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# High Energy Rechargeable Lithium-Metal Cells: Fabrication and Integration

JIE XIAO (PI) AND JUN LIU
PACIFIC NORTHWEST NATIONAL LABORATORY
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2018 DOE VEHICLE TECHNOLOGIES PROGRAM
ANNUAL MERIT REVIEW

Project ID #: Bat369

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# Overview

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## Timeline

- Project start date: December 2016
- Project end date: October 2021
- Percent complete: 30%

## Barriers

- Low energy: Li metal anode will boost cell energy
- Short battery Life: mitigating side reactions will extend the cycling stability

## Budget

- Total project funding: $50M
  - DOE share: 100%
- Funding for FY 2017: $10M
- Funding for FY 2018: $10M

## Partners

- Battery 500 PIs
- BNL,ARL,INL,SLAC
- 10 universities
- GM, Navitas Systems

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# Relevance/Objectives

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- **Overall Objectives**
  - Overcome the fundamental issues in building high-energy rechargeable Li metal batteries
  - Demonstration of long-term cycling of 500 Wh/kg Li metal cells
- **Objectives of this period**
  - Identify the cell-level scientific challenges in high-energy rechargeable Li metal batteries: Li/NMC and Li-S
  - Demonstrate 300 Wh/kg Li metal pouch cells for at least 50 stable cycling
- **Impacts**
  - Accelerate the development of high-energy rechargeable Li metal batteries for future vehicle electrification

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# Milestones: Keystone Project 3 for Cell Fabrication, Testing and Diagnosis

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| Milestones and Go/No-Go Decisions | Date | Status |
|---|---|---|
| Investigate methods to extend the cycling and stability of Li metal pouch cells. | 12/31/2017 | Completed (Jason Zhang) |
| Develop stage 2 coin cell and stage 1 pouch cell testing protocols | 3/31/2018 | Completed (Jie Xiao/Eric Dufek) |
| Develop procedures to identify the failure of Li-metal anode in coin cells and pouch cells | 6/30/2018 | On track |
| Deliver 350 Wh/kg Li metal pouch cell (> 50 cycles and < 20% capacity fading) | 9/30/2018 | On track |

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# Approach

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- Pouch cell design and analysis to provide a clear roadmap to build high-energy Li metal cells.
- Identify the key factors that limit the cycling of rechargeable Li metal cells
- New electrolytes and cell optimization to extend reversible cycling of lithium metal anode
- Close the gap between coin cell evaluation and pouch cell testing for fast screening of innovative and effective approaches

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# Technical Accomplishments

## Design and Fabrication of 300 Wh/kg Li/ $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) Pouch Cell

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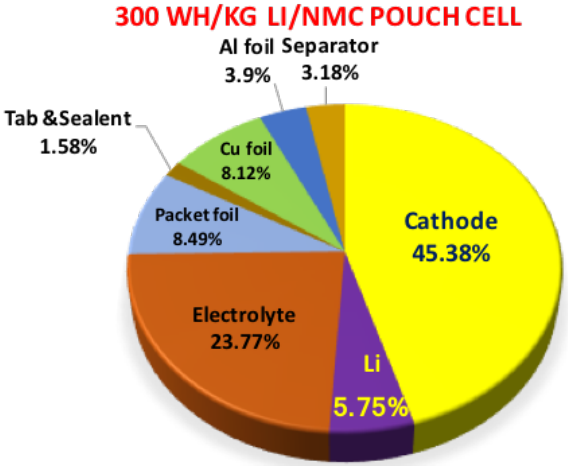
| | Parameters | Real Value |
|---|---|---|
| Cathode | Material | $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ |
| | 1st dicharge capacity (mAh/g) | 180 |
| | Active material Loading | 96% |
| | Coating weight (mg/cm$^2$ each side of Al) | 21.8 |
| | Areal Capacity (mAh/cm$^2$ each side of Al) | 3.8 |
| | Electrode press density (g/cm$^3$) | 3.0 |
| | Electrode thickness(each side of Al foil) (μm) | 72 |
| | Al foil thickness (μm) | 12 |
| | Cathode Layers | 7 |
| Anode | Material | Li |
| | Areal Capacity (mAh/cm$^2$ each side of Cu) | 10 |
| | Cell Balance (N/P ratio) | 2.6 |
| | Electrode thickness(each side of Cu) (μm) | 50 |
| | Cu foil thickness (μm) | 8 |
| Electrolyte | Electrolyte/capacity (g/Ah) | 3.1 |
| | Weight (g) | 3.3 |
| Separator | Thickness (μm) | 20 |
| Packaging Foil | Thickness (μm) | 115 |
| Pouch Cell | Voltage (V) | 3.8 |
| | Capacity (Ah) | 1.07 |
| | Energy density (Wh/Kg) | 300 |




- Appropriate cell designs guide the fabrication of pouch cells with different energy/power and cycling requirements.
- Cathode areal capacity, N/P ratio and electrolyte content are interrelated parameters that dynamically impact the cell energy and cycling stability simultaneously.

