Process Development and Scale-Up of Advanced Active Battery Materials

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Argonne National Laboratory
Project ID: BAT167

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Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2023
- Percent complete: On-going

Budget

- Funding for FY2023 = $1,475,000
- Funding for FY2022 = $1,200,000

Barriers

- Cost: Reduce manufacturing costs with scalable continuous processes
- Availability: Advanced cathode materials needed for research are not commercially available with the desired composition or morphology
- Performance & Life: High energy density advanced cathode materials have major performance and life issues

Partners

- EaCAM consortium
- DRX consortium
- ReCELL subgroups
- Anthony Burrell, BTMS
- Feng Wang (ANL), Ke Chen and Jianming Bai (BNL)
- Pallab Barai and Venkat Srinivasan (ANL)
- Prof. Sahar Vahabzadeh, Northern Illinois University
- Prof. Feng Lin, Virginia Tech
- Prof. Mark Hersam, Northwestern University
- Prof. Corie Cobb, University of Washington
- Prof. Zheng Chen, University of California, San Diego
- Damien Despinoy, Volexion Inc.

OBJECTIVES AND RELEVANCE

- The objective of this project is to provide a systematic research approach to:
  - Produce and provide **sufficient quantities of high quality** battery materials for large scale evaluation and to support further research
  - Evaluate **emerging synthesis technologies** for the production of experimental precursor of cathode materials (pre-CAMs) and final CAMs.
  - Develop **cost-effective, scalable** processes for manufacturing of advance materials that are not commercially available
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between invention of new advanced cathode materials, market evaluation of these materials and high-volume manufacturing
  - Enabling full-scale evaluation by multiple R&D groups
- This program provides large quantities of materials with consistent quality
  - For prototyping in large format cells
  - To allow battery community access to new materials and advance further research

MILESTONES

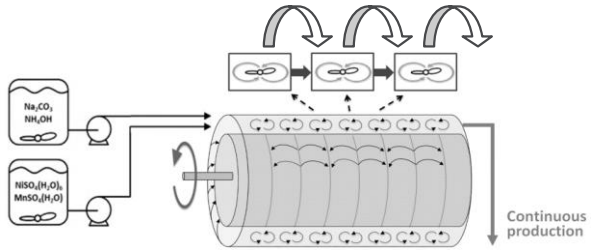
Description of Tasks/Milestones	Planned End Date	Type	Status
Co–free cathode active materials (EaCAM) Baseline formulations are identified: Li/Mn-rich (MnNi) oxides, Co-free high Mn, Low Ni oxides: (Varying Ni (↓) and Mn (↑) mol ratios & Replacing cobalt with other elements) M.1: Process R&D and synthesis: Carbonate vs hydroxide co-precipitation M.2: Produce and distribute 3 -5 materials at 50-250 g scale	**12/31/2025**	**Annual (Regular)**	**On-going**
Taylor Vortex Reactor (TVR) - residence time M.3: Investigate process parameters to produce desired materials morphology for various precursors using Taylor Vortex reactors: slow vs fast reactions (completed) M.4:Co-precipitation process for producing monocrystalline precursors (planned)	**12/31/2023**	**Annual (Regular)**	**On-going**
Calcination scale-up and optimization Investigate temperature, time, oxygen partial pressure, and furnace design/modification. M.5:Conduct process R&D to establish relationship between calcination parameters and material performance (completed) M.6: Develop optimized calcination parameters for high Ni and high Mn materials and assess scalability of the process	**12/31/2024**	**Annual (Regular)**	**On-going**
Material support for US battery community M.7: Ni-rich pre-CAMS and final CAMs (completed) M.8: Disordered rock-salt CAMs M.9: Size specific CAMs M.10: CAMs with different architectures (mono/poly - crystalline) at scale (planned)	N/A	**Annual (Stretch)**	**On-going**

APPROACH

- Develop scalable processes by implementing conventional and/or emerging synthesis technologies
- "Material compositions and particle size/morphology" requests are diverse

Taylor Vortex Reactor (TVR)

PLUG-IN-FLOW + TANK



Scalable, continuous co-precipitation

1 L TVR: 14 × 71.4 mL batch TRs equivalent

10 L TVR: 14 × 714 mL batch TRs equivalent

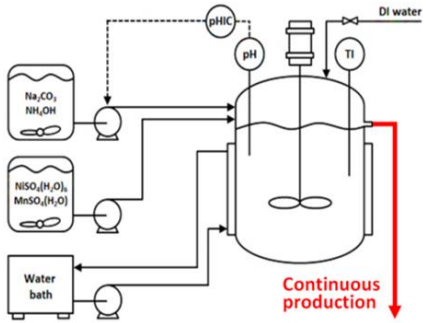
- Homogeneous intense micro-mixing zone; high mass & heat transfer
- Self particle size control
- Reduces residence times 3-fold vs same scale CSTRs (e.g. τ = 4h for TVR vs 12h for CSTR)
- Main synthesis platform to synthesize pre-CAMs

To address US battery community material needs as quickly as we can:

Providing high quality cathode precursors & cathodes that are not commercially available

Scaling up promising chemistries up to kg quantities for large scale evaluation

Continuous Stirred Tank Reactor (CSTR)



4L CSTR – conventional

Rate: 30 g/h

- For large NMC secondary particles synthesis

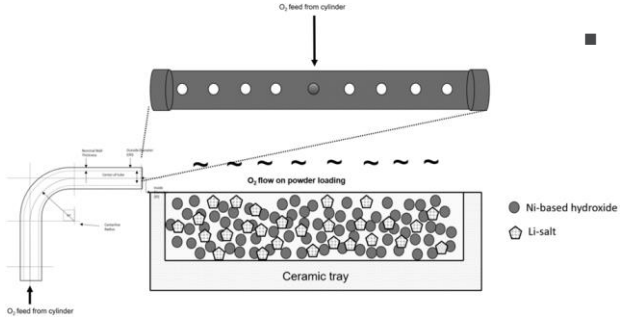
High Energy Planetary Ball Mill (batch)

