Development of Specialized Li-ion Batteries for a Venus Aerobot Mission

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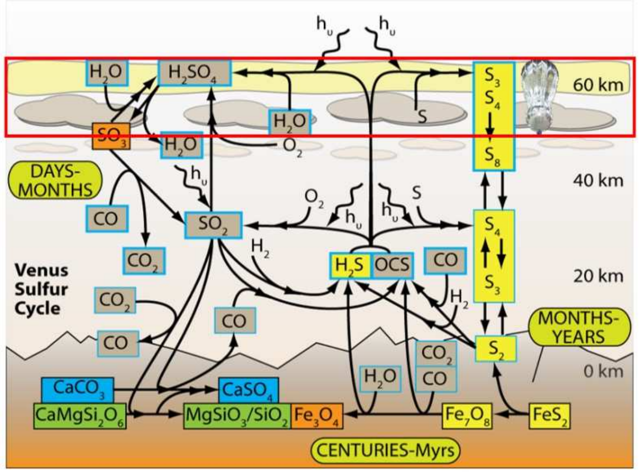
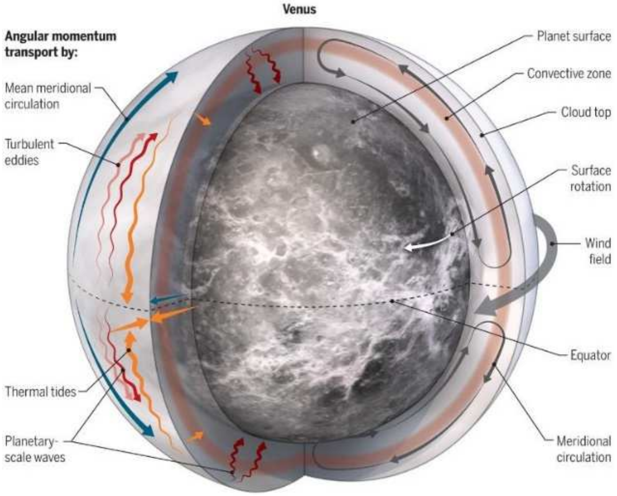
4/25/2024


Venus Cloud Explorer New Frontiers Mission Concept

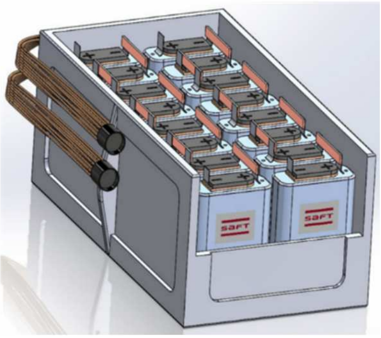
- <u>Mission Concept: </u>Send a variable-altitude balloon spacecraft to the Venus atmosphere 50-60 km above surface
- Atmospheric chemistry measurements:
  - Assess full chemical inventory of all major chemical cycles
  - Determine chemistry of aerosols and gases present
- Atmospheric dynamics measurements:
  - Cause of super-rotation
  - Vertical transport of energy and momentum
  - Atmospheric waves
- Surface dynamics (via infrasound measurements):
  - Seismic activity
  - Volcanic activity
- Surface imaging below cloud layer
- Magnetic mapping measurements





Overview of Battery Effort

- Energy storage for a Venus aerobot mission is very challenging:
  - Battery temperatures will vary from -30^{o}C to +100^{o}C.
  - No battery cell chemistry can survive over this temperature range.
- JPL with Saft America and Saft Poitiers is developing a wide operating temperature battery cell for the mission
  - JPL develops, screens, and tests new electrolyte formulations with increased temperature range and survivability.
  - Saft infuses JPL's electrolyte formulations into an existing high TRL cell format.
    - NMC 1:1:1 cathode, graphitic anode (cannot change)
  - Saft delivers flight-like cells to JPL for testing.



Technical Approach

- Screen a large number of electrolyte variants in coin cells
  - Focus on prior wide operating temperature electrolyte formulations developed in house[1] and reported in literature
  - Focus on high temperature resilience (low discharge rate at low T, could bring heaters)
- Downselect promising electrolyte variants prepare three-electrode cells:
  - Carry out detailed electrochemistry studies (EIS, Tafel polarization, rate capability, etc. on each electrode)
  - Perform DPA and various post-mortem analyses on cell components
- Provide Saft with promising electrolyte compositions for incorporation into flight-like MP-xtd format
- Characterize Saft cells with JPL electrolyte against mission simulation load profiles
- Correlate three-electrode data with Saft cell data to assure laboratory cell data matches Saft cell data

Coin cell

3-electrode cell

Saft MP-xtd cell

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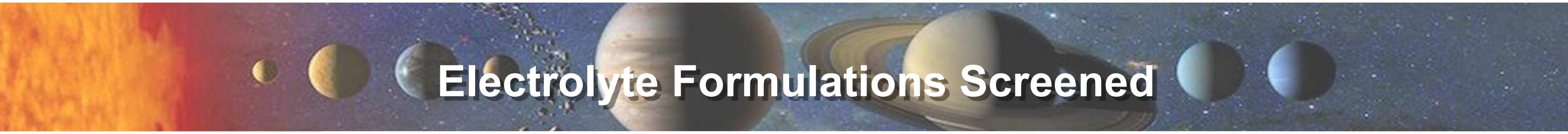
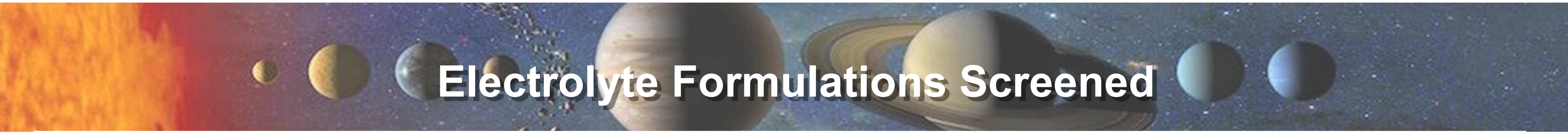
[1] See for example: ECS Transactions, 25 (36) 37-48 (2010).



