# Cobalt-Free Cathodes for Next Generation Li-Ion Batteries

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Nexceris, LLC

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Project ID: bat417



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# Overview

## Timeline

- Project Start Date: Jan. 2019
- Project End Date: Dec. 2021
- Percent Complete: ~ 30 %

## Budget

- Total Project Funding: $3.08 M
  - DOE share: $2.46 M
  - Cost share: $620 k
- Funding for FY2019: $1.04 M
- Funding for FY2020: $1.01 M

## Barrier and Technical Targets

- Barriers addressed:
  - Cycle Life: 1000 cycles C/3 deep discharge with < 20 % energy fade
  - Cost: < $100/kWh

## Partners

- Ohio State University: Dr. Jung-Hyun Kim
  - Battery testing
  - Cell chemistry development
- Navitas Systems Dr. James Dong
  - Large-scale electrode fabrication
  - 2-Ahr battery manufacture and testing

# Relevance

## Impact

- The increased demand for EVs will drive demand for battery materials.
- Renewed interest in reduced or cobalt free Li-ion battery cathode formulations
  - Opportunity to reestablish U.S. dominance in batteries

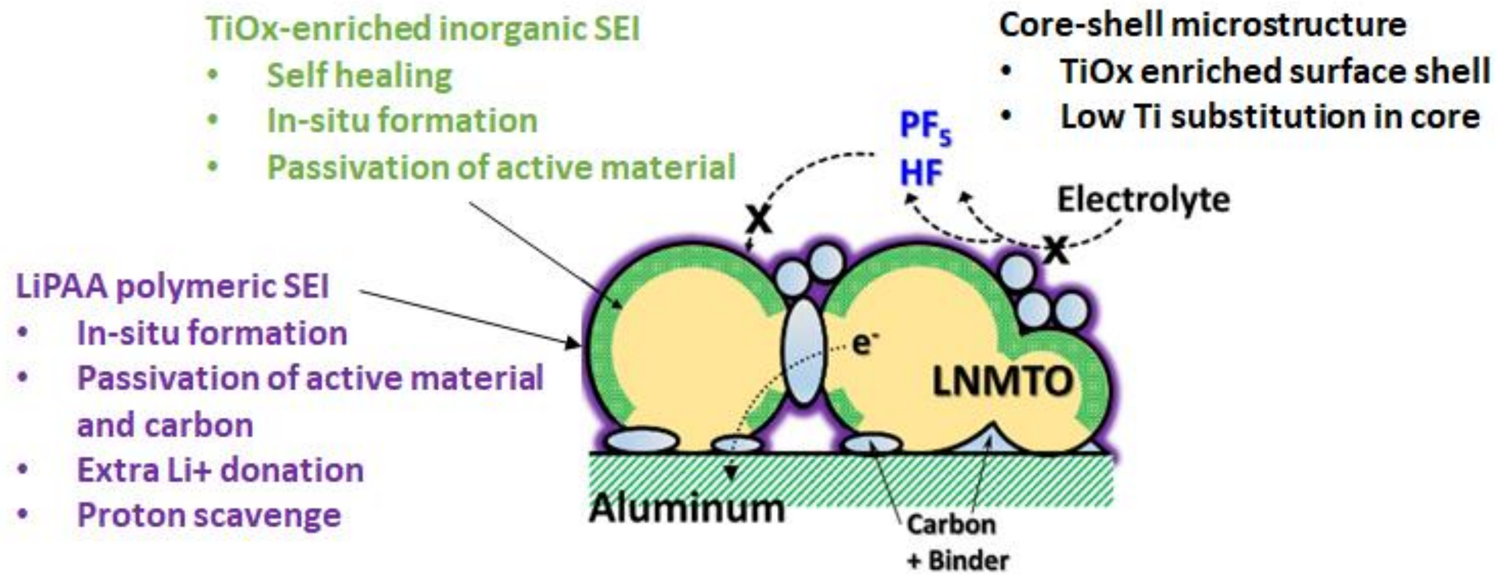
## Objective

- Develop high performance and cobalt-free lithium ion battery based on high voltage lithium manganese nickel titanium oxide (LNMTO) cathode
  - Identify low-cost, scalable manufacturing process for LNMTO cathode powder
  - Identify compatible electrolyte to minimize degradation (> 1000 cycles with < 20 % energy fade)
- To date:
  - Demonstrated potential of Ti-substituted LNMTO to improve stability
  - Pouch-type testing has highlighted the importance of the electrolyte to achieve required cycle life

# Approach

## Develop cobalt-free cell based on high-voltage $LiNi_{0.5}Mn_{1.2}Ti_{0.3}O_4$ (LNMTO) cathode

- Improve cycle and calendar life of high-voltage spinel cathodes by forming a solid-electrolyte interface that effectively passivates the cathode surface
- Create novel LNMTO core/shell microstructures where Ti is preferentially located at surface
- Incorporate optimized binder/electrolyte chemistries



# Approach/Strategy - Milestones

## FY19 cumulated in testing of 2 Ah PPCs and demonstrating improved cycle performance of down-selected LNMTO cells compared to LNMO baseline

| | FY 2020 | | | | FY 2021 | | | |
|---|---|---|---|---|---|---|---|---|
| **Milestone/Decision Point** | **Q1** | **Q2** | **Q3** | **Q4** | **Q1** | **Q2** | **Q3** | **Q4** |
| PPC post-mortem analysis completed | | ◆ | | | | | | |
| **Decision Points:** Candidate core-shell LNMTO powders down-selected | | | ◆ | | | | | |
| Promising cell chemistries down-selected | | | | ◆ | | | | |
| **Go/No-Go Decision Point:** Testing of 2-Ahr cells completed<br>*Demonstrate that core/shell modification enhances cathode performance* | | | | ◆ | | | | |
| Intermediate 2 Ah cells post-mortem analysis completed | | | | | | ◆ | | |
| Down-select: Cell chemistries (inc. LNMTO powder) and fabrication and conditioning full defined for PCCs | | | | | | | ◆ | |
| **Final Project Performance Target:** PCC cells achieve target performance/durability criteria | | | | | | | | ◆ |

Cycle life > 500 cycles
< 20 % energy fade (C/3, 25 °C)

1. Cycle life > 1,000 cycles < 20 % energy fade (C/3, 25 °C)
2 Specific energy (cathode) > 600 Wh/kg (C/3)
3. Compatibility with cell cost of less than $100/kWh

