Lithiation Method for High-Energy, Long-Life Lithium-Ion Battery (L3B)

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National Renewable Energy Laboratory
6/12/2019

DOE Vehicle Technologies Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID # bat391

Overview

Timeline

- Project start date: 10/01/2016
- Project end date: 9/31/2019
- 80% Percent complete

Budget

- Total project funding: $1.2M
  - DOE share: 100%
- FY 2017: $600K
- FY 2018: $600K
- FY 2019: Carry-over Funding

Barriers

- High energy density lithium-ion batteries using Si anodes have limited cycle life
- Loss of lithium ions limits cycle lifetime of cells with Si and graphite anodes
- Prelithiation techniques are cost-prohibitive and extra lithium can only be initially inserted

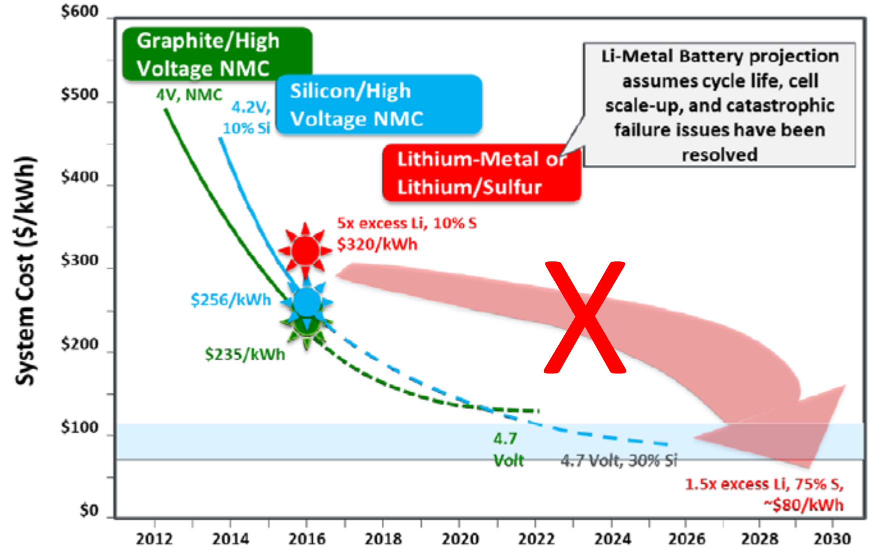
Partners

- Lead: NREL
- Partners/Collaboraters
  - ANL-CAMP
  - Coulometrics
  - Nanograf/Si-Node

Life, Energy Gaps in Near-Term Battery Technology

Graphite/NMC 150-250Wh/kg

- 10+ year automotive life requires extra cost (oversizing, thermal management)
- Grid applications demand 20+ years, 10000+ cycles



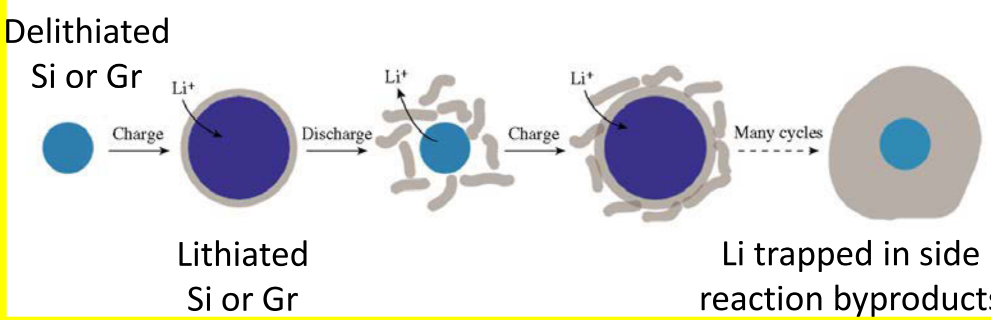
Steven Boyd, 2018 DOE Annual Merit Review

Silicon/NMC >300 Wh/kg

- Prelithiation needed to achieve high energy. Adds manufacturing time and cost
- Severe calendar and cycle life limitations
- SOA life: 500 cycles vs. 1000 cycles EV requirement

Overarching problem:

