



Materials Development for Behind-the-Meter Storage

Kyusung Park

National Renewable Energy Laboratory (NREL)

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DOE Vehicle Technologies Program

2021 Annual Merit Review and Peer Evaluation Meeting

Project ID # bat472

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Overview

Timeline

- Project start date: 10/1/2019
- Project end date: 9/30/2025
- Percent complete: 33%

Budget

- Funding for FY 2020: \$500,000
- Funding for FY 2021: \$500,000

Barriers

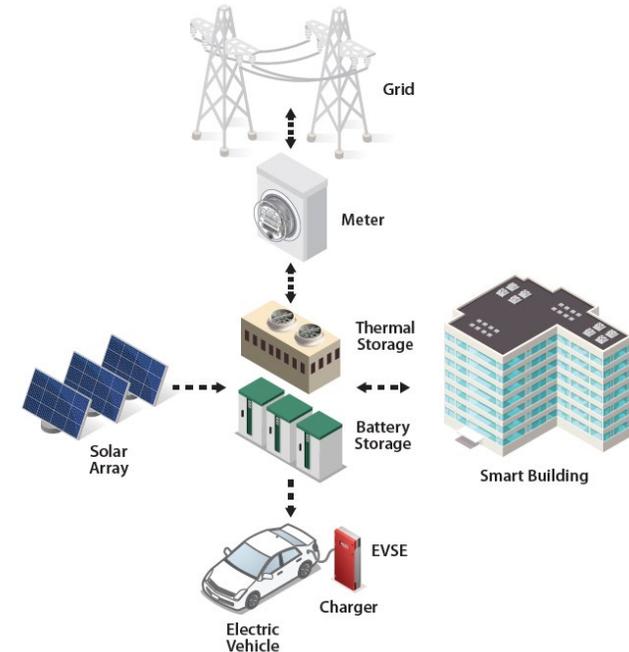
- To develop critical-material-free cell chemistries for high-energy-density Li-ion batteries.
- To develop thick electrodes and improve their utilizations.

Partners

- NREL (lead)
- Argonne National Laboratory (ANL)
- Idaho National Laboratory (INL).

Relevance and Objectives

- **Objective:** To develop critical-material-free battery chemistries that enable safe, long-term operations for behind-the-meter storage (BTMS) applications.
- VTO battery program has enabled infrastructure, capabilities, and materials development to tackle major technical barriers such as high cost, low energy density, and short battery life.
- BTMS Materials Development Project aims to:
 - Reduce battery costs
 - Create a sustainable materials supply
 - Develop high-energy-density batteries
 - Extend battery life.
- Successful development of BTMS batteries could deal with electric vehicle (EV) fast-charging loads in commercial buildings.

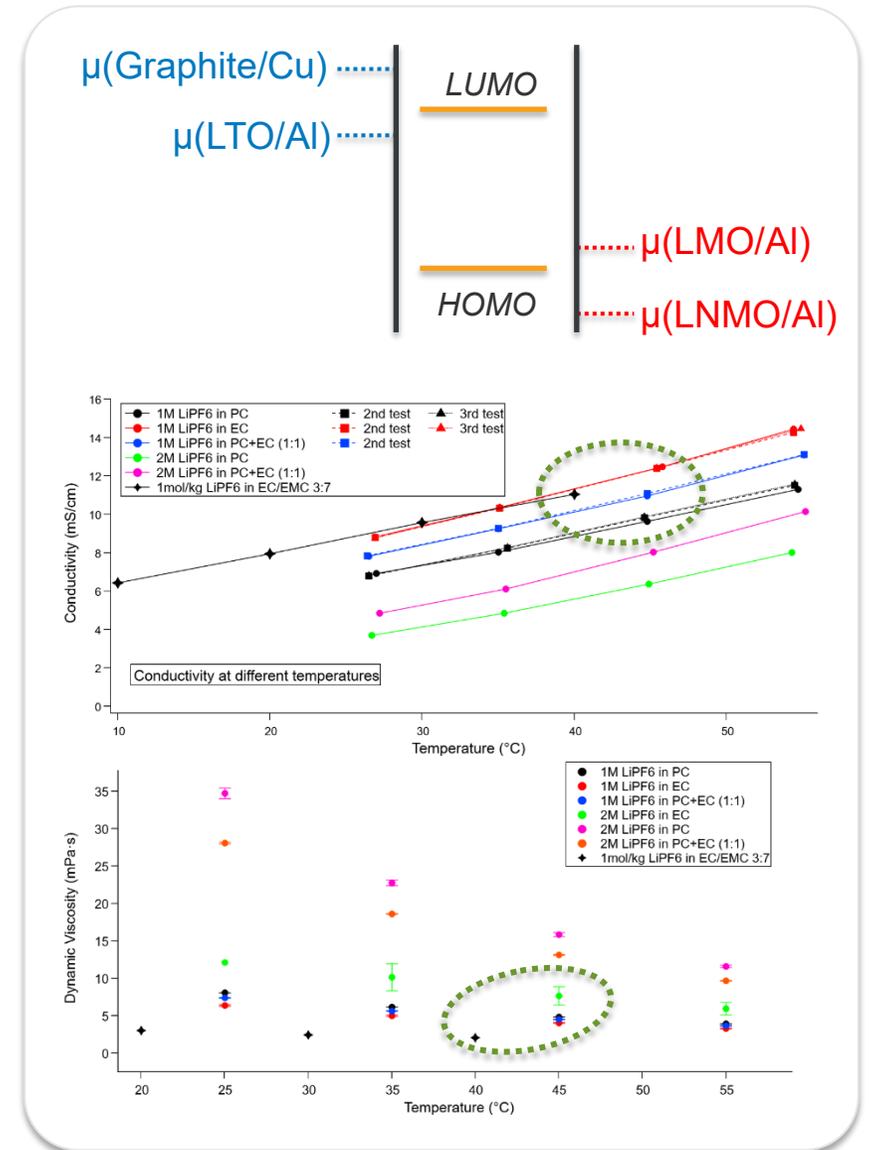


Approach

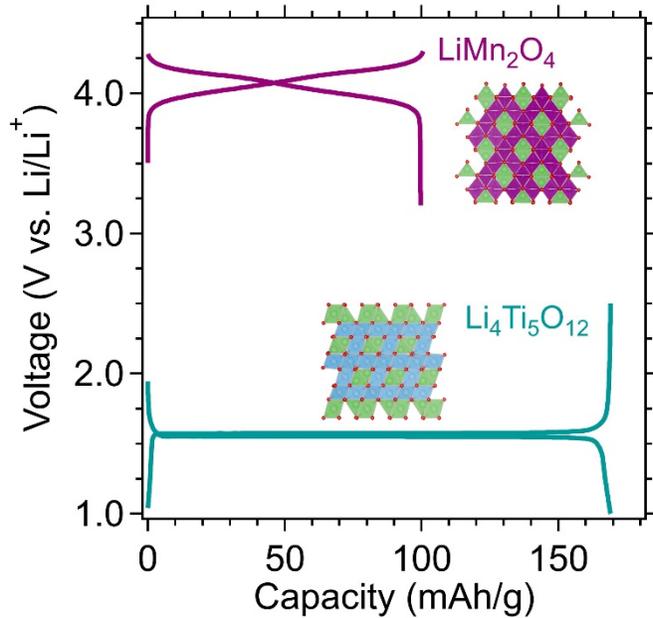
- **Design considerations for BTMS batteries**
 - Critical-material-free chemistry: sustainability and low cost
 - Long service life
 - High-energy cell: electrode engineering, high-temp operation
 - Safety: electrolyte screening – testing cyclic carbonate electrolytes
- **LiMn₂O₄/Li₄Ti₅O₁₂ (LMO/LTO) as a starting cell chemistry**
 - NREL screens electrolytes and evaluates electrochemical performance in small cell formats
 - ANL’s Cell Analysis, Modeling, and Prototyping (CAMP) facility fabricates high-loading electrodes and tests electrochemical properties in large cell formats.
- **FY21 Q4 milestone**
 - To have critical-material-free batteries (2 Ah) prepared and on test using BTMS protocols.

	Combustible		Flammable				
	EC	PC	EMC	DEC	EC/EMC (0.34/0.66)	EC/DEC (0.37/0.63)	1 M LiPF ₆ in EC/EMC (0.5/0.5)
Flash pt. (°C)	143	132	24	25	26	34	24

Source: G.G. Eshetu et al. “In-depth safety-focused analysis of solvents used in electrolytes for large scale lithium ion batteries.” *Phys. Chem. Chem. Phys.* 15 (2013): 9145–9155.