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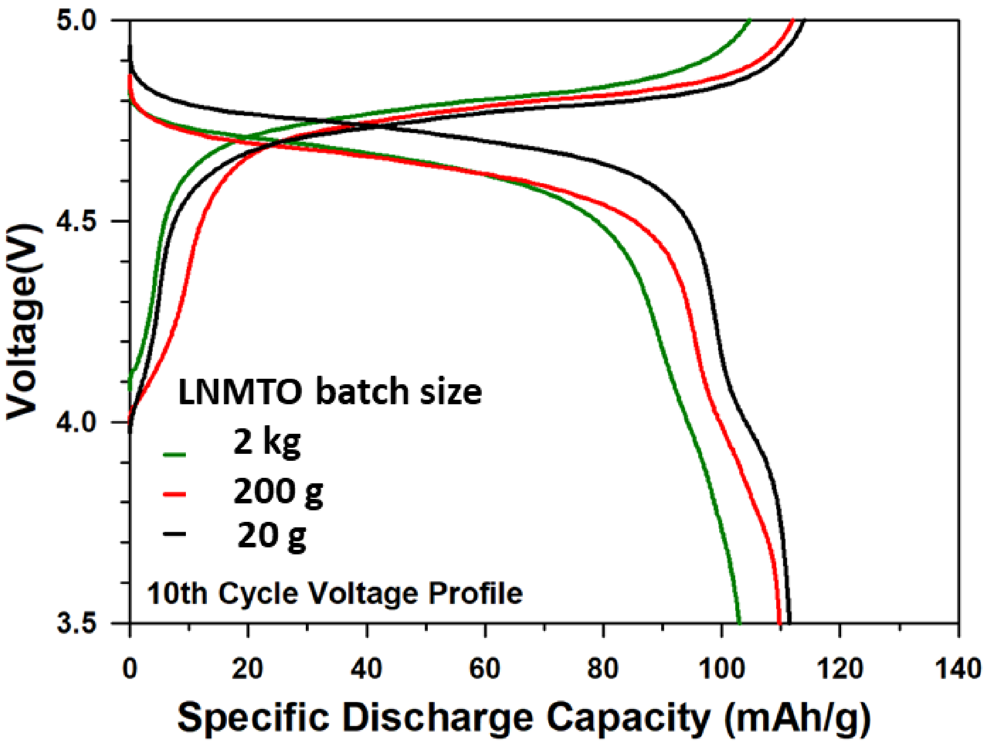
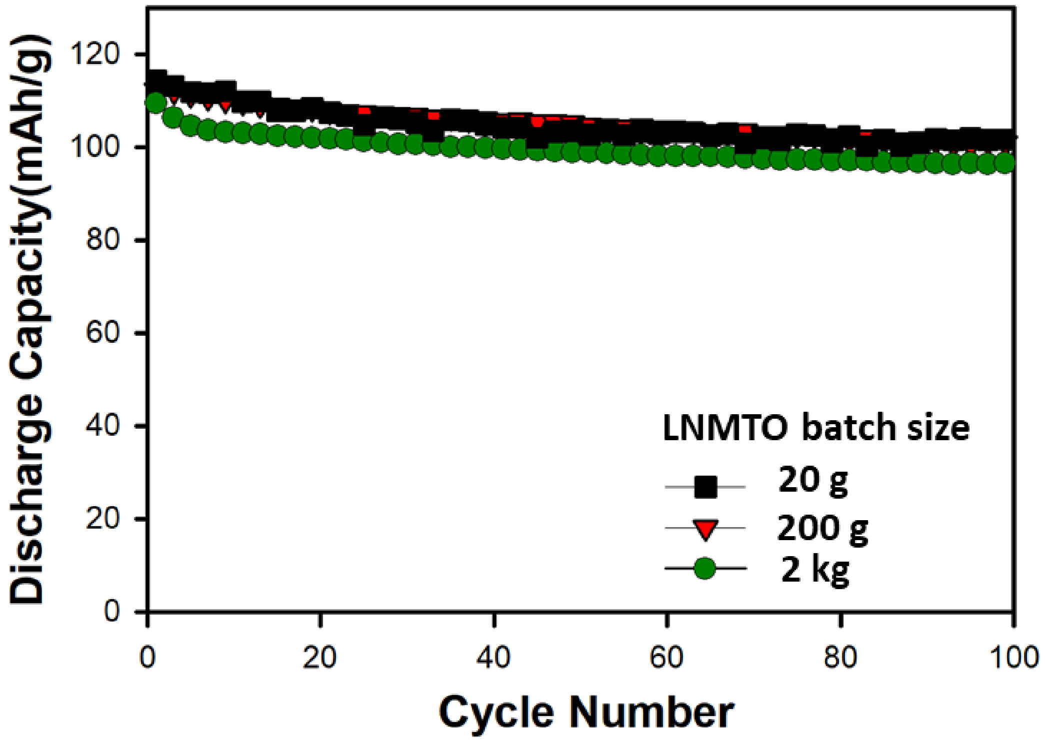
# Accomplishment: LNMTO Solid State Powder Synthesis

Successfully scaled solid-state process to 2 kg and powder homogeneity increased from 87 % to 94 %

