



## LEO Cycling Performance after Zero Volt Storage of 8 Series Test Module with EnerSys Lithium Ion Chemistry for the Aerospace Application





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## Outline

1. History of product development in EnerSys Advanced Systems (EAS) – ABSL – Quallion

## 2. Introduction of ZeroVolt technology (Cell level tests)

- 1. ZeroVolt chemistry design verification
- 2. ZeroVolt cell characterization for aerospace application

## 3.8 cell series module evaluation

- 1.0V storage characterization for 4 months
- 2. Module characterization during 20% DOD LEO cycling after 0V storage

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# EnerSys Advanced Systems

## \$100M Division Consisting of 6 Business Units

- Space
  - Launch Vehicles
  - Satellites
  - Manned
  - Interplanetary & Landers

### • Aviation

- Fixed Wing & Rotary Aircraft including F16/18 & 777
- UAV's & Target Drones

## • Munitions

- Missiles & Smart Weapons
- Guided Bombs & Projectiles
- Electronic Fusing
- Land
  - Combat, Tactical & Unmanned Ground Vehicles
  - Microgrids & Forward Operating Bases
- Sea
  - Submarines
  - Unmanned Underwater Vehicles
- Medical
  - Cochlear Implant Speech Processors
  - Neromodulation
  - Pumps









Aviation









# **Facility Locations**

## EnerSys Advanced Systems

- EAS Manufacturing Facilities
  - Sylmar, CA
  - Santa Clarita, CA
  - Longmont, CO
  - Warrensburg, MO
  - Horsham, PA
  - Tampa, FL
  - Culham Oxfordshire, UK
  - Newport, UK
  - Zwickau, DE



#### **Product Line Main Manufacturing Locations Brands** Technology Lithium-Ion Materials, Cells & ABSL/Quallion Longmont CO, Sylmar CA, Culham UK Space **Batteries** Medical Quallion Lithium-ion Cells & Batteries Sylmar CA Munitions EAS, Enser Lithium Primary/Liquid Reserve Horsham PA, Tampa FL Land & Sea Hawker/Armasafe Lead Acid (Thin Plate), NiZn Warrensburg MO, Zwickau DE Lead Acid (Thin Plate), Ni-Cd & Warrensburg MO, Sylmar CA, Aviation Hawker/Quallion Newport UK, Zwickau DE Lithium-ion

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## Overview of Battery Industry Battery Market Stratification



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EAS / Quallion is a full service provider with expertise at all stratifications of the battery market.

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## ABSL – Quallion – EnerSys Advanced Systems Aerospace Application



## Quallion – EnerSys Advanced Systems Medical Application





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# **Single Cell Evaluation**

- 1. ZeroVolt chemistry design verification (Comparison with conventional LIB)
- 2. ZeroVolt cell characterization for aerospace application
  - 1. 200mAh test cell, 0V storage + LEO cycling test
  - 2. 15Ah cell, low voltage storage + LEO cycling test
  - 3. 75Ah cell, low voltage storage + calendar life test

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## Introduction of ZeroVolt Technology Comparison with Conventional LIB, Test Method



### Test sample cell

- Quallion 18650 cell (Zero-Volt<sup>™</sup> technology)
- Sony 18650H2 cell (Hard carbon cell)

### Test procedure

- 1. Capacity check to determine baseline capacity (before storage)
- The cells are cycled three times at room temperature according to the following standard procedures.
  - a) CC charge at C/2 rate to 4.2V
  - b) CV charge at 4.2V with a current cutoff of C/20
  - c) CC discharge at C/2 rate to 2.7V
- 2. Simulate 0V state by short-circuiting the cell with a 20 ohm resistor.
- 3. Storage at room temperature for 3 days.
- 4. Charge the cells at room temperature in two steps
- CC charge at C/200 rate to 3.0V
- CC charge at C/20 rate to 4.2V
- 5. Repeat the capacity check test from step 1 to determine the cell capacity after 0V storage.