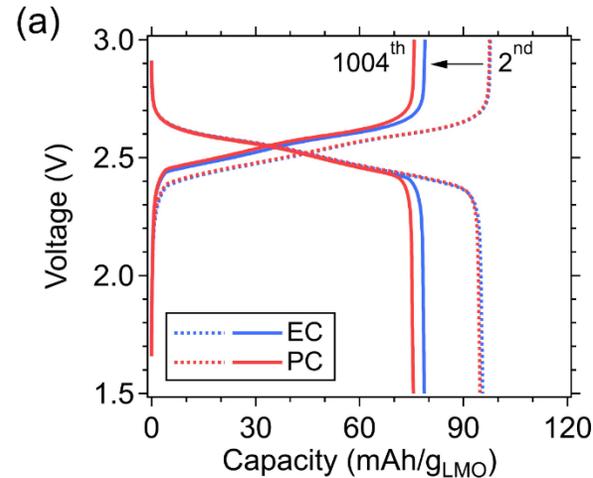


LTO/LMO Cells with 100% Cyclic Carbonate Electrolytes

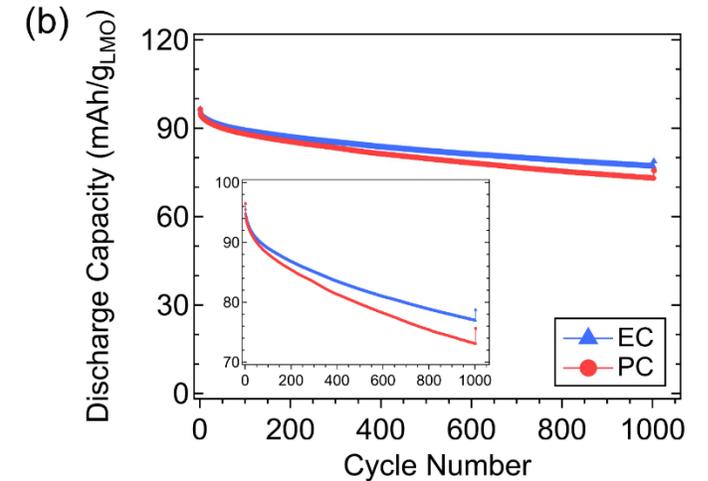


1 M LiPF₆ in EC vs. 1 M LiPF₆ in PC at 45°C

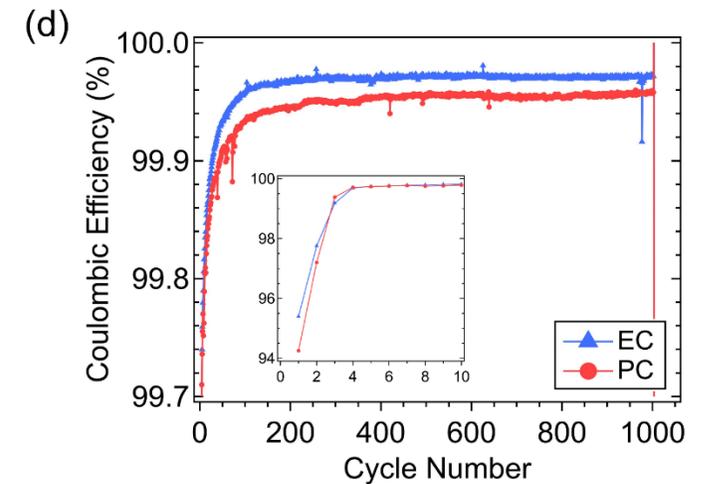
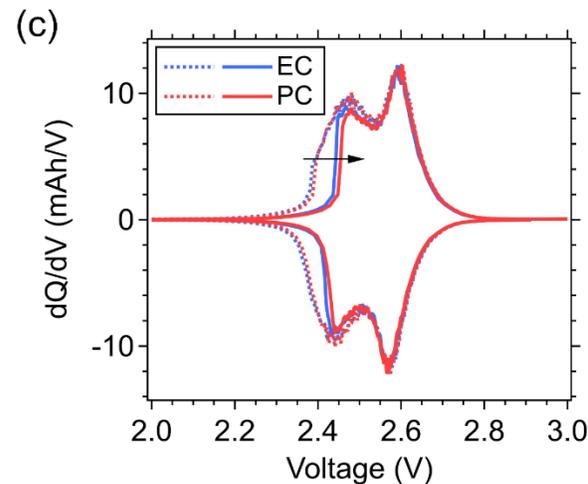
Initial vs. Final Cycles at C/10



Long-Term Cycle Performance at 1C

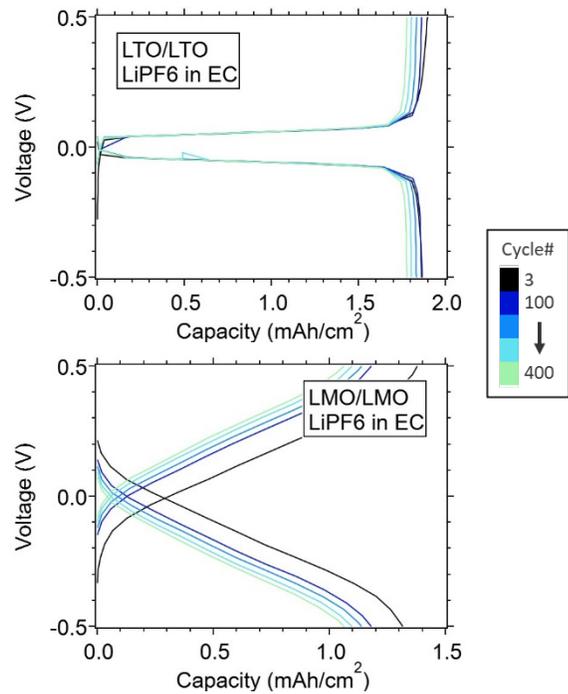


- Both EC and PC cells exhibit capacity retention of ~80% and CE > 99.95% at 45°C
- The EC cell shows slightly higher capacity retention (81% vs. 78%) and coulombic efficiency (99.97% vs. 99.96%)
- The lower-voltage dQ/dV peak (~2.45 V) shows a partial degradation.

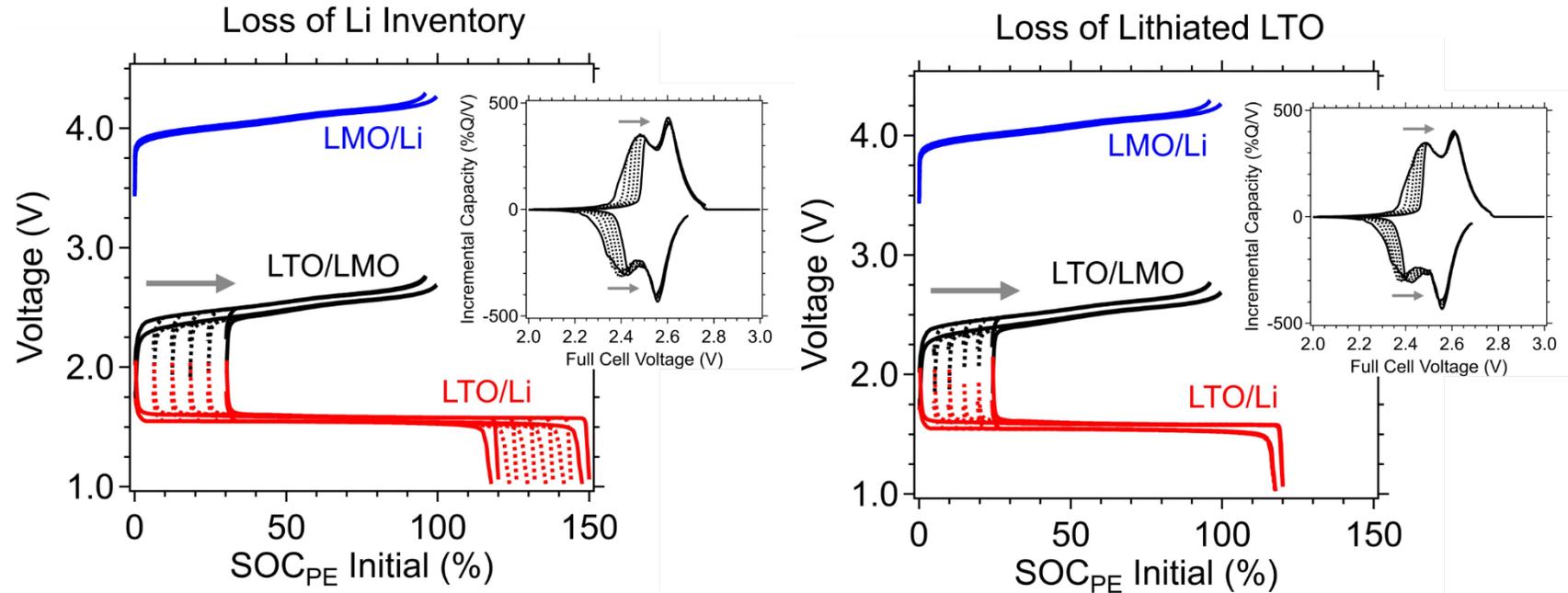


Degradation Mode Analysis

- Symmetric cell tests show that the major degradation modes of LTO are losses of “Li inventory” (LLI) and/or “active material” (LAM). For the cathode, the cell impedance increase due to degradations of active materials and/or electrolyte should be the major issue.
- The dQ/dV results indicate that the anode degradation is dominant, but the exact origin needs to be unveiled.



