High Temperature Batteries for Planetary Missions

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Space Power Workshop 2025

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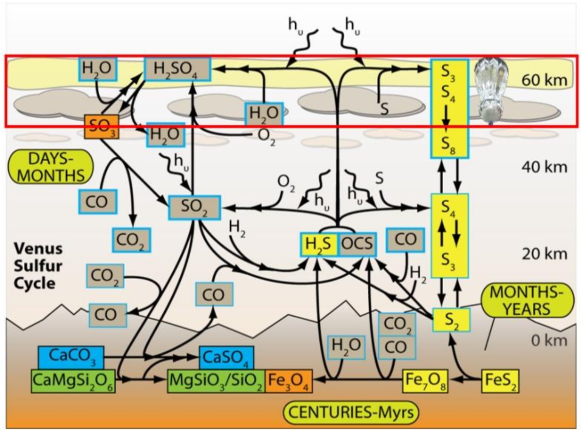
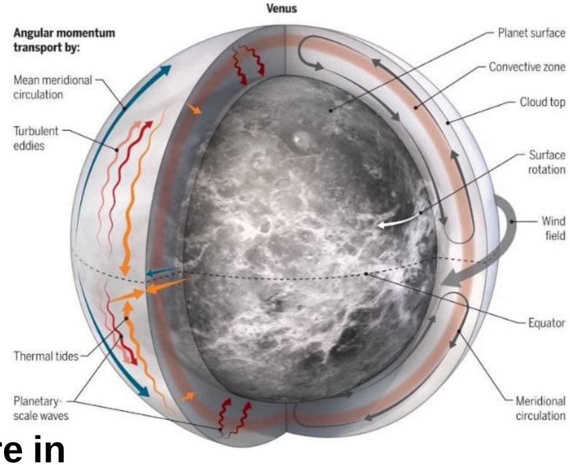
Venus Atmosphere is Relatively Unexplored

- <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
- **Only missions to the Venusian atmosphere were in the 1980s**
  - Short-lived, fixed altitude balloon

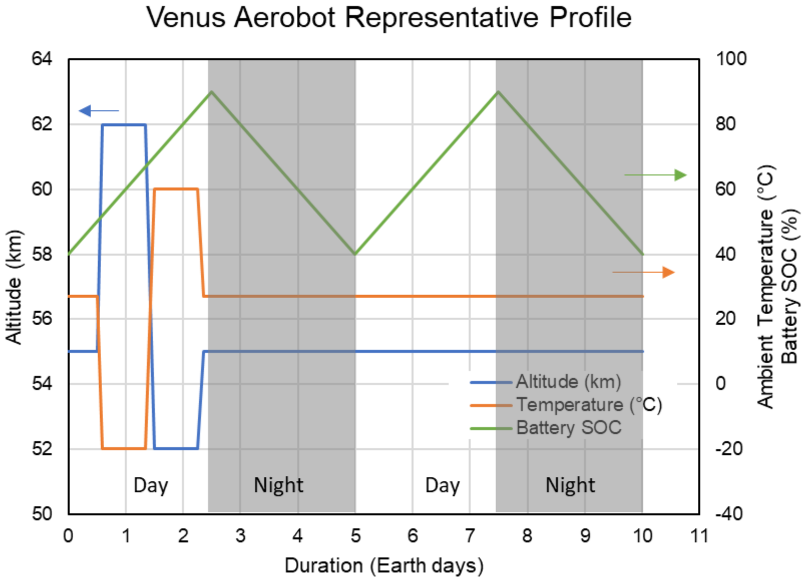


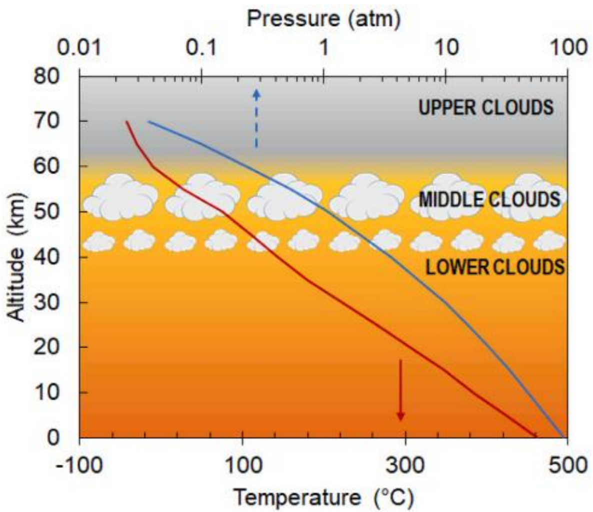


Pre-Decisional Information -- For Public Release, Planning and Discussion Purposes Only

Venus Mission Driver for High Temperature Batteries

- Venus Aerobot mission concepts would deploy a variable altitude balloon to the Venus cloud layer
- Atmospheric winds carry the balloon around the planet in five days with 60 hours in sunlight and 60 hours in darkness