Multiple uses:

- To produce disordered rock salt materials
- Particle size reduction/mixing
  - Dry/solvent milling
- 4 stations: max. 1200rpm
- YSZ jars/beads: 2 × 50ml & 2 × 500ml
- Yield: 5g (50ml) – 100g (500ml) / jar / batch

Image credit: https://www.retsch.com/imgdb/-700x-max/sl/5516bd1033aa7142326d67b6d07189c0.png

Modified Commercial Box Furnaces



- Improving gas flow patterns in commercial box furnaces by design; for high gas flow efficiency for calcination

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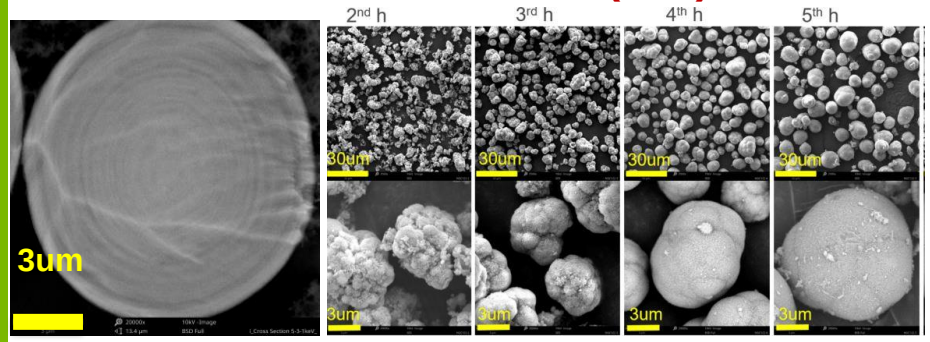
TECHNICAL ACCOMPLISHMENT

LMR-NMC Synthesis: Pre-CAM Particle Formation - Reducing Residence Time, (τ = 1 h)

- **Carbonate Route – Continuous**
  - Particles are developed as early as in 3τ
  - Nodular to spherical: after 4 τ

τ = 4h (slow) τ = 1h (fast)

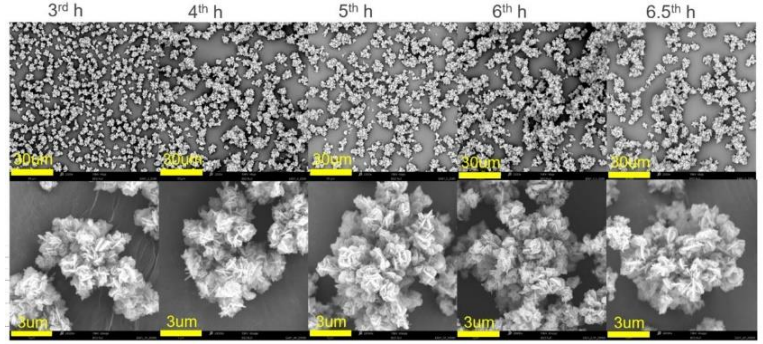


PSD (μm) → f(τ)

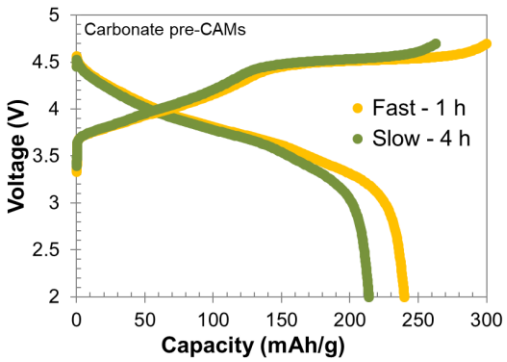
μm	1h	4h
D10	5.4	7.2
D50	9.1	16.9
D90	14.8	34.8
TD	1.7 g/cc	2.0 g/cc

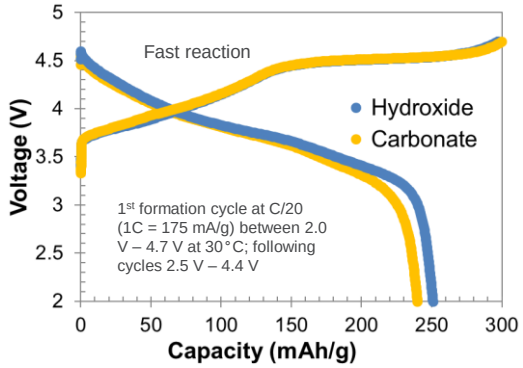
- **Hydroxide Route – Continuous**
  - Low density aggregates, consistent throughout the reaction
  - Primaries: < 1 μm size platelets with ~100nm thickness

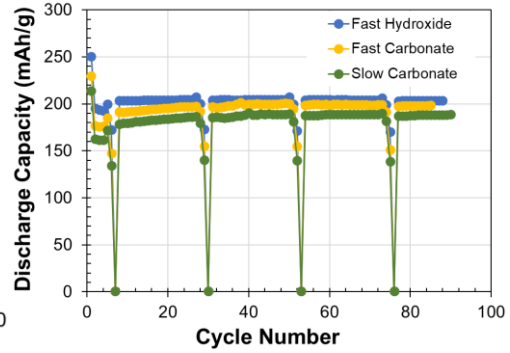
τ = 1h (fast)