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# Technical Accomplishments

## Li/NMC622 Pouch Cells Have Very Limited Cycling in Carbonate-based Electrolyte

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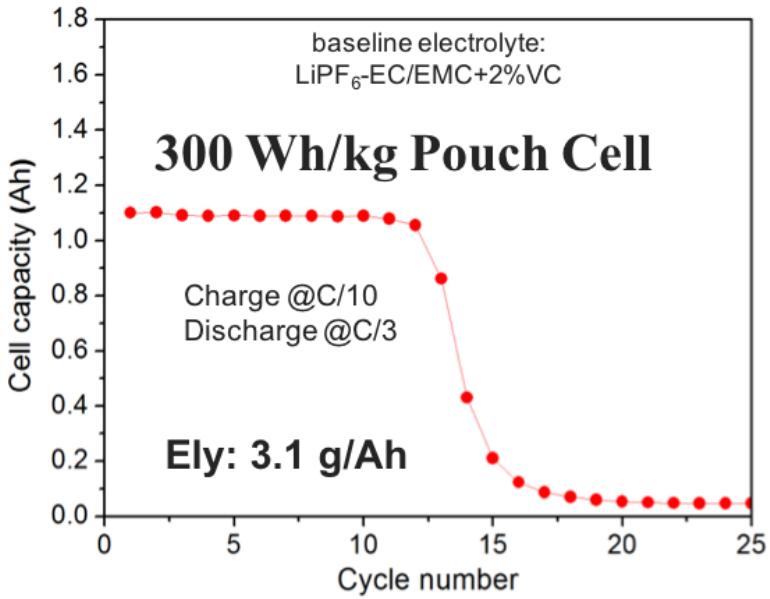


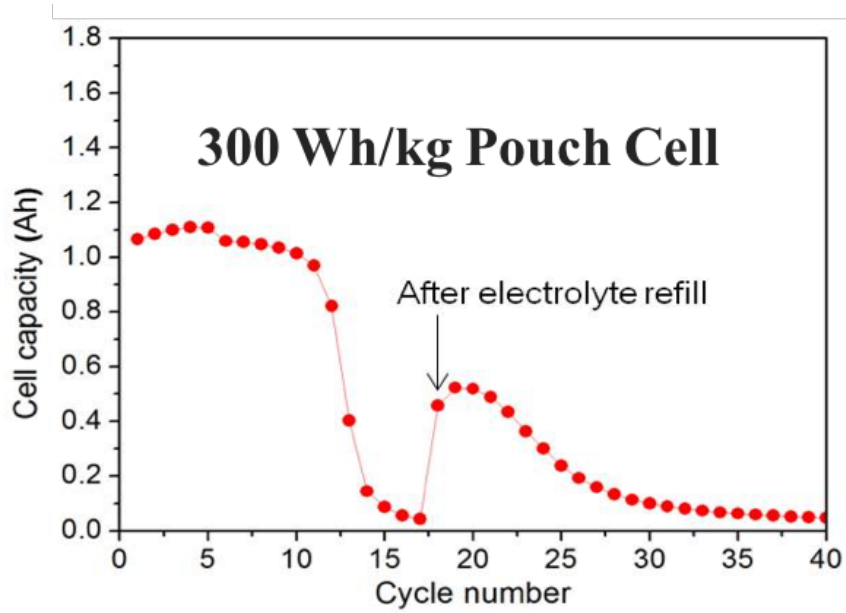


- Pouch cell capacity always ”dives” after 12 cycles regardless of electrolyte amounts.
  - NMC622 cathodes still works well in re-assembled cells (backup slide)
  - Cell is not short as reflected by the voltage profiles after failure (backup slide).
- Refilling electrolyte only partially recovers the capacity.
  - Electrolyte drying out is NOT the only reason for fast capacity decay.
  - Li is also being depleted after 15 cycles!

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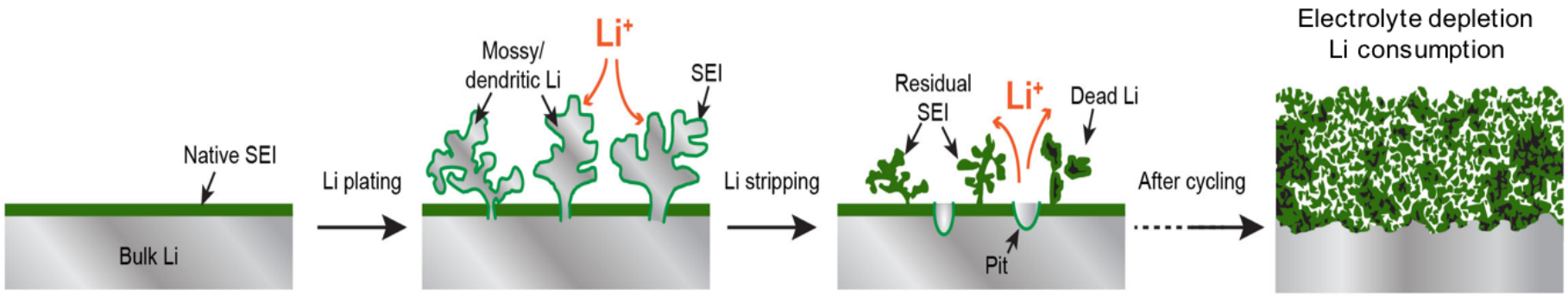
# Technical Accomplishments
## SEI Formation Consumes both Electrolyte and Li




- Electrolyte is continuously consumed to form SEI on newly exposed Li surfaces.
- Part of Li is tightly “wrapped” by insulating SEI layers and loses electronic contact with anode: “dead” Li formation
- ”Dead” Li is continuously accumulated during cycling: Li depletion