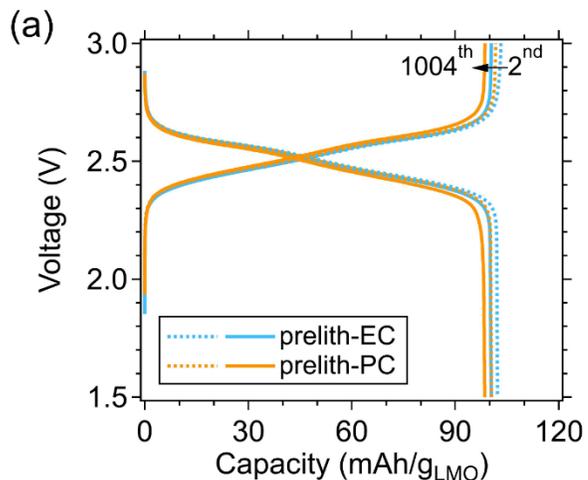
LTO/LTO and LMO/LMO symmetric cells



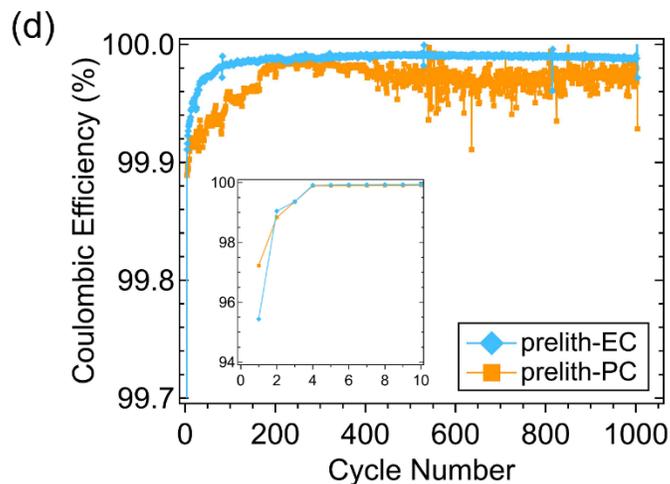
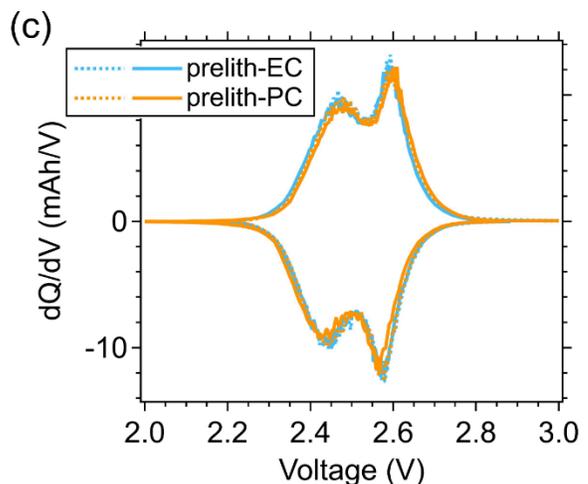
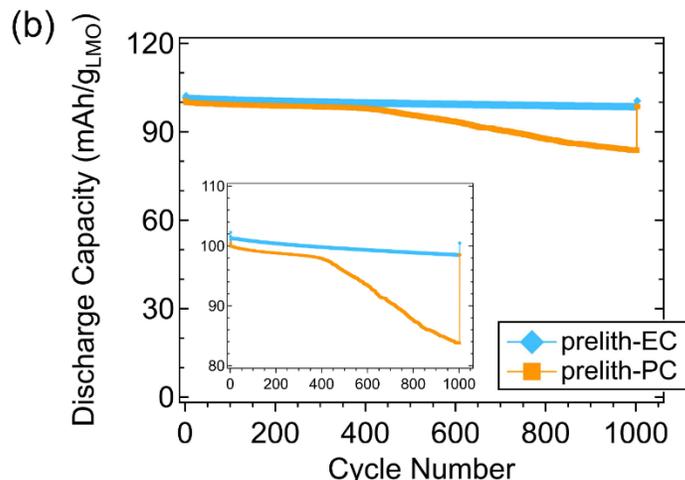
Simulated LTO/LMO voltage profiles ('Alawa battery emulation toolbox software)

LTO/LMO Cells with Extra Li Inventories

Initial vs. Final Cycles at C/10

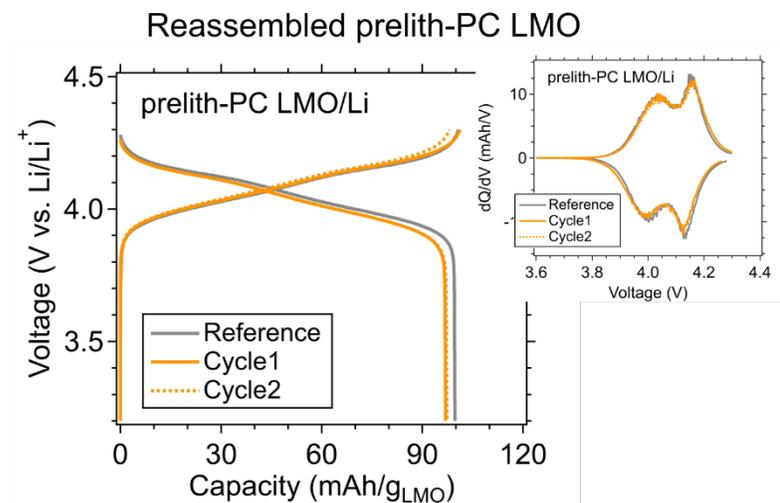
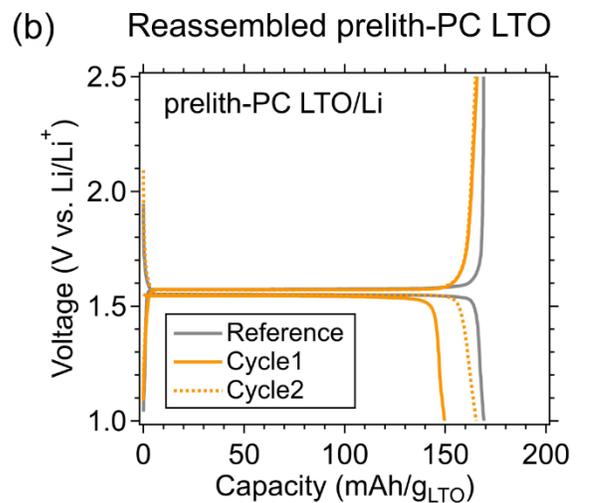
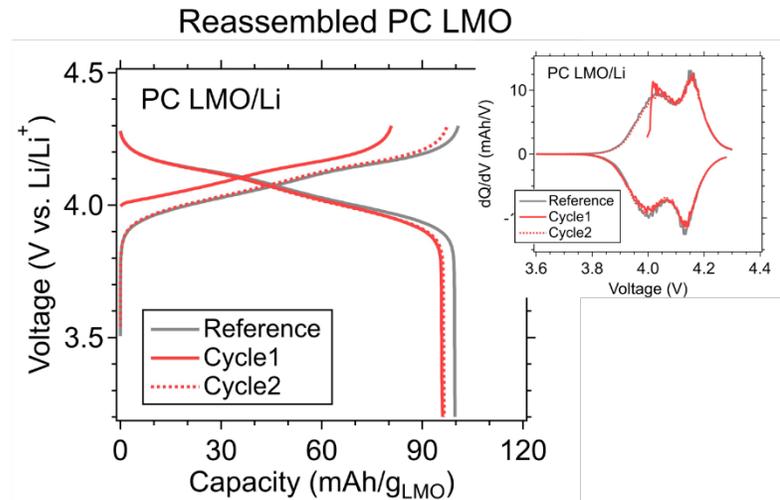
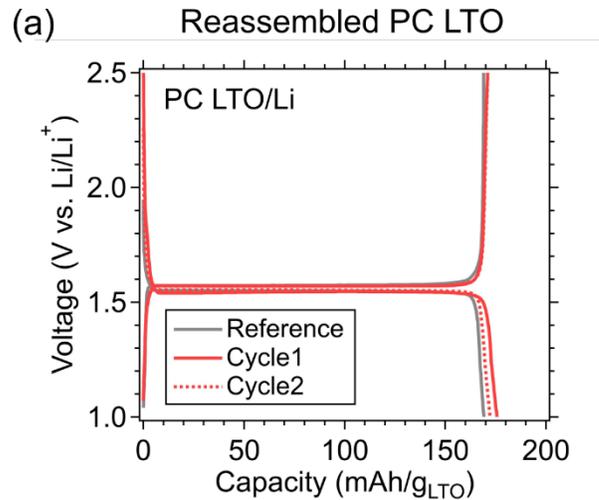


Long-Term Cycle Performance at 1C



- To distinguish LLI and $LAM_{(LTO)}$, extra Li was added to LTO by electrochemical prelithiation.
- The prelithiated LTO/LMO cells do not show the dQ/dV peak degradation, suggesting that the LLI is the major degradation mode.
- During the 1C rate cycling, the prelith-EC cell shows 98% capacity retention after 1,000 cycles and 99.99% coulombic efficiency; the prelith-PC cell shows significant impedance rise.

Validation of the LLI Model



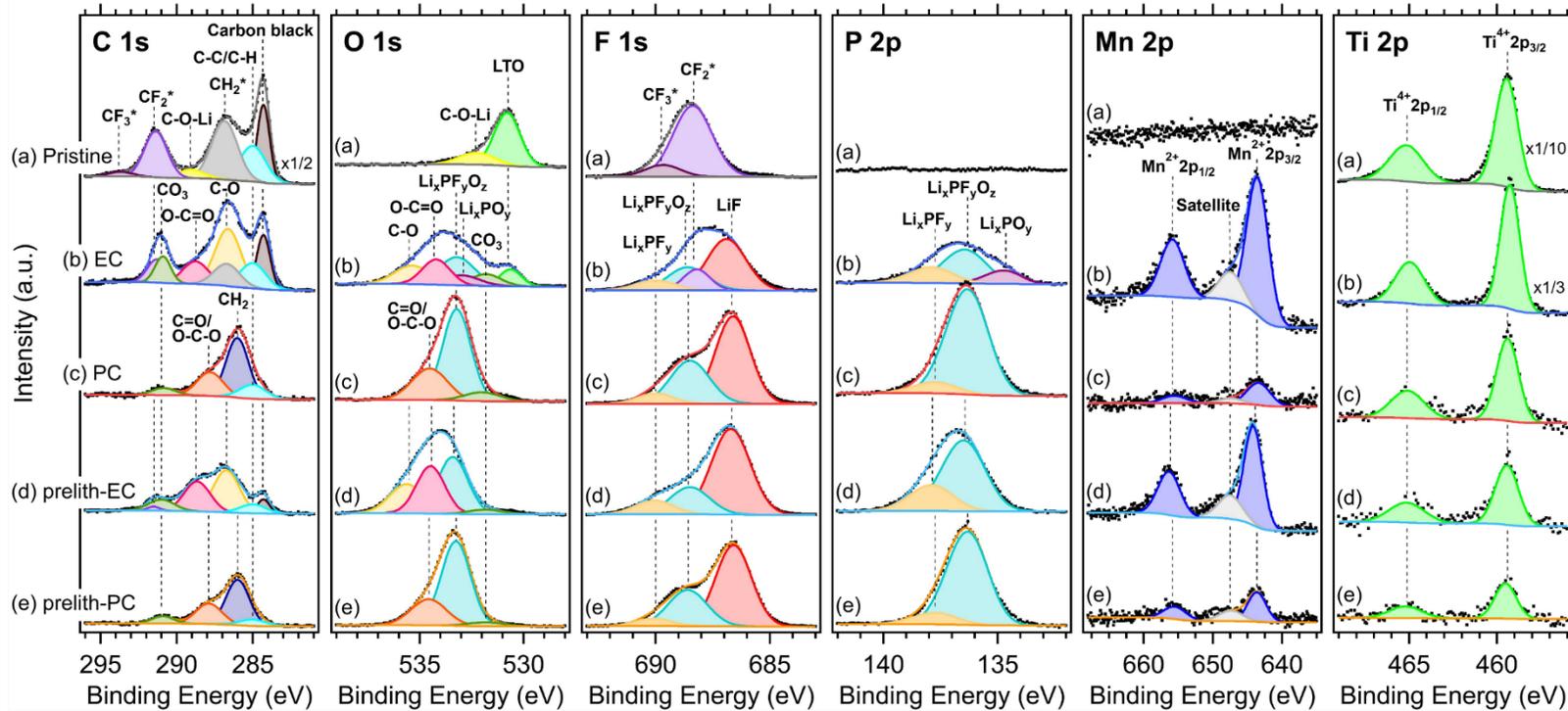
- PC LTO electrode shows no degradation; LMO electrode shows a higher state of charge.
- Prelith-PC LTO shows smaller first lithiation capacity—remaining Li amount of 0.19 mAh/cm² (vs. 0.42 mAh/cm²); LMO electrode is in a fully discharged state.