Electrolyte Formulations Screened

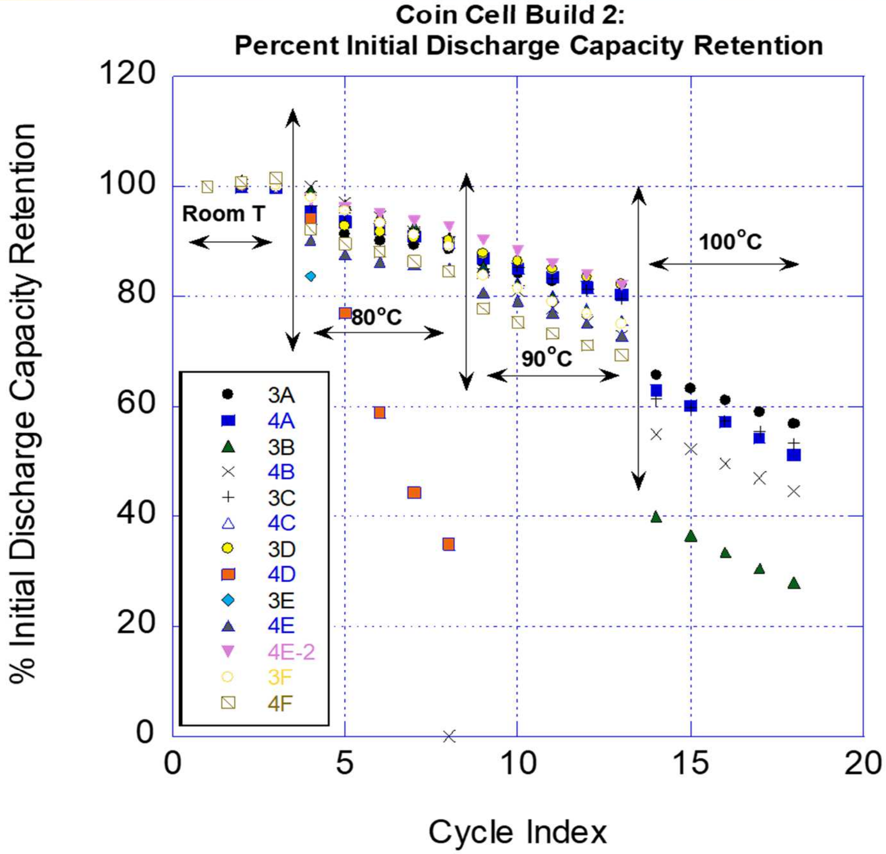
	Electrolyte component	Rationale
A	1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +2% vinylene carbonate (VC)	Polymerization of VC to yield more uniform and stable SEI on graphite
B	1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +2% lithium oxalate	Lithium oxalate to provide more stable SEI/CEI at elevated temperature
C	1.0M $LiPF_6$, 0.10 M LiBOB in EC+EMC (50:50 v/v)	LiBOB to prevent unwanted deposition on NMC cathode and form stable SEI on graphite
C1	1.0M $LiPF_6$, 0.10 M LiDFOB in EC+EMC (50:50 v/v)	LiDFOB may have less gas generation relative to LiBOB with better CEI forming ability
D	1.0M $LiPF_6$, 0.10 M LiFSI in EC+EMC (50:50 v/v)	LiFSI to expand the electrochemical window at high temperature
E	1.0M $LiPF_6$, FEC+EMC (50:50 v/v) + 2% VC	FEC has been reported to provide beneficial F-rich SEI and thin CEI
F	1.0M $LiPF_6$, EC+DMC+DEC (1:1:1 v/v)	Baseline electrolyte
G	1.0M $LiPF_6$ in EC+EMC+ BB (50:30:20 v/v) + 2% VC	Higher molecular weight ester to improve high temperature performance
I	1.0M $LiPF_6$ EC+MPC (50:50 vol %) + 2% VC	MPC has higher boiling point, should be preferred at high T

