Lithium Ion Cells Capable of Storage at 0-Volts and Recovery from Dead Bus Events

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Approved for Public Release

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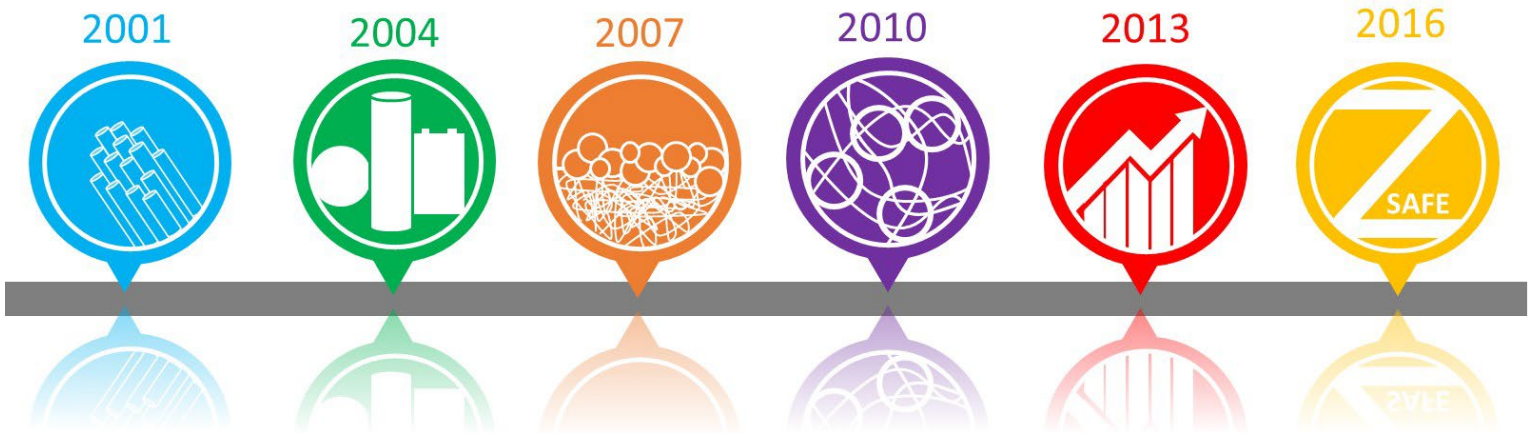
Material and Cell Developments



Cellec Technologies Inc.

Cellec Technologies is pursuing a lithium balancing approach to 0V capability (Z-Safe) in any lithium ion cell chemistry without sacrificing energy or power density (Wh/L and Wh/kg). This novel approach improves the overall safety of the cells, and eliminates the need for storing and transporting lithium ion cells at a partial state of charge.

Applications of Z-Safe Technology

Increase safety of Li^+ cells in a user-inactive state during storage/shipping and improve resiliency during use.

