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

POWERED by

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Outline


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
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
### 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

**EnerSys Headquarters: Reading, PA**
(*US Owned Company*)

### Facility Locations

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<th>Technology</th>
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<td>ABL/Quallion</td>
<td>Lithium-Ion Materials, Cells &amp; Batteries</td>
<td>Longmont CO, Sylmar CA, Culham UK</td>
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<tr>
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<td>Lithium Primary/Liquid Reserve</td>
<td>Horsham PA, Tampa FL</td>
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<tr>
<td>Land &amp; Sea</td>
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<td>Warrensburg MO, Zwickau DE</td>
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<tr>
<td>Aviation</td>
<td>Hawker/Quallion</td>
<td>Lead Acid (Thin Plate), Ni-Cd &amp; Lithium-ion</td>
<td>Warrensburg MO, Sylmar CA, Newport UK, Zwickau DE</td>
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</table>

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Overview of Battery Industry
Battery Market Stratification

Materials
Chemistries can be varied for high-energy, power, rate and capacity, safety.

Cell Design
Cell configurations include prismatic, cylindrical, flat stack, wound, large, small, polymer (pouch), hard case.

Electronics
Cell and battery management, power, safety, interface, communication (e.g., SM/CAN), balancing, state of health monitoring, modeling, grade of board parts.

Battery Pack
Pack design considerations: safety, interconnects, spacing of cells, thermal gradients, heat ejection, environmental requirements, interface to

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

- **1998**
  - Quallion established in California, USA

- **2000**
  - ABSL: The 1st space flight battery manufacturer to qualify lithium-ion cells for space flight

- **2001**
  - ABSL: The 1st lithium-ion battery to orbit Mars (ESA’s Mars Express)

- **2003**
  - Quallion registered ISO 9001 & 13485; Zero-Volt™ technology patented

- **2004**
  - ABSL: The 1st lithium-ion battery to power a comet probe (ESA’s Rosetta)

- **2005**
  - ABSL: The 1st lithium-ion battery to orbit Venus (ESA’s Venus Express)

- **2006**
  - ABSL: The 1st lithium-ion battery to power a NASA spacecraft (NASA’s ST-5)

- **2007**
  - ABSL: 100th lithium-ion battery launched

- **2009**
  - ABSL: Powering NASA’s return to the moon (NASA’s LRO & LCROSS)

- **2011**
  - EnerSys acquired Quallion. ABSL & Quallion combine space technologies

- **2012**
  - Quallion: 1st satellite battery launched into orbit. Powers U.S. Military Satellite (TacSat 4)

- **2013**
  - ABSL: Powering NASA’s return to the moon (NASA’s LRO & LCROSS)

- **2014**
  - ABSL: Powering NASA’s return to the moon (NASA’s LRO & LCROSS)

Los Angeles County, CA & Boulder County, CO

EnerSys Headquarters: Reading, PA (US Owned Company)

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Quallion – EnerSys Advanced Systems
Medical Application

1998
Quallion Established in California, USA

2003
Commercial launch of Advanced Bionics’ Cochlear Implant with Quallion Behind the Ear battery

2004
Quallion registered ISO 9001 & 13485; Zero-Volt™ technology patented

2012
Manufactured 100,000th implantable medical battery

2013
10 years of safety and reliability in implanted medical applications

2014
EnerSys acquired Quallion.

Locations:
Quallion Facility- Los Angeles County, CA
EnerSys Headquarters- Reading, PA

Commercial launch (EU) of Sequana Medical’s implanted pump with Quallion implanted battery

Impulse Dynamics launches Optimizer IV using Quallion implanted battery

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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
Introduction of ZeroVolt Technology
Comparison with Conventional LIB, Test Method

Test sample cell
- Quallion 18650 cell (Zero-Volt™ 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.
ZeroVolt Cell Characterization
Before and After 3-day Storage at Zero Volt

SONY 18650

- Room temperature storage
- 40°C storage

Permanent cell damage after 0 volt storage

Quallion 5A-2 zero-volt 18650

- Room temperature storage
- 40°C storage

No cell damage observed
ZeroVolt Cell Characterization Protocol for Aerospace Application

Test cell
- 200 mAh simulation cell
- Hermetic

50 Ω resistor attached across the positive & negative terminals of SCS cell

**Pre-0V storage**
1. Take ACIR/OCV measurements
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

**0V storage**
1. Characterization for Zero Volt Storage
   1. Discharge: 0.05C to 2.7 V @ 23 °C
   2. Rest 10 minutes
2. Attach 50 Ω resistor across positive & negative terminals of SCS cells
   - Incubator storage @ 23 °C for 14 or 29 months

**Post-0V storage**
1. Remove 50 Ω resistor from SCS terminals
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
Zero Volt Cell Characteristics in Aerospace Use
40% DOD LEO Cycle Performance after 0V Storage (29 months)
(200mAh wound type model cell)

Storage Condition
For **29 months**,
- 100% SOC (3 cells)
- 50% SOC (3 cells)
- 10% SOC (3 cells)
- 0V (3 cells)
(at room temperature)

**Cycle condition**
- LEO cycle (40% DOD)

**Capacity check**
- 100% DOD
  at every 500 cycles
  (at 20°C)

**No difference in cycle performance**
≈ 14,000 cycles

Test location / equipment changed.