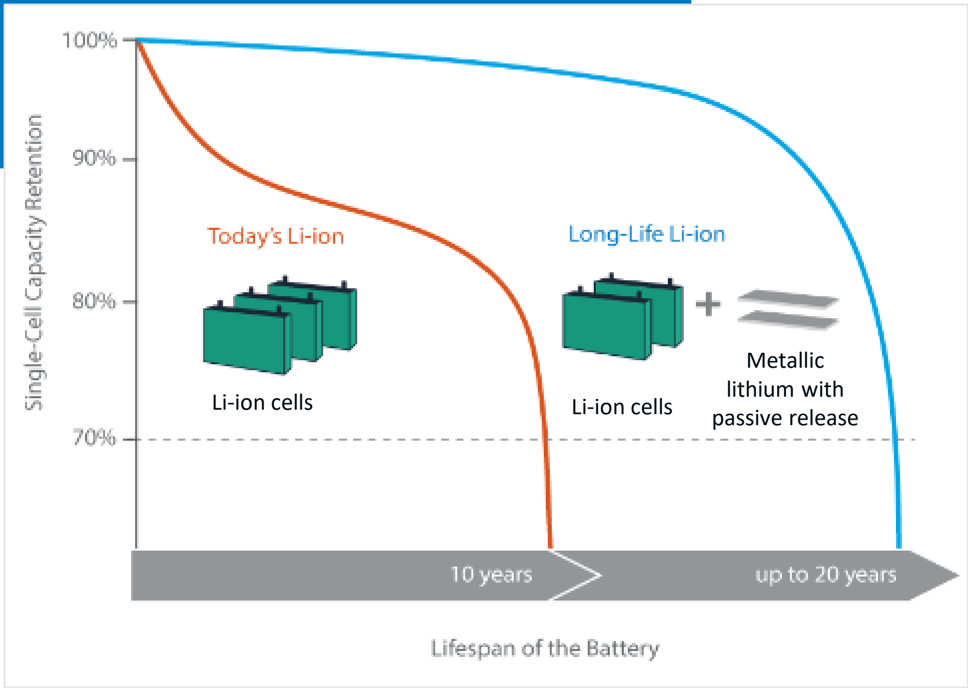
Loss of lithium inventory



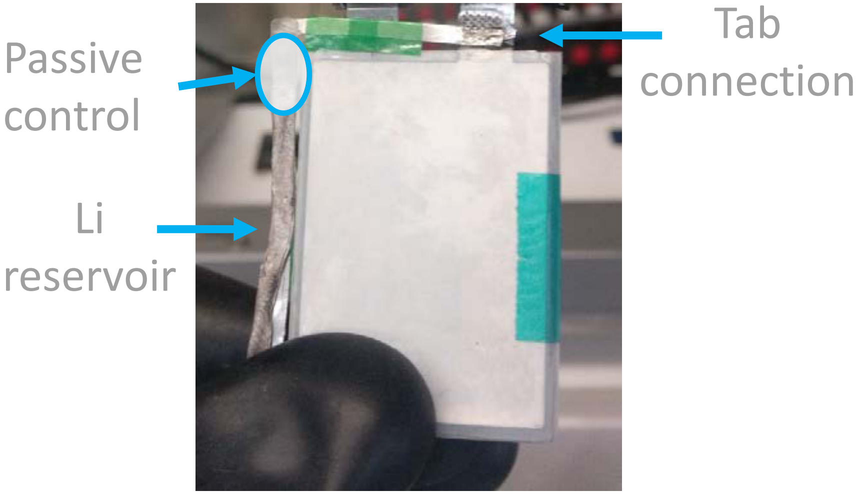
Ma, Nano-Micro etters (2014)

Approach

- **Cell-internal** lithium reservoir with passive control of release
  - Enables both continuous and on-demand Li release
  - <5% impact to cell volume, mass and cost
  - No third terminal required
- Li-ion **lifetime can be doubled** in many real-world scenarios
- **Pre+relithiation** enables EV-ready **lifetime** for **high energy silicon anodes**
- Patent pending (filed Aug. 2016)

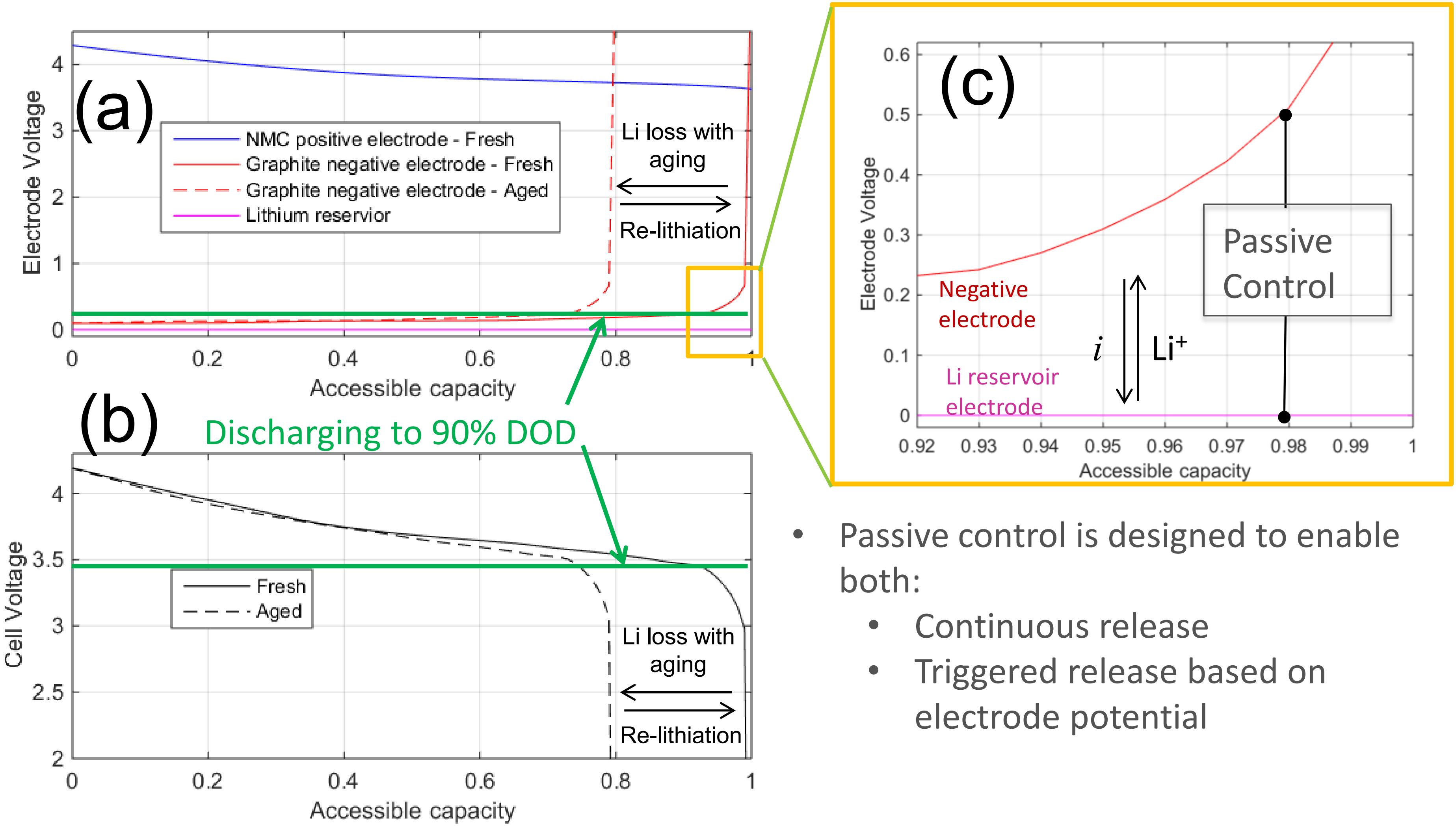


Example implementation
400mAh Gr-Si/NMC pouch cell jellyroll



Approach: Passive Control

- Passive control is possible because electrode potentials are positive relative to lithium



- Passive control is designed to enable both:
  - Continuous release
  - Triggered release based on electrode potential

Target Markets

48V&HEV: 15+ year, low cost
Reduced cooling. Underhood packaging.

