Investigation of Nonflammable Electrolytes for Behind-the-Meter Storage Batteries

Drew J. Pereira,* Kae Fink, Katharine L. Harrison

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Presentation Content

Brief Introduction to Self and NREL

Introduction to the Behind-the-Meter Storage Project

Brief Background on Nonflammable Electrolytes

DOE to Evaluate E-Chem and Safety Performance of NF Electrolytes

Initial Results

Questions and Discussion

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Experience

- B.S. in Chemical Engineering

- Ph.D. in Chemical Engineering

  Battery modeling under Prof. Weidner
  - Cell Modeling Engineer

    Modeling battery volume change
  - SCGSR Fellow

    Modeling and Advanced Characterization

- R&D Manager/Senior Engineer

  Emphasis on battery longevity and safety
- Postdoctoral Researcher

  Electrochemistry and Battery Materials

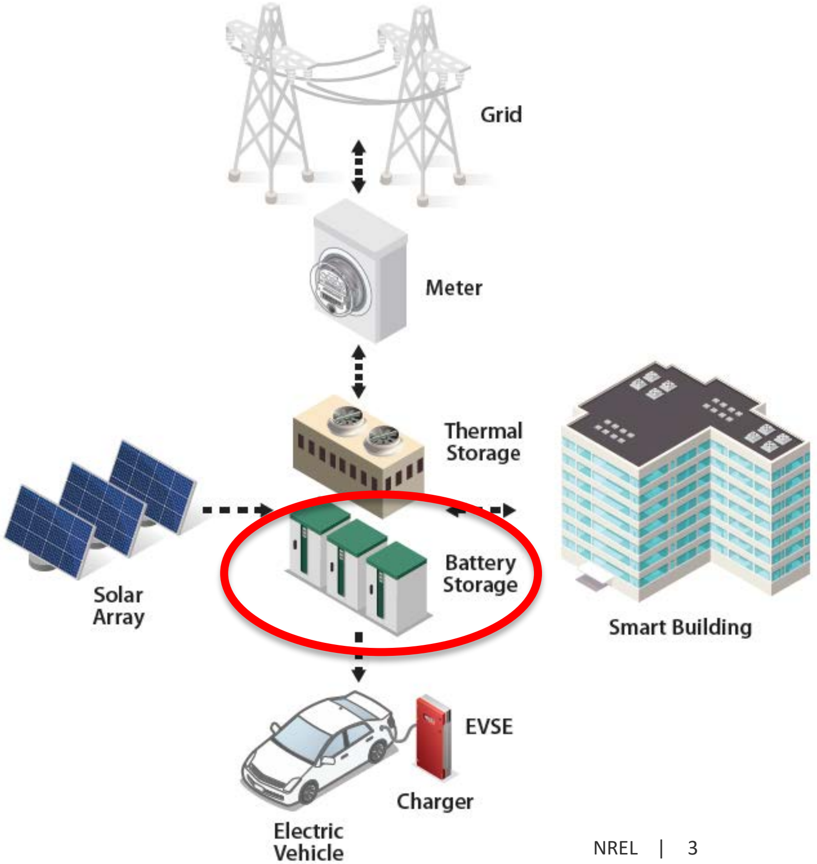
National Renewable Energy Laboratory

Presentation Content

Behind-the-Meter Storage Mission

Utilize Battery ESS to facilitate:

- EV charging integration
- Solar power generation integration
- Energy-efficient buildings integration
- Minimize system and operating cost
- Minimize grid impacts



Funded by BTMS Consortium

A partnership with the DOE VTO, BTO, OE, and SETO.

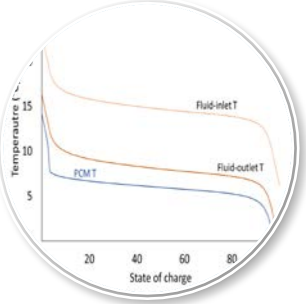
NREL Transforming ENERGY | Idaho National Laboratory | Sandia National Laboratories | Argonne National Laboratory | Pacific Northwest National Laboratory

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

BTMS Efforts

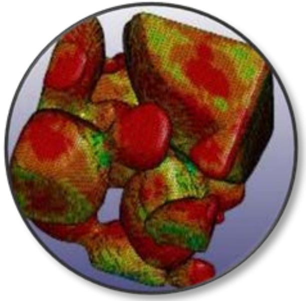
Metrics and target determination

Informing low-TRL R&D



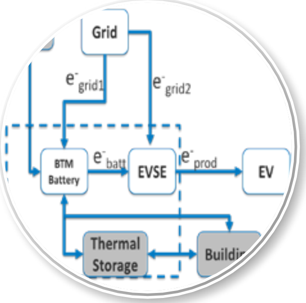
Multi-scale characterization

Materials to systems



Materials Discovery

Metric-informed R&D

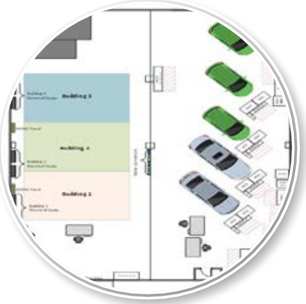


Integrated-system modeling and design

Strategies for battery + thermal storage systems

Full System Design

Technology transfer where prototypes are produced for qualification



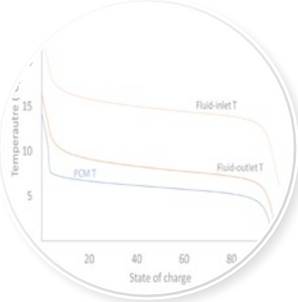
Integration experiments

Demonstrating controls and interoperability of technologies

BTMS Efforts

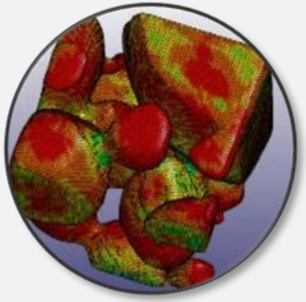
Metrics and target determination

Informing low-TRL R&D



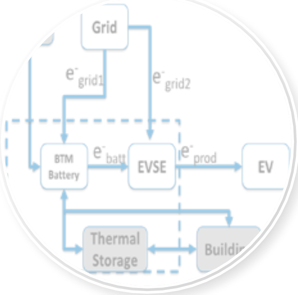
Multi-scale characterization

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

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Demonstrating controls and interoperability of technologies