→ *Confirms that the LTO/LMO cell degradation arises from LLI.*

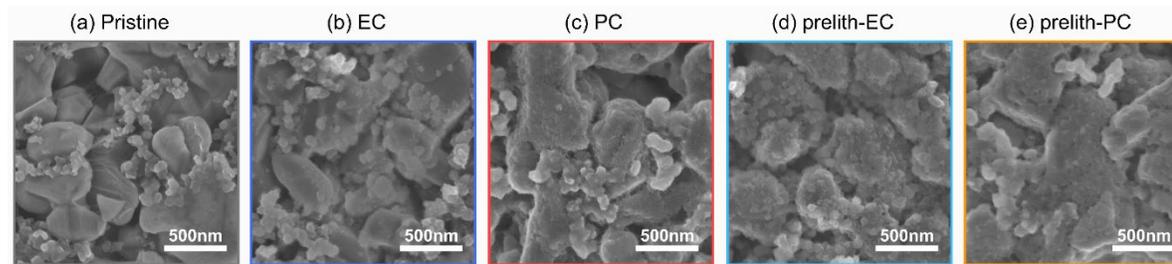
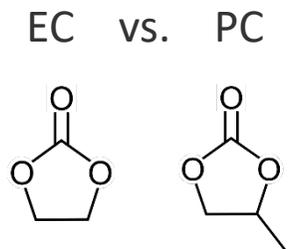
- Both cells exhibit negligible loss of cathode active material (~2%–3%)

Continuous electrolyte decomposition at the LTO electrode and LLI causes the failure of LTO/LMO cells.

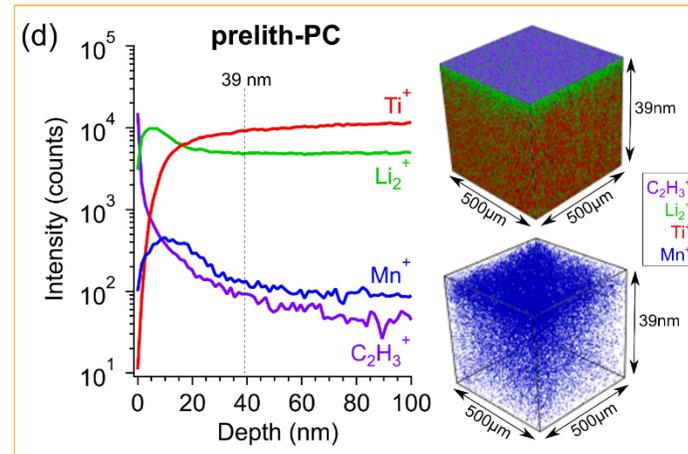
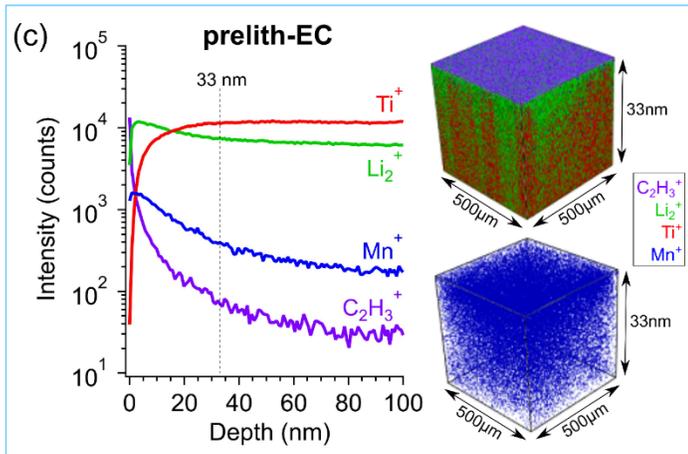
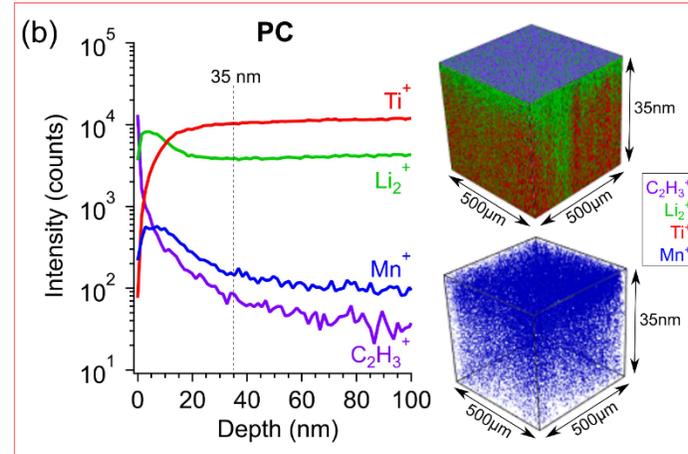
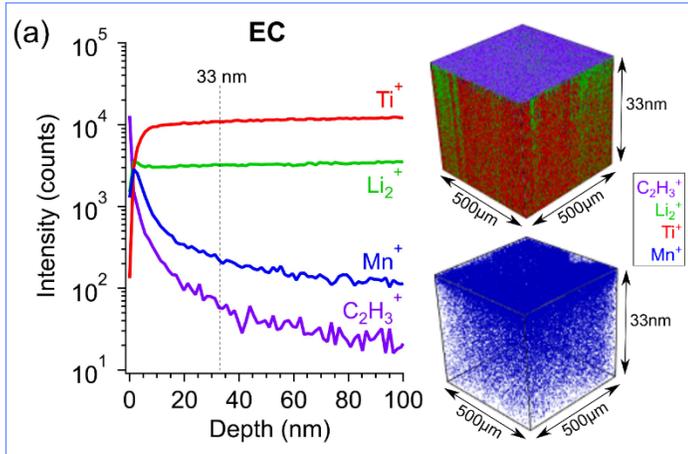
X-Ray Photoelectron Spectra of the Cycled LTO Electrodes



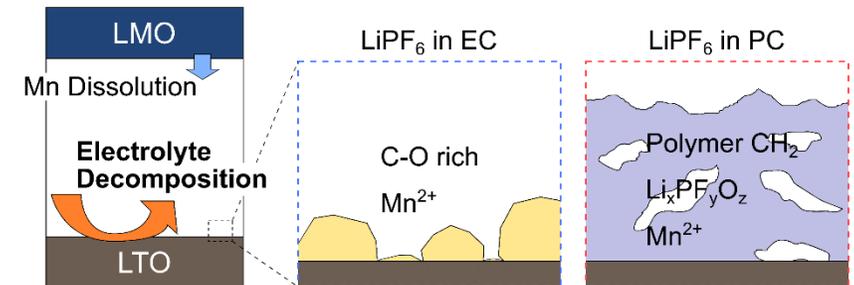
- PC electrolyte creates thicker surface films (weaker Ti 2p signals)
- Stronger salt decomposition product signals (Li_xPO_y, Li_xPF_yO_z, Li_xPF_y, LiF) detected from the PC electrolyte cells indicate greater electrolyte decomposition
- Decomposition of EC and PC creates C-O and CH₂-rich compounds, respectively, with distinct C 1s and O 1s signals
- Mn dissolved from the cathode migrates and deposits on the LTO surface.



