National Aeronautics and Space Administration

FY24 Strategic Initiatives Research and Technology Development (SRTD)

Advanced, Wide Operating Temperature Batteries for Venus Aerobot Missions

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Strategic Focus Area: Technologies for Venus Cloud Environments /Venus In-Situ Aerosol Measurement Technologies **| Strategic Initiative Leader:** James A Cutts

Objectives: The overall task objective was to develop a wide operating temperature flight-worthy Li-ion battery module that could meet the required temperature range, cycle life, and energy requirements of a Venus Aerobot mission. In the third year, the specific objectives were to:

1. Carry out a follow-on operational test of the Li-ion battery module designed and fabricated in Year 2 in thermal vacuum chamber to better envelop allowable flight temperature (AFT) predicts.
2. Continue wide-operating temperature electrolyte development
3. Hold a Technology Readiness Assessment (TRA) targeting TRL 5.

Background: The 4x directorate seeks to develop technologies that will enable a mission with a Venus-deployed variable altitude aerobot for near-term New Frontiers or Discovery Class opportunities. The expected temperature range of an aerobot operating in the Venus atmosphere is quite challenging, spanning from low temperatures of about -15ºC to -30ºC up to about 80ºC to 100ºC depending on the diurnal cycle and aerobot elevation between 52 to 62 km in the Venus cloud layer. While space-rated Li-ion cells can be tailored to meet the lower temperature limit, operating or storage temperatures higher than about 60ºC can rapidly degrade cell performance. Although there is a specialized Li-ion battery cell type offered by one vendor with a state-of-the-art specific energy that can approach operating at this temperature range (-30ºC to +85ºC), it cannot meet the upper temperature requirement of 100ºC. Furthermore, this cell degrades rapidly even when held at 85ºC, and experiences swelling and steep capacity fade in tens of days. At 100ºC, it is likely this cell would fail catastrophically after extended high temperature exposure. As such, a new mission-enabling battery cell technology must be developed that can tolerate the temperature extremes of the Venus atmospheric mission.

Approach and Results:

- The four-cell battery module was tested in an operating thermal vacuum cycle to simulate a single diurnal cycle. The first charge-discharge cycle data is shown in Figure 1, where the charging is anticipated during the Venus daytime at the maximum temperature over approximately five hours while the photovoltaic panels are illuminated. The discharge is anticipated to occur in the nighttime when no photovoltaic power is available and the spacecraft is set into sleep mode with minimal power requirements. This charge/discharge test routine was then set to 90ºC to 100ºC charge at C/5 (where C is taken as 5.5A) and discharge is set to -30ºC to -5ºC at C/100. Figure 1 shows the battery module mounted in the thermal vacuum chamber. As shown in Figure 2, the battery module and cells were able to survive thermal vacuum testing in the desired temperature range, providing approximately 4.7Ah capacity at 16.4V – 12V. These battery modules can in principle be configured in multiple parallel units to provide greater capacity and allow for even distribution of mass around the Venus Aerobot spacecraft.
- The development of novel wide-operating temperature electrolytes continued. Preliminary results described in the Year 2 final report were further elaborated in Year 3. For example, the previously developed baseline electrolyte, 1.0 M lithium hexafluorophosphate ($LiPF_6$) in 1:1 ethylene carbonate (EC):ethyl-methyl carbonate (EMC) (v/v) with 2 wt.% vinylene carbonate (VC), was altered to observe the effects of the lithium salts lithium difluoro(oxalato)borate (LiDFOB) and lithium difluorophosphate (LiDFP), and the fluorinated co-solvent 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE). The resulting formulations showed significantly improved capacity retention at 100°C in multiple cell configurations. X-ray photoelectron spectroscopy (XPS) characterization of the electrodes following cycling at high temperatures with the improved electrolyte revealed the cathode-electrolyte-interphase (CEI) to be boron-rich, while the graphite anodes were found to have little boron but were more fluorine rich compared to the baseline anodes. Overall, the use of various Li salts as well as the TTE co-solvent improved specific capacity retention and reduced cell-to-cell variability at 100 °C as shown in Figure 3. Furthermore, improvements in both the anode and cathode impedances were observed in the cells with TTE-based electrolytes relative to the baseline electrolyte (Figure 4).
- The team convened a Technology Readiness Assessment (TRA) board to establish the TRL of the Venus Aerobot battery module, with a target TRL 5. The conclusion reached by the review board was the battery module could be reasonably assessed at TRL 6. This outcome is being documented in an Interoffice Memorandum (IOM #3466-24-001).

