Electrolyte and Cutoff Potential Effects on Cycle Life of $Li_4Ti_5O_{12}/LiNi_{0.9}Mn_{0.1}O_2$ Batteries for Behind-the-Meter Storage Applications

Drew J. Pereira,* Yicheng Zhang, Yeyoung Ha, Maxwell Schulze, Jihyeon Gim, Stephen Trask, Anthony Burrell, Katharine L. Harrison

May 26th, 2024 14:20

A02 Lithium-Ion Batteries

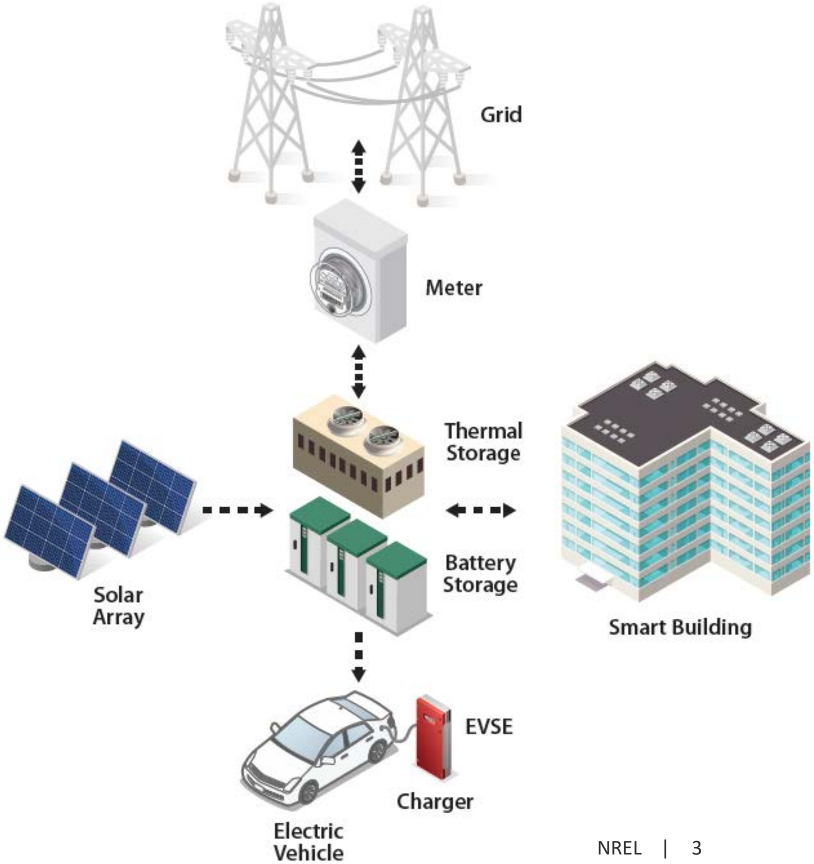
Drew.Pereira@nrel.gov

What is Behind-the-Meter Storage

Utilize Battery ESS to improve:

- EV charging integration
- Solar/Wind power generation integration
- Utility costs
- Impact on the grid