TOF-SIMS Depth Profiles and 3D Tomography Images



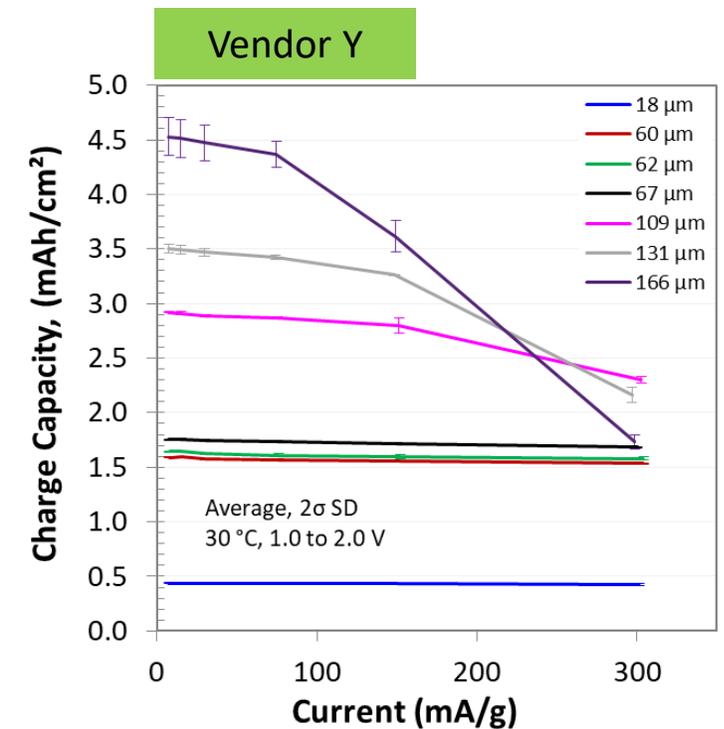
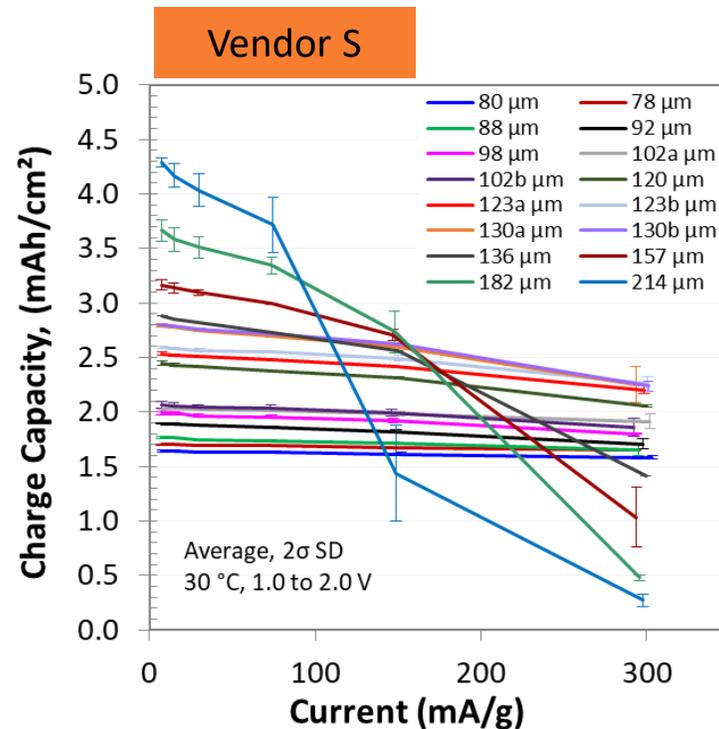
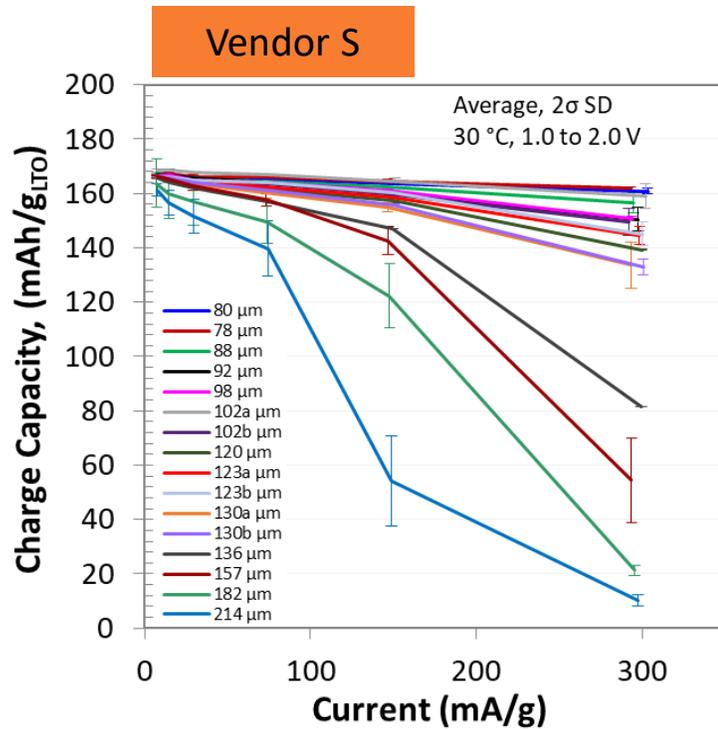
- Thicker, CH-rich surface layer formation with the PC electrolyte
- Whereas the maximum Mn⁺ signal intensity is higher in the EC electrolyte samples, PC electrolyte samples show broader, sparse Mn⁺ distribution.



TOF-SIMS: time-of-flight secondary-ion mass spectrometry

Thick Electrode Development – LTO Anode

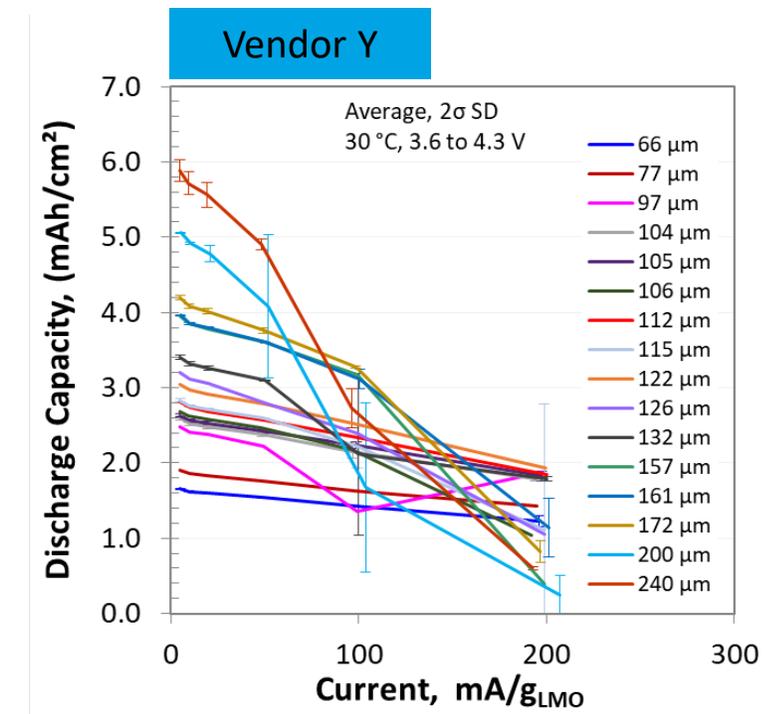
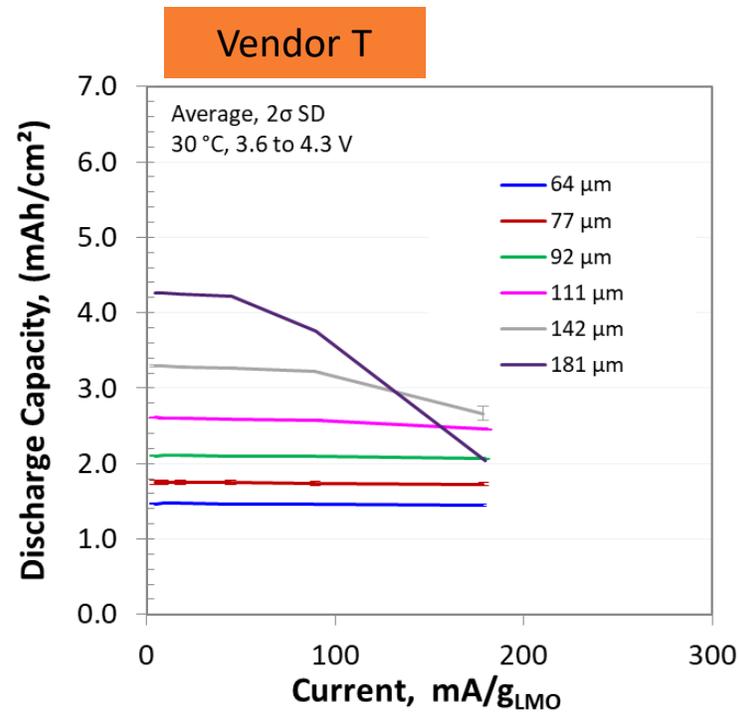
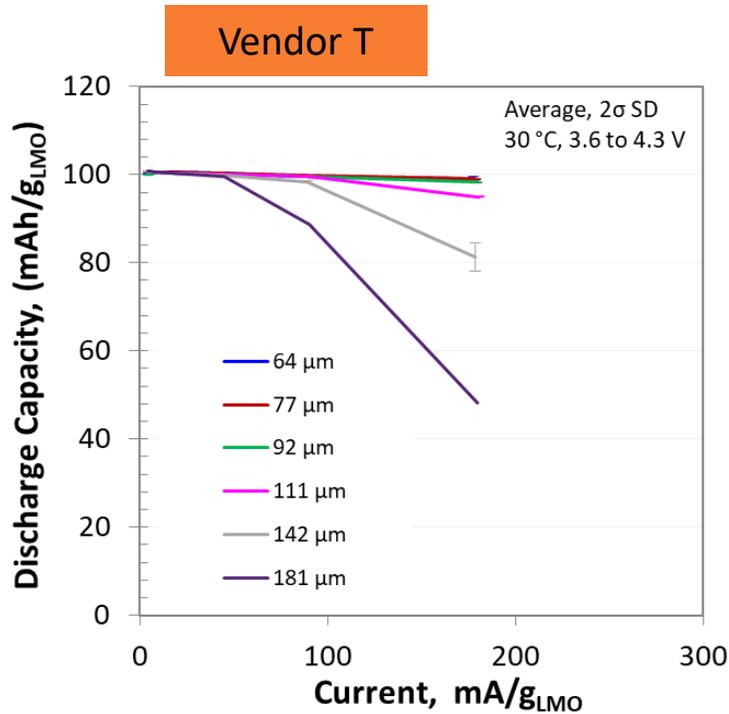
- Several LTO samples from different vendors have been used for thick electrode fabrication
- LTO electrodes >130 μm thick (>3 mAh/cm² loading) show poor performance at 2C in coin cells with Li-metal counter electrode.