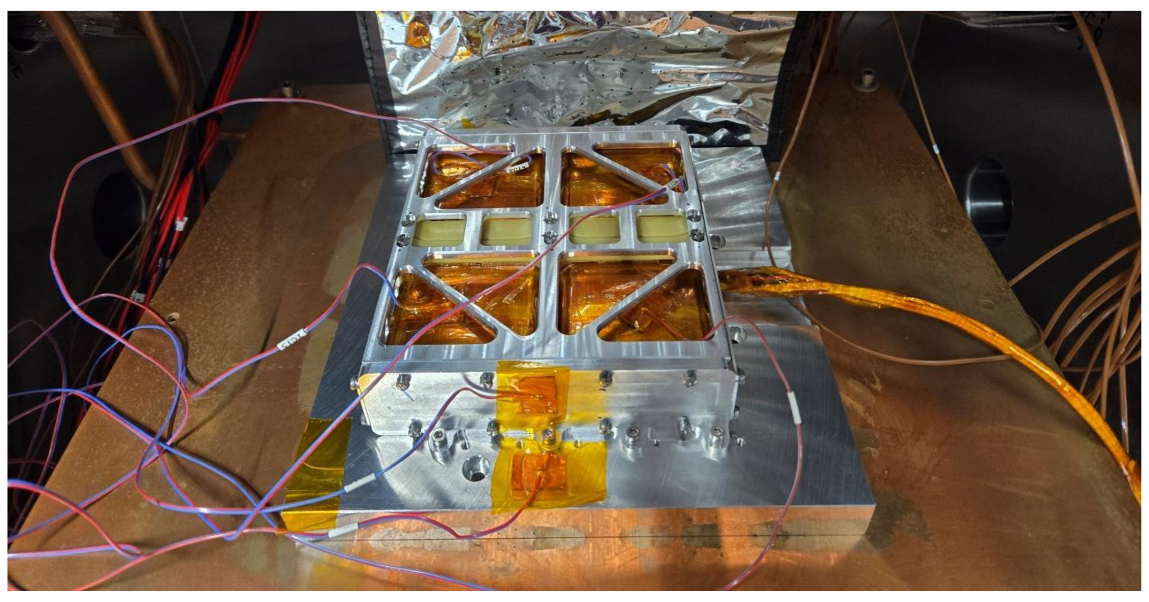

Figure 1. Four cell (4s1p) Venus Aerobot battery module mounted in the thermal vacuum chamber for re-test under wider temperature range of -10ºC to +95ºC during operation.

