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High-Performance Electrolyte for Lithium-Nickel-Manganese Oxide (LNMO)/Lithium-Titanate (LTO) Batteries

Project ID: bat441

April 27, 2020

Principle Investigator/Presenter:
Dr. Jennifer Hoffmann For Gotion, Inc.

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Overview

Timeline

- Start: March 20, 2019
- End: March 20, 2022
- Status: ~45% Completed

Budget

- Total Project Funding: $3.1 Million
  - DOE: $1.5M
  - Industrial Cost Share: $1.6M

Partners

- University of Rhode Island (URI)

Barriers[1]

- Cost: The cost of current high-energy lithium ion batteries is approximately 2-3x too high with raw materials being one of the main contributing factors.
- Performance: Higher energy density materials can reduce cost and weight but suffer from life and performance issues to match gas powdered vehicles' performance and customer convenience.
- Life: Next generation technologies suffer cycle and calendar life issues

[1]US DRIVE Electrochemical Energy Storage Technical Team Roadmap September 2017
https://www.energy.gov/sites/prod/files/2017/11/f39/EESTT%20roadmap%202017-10-16%20Final.pdf

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Relevance

Objectives

- Analyze and understand LTO and LNMO materials through study of electrolyte interactions, gas analysis, and failure mechanisms
- To develop and evaluate LTO electrolytes and electrolyte additives that demonstrate minimal gassing, high cycle life, high power charge/discharge capabilities, wide operating temperature, and competitive cost
- To develop and evaluate LNMO electrolytes and electrolyte additives that demonstrate minimal gassing, high cycle life, high power charge/discharge capabilities, wide operating temperature, and competitive cost

Impact

- LTO is a sought-after anode material due to its improved safety, cycle and calendar life, and operating temperature range in comparison to graphite anode. By optimizing the electrolyte to mitigate the known gassing issues moves this material closer to commercial viability.
- LNMO is a high voltage (>4.9V) cathode material that increases energy density while reducing cost due to the elimination of cobalt. However, modern electrolyte is not compatible. New additives, electrolyte formulations, and mechanistic understanding can make this technology more accessible.
- Combining LNMO/LTO, which is the ultimate objective of the project, allows for a balance of the benefits of each material. The high-voltage LNMO improves the high working potential of LTO and balances the battery cost while the LTO provides improved cycle life and safety.

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Milestones

**Delays are primarily being caused by COVID-19 orders and response and political differences between the USA and China. The true impact of the delays are being monitored closely and communicated in real time with all relevant parties*

Month/Year	Description of Milestone or Go/No Go Decision	Status
Oct. 2019	Synthesis and screening of first 5 electrolyte additives. Confirm that targeted structures and functional groups are effective. Optimize synthesis strategy.	Completed
Jan. 2020	Synthesis and screening of additional 5 electrolyte additives based on optimized synthesis strategy.	Completed
Oct. 2020	Of developed additives, determine which should be scaled up for large scale testing	On Schedule
Nov. 2019	Based on 2 Ah MLPC LTO vs Lithium Nickle Cobalt Manganese Oxide (NCM) cathode testing, compile data package of analytical findings for further development of LTO anode.	Completed
July 2020 (Original Nov. 2019)	Based on 2 Ah MLPC Carbon Anode vs high-voltage LNMO testing, compile data package of analytical findings for further development of LNMO cathode.	Extended
July 2020	Based on LTO/LNMO 2Ah MLPC testing, deliver twenty 2 Ah LTO/LNMO MLPC containing selected electrolyte formulations to USABC for further evaluation	Behind Schedule*
Feb. 2021	Determine final electrolyte additives and formulations for 10 Ah cells	Behind Schedule*
March 2021	Deliver thirty 10 Ah LTO/LNMO MLPC to USABC for further evaluation	Behind Schedule*
Moving Target	Publication through journal paper and/or patent of any additives and/or other discoveries considered appropriate	On Going

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Approach

Multi-Layer Pouch Cell (MLPC) Performance Testing

In 2Ah and 10Ah MLPC, the following testing is being conducted to gain information on performance in tandem with gas analysis for failure mechanism understanding, surface analysis for electrolyte-electrode interaction understanding, and Manganese dissolution tracking:

- -20°C Cycling
- 25°C Cycling
- 45°C Cycling
- 45°C, 1 week, 100% SOC Storage Testing
- 45°C, 4 week, 100% SOC Storage Testing

Electrolyte Intrinsic Property Study

In order to track the possible trends associated with the electrolyte properties and how they are can be applied, the following is conducted and analyzed:

- Electrochemical Stability (Voltammetry & Floating Testing)
- Vapor Pressure
- Flashpoint
- Viscosity (30°C and -30°C)
- Specific Conductivity (30°C and -30°C)
- Water and Hydrofluoric Acid (HF) Content
- Lithium Transference Number

Additive Synthesis

In partnership with URI, new multi-functional additives that will focus on solid electrolyte interphase (SEI) formation that improves gas generation, MN dissolution, and/or electrolyte stability are being synthesized and tested to improve the electrolyte properties and cell testing

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Technical Accomplishments & Progress

Electrolyte Chemical Property Testing

- Water and HF content requirements have been routinely accomplished
- Specific conductivity and vapor pressure techniques have been improved
- Compounds that improve specific conductivity at 30°C and -30°C have been identified
- Relationship(s) between certain parameters have been identified and are undergoing further investigation

Task 1 – Additive Synthesis

- 11 novel additives have been synthesized and screened in coin cells
- One of three additives evaluated showed gas reducing benefits in LTO/NCM MLPC testing
- All additives developed show 25°C cycling performance similar to or better than the baseline in 4.9V LNMO/C MLPC
- Impact on impedance and gas generation in 4.9V LNMO/C MLPC is underway
- Principle Component Analysis is being employed to further narrow additive development
- Patent application for one of the novel additives created has begun