Storage

http://rebuiltcarbatteries.blogspot

Shipping

Aerospace

http://money.cnn.com/2016/02/23/news/companies/

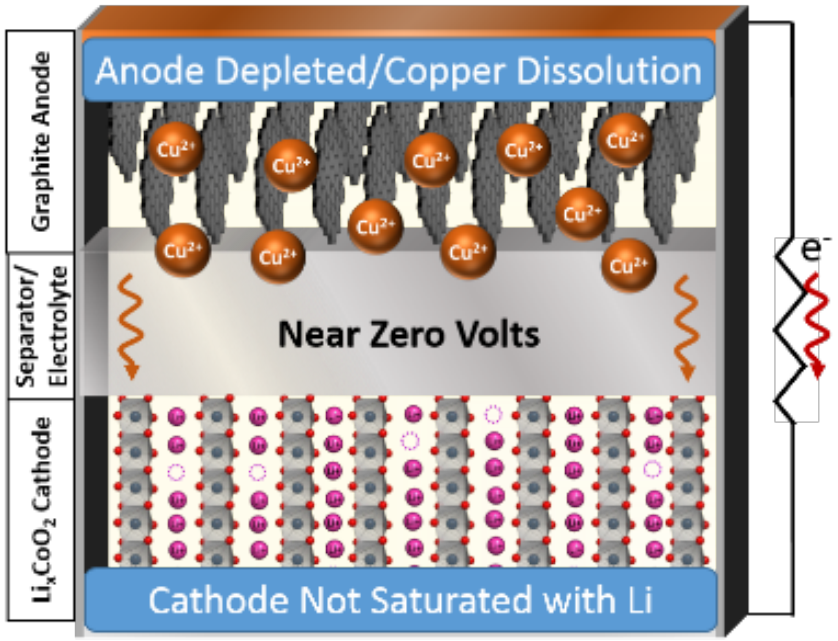
Handling

http://www.epectech.com

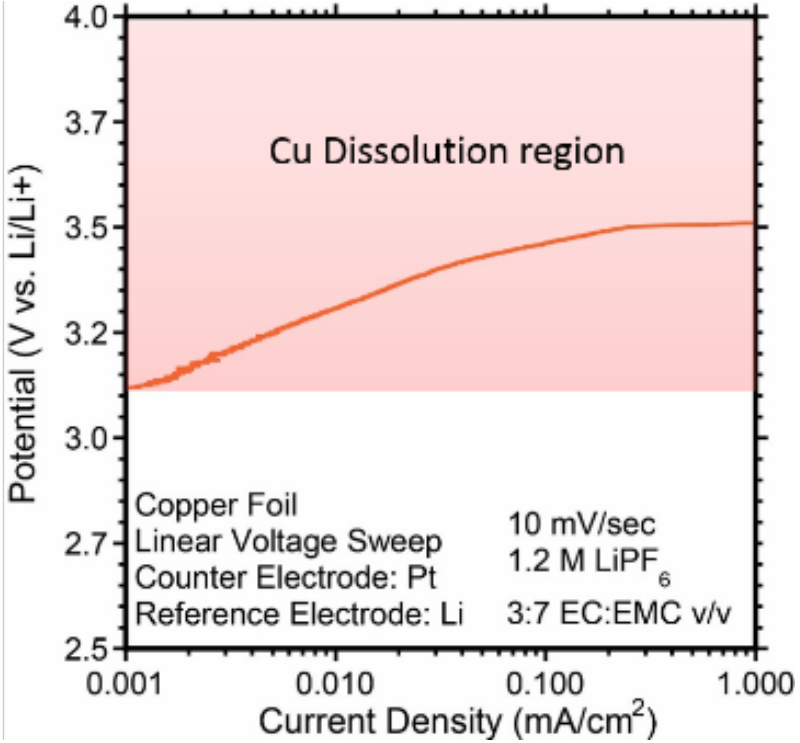
Aerospace Advantages

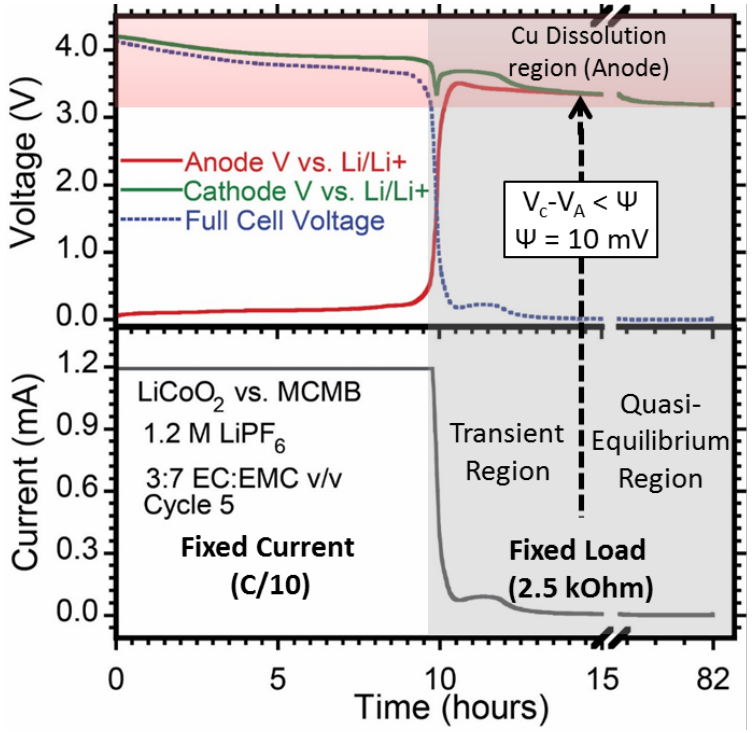
1. **Eliminate assembly risk for human technicians** when constructing systems since cells are in safe 0-Volt state.
2. ***No trickle charging umbilical*** during storage prior to use which lowers costs and complexity.
3. Assembly and integration of **multiple hardware units** that can be **stored at 0-Volts until use**.
4. Stowed payload for deferred use or a system which is indefinitely “dark” with primary integrated.
5. Provides cell stability for over discharge which can aid in recovery from “**dead bus**” scenario.

0-Volt Storage Tolerance with Anode Pre-lithiation



Crompton and Landi, Energy Environ. Sci., 2016,**9**, 2219-2239





Crompton and Landi, Energy Environ. Sci., 2016,**9**, 2219-2239

Traditional lithium ion cells are not stable at 0-Volts state-of-charge because the copper foil current collector experiences a voltage above the dissolution potential of copper.

Approaches to Mitigate Copper Dissolution

Two general approaches to avoid this degradation mechanism:

Approach 1: Render anode current collector stable against high potentials.

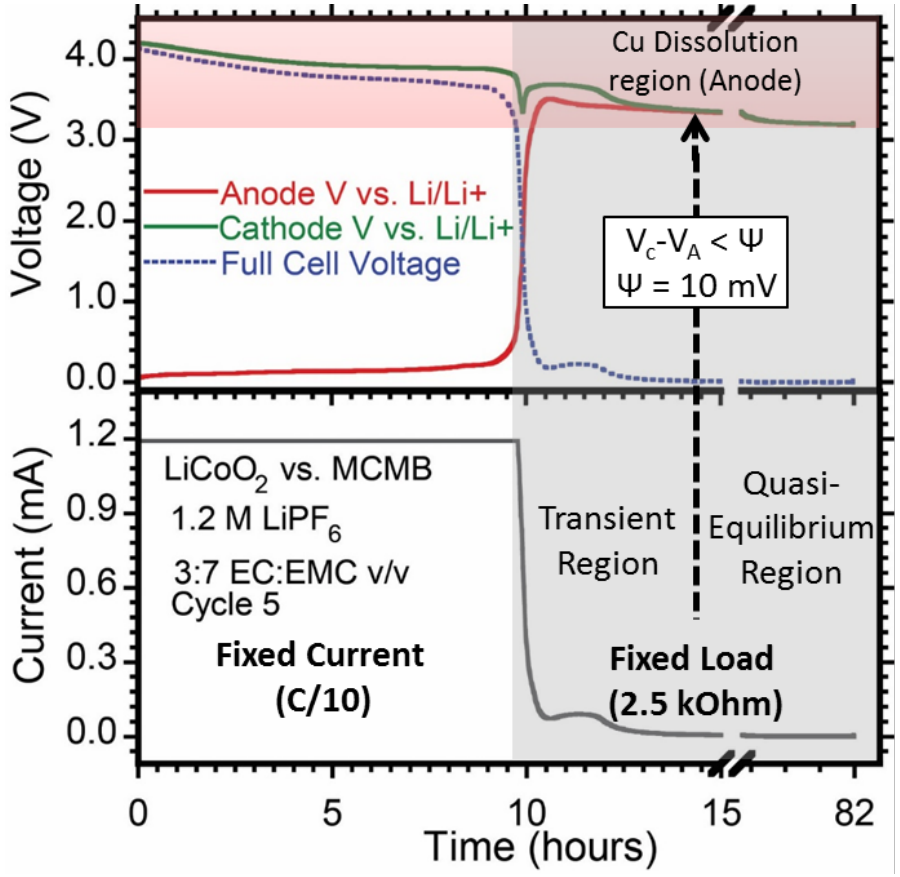
- Titanium replacement for copper (stable up to ~4.0 V vs. Li/Li^+)
  - *Titanium foils typically thicker and more expensive than copper foils*
  - *Titanium is about 25X less conductive than copper*
- Copper passivation (succinonitrile) – prevents copper dissolution
  - *Increases cell impedance, especially on cathode*
- *Carbon Nanotube (CNT) current collectors – modify SEI through electrolyte modification*

Approach 2: Modify cell to prevent high anode potential when cell is discharged to near zero volts by a fixed load.