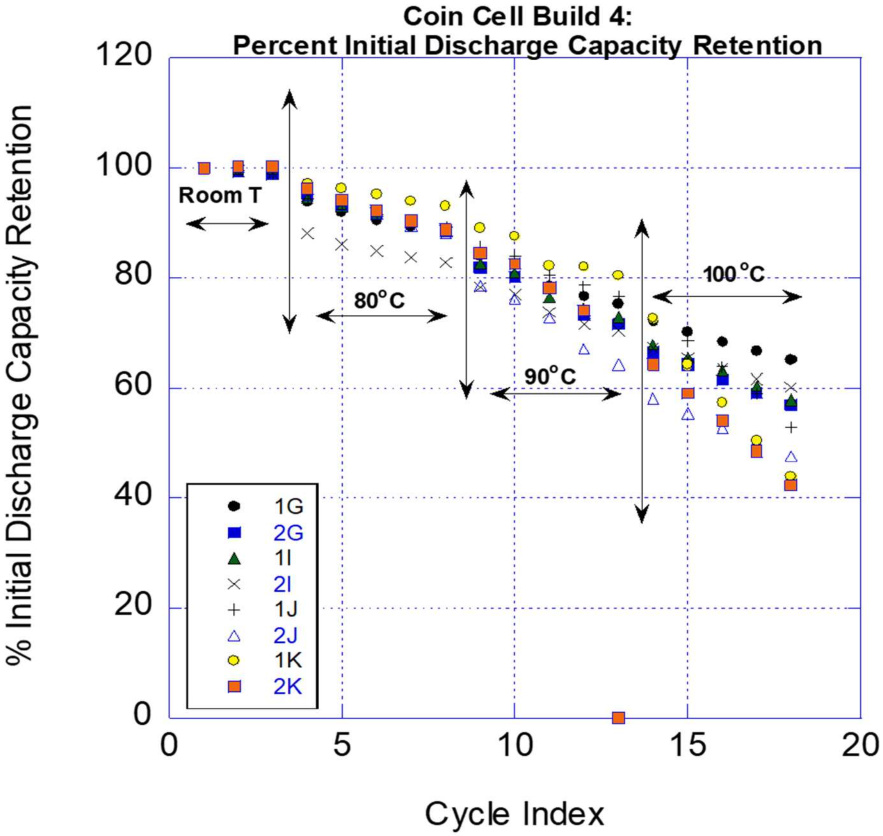


Electrolyte Formulations Screened

	Electrolyte Component	Rationale
J	1.0M $LiPF_6$ in EC+EMC+DMC (50:30:20 v/v) + 2% VC	Variant on Saft baseline formulation replacing binary with ternary carbonate blend for wider temperature tolerance
K	0.6M LiTFSI – 0.4M LiDFOB in 50:50 EC:EMC + 2% VC	Alternative salt for $LiPF_6$ to prevent potential PF_6- induced degradation
L	1.0 M LiTFSI + 0.50 M LiDFOB in EC+EMC+TPP (50:40:10 vol %) + 2% VC	TPP is beneficial for high voltage and long cycle life; could also be beneficial for high temperature
M	1.0 M $LiPF_6$ in EC+EMC (50:50 v/v %) + 4% FEC + 2% VC	Combination of FEC and VC for synergistic improvements
N	1.0M $LiPF_6$ in EC+EMC (50:50 v%) + 2% VC + 2% PS	Propane sultone (PS) to reduce gas generation
O	1.0 M $LiPF_6$, 0.10 M LiFSI, EC+EMC (50:50) + 2% VC	Combination of LiFSI and VC for synergistic improvements
P	Saft proprietary blend	Used in prior SAFT high-temperature cells
Q	Saft proprietary blend with additional VC	Additional VC currently used in SAFT baseline cells