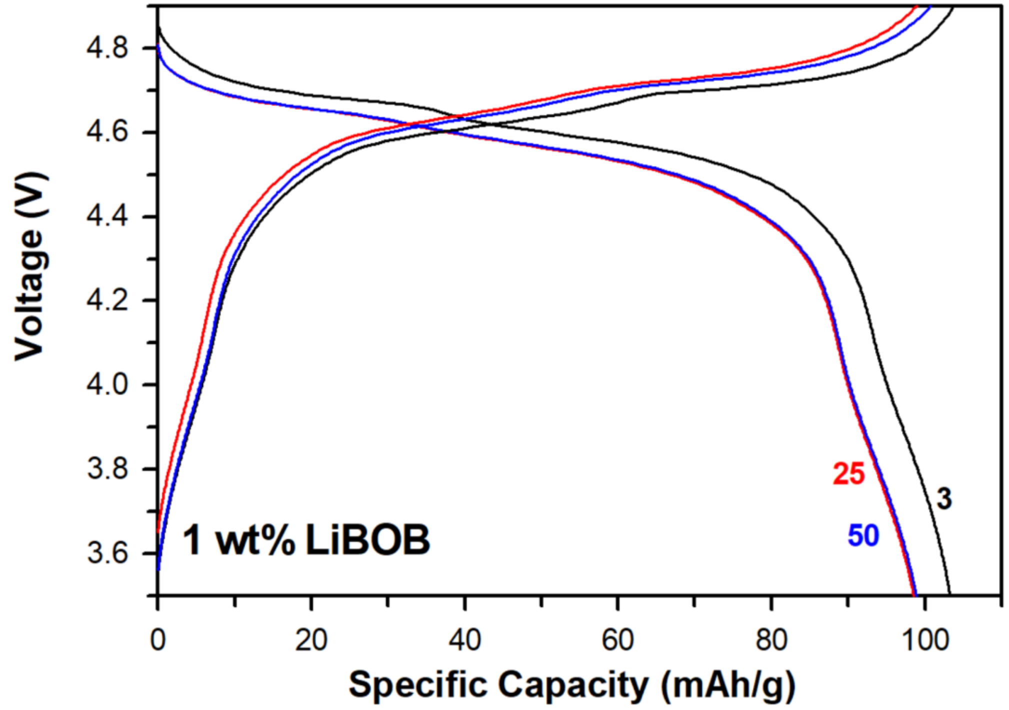


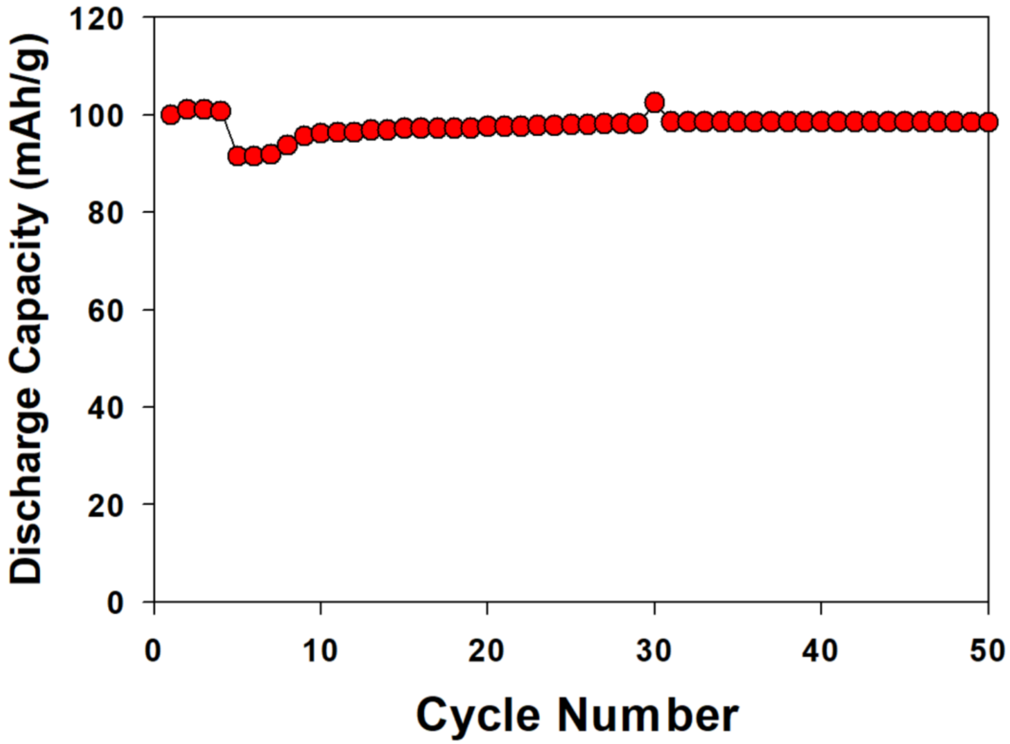




Coin-type half-cells - Cathode: LNMTO PVdF binder; Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC
Cycling conditions: Cycle 1: C/10 then C/5 (Ch) and C/2 (dis) at 25 °C

# Accomplishment: Down-selected optimal cell chemistry

After extensive screening, down-select PPC cell chemistry incorporated LiPAA binder and LiBOB electrolyte additive




Single-Layer Pouch cells - Cathode: LNMTO, LiPAA binder, Anode: Graphite, Electrolyte: 1 M $LiPF_6$ in 1:1 wt. EC/EMC with 1 wt.% LiBOB
Cycling conditions: 4.9 V to 3.5 V, Cycle 1: C/10 then C/5 (Ch) and C/2 (dis). at 25 °C

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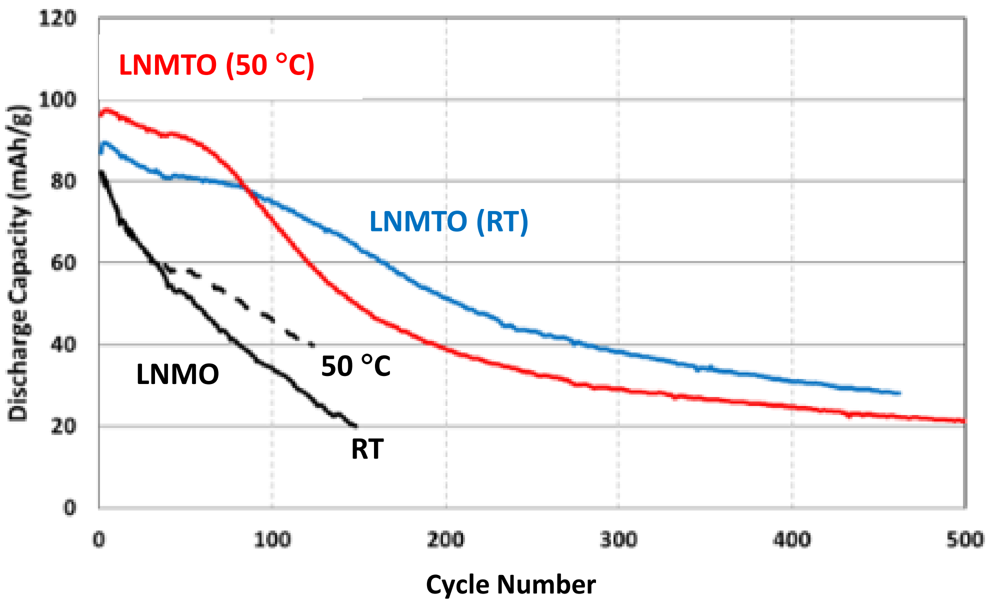
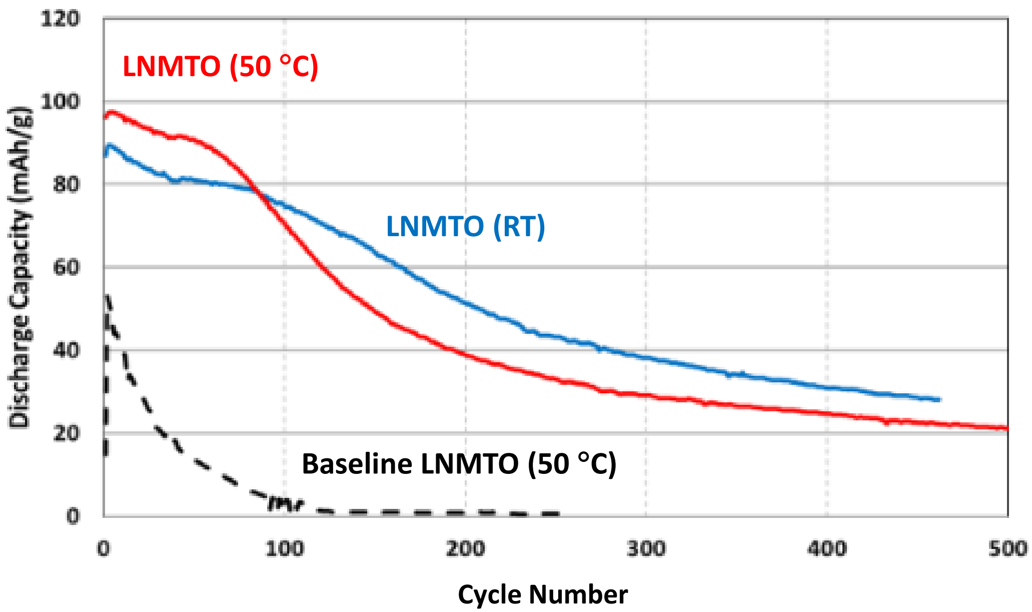
# Accomplishment: Manufactured and tested 2 Ah PPCs