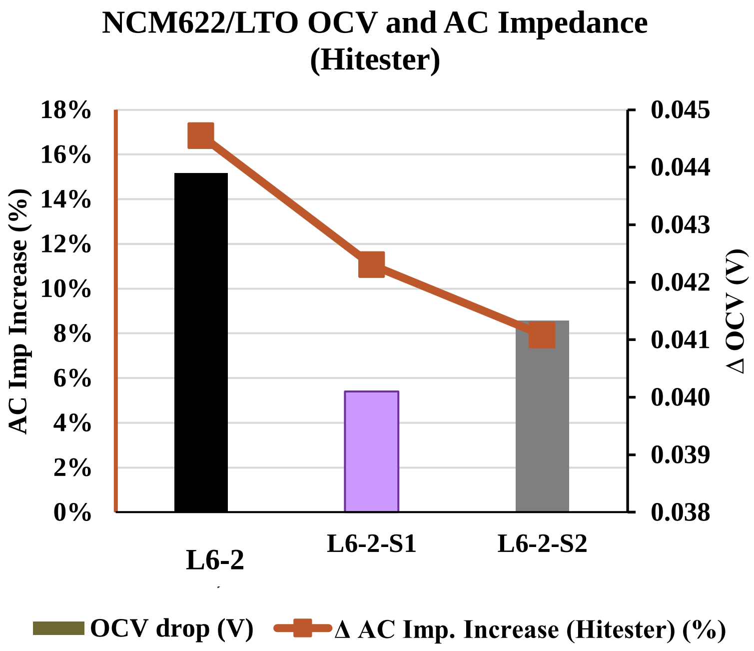
Technical Accomplishments & Progress

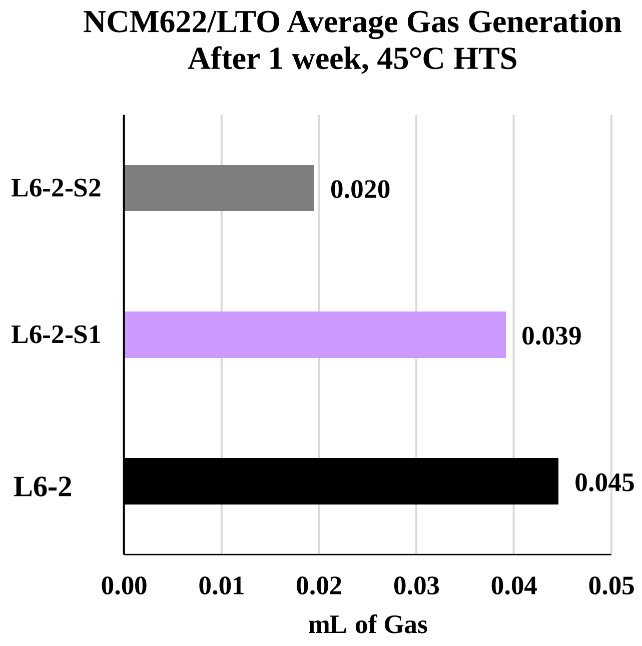
Task 2 – NCM/LTO MLPC Testing

- Task has been completed as of Nov. 2019
- Capacity retention and volume targets for 45°C Cycling, 45°C were met
- Capacity retention, capacity recovered, and volume targets for 1 Week 100% SOC storage testing and 45°C, 4 Week 100% SOC storage testing were met
- Evaluation of compatibility between unique solvents and additives and LTO anode were confirmed for next step testing

Task 3 – 4.9V LNMO/C MLPC Testing

- Multiple additives have been evaluated and show improvements to 25°C cycling performance, impedance, and/or gas reduction when compared to the baseline and/or leading common knowledge additives
- Understanding of the gassing mechanism has advanced based on gas analysis findings





Graphs show some of the high temperature storage data comparing the baseline (L6-2) to the baseline with novel additives synthesized for the project (S1 is additive 1 and S2 is additive 2). Additives show reduced gassing, improved impedance, and better cell stability during storage testing.

Technical Accomplishments & Progress

USABC Gap Chart of Advanced Electrolytes					
Parameter		Unit	USABC Goal	End Target	Current
Cost at a yearly production volume no more than 20,000 ton/year		$/kg	< 10	8-10	12
Electrochemical Stability	Upper Voltage	V vs. Li/Li+	5	5	~5
	Lower Voltage		0	0.5	1.0
Vapor Pressure at 30°C		mm Hg	< 1	10	10
Flashpoint		°C	> 100	40	26
Viscosity	at 30°C	cP	< 5	5	<5
	at -30°C		< 20	20	30
Specific Conductivity	at 30°C	mS/cm	> 12	10-12	10.66
	at -30°C		> 4	4	3.164
Li^+ Transference Number			> 0.35	0.3	0.2
Components Purity		%	> 99.99	99.98	99.0-99.95
Lithium Salt Solubility		M	1	up to 1.4	1.2
Water Content		ppm	< 20	< 15	3.2
HF Content		ppm	< 50	< 40	28.7
USABC End Target Currently Being Met					
Status is above start of project but below end target					
The current status is below start of project and/or end target					