- Secondary active materials with intermediate discharge potentials
  - *Can reduce energy density, stability concerns*
- High loss cathode additives like Li_2NiO_2 to offset SEI loss
  - *Gassing, reduction in energy density and cell stability*
- *Develop reversible lithium management in cell that maintains anode potential below copper dissolution value*

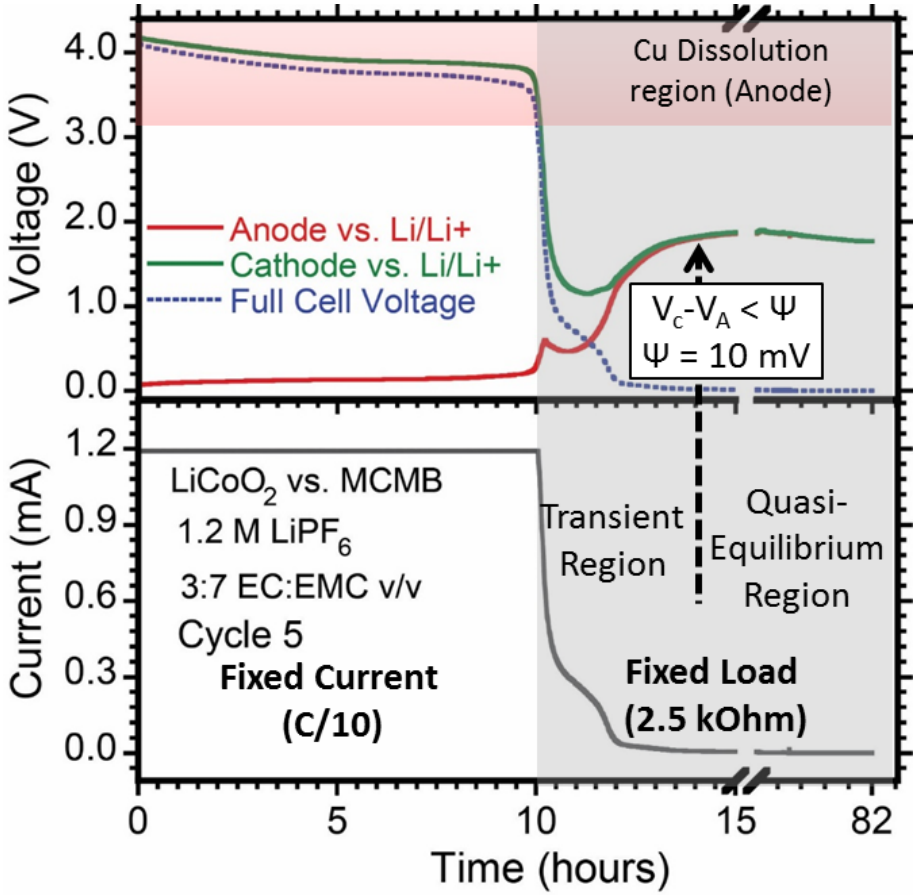
RLE Approach to Zero Volt Tolerance

Conventional Cell (No RLE)



Crompton and Landi, Energy Environ. Sci., 2016,**9**, 2219-2239

Zero-Volt Tolerant (With RLE)



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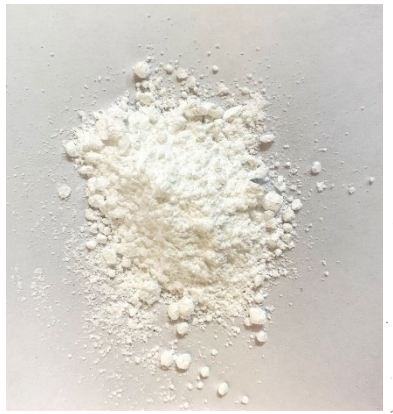
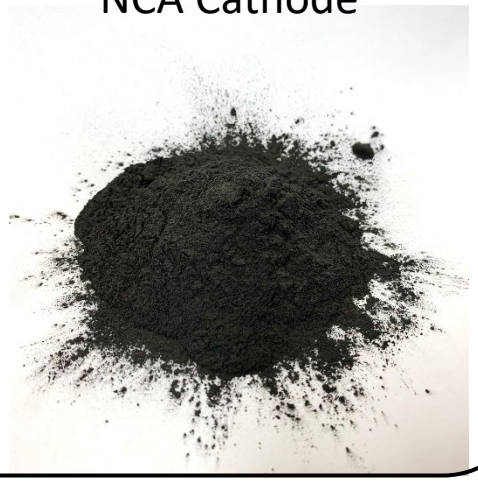
Anode and Cathode Materials For Slurries

PVDF Powder



Carbon Black

NCA Cathode

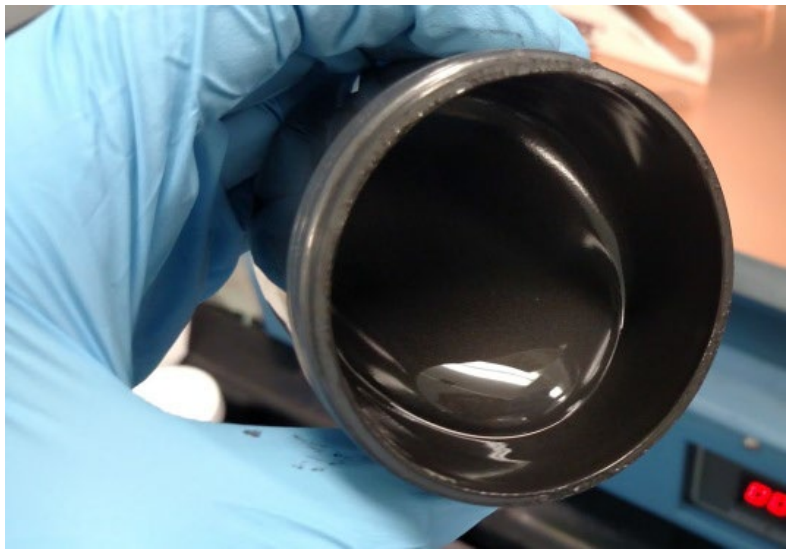


SBR Solution

Carbon Black

Graphite Anode

Cathode & Anode Slurries



No significant modifications to the materials or structure of the electrodes is required.