# Technical Accomplishments

## Li and Electrolyte Contents are Drastically Different in High- Energy Pouch Cells and Lab-testing Coin Cells

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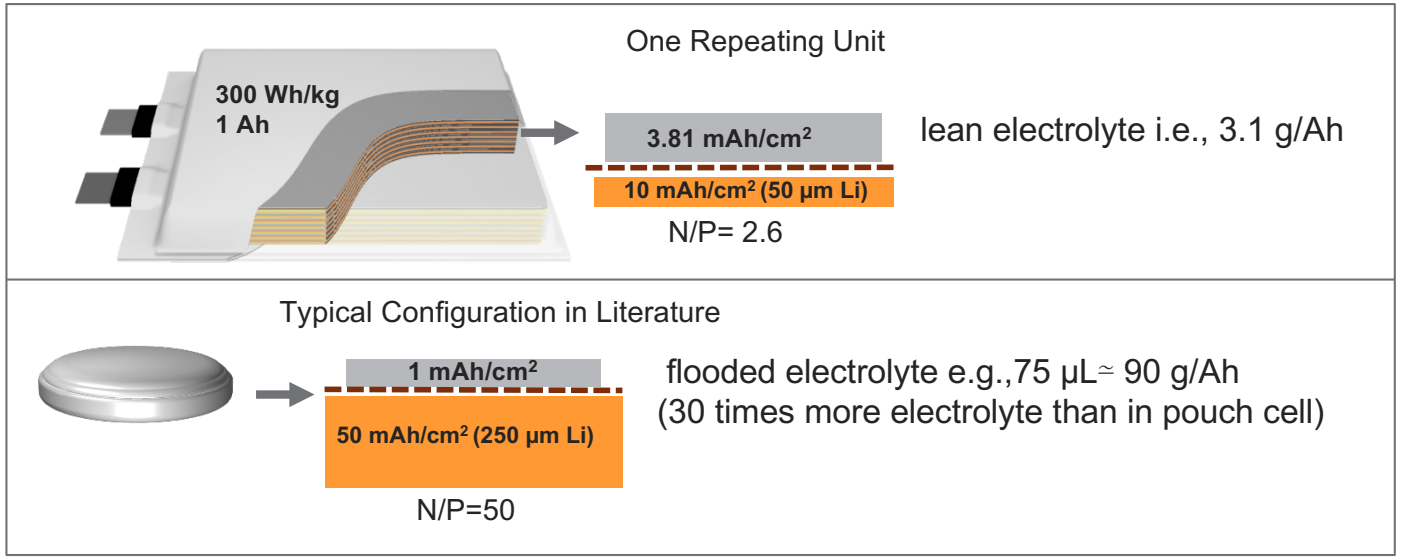


- During each cycle: both electrolyte and Li are irreversibly consumed
  - Pouch cells: very restricted amounts of Li and electrolyte so the cell degrades very fast
  - Coin cells: almost unlimited amounts of Li and electrolyte thus hundreds of stable cycling is often seen in literature
- A standard coin cell testing protocol has been developed to close the gap between coin cell evaluation and pouch cell fabrication.

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# Technical Accomplishments

## Both Li and Electrolyte Contents Significantly Impact Cycling Stability of Li Metal Cells

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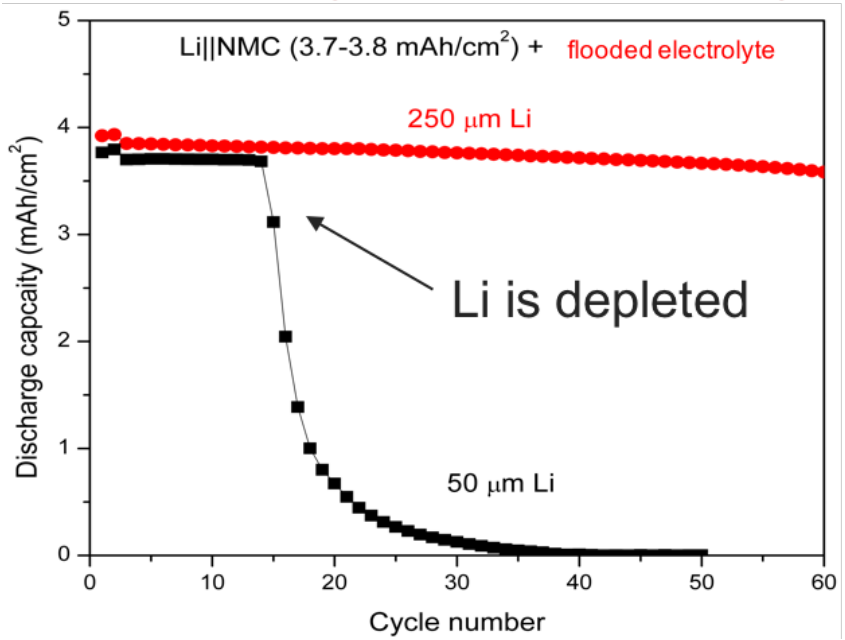
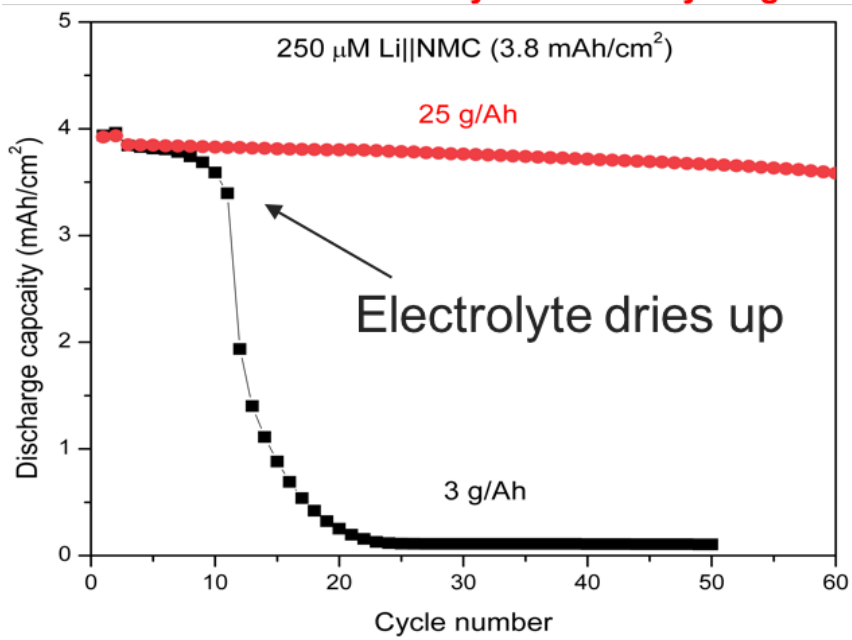
**sufficient electrolyte: Li amount determines cycling**




**sufficient Li: electrolyte dictates cycling**




- Cells are terminated once Li or electrolyte (or both) is completely drained, whichever comes first.
- Pouch cells consist of thin Li (50 um) and lean electrolyte (3 g/Ah)
- Confirm that the continuous consumption of thin Li and lean electrolyte leads to fast pouch cell degradation.