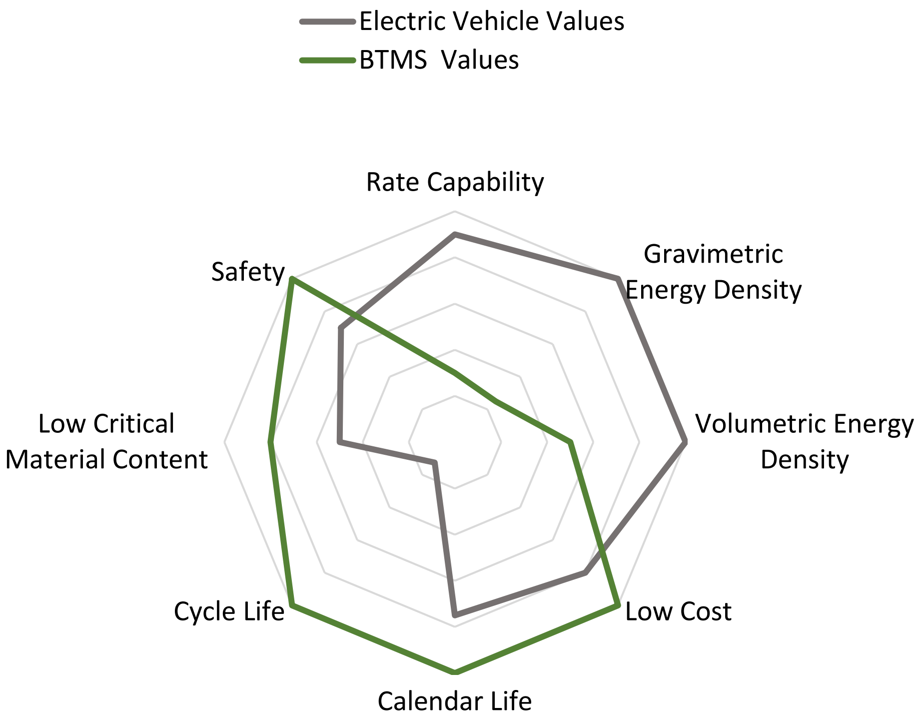
Why BTMS-specific materials discovery?

BTMS battery needs

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

BTMS batteries not as reliant on

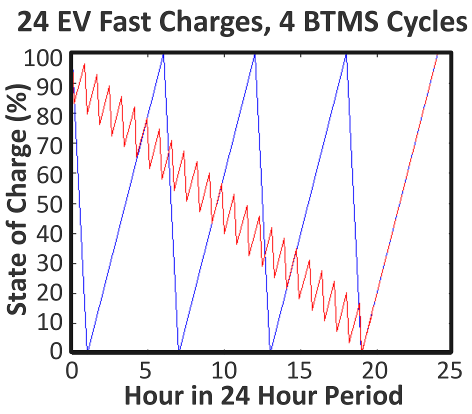
- Gravimetric energy density
- Volumetric energy density
- Rate capability



BTMS battery targets and material consideration

1-10 MWh battery:

- $100/kWh
- 8000 cycles
- 20 y calendar life
- 4 BTMS cycles/day
- 24 EV fast charges/day
- 10 min EV charge
- 1C rate for BTMS max



Initially considered

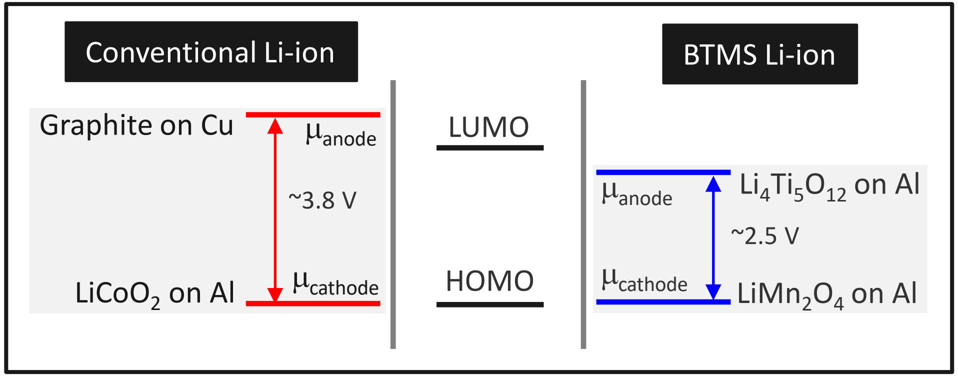
- Graphite/NMC
- LTO/NMC
- LTO/LMO
- LTO/LNMO
- Ni-Zn
- Pb Acid
- Graphite/LFP
- Zn-air

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

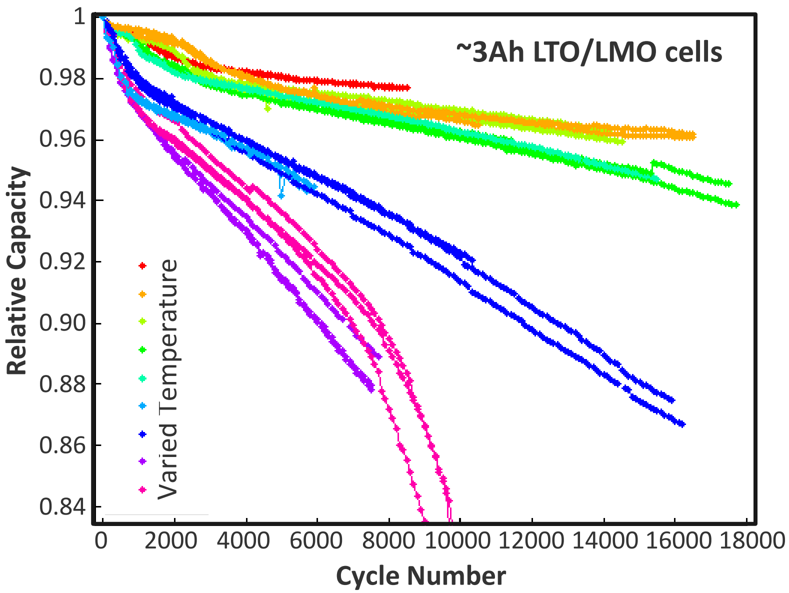
Grid buffering with batteries can be cost effective at $100/kWh but achieving long cycle/calendar life goals with minimal critical materials is a significant research challenge.

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 safety attributes
- *LTO/LMO tradeoff is lower energy density/specific energy*



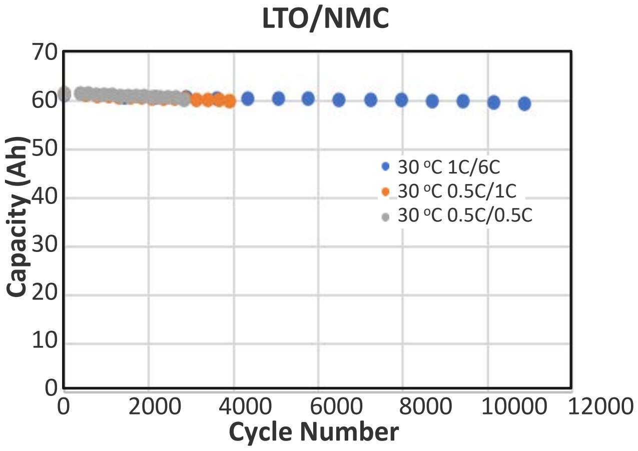
Commercial LTO/LMO cells exhibit excellent cycle life, even at elevated temperature