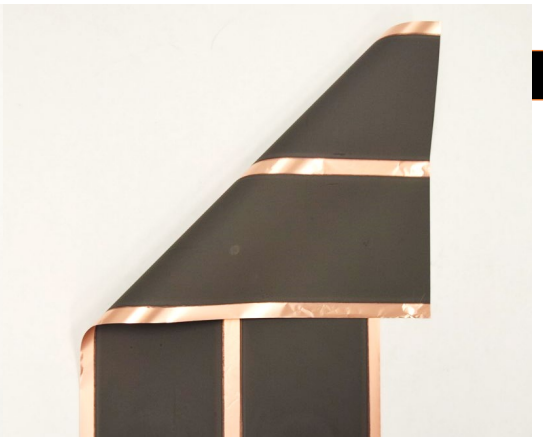
Cell Fabrication Process

Roll-to-Roll Coater

Roll-to-Roll Calender

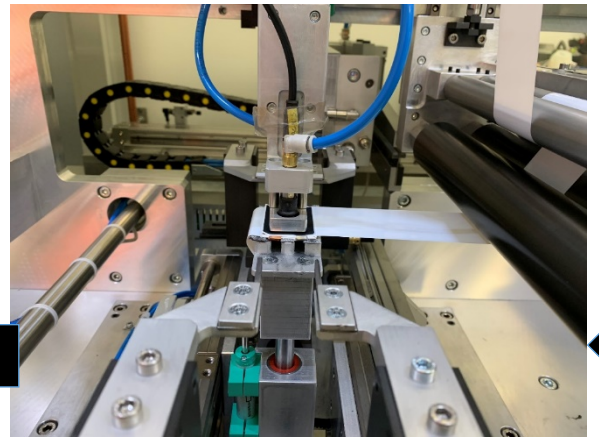
Double-Sided Cathode Coating

Double-Sided Anode Coating

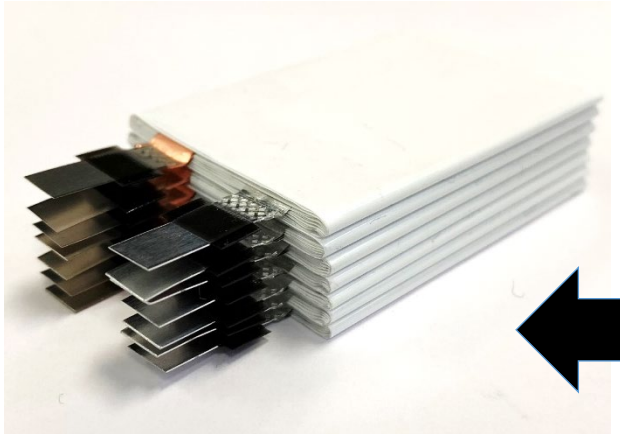


Punch Electrodes

Semi-Automated Z-Stacker



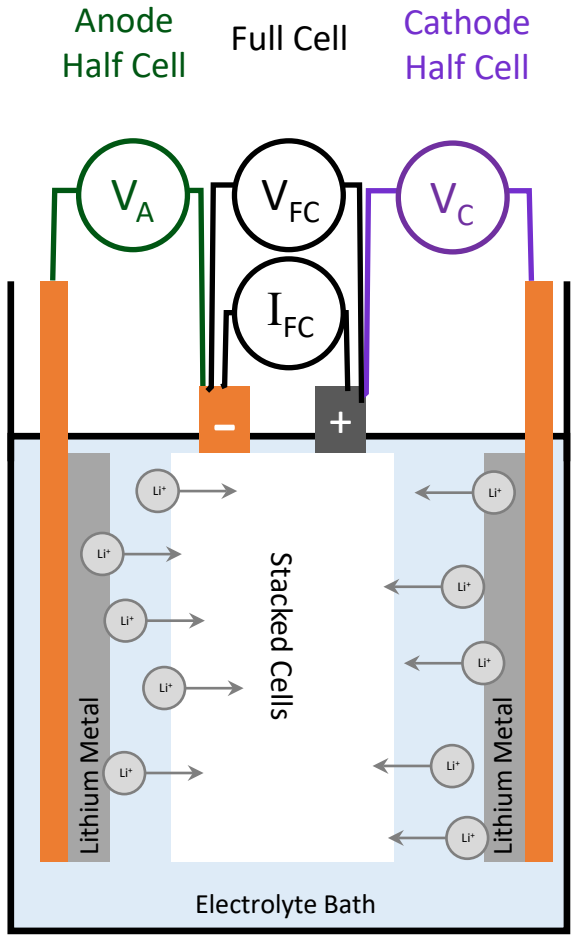
Stacked Electrodes



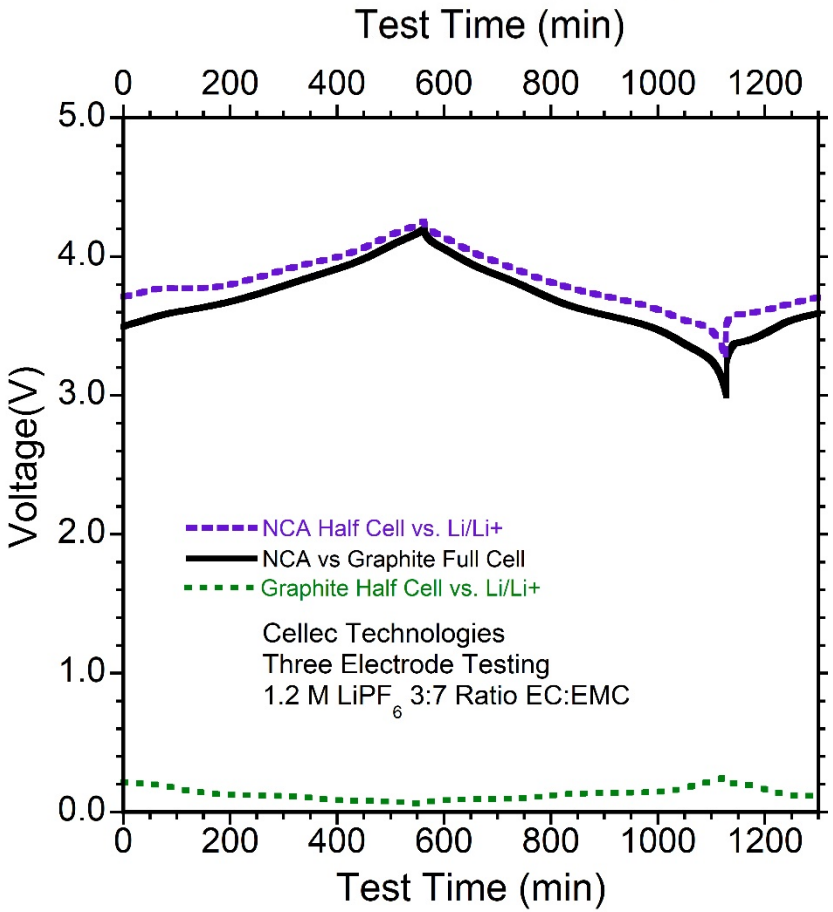
Finished Battery