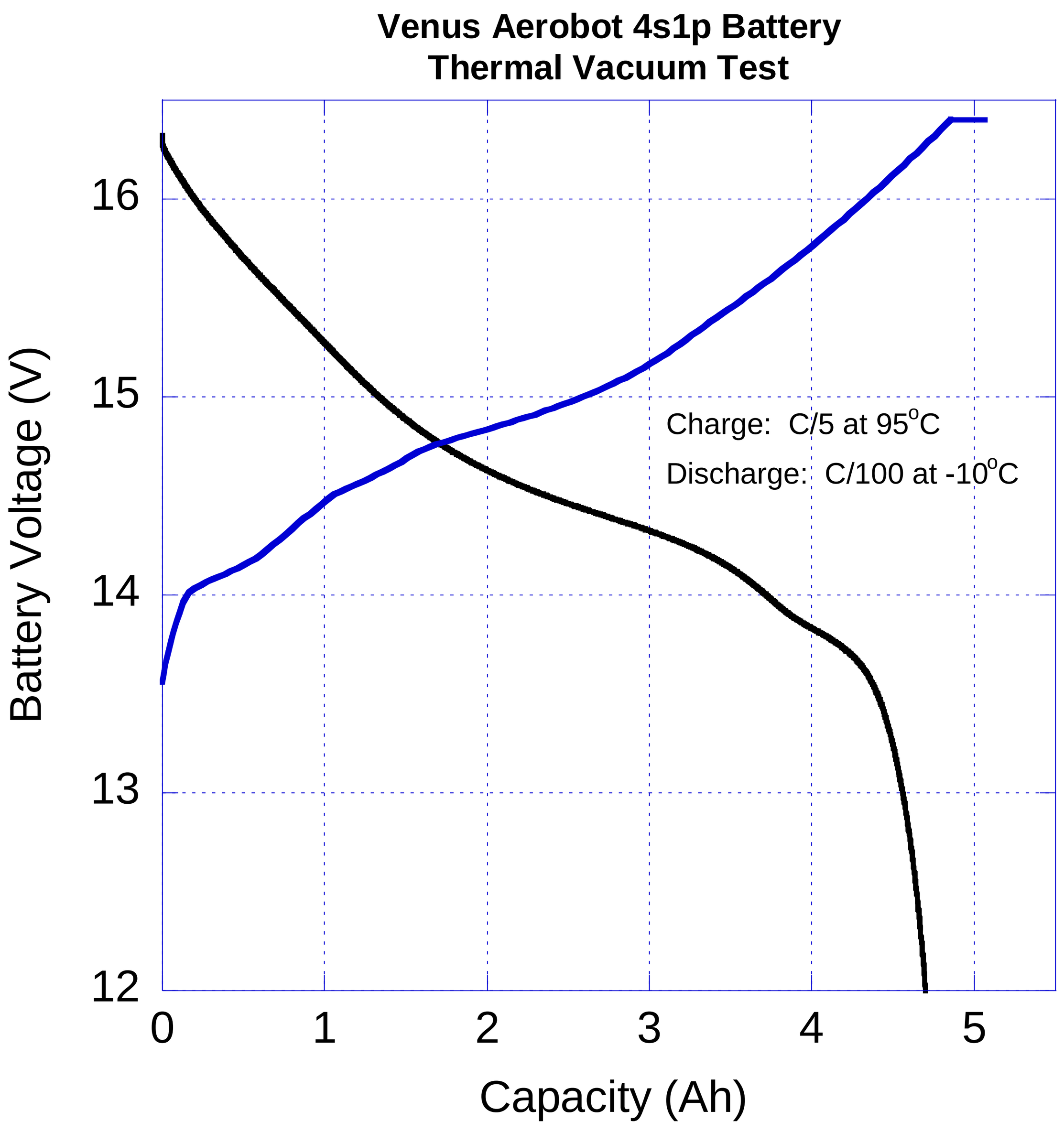

Figure 2. Charge-discharge profile for the 4s1p battery module. The charging was carried out at a C/5 rate at 95ºC and discharged at C/100 at -10ºC, where the nominal cell capacity is 5.6 Ah.