Same energy retention trend
- Fresh cell (no storage)
- 29mo. 0V-stored cell
Zero Volt Capability
Capacity Retention and Cell Voltage after 0V Storage (49 months)
(QL015KA cell, 40% DOD LEO Cycle Performance)

<table>
<thead>
<tr>
<th></th>
<th>Cell Voltage during Storage / Volts</th>
<th>Discharge Capacity / Ah</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Storage</td>
<td>After Storage (49 months)</td>
</tr>
<tr>
<td>X06H532</td>
<td>0.656</td>
<td>14.6</td>
</tr>
<tr>
<td>X06I004</td>
<td>0.180</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Discharge Capacity

Cell Voltage @ End of Discharge

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Zero Volt Capability
Capacity Retention after 0V Storage (40 months)
(QL075KA cell, 20% SOC Storage Performance)

QL075KA
- 0 - 40th Month: 0V Storage at room temp
- After 40th Month: 20% SOC Storage at room temp

Capacity Check Cycle
- Charge: 0.5C / 4.1V till C/20 at room temp
- Discharge: 0.5C to 2.7V at room temp

After 0 volt storage
- No capacity fade
- Same storage capability to fresh cell
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
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.
Cell Configuration & History of cells selected for 0 V Study:

- Form factor: 200mAh simulation cell (SCS cell)
- Feb ~ Mar/2010: Cell Assembly:
  (Cells under storage at 3.64 - 3.67 V for ~ 2 years before Module assembly and Module 0V storage characterization)
- Jan/2012: Module Assembly
- Jan ~ May/2012: 0V storage
- Jun/2012~: 20% DOD LEO cycling
8S 200mAh Test Module
0V 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
   4. Attach resistance across positive & negative terminals of module
      8S module: 400 Ω resistance (= 50 Ω per cell)

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 Ω resistors in series across module terminals
0V storage characterization for 4 months
Characterization of Modules before 0V Storage, Month 4
Capacity Check Cycling, 8S Modules

8S Module, Module and Cell Voltage

- **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
8S Module, Voltage and ΔV* vs. Time

ΔV defined as the max. difference between cell voltages during cycling

- **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
8S Module, Voltage and ΔV* vs. Time

* ΔV defined as the max. difference between cell during cycling

- **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

Max. ΔV among 8 cells were in 8S module:
- @ 50% DOD = 10 – 25 mV
- @ 100% DOD, 2.7 V = 360 – 480 mV
Characterization of Modules after 0V Storage
8S Modules, Month 0
Cell Voltages during 0V Storage in Modules *

8S Module, Discharge to 0V

* Voltage profile after attachment of resistors across positive and negative terminals of module during first month of 0V storage

→ 8S module: 2 cells showed reverse voltage between -1 V and -2 V.

Module Voltage: 0V

Cell Voltage

High degree of reverse voltage

Module Voltage

Characterization of Discharge to 0V with Resistor:

Previous Step: Discharge C/10 until first cell reaches 0V
Rest: 2 hours
Discharge: Attach 400 Ω resistance across module terminals
Storage: 1 month, RT
Discharge Curves

- **Capacity Check Cycling Condition**
  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

**Discharge Capacity Retention, 8S Module:**
No change during 0V storage
Characterization of 8S Modules after 0V Storage
DC Resistance Dependency on DOD

DC resistance vs. Depth-of-Discharge

- DC resistance 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

→ DC-IRs at any DOD did not show any change after 0V, 4 months in 8S module.
During 0V storage for 4 months, the following were found at periodic characterization (capacity check cycles):

**Discharge Capacity:**
- **100% 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:**
- **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.
8S Module characterization during 20% DOD LEO cycling after 0V storage

(15,431 Cycles as of Nov. 2016)
8S Module Characteristics under 20% DOD LEO Cycling after 0V Storage
Discharge Capacity and End-of-Discharge Voltage

**Discharge Capacity**

SCS 8S Module: Module Discharge Capacity (Ah)

- 0.182 Ah after 500 cycles
- 0.185 Ah after 12,875 cycles
- 0.182 Ah after 0V storage

**Cycle Index**

- 15,431 cycles

**SCS full cell, 8S Module after 0V Storage, 4 months**

- 20% DOD, LEO cycling conditions:
  - Charge: CCCV 0.3 C to 4.1 V, 0.05 C cutoff @ room temperature, 54 min
  - Discharge: 0.33 C to 2.7 V @ room temperature, 36 min

- Capacity Check every 500 cycles:
  - Charge: CCCV 0.5 C to 4.1 V, 0.05 C cutoff @ room temperature
  - Discharge: CC 0.5 C to 2.7 V

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

SCS 8S Module: Cell and Module Voltage at End of Discharge

Module Voltage

Cell Voltages

Test cable connection issue

Cycle Index

Cell Voltage EODV (V)

Module Voltage EODV (V)

20% DOD, LEO cycling conditions:
Charge: CCCV 0.3C to 4.1V, 0.05C cutoff @ room temperature, 54 min
Discharge: 0.33C to 2.7 V @ room temperature, 36 min
Capacity Check every 500 cycles:
Charge: CCCV 0.5C to 4.1 V, 0.05C cutoff @ room temperature
Discharge: CC 0.5C to 2.7 V

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8S Module Characteristics under 20% DOD LEO Cycling after 0V Storage
Maximum ΔV between Cells at End-of-Discharge Voltage

End-of-Discharge Voltage

SCS 8S Module: Cell Voltage at End of Charge and Discharge; and ΔV

- ΔV (Charge) = 25mV
- ΔV (Discharge) = 22mV

After 15,431 cycles

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

No significant change in discharge curves

Capacity Check Cycle:
Charge: CCCV 0.5C until first cell reaches 4.1 V, C/20 cutoff
Rest: 10 minutes
Discharge: CC 0.5C until first reaches 2.7 V
8S Module Characteristics under 20% DOD LEO Cycling after 0V Storage

DC Resistance Dependency on DOD

No significant change in DC resistance of cells in test module

DC resistance during 0V storage before LEO cycle

DC resistance after 12,500 LEO cycles
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 ΔV @ end of charge = 25 mV
  - Max. ΔV @ 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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