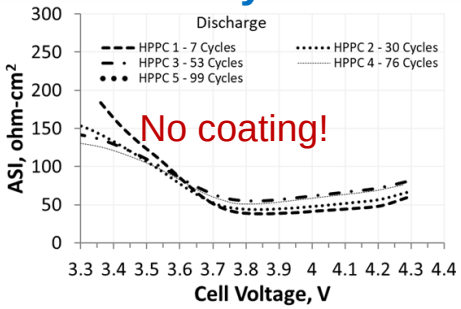
Performance comparison - f(co-precipitation routes and τ)



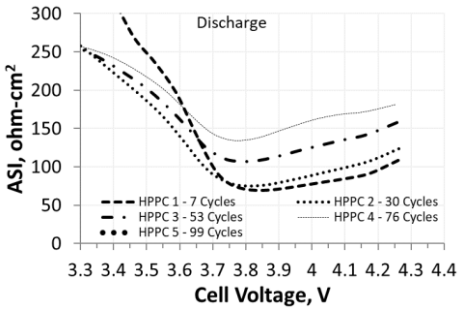




Fast hydroxide



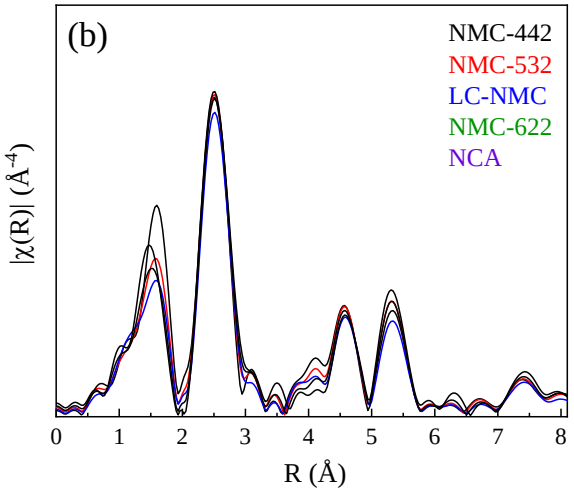
Fast carbonate



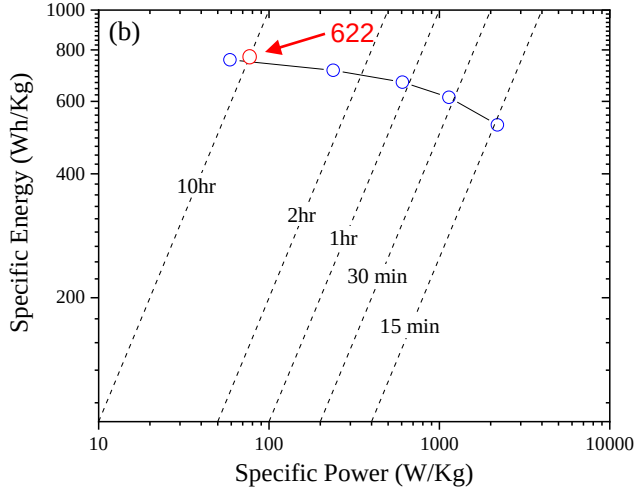
➢Reaction parameters that control **particle architectures** must be better understood for Mn-rich cathodes in order to achieve optimal performance

TECHNICAL ACCOMPLISHMENT

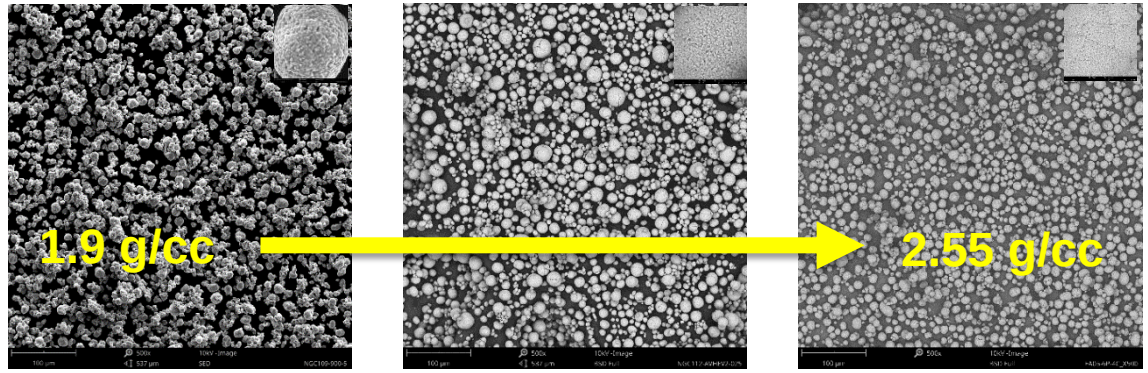
‘High Mn’, Low Ni Oxides



Croy et al., J. Power Sources, 440, 227113 (2019)



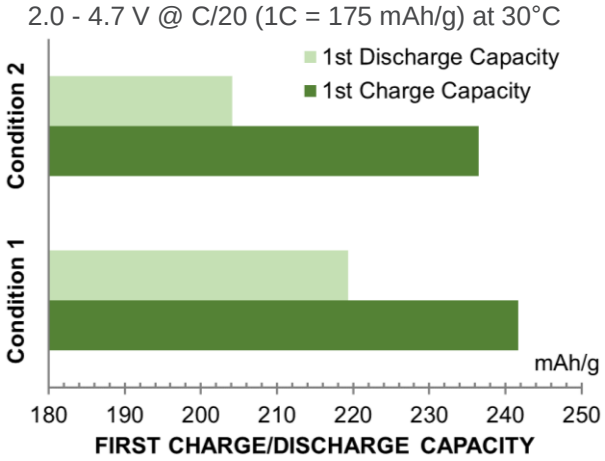
- Morphology change and PSD improvement by process R&D