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

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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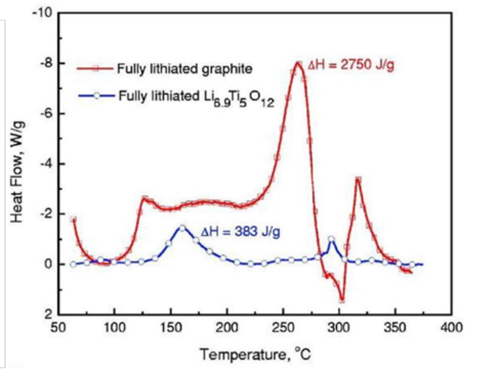
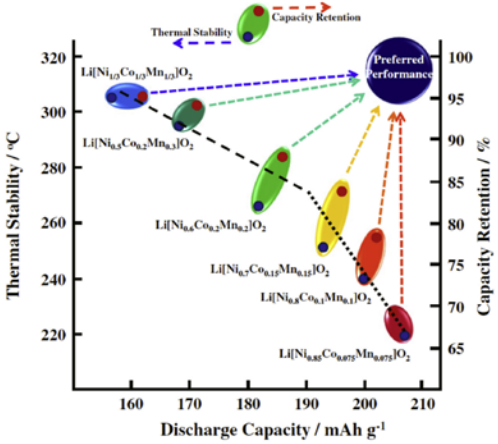


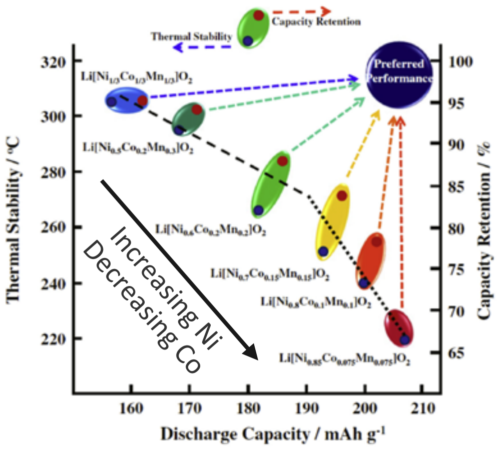
Xu, G., Han, P., Dong, S., Liu, H., Cui, G. and Chen, L., 2017. *Coordination Chemistry Reviews*, 343, pp.139-184.



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

System for this Study: $Li_4Ti_5O_{12}/LiNi_{0.9}Mn_{0.1}O_2$ (LTO/NM90-10)

- LTO/NMC90-10-0 cathodes showed significant capacity fade in previous BTMS study
  - Higher Ni content associated with decreased thermal stability and capacity retention
    - H2→H3 phase transition causes c axis expansion and particle cracking
    - H3 less stable → exothermic O_2 evolution, $LiNi_2O_4$ + NiO transition, poor thermal stability
    - Ni^{4+} reacts with electrolyte → transition metal dissolution and structural damage



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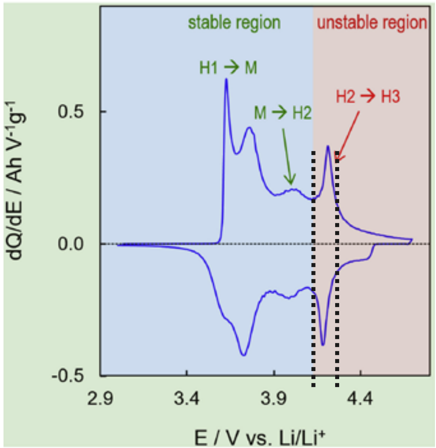
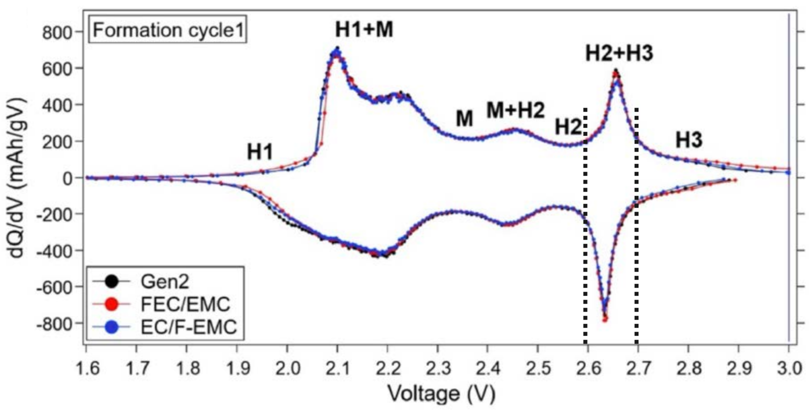
H3 ~ 4.15-4.25 V in half cell



H3 ~ 2.6 – 2.7 V in LTO/NMC90-10-0 cell



Zhang, Y., Teeter, G., Dutta, N.S., Frisco, S. and Han, S.D., 2023. Chemical Engineering Journal, 460, p.141239.

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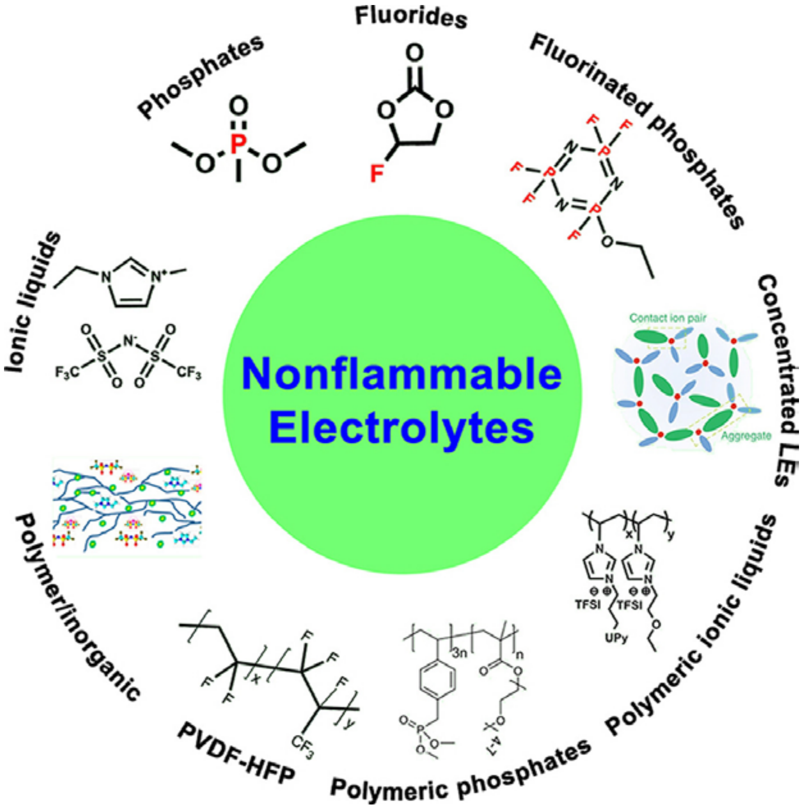
Nonflammable Electrolytes

NFPA definition:
Flash point below 100°C
200°C for category 3b

OSHA definition:
Flash point below 199.4°C



Deng, Kuirong, Qingguang Zeng, Da Wang, Zheng Liu, Guangxia Wang, Zhenping Qiu, Yangfan Zhang, Min Xiao, and Yuezhong Meng. "Nonflammable organic electrolytes for high-safety lithium-ion batteries." *Energy Storage Materials* 32 (2020): 425-447.