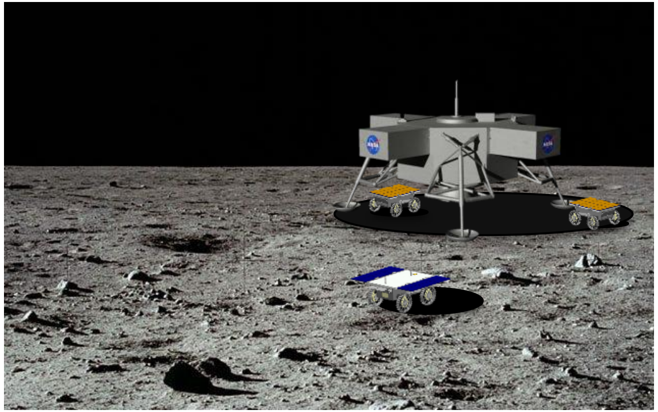


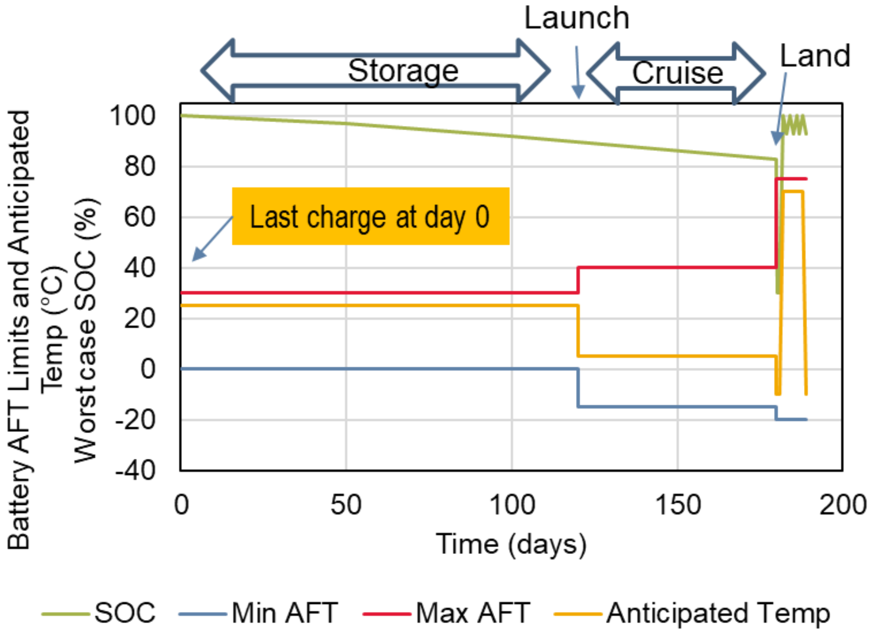
Bugga et al. Acta Astronautica 197 (2022) 69–80

- Ambient temperature in the range of -20 °C to +60 °C means that the battery would warm to >80 °C during daytime operation
- Standard electronics limit upper allowable flight temperature (AFT) to ~85 °C
- Battery would need temperature margin over 85 °C
- 100 °C upper operation of battery selected for design work
  - No current COTS high energy Li-ion batteries are rated for such a high temperature
- Relatively slow battery cycles allow focus to remain on high temperature

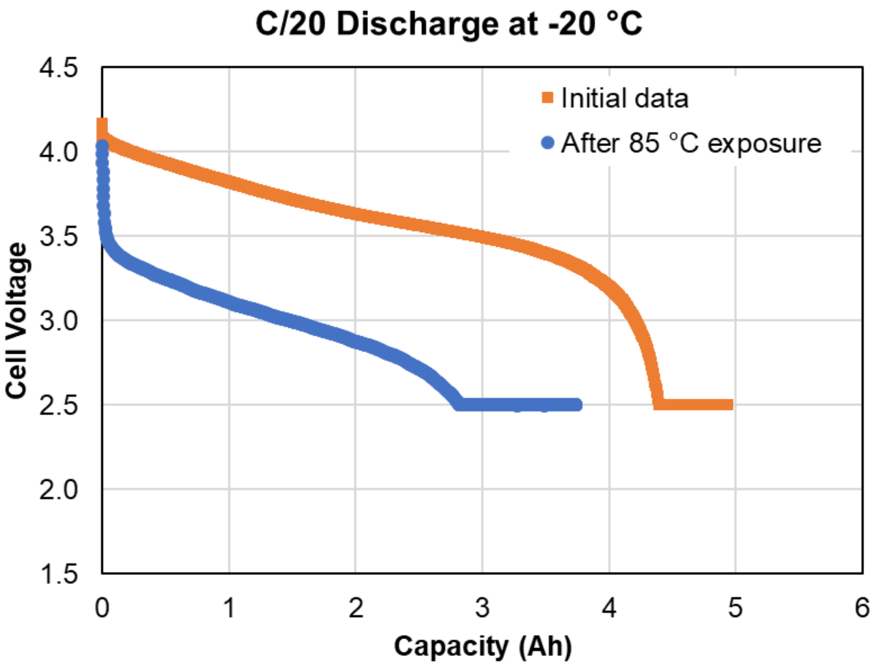
Lunar Mission Driver for High Temperature Batteries

- Approximate Temperature range: -170 to +120 °C
  - Thermal management limits extreme temperature exposure
- Desire to survive multiple diurnal cycles (i.e. multiple months)
- Cooperative Autonomous Distributed Robotic Exploration (CADRE) rovers designed for 14 Earth days (illuminated period on surface) of operation from -10 to 75 °C (AFT)
  - Used Saft MP-xtd cells in 4s1p battery
  - Planned launch in late 2025-early 2026 on IM-3