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# Technical Accomplishments
## New Electrolyte Mitigates Side Reactions between Li and Electrolyte

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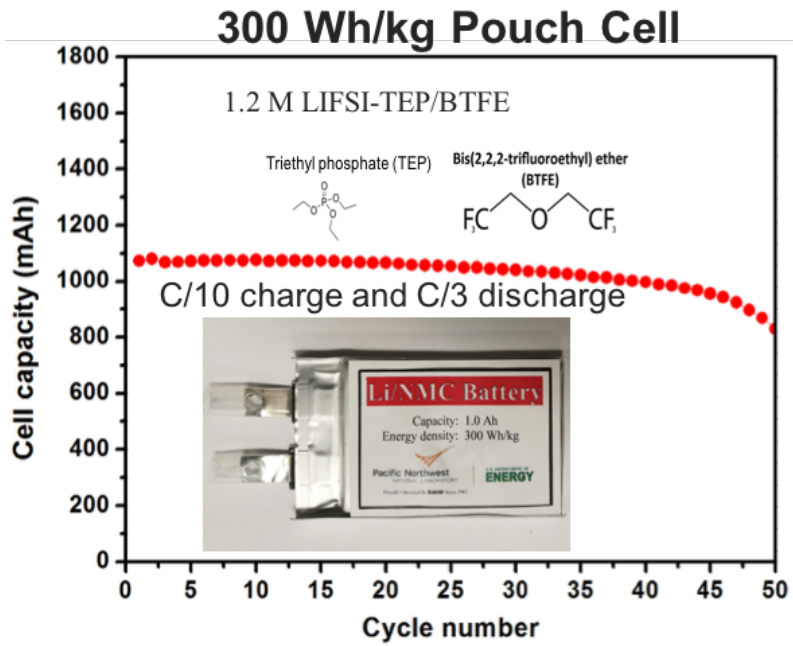


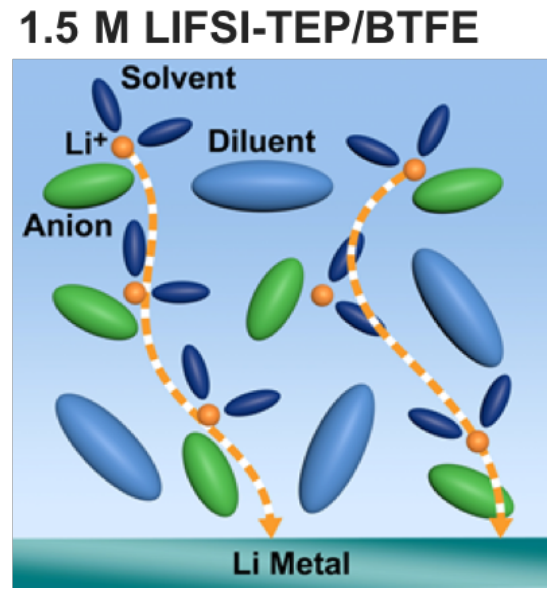


** J.-G.Zhang et al, Advance Materials, 2018, DOI: 10.1002/adma.201706102*

- New electrolyte (1.5 M LiFSI-TEP/BTFE) greatly extends pouch cell lifespan (project #Bat362).
  - Less amount of electrolyte and Li are consumed each cycle
  - Improved SEI quality to slow down “dead” Li formation
  - Non-flammable, low viscosity and good wetting
- Independent pouch cell testing at INL demonstrated > 100 stable cycles (project # Bat368)

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# Technical Accomplishments

## New Electrolyte Slows Down the Side Reactions between Thin Li and Lean Electrolyte

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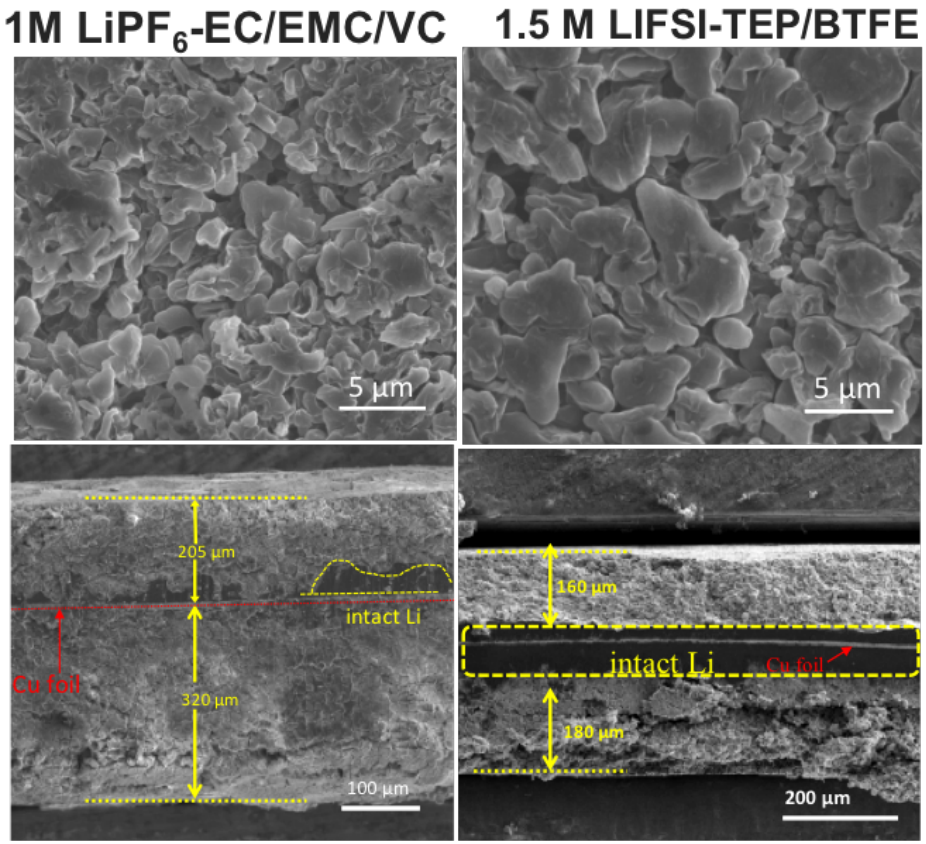
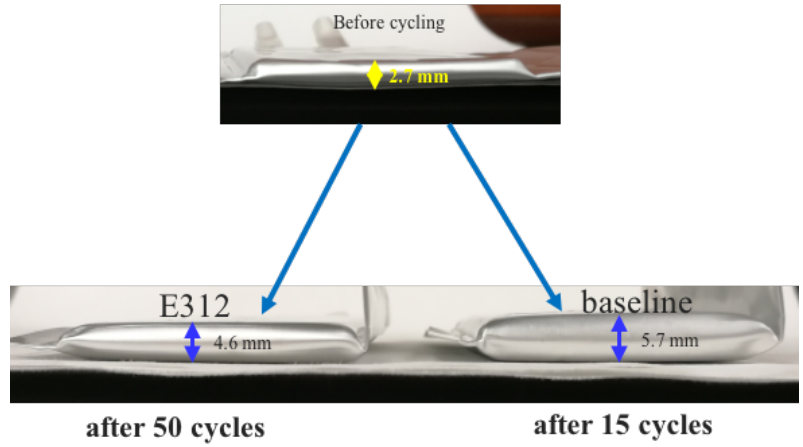



after 15 cycles after 50 cycles




- In new electrolyte (300 Wh/kg cell):
  - Cycled Li has larger average particle sizes: less surface areas for side reactions.
  - Li shows less expansion and cell volume expansion is also reduced.
  - No uniform external pressure applied yet in both tests.
- Intact Li is found in the cell tested in new electrolyte.

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# Technical Accomplishments

## New Electrolyte is also Compatible with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) Cathode

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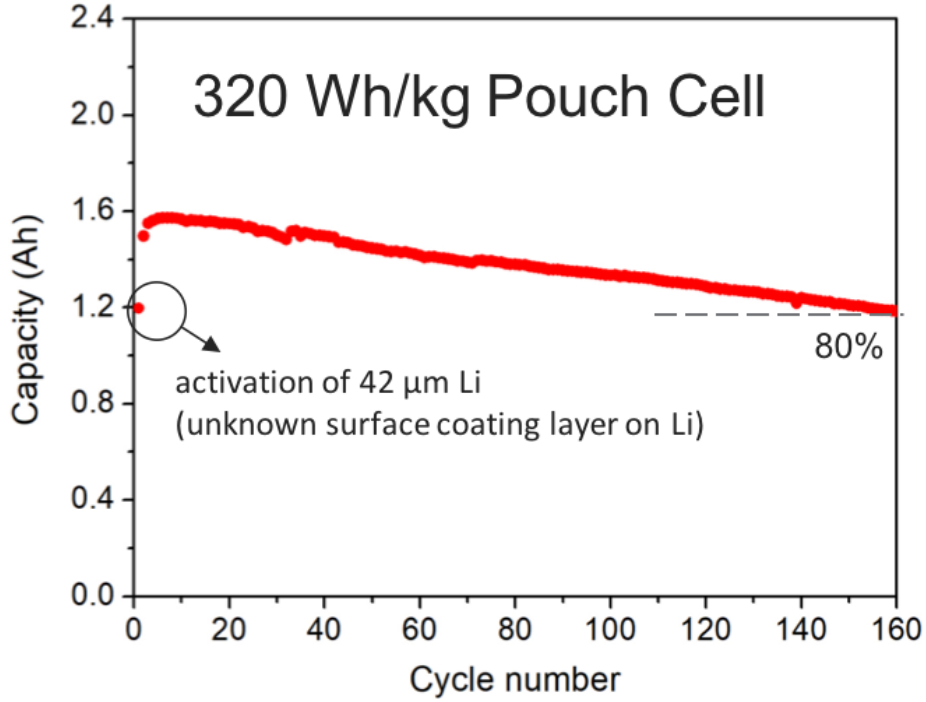