EV: 1000-cycle 400 mi.
Si anode. Prelithiation. Continuous relithiation.

Grid: 20+ year life
Increased useable energy.

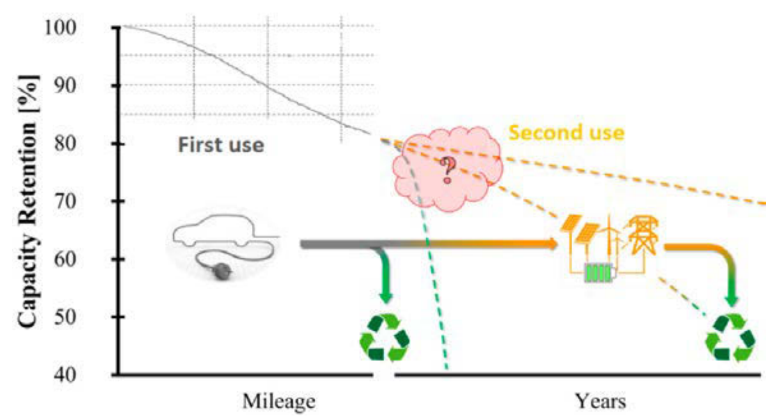
www.auto evolution.com

www.jeepoffroadadventures.com

www.autoguide.com

www.energystoragenetworks.com

2nd Use Repurposing



www.mdpi.com

Applicable to all of today's large-scale Li-ion products

$69B by 2022

16% annual growth

www.marketwatch.com

FY2018 Milestones

Milestone	Date	Status
M5: Integration of device with ANL/ABR Si-based pouch cells	12/31/2017	Complete
M6: Data for NMC/Si-based system showing 5% or more capacity improvement after aging for >50 cycles	3/31/2018	Complete
M7:Demonstrate tunable passive release rate via circuit	6/30/2018	Complete
M8: Method to quantify non-uniformity of Li with release rate and cell design using models and experiments. Measure power capability/internal resistance before and after re-lithiation	9/30/2018	Complete

FY2019 Milestones

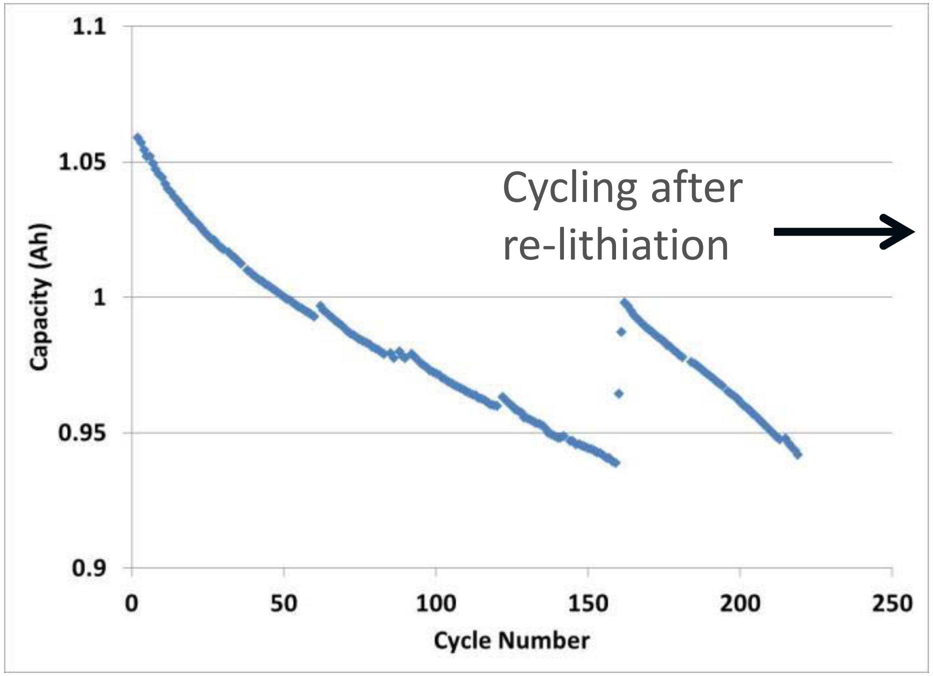
Milestone	Date	Status
M9: Experimental demonstration of passive circuit implemented entirely inside cell. Analysis confirming commercial EV-cell applications where device occupies less than 5% of cell volume while adding >50% life improvement (to 80% remaining capacity) and/or >10% increased energy density	12/31/2018	Complete
M10: Initiation of work with industry partner(s) to demonstrate concept in commercial cell	3/31/2019	Complete
M11:Successful mitigation of over-lithiation safety risk through design and controls, supported by data and analysis	6/30/2019	On-track
M12: Data demonstrating 50% life improvement to 80% remaining capacity through cycling at elevated temperature (graphite & Si systems) and 10% capacity* improvement at cycle 10 (Si system)	9/30/2019	On-track

Technical Accomplishments and Progress

Life extension with external control: A123 Gr/FeP 18650 cell

- Custom 3-electrode fixture built for proving concept
- Cell was cycled 150 times and then paused
- Relithiation done with second cycler channel

C/3 cycling at 55 °C (increase Loss of Lithium Inventory)