Effect of high temperature exposure

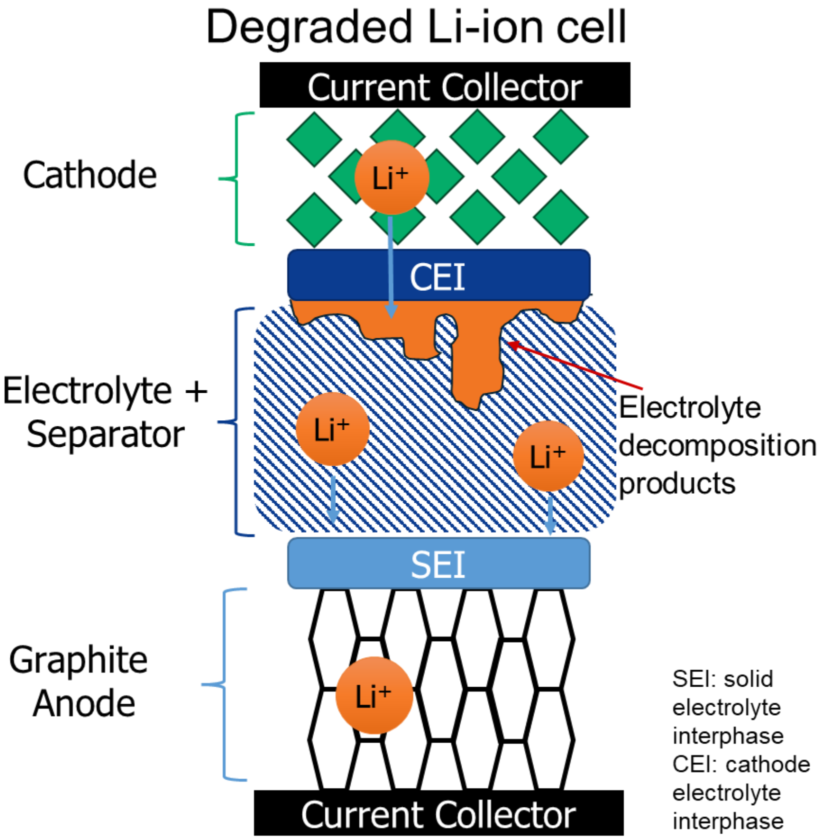


Charge: C/20 to 4.2 V until current dropped to <C/200 at -20 °C
Discharge: C/20 to 2.5 V until current dropped to <C/200 at -20 °C

- Cells survive high temperature exposure, but at the expense of significant impedance growth during operation
- Cells used for temperature and rate performance testing were subsequently screened at -20 °C
- Cell exposed to very stressful conditions (4.2 V charge, high and low rate) for 18 days
- Results indicate ~60% loss of capacity at C/20

What is the Failure Mechanism at High Temp?

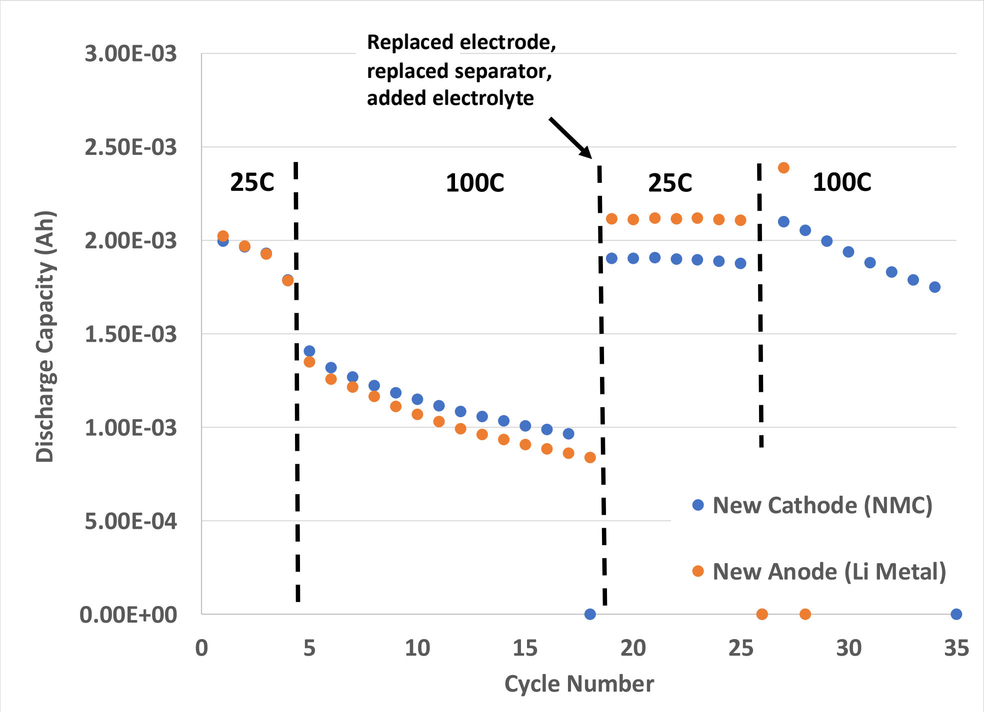
- Active materials are all stable at >100 °C
- Electrolyte components by themselves are stable to >100 °C
- The cathode electrolyte interphase (CEI) and solid electrolyte interphase (SEI) are two prime candidates for instability
- Both are formed by breakdown products from the electrolyte and serve to stabilize the cell over hundreds-thousands of cycles
- Breakdown products lead to stranded lithium which leads to capacity fade[1]