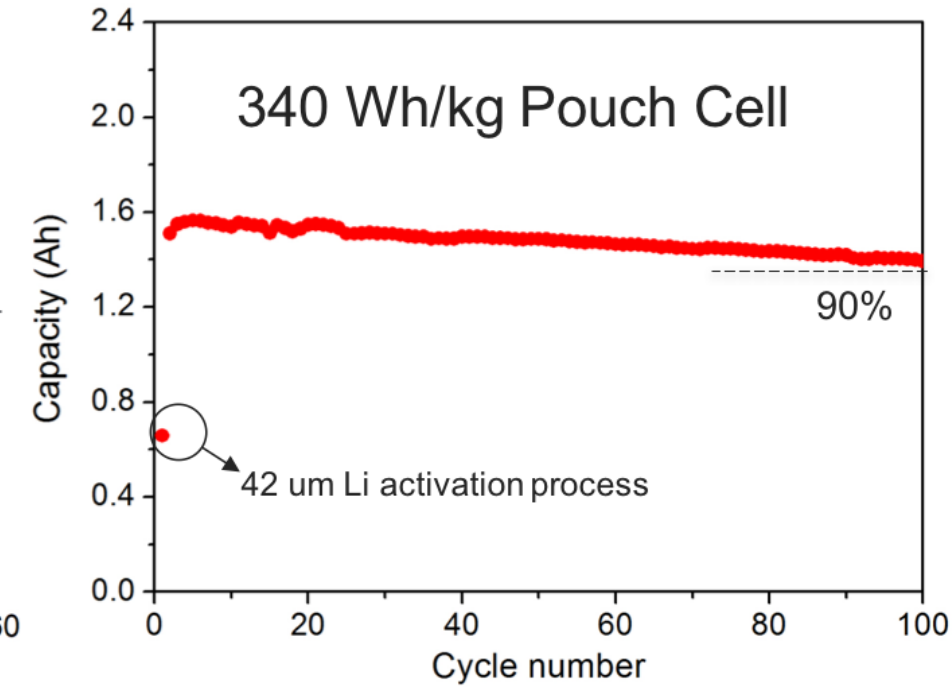


**Testing conditions:**
first 2 cycles: C/10 for charge/discharge
subsequent cycles: C/10 charge and C/3 discharge

- Li/NMC811 chemistry further increases cell energy to > 300 Wh/kg.
- Optimized cell design is critical to extend stable cycling to beyond 100 cycles.

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# Responses to Previous Years Reviewers' Comments

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- This project was not reviewed last year.

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# Collaboration and Coordination with Other Institutions

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- Industry:
  - General Motors: independent testing of PNNL's thick S electrodes
  - Navitas System: new coating method
- University:
  - UT Austin: Supplied high-Ni NMC to PNNL for evaluation
  - Univ. Washington: separator coating
  - SUNY Binghamton: cell fabrication
  - UC San Diego: testing on industry-made electrodes and PNNL electrolytes
  - Univ. Pittsburg: supplied S/C composite for electrode coating
  - Penn State Univ.: testing of thick NMC and S electrodes made
  - Univ. Houston: testing of PNNL new electrolyte
  - Stanford: S electrodes testing
  - Univ. Maryland/Army research Lab: electrolyte development
- National Laboratory
  - Idaho National Lab: independent testing of PNNL-made pouch cell
  - Brookhaven Nation Lab: characterization of PNNL fabricated electrodes/electrolytes
  - SLAC: new electrolyte characterization

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# Remaining Challenges and Barriers

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- Push the cell energy towards 500 Wh/kg by appropriate cell designs and new electrolytes
- Balance of high energy and cycle life of Li metal cells
- Dendrite-induced cell shorting (C/10 charging rate is used in FY18 to decouple cell shorting and cell failure caused by Li/electrolyte depletion.)

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# Proposed Future Work

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- FY18 (Q4): **Demonstrate 350Wh/kg pouch cell with >50 stable cycling and <20% fading**
- FY19:
  - Cell design to balance energy and cycling
  - Optimization of the new electrolyte to further enhance the cycling stability of Li/NMC811 pouch cells
  - Electrolyte and separator modifications to improve Li-S pouch cell cycling ability
  - Li metal modification to improve the anode stability

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

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# Summary

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- ≥300 Wh/kg Li metal pouch cells have been successfully fabricated and demonstrated >100 stable cycling.
- Cell-level fundamentally new challenges are identified.
  - Pouch cells contain very limited amounts of Li and electrolyte.
  - The fast depletion of both Li and electrolyte leads to the quick cell degradation.
- New electrolyte has been developed to enhance Li stability and is also compatible with high-Ni NMC cathodes.
- A standard coin cell testing protocol has been developed and shared across the team to accelerate innovations at relevant scales.

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# Acknowledgement

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- DOE/EERE/VTO: Battery500
- Key contributors: C. Niu, D. Lv, S. Chen, H. Lee, X. Ren, S.Q. Wilson, Q. Li, W. Xu and J. Zhang
- Battery500 PIs and their teams


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# Technical Backup Slides

# Harvested NMC622 Cycles Well in Coin Cells with Fresh Li Metal

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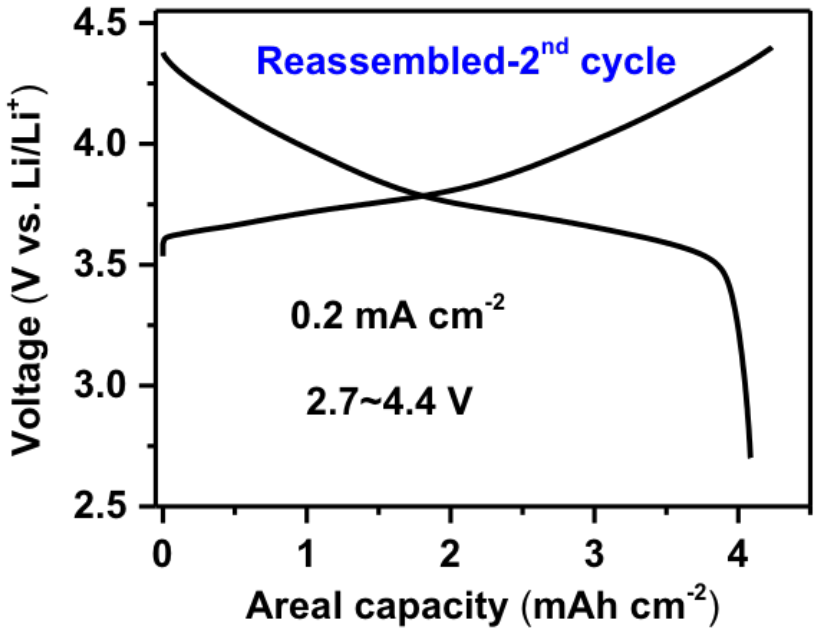