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## ZeroVolt Cell Characterization Before and After 3-day Storage at Zero Volt









## ZeroVolt Cell Characterization Protocol for Aerospace Application



### <u>Test cell</u>

- 200 mAh simulation cell
- Hermetic



 $50 \ \Omega$  resistor attached across the positive & negative terminals of SCS cell

### Pre-0V storage

- 1. <u>Take ACIR/OCV measurements</u>
- 2. Capacity Check Cycling (2 cycles)
  - 1. Charge: CCCV 0.5C to 4.1 V, 0.05 C cutoff @ 23 °C
  - 2. Rest: 10 minutes
  - 3. Discharge: 0.5C to 2.7 V @ 23 °C
  - 4. Rest 10 minutes

### OV storage

- 1. Characterization for Zero Volt Storage
  - 1. Discharge: 0.05C to 2.7 V @ 23 °C
  - 2. Rest 10 minutes
- 2. <u>Attach 50 Ω resistor across positive & negative terminals of SCS cells</u>
  - Incubator storage @ 23 °C for 14 or 29 months

### Post-0V storage

- 1. <u>Remove 50 Ω resistor from SCS terminals</u>
- 2. Recovery from Zero Volt Storage, Characterization
  - 1. Charge: CCCV 0.005C (C/200) to 3.0 V @ 23 °C
  - 2. Charge: CCCV 0.05C (C/20) to 4.1 V @ 23 °C
  - 3. Rest: 10 minutes
  - 4. Discharge: 0.5C to 2.7 V @ 23 °C
  - 5. Rest 10 minutes
- 3. Run 2 cycles of capacity check
  - 1. Charge: CCCV 0.5C to 4.1 V, 0.05C cutoff @ 23 °C
  - 2. Discharge: CC 0.5C to 2.7 V @ 23 °C
- 4. Proceed to long-term cycling tests

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Zero Volt Cell Characteristics in Aerospace Use 40% DOD LEO Cycle Performance after 0V Storage (29 months) wer/Full Solutions (200mAh wound type model cell)

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Zero Volt Capability

Capacity Retention and Cell Voltage <u>after 0V Storage (49 months)</u> (QL015KA cell, 40% DOD LEO Cycle Performance)





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	Cell Voltage during Storage / Volts	Discharge Capacity / Ah		
		Before Storage	After Storage (49 months)	After 5000 cycles
X06H532	0.656	14.6	14.6	14.9
X06I004	0.180	14.7	14.4	14.5

Cell Voltage @ End of Discharge

## **Discharge Capacity**





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## 8 Series Module (200 mAh Test Cell) Characterization

1.0V storage characterization for 4 months

2. Module characterization during 20% DOD LEO cycling after 0V storage

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## **Scope of Work**

- 1. To perform 0V storage with 200mAh simulation module configured in series of 8 cells\*
- 2. To understand the influence of 0V storage with module configuration to electrochemical performance at pre-/post- 0V storage
- 3. To characterize the 8-cell module in 20% DOD LEO cycling after 0V storage

\*Cell level characterization of 0V storage has been done separately. This study is extension of understanding 0V capability with ZeroVolt chemistry in application use.

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8S 200mAh Test Module Preparation ABSL QUALLION

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**Cell Configuration & History of cells** selected for 0 V Study:

- Form factor: 200mAh simulation cell (SCS cell)
- Feb ~ Mar/2010: Cell Assembly:

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ower/Full Solutions

(Cells under storage at 3.64 - 3.67 V for ~ 2 years before Module assembly and Module OV storage characterization)

- Jan/2012: •
- Jan ~ May/2012: 0V storage ٠
- Jun/2012~:



## 8S 200mAh Test Module **OV Characterization Protocol**



### 1. Take ACIR/OCV measurements

### 2. Capacity Check Cycling (2 cycles)

- 1. Charge: CCCV 0.5C until first cell reaches 4.1 V, C/20 cutoff @ 23 °C
- 2. Rest: 10 minutes
- 3. Discharge: 0.5C until first cell reaches 2.7 V @ 23 °C
- 4. Rest 10 minutes

### 3. DCIR Test (1 cycle)

- 1. Charge: CCCV 0.2C until first cell reaches 4.1 V, C/20 C cutoff @ 23 °C
- 2. Rest: 10 minutes
- 3. Discharge: 0.2 C for 30 minutes or to 2.7 V @ 23 °C
- 4. Pulse: 1C for 5 seconds
- 5. Repeat Discharge and Pulse until first cell reaches 2.7 V

### 4. Characterization for Zero Volt Storage

- 1. Discharge: 0.1C until first cell reaches 0 V @ 23 °C
- 2. Rest: 1 hour
- 3. Take ACIR/OCV measurements
- <u>Attach resistance across positive & negative terminals of module</u>
  <u>BS module: 400 Ω resistance ( = 50 Ω per cell)</u>
- 5. Incubator storage @ 23 °C for specified period

### 6. Recovery from 0V storage

- 1. After removing resistors, take ACIR/OCV measurements
- 2. Charge: CC C/200 until first cell reaches 3.0 V
- 3. Charge: C/20 until first cell reaches 4.1 V
- 4. Discharge: CC 0.5C until first cell reaches 2.7 V