SEI: solid electrolyte interphase
CEI: cathode electrolyte interphase

[1]Floras et al 2025 J. Electrochem. Soc. 172 020514

Electrode Replacement Studies

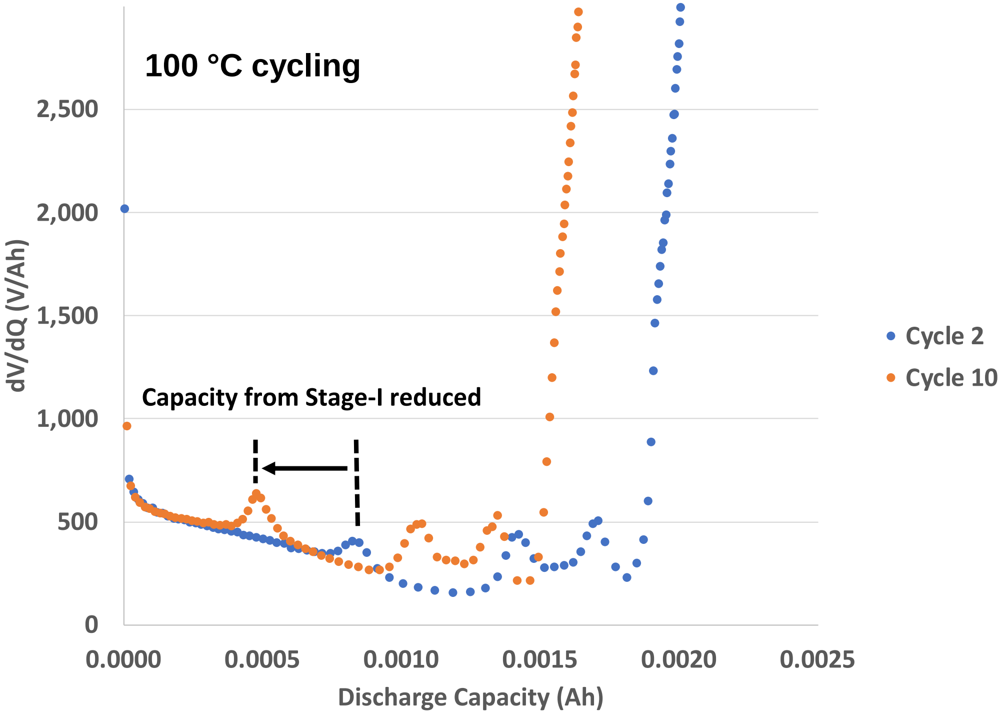


1.0 M $LiBF_4$ in EC+EMC (1:1 vol.) + 2% VC
Graphite / NMC 111 Swagelok Cells
4.1 to 3.2 V, C/5 cycling

- Replacing electrodes with lithium metal shows virtually full capacity recovery after high temperature exposure
- Suggests that both cathode and anode are relatively stable at +100 °C
- Lithium inventory loss probable cause for capacity fade

Hawkins et al. *Journal of The Electrochemical Society*, **2023** 170 100522.
https://doi.org/10.1149/1945-7111/acfc36

Electrode Replacement Studies



1.0 M $LiBF_4$ in EC+EMC (1:1 vol.) + 2% VC

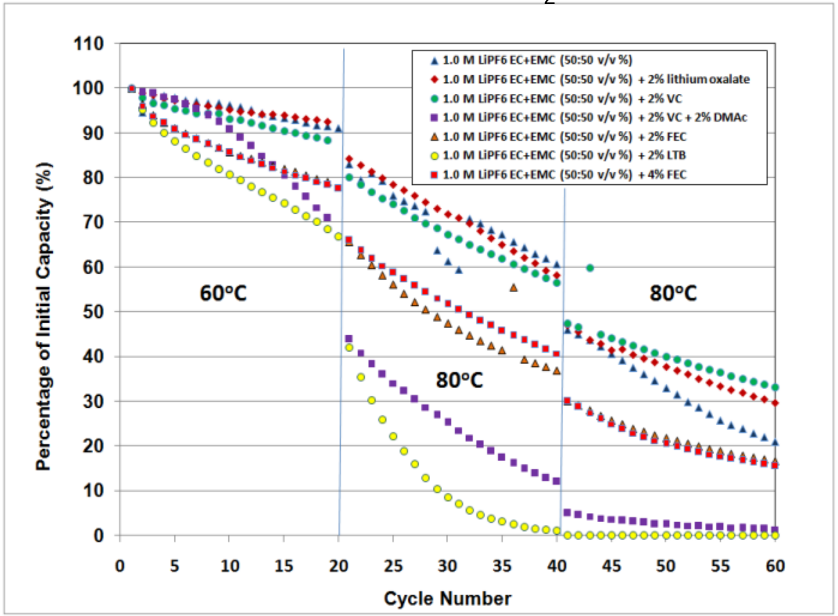
- dV/dQ analysis indicates that loss of lithium associated with Stage I graphite intercalation
- Capacity associated with other stages remains relatively constant
- Supports stability of anode (at least) during high temperature exposure

Hawkins et al. *Journal of The Electrochemical Society*, **2023** 170 100522. https://doi.org/10.1149/1945-7111/acfc36

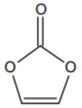
Prior studies of high temperature electrolytes

- Prior studies of high temperature electrolytes indicated that high EC content helped to alleviate high temperature survivability
- EC is essential to forming a good SEI, so higher EC content is likely re-forming an SEI as it is degraded
- 1.0 M $LiPF_6$ in EC+EMC 50:50 used as baseline
- 2% VC as an additive showed best performance

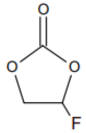
MCMB - $LiNiCoO_2$ cells



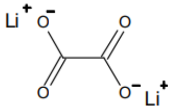
Smart et al. ECS Transactions, 25 (36) 37-48 (2010)