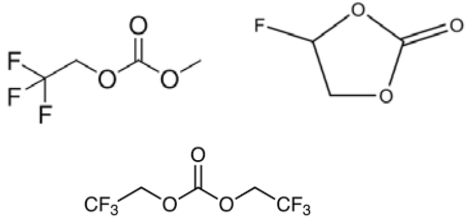
Nonflammable Electrolytes: Down-selected

Category	Sub-category	Examples	Justification
"Non-flammable, standard" Solvents	Cyclic Carbonates	EC, PC	High flash point, low cost, contributes to high cycling stability
Flame-Retardant Solvents	Hydrofluorocarbons	FEC, F-EMC, etc.	Radical capturing, similar stability
	Organophosphorous	TEP, TMP, etc.	Radical capturing, low cost
Flame-Retardant Additives	cyclophosphazenes	PFPN, FPPN	Radical capturing, decreased viscosity
High/Locally High Concentration Electrolytes	-	LIFSI/LiTFSI in DME/TTE	High salt concentration reduces volatility and flammability of solvents

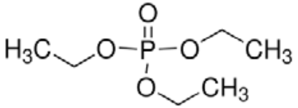
High-level NF electrolyte mechanism.

1. Short/defect/degradation occurs generating heat
2. High temperatures force O_2 into a reactive spin-paired state, $^1O_2$
3. By hydrogen abstraction, hyperperoxide and hydroxyl radicals are formed
4. During chain branching, oxidizing species are formed and react with hydrocarbons to form fuel radicals
5. Fuel radicals, H·, O·, and HO·, are consumed in combustion cycle at ignition, or preferably inhibited by radical scavengers.

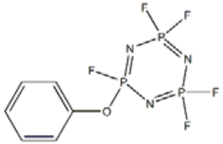
hydrofluorocarbons



organophosphorus



cyclophosphazene



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Design of Experiment

Electrochemical Evaluation	Safety Evaluation

Electrochemical Evaluation

1. Oxidative Stability Testing
2. Voltage Hold Testing
3. Formation and Rate Testing
4. Cycle Life Testing

Safety Evaluation

1. Flash Point Measurement
2. Self-Extinguishing Test (SET)
3. Differential Scanning Calorimetry (DSC)
4. Electrolyte Ignition and Heat Release Measurement
5. Accelerating Rate Calorimetry (ARC) Test on Full Cell

Proper* Electrolyte Preparation

Drying Salt

1. Dry salt at stable temperature (80°C for $LiPF_6$) under vacuum for 24 hours.

Drying Solvent

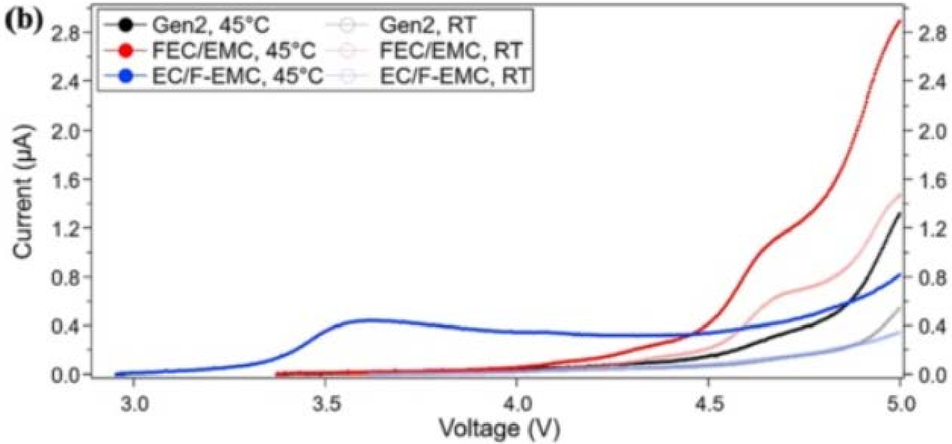
1. Dry activated alumina (AA) under vacuum for 100°C for 24 hours.
2. Continue drying at 200°C for 24 hours.
3. Expose solvent to dried AA in a 4:1 ratio by volume for 48 hours.
4. Filter AA from solvent.
5. Confirm water content with KF

Mixing Electrolyte

1. Dry and hot-load all tools/consumables into glovebox.
2. Obtain dried solvent add to hot-loaded PTFE container.
3. Add any co-solvent as necessary to achieve desired co-solvent ratio.
4. Weigh and add dried Li salt to achieve desired molarity.
5. Add any additives as to desired content.
6. Add hot-loaded stir bar to container and stir overnight under no heat.
7. Confirm water content with KF

Oxidative Stability Testing

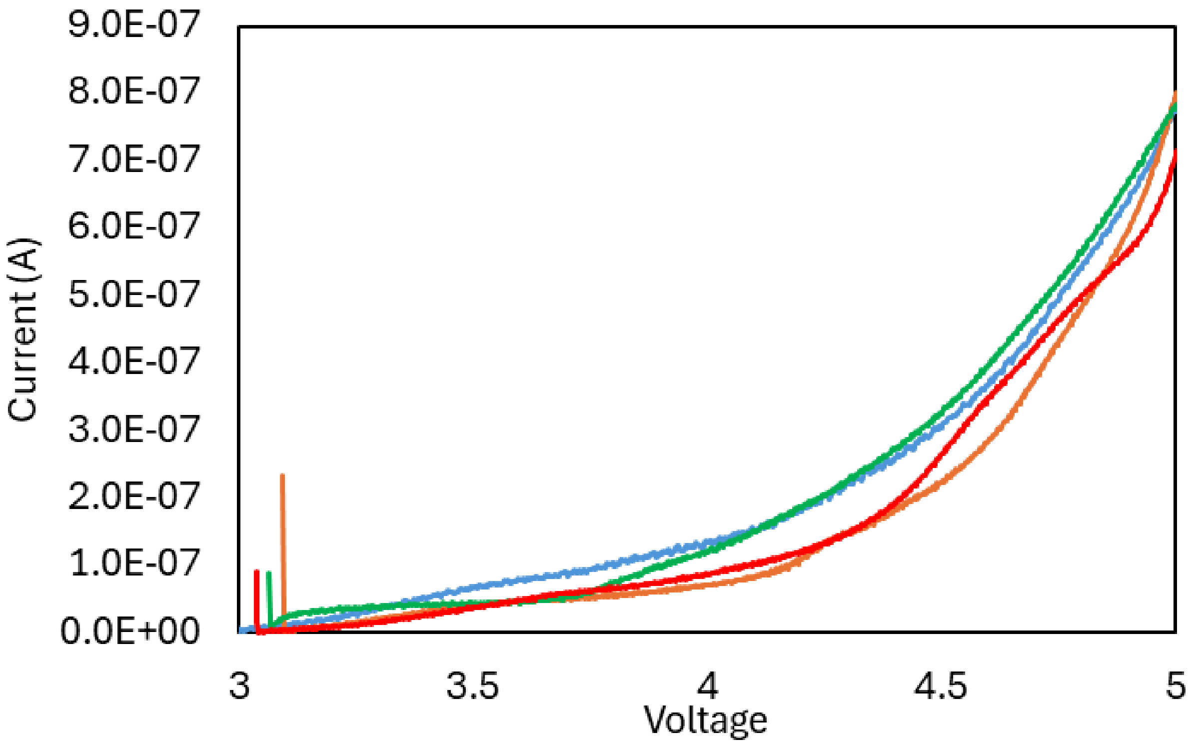
3-electrode cell



1. Prepare working electrode (Pt, Al, or cathode) and insert into electrochemical cell
2. Prepare Li-metal counter and reference electrodes and insert into cell
3. Add 5mL of prepared electrolyte into cell (only Li metal and working electrode should be exposed to electrolyte)
4. Perform Linear Sweep Voltammetry from OCP to 5V (25mV/s)

Zhang, Y., Teeter, G., Dutta, N. S., Frisco, S., & Han, S. D. (2023). Mechanistic understanding of aging behaviors of critical-material-free Li4Ti5O12//LiNi0. 9Mn0. 1O2 cells with fluorinated carbonate-based electrolytes for safe energy storage with ultra-long life span. *Chemical Engineering Journal*, *460*, 141239.