## LNMTO demonstrates a significant improvement over LNMO 2-Ahr cells
## Down-selected LNMTO cell chemistry shows improved performance to baseline LNMTO




Down-select 2 Ah PPC cells: Solid-state LNMTO, LiPAA binder; Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC with 1 wt.% LiBOB
2 Ah LNMO cells: Same as PPCs but with PVdF binder
Baseline Cathode: LNTMO, PVdF binder; Anode: Superior Graphite; Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC no additive
Cycling conditions: 4.9 V to 3.5 V, C/3 (Ch) and C/3(dis) at 25 °C

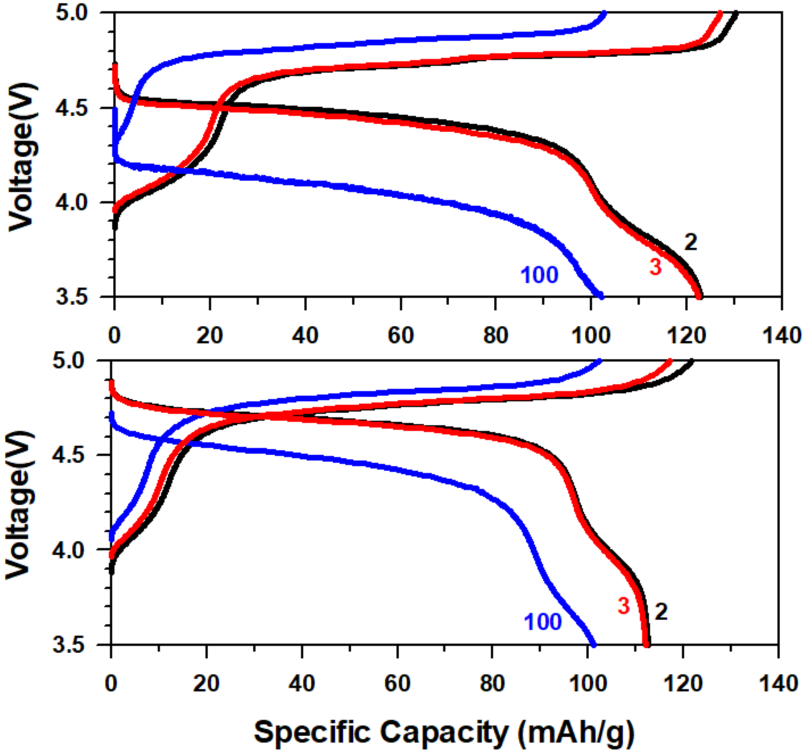
# Accomplishment: Parallel development of precipitation synthesis process

Developed parallel co-precipitation synthesis process to improve homogeneity of LNMO and LNMTO powders