3-Electrode Cell Testing

Open Bath Formation to Achieve RLE Zero-Volt Capability



3-Electrode Voltage Curves

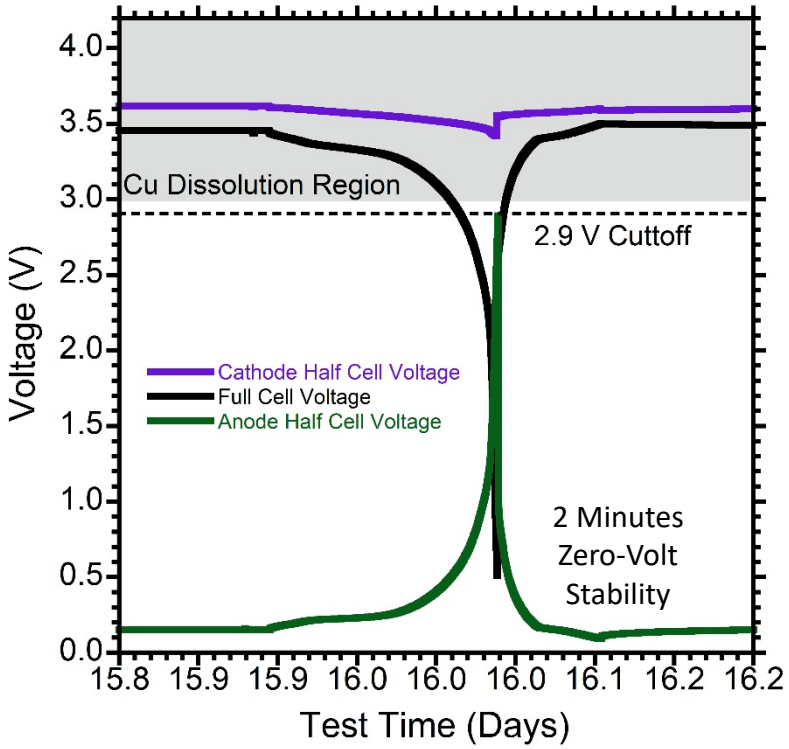


3-Electrode Measurement Technique

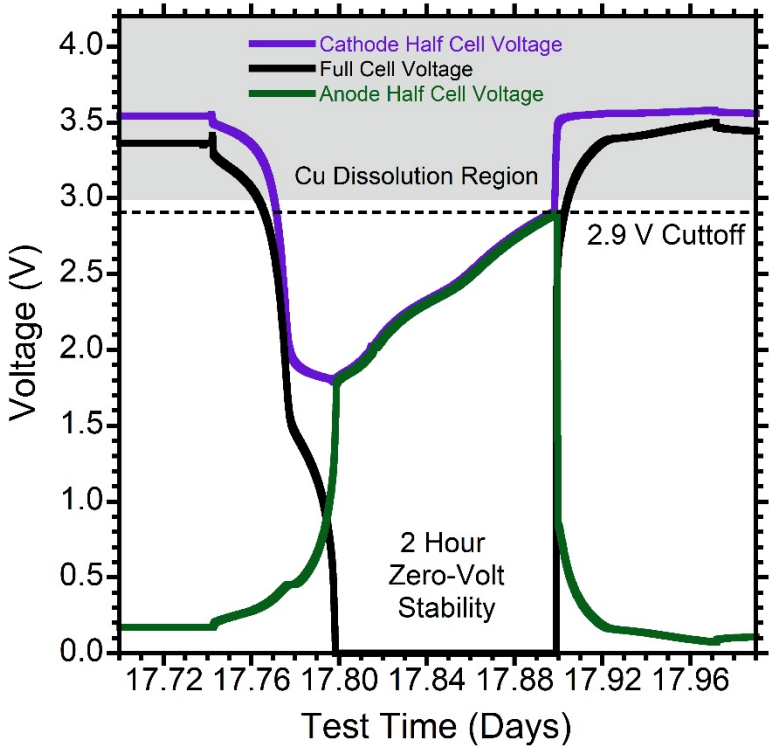
- Three electrode measurements were performed on the multi-layer pouch cells.
- Using reference Lithium electrodes enables simultaneous monitoring of the full cell voltage and anode/cathode half cell voltages.