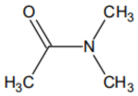
VC



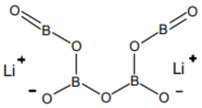
FEC



Lithium oxalate



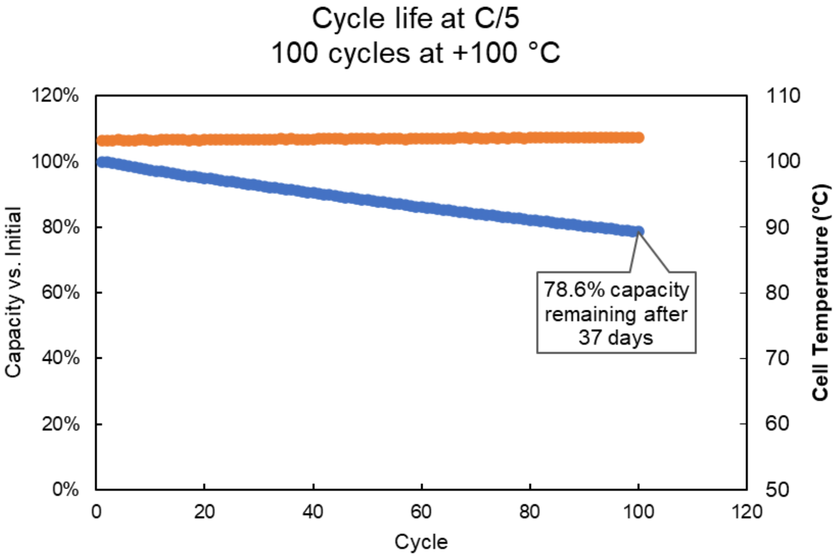
DMAc

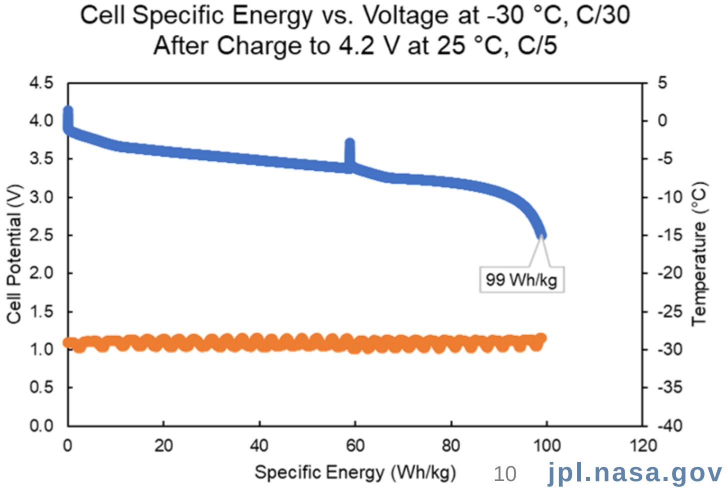


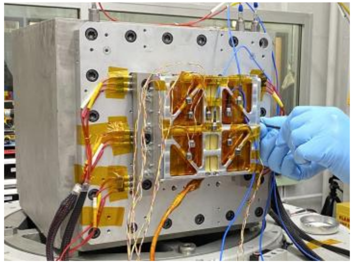
LTB

Commercial Cell Build and Testing

- Custom Saft MP-xtd cells filled with JPL electrolyte:
    - 1.0 M $LiPF_6$ in EC:EMC (50:50 v/v) + 2 wt % VC + 2 wt % LiDFP
    - LiDFP was selected to help stabilize the CEI based on prior work[1]
- Cells operate for 100 cycles, or 37 days to 80 % capacity when cycled at C/5, 100 °C
- Cells still provide reasonable energy (100 Wh/kg) at -30 °C at benign rates
- Performance meets mission requirements for notional Venus Aerobot battery duration
- Cells built into battery and vibration and Tvac tested to demonstrate TRL 6



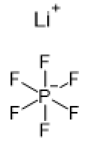




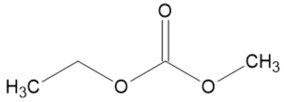
[1]Wang et al., Ionics, 27, 4135 (2021).

Continued 100 °C Electrolyte Development

Baseline components

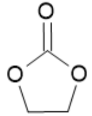


$LiPF_6$
Lithium
Hexafluorophosphate

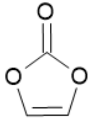


EMC
Ethyl Methyl
Carbonate

SEI formation / stabilization

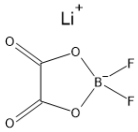


EC
Ethylene
Carbonate

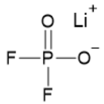


VC
Vinylene
Carbonate

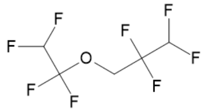
New components focused on cathode



LiDFOB
Lithium
Difluoro(oxalate)borate



LiDFP
Lithium
Difluorophospahte



TTE
1,1,2,2-tetrafluoroethyl-
2,2,3,3-tetrafluoropropyl ether

CEI formation / stabilization

High oxidative stability

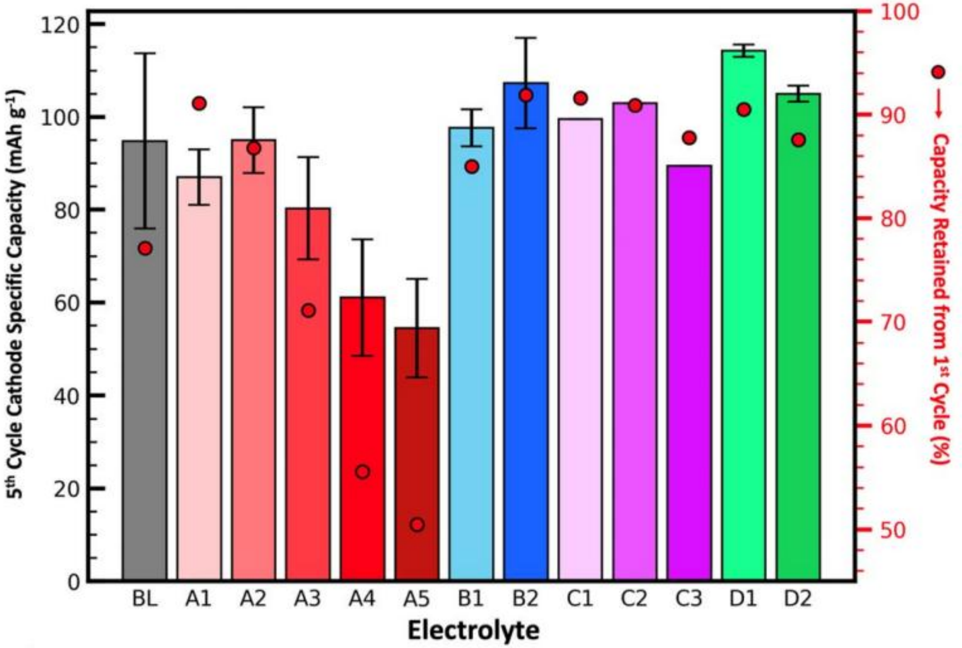
- Screened 100s of electrolytes in coin cells sealed in epoxy
- Graphite anode, NMC111 cathode
- Formed at room temp
- Cycled at +100 °C, C/5 from 4.2 to 2.5 V
- Identified three additional beneficial components:
  - Lithium difluoro(oxalato)borate (LiDFOB)
  - Lithium difluorophosphate
  - 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE)
- Other things that didn't work:
  - LiTFSI and LiFSI, other Li salts
  - Ionic liquids
  - FEC
  - Blends without a high EC content