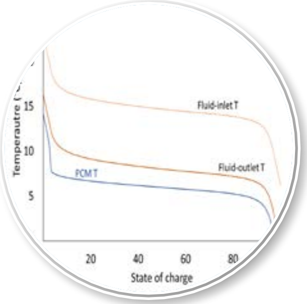
Catalyze transition to clean energy



BTMS Consortium Efforts

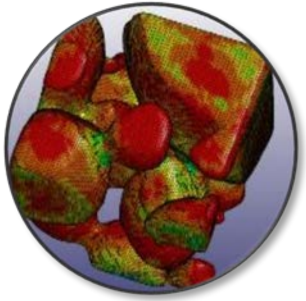
Metrics and target determination

Informing low-TRL R&D



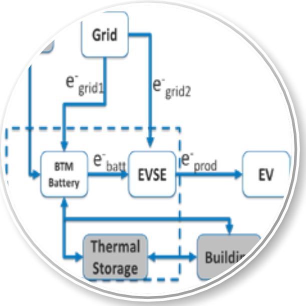
Multi-scale characterization

Materials to systems



Materials Discovery

Metric-informed R&D



Integrated-system modeling and design

Strategies for battery + thermal storage systems

Full System Design

Technology transfer where prototypes are produced for qualification

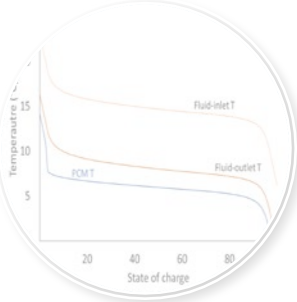
Integration experiments

Demonstrating controls and interoperability of technologies

BTMS Consortium Efforts

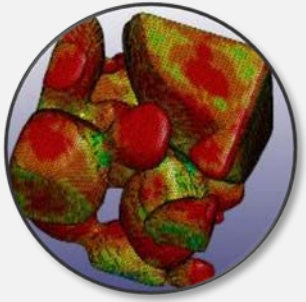
Metrics and target determination

Informing low-TRL R&D



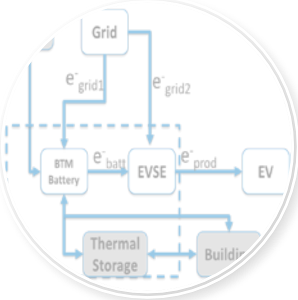
Multi-scale characterization

Materials to systems



Materials Discovery

Metric-informed R&D



Integrated-system modeling and design

Strategies for battery + thermal storage systems

Full System Design

Technology transfer where prototypes are produced for qualification

Integration experiments

Demonstrating controls and interoperability of technologies

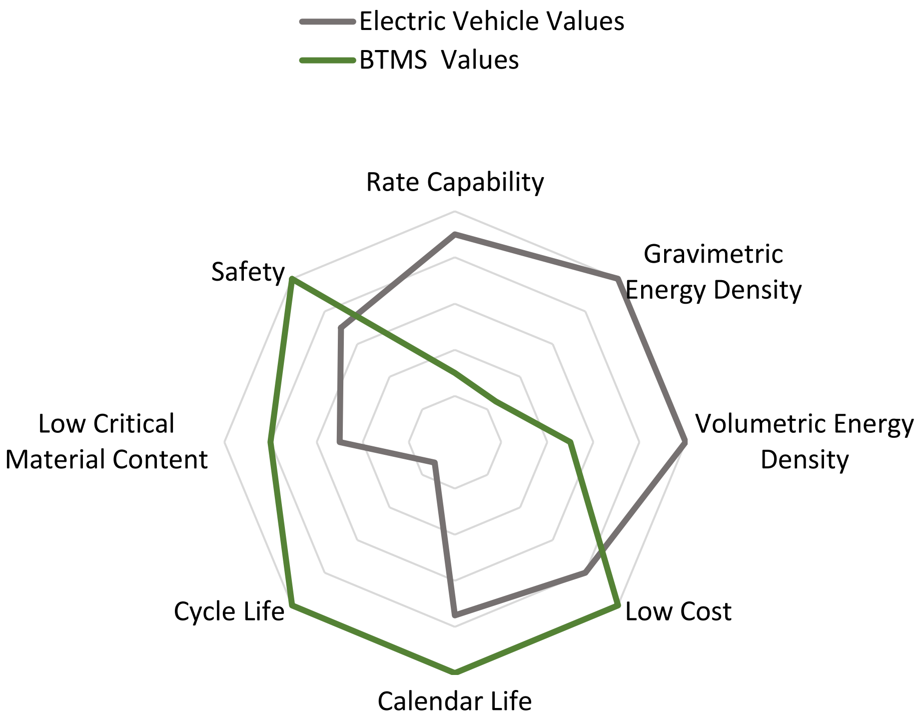
Why BTMS-specific materials discovery?

BTMS battery needs

- Minimize critical materials use
- Maximize cycle life
- Maximize calendar life
- Maximize safety

BTMS batteries not as reliant on

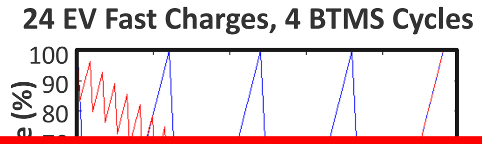
- Gravimetric energy density
- Volumetric energy density
- Rate capability



BTMS battery targets and material consideration

1-10 MWh battery:

- $100/kWh
- 8000 cycles
- 20 y calendar life
- 4 BTMS
- 24 EV f
- 10 min
- 1C rate



See invited speaker: Katie Harrison for more in-depth background on early BTMS work

A02-0401 10:20-11:00 am
Wednesday, May 29th 2024

Initially considered

- Graphite/NMC
- LTO/NMC
- LTO/LMO
- LTO/LNMO
- Ni-Zn
- Pb Acid
- Graphite/LFP
- Zn-air

NREL developed EVI-EDGES model to evaluate how BTMS can mitigate costs and grid impacts of EVs.

Grid buffering with batteries can be cost effective at $100/kWh but achieving long cycle/calendar life goals with minimal critical materials is a significant research challenge.

Motivation

Knowing that Ni-rich layered oxide materials have historically had poor capacity retention and thermal stability:

- Can we mitigate these issues in Ni-rich, No-Co material by adjusting operating voltage or appropriate electrolyte design, while still retaining benefits for BTMS applications?

Electrolyte and Cutoff Potential Effects on Cycle Life of $Li_4Ti_5O_{12}/LiNi_{0.9}Mn_{0.1}O_2$ Batteries for Behind-the-Meter Storage Applications

Cycle Life Study

Coin Cell Assembly:

Steel Cap (Hohsen Corp.)

1mm steel spacer (welded, Hohsen Corp.)
14mm dia. $LiNi_{0.9}Mn_{0.1}O_2$ (90%, CAMP)

40uL electrolyte

Separator (celgard 2325 for Gen 2 and EMC, delfort DWG20 for EC and FEC)

40uL of the same electrolyte

15mm dia. LTO (92%, CAMP) (N:P≈0.9)
0.5mm steel spacer (welded)

Button and O-ring (Hohsen Corp.)

Electrolyte Selection:

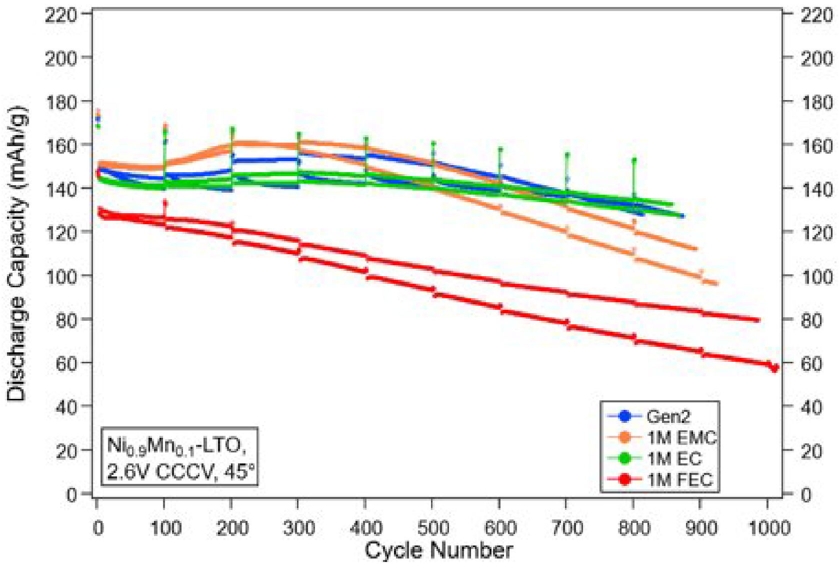
- Gen2 (1.2M $LiPF_6$ in 3:7 EC/EMC by wt.)
- 1M $LiPF_6$ in ethyl methyl carbonate (EMC)
- 1M $LiPF_6$ in ethylene carbonate (EC)
- 1M $LiPF_6$ in fluoroethylene carbonate (FEC)

BTMS Cycling Protocol (1.4-2.6V OR 1.4-2.7V):

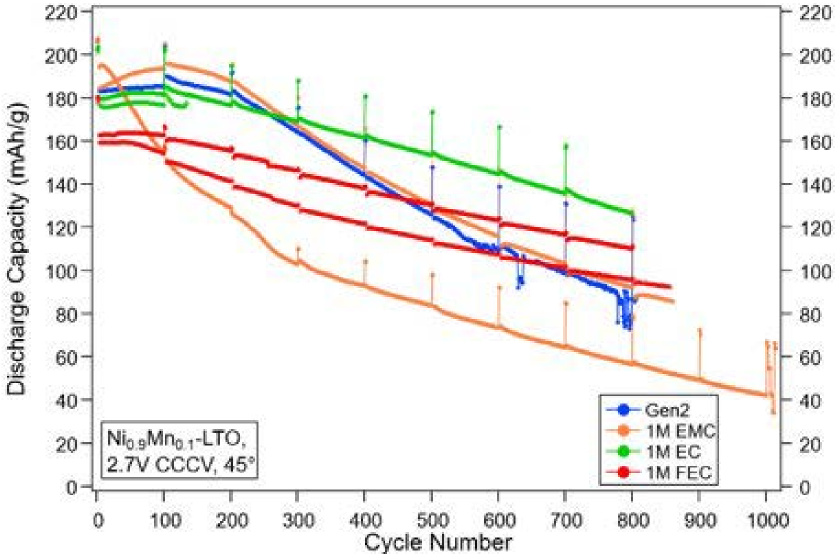
1. Initial Formation and Rate test (CCCV charge, CC discharge)
   a) Cycles: 3 @ C/10, 3 @ C/3, 3 @ 1C, 3 @ 2C
2. Repeating cycling sequence (until reaching 1000 cycles)
   a) 2 cycles @ C/10
   b) 1 HPPC cycle
   c) 97 cycles @ 1C
3. End-of-Life Rate test