**Solid State**

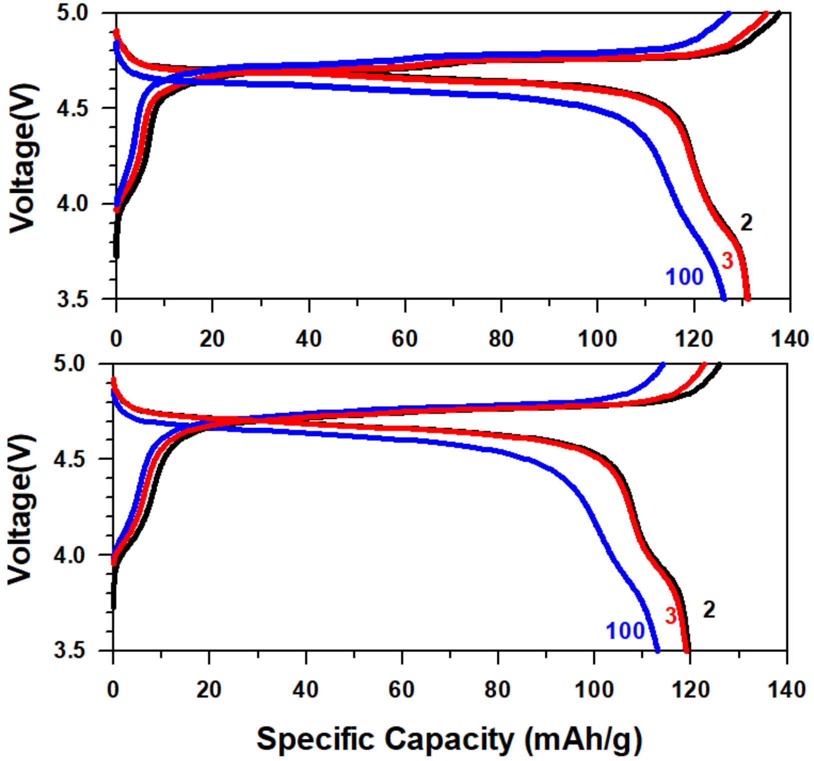
LNMO

LNMTO




Increased capacity

**Co-Precipitation**




LNMO

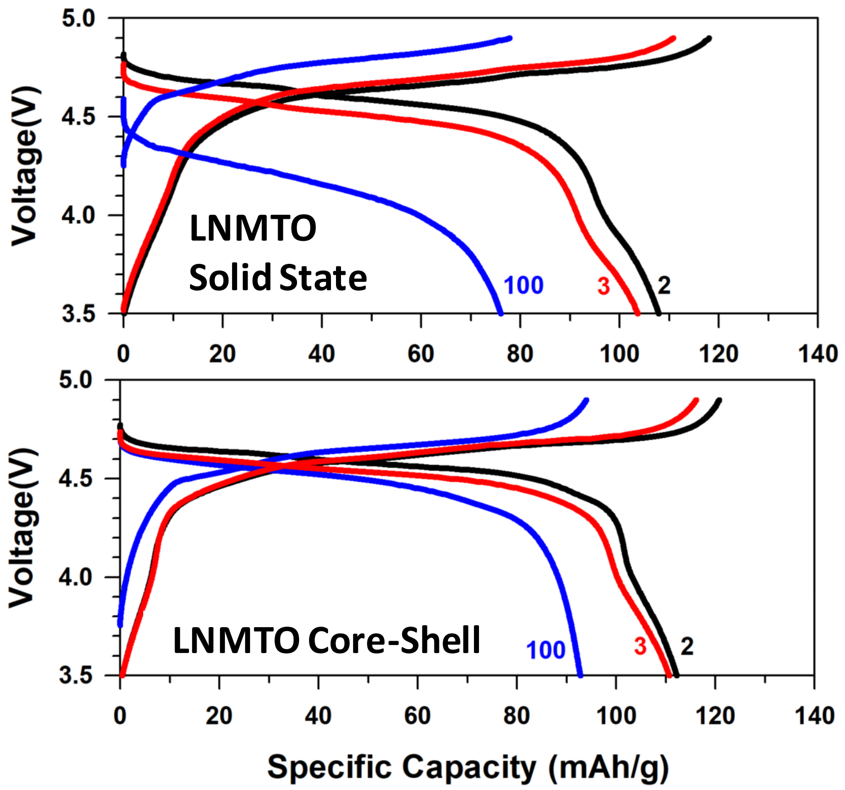
LNMTO

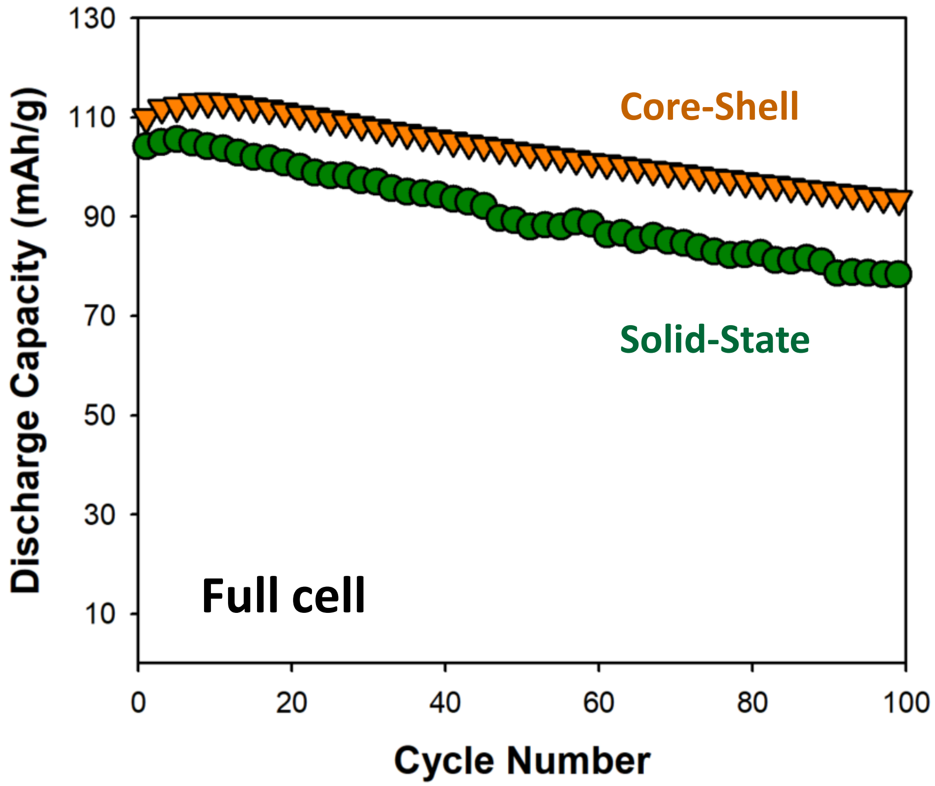
Coin-type half-cells – Cathode: LNM(T)O, PVdF binder, Anode: Li, Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC

Cycling conditions: Cycle 1: C/10 then C/5 (Ch) and C/2 (dis) at 25 °C

# Accomplishment: Demonstrated the feasibility of core/shell approach

## Potential of core/shell LNMTO microstructure to enhance performance demonstrated




Coin-type full-cells - Cathode: LNMTO, PVdF binder, Anode: Graphite, Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC

Cycling conditions: Cycle 1: C/10 then C/5 (Ch) and C/2 (dis) at 25 °C



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# Collaboration and Coordination with Other Institutions

| Project Team Member | Relationship |
|---|---|
| The Ohio State University | ○ Coin-cell and SLP cell screening of cell chemistries<br>○ Cell chemistry (additives/binder) development<br>○ Analytical characterization of cathode materials and electrodes |
| Navitas Systems | ○ Electrode scale-up<br>○ Large format 2-Ahr battery fabrication and testing |

## Other Collaboration Activities

- Very helpful discussions with teams at ANL
  - Incorporating electrolyte/electrode sample testing into FY20 development plan
- Engaged with automakers and potential end users to better understand value-proposition and T2M strategy

# Proposed Future Research

| Future Work | Justification |
|---|---|
| **Postmortem characterization of PPCs (FY20)**<br>○ Expedited analysis of SLP cells, waiting on PPCs<br>○ Ensure strategies to address degradation are incorporated into development plan<br>○ Identify collaboration opportunities | ○ Understand primary degradation mechanisms<br>○ Identify opportunities to improve cell performance (e.g., optimization of formation protocol to minimize gas generation) |
| **Refine co-precipitation synthesis process (FY20)**<br>○ Incorporate process improvements to make the process more cost-effective and scalable | ○ Current precipitation process will be difficult for Nexceris to scale |
| **LNMTO core/shell development (FY20/FY21)**<br>○ Develop approach identified in FY19 | ○ LNMO core with Ti-enriched surface enables an increase cycle-life without degrading capacity |
| **Tailoring of cell chemistries for high V cathode (FY20/FY21)**<br>○ Identification of advanced binders and electrolyte additives that complement high voltage LNMTO cathode<br>○ Address electrolyte oxidation/gas generation | ○ Primary degradation mechanisms are caused by electrode-electrolyte interactions<br>○ Critical to achieve required cell stability and cycle life |



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# Summary

## Accomplishments

- Developed a scalable solid-state process for synthesizing LNMTO cathode powder
- Down-selected a compatible cell chemistry to improve the stability of the high voltage LNMTO cell
- Completed manufacturing and testing of 2 Ah PPCs
  - Demonstrated improvement in cycle life versus LNMO baseline