Wang *et al.* 2024 *J. Electrochem. Soc.* **171** 120517 DOI: 10.1149/1945-7111/ad9b52

Selected Electrolytes

Li Salt	Solvent (v/v)	Additive	Abbreviation
1.0 M $LiPF_6$	1:1 EC:EMC	2 wt % VC	BL
0.25 M LiDFOB, 1.0 M $LiPF_6$	1:1 EC:EMC	2 wt % VC	A2
0.25 M LiDFOB, 1.0 M $LiPF_6$	1:1 EC:EMC	2 wt % VC, 2 wt % LiDFP	B2
0.125 M LiDFOB, 0.5 M $LiPF_6$	1:1:2 EC:EMC:TTE	2 wt % VC, 2 wt % LiDFP	D1
0.25 M LiDFOB, 0.5 M $LiPF_6$	1:1:2 EC:EMC:TTE	2 wt % VC, 2 wt % LiDFP	D2

- 5^{th} cycle capacity turned out to be enough to separate electrolytes
- High degree of variability observed in cells operated at high temp
- Blends with TTE (solvent), LiDFOB (co-salt) and LiDFP (additive) showed best overall performance
- TTE as a co-solvent dramatically improved reproducibility



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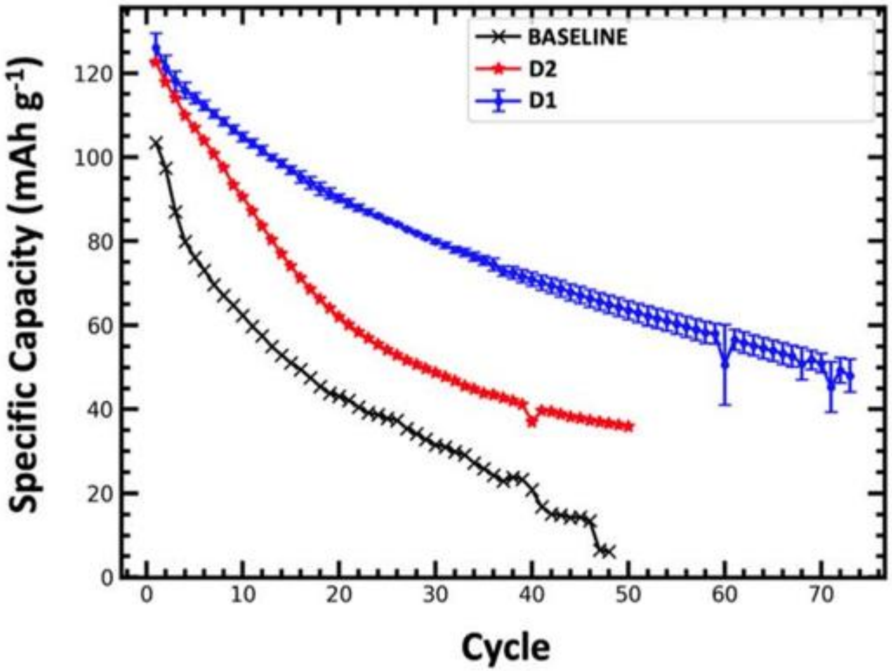
Long Term Cycling at 100 °C

Li Salt	Solvent (v/v/v)	Additive	Abbreviation
1.0 M $LiPF_6$	1:1 EC:EMC	2 wt % VC	BL, Baseline
0.125 M LiDFOB, 0.5 M $LiPF_6$	1:1:2 EC:EMC:TTE	2 wt % VC, 2 wt % LiDFP	D1
0.25 M LiDFOB, 0.5 M $LiPF_6$	1:1:2 EC:EMC:TTE	2 wt % VC, 2 wt % LiDFP	D2

- The D1 long term cycling data shows an average specific capacity of three coin cells with error bars
  - One cell reached 73 cycles at 100 °C and the other two reached the 100 cycle limit with a standard deviation of ± 8.8 mAh/g
- The plotted data shows the Baseline and D2 cell with the highest achieved cycle number for this study