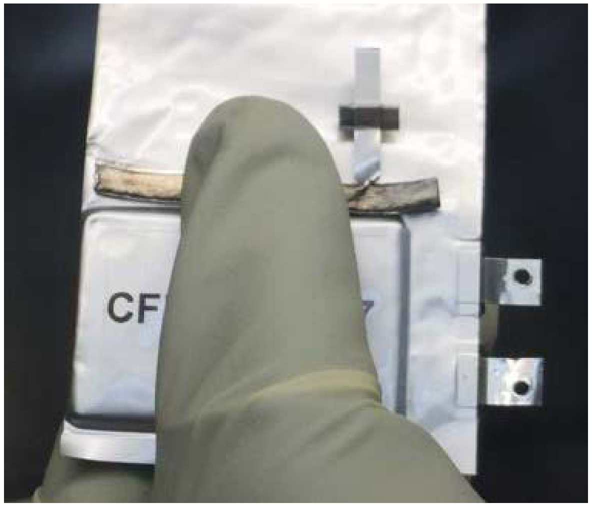


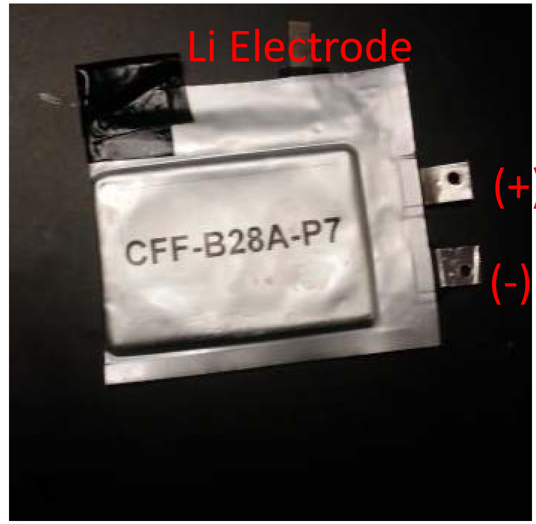
Lithium discharged capacity was 80 mAh at 200 uA (17 days) and 60 mAh capacity recovered

Custom Teflon fixtures for 18650 jelly rolls with lithium reservoir at the bottom

Life extension with external control: 400 mAh Gr-Si/NMC Pouch Cells

Inserting lithium reservoir into ANL-CAMP Pouch Cell

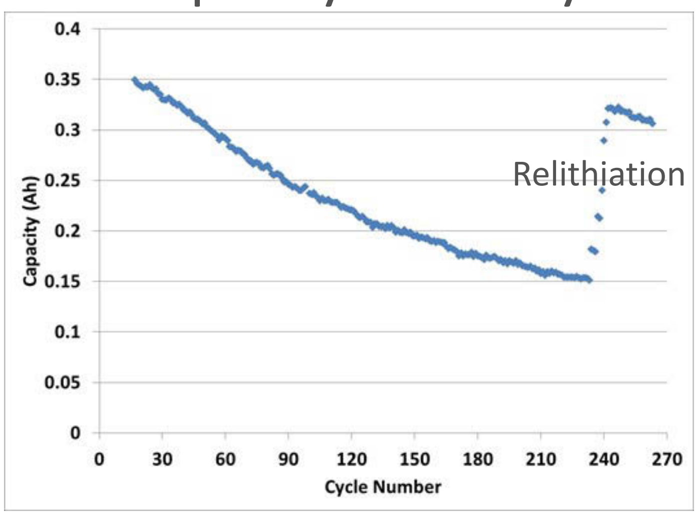


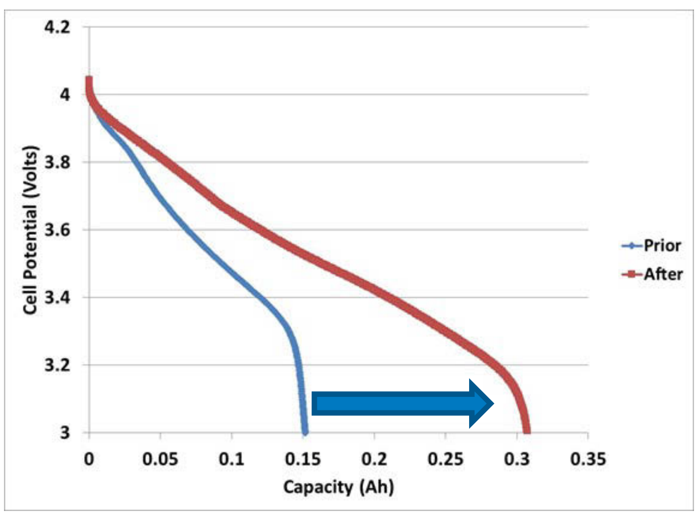


M5: Integration of device with ANL/ABR Si-based pouch cells

- Anode: Gr-Si (73-15 wt. %)
- Cathode: NMC532
- Cell type: 400mAh pouch
- Jellyroll fabrication: Argonne CAMP
- Voltage: 3-4.1V
- Room temperature cycling