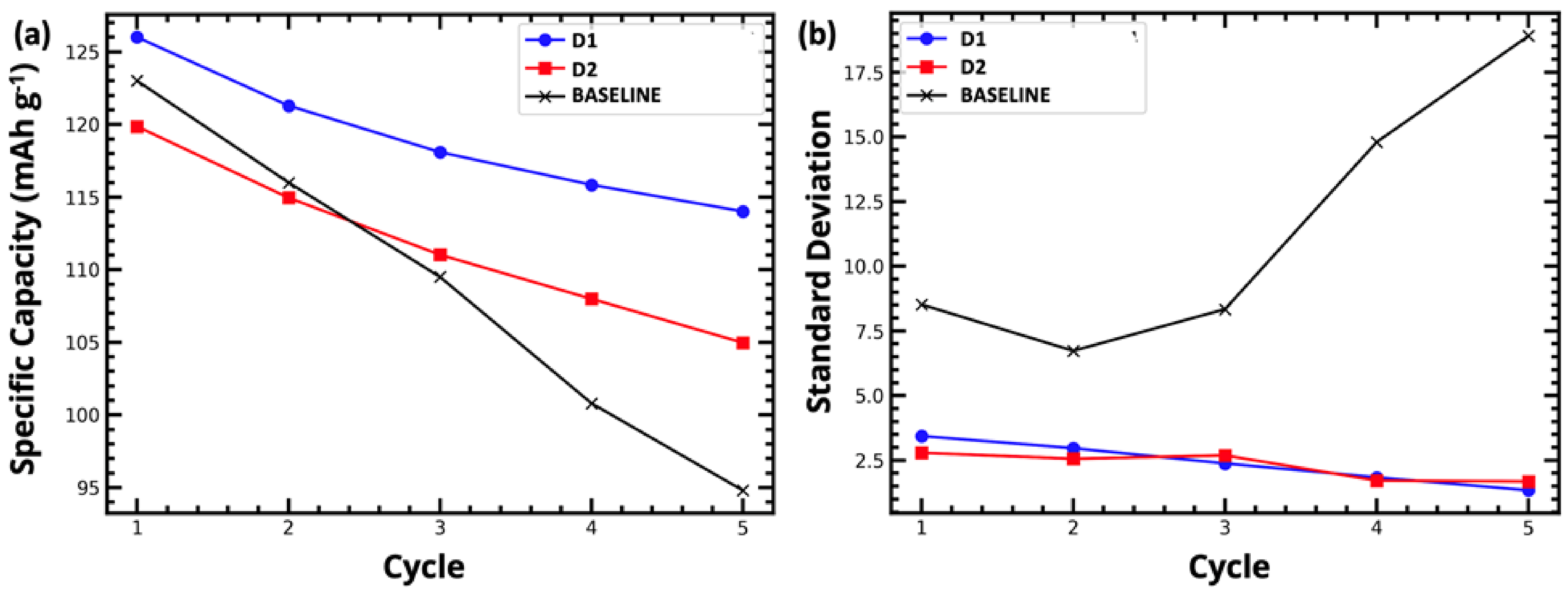

Figure 3. Galvanostatic charge/discharge experiments of Li-ion graphite-NMC111 coin cells showing at C/5: (a) Discharge specific capacity of the 1st five cycles at 100 °C in coin cells. (b) Standard deviation of these cycles for the baseline vs. D1 (0.125 M LiDFOB 0.5 M LiPF6 in 1:1:2 EC:EMC:TTE + 2 wt. % VC, 2 wt. % LiDFP) and D2 electrolyte (0.25 M LiDFOB, 0.5 M LiPF6 in 1:1:2 EC:EMC:TTE + 2 wt. % VC, 2 wt. % LiDFP). The points represent averages of multiple cells: Electrolyte D1 (5 cells), electrolyte D2 (4 cells), and the baseline (4 cells).