Initial Results

2.6V CCCV



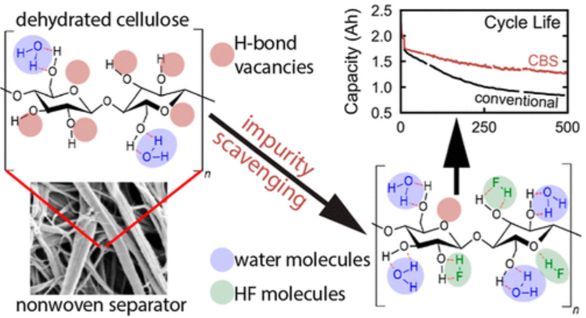
2.7V CCCV

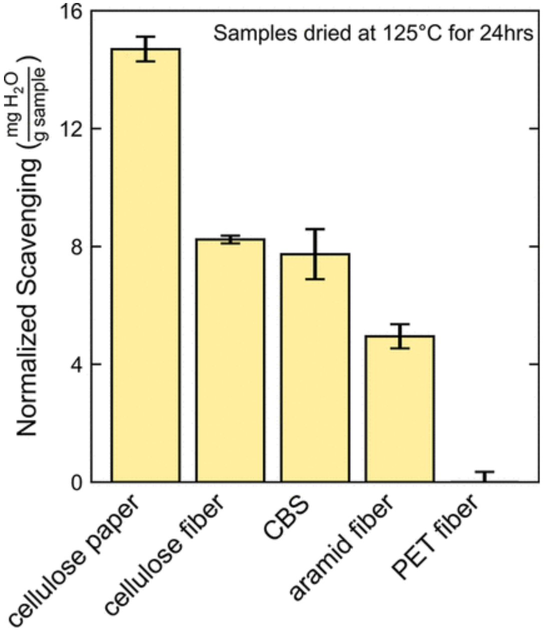


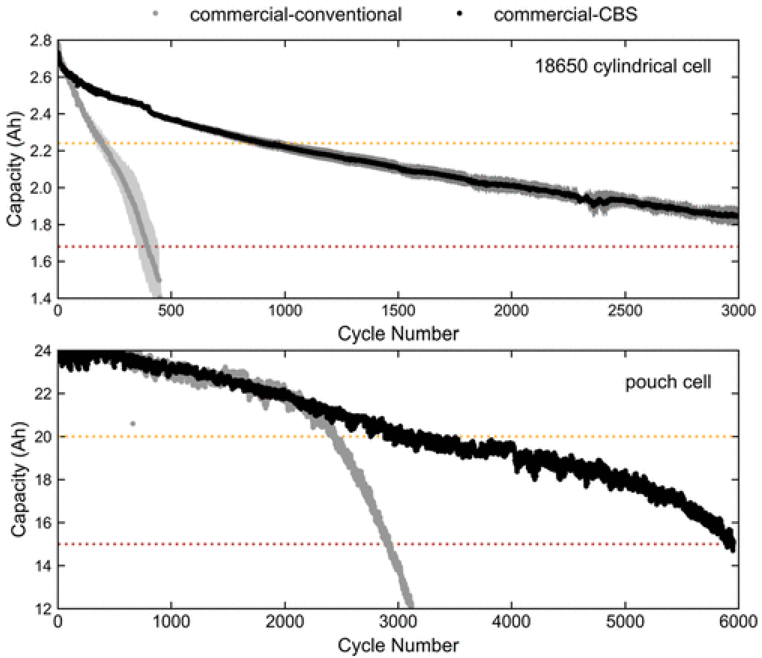
- 2.7V unlocks higher capacity for all electrolytes
- EC seems to demonstrate the best stability at both 2.6V and 2.7V
- At the sacrifice of initial capacity, FEC shows promise as a non-flammable with similar retention to EC at both voltages
- However, a complication….

Good and Bad: Cellulose-based Separator

Cellulose-based separator, like ours, has been shown to significantly enhance cycle life.







Pereira, D. J., McRay, H. A., Bopte, S. S., & Jalilvand, G. (2024). H2O/HF Scavenging Mechanism in Cellulose-Based Separators for Lithium-Ion Batteries with Enhanced Cycle Life. *ACS Applied Materials & Interfaces*.

Adjusted Cycle Life Study

Coin Cell Assembly: Wetting Steps

Steel Cap (Hohsen Corp.)

1mm steel spacer (welded, Hohsen Corp.)
14mm dia. $LiNi_{0.9}Mn_{0.1}O_2$ (90%, CAMP)

40uL electrolyte

Separator (delfort DWG20 only)

40uL of the same electrolyte

15mm dia. LTO (92%, CAMP) (N:P≈0.9)
0.5mm steel spacer (welded)

Button and O-ring (Hohsen Corp.)

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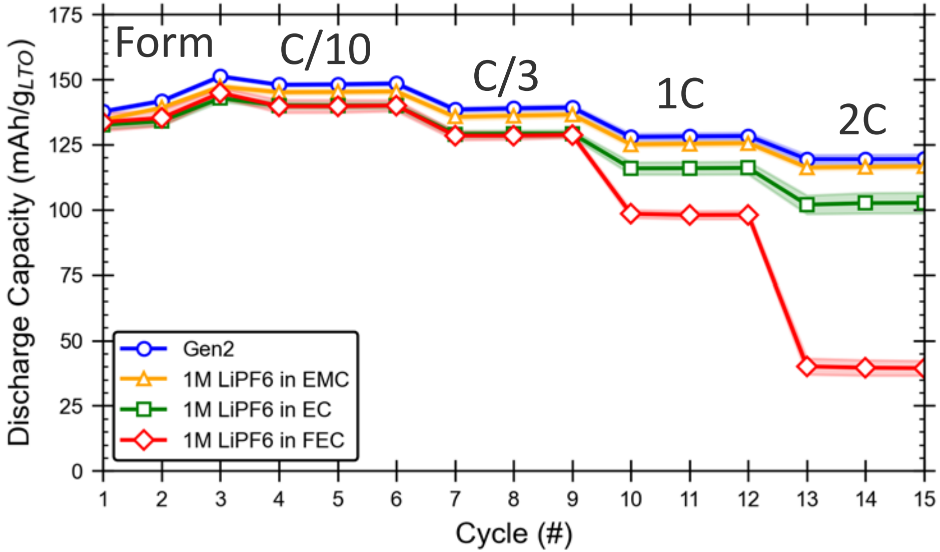
- 1M $LiPF_6$ in ethylene carbonate (EC)
- 1M $LiPF_6$ in fluoroethylene carbonate (FEC)

BTMS Cycling Protocol (1.4-2.6V OR 1.4-2.7V):

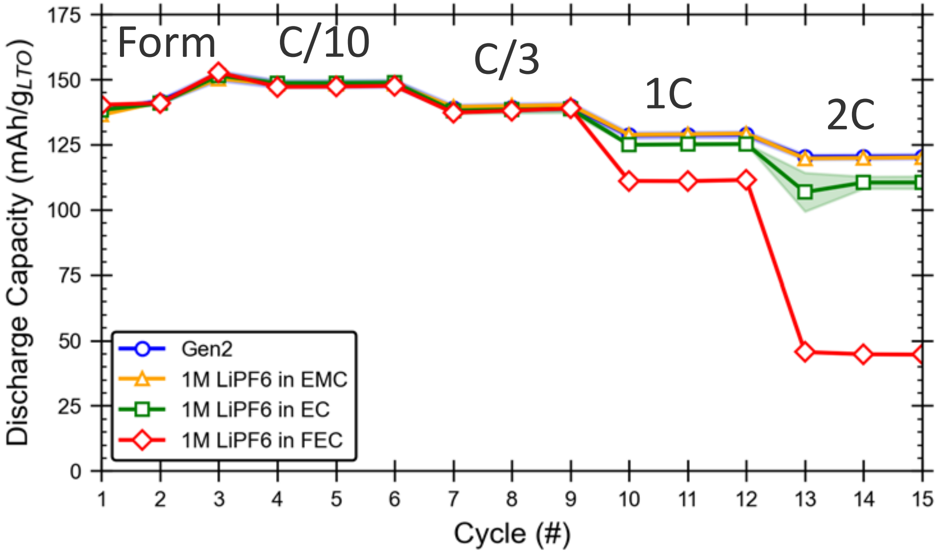
1. Initial Formation and Rate test (CCCV charge, CC discharge)
   a) Cycles: 6 @ C/10 (2 CC, 4 CCCV), 3 @ C/3, 3 @ 1C, 3 @ 2C
2. Repeating cycling sequence (until reaching 1000 cycles)
   a) 2 cycles @ C/10
   b) 1 HPPC cycle
   c) 97 cycles @ 1C
3. End-of-Life Rate test