50% capacity recovery has been demonstrated for multiple cells



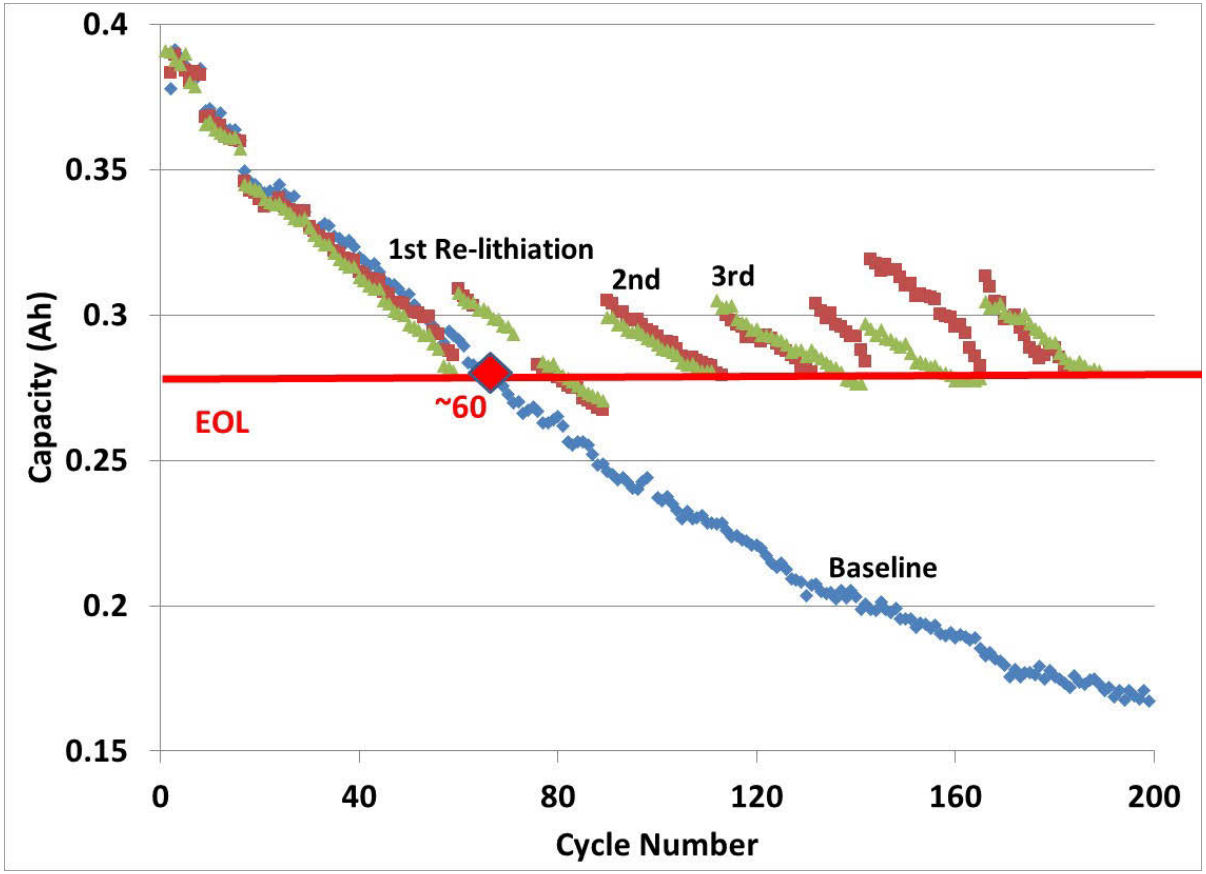


M6: Data for NMC/Si-based system showing 5% or more capacity improvement after aging for >50 cycles

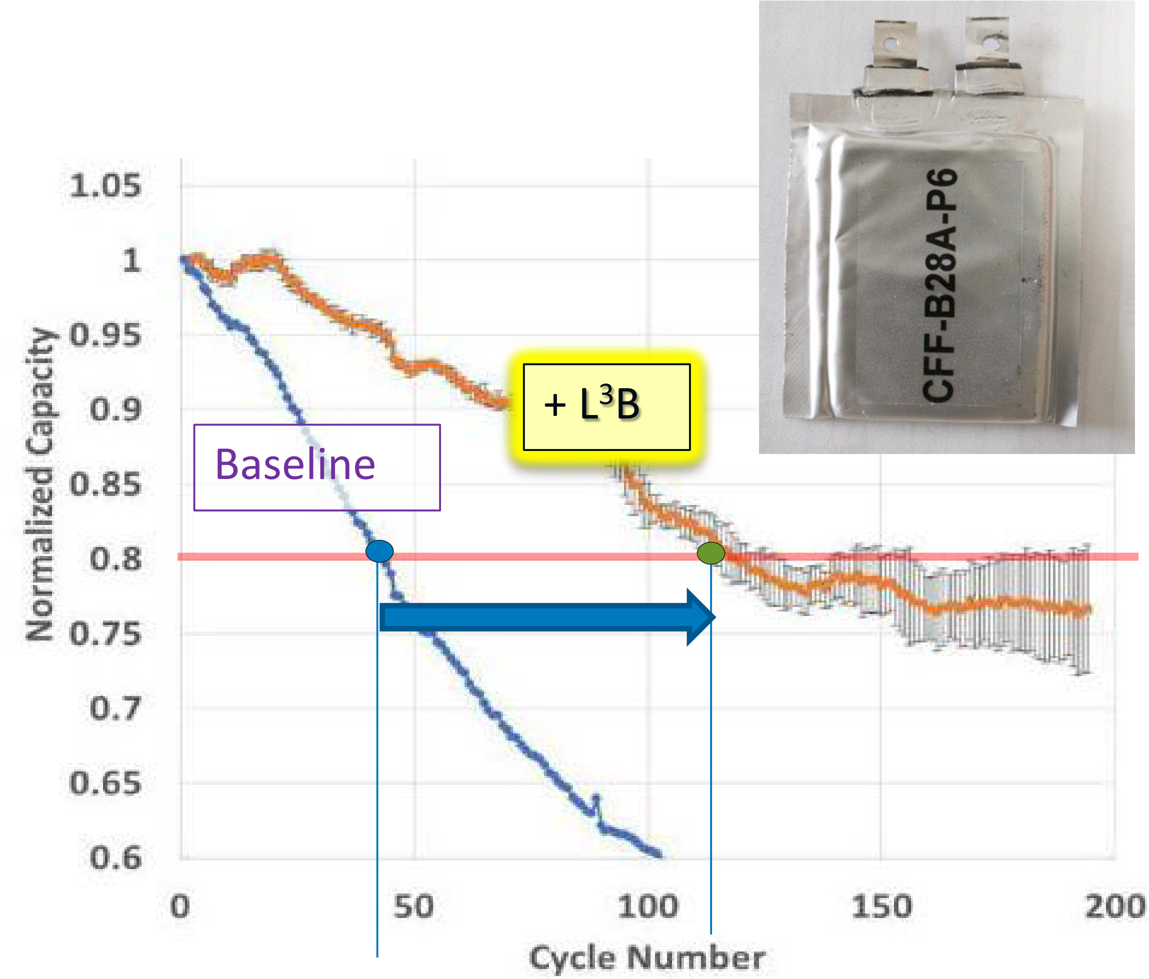
Relithiation done at 100 uA (70% efficiency)

Life extension with external control: 400 mAh Gr-Si/NMC Pouch Cells

- Life extension of 200% demonstrated with multiple, triggered relithiations (C/3 cycling at room temperature)
- Baseline cells fades to 280 mAh after 60 cycles
- Cells with relithiation have a capacity of 280 mAh after 180 cycles