Establishing RLE For Zero-Volt Stability

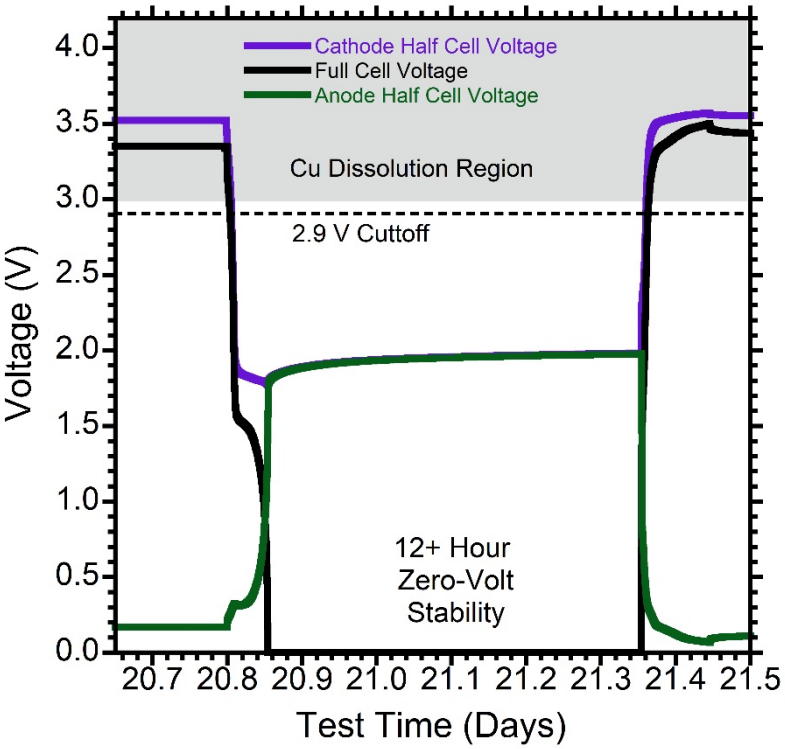
1% Additional Li Capacity



11% Additional Li Capacity

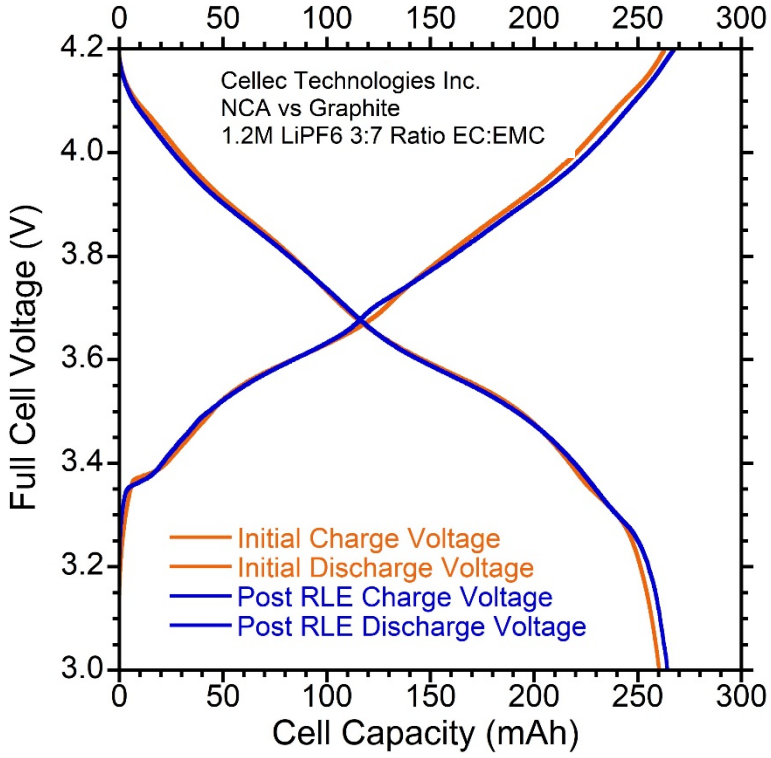


21% Additional Li Capacity

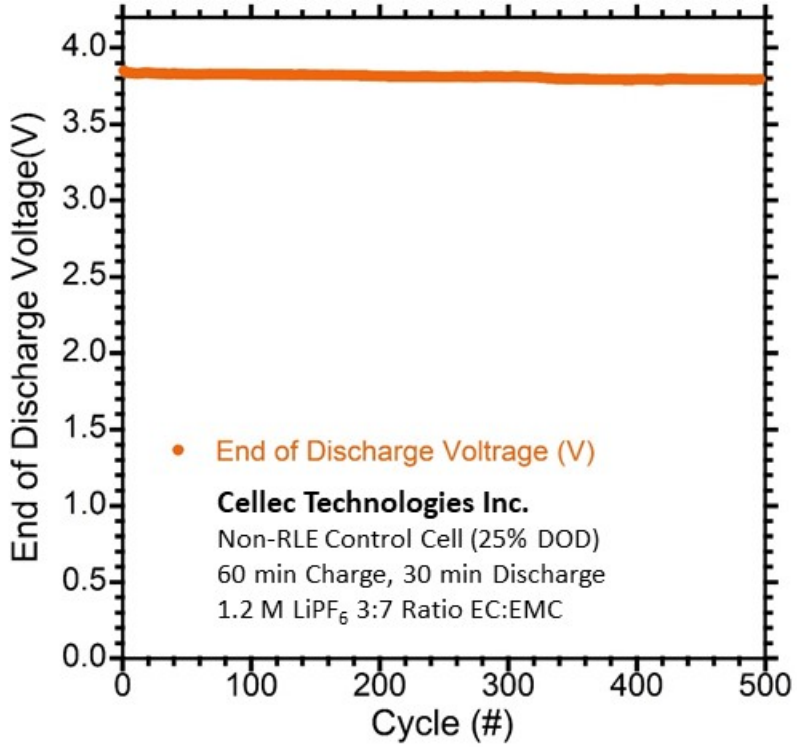


Additional lithium was added to the stacked electrodes in the bath lithiation process to alter the cell's EAP. The EAP was measured and the EAP was measured at 0-Volts