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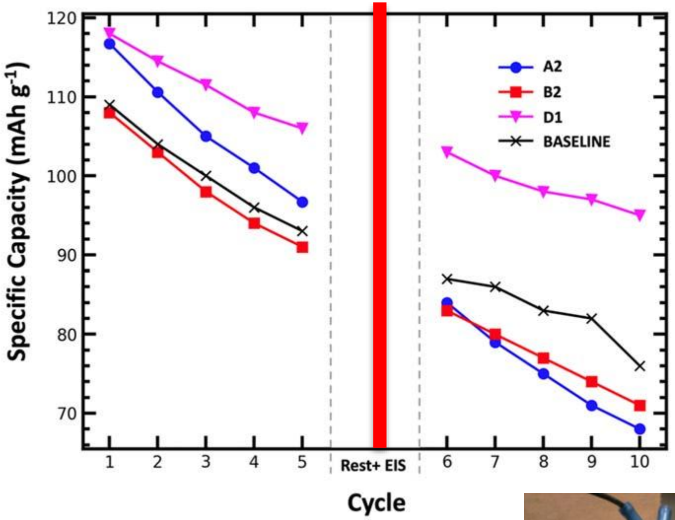
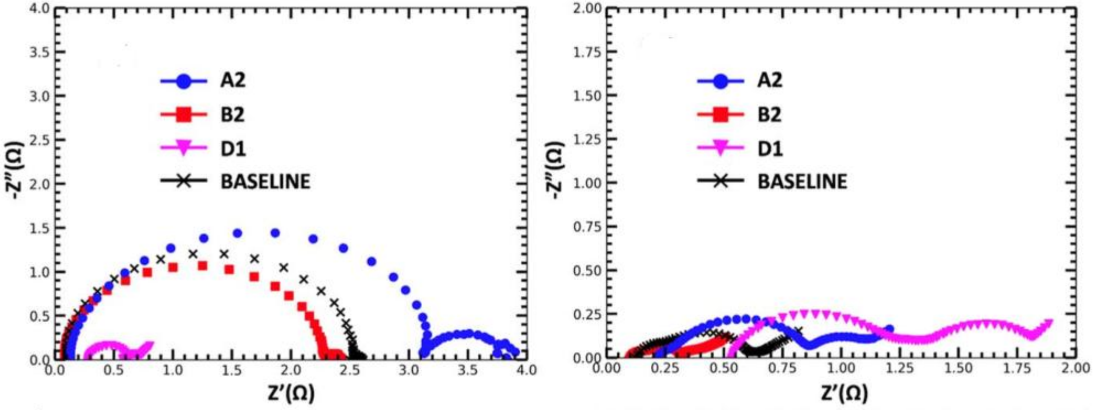
EIS on 3-Electrode Cells After 100 °C



Post 5-cycles at 100 °C

Cathode

Anode



Baseline: 1 M $LiPF_6$ 1:1 EC:EMC + 2 wt% VC
A2: 0.25 M LiDFOB 1 M $LiPF_6$ 1:1 EC:EMC + 2 wt% VC
B2: 0.25 M LiDFOB 1 M $LiPF_6$ 1:1 EC:EMC + 2 wt% VC + 2 wt% LiDFP
D1:0.125 M LiDFOB 0.5 M $LiPF_6$ 1:1:2 EC:EMC:TTE + 2 wt% VC + 2 wt% LiDFP

- Post-formation: Both cathode (< 0.15 Ohm) and anode (< 0.4 Ohm) impedance are low
- Post 5-cycle 100 °C: Significant increase in cathode impedance (up to 3 Ohm) for all compositions except D1, anode impedance for D1 increases more than other compositions
- **TTE-containing electrolyte significantly improves CEI stability after 100 °C cycling**

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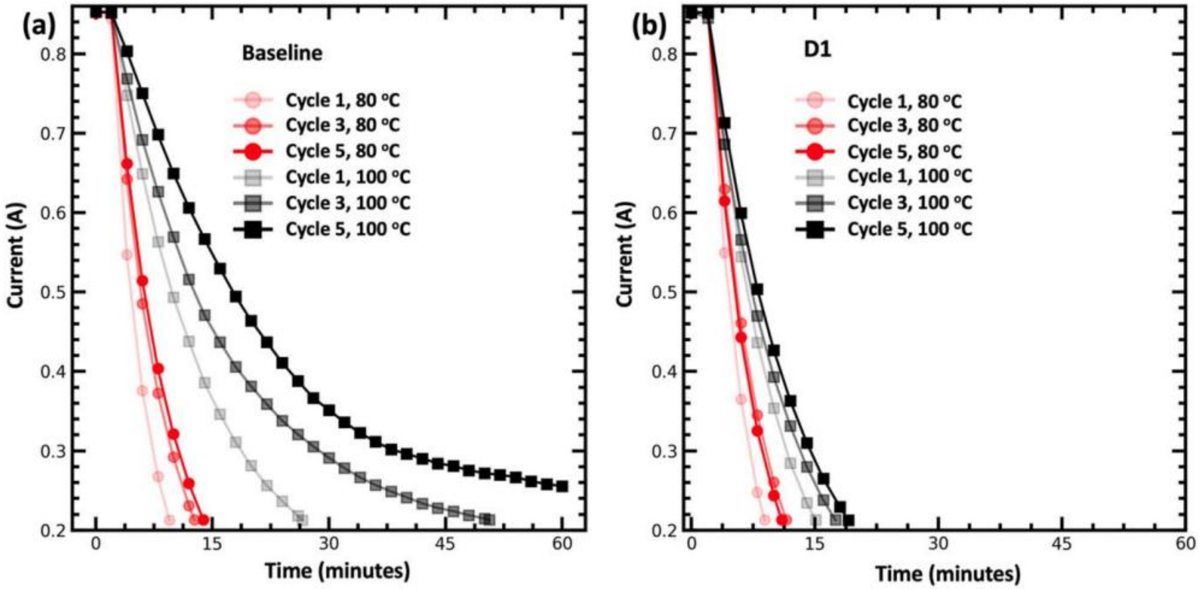
Charge Taper

Baseline: 1 M $LiPF_6$ 1:1 EC:EMC + 2 wt% VC

D1:0.125 M LiDFOB 0.5 M $LiPF_6$ 1:1:2 EC:EMC:TTE + 2 wt% VC + 2 wt% LiDFP



- Cells charged at C/5 to 4.2 V
- Held at 4.2 V until current falls below C/50 or 1 hour has passed
- Cells behave similarly at 80 °C
- TTE-containing electrolytes consistently tapered for much less time than non-TTE-containing electrolytes at 100 °C
- Time and current passed during taper indicates formation of breakdown products, rather than charge storage
  - Corresponds to steep capacity fade

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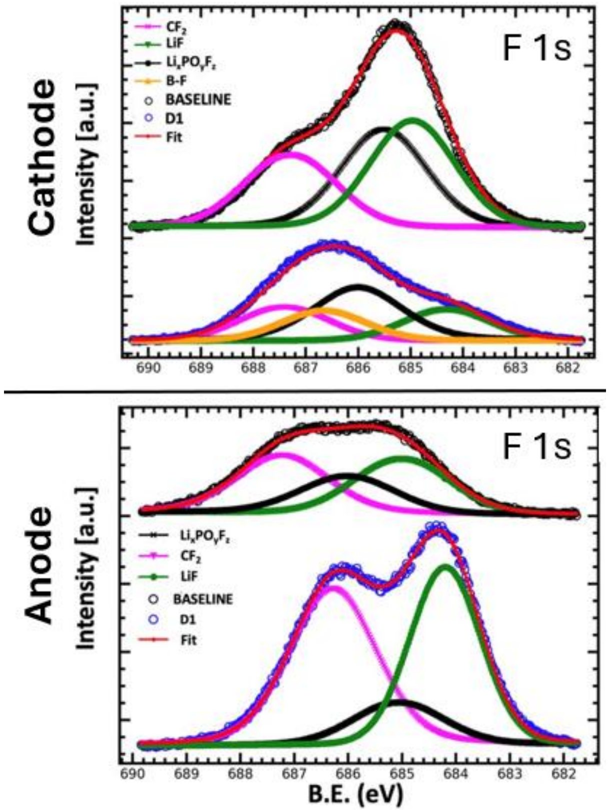
XPS Analysis After 100 °C



- XPS investigation of the harvested anode and cathode from cells cycled at 100 °C
- These findings demonstrate the significant impact of LiDFOB, LiDFP and TTE on electrode film formation at 100 °C
- Both cathode and anode films are substantially different when we switch from the baseline to TTE-containing electrolyte

Baseline: 1 M $LiPF_6$ 1:1 EC:EMC + 2 wt% VC
D1:0.125 M LiDFOB 0.5 M $LiPF_6$ 1:1:2 EC:EMC:TTE + 2 wt% VC + 2 wt% LiDFP

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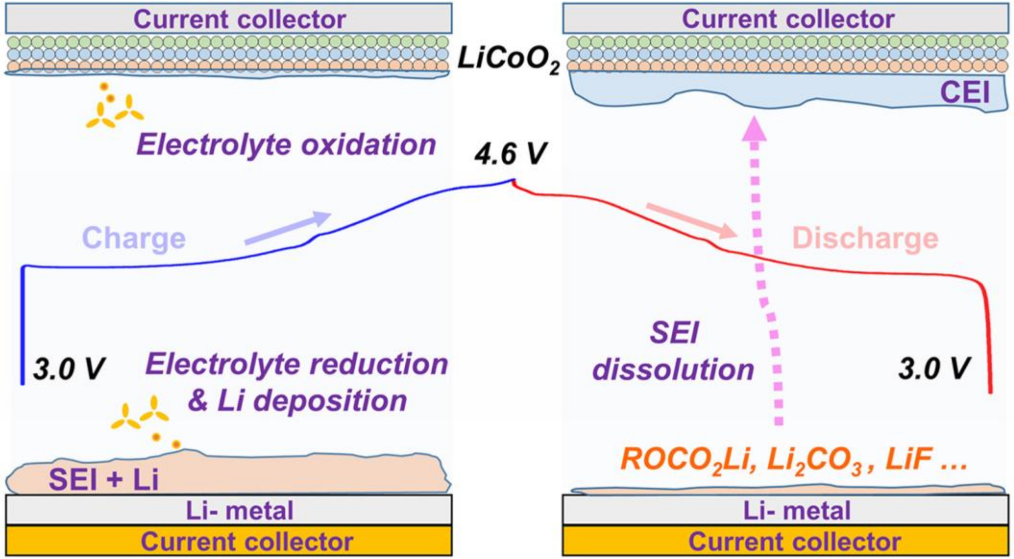
What is TTE Doing?

- High oxidative stability (shouldn't decompose)
- Low polarity means less interaction with Li^+
- Changes the CEI and SEI
- Likely changes electrolyte solvation structure
- Possibly affects solubility of SEI and CEI components?
  - TTE may improve high temperature performance by being a worse solvent for SEI and CEI products
  - We did not find strong evidence to support this hypothesis, but it's also consistent with our observations



Zhang et al., Energy Storage Mater., 14, 1 (2018) doi.org/10.1016/j.ensm.2018.02.016.

Conclusions

- Demonstrated TRL 6 battery that could support a notional Venus aerobot mission and future lunar missions surviving multiple days
- Continued high temperature electrolyte development has shown promise in lab cells
- TTE as a co-solvent dramatically improved performance at 100 °C
- CEI stabilization is clearly important
- How TTE stabilizes CEI is still unclear
- 100x custom 18650s have been procured with high temp electrolytes to demonstrate new formulations in high energy designs

Custom Moli 18650s

Custom Saft MPs

Acknowledgements

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