Oxidative Stability initial result



Voltage Hold Test

Coin Cell Assembly:

Steel Cap (Hohsen Corp.)

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

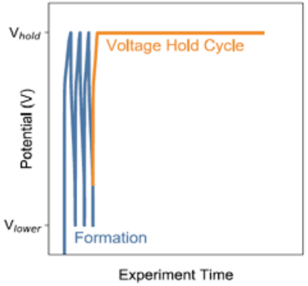
40uL electrolyte

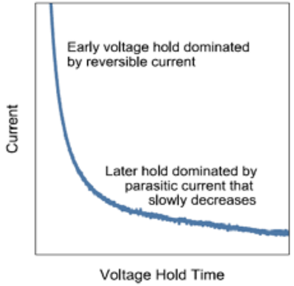
Separator

40uL of the same electrolyte

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

Button and O-ring (Hohsen Corp.)



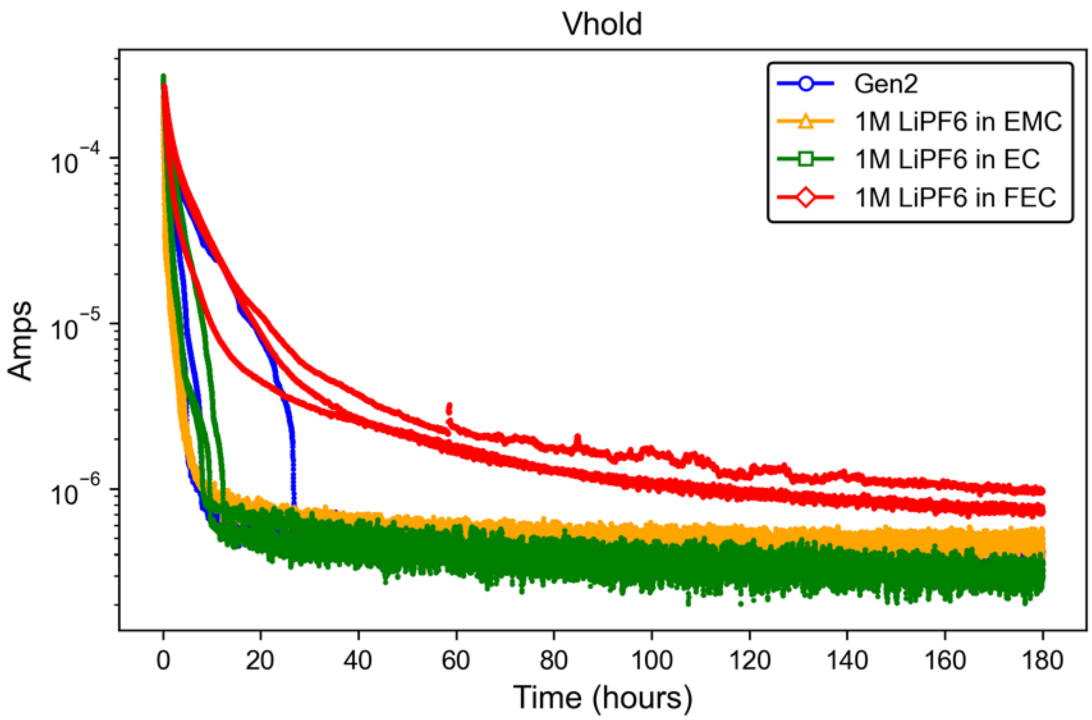


Schulze, M.C., Rodrigues, M.T.F., McBrayer, J.D., Abraham, D.P., Apblett, C.A., Bloom, I., Chen, Z., Colclasure, A.M., Dunlop, A.R., Fang, C. and Harrison, K.L., Liu, G., Minteer, S.D., Neale, N.R., Robertson, D., Tornheim, A.P., Trask, S.E, Veith, G.M., Verma, A., Yang, Z., and Johnson, C., 2022. Critical evaluation of potentiostatic holds as accelerated predictors of capacity fade during calendar aging. *Journal of the Electrochemical Society*, *169*(5), p.050531.

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

BTMS Protocol: Voltage Hold



Form/Rate and 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

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.)

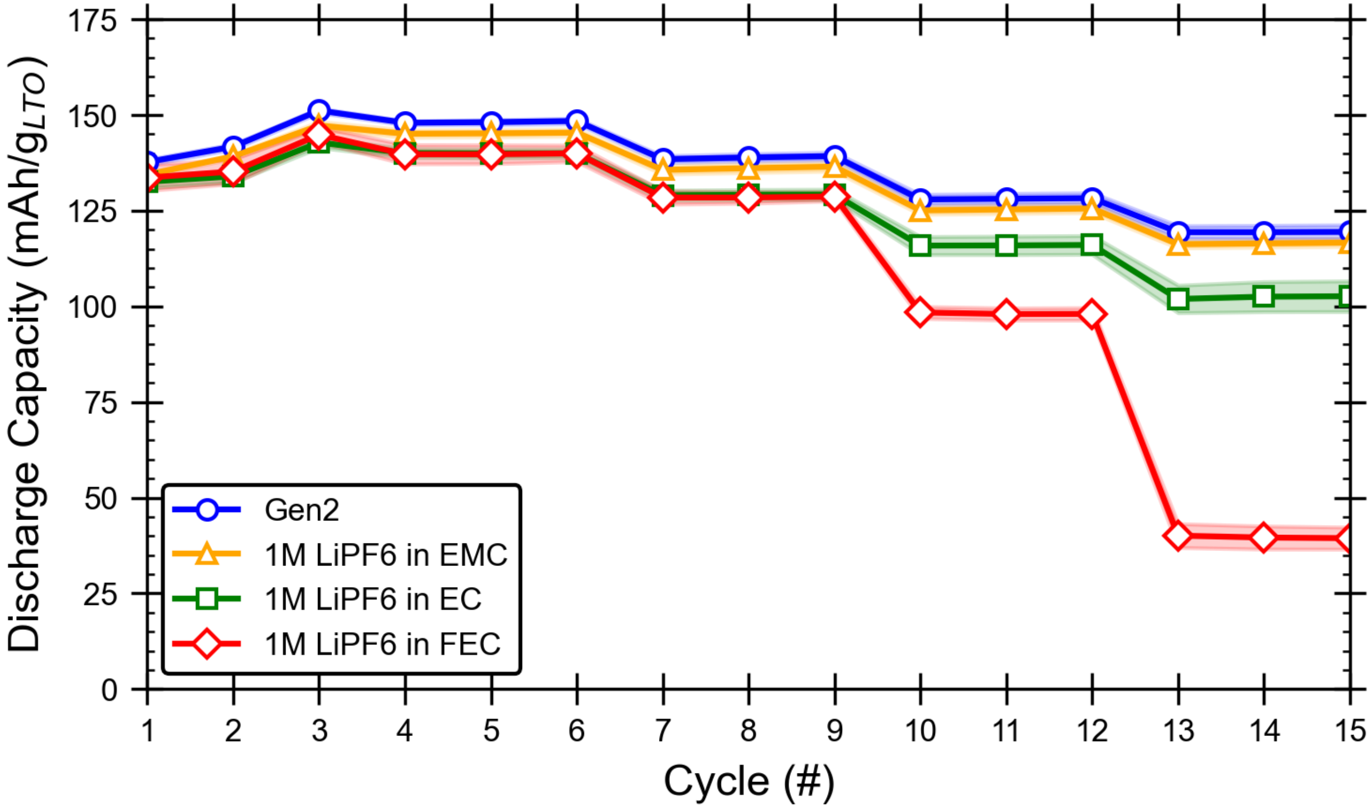
BTMS Form/Rate Protocol (1.4-2.6V):

1. Initial Formation and Rate test (CCCV charge, CC discharge)
   a) Cycles: 3 @ C/10, 3 @ C/3, 3 @ 1C, 3 @ 2C

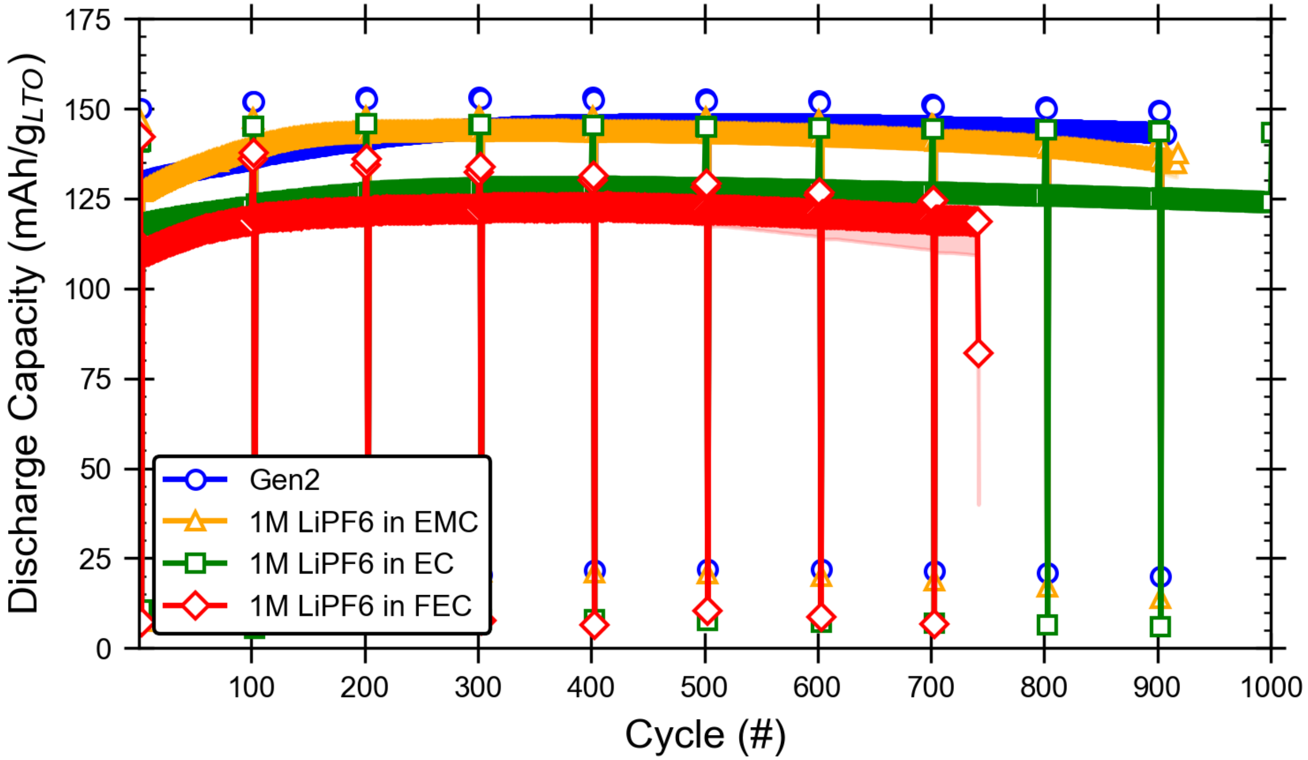
BTMS Cycle Life Protocol (1.4-2.6V):

1. Repeating cycling sequence (until reaching 1000 cycles)
   a) 2 cycles @ C/10
   b) 1 HPPC cycle
   c) 97 cycles @ 1C
2. End-of-Life Rate test

Formation and Rate Test

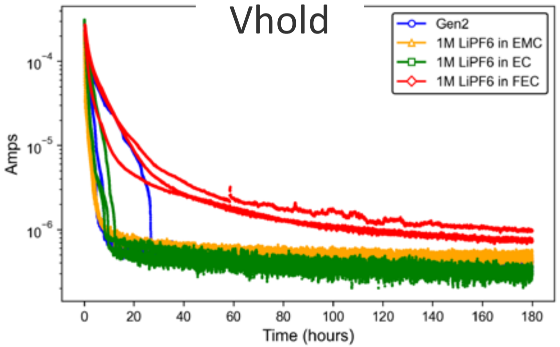


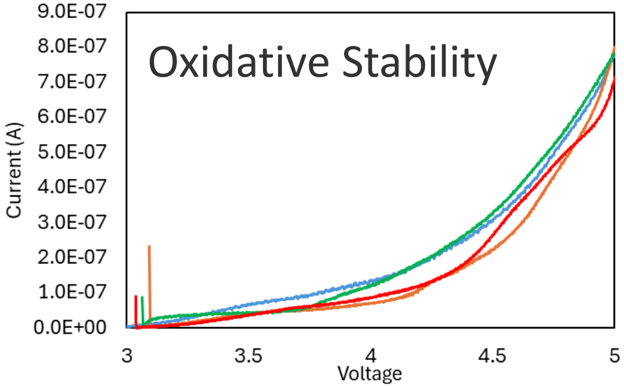
Cycle Life

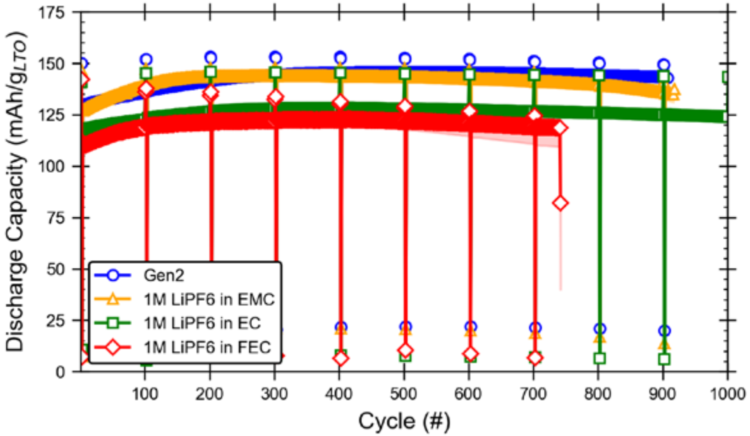


Discharge Capacity (mAh/g$_{LTO}$)
Cycle (#)
175
150
125
100
75
50
25
0
100
200
300
400
500
600
700
800
900
1000
Gen2
1M LiPF6 in EMC
1M LiPF6 in EC
1M LiPF6 in FEC