Representative Coin Cell Data

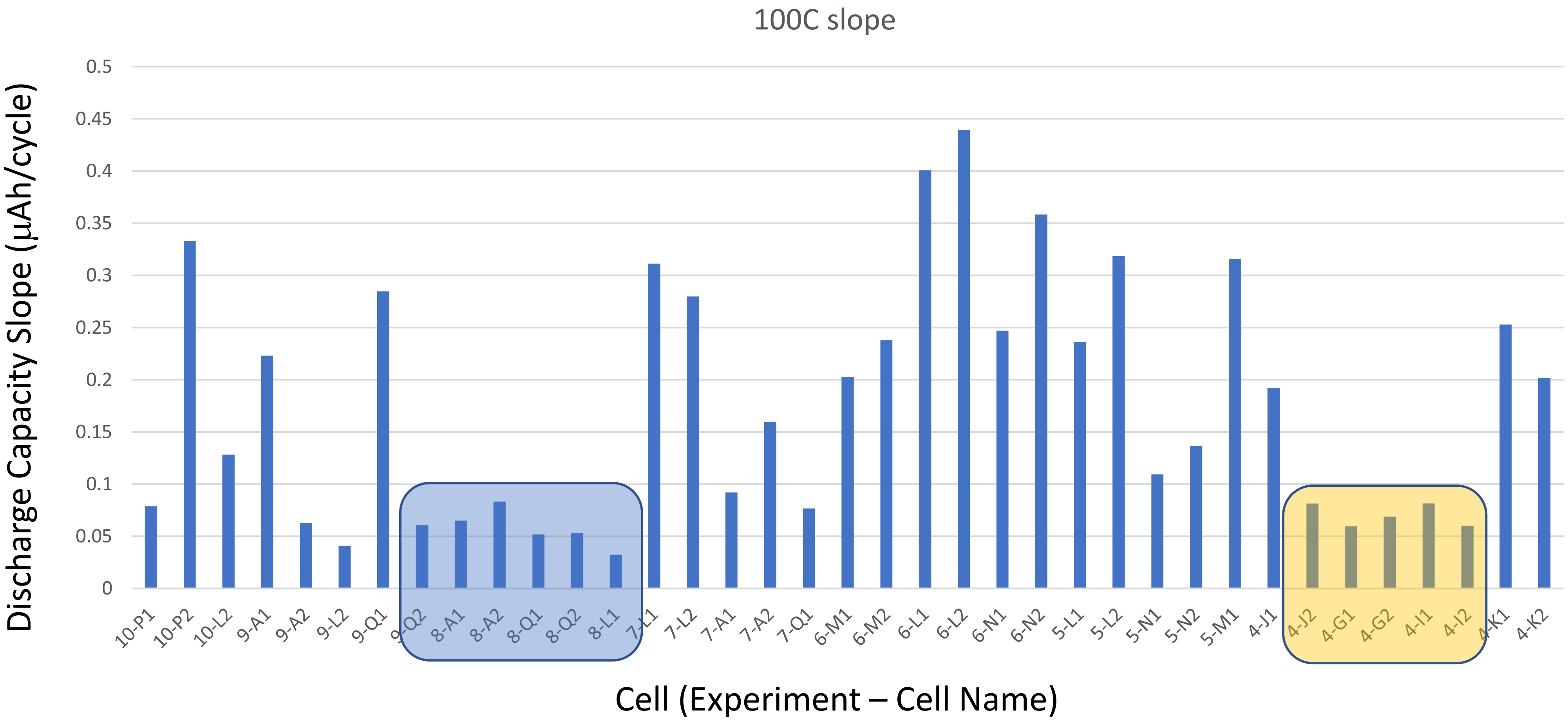

Coin Cell Build 2:
Percent Initial Discharge Capacity Retention


Coin Cell Build 4:
Percent Initial Discharge Capacity Retention

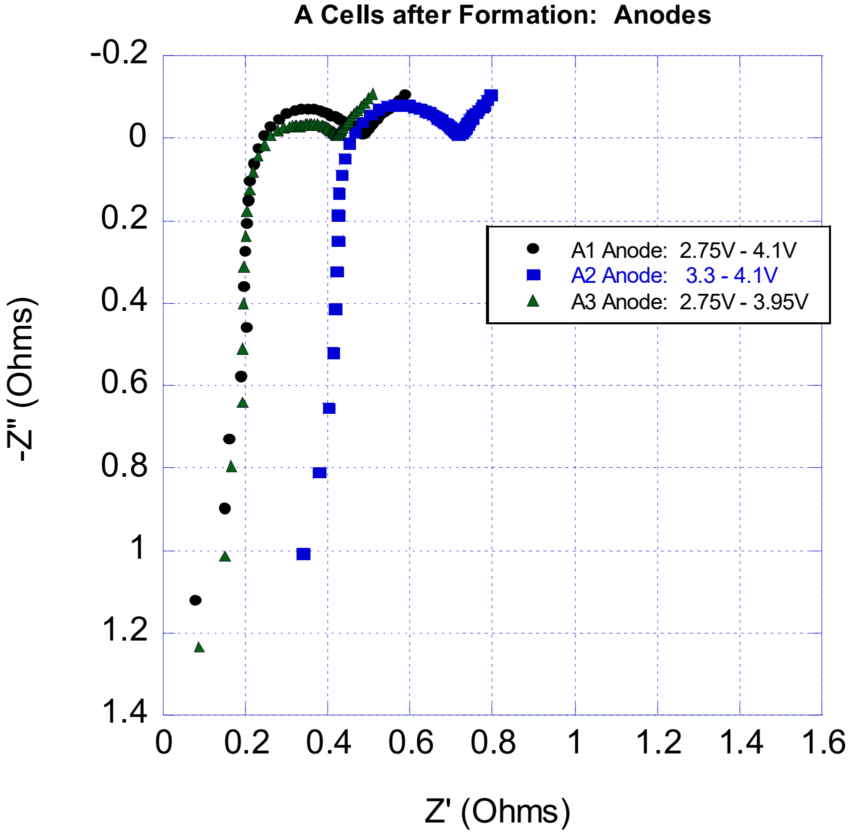
A Electrolyte: 1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +2% VC
G Electrolyte: 1.0 M $LiPF_6$ in EC+EMC+ BB (50:30:20 v/v) + 2% VC

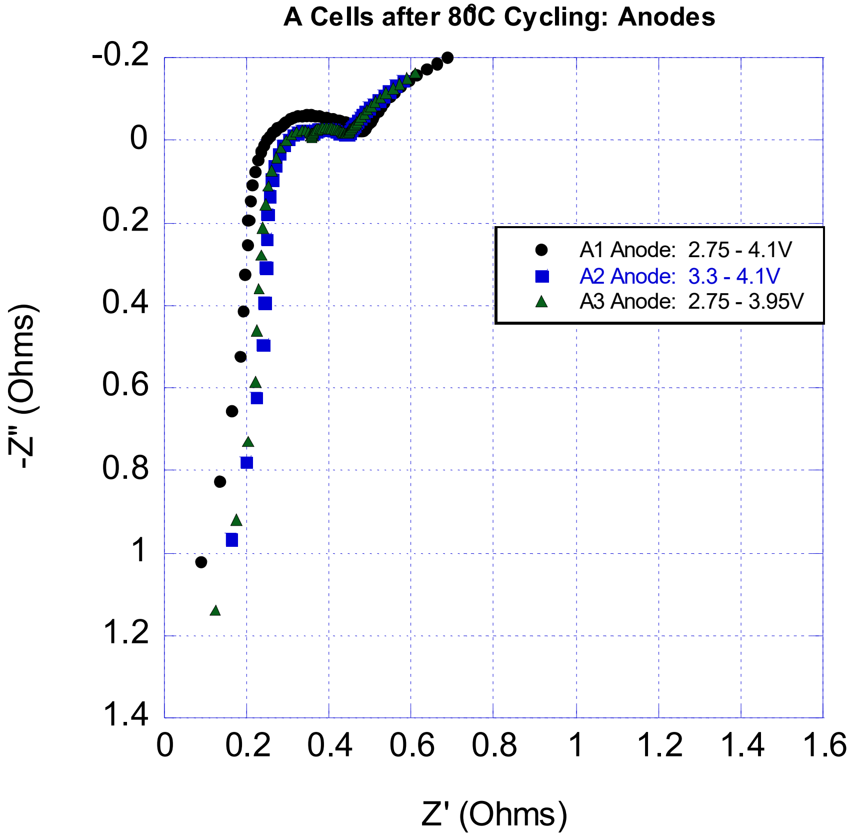
Representative coin cell cycling data to evaluate various electrolytes

Summary of Discharge Capacity Fade vs. Formulation (100°C)



3-Electrode EIS Studies: Anode

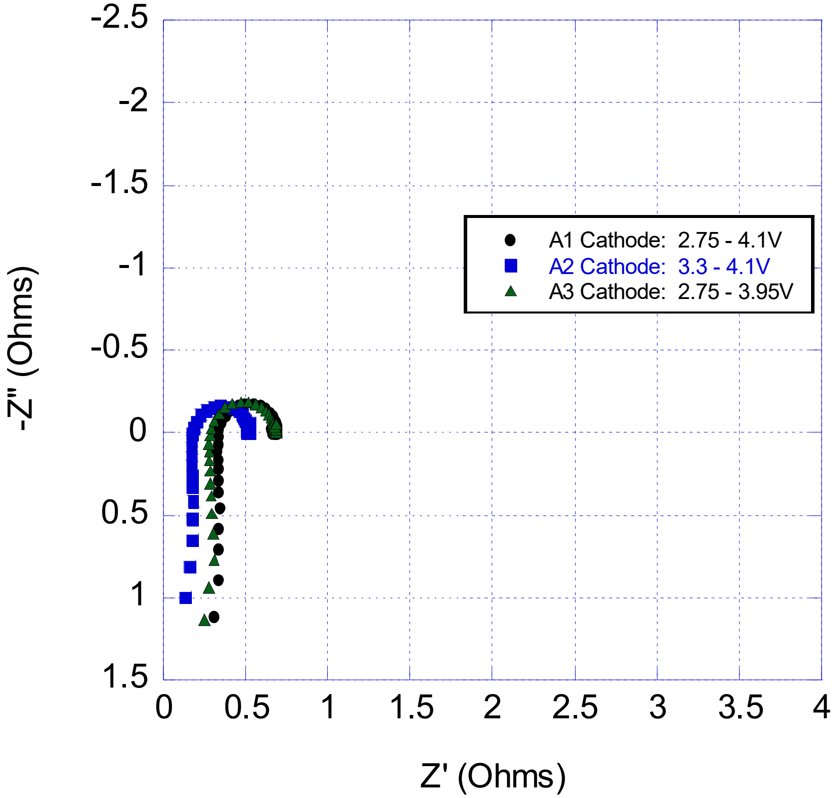




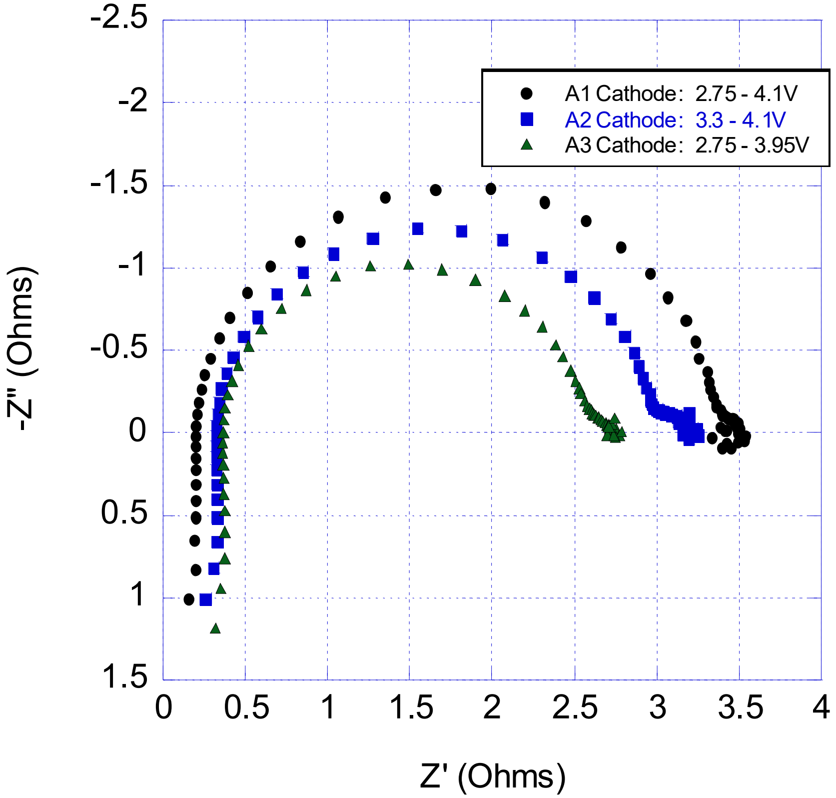
A Electrolyte: 1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +2% vinylene carbonate (VC)

Anode impedance does not appreciably change after 80°C cycling

3-Electrode EIS Studies: Cathode



A Cells after Formation: Cathodes



A Cells after 80°C Cycling: Cathodes

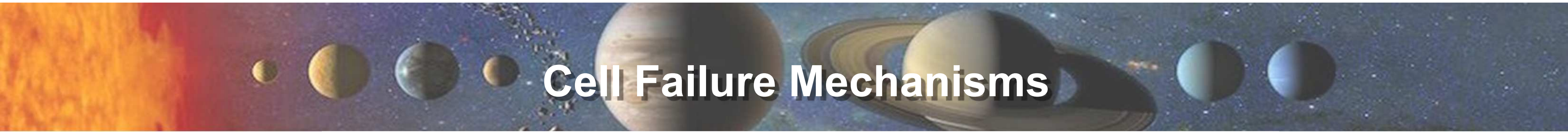
A Electrolyte: 1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +2% vinylene carbonate (VC)

Cathode impedance sharply increases after 80°C cycling

Impedance Studies

Cell	Voltage Range (V)	Cathode after Formation (Ohms)	Anode after Formation (Ohms)	Electrolyte after Formation (Ohms)	Cathode after 80C (Ohms)	Anode after 80C (Ohms)	Electrolyte after 80C (Ohms)	Cathode Impedance Growth (%)	Anode Impedance Growth (%)	Electrolyte Impedance Growth (%)
A1	2.75-4.1	0.686	0.486	0.566	3.51	0.49	0.428	411.6618	0.823045	-24.3816
A2	3.3-4.1	0.525	0.721	0.679	3.21	0.451	0.552	511.4286	-37.448	-18.704
A3	2.75-3.95	0.689	0.418	0.531	2.75	0.442	0.615	299.1292	5.741627	15.81921
L1	2.75-4.1	0.564	0.514	0.514	2.03	0.502	0.515	259.9291	-2.33463	0.194553
L2	3.3-4.1	0.592	0.366	0.609	2.07	0.437	0.584	249.6622	19.39891	-4.10509
L3	2.75-3.95	0.607	0.656	0.609	1.72	0.701	0.727	183.3608	6.859756	19.37603

Cell impedance growth is dictated by the cathode. Anode and electrolyte impedance changes are trivial.



Cell Failure Mechanisms

Cell failure mechanisms investigated:

- We have observed (as expected) that high temperature cycling of the cells leads to failure by two process:
  1) The cells current-carrying capability continually decreases
  2) The cells’ capacity continually decreases
- Electrochemistry study identified the cause of 1): Cell impedance growth occurs almost exclusively at the cathode
- Cell component replacement study[1] determined that 2): Capacity loss is associated with Li inventory loss
  - Furthermore, coupled with rationale for 1), almost certainly Li is consumed in film growth at the cathode
- These findings allow us to tightly focus our mitigation approaches. Other possible failure mechanisms such as crystallographic degradation of graphite or NMC can be discounted.