Nodular, bimodal PSD | Spherical, bimodal PSD | Nodular & spherical, narrow PSD

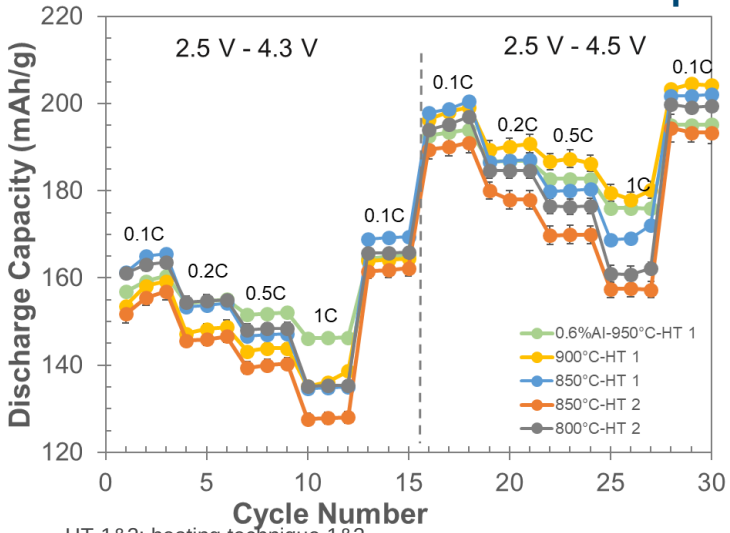
- Previous Deep Dive consortium on low cobalt cathodes developed layered materials with ‘high’ Mn contents (>30%) and ‘low’ Ni contents (<60%) with ≤5% Co showing performance on par with NMC-622
- MERF is now developing advanced versions of these materials through synthesis studies to help i) increase Mn contents while lowering Ni contents, ii) optimize select dopant incorporation in the co-precipitation process, iii) maximize particle densities while maintaining performance, and iv) transfer knowledge to scale-up efforts for distribution to the EaCAM team for further study
- Initial studies have focused on optimization of co-precipitation conditions as well as calcination/lithiation of precursors
- Synthesis and processing of Mn-rich, layered oxides are being fully explored to help meet the goals of VTO’s EaCAM consortium

1st Cycle Performance



Variables	1st D.Cap	1st C.E.
Condition 1	219 mAh/g	90.8%
Condition 2	204 mAh/g	86.3%

Rate Performance vs Calcination Temp



HT-1&2: heating technique 1&2
2-cell average*

- Calcination temp, time and atmosphere are being tailored to optimize capacity and rate

TECHNICAL ACCOMPLISHMENT

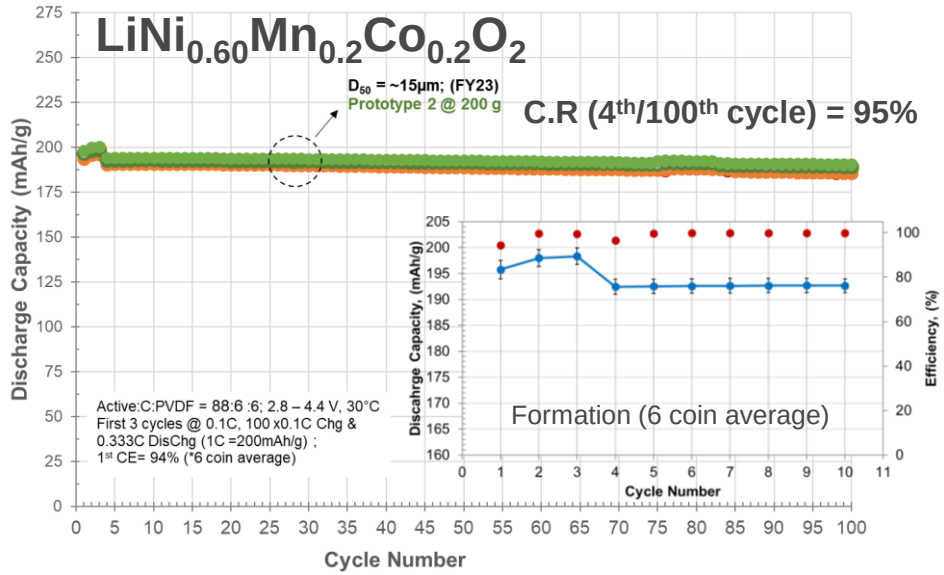
LNO-based cathodes – Calcination studies for efficient oxygen flow

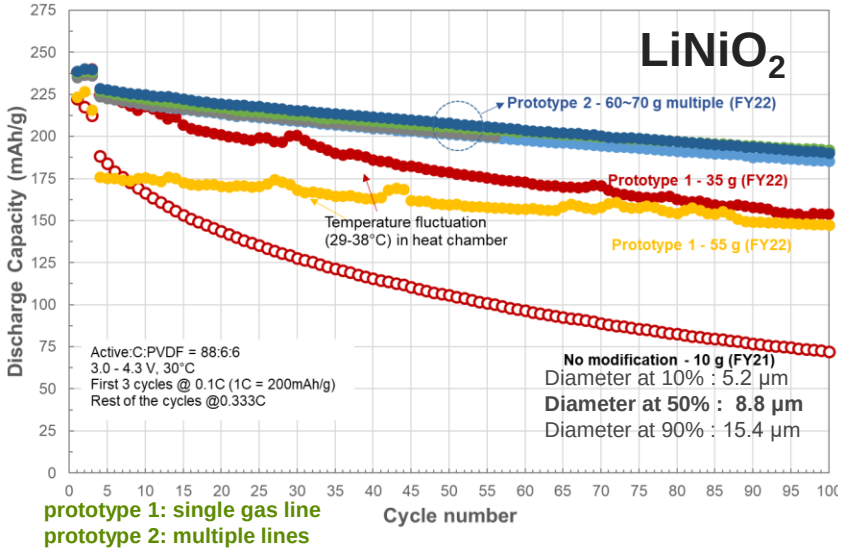
Issue: Inefficient oxygen partial pressure on powder loading in box furnaces due to the irregular gas flow/exhaust pattern, leading to poor O_2 gas diffusion to the bath – high O_2 pp is essential for the lithiation of LNO-based oxides