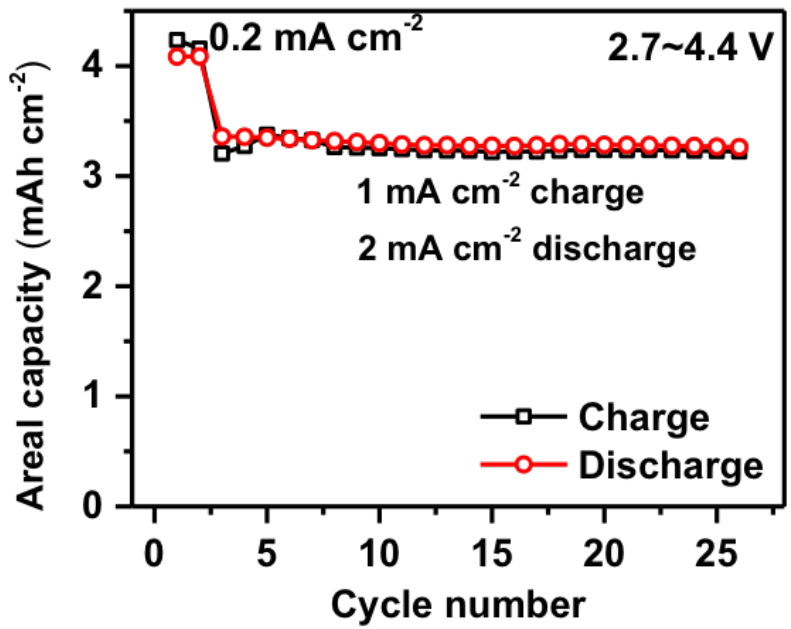


- Cathodes punched from failed/disassembled Li/NMC622 pouch cells (in baseline electrolyte) are re-assembled into coin cells.
- Normal voltage profiles and stable cycling are seen from harvested NMC622 i.e., cathode is NOT the reason for the fast pouch cell degradation in baseline electrolyte.
- Lithium and electrolyte are both in excessive amounts to evaluate cycled NMC622.

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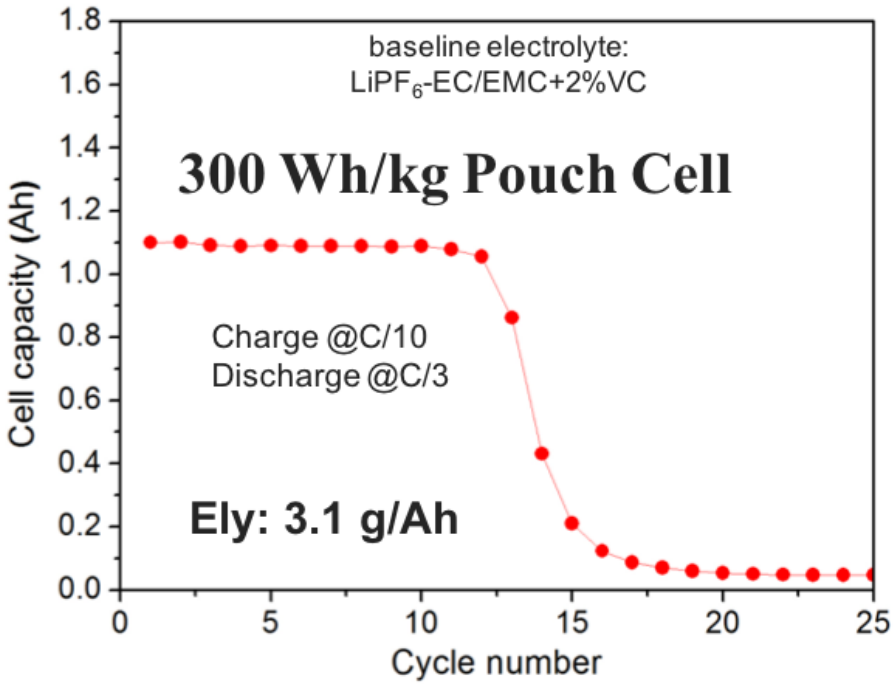
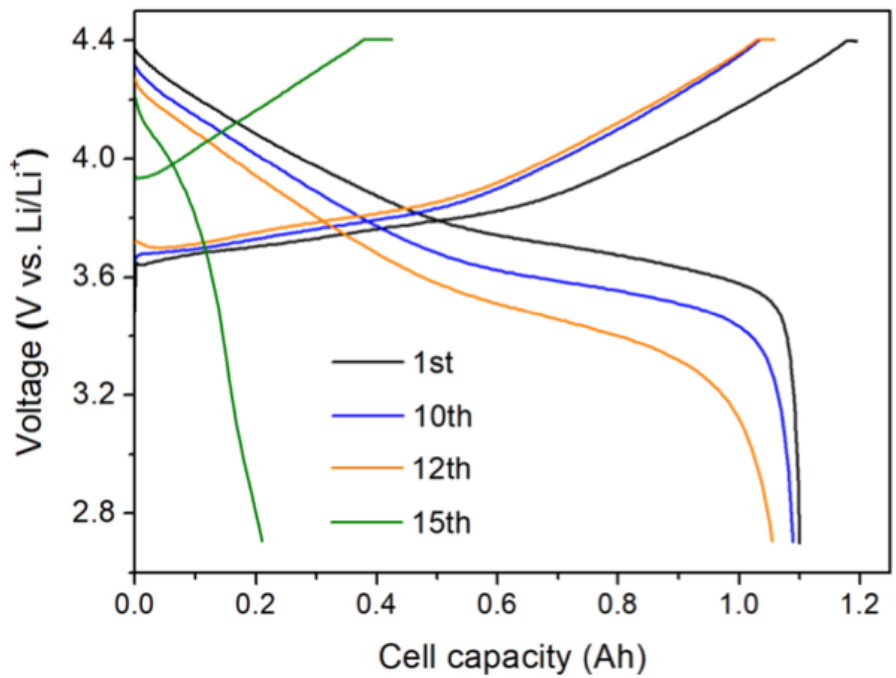
# Failed Li Metal Pouch Cell is Not Short