Life extension with passive control: 400 mAh Gr-Si/NMC Pouch Cells

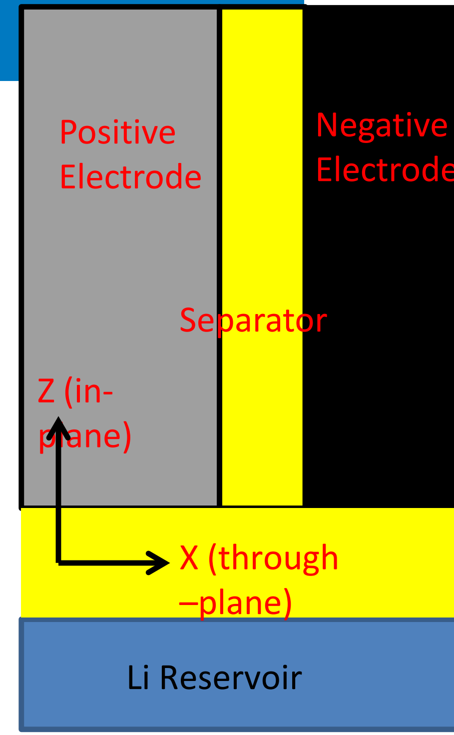


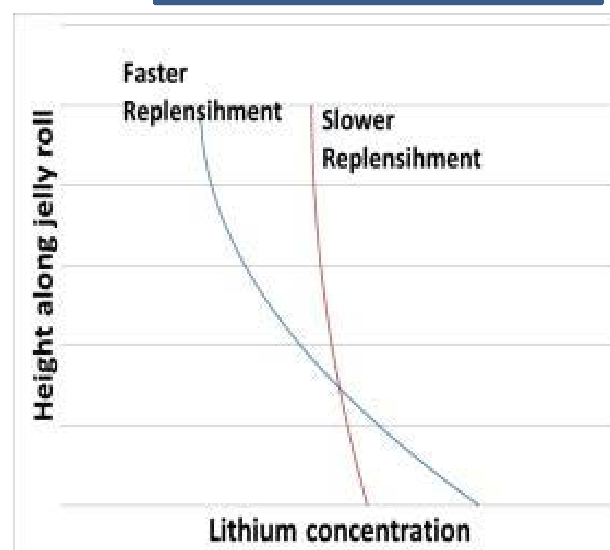
>2x life extension

- Relithiation done continuously cycling with passive control
- Room temperature cycling at C/3
- Relithiation has no measurable impact on resistance

2D Transport Model for Investigating lithium distribution

- If lithium is replenished at too high a rate, then lithium will be preferentially inserted near the lithium reservoir
- This non-uniformity could result in over-lithiation/lithium plating near bottom edge of jelly roll
- A transport model was developed to investigate limitations in relithiation rate:
  - 2D model (assumes symmetry between multiple layers or jelly roll winding)
  - Considers Li+ transports for through-plane direction (between anode and cathode) and in-plane (between Li-reservoir and electrodes)

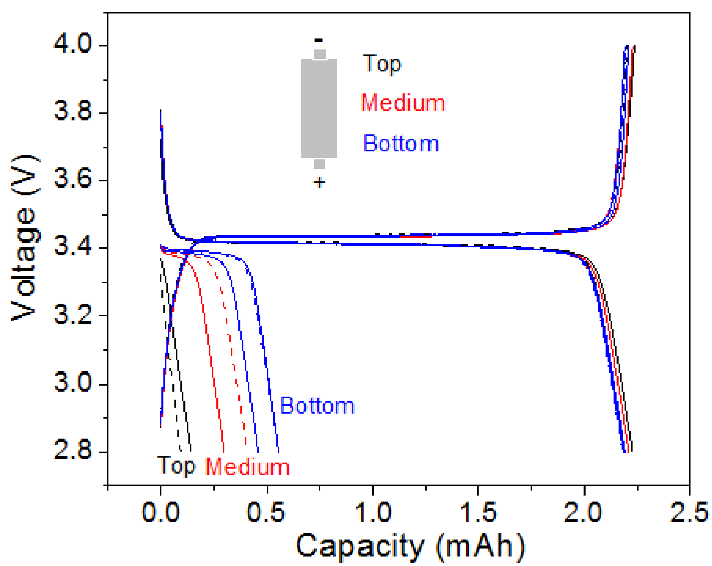




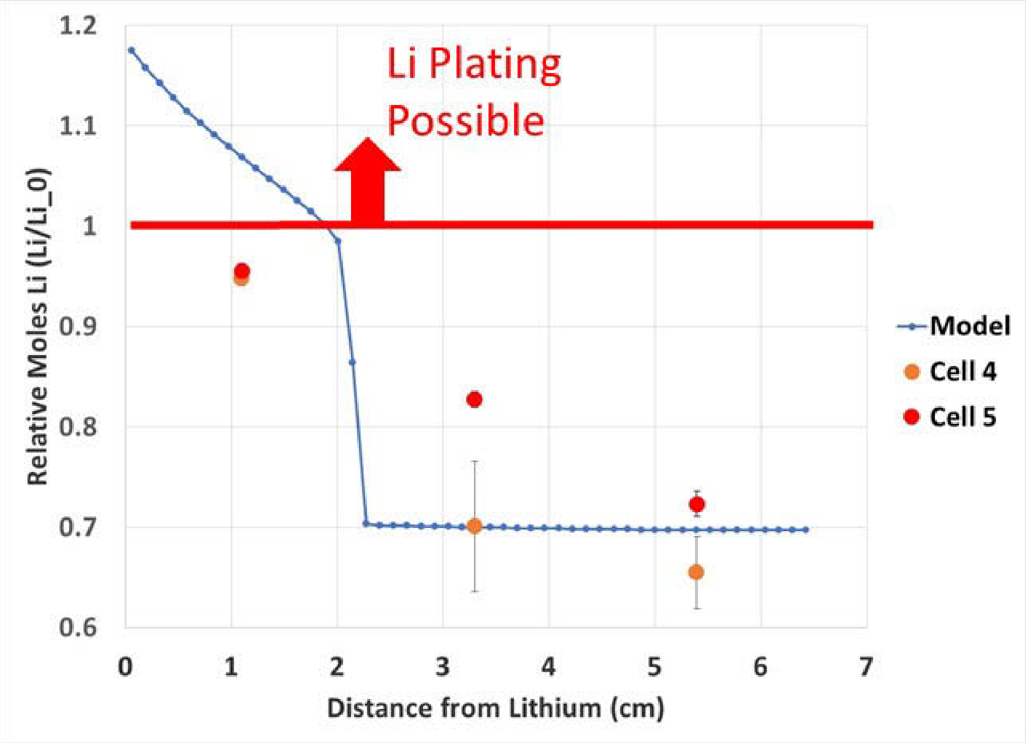
Lithium distribution from re-lithiated A123 jelly roll (M8)

- Coin cells are harvested from cycled jelly rolls/pouch cells and 1st cycle coulombic efficiency is used to determine lithium inventory
- Model is conservative and predicts more lithium non-uniformity than measured
- Challenging chemistry for relithiation due to flat OCP of graphite/LFP

1st Cycle for LFP cathode half-cells



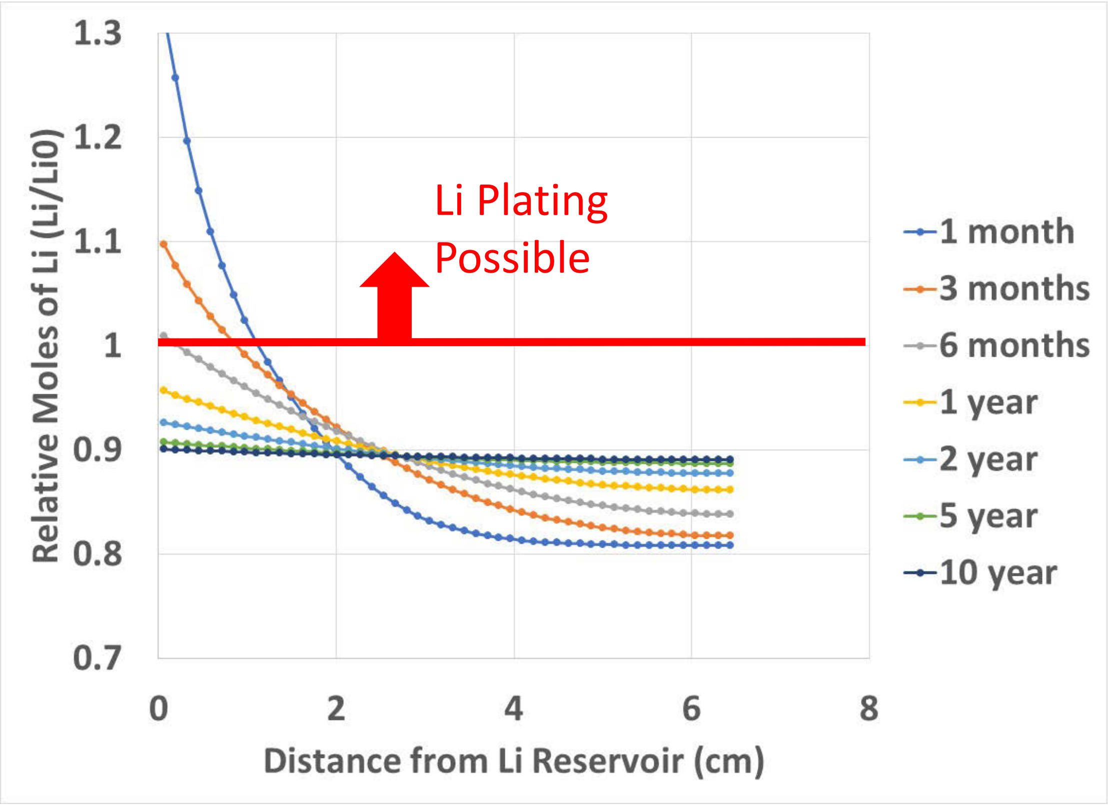
Li reservoir near top position



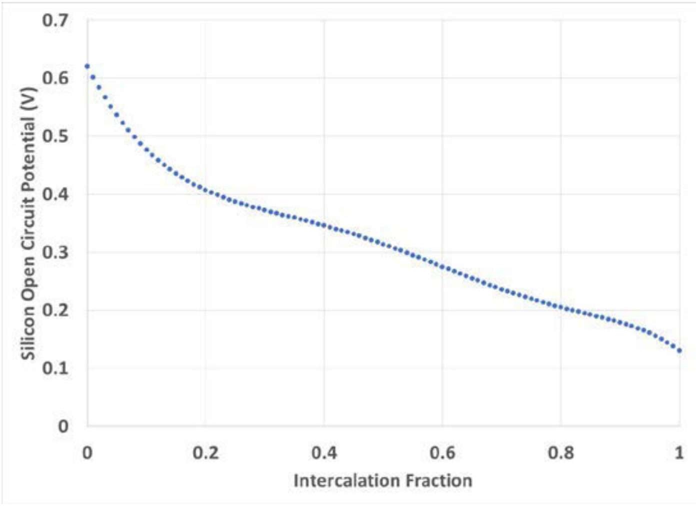
M8: Method to quantify non-uniformity of Li with release rate and cell design using models and experiments. Measure power capability/internal resistance before and after re-lithiation

Model predictions for lithium distribution as a function of re-lithiation rate

- Model parameters developed based on:
  - Gen 2 electrolyte properties at 45 °C
  - High energy density Si/NMC cell of 680 Wh/L (3.2 Ah 18650 cell)
- 20% re-lithiation over different time periods
- Recovery over time-scales longer than 6 months predicted to have reasonably uniform lithium distribution