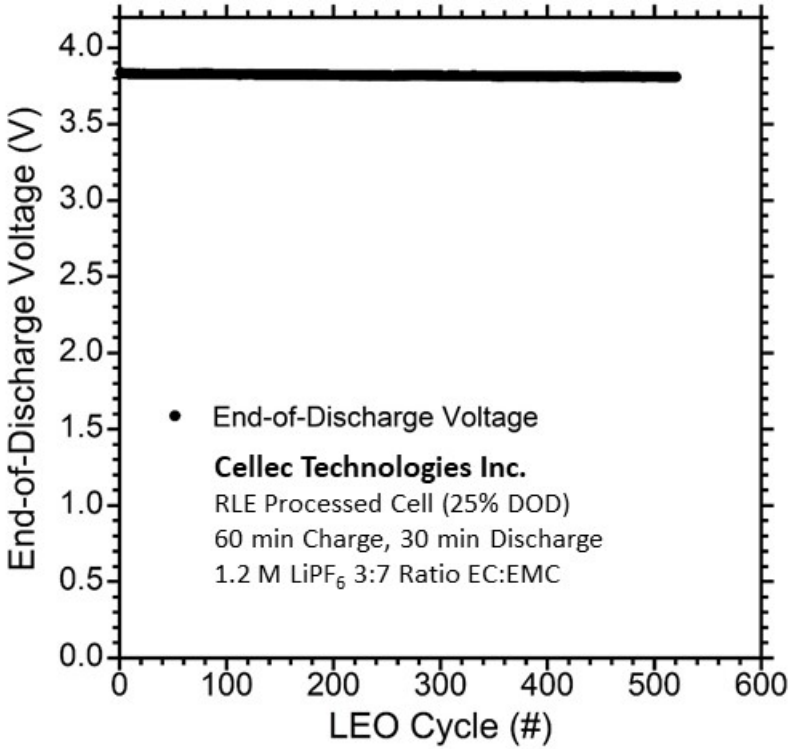
Voltage Profile Before and After RLE



Non-RLE 0-Volt Cell LEO Cycling



RLE 0-Volt Cell LEO Cycling



Voltage Profile and LEO Cycle Life Testing

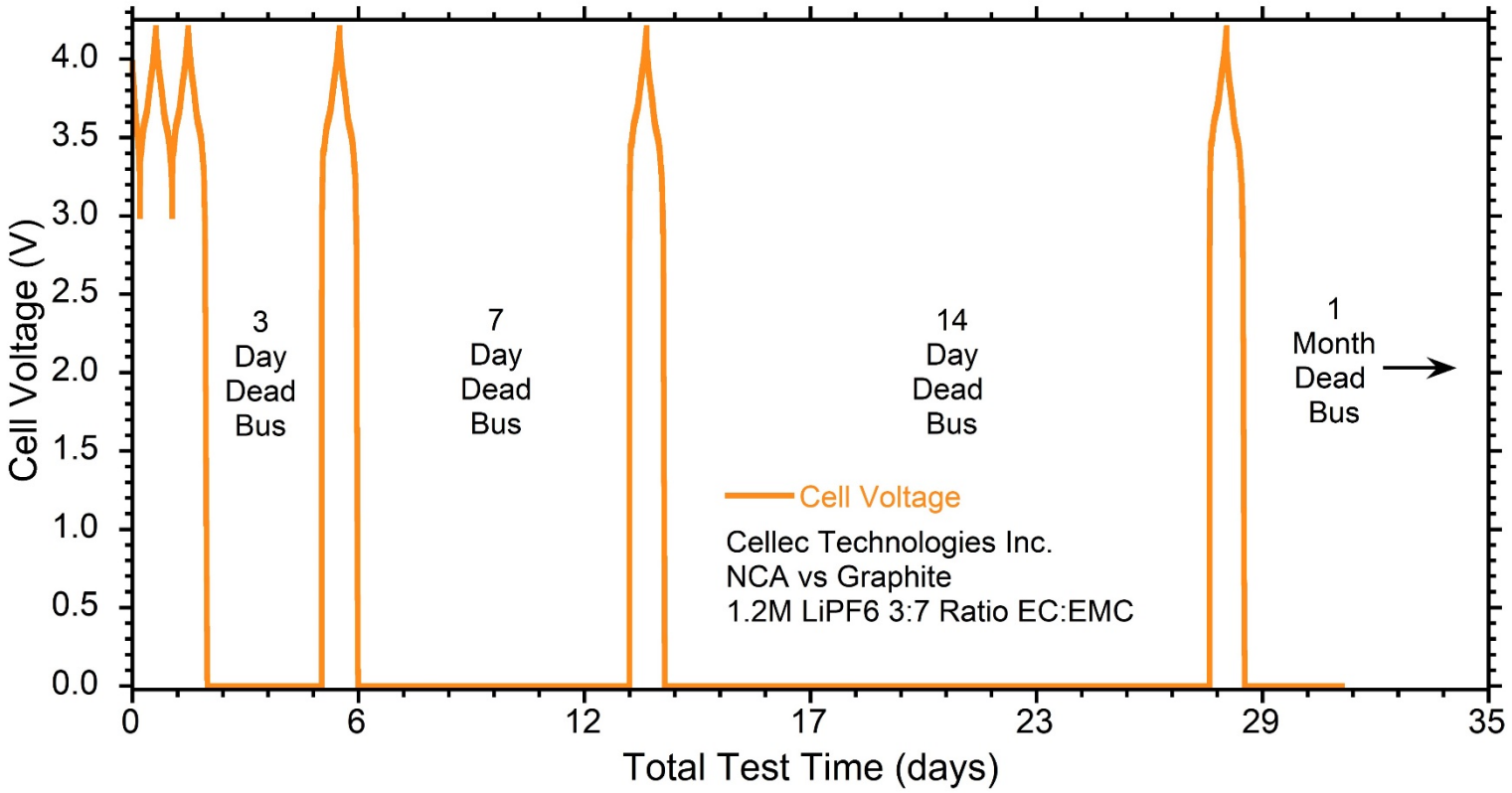
- The voltage profiles of a multi-layer pouch cell were compared before and after the RLE process. Minimal change was measured in the structure of the voltage profile
- LEO cycling of the cells with and without RLE zero-volt tolerance shows little difference in their stability and end-of-discharge voltages.

Beginning of Life Storage at 0-Volts

Beginning of Life Cell Storage at 0-Volts

- RLE processed Li^+ cells were subjected to increasing shelf life storage at 0-Volt SOC.
- 3, 7, and 14 day storage periods were tested for a RLE NCA vs Graphite cell with copper current collectors on the anode electrodes.
- Following each 0-Volt storage period, the cells were charged to 4.2 volts to confirm viability before being discharged back down to 0-Volt for another storage period.

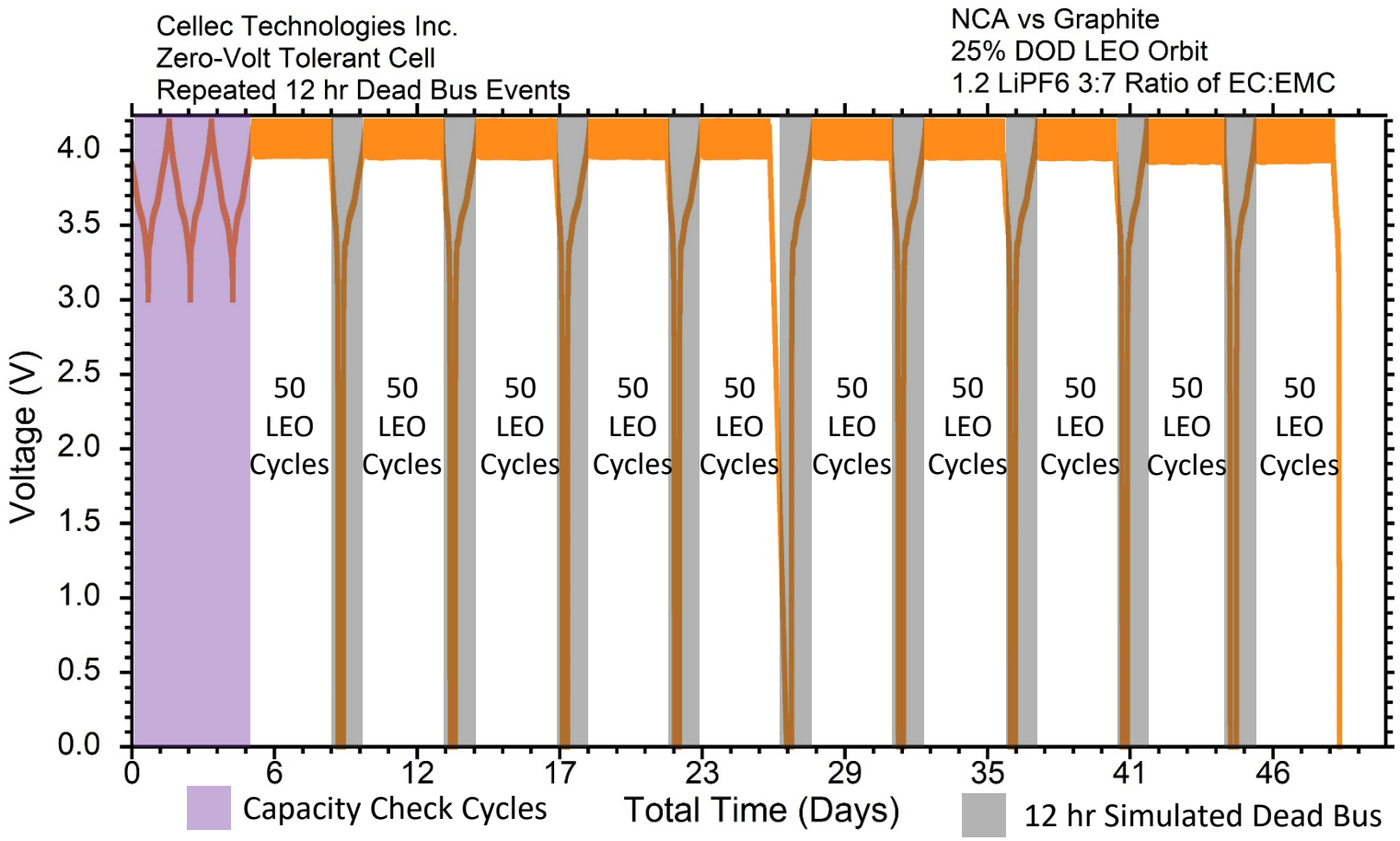
BOL Shelf Life Storage at 0-Volts for Increasing Periods of time



