

PROPULSION & POWER DIVISION NASA Johnson Space Center, Houston, Texas



Calendar Life Aging of Two Models of 18650 Lithium Ion Cells

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Introduction

| Preser | ^{iter} S. Rus | S. Russell | | |
|--------|------------------------|------------|--|--|
| Date | 26 Apr 2018 | Page 2 | | |

- Interim calendar life test results for two models of 18650 lithium ion cell used in Human Spaceflight
 - Test conditions derived from low rate, low cycle, extended storage application requirements
 - Test cells selected from date code traceable populations
 - Moli ICR18650J, Apr 2007
 - Samsung ICR18650-26F, Dec 2013
- This work is administered by NASA Johnson Space Center in support of the EVA Office and the International Space Station
- Test is performed by Symmetry Resources Inc, Arab AL





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Test Protocol

| Presenter | | S. Ru | ssell |
|-----------|----|----------|--------|
| Date | 26 | Apr 2018 | Page 3 |

- Calendar Life Test is an on-going, full factorial, self discharge and irreversible capacity loss experiment of twelve conditions with 3 groups of 3 cells per condition for a total of 108 cells
 - Storage Conditions:
 - Cells stored in sealed, dry containers
 - SOC: 0%, 30%, 100%, 110%
 - Temperature: 10°C, 25°C, 35°C

- SOC Definition (Moli/eSDI): 0% = 3.2/3.2V 30% = 625/720 mAh charge input 100% = 4.12/4.1V, taper to 60mA 110% = 4.2/4.2V, taper to 60mA
- Cycle Protocol: C/2 cycling between 3.2-4.2V
 - During discharge pulse at 2C for 1s every 10% SOC
 - Terminate final charge cycle at storage condition
- Test Protocol: Measure OCV and/or cycle at ambient conditions
 - Year 1: cycle at 90, 180, 270, and 365 day intervals
 - Year 2+: cycle at 182, 365, and 730 day intervals
 - Group 4 (spare cells) to be tested with 730 day interval if not used
 - When cell group average fails to deliver 1.66 Ah (~70%)
 - Charge at C/2, discharge at 563mA for 5s then 238 mA to 3.2V
 - If unable to deliver 1.66 Ah, terminate storage





Storage Environment



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Date 26 Apr 2018 Page 4

 Test Temperature has been maintained within +/- 2 °C since 2008 except during periods of cell access or extended power outage (interim years not shown)



Lithium Ion Cell Calendar Life Testing, SRI Job# 83A & 53H



S. Russell

Page 5

Presenter

26 Apr 2018

Date

• 108 month self discharge results for the Moli cell, 182 day cycle group



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• 108 month self discharge results for the Moli cell, 365 day cycle group



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108 month self discharge results for the Moli cell, 730 day cycle group •



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30 month self discharge results for the Samsung cell, 182 day cycle group



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Presenter S. Russell 26 Apr 2018 Page **9**

Date

30 month self discharge results for the Samsung cell, 365 day cycle group



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Self Discharge

- Presenter S. Russell
 Date 26 Apr 2018 Page 10
- 30 month self discharge results for the Samsung cell, 730 day cycle group



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Cell Failures



Presenter S. Russell Date 26 Apr 2018 Page 11

- Initial Findings
 - None of the 216 cells have failed anomalously
 - Several high temperature and/or high SOC groupings have failed

| | | Cvcle | Total Storage Time to Group | | |
|---------------|------------|-------------------|-----------------------------|------------|--|
| Storage Temp. | SoC (%) | Interval (mo.) | Capacity Failure | | |
| (°C) | | | C/2 Discharge | 0.238A | |
| | | | | Discharge | |
| 35 | 110 | 6 | 24 months | 36 months | |
| 35 | 110 | 12 | 36 months | 48 months | |
| 35 | 110 | 24 | 36 months | 60 months | |
| 35 | 100 | 6 | 42 months | 66 months | |
| 25 | 110 | 6 | 42 months | 66 months | |
| 35 | 100 | 12 | 48 months | 72 months | |
| 25 | 110 | 12 | 48 months | 84 months | |
| 35 | 100 | 24 | 60 months | 84 months | |
| 25 | 110 | 24 | 60 months | 108 months | |
| 25 | 100 | 6 | 72 months | | |
| 25 | 100 | 12 | 96 months | | |
| 25 | 100 | 24 | 108 months | | |