Measurements have not yet been conducted					

- The gap chart is used to track progress of the parameters being measured
- Important to note about the gap chart, it is not representative of one formulation but rather all formulations measured.
  - The formulation that meets the conductivity requirement and shows target met on the gap chart may or may not be different than the formulation that meets the flashpoint requirement displayed on the gap chart.
- Electrochemical stability shows upper voltage stability of ~5V based on floating tests in half cell coin cell. This does not mean the electrolyte is stable in full cell cycling tests.
- How these parameters relate to performance and each other is still under evaluation
- The biggest challenge so far is vapor pressure and making vapor pressure agree with conductivity.

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Technical Accomplishments & Progress

USABC Gap Chart of Cell Testing				
Parameter		**Unit**	**End Target**	**Current**
-20°C Cycling (LT Cycling)	Volume Change after 300 Cycles	mL, %	< 5%	N/A
	Capacity Retention at 25°C after 300 LT Cycles	%	80%	N/A
25°C Cycling (RT Cycling)	Volume Change after 600 Cycles	mL, %	< 8%	HVS/C: ~20% after 100 cycles NCM622/LTO: Not measured
	Capacity Retention Projected to 1500 Cycles	%	80%	HVS/C: 80% at ~120-150 cycles NCM622/LTO: Not measured
45°C Cycling (HT Cycling)	Volume Change after 600 Cycles	mL, %	< 10%	HVS/C: Not yet measured NCM622/LTO: < 10% Achieved
	Capacity Retention Projected to 1000 Cycles	%	80%	HVS/C: Not yet measured NCM622/LTO: 100% After 300 cycles
45°C, 1 Week at 100% SOC Storage	Retained Capacity	%	95%	HVS/C: Pending NCM622/LTO: 95% Reached
	Recovered Capacity	%	97%	HVS/C: Pending NCM622/LTO: 99% Reached
	Volume Change	mL, %	< 10%	HVS/C: Pending NCM622/LTO: <3% Reached
45°C, 4 Week at 100% SOC Storage	Retained Capacity	%	95%	NCM622/LTO: 89% Reached
	Recovered Capacity	%	97%	NCM622/LTO: 99% Reached
	Volume Change	mL, %	< 10%	NCM622/LTO: <3% Reached