Capacity utilization (delithiation; full-cell discharge) as a function of electrode thickness under various delithiation rates for LTO versus Li metal in coin cells (Gen2 electrolyte, 30°C, 1.0–2.0 V).

Thick Electrode Development – LMO Cathode

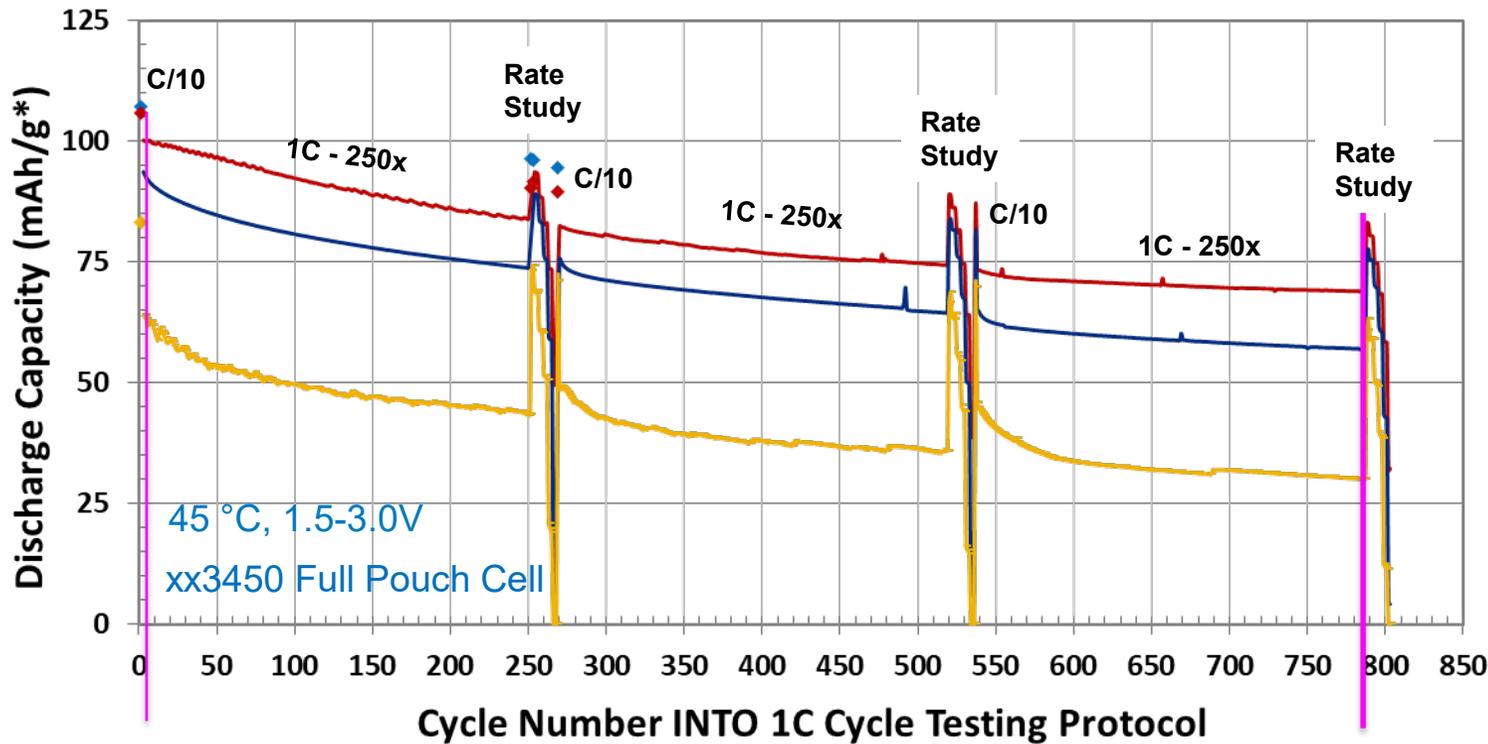
- Several LMO samples from different vendors have been used for thick electrode fabrication.
- Vendor T LMO shows better performance at higher rates (power) but has ~15 mAh/g less capacity at slower rates (energy) than the vendor Y LMO.



Capacity utilization (lithiation; full-cell discharge) as a function of electrode thickness under various lithiation rates for LMO versus Li metal in coin cells (Gen2 electrolyte, 30°C, 3.6–4.3 V).

Pouch Cell Evaluation of Thick LTO/LMO Electrodes

- xx3450 full pouch cells were made with thick LTO and LMO electrodes.
- Reasonable cycle performance was achieved with up to ~3 mAh/cm² loading electrodes.
- >4 mAh/cm² loading is too thick to fully utilize the electrode during 1C cycling at 45°C.



VENDOR Y LMO | VENDOR S LTO 1C Cycling – Representative Cells

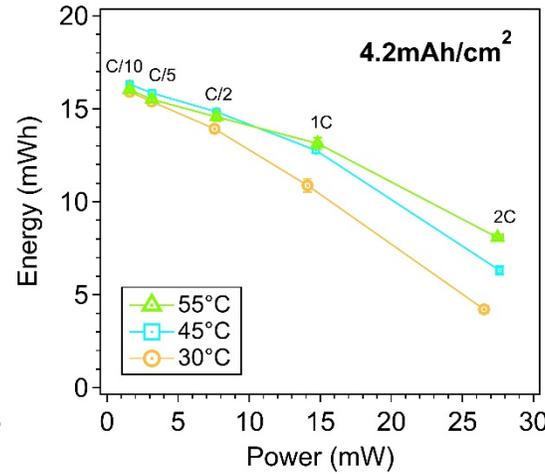
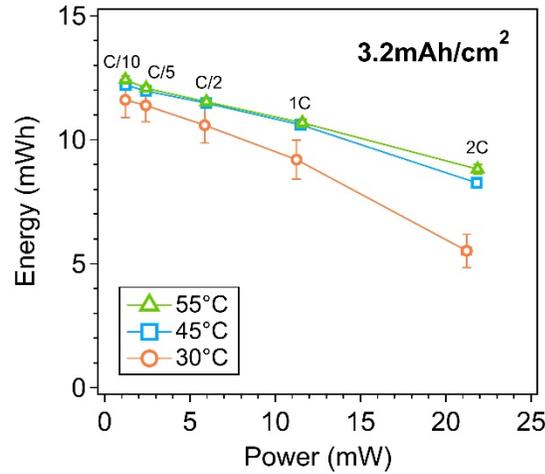
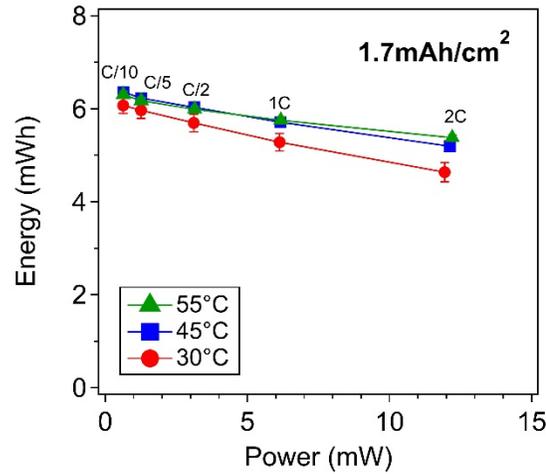
- Loading #1
- Loading #23
- Loading #27



		Coating Thickness	C/10 mAh/cm ²	Total Coating Loading, mg/cm ²
LTO	#1	80 μm	1.65	11.28
LMO	#1	66 μm	1.67	16.19
LTO	#23	157 μm	3.14	22.09
LMO	#23	126 μm	3.22	31.22
LTO	#27	214 μm	4.15	29.58
LMO	#27	172 μm	4.21	41.06

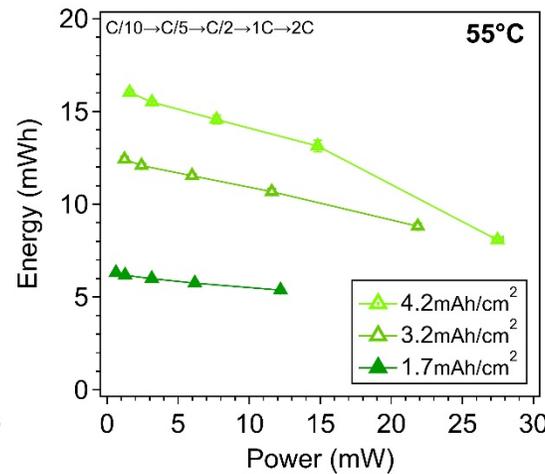
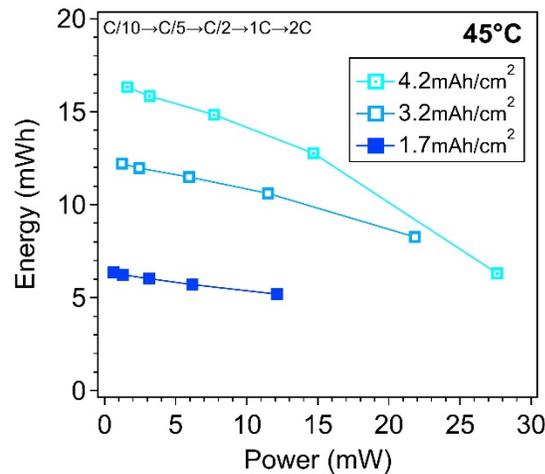
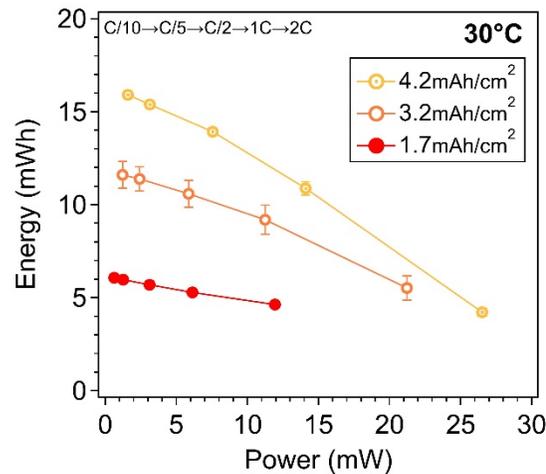
Ragone Plots of LTO/LMO Cells: Loading and Temperature