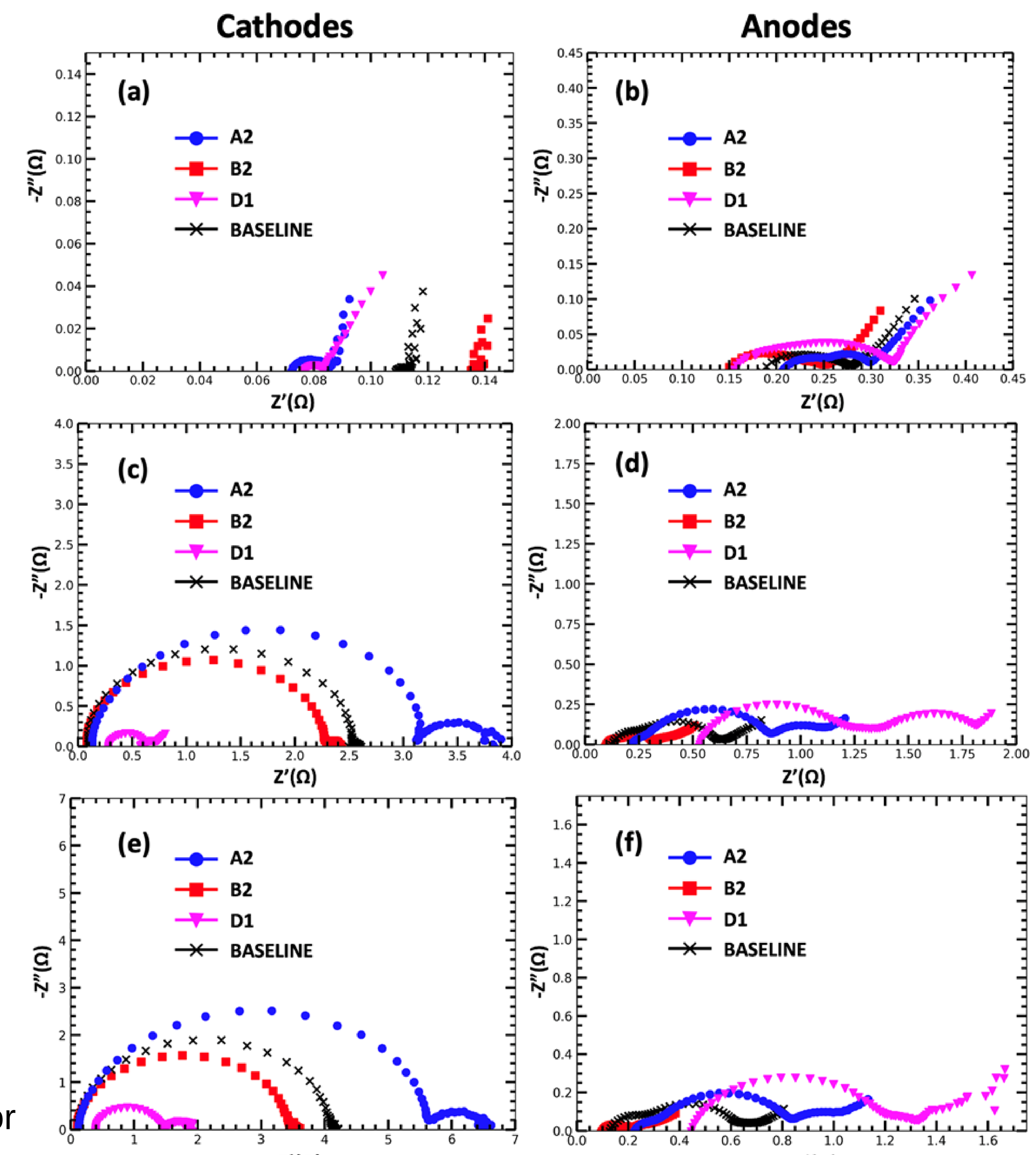

Figure 4. Complex-plane plots of (a) NMC111 cathodes cycled through formation cycling at room temperature, (b) graphite anodes cycled through formation cycling at room temperature, (c) NMC111 cathodes cycled through 5 cycles at 100ºC, (d) graphite anodes cycled through 5 cycles at 100ºC, (e) NMC111 cathodes cycled through 10 cycles at 100ºC, and (f) graphite anodes cycled through 10 cycles at 100ºC.

Significance/Benefits to JPL and NASA: This year's effort resulted in:

1. Further understanding of variables of the cell makeup that can enable improved performance of the battery technology for operation over a wide temperature range.
2. A submitted manuscript now under external peer review describing new electrolyte formulations.
3. The re-test of the 4s1p battery module under operating thermal vacuum conditions under a wider temperature range, confirming the performance of the module can survive charging in vacuum at elevated temperatures near the maximum AFT and discharge in vacuum at low temperatures.
4. Successfully passed a Technology Readiness Assessment at TRL 6 paving the way for infusion of the battery module into future lunar or Venus atmospheric missions.

National Aeronautics and Space Administration

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PFY24 Publications and NTRs:

- "Fluorinated Ether Co-solvents to Enable High Operating Temperature Li-ion Batteries", Jonah Wang, Michael J. Keating, Harrison Asare, Elizabeth J. Biddinger, Robert J. Messinger, William C. West, and John-Paul Jones, *J. Electrochem Soc., (in review).*
- " "Fluorinated Ether Co-Solvents Enable Wide Operating Temperature Lithium-Ion Cells", William West, John-Paul Jones, and Jonah Wang, *New Technology Report #52816,* (2023).

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