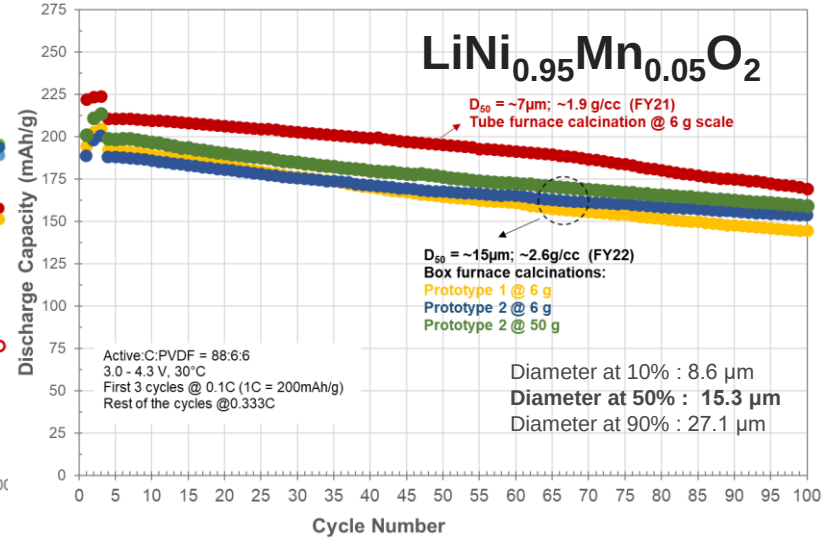
- Two prototypes of gas line fixtures (metal) were designed for commercial lab scale box furnaces for high and homogeneous gas flow
- Cathodes were calcined under oxygen flow for 12 h: (composition dependent T_{calc} between: 650°C – 800 °C)

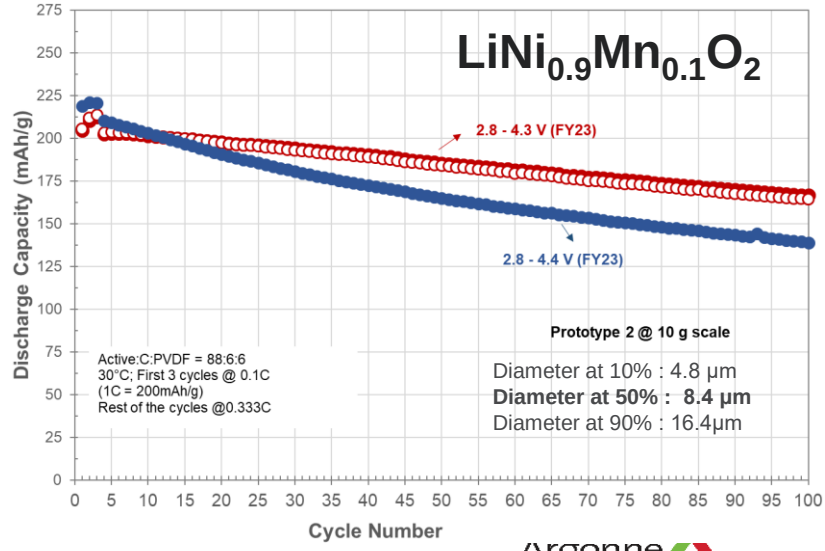
➢ All CAMs are pristine with no surface coatings → improved capacity retentions (e.g. 81% for $LiNiO_2$, 82 % for both $LiNi_{0.95}Mn_{0.05}O_2$ and $LiNi_{0.9}Mn_{0.1}O_2$ after 100 cycles.

➢ Calcination batches were successfully scaled up: initially from 5-10 g to 30-50 g; and to 200 g single batch operation (e.g. for NMC622)









➢ Metal fixtures worked well at lower temperatures (≤800°C). High T calcinations requires different metals/alloys.

TECHNICAL ACCOMPLISHMENT

BAT183, BAT402

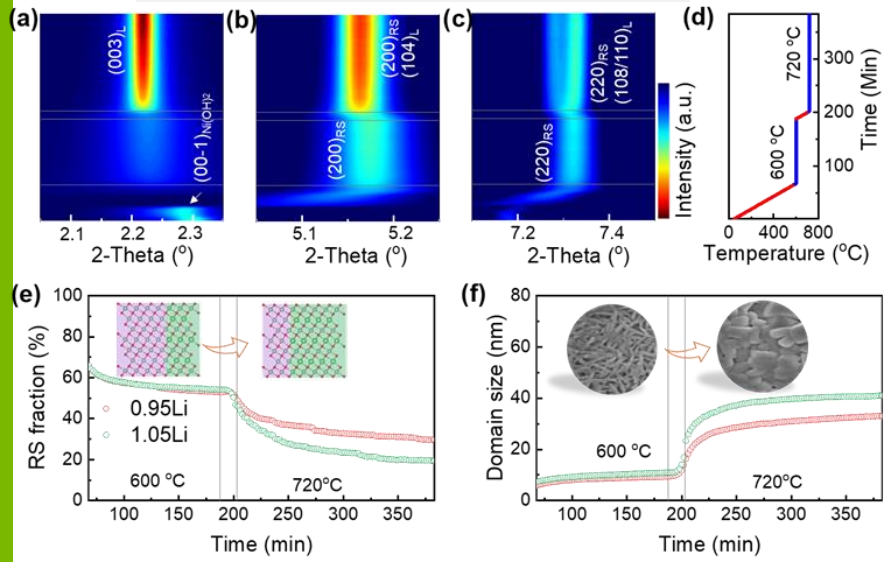
Stabilizing Co-free Ni/Mn-Based CAMs

- Identify the impact of lithium stoichiometry on structural and morphological tuning of Ni-based Co-free cathode materials (low/no cobalt Deep-Dive chemistries) during calcination.