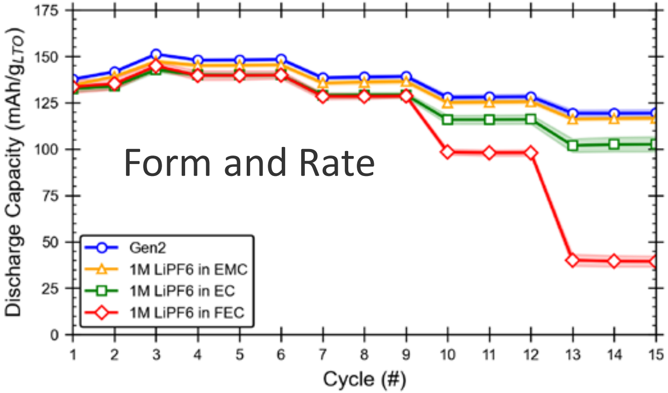
Data Comparison



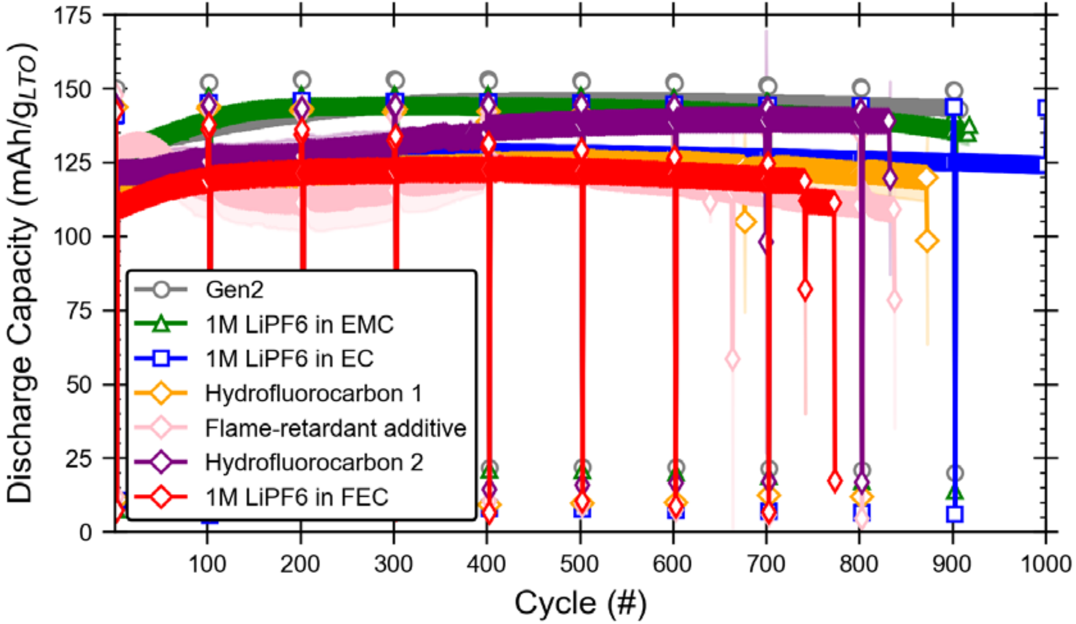




Cycling



Progressing Cycle Life



General Takeaways:

EC enhances stability

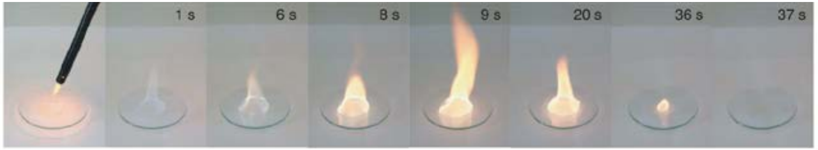
Organophosphorous compounds not stable at high voltages.

Flame-retardant additive impacting performance.

Hydrofluorocarbons showing promise.

Materials-Level Safety Measurements

Flash Point

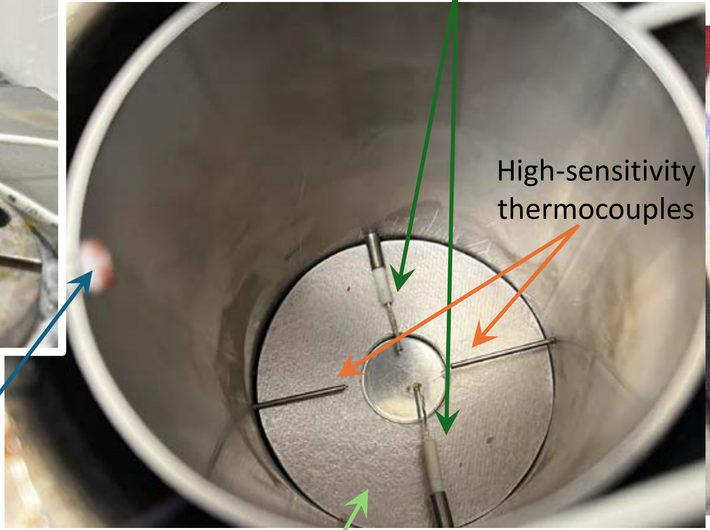


Self-Extinguishing Time (SET)

	Flash Point	Self-Extinguishing Time (SET)
How Test Works	Gradually raise temperature of sample during exposure to ignition source until it ignites; closed-cup methods use sealed vessel	Directly ignite electrolyte and measure (1) time to ignite and (2) time to self-extinguish (i.e., time for flame to burn out)
Purpose	Closed-cup methods are reliable & reproducible; can compare to ASTM/literature standards	Most directly simulation of real-world safety conditions
Status	Instrument procurement at NREL.	**In-house design/build – see next slides**
Challenges	Wetted parts are not ideal for electrolytes; requires new system with inerted components	No literature or ASTM standard for liquids, so all literature reports use a different approach to prep/methods

SET Test: Refinement for Consistency

Kae Fink and Josh Major (NREL) responsible for design and build support!



Spark gap igniter

High-sensitivity thermocouples

Photocell detector

High-T mica stage
(machined to hold coin cell cap)

Materials-Level Safety Measurements

Differential Scanning Calorimetry (DSC)

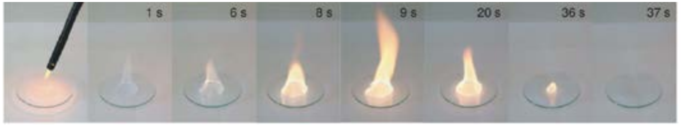
How Test Works	Gradually raise temperature of sample and measure varied heat output from material breakdown.
Purpose	Used to evaluate how material heat output may contribute to full-cell heat output.
Status	Instrument online at NREL.
Challenges	Large matrix to evaluate due to interaction between electrode and electrolyte. Focusing now on electrolyte only.