Impedance/EIS, Rate Performance, ICE, and OCV measurements are conducted, analyzed, and considered during the project but are not in the testing targets so they are left out of the gap chart.

- USABC End Target Currently Being Met
- Status is above start of project but below end target
- The current status is below start of project and/or end target
- Measurements have not yet been conducted

- Similar to the last gap chart, the chart reflects the best formulation for the parameter being measured and may not be the same across parameters.
- The NCM/LTO testing was very successful and consequently discontinued. It was never scheduled to run low temperature testing in the scope of this project.
- LNMO/C testing struggled to perform testing higher than 25°C, but continued testing for additive development is extended with the possibility of high temperature testing being revisited.
- The main motivation of the project is the LNMO/LTO combination which just started testing and therefore is not yet displayed on the gap chart.

HVS = High Voltage Spinel = LNMO

Collaboration/Partnerships

University of Rhode Island – Dr. Brett Lucht and Group

- Additive Synthesis
- Surface Analysis
  - X-Ray Photoelectron Spectroscopy (XPS)
  - Fourier Transform Infrared (FTIR)
  - Scanning Electron Microscopy (SEM)
- Manganese Dissolution Analysis
  - XPS
  - Inductively Couple Plasma – Mass Spectrometry (ICP-MS)

THE UNIVERSITY OF RHODE ISLAND

Battery Envisions, LLC. (BEL) – Dr. Zhiqiang Xu

- Cell design specialist
- MLPC supplier

Remaining Challenges and Barriers

- Principle component analysis and/or other methods for narrowing the additive development scope need to be employed in order to more efficiently discover correlations and select the best additives for scale up and/or commercial development.
- During the high voltage LNMO/C testing, complexities were discovered that made the need for some testing to be extended. This system continues to be challenging even under room temperature testing with initial coulombic efficiency (ICE), capacity fade, and gassing still very much a challenge.
- The start of LNMO/LTO MLPC testing showed more capacity fade than originally predicted. Improving the capacity fade and gas generation is a key challenge for moving toward making this system viable.
- Gotion will need to improve the high amperage cycling capabilities at their site in order to perform the scheduled 10 Ah testing. While this barrier was initially resolved through an internal expansion, delays due to political unrest between China and the USA delayed this process.

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Proposed Future Research

Multi-Layer Pouch Cell (MLPC) Performance Testing

In LNMO/LTO 2Ah and 10Ah MLPC conduct following testing to gain information on performance in tandem with gas analysis for failure mechanism understanding, surface analysis for electrolyte-electrode interaction understanding, and Manganese dissolution tracking:

- -20°C Cycling
- 25°C Cycling
- 45°C Cycling
- 45°C, 1 week, 100% SOC Storage Testing
- 45°C, 4 week, 100% SOC Storage Testing

Electrolyte Intrinsic Property Study

Continue measurements such as those listed here on the most promising electrolytes for LNMO/LTO to determine trends and meet electrolyte expectations:

- Electrochemical Stability (Voltammetry & Floating Testing)
- Vapor Pressure
- Flashpoint
- Viscosity (30°C and -30°C)
- Specific Conductivity (30°C and -30°C)
- Water and Hydrofluoric Acid (HF) Content
- Lithium Transference Number

Additive Synthesis

Scale up and optimize novel additives and perform testing in LNMO/C and LNMO/LTO MLPC for development. Evaluate data collected with principle component analysis to further narrow the scope and develop the most promising candidates.