By loading:



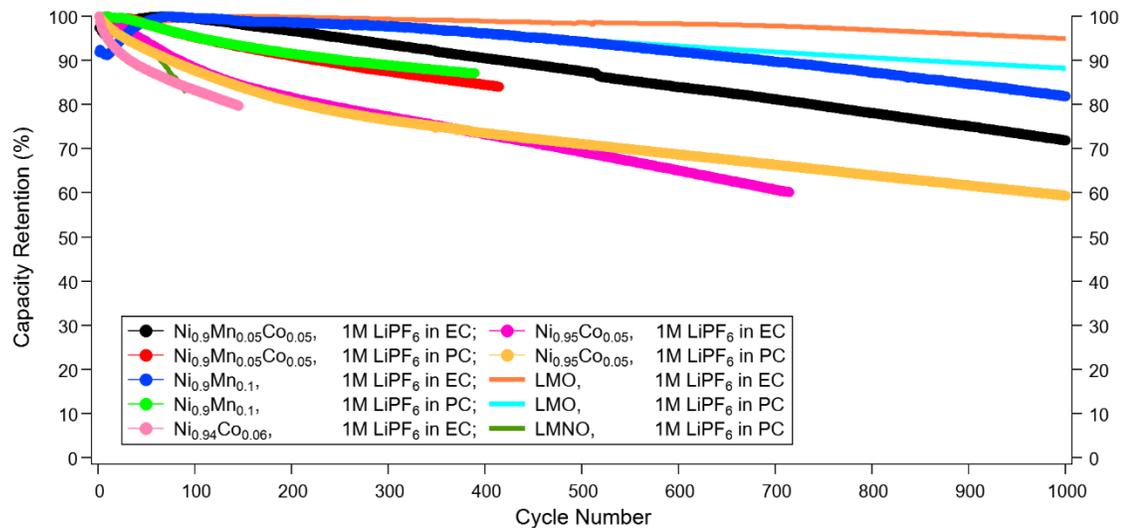
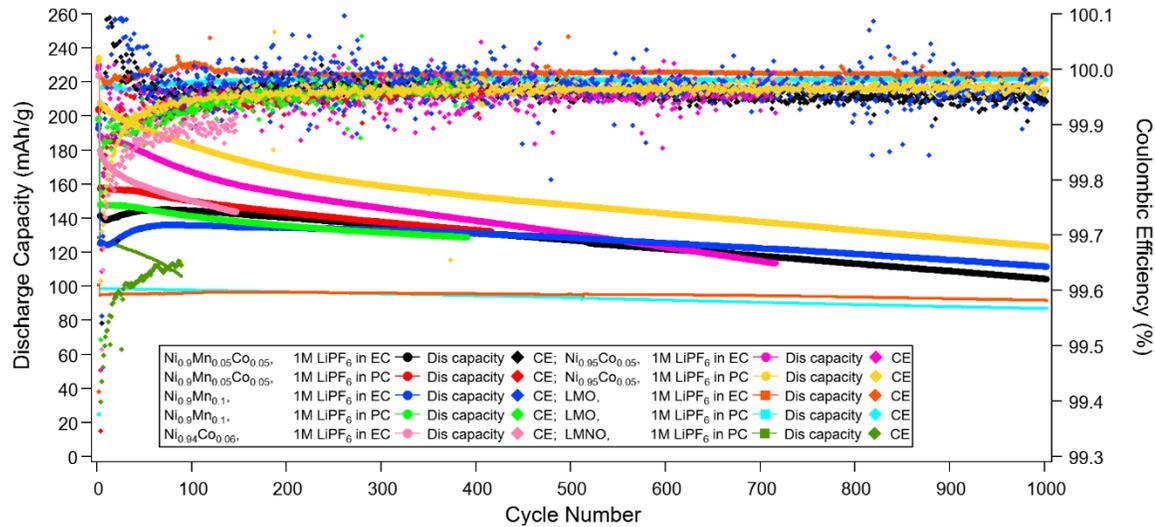
		Coating Thickness (μm)	Areal Capacity (mAh/cm ²)
#1	LTO	80	1.65
	LMO	66	1.67
#2	LTO	157	3.14
	LMO	126	3.22
#3	LTO	214	4.15
	LMO	172	4.21

By temperature:



Thick electrodes show less electrode utilization at higher C-rates, but the higher operating temperature can improve the kinetics.

Evaluation of No-/Low-Co Layered Cathodes



- $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ have shown promising electrochemical performance.
- EC-based electrolyte preforms better than PC-based electrolyte, possibly due to stable solid-electrolyte interface (SEI) formed by EC-based electrolyte.*

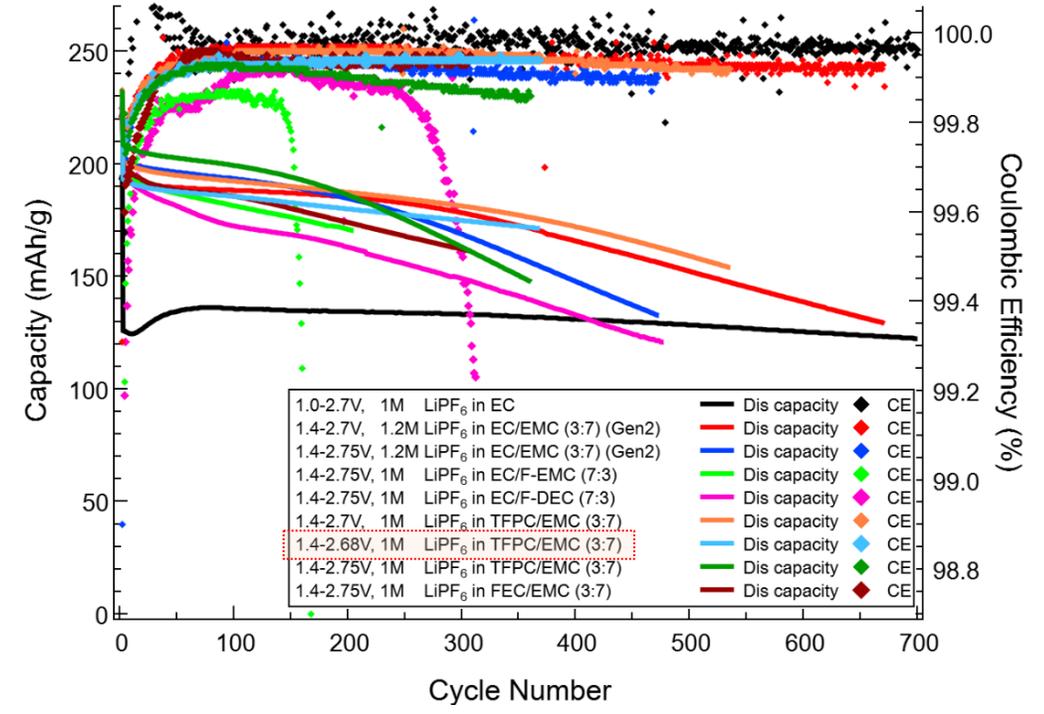
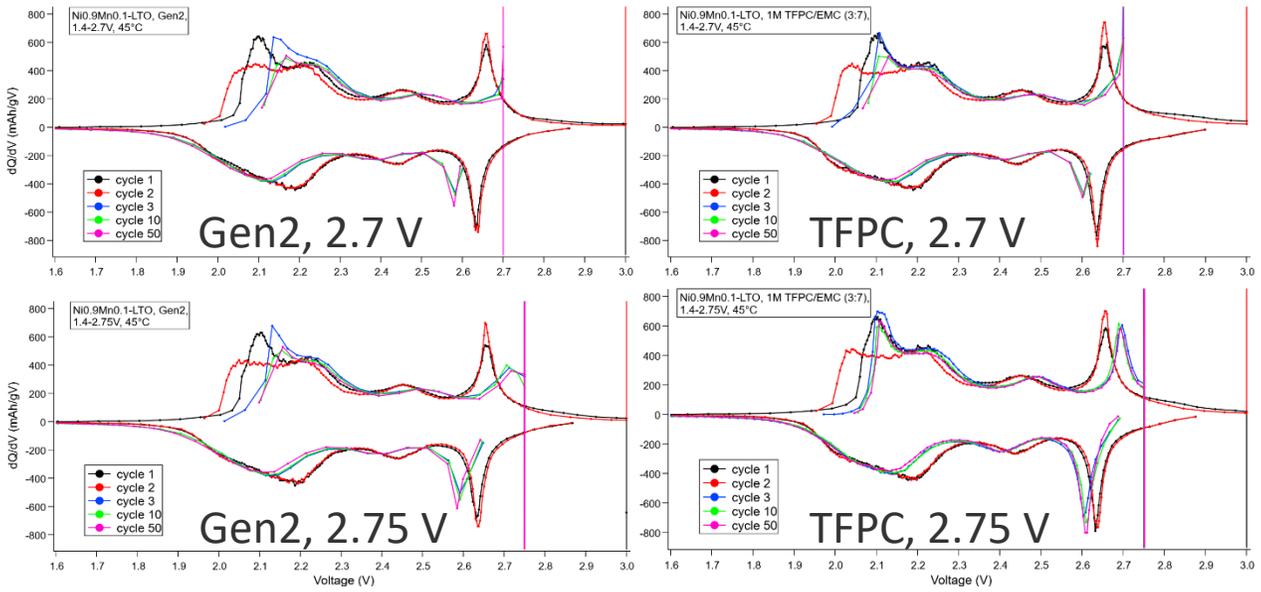
Electrochemical cycling condition:

- Electrolyte: 1.0 M LiPF_6 in EC (or PC); anode: $\text{Li}_4\text{Ti}_5\text{O}_{12}$, N/P ratio: 1.09–1.22
- Protocol: two formation cycles at C/10 + 1,000 aging cycles at 1C in the voltage range of 1.0–2.7 V at 45°C.