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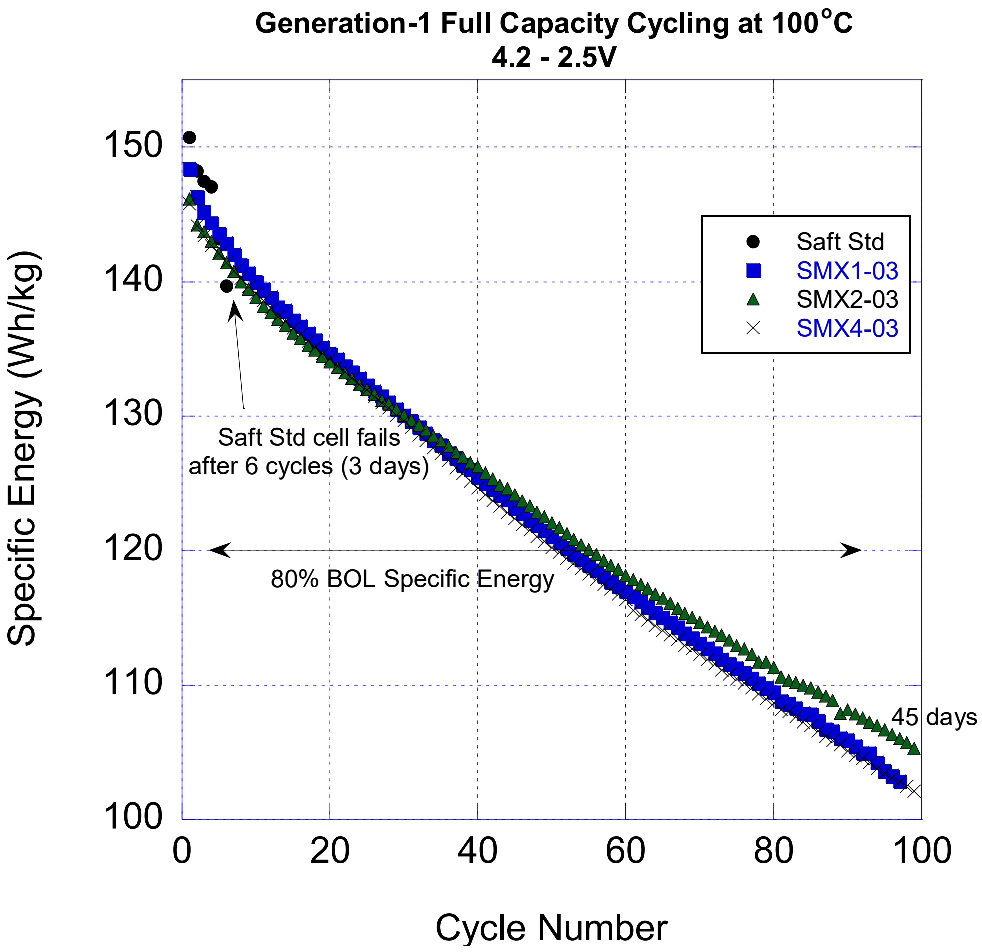
1. “Elucidating Failure Mechanisms in Li-ion Batteries Operating at 100 °C”, Brendan E. Hawkins, Harrison Asare, Brian Chen, Robert J. Messinger, William West, John-Paul Jones, *J. Electrochem. Soc.,* **170**, 100522 (2023) DOI 10.1149/1945-7111/acfc36.

Full Capacity Cycling Tests



Capacity after 35 cycles:

- Full capacity cycling (4.2-2.5V): **127 Wh/kg**
- Shallow cycling (4.1-3.2V): **117 Wh/kg**
- Very shallow cycling (3.75-3.2V): **70 Wh/kg**
- Standard Saft cell fails after only six cycles
- All three JPL electrolytes continue to cycle above 80% BOL specific energy for more than 50 cycles
  - No cell failures after more than 45 days at 100°C and 100 cycles

SMX1: 1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +2% VC
SMX2: 1.0M $LiPF_6$ in EC+EMC (50:50 v/v) +3% VC
SMX4: 1.0M $LiPF_6$, 0.10 M LiDFOB in EC+EMC (50:50 v/v) + 3% VC

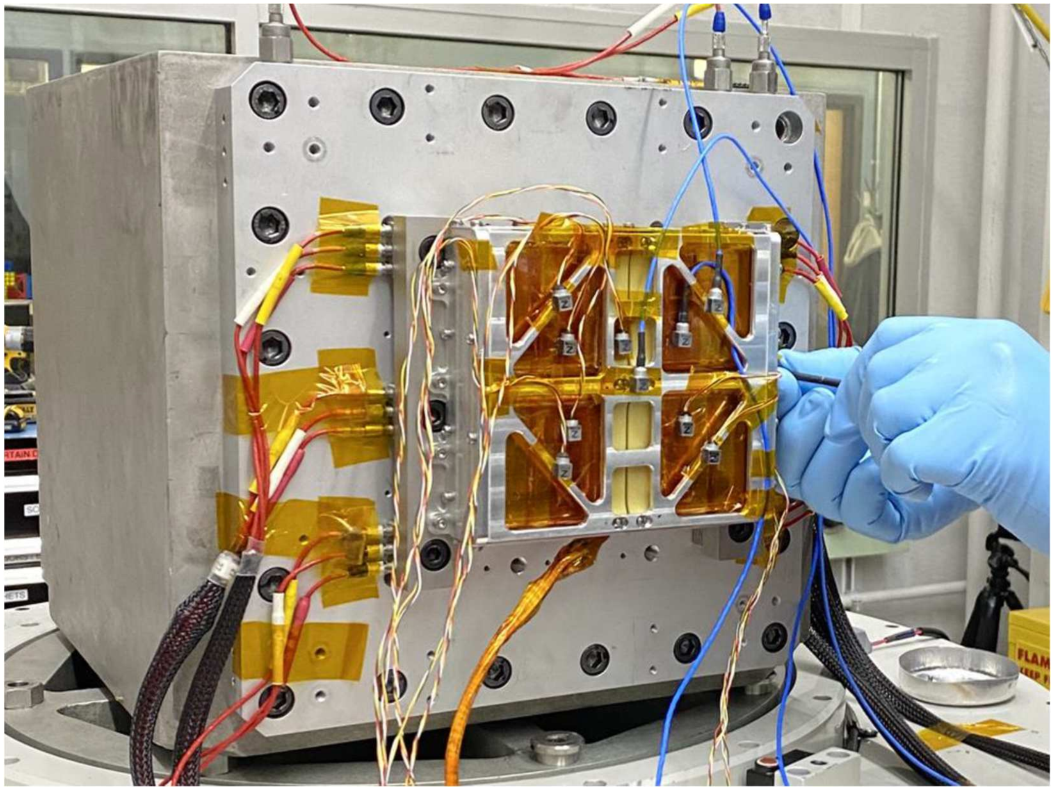
Fabrication of Venus Aerobot 4s1p Battery Module