## Technical Highlights

- Identified strategies to close performance gap
  - Developed co-precipitation synthesis processes for LNMO and LNMTO powders
  - Demonstrated the potential of core/shell approach


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# Technical Back-Up Slides



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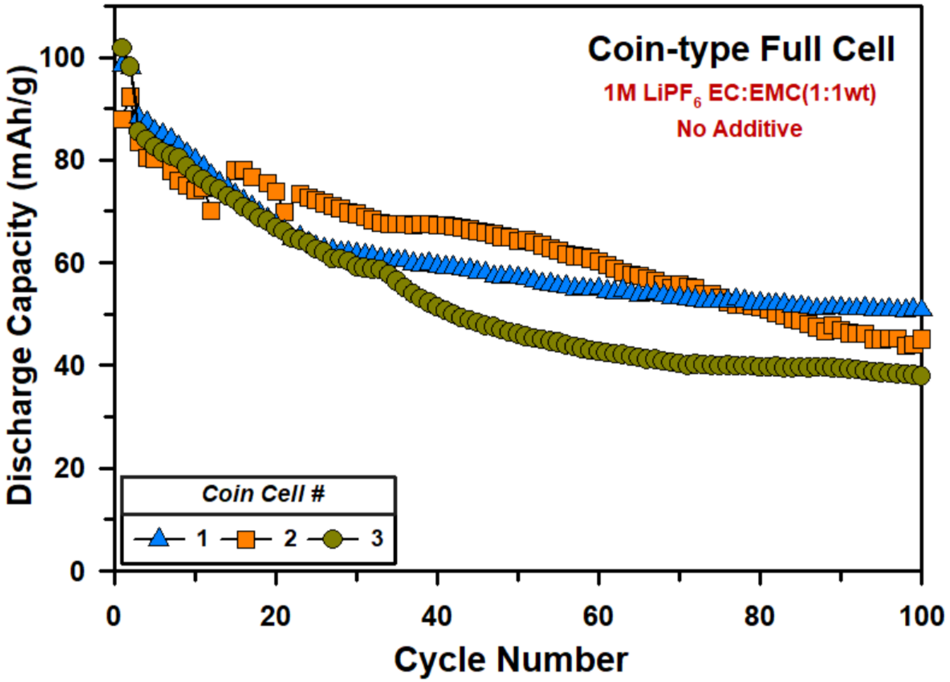
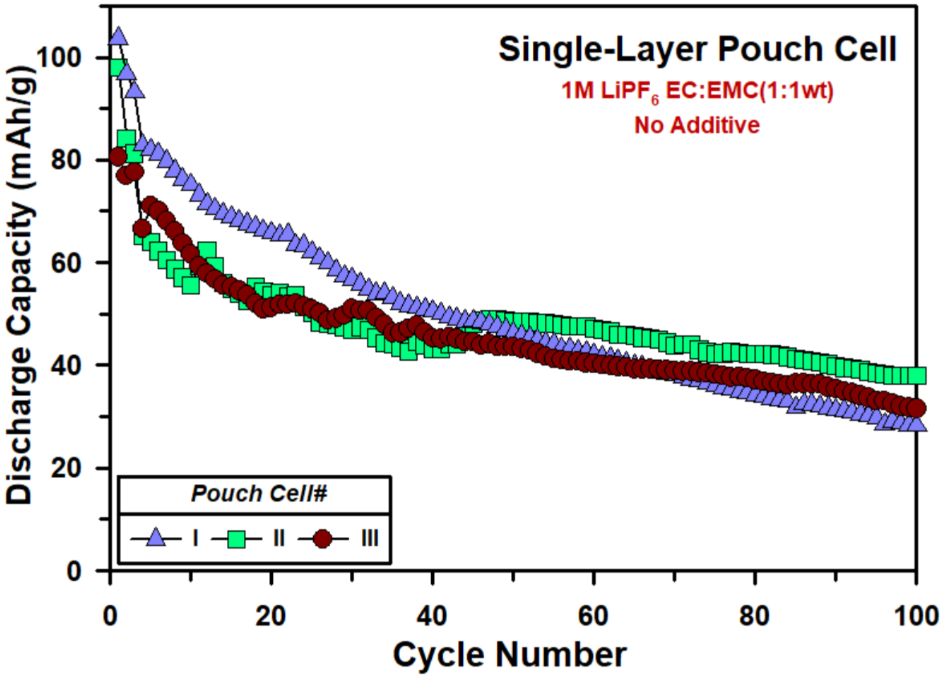
# SLP cells were used for cell chemistry optimization

SLP cells provided intermediate step to mitigate risk with manufacture of 2 Ah cells
Successfully replicated full-cell coin cell and SLP cell data