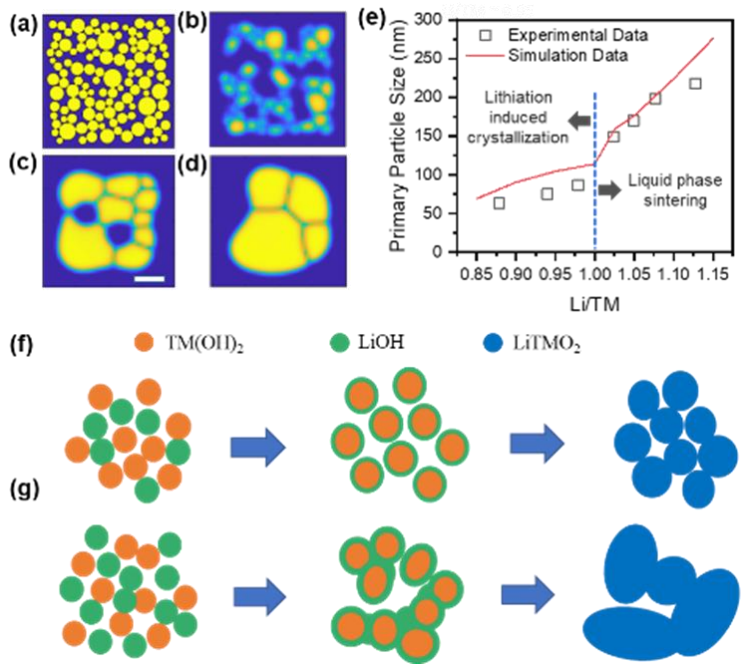
$Ni_{0.95}Mn_{0.05}(OH)_2$ with varying Li:TM molar ratios

$Li_xNi_{0.95}Mn_{0.05}O_2$; $(0.9 \le x \le 1.1)$

Real time tracking
(*in situ* XRD)



Multiscale Modeling
(correlated with experimentation)



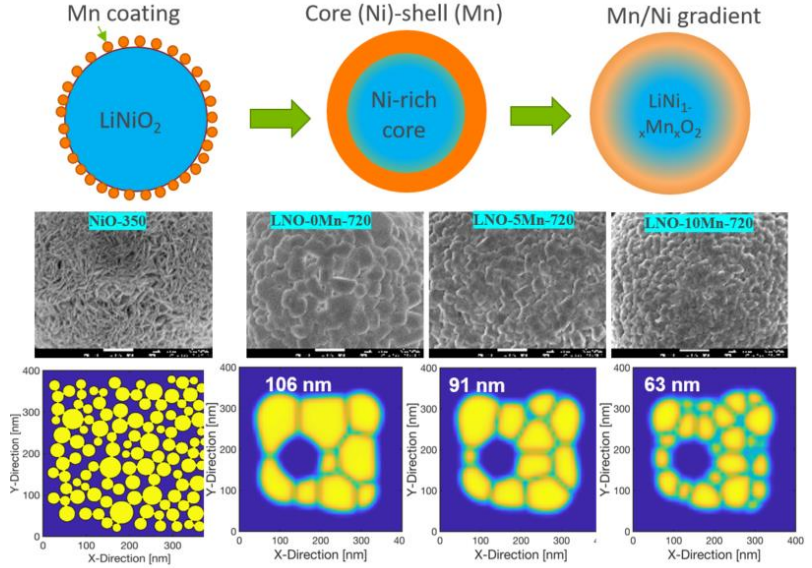
- Li-deficiency: hindering crystallization and inter-particle fusion, resulting in rocksalt/layered composites
- Li-stoichiometry control: a generic approach for stabilizing Co-free Ni/Mn-based CAMs

*Paper publication is submitted

Data (FY23) credit: Drs. Feng Wang, Pallab Barai, Venkat Srinivasan (ANL), and Jianming Bai and Ke Chen (BNL)

NiO (*pretreated* $Ni(OH)_2$) with varying Mn-dopant*

$LiNi_{1-x}Mn_xO_2$; $(0.0 \le x \le 0.1)$



$Ni(OH)_2 \xrightarrow{350°C}$ NiO

- **Size decrease with Mn-substitution**
  - Surface energy of Mn-substituted LNO is very similar to LNO
  - Mn-dopants limit the grain boundary mobility

*On-going collaborative activity (BAT183; BAT402)

All materials are TVR-products

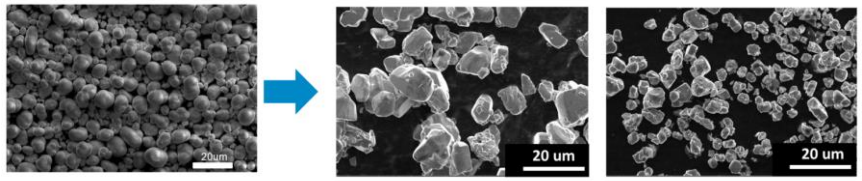
TECHNICAL ACCOMPLISHMENTS

Providing Materials for US DOE Battery Community

RECELL Sub-groups (continued support)