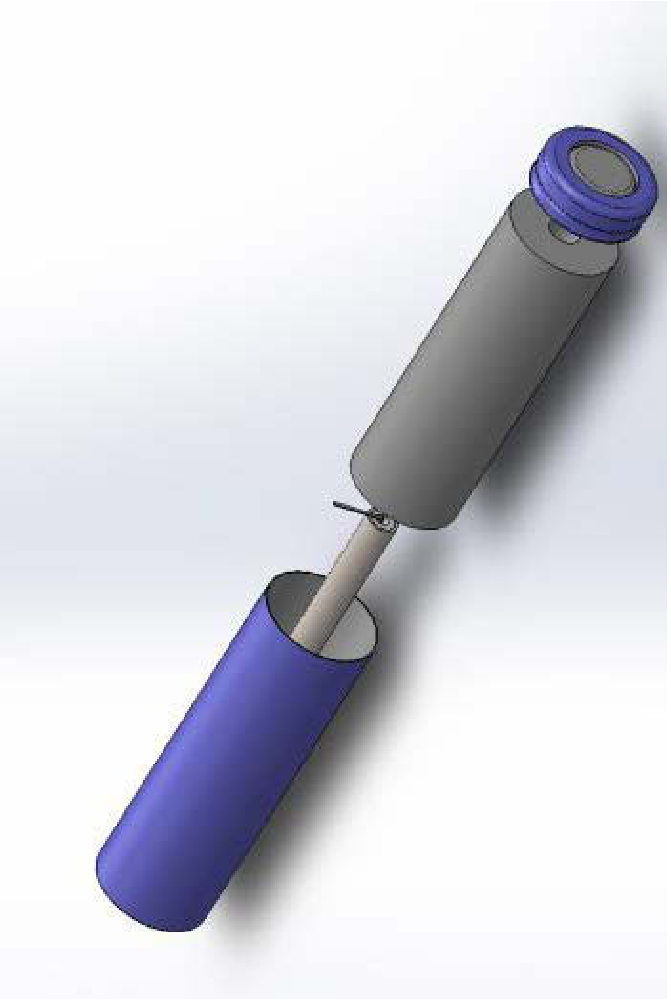
Sloped OCP of Silicon helps promote lithium uniformity



Designs for Cylindrical Cells

1.) Cup placed at bottom

2.) Inner Mandel



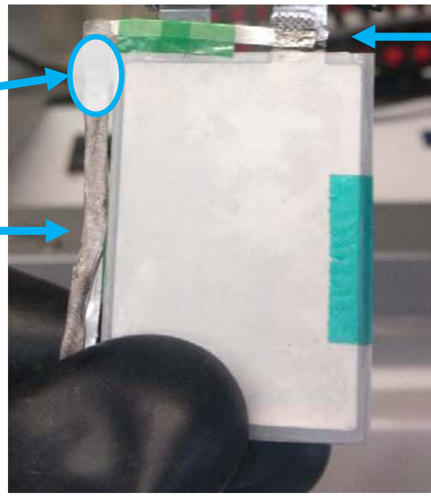
M3. Design drawings of Li reservoir and circuit packaging concepts that occupy less than 5% volume of 18650 cell

Device development for Pouch Cells

Example implementation
400mAh Gr-Si/NMC pouch cell jellyroll

Passive control

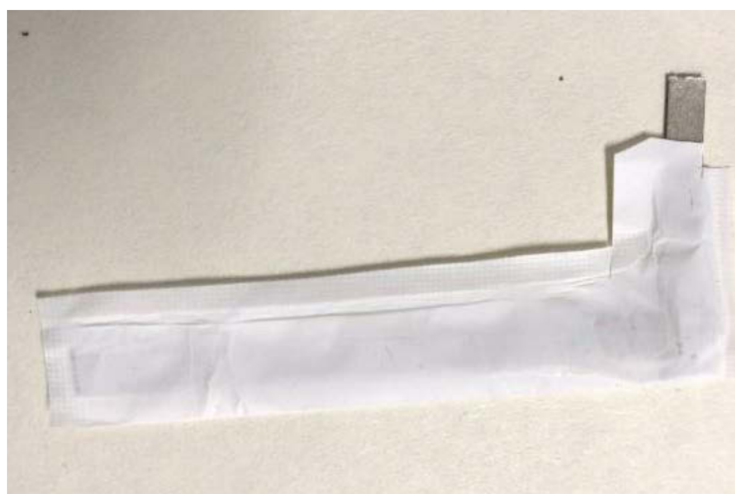
Li reservoir



Tab connection

Carried out X-ray CT. The Li and Al components are transparent to X-rays

Li reservoir and passive control are wrapped in separator that is then sealed on one side



Responses to Previous Year Reviewers' Comments

- Project has not been reviewed previously

Acknowledgements

- Supported by DOE Office of Vehicle Technologies
  - Brian Cunningham, Program Manager

Collaboration and Coordination

Category	Institution	Role
National Laboratories	Argonne National Lab (CAMP)	Fabrication of 400 mAh pouch cells utilizing 15 wt% Si anodes.
Industry	Coloumetrics	Canning of 18650 graphite-NMC cells
	Nanograf/Si-Node	Supplying SOA Si/graphene electrodes for device demonstration

Remaining Challenges and Barriers

- Proposed device needs to be demonstrated in larger capacity cells suitable for EV applications
- Safety implications of proposed device
- Device packaging
  - Enable handling in dry room
  - Minimal changes to manufacturing line
- Other degradation modes
  - Electrolyte dry out
  - Particle isolation/cracking from mechanical swelling

Proposed Future Research

- Implement device into large capacity cells suitable for EV applications
  - Submitted TCF with GM and Zenlabs
  - 10 and 50 Ah cells
- Develop control strategies to prevent over-lithiation for safety
- Quantify capacity fade from different fade mechanisms for SOA high energy Si cells using relithiation
- Investigate if proposed device can be used as alternative to pre-lithiation (discharge Li at high rates over course of few days)

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

Summary

- Life extension device is composed of metallic lithium reservoir and passive control internal to cell (no third terminal)
- Device has been shown to at least double the lifetime of both traditional graphite and next generation Si cells
- Device occupies less than 5% of the volume, weight, and cost of high energy density cells
- Device has been incorporated in both pouch and cylindrical cells with multiple lithium-ion chemistries
  - Anodes: Gr, Si
  - Cathodes: NMC, FeP, LMO

Thank You

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NREL/PR-5400-73615

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