RLE Processed cells can tolerate extended exposure to 0-Volt conditions at beginning of life.

Dead Bus Simulations and Recovery

12 hr Dead Bus every 50 LEO Cycles



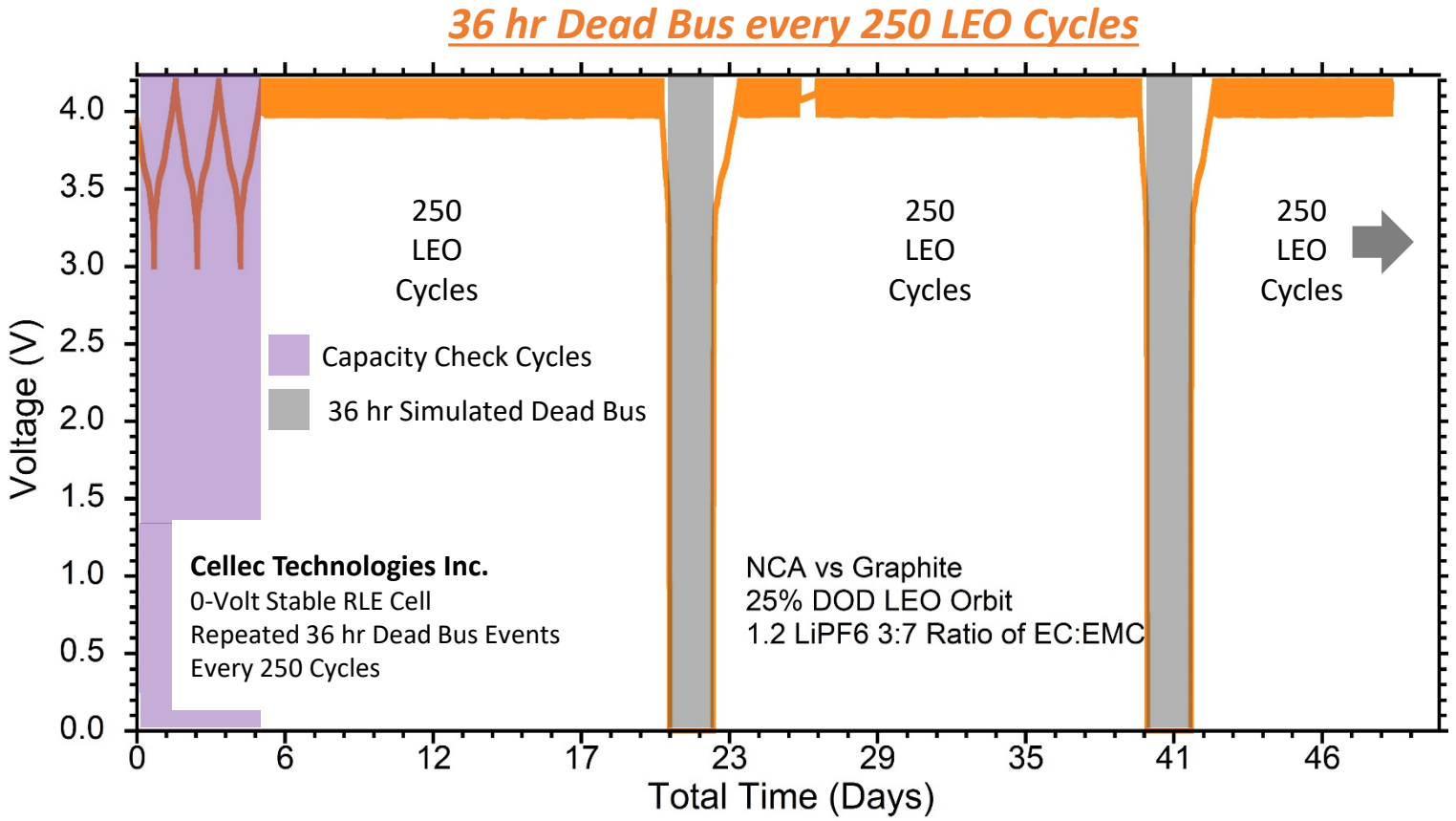
LEO Cycling with Dead Bus Simulation

- 0-Volt stable RLE cells were subjected to 12 hour long multiple dead bus events every 50 cycles to determine if the technology can feasibly recover from a catastrophic failure during flight.
- The RLE Cells successfully recovered from the dead bus event and were able to be recharged and continue charge/discharge testing.

Testing Conditions:

- 90 min LEO Orbit (60 min charge, 30 min Discharge)
- 20% Depth of Discharge

Voltage Profile Before and After RLE



LEO Cycling with Dead Bus Simulation

- 0-Volt stable RLE cells were subjected to 36 hour long multiple dead bus events every 250 cycles to determine if the technology can feasibly recover from a catastrophic failure during flight.
- The RLE cells successfully recovered from the dead bus event and were able to be recharged and continue charge/discharge testing.

Conclusions

- Using the RLE approach to achieve cell stability at 0-Volts is possible without negatively impacting the cell performance or adding non-standard materials to the cell chemistry.
- The cells successfully demonstrated stability at 0-Volts as beginning of life as well as during their use phase.
- The cells were able to recover from multiple dead-bus exposure events during LEO cycling that help ensure continued mission success

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