- Heavily leverage Cooperative Autonomous Distributed Robotic Exploration mission (CADRE) battery module design
- Fabricated battery housing including frame and Ultem mounts
- Installed three layers of Kapton tape on cells
- Soldered pigtailed leads on terminals
- Completed bin testing on five of the PFD-variant cells
  - Room temperature capacity tests
  - Binned cell lot
  - Voltage leveling of binned cells
- Mounted cells in Ultem slots with custom Arathane encapsulation adhesive
- Connected harness to pigtailed leads
- Torqued/staked the assembly fasteners
- Carried out post-assembly capacity tests

4s1p battery module

Venus Aerobot Battery Operating Random Vibration Tests

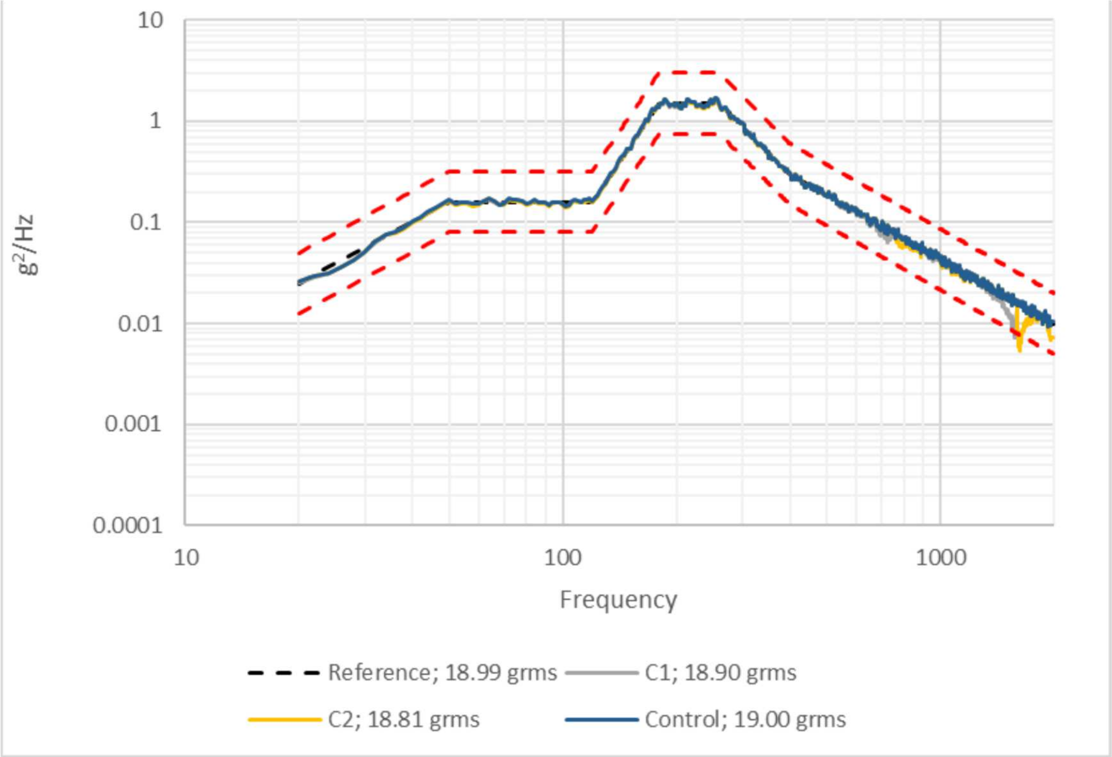
- Battery was mounted onto the cube which is then mounted to the shaker
- Low-level random signature surveys were done before and after application of full-level vibration requirements in each axis.
- Low-level vibration runs preceded the qualification level runs.
- Vibration testing was carried out based on CADRE mission qualification levels on all three axes.
- The battery was actively discharged during vibration testing.