### 7. After 4 months, 0V storage, place modules on 20% DOD, LEO Cycling

Current across module with 2.7 V / cell when resistors are attached does not exceed 0.3 C rate

## 8S Module under 0V Storage



50  $\boldsymbol{\Omega}$  resistors in series across module terminals

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## **0V storage characterization for 4 months**

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Characterization of Modules before 0V Storage, Month 4 **EnerSys**. Capacity Check Cycling, 8S Modules

## **8S Module, Module and Cell Voltage**



- 1. Charge: CCCV 0.5C until first cell reaches 4.1 V, C/20 cutoff @ 23 °C
- Rest: 10 minutes 2
- Discharge: 0.5C until first cell reaches 2.7 V 3. @ 23 °Č
- Rest 10 minutes 4



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## 8S Module, Voltage and ΔV\* vs. Time

 $\Delta V$  defined as the max. difference between cell voltages during cycling



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# Modules after 0V Storage, Months 0 - 4

## 8S Module, Voltage and ΔV\* vs. Time

\*  $\Delta V$  defined as the max. difference between cell during cycling

• Capacity Check Cycling (2 cycles)

- Charge: CCCV 0.5C until first cell reaches 4.1 V, C/20 cutoff @ 23 °C
- 2. Rest: 10 minutes
- Discharge: 0.5C until first cell reaches 2.7 V @ 23 °C
- 4. Rest 10 minutes

Max.  $\Delta V$  among 8 cells were in 8S module:

- @ 50% DOD = 10 25 mV
- @ 100% DOD, 2.7 V = 360 480 mV



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Characterization of Modules after 0V Storage 8S Modules, Month 0



Rower/Full Solutions Cell Voltages during 0V Storage in Modules \*



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## Power/Full Solutions Discharge Curve Comparison in Month 0, 1, 2, 3, and 4

## **Discharge Curves**

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### Capacity Check Cycling Condition

- Charge: CCCV 0.5C until first cell reaches 4.1 V, C/20 cutoff @ 23 °C
- 2. Rest: 10 minutes
- Discharge: 0.5C until first cell reaches 2.7 V @ 23 °C
- 4. Rest 10 minutes

### **Discharge Capacity Retention,** 8S Module:

No change during 0V storage



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## DC resistance vs. Depth-of-Discharge

ower/Full Solutions



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Performance Summary



During 0V storage for 4 months, the following were found at periodic characterization (capacity check cycles):

### **Discharge Capacity:**

**<u>100%</u>** discharge capacity retention for 4 months at 0V

Discharge capacity: from 0.183 Ah to 0.183 Ah

### Maximum ΔV:

No change in voltage divergence among 8 cells

- □ Max ΔV @ 100% DOD= 360 480 mV
- Max. ΔV @ 50% DOD = 10 25 mV

## DCIR:

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**No change** in DC resistance across a range of DOD during 0V storage for 4 months

## AC-IR:

**No change** in AC-IR values was observed.

# The test module demonstrated the 0V storage capability without any degradation.

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## 8S Module characterization during 20% DOD LEO cycling after 0V storage

(15,431 Cycles as of Nov. 2016)

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## **Discharge Capacity**



SCS 8S Module: Module Discharge Capacity (Ah)

8S Module Characteristics under 20% DOD LEO Sys. Cycling after 0V Storage Discharge Capacity and End-of-Discharge Voltage



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8S Module Characteristics under 20% DOD LEO Cycling

after 0V Storage

**Maximum**  $\Delta V$  between Cells at End-of-Discharge Voltage



## End-of-Discharge Voltage



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8S Module Characteristics under 20% DOD LEO Cycling after 0V Storage Cell and Module Discharge Curves

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### 8S Module Characteristics under 20% DOD LEO Cycling after 0V Storage DC Resistance Dependency on DOD



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8S 200mAh Test Cell Module, 20% DOD LEO Cycling ABSL QUALLION Performance Summary

During 20% LEO cycling after 4 months of 0V storage with 8S module, the following were observed:

### **Discharge Capacity Retention:**

### No change after 12,500 cycles:

Discharge capacity in the 8S module: from 0.183 Ah to 0.185 Ah

### Maximum ΔV during cycling:

No significant increase of cell voltage divergence in module during 15,451 cycles

Max $\Delta V$ @ end of charge	= 25 mV
Max. $\Delta V$ @ end of discharge	= 22 mV

## DCIR:

No change in DC resistance of cells across a range of DOD after 12,500 cycles

# ➔ The test module demonstrated the superior LEO cycling performance for aerospace application after 0V storage.

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