Comprehensive Safety Matrix for Electrolytes

Goal to link material scale results to each other and safety performance at the cell level

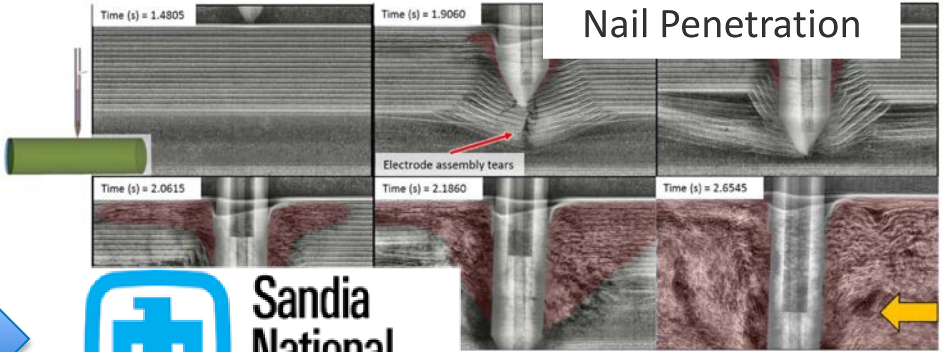
Flash Point

SET



DSC

Nail Penetration



Sandia National Laboratories

ARC

Thanks to the
BTMS Consortium Team

Thank you, questions?

www.nrel.gov

NREL/PR-5K00-90689

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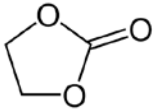
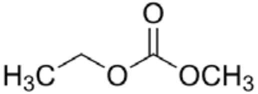
Acronyms

$LiPF_6$:
lithium hexafluorophosphate

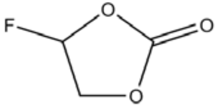
EC:
ethylene carbonate



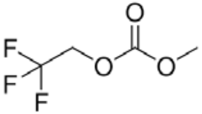
EMC:
ethyl methyl carbonate



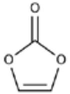
FEC:
fluoroethylene carbonate



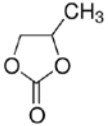
F-EMC:
methyl (2,2,2-trifluoroethyl) carbonate



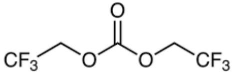
VC:
vinylene carbonate



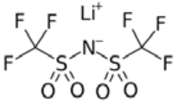
PC:
propylene carbonate



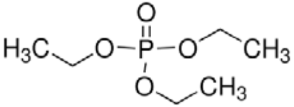
DF-DEC (F-DEC):
di-(2,2,2-trifluoroethyl) carbonate



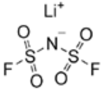
LiTFSI:
lithium bis(trifluoromethane)sulfonimide



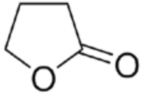
TEP:
triethyl phosphate



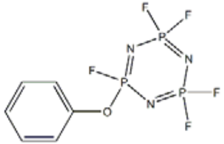
LiFSI:
lithium bis(fluorosulfonyl)imide



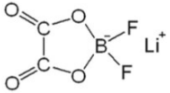
GBL:
gamma-butyrolactone



FPPN:
(phenoxy)pentafluorocyclotriphosphazene



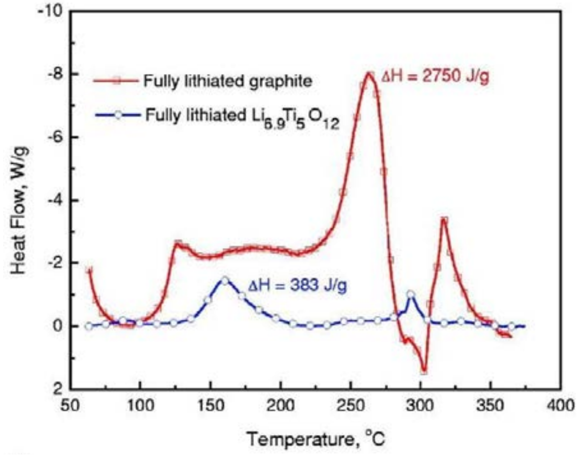
LiODFB:
lithium difluoro(oxalato)borate



Safety is very important for large BTMS batteries located near buildings

- Require no rack-to-rack propagation
- Desire no cell-to-cell propagation
- Reduce onset temperature, self-heating rate, and thermal runaway enthalpy

Differential Scanning Calorimetry (DSC)



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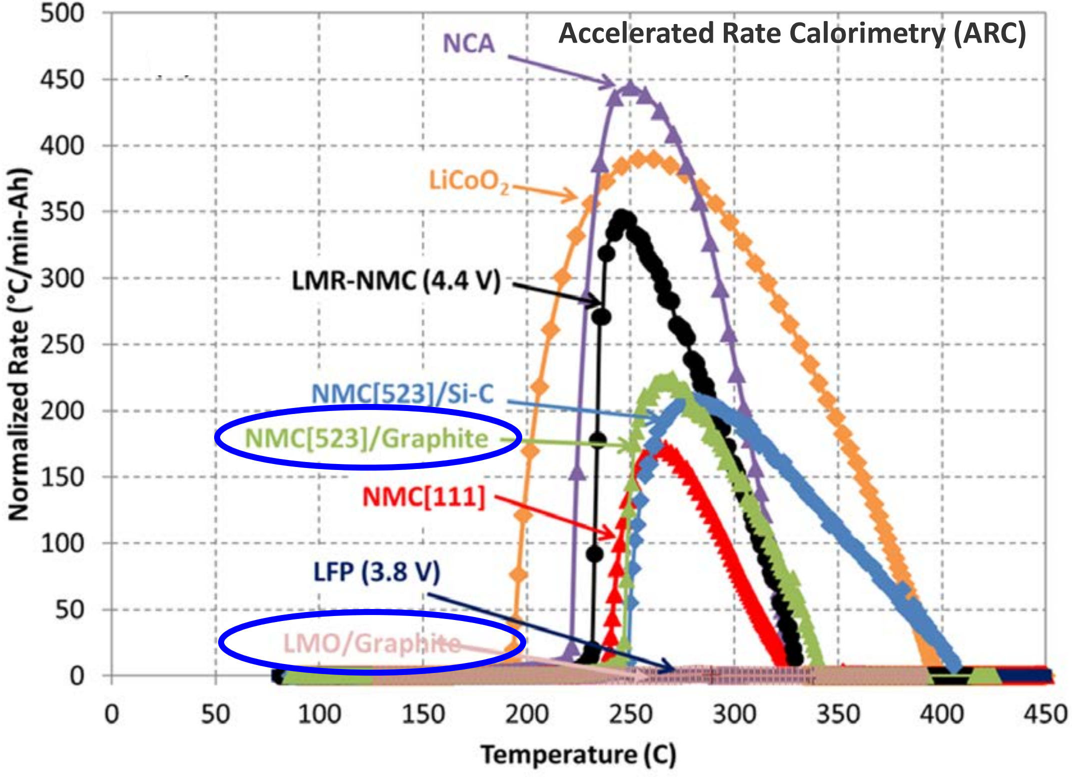

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