*Yeyoung Ha et al. "Long-term cyclability of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ cells using carbonate-based electrolytes for behind-the-meter storage applications." *Energy Storage Mater.* 38 (2021): 581–589.

Electrolyte Screening and Voltage Window Tuning

LiNi_{0.9}Mn_{0.1}O₂/LTO Cell Chemistry



Electrolyte Screening

- Several fluorinated cyclic and/or linear carbonate solvents were evaluated to enhance electrochemical stability, transport properties, and safety.

Optimization of Cycling Conditions

- Electrochemical cycling with lower upper cut-off voltages (UCVs) demonstrates the improved capacity retention, possibly due to less electrolyte decomposition and preserved structure.

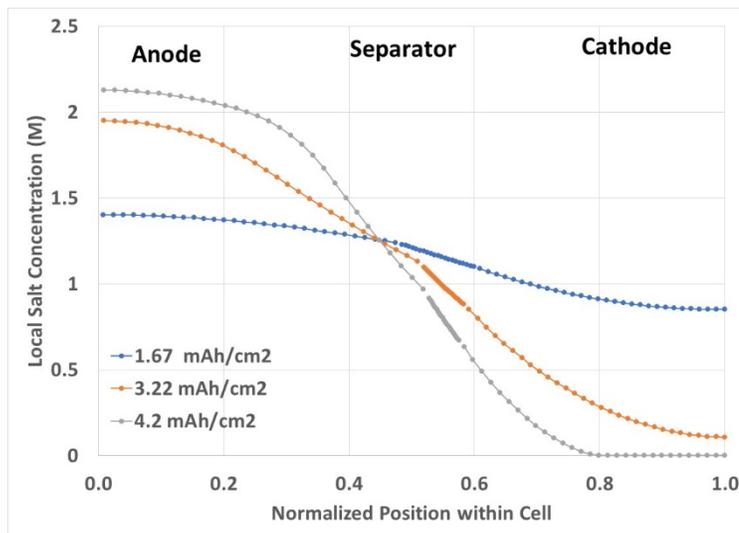
Collaboration and Coordination

- We gratefully acknowledge continuous support from David Howell and Samm Gillard of the U.S. Department of Energy's Vehicle Technologies Office.
- NREL team (lead): *Electrochemical and materials characterizations of BTMS cell chemistries*
 - Anthony Burrell
 - Kyusung Park
 - Yeyoung Ha
 - Yicheng Zhang
 - Sang-Don Han
 - Andrew Colclasure
- CAMP, Argonne National Laboratory collaborators: *Thick electrode development and cell tests*
 - Andy Jansen
 - Steve Trask
 - Alison Dunlop
- Idaho National Laboratory collaborators: *Battery modeling*
 - Eric Dufek
 - Tanvir Tanim

Remaining Challenges and Barriers

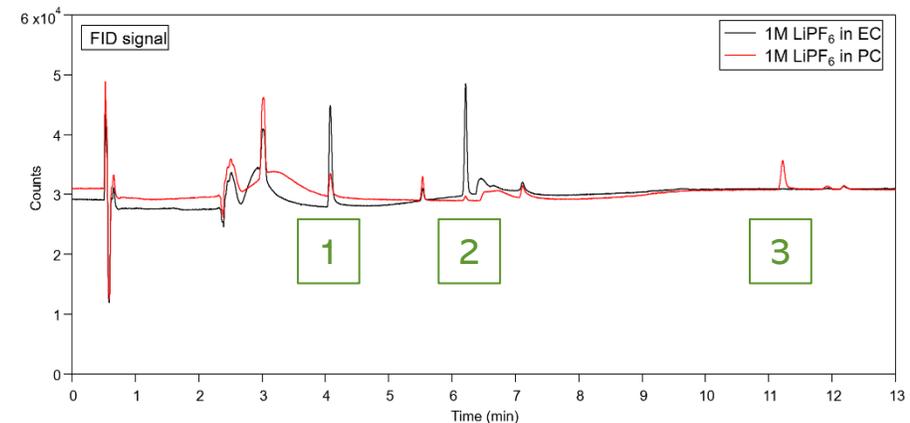
- Electrochemical utilization of thick LTO and LMO electrodes at higher C-rates is limited, likely due to electrolyte limitations.
- The gas evolution from LTO is still a major issue for long-term safe cell operation.
- The energy density of LMO is still low.

Local salt concentration profiles at 2C and 45°C at the end of discharge



*Modeling done by Andrew Colclasure, NREL

Gas evolution from LTO/Li half cells after 1-day rest

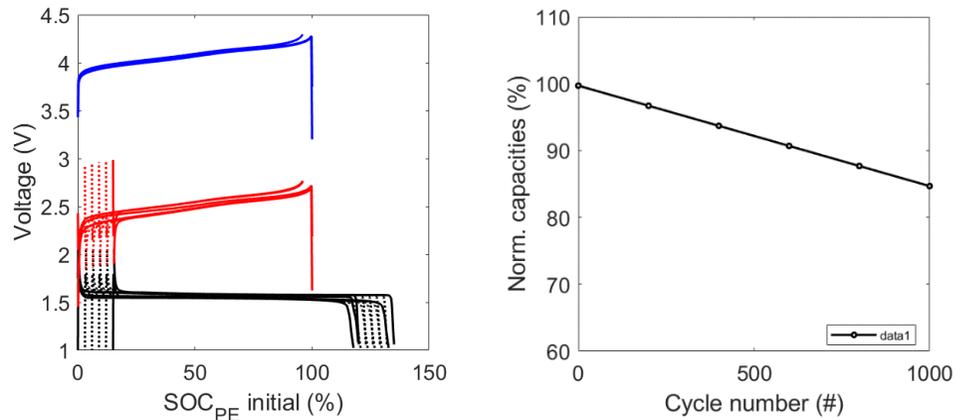


	1(CO ₂)	2(C ₂ H ₄)	3(C ₃ H ₆)
EC electrolyte	32.1	40.1	0.0
PC electrolyte	3.1	2.2	25.8

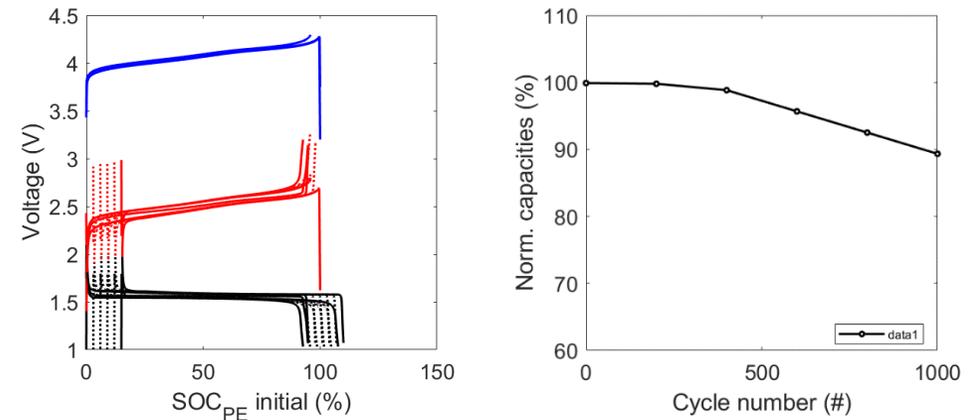
Proposed Future Research

- Test gas evolution from LTO anode and find ways to mitigate the outgassing issue
- Test new electrolyte systems (e.g., localized high-concentration electrolytes – Xiaolin Li at Pacific Northwest National Laboratory)
- Test chemical prelithiation of LTO to mitigate the LLI issue
- Test N/P ratio effect on the LMO/LTO cell performance
- Test alternative cathode materials (layered transition metal oxide cathode) for higher energy densities
- Prepare critical-material-free batteries (2 Ah) and put them on test using BTMS protocols (FY21 Q4 milestone).

N/P = 1.2



N/P = 0.95



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

Summary

- **LTO/LMO cell chemistry has been evaluated using 100% cyclic carbonate (EC, PC) electrolytes**
 - 100% EC and PC electrolytes have high Li⁺ conductivities and low viscosities at 45°C
 - The major capacity fade originates from continuous electrolyte decomposition at the anode
 - By creating a “good” surface layer with EC electrolyte and supplying additional Li source by prelithiating the LTO electrode, LTO/LMO cycle performance can be greatly enhanced.
- **Thick electrode development shows promises and limitations**
 - Maximum 214- μm -thick LTO electrode was coated, and >130- μm -thick LTO electrodes (>3-mAh/cm² loading) show kinetic limitations at 30°C
 - A higher cycling temperature is beneficial to increase rate capability
 - 2C rate is maximum current density to achieve a reasonable rate capability with a thick electrode.
- **Low-/no-Co layered cathode materials have been evaluated**
 - Higher energy densities and thinner cathode composite coating are beneficial
 - Long-term cycling performance is reasonable, and it could be enhanced by fluorinated electrolytes.

Thank You

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NREL/PR-5K00-79860

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Technical Back-Up Slides

Rate Capability Tests with Pouch Full Cells

Gen 2 cells Charge AND Discharge Capacity (mAh/g) per Cycle

*45°C, 1.5–3.0 V