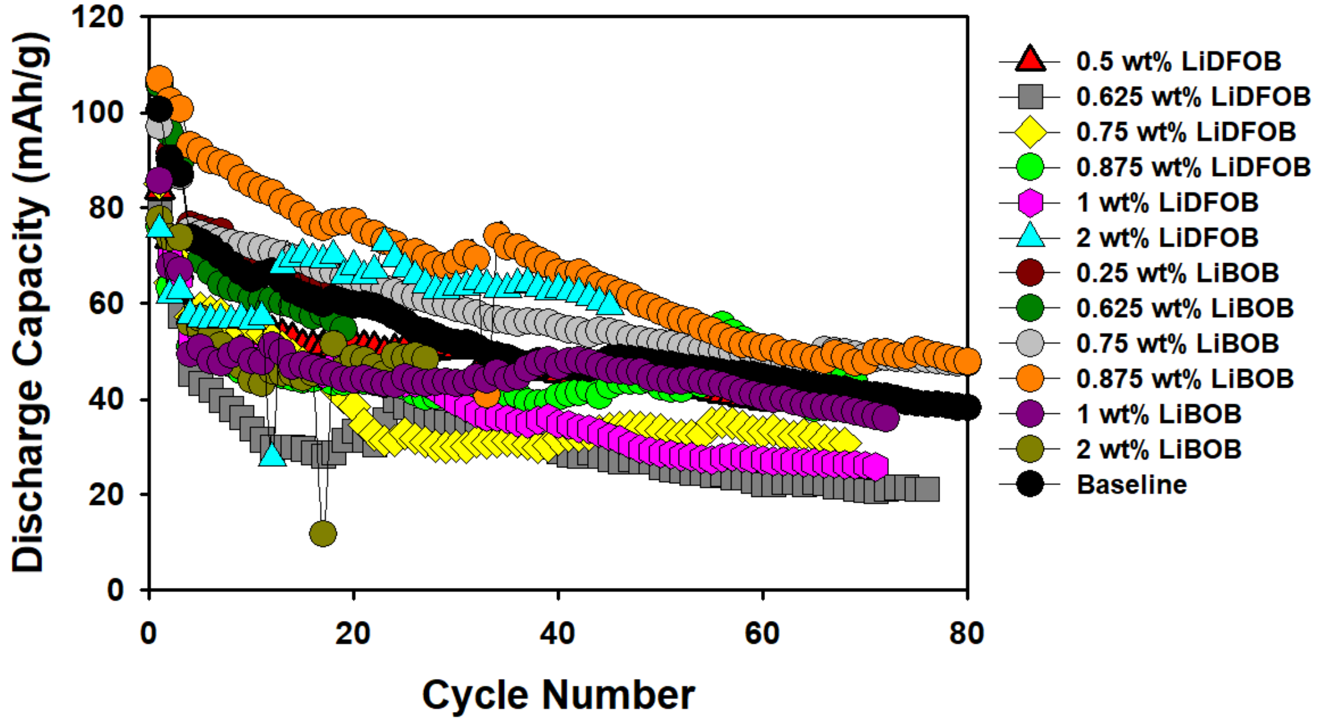



Coin and SLP-cells: Cathode: LNMTO w/ LiPAA binder, Graphite anode, Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC no additive
Cycling conditions: 4.9 V to 3.5 V, Coin: Cycle 1,2: C/10 then C/3 (Ch) and C/2 (Dis), SLP: Cycle 1 C/20, Cycles 2,3 C/10, then C/5 (Ch) and C/2 (Dis), at 25 °C

# Electrolyte Additive Screening

In FY19 screened a wide-range of potential electrolyte additives and identified LiBOB as the most effective
In FY20 a more systematic screening is being conducted based on an extensive literature review




SLP-cells: Cathode: LNMTO w/ LiPAA binder, Graphite anode
Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC with various additives
Cycling conditions: Cycle 1: C/20, C/10 (2 cycles) then C/3 (Ch/Dis) at 25 °C

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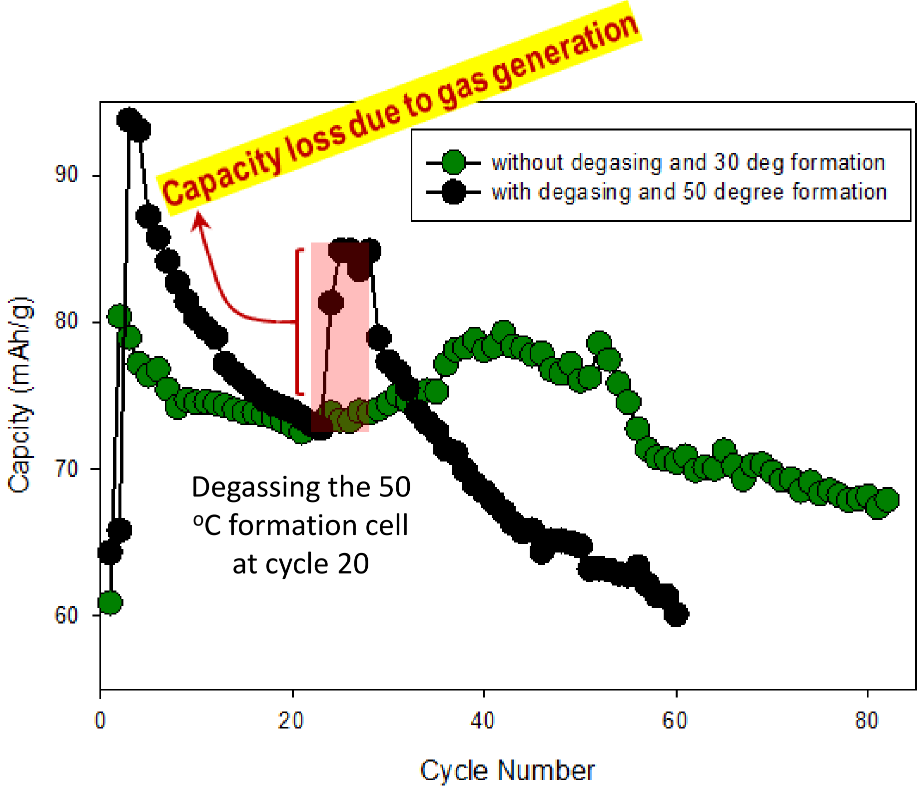
# Optimization of formation cycle protocol

Identifying the correct formation/passivation strategy key to long-term cycle life of high voltage cells

## Optimization of formation cycle procedure to address gas generation

- 50 ºC aging condition increase initial capacity at low C-rate but suffers from large cell impedance and low cycle life.
- 30 ºC aging condition shows lower initial capacity but retains cycle life
- This trend agrees very well with 2 Ah PCC cell data




SLP-cells: Cathode: LNMTO w/ LiPAA binder, Graphite anode, Electrolyte 1 M $LiPF_6$ in 1:1 wt. EC/EMC
Formation procedure: CC-CV charge to 4.9V then storage for 24 h at 50 C and 30 C. Discharge to 3.5V vacuum sealed
Cycling conditions: Cycle 1-3: C/10 then continuous C/3 (Ch/Dis) with intermittent C/20 cycle at 25 °C