BoL Formation and Rate Test

2.6V Form and Rate



2.7V Form and Rate

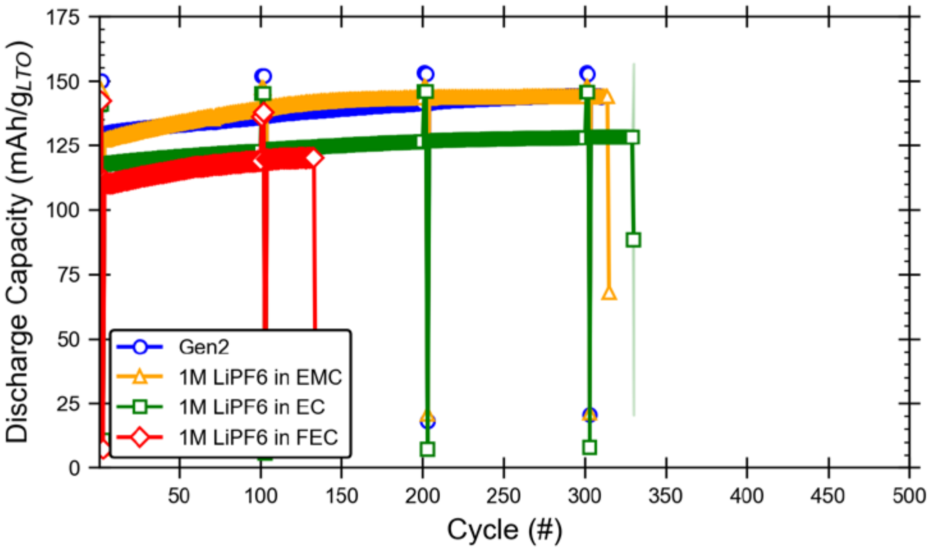


Initial Takeaways:

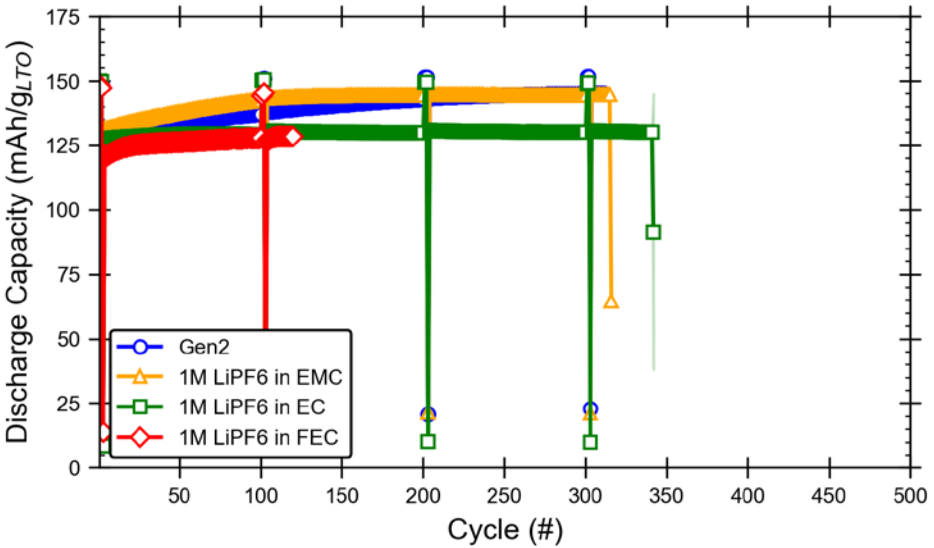
- Slightly higher capacities accessible at 2.7V, but not to the degree we saw in initial test.
- EC and FEC electrolytes slack at the BTMS-relevant 1C rate.
- Interesting phenomena at 2.7V where the low-rate capacities of all electrolytes are equivalent.

Progressing Cycle Life

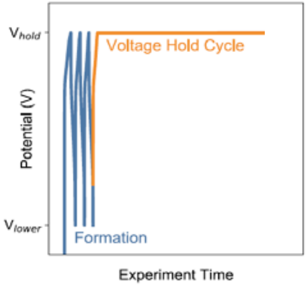
2.6V Cycling

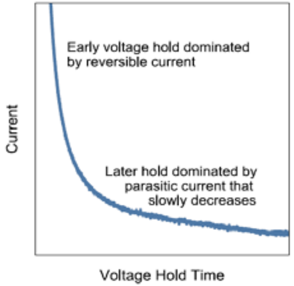


2.7V Cycling



BTMS Protocol: Voltage Hold





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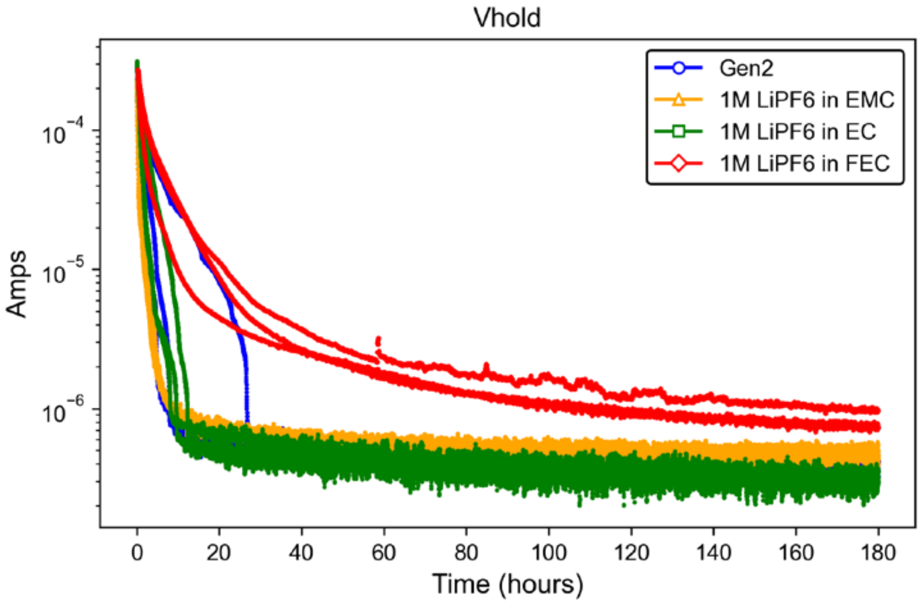
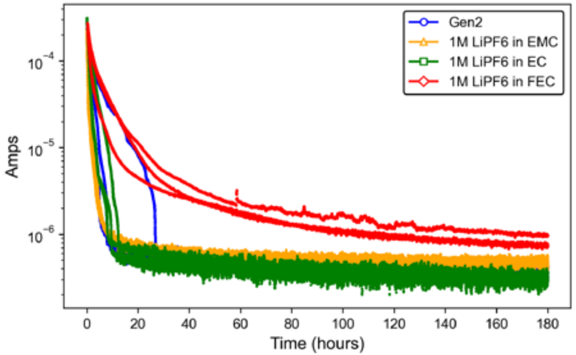


Initial Takeaways:

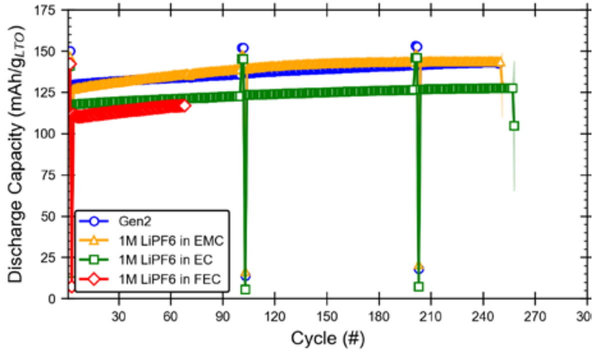
- EC shows lowest Vhold current, with Gen2 showing similar performance
- FEC showing highest current.

Data Comparison

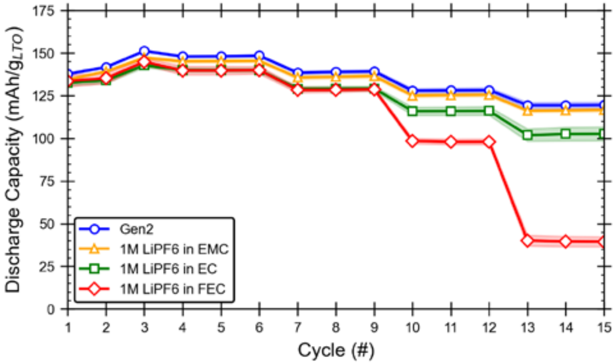
Vhold



2.6V Cycling



2.6V Form and Rate



Initial Takeaways:

- Parasitic current and 1C rate capability contributed to low FEC capacity
- EC shows best Vhold current, but has lower capacity, seemingly only performance related
- Gen2 and EMC show nearly identical performance in early cycling.

Helpful Information (So Far)

- Nonwoven, cellulosed-based separator impacts (enhances!) cycle life
- FEC stock aging seems to significantly impact performance.
- Appropriate formation protocol as well as an initial rate and Vhold tests may help to predict future cycling performance.

Future Work

- Expand beginning-of-life testing to predict performance
  - Oxidative Stability
  - More.
- Expand electrolyte evaluation to many more nonflammables
- Safety testing
  - Material scale
  - Large format cell scale

Thanks to the
BTMS Consortium Team

See: Strategic Cutoff Potential Selection Enables Safe and Long Cycle Life $Li_4Ti_5O_{12}$/$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ Batteries for Behind-the-Meter (BTMS) Storage Applications

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Thank you, questions?

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Current BTMS Team:
Andrew Meintz, Brian Perdue, Eric Dufek, Jack Deppe, Andrew Jansen, John Farrell, Kandler Smith, Kevin Gering, Matthew Keyser, Steve Trask, Drew Pereira, Kae Fink, Donald Karner, Sergiy Sazhin, Alastair Thurlbeck, Vaibhav Pawaskar, Alison R Dunlop, Matthew Shirk, Paul Gasper, Richard Carlson, John Kisacikoglu, Ed Watt, Ryan Tancin, Bertrand Tremolet de Villers, Noah Schorr, Katie Harrison, Anthony Burrell

Electrolyte Preparation

Pre-made electrolyte (Tomiyama):

- Gen2 (1.2M $LiPF_6$ in 3:7 EC/EMC by wt.)
- 1M $LiPF_6$ in ethylene carbonate (EC)

1. Used Karl Fischer measurement to confirm water content below 20ppm
   - Using appropriate KF reagents for battery solvents

Manually-made electrolyte:

- 1M $LiPF_6$ in ethyl methyl carbonate (EMC)
- 1M $LiPF_6$ in fluoroethylene carbonate (FEC)

1. Used Karl Fischer measurement to confirm water content below 20ppm
   - Tomiyama EMC and FEC, using appropriate KF reagents for battery solvents
2. Dry $LiPF_6$ salt (Sigma Aldrich) in Buchi oven (inside glovebox) at 80°C under vacuum, 24 hrs
3. Combine salt and solvent, stirring 24 hrs before use.

Early BTMS success with LTO/LMO

- LTO → operates at 1.55 V, inside electrolyte stability window
- LTO → zero-strain material, enabling excellent cycle life
- LTO → contains relatively abundant elements
- LMO → no Ni or Co, so inexpensive and easier supply chain
- LTO/LMO → excellent safet
- *LTO/LMO tradeoff is lower e*

See invited speaker: Katie Harrison for more in-depth background on early BTMS work

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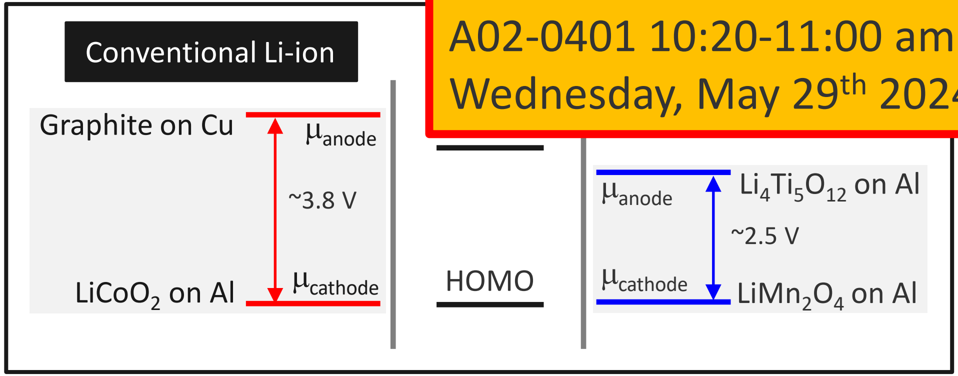
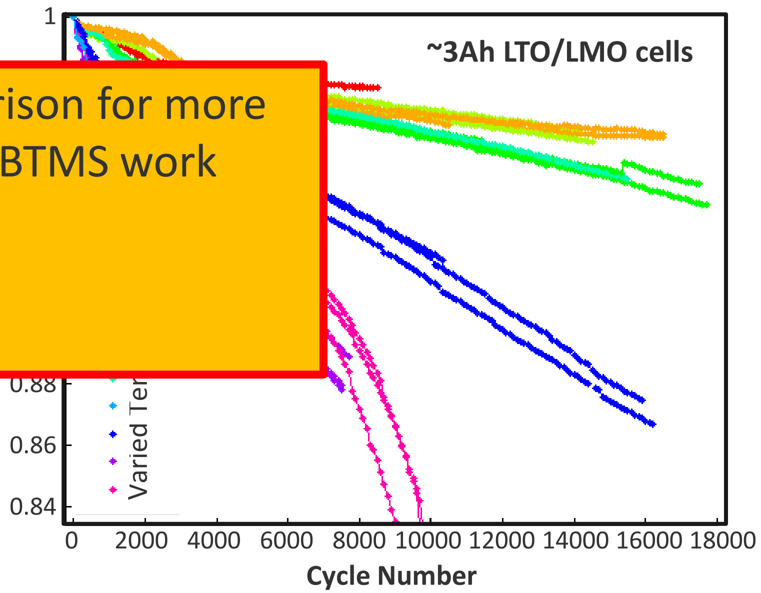


Commercial LTO/LMO cells exhibit excellent cycle life, even at elevated temperature

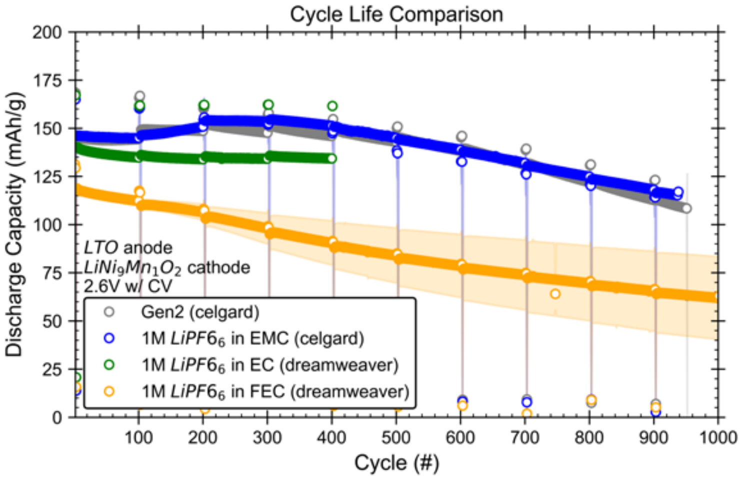


Burrell, A., 2021. *Department of Energy Annual Merit Review presentation*, bat442.
Data courtesy of Matthew Shirk and BTMS team.