Moli J Cell Group Failure Chronology

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Date 26 Apr 2018 Page 12

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- Internal Resistance growth provides a clear indication of cell degradation
 - Effect of SOC at 25 degree C for both Moli and Samsung cell



Data provided by Lithium Ion Cell Calendar Life Testing, SRI Job# 53H & 86A, Feb 20, 2018





cell

Internal Resistance



Page 13

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26 Apr 2018

Date

- Internal Resistance growth provides a clear indication of cell degradation
 - Effect of temperature at 0% and 110% SOC for both Moli and Samsung



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Capacity Decay

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Date 26 Apr 2018 Page 14

- Mechanism does not appear to be strongly coupled to cycling
 - Maximum number of cycles shown on plot are 17

Cycle Life Test Results Shown for Reference Only

5S Moli Cell Cycling

| Cycle | Сар | % Cap |
|-------|-------|---------|
| 1 | 2.199 | 100.00% |
| 10 | 2.198 | 99.98% |
| 50 | 2.197 | 99.94% |
| 100 | 2.196 | 99.88% |
| 150 | 2.195 | 99.83% |
| 200 | 2.194 | 99.78% |

SRI Job# 86A, Oct 20, 2009

4S Samsung Cell Cycling

| Cycle | Average | % Cap |
|-------|---------|---------|
| 1 | 2.381 | 100.00% |
| 10 | 2.354 | 98.85% |
| 50 | 2.317 | 97.32% |
| 100 | 2.273 | 95.47% |
| 150 | 2.244 | 94.24% |
| 200 | 2.225 | 93.44% |

PCTest Job# 4M1702100015-2, Jan 17, 2018



Data provided by Lithium Ion Cell Calendar Life Testing, SRI Job# 53H & 86A, Feb 20, 2018



Self Discharge



Date 26 Apr 2018 Page 15

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- 24 Month Interval test provides insight into Self Discharge Rate
 - Rate is minimized at 30% SOC for tested temperatures



SELF DISCHARGE RATE mV/mon

First Interval (Month 15-36*)

| | 0% | 30% | 100% | 110% |
|-----|-----|-----|------|------|
| 10C | 0.3 | 0.1 | 1.2 | 1.5 |
| 25C | 1.7 | 0.2 | 1.7 | 2.2 |
| 35C | 4.0 | 0.2 | 2.2 | 3.1 |

Rate is calculated by subtracting final OCV from initial OCV and dividing by 15 months. **Note, interval is incomplete.*

Data provided by SRI Job# 53H





Self Discharge

Presenter S. Russell Date 26 Apr 2018 Page 16

 Extended 24 month interval testing offers insight into Self Discharge Rate change with continued storage (30% is still preferred)



SELF DISCHARGE RATE (mV/mon)

First Interval (Month 15-36)

| | 0% | 30% | 100% | 110% |
|-----|-----|-----|------|------|
| 10C | 1.1 | 0.1 | 0.7 | 1.2 |
| 25C | 8.7 | 0.2 | 1.5 | 2.2 |
| 35C | 8.7 | 0.7 | 2.0 | 3.0 |

Fourth Interval (Month 87-108)

| | 0% | 30% | 100% | 110% |
|-----|-----|-----|------|------|
| 10C | 0.9 | 0.1 | 0.5 | 0.8 |
| 25C | 2.6 | 0.1 | 0.8 | 0.9 |
| 35C | 5.6 | 0.2 | 0.2 | 0.1 |

Rate is calculated by subtracting final OCV from initial OCV and dividing by 21 months

Data provided by SRI Job# 83A





Degradation Mechanism

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• Initial review by National Renewable Energy Laboratory suggests a single mechanism dominates observed degradation



Preliminary Look at NASA Cell-Life Data, NREL, K. Smith, Sep 18, 2015





Summary

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|-------|-------------|------------|--|--|
| Date | 26 Apr 2018 | Page 18 | | |

- Temperature and SOC storage conditions are being assessed on two models of commercial lithium ion cell
 - Test protocols derived from low rate, low cycle, extended life application
 - Test offers insight into self discharge rate and effect of storage condition
 - Results used to validate operational storage conditions and approximate end of asset life
 - Mechanistic modeling has been considered as forward work
 - Current method assumes observed degradation is linear and mathematically averages degradation based on time at condition

 $X(t) = X(t-1) * \left[1 + /-\left(Annual Cycle Loss * Annual Cycles + \frac{\sum Condition Loss * days at Condition}{365 days} \right) \right]$

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- Questions?