Any proposed future work is subject to change based on funding levels

Summary

- Accomplishments
  - NCM/LTO MLPC testing met all performance and gassing targets in high temperature testing
  - 11 novel additives have been synthesized with one entering patenting phase
  - Compounds that improve electrolyte conductivity have been identified with major impact at low temperature (-30°C)
- Technical Highlights
  - Complexities of the high voltage LNMO/C system have been exposed further thus leading to extended work being carried out
  - Work on the deliverable design LNMO/LTO has started based on knowledge gained from the other testing
- Impact
  - This work is allowing entry into next generation materials to be realized with safety and cost being considered along with performance. The large scope of work is designed to gain as much knowledge as possible to make commercial viability a reality for these systems and share that knowledge with the scientific community to continue to push electromobility and energy storage even further.

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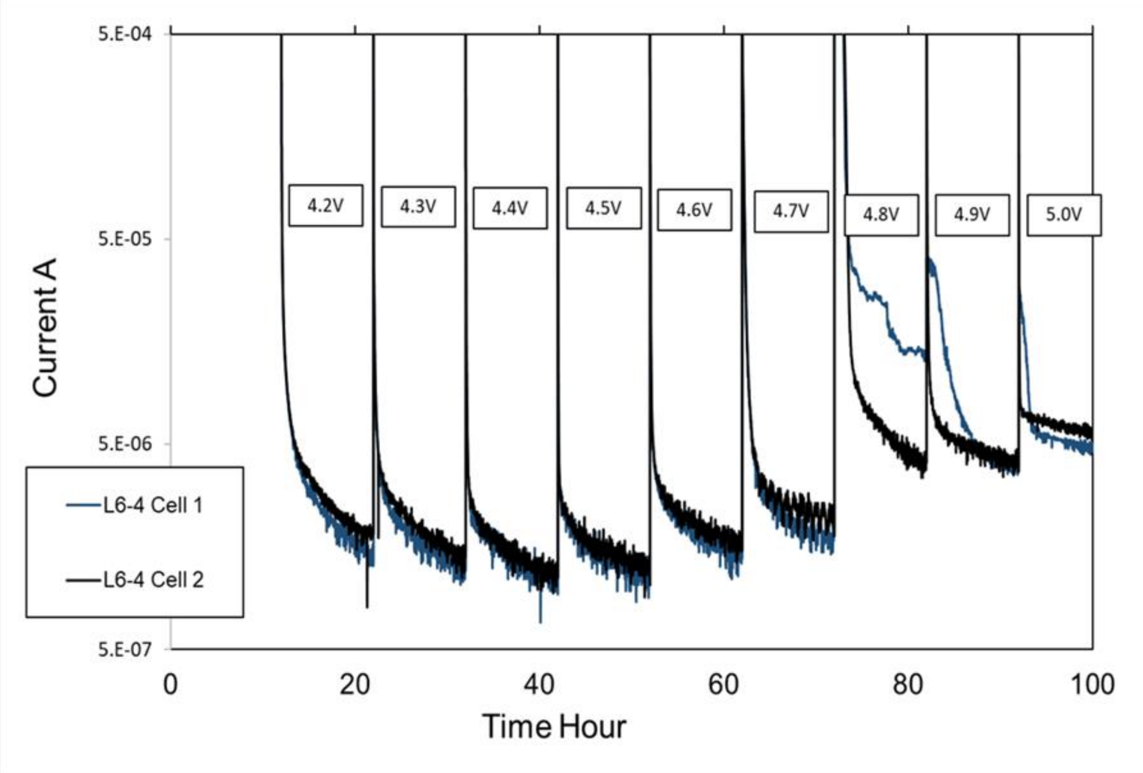
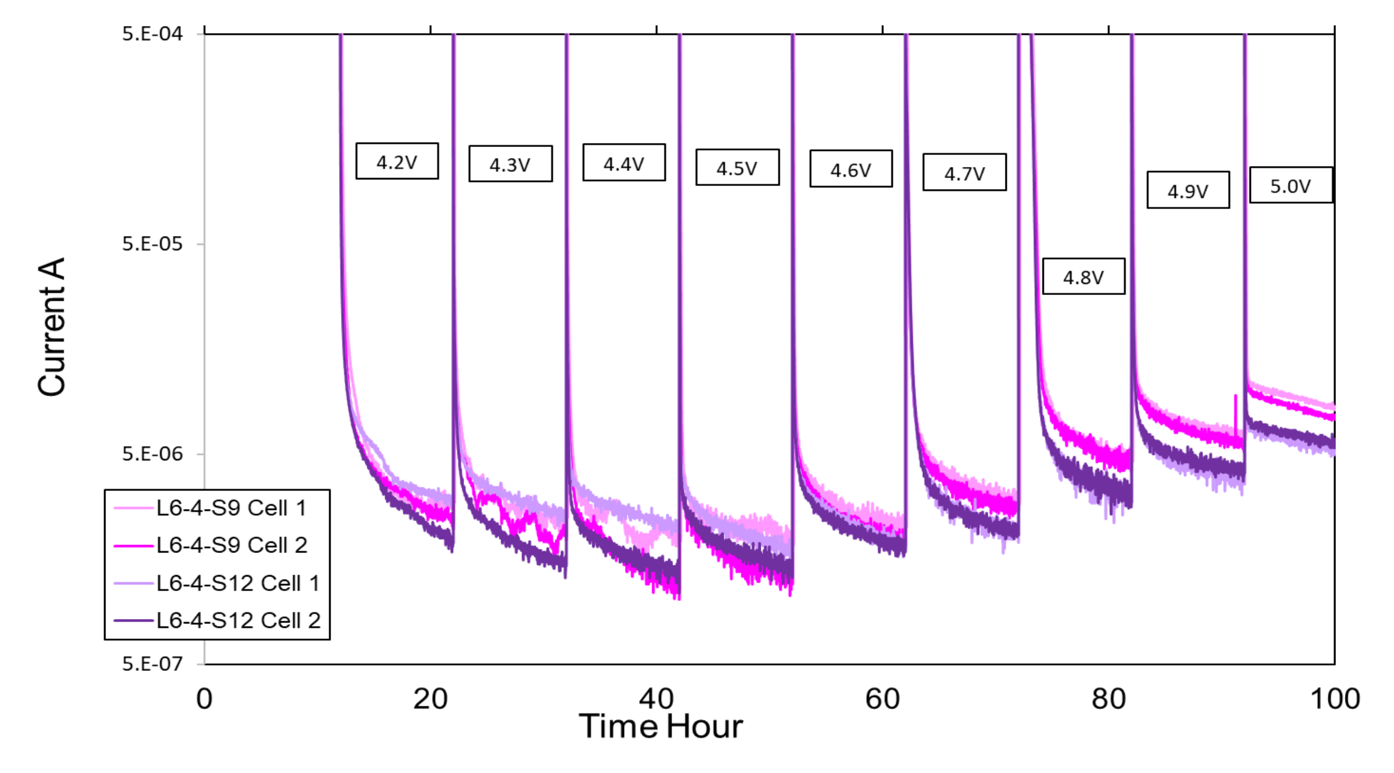
Technical Back Up Slides