Objective: Ni precursor is used to convert low-Ni cathode into high Ni-cathodes
- TVR-made pure β-Ni(OH)$_2$ mixed with NCM111→ Upcycled NCM622 and NCM811

Request: pure β-Ni(OH)$_2$ (**≥ 400 g**)
➢ Address future needs to enable UCSD's technology

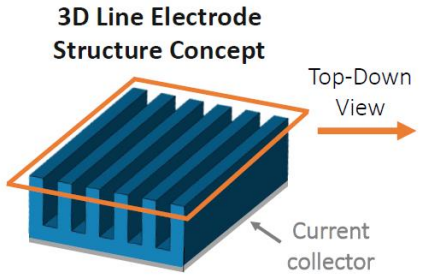


β-Ni(OH)$_2$ Upcycled NCM622 Upcycled NCM811

Prof. Zheng Chen, Hongpeng Gao, Xiaolu Yu from University of California, San Diego

University of Washington (UW), AMMTO project DE-EE00009112 (new)

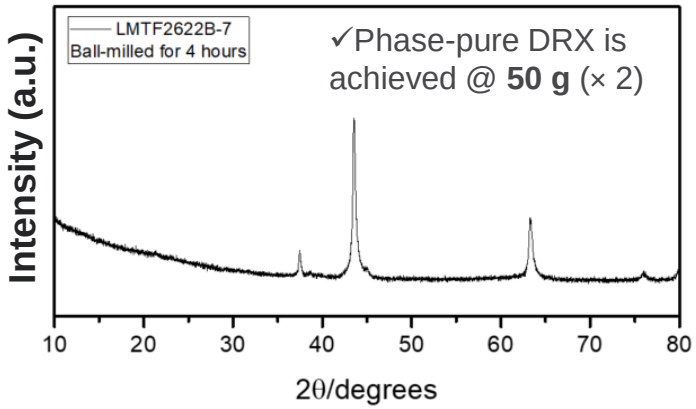
Objective: Use acoustic additive manufacturing process to pattern thick, fine feature 3D Lithium-ion battery electrodes over large areas
Target: minimum of a 10% improvement in Wh/L and Wh/kg over conventional Lithium-ion battery pouch cells
Request: $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ material (made by CSTR) with large particles (D_{10}:~10μm; D_{50}:~20μm; D_{90}:≤35μm) with narrow particle size distribution (**~1 kg**)
Preliminary Results: The MERF NMC-622 improves UW's 3D electrode structures and acoustic process consistency relative to commercially available materials

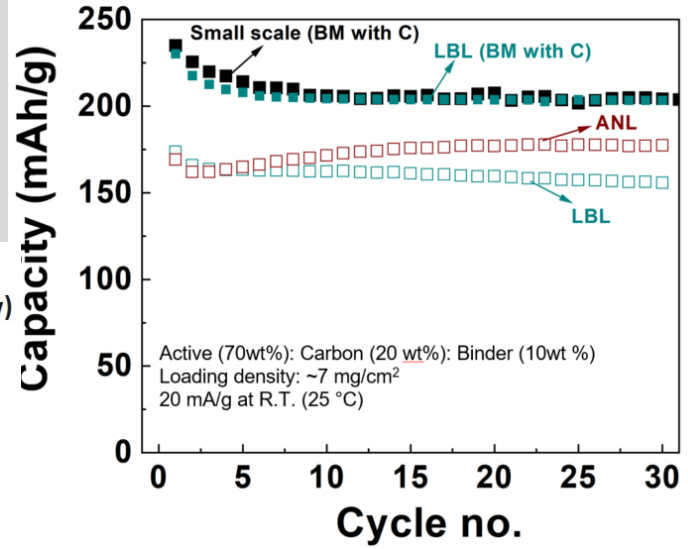


DRX Consortium (new)

Request: Scale up DRX Gen1 cathode from ~5 g scale to ~50 g

Approach: Use a high energy planetary ball mill, followed by calcination





E-chem data by Haegyum Kim

Accomplishments:
- Eliminated the need of pelletizing
- Achieved phase-pure DRX structure at 50 g scale (× 2)

Feedback from DRX partners:
✓ANL and LBL samples show similar specific capacity and stable cycling.
✓ANL sample shows slight capacity increase for initial 10-15 cycles.

For more details, see:
BAT570 (Gerd Ceder)
BAT589 (Guoying Chen)
BAT597 (Bryan McCloskey)
BAT598 (Robert Kostecki)

TECHNICAL ACCOMPLISHMENTS

Providing Materials for US Battery Community

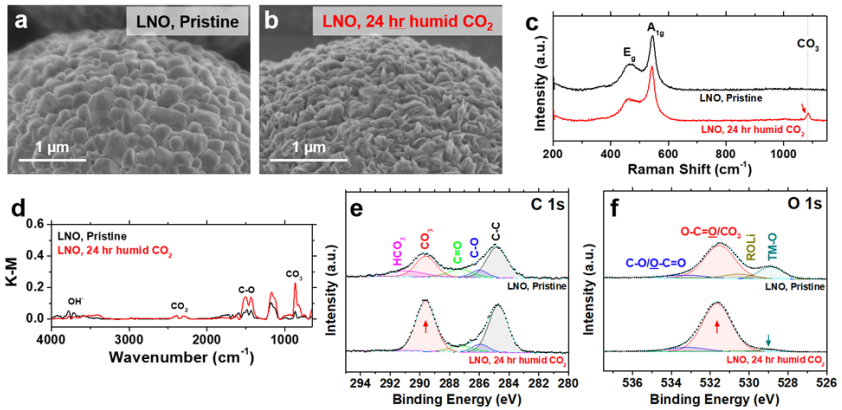
Northwestern University (continued support)