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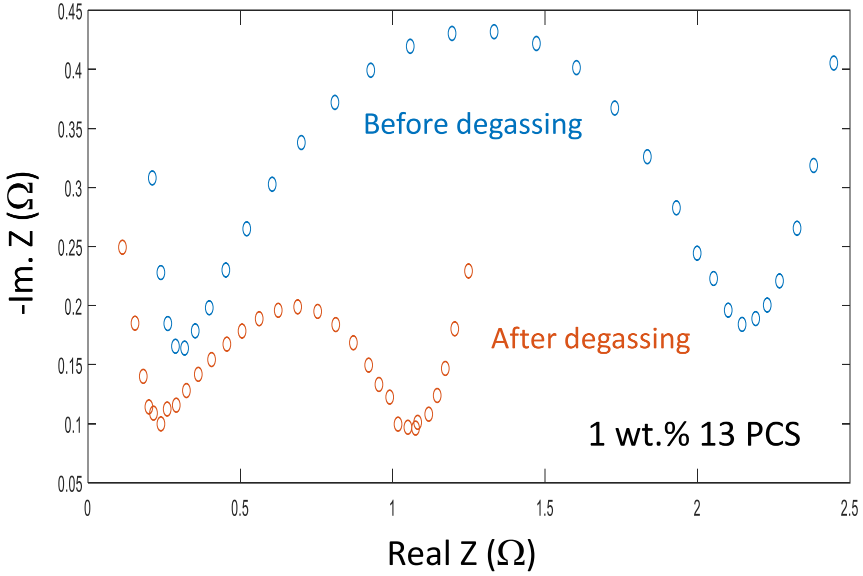
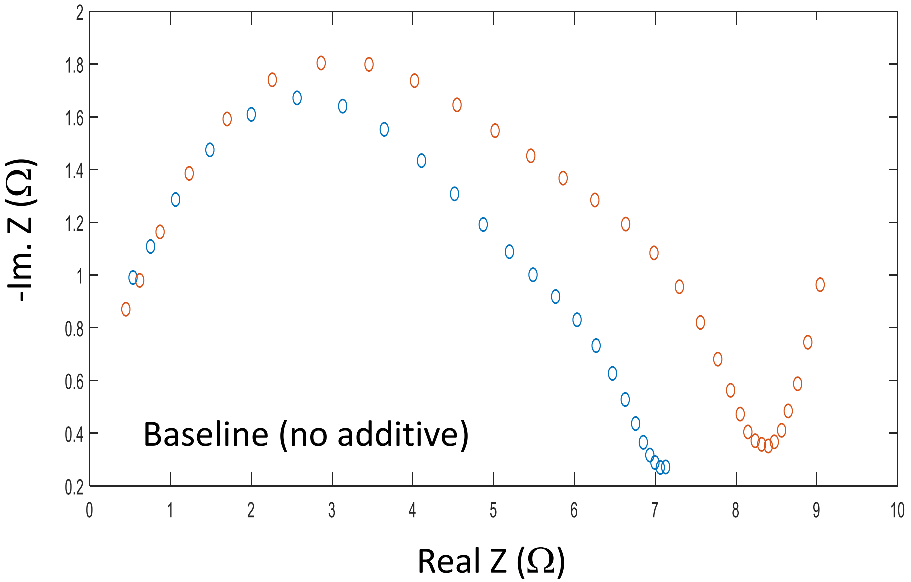
# Use of additives to reduce gas generation

## Using EIS to assess the effect of additives on gas generation




### SLP cell with 1 wt. % 13 PCS additive

- Decrease in impedance after degassing during cycling

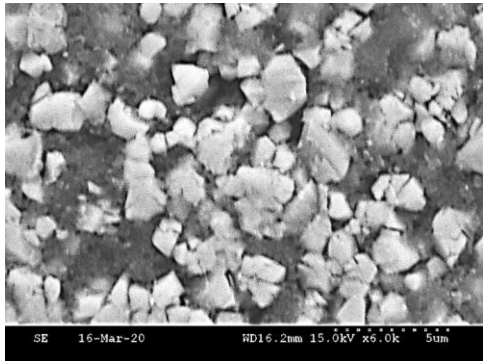
### Baseline SLP Cell (no additive)

- Slight increase in impedance after degassing during cycling (too much electrolyte removal from the cell)

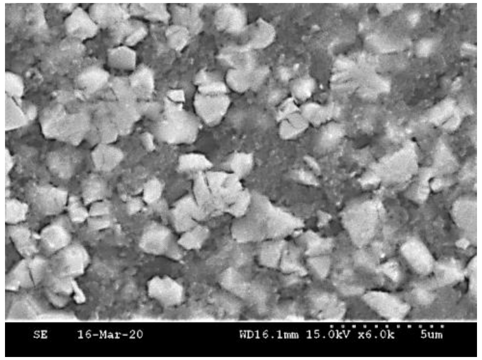
# SLP Cell Post-Mortem Characterization

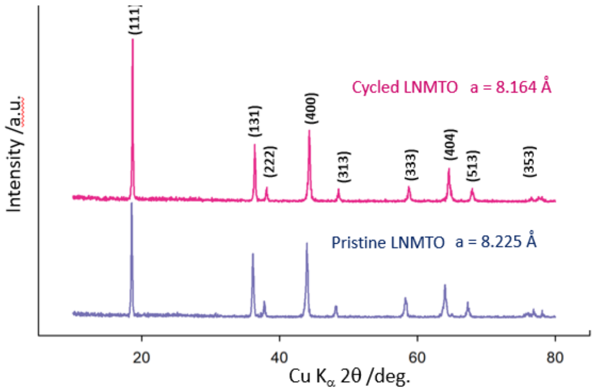
## Cycled anode SEI is destabilized by TM dissolution that occurs at cathode due to electrolyte oxidation

Pristine Cathode



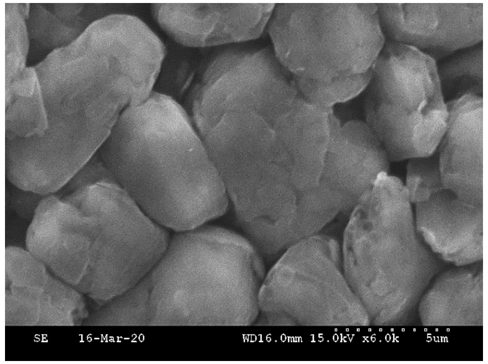

Cycled Cathode



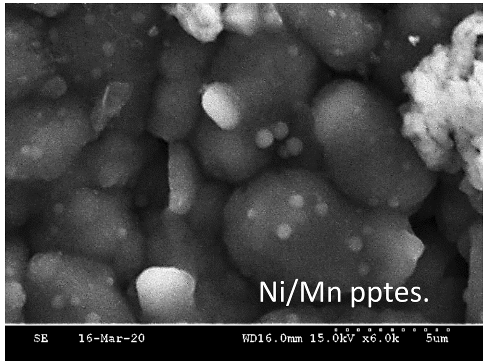



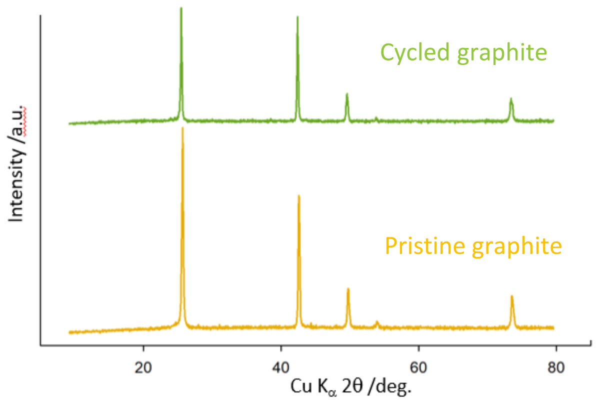

- Cathode surface looks similar before and after cycling
- ↓ lattice parameter indicates Li-loss

Pristine Anode




Cycled Anode




- Cycled anode shows graphite particles fused together due to SEI products
- TM species are reprecipitated in a reduced form at the graphite SEI
- Destabilizes SEI