Electrolyte Property Testing

- Floating Test:
  - Half cells with HV-LNMO cathode were held for 10 hours at each voltage step
  - Voltage steps started at 4.2V and increased by 0.1V up to 5V

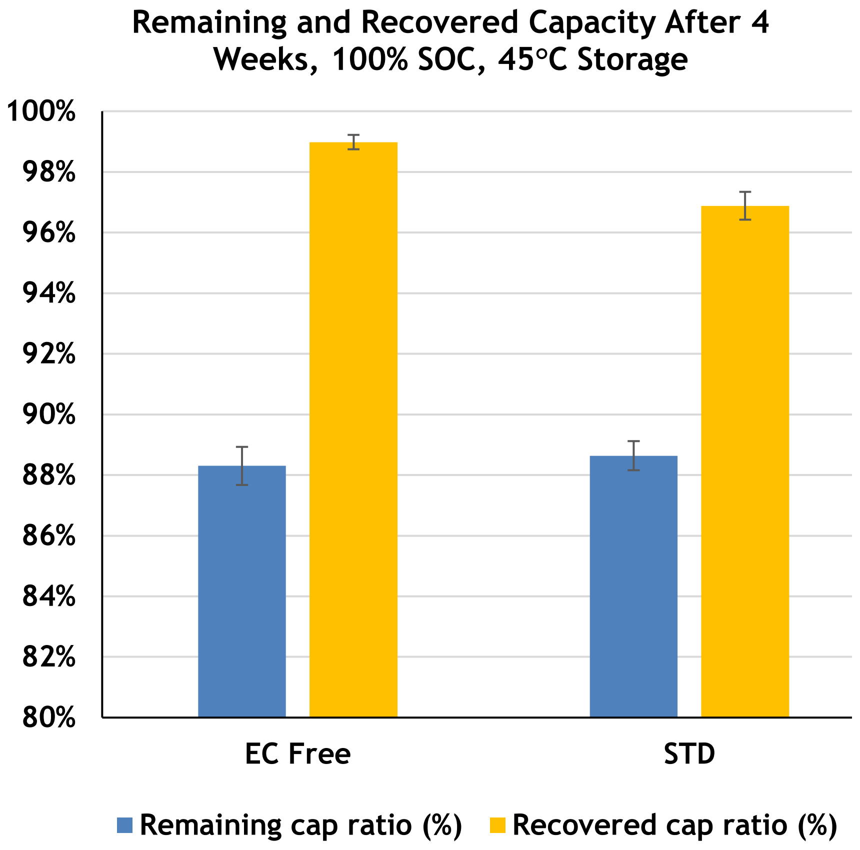
- Baseline (L6-4) shows decent stability through 5V, but a clear change at 4.8V. The formulations containing additives show reduced instability at the 4.8V step.

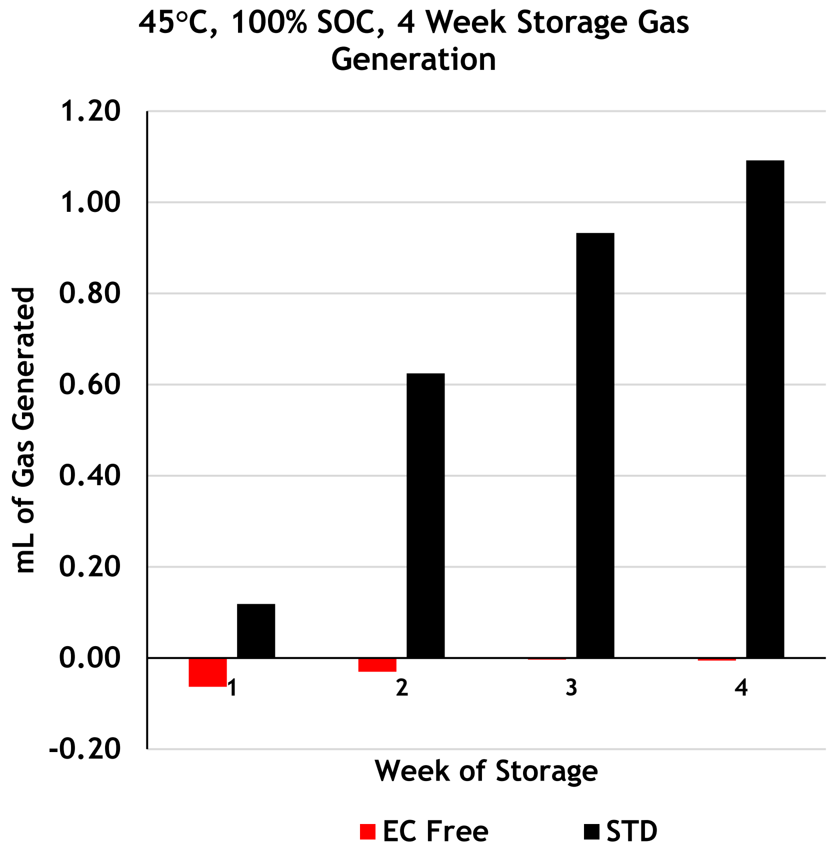




NCM/LTO MLPC Testing

- Testing for the set of data was conducted in 2 Ah NCM622/LTO MLPC
- 4 Week, High Temperature storage testing of NCM/LTO shows improvements made in performance and gas reduction when using EC free electrolyte versus the standard electrolyte
- Findings showed that the optimized formulation without EC also improved gas generation





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LNMO/C MLPC Testing

- While 4.9V LNMO/C testing has proven challenging, improvements have been seen in capacity retention and gas reduction through the use of novel additives and combinations of additives
- Not shown is the EIS impedance is measured alongside performance and gas measurements to understand the impacts being made