X-Axis mounting of the Venus Aerobot Battery Assembly on vibration fixture

Venus Aerobot Battery Operating Random Vibration Tests

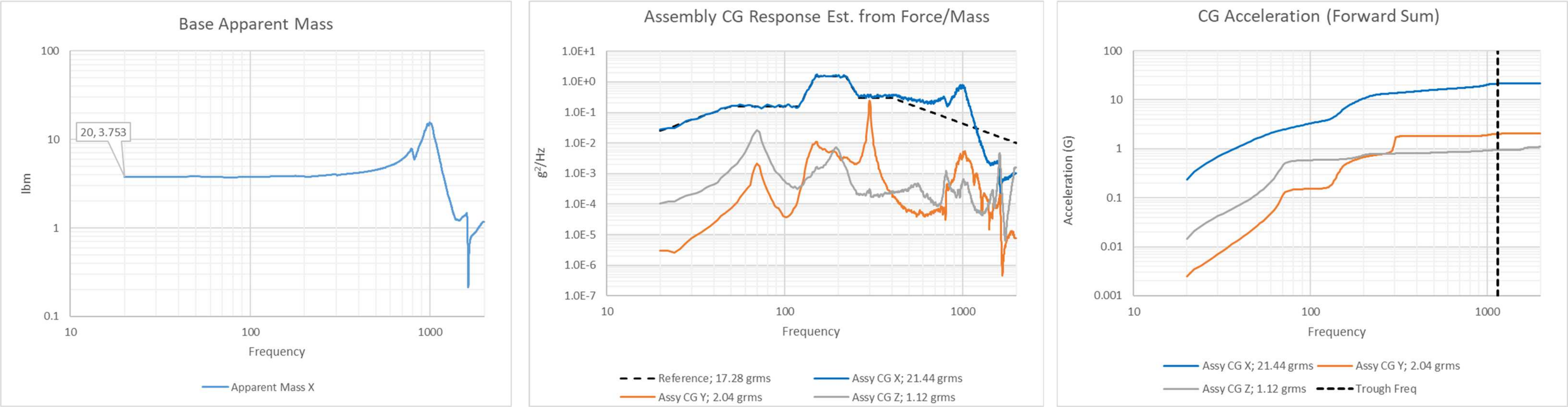
- The battery assembly underwent random vibration tests in all three orthogonal axes.
- The battery module successfully met the criteria for passing the qualification-level vibration test.
- Analysis of the acceleration responses and visual inspection indicated nothing anomalous except for the Kapton tape loosening near one accelerometer on the battery on the x-axis run.
- The battery was actively discharged during vibration testing.
  - No voltage/current chatter was observed.



Representative (z-axis) pre/post signature overlays.

Venus Aerobot Battery Quasi-Static Assessment (from random vibration test data)

X-Axis Quasi-Static Loading from RV Vibration CG Response

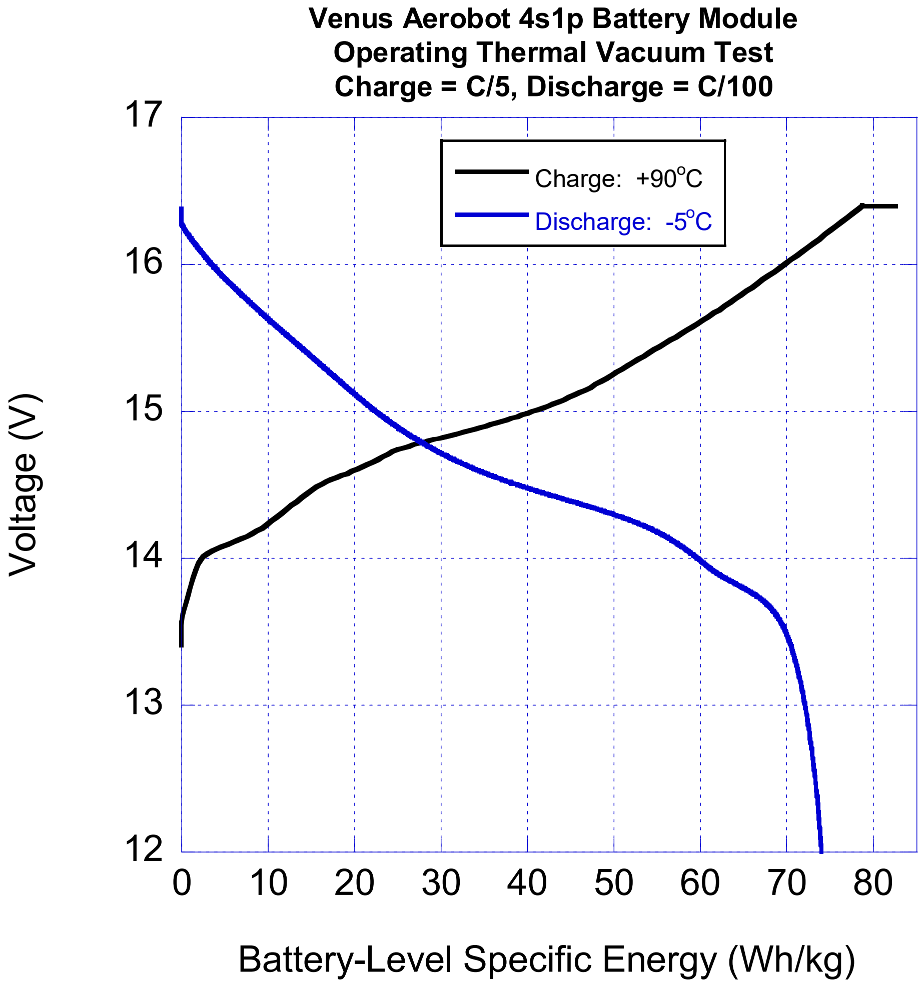


- Random vibration test data provide the means to estimate quasi-static loads

Quasi-Static Load Calc (X-Axis)

Peak Freq:	998Hz
Trough Freq:	1452Hz
Grms at Freq:	21.43G
3-Sigma Peak:	**64.29G**

Operating Thermal Vacuum (TVAC) Test of the Battery Module



- Successfully charged and discharged 4s1p battery module in thermal vacuum
- The battery module passed operating thermal vacuum test
- Cell-level specific energy:
  - Charge = 142 Wh/kg, 90°C, C/5
  - Discharge = 127 Wh/kg, -5°C, C/100

Summary

- Screened a large number of electrolyte variants
  - Focus on high temperature resilience
- Via a wide range of materials and electrochemical experiments, determined that:
  - Cathode is the culprit in elevated temperature impedance growth
  - Capacity fade is due to Li inventory loss
- Down-selected and infused promising electrolyte variants into flight-like cells
- Fabricated a 4s1p battery module using the CADRE battery design and successfully tested it via:
  - Thermal ambient cycling
  - Thermal vacuum cycling
  - Operating random vibration
    - Quasi-static load

Acknowledgements

This research was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA).

Backup