- In baseline electrolyte: Cell voltage and polarization increase significantly after cell failure.
- Cell failure is NOT caused by Li dendrite-induced shorting.
- Consistent with the conclusion that Li and electrolyte depletion is the main reason for cell termination.

# Voltage Profiles of Li/NMC811 Pouch Cells

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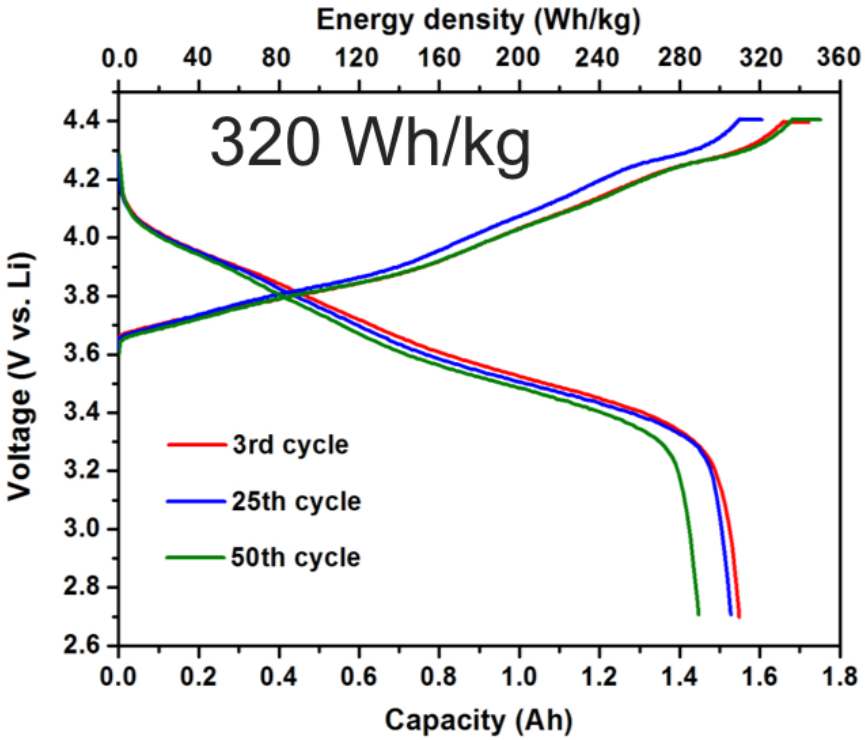


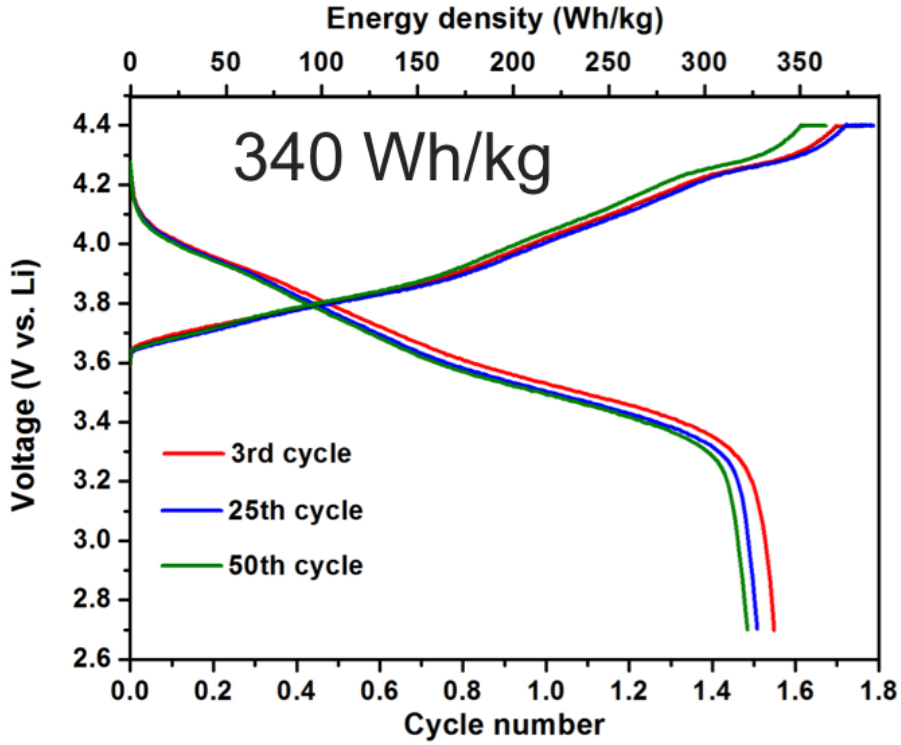


- In electrolyte and optimized cell design: Slight polarization increase is seen during cycling.
- Further optimization on the cells is underway.

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