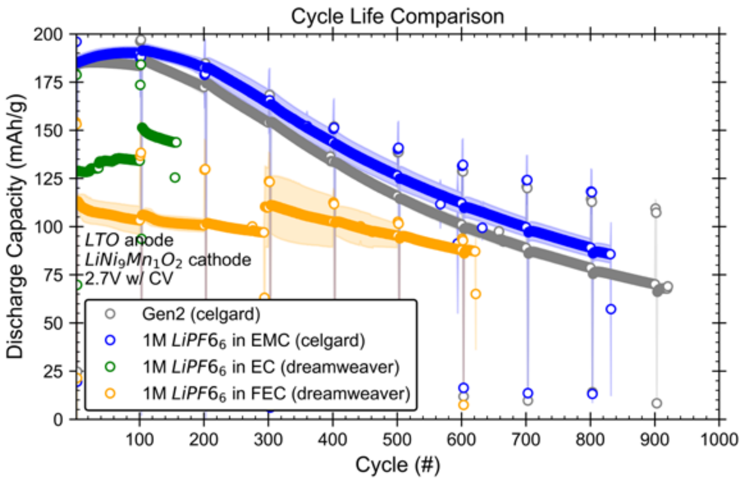
Backup

- FEC/EC wetting issues.
- FEC aging issues.

2.6V CCCV



2.7V CCCV



Voltage Hold Test

Coin Cell Assembly:

Steel Cap (Hohsen Corp.)

1mm steel spacer (welded, Hohsen Corp.)
15mm dia. LFP (CAMP)

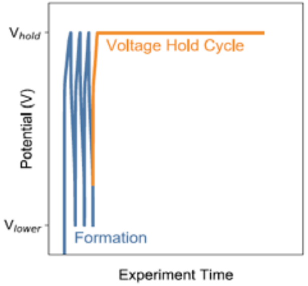
40uL electrolyte

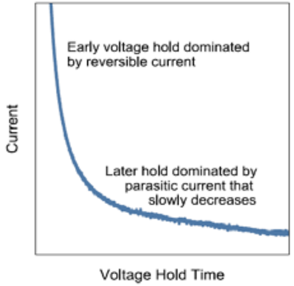
Separator (delfort DWG20 only)

40uL of the same electrolyte

14mm dia. LTO (92%, CAMP)
0.5mm steel spacer (welded)

Button and O-ring (Hohsen Corp.)





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Process:

1. Build LTO/LFP cell (N:P << 1)
2. Form SEI on LTO electrode
   a) 2 CC C/10 cycles
   b) 1 CCCV C/10 cycle (C/100)
   c) 3 CCCV C/10 cycles
3. Voltage Hold
   a) Fully charge LTO at C/10
   b) Maintain Voltage for 180 hours, monitor current
4. Post hold cycles
   a) 3 CCCV C/10 cycles

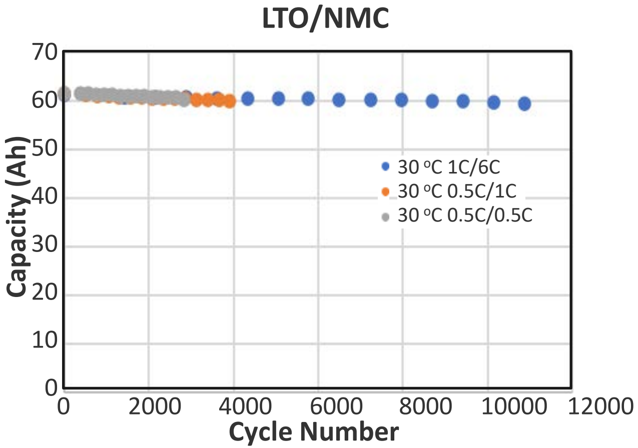
Consideration of LTO/Layered Oxides for BTMS

LTO/NMC cells showed strong capacity retention in commercial cells

LTO significantly enhances safety of cells

NMC prices reaching record low, despite increasing Co and Ni prices increasing

- Ni-rich NMC tends to have poor thermal stability (safety)
- Ni-rich NMC tends to have poor cyclability



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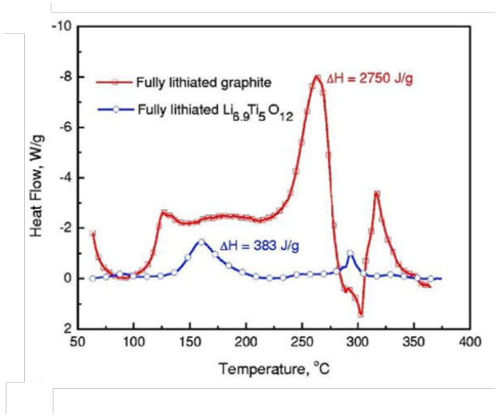
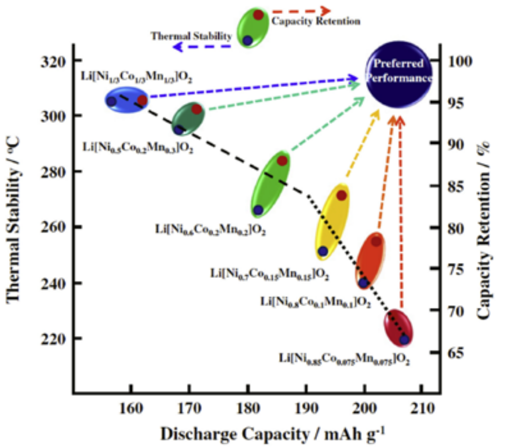


Xu, G., Han, P., Dong, S., Liu, H., Cui, G. and Chen, L., 2017. *Coordination Chemistry Reviews*, 343, pp.139-184.



Zhang, S.S., 2020. Problems and their origins of Ni-rich layered oxide cathode materials. Energy Storage Materials, 24, pp.247-254.