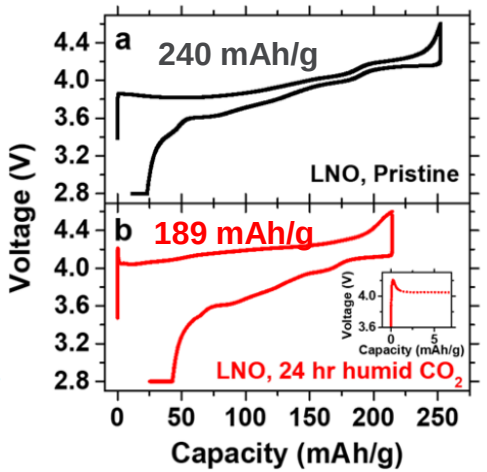
Request: surface clean $LiNiO_2$ → synthesized using modified box furnaces

FY22-23 objective*: TVR-made materials (≤8 μm) were used as baseline materials for "enabling ambient storage of $LiNiO_2$ lithium-ion battery cathodes via a conformal, hydrophobic graphene-ethyl cellulose coating"

Address future needs; support & provide Mn-rich NMC materials at scale

Smooth surface (pristine) → rough surface (humid CO_2)





Raman, DRIFTS-FTIR and XPS spectroscopic results:

- Relatively clean surfaces for pristine LNO
- New, carbonate-rich layer for the LNO surface during exposure to humid CO_2
- Surface clean LNO by MERF has higher Ch./DisCh. capacities with minimal polarization vs humid CO_2 exposed LNO

Activation cycle: 2.8 V – 4.6 V vs. Li/Li^+ at C/10 (A:C:PVD=90:5:5)

*Paper publication is submitted

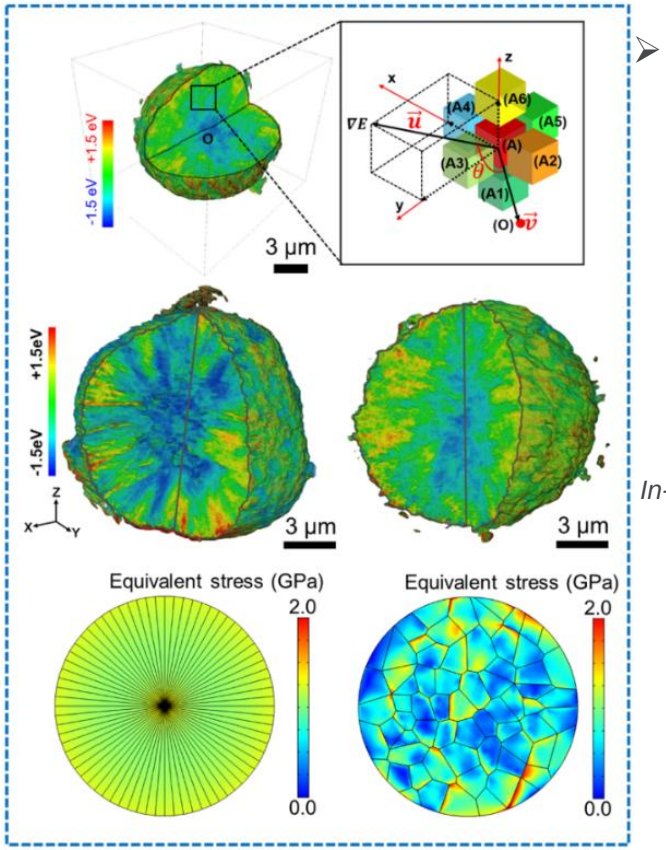
Prof. Feng Lin at Virginia Tech (FY23, new)

Request: Wide range of pre-CAMs with different particle sizes

Objective: VT investigates how different precursors can lead to different grain growth behaviors and different battery electrochemical and safety characteristics

Material support (by TVR): 14 different pre-CAMs at ~**1.1 kg**

SOC distribution within a single particle



- TVR-made materials have being used to synthesize CAMs with different microstructures to investigate how the microstructures impact the SOC distribution

In-situ transmission X-ray microscopy

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project wasn't reviewed last year.

COLLABORATIONS

- Earth Abundant Cathode Active Materials Consortium (EaCAM), earlier Low/No Cobalt Deep-Dive
  - Several institutions, inter/intra project subgroup collaborations (MERF, CAMP, BTMS, Deep-Dive)
- Pallab Barai, Venkat Srinivasan (BAT 402, ANL) and Feng Wang (ANL), Jiangming Bai, Ke Chen (BNL) (BAT183)
  - In-situ spectroscopy and modelling studies for Ni100- and Ni95-compositions
- ReCELL subgroups
  - Eva Allen, Albert Lipson → Co-precipitation byproducts for upcycling NMC pre-CAMs (~100L) and 4L CSTR runs
  - Prof. Zheng Chen, Hongpeng Gao (UCSD) → pure β-$Ni(OH)_2$
- DRX Consortium subgroups → scaled up GEN 1 DRX material
  - Gerd Ceder, Guoying Chen, Robert Kostecki, Vince Battaglia, Haegyum Kim, Bryan McCloskey and DRX team
- Jianlin Li (ORNL) → CAMs with different architectures (planned)
- Francis Kim (PhD candidate) and Prof. Sahar Vahabzadeh (NIU) → supporting young researchers in local universities
- Jonathan Pistorino, Damien Despinoy (Volexion Inc.)→ continued materials support for encapsulation technology improvement
- Norman Luu, Mark Hersam (NU) → material support for basic R&D
- Emilee Armstrong (PhD Candidate) and Prof. Corrie Cobb (UW) → supporting AMMTