA TECHNOLOGY SPACE

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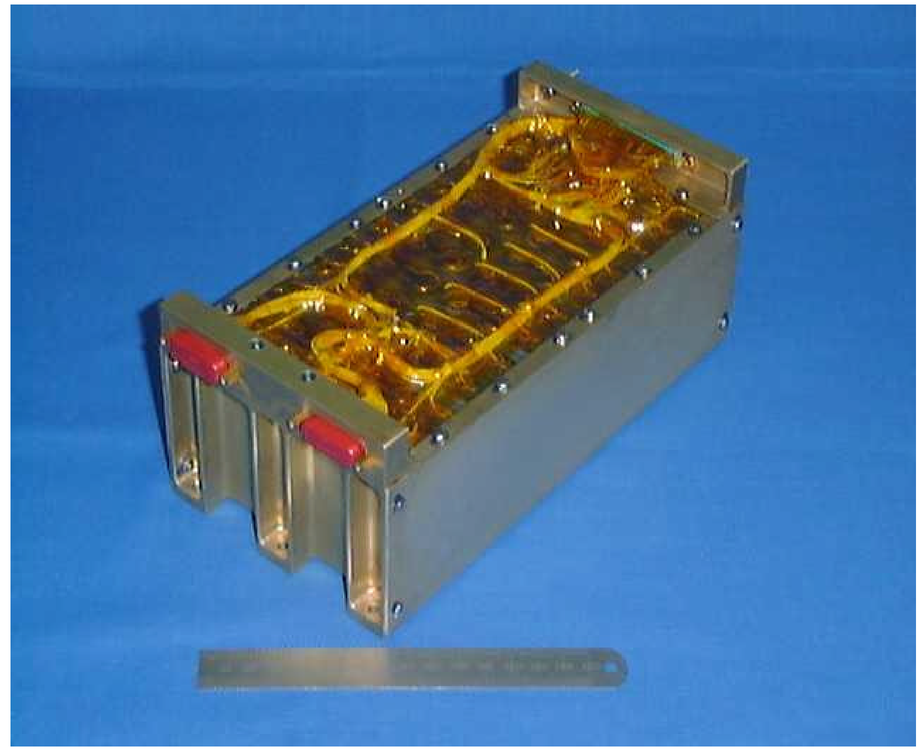
SUPPLEMENTARY DATA

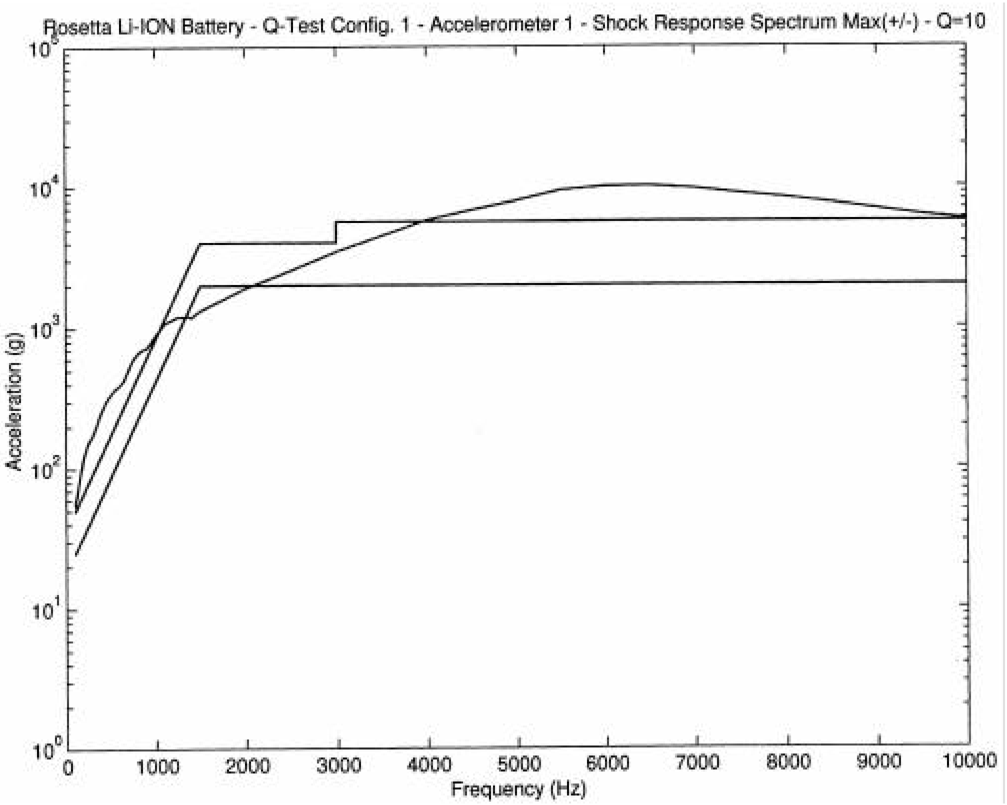
ROSETTA Satellite Battery

- ESA Cornerstone mission to comet Wirtanen
- Battery of 1070 Wh
- Three modules, each 6s - 11p
- Battery mass 9.99 kg
- Battery energy 107 Wh/kg
- Qualification complete
- Flight models manufactured and undergoing acceptance testing
- Launch date: 2003



Shock

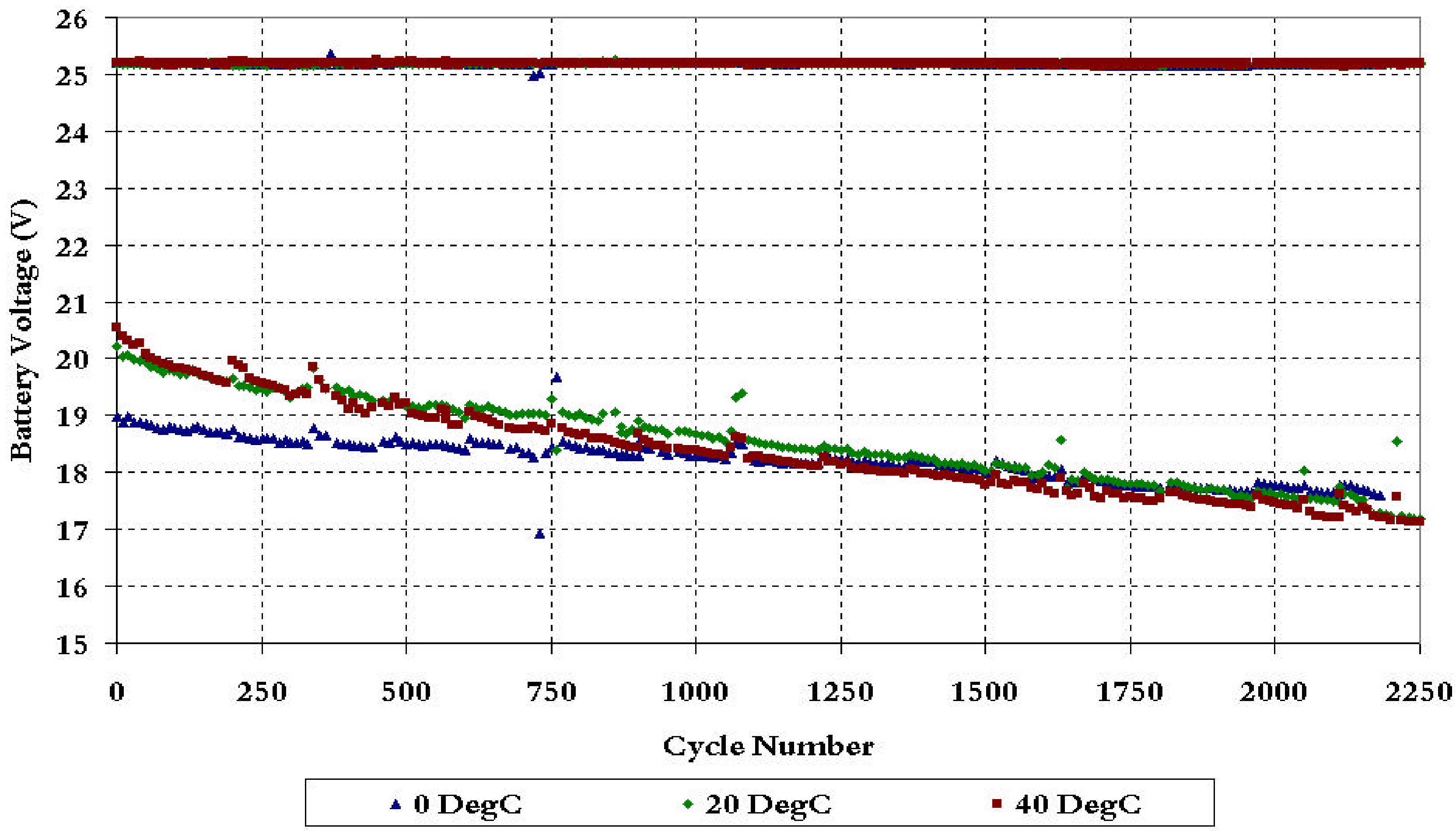
- Recent spacecraft requirements well in excess of IEC 5.2.1
- ROSETTA qual at 2,000g at 1.5 to 10 kHz (+9dB,-6dB)
- Actual pyrotechnic qualification test achieved peak levels >10,000g at 6kHz
- Repeated in all three axes
- Followed by sine and random vibration
- No failures



Reverse Polarity - 1

- Three batteries undergoing life-test at 0, 20, 40degC
- Battery configuration 6s-2p
- GEO throughput cycling regime - 60% constant DOD
- Accidental reverse polarity at 350 cycles following a capacity measurement
- Battery cells severely imbalanced
- Half of the cells over discharged
- Half the cells overcharged to almost 4.3V
- Since completed 2,250 cycles and ongoing (equivalent to a 25 year life)
- The incident had no apparent effect upon battery cycle-life

Reverse Polarity - 2

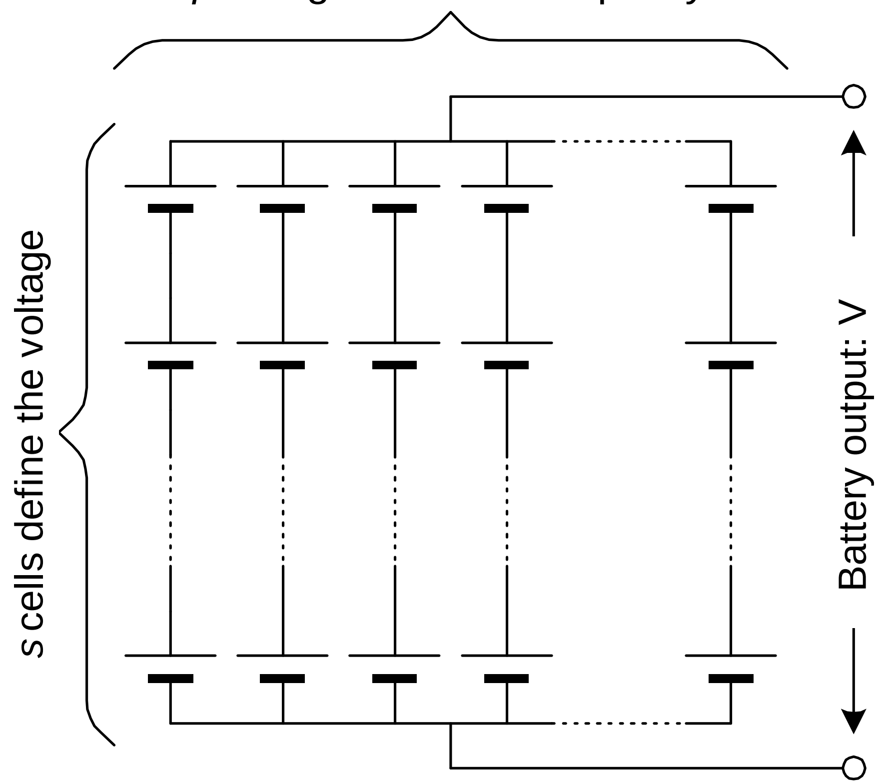


An Alternative Crush Test!

- Sony cells from a mobile phone
- Phone crushed by a SUV - cell ends severely crushed!!
- Cells still work fine!
- Capacity 1.36 Ah each
- Energy 4.99 Wh
- Some capacity fade from 2 years use, as expected

Battery Protection

- Charge/discharge at battery level voltage to *s x 4.2V*
- Cell O/C failure
  - Loose a string (not acceptable for ‘big’ cells)
- Cell C/C failure
  - Overcharge cells in the same string
  - Each string has many other ‘fuses’ in series with failed cell
  - Loose string O/C (for Sony cell)
- Topology is highly robust to cell failures

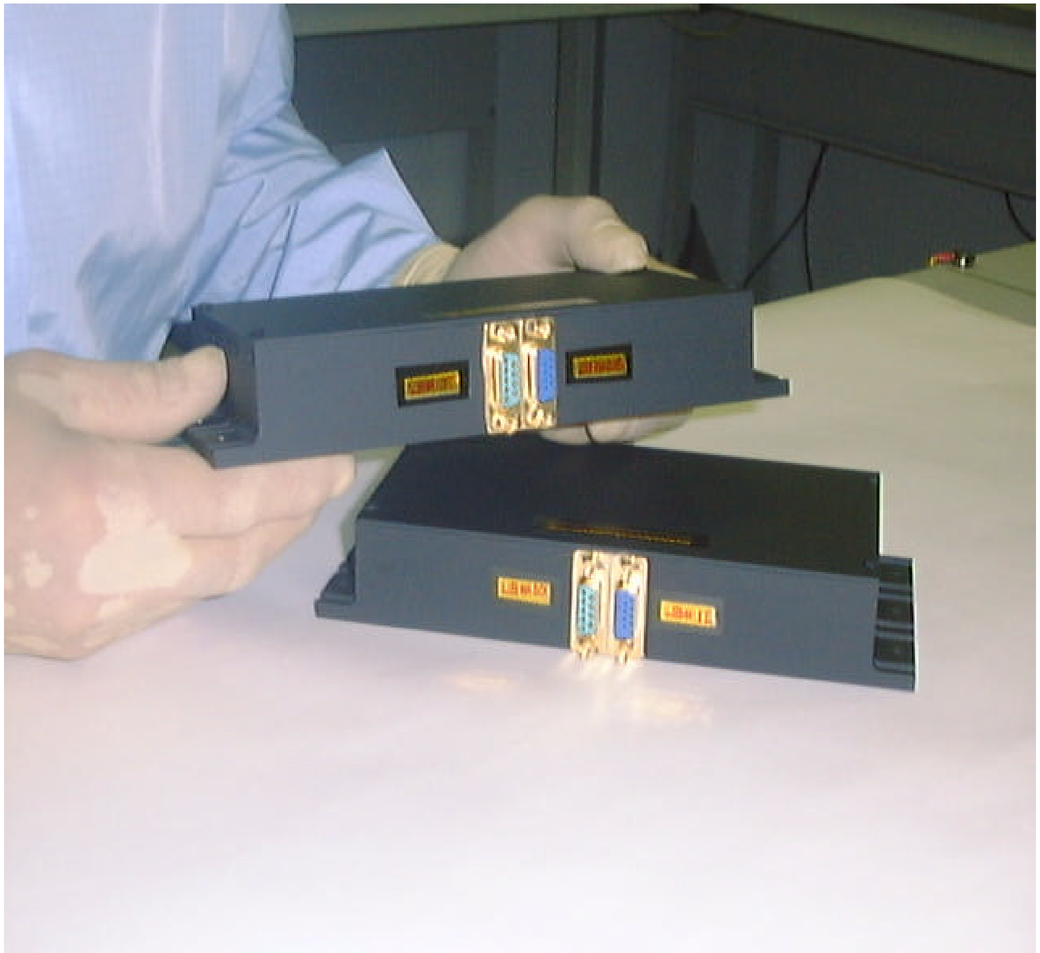


s-*p* topology

Conclusions

- Over 2 million cell-hours of space testing, plus many more cells used to make military batteries from Sony cells, without serious incident
- Safety reviews conducted by ESA and most European Primes in anticipation of forthcoming launches of:
  - Mars-Express
  - PROBA
  - RoLand
  - ROSETTA
  - Beagle2 batteries
- STRV-1d battery also passed full safety reviews by Arianespace
- Successfully launched on Ariane 507 last night (November 15th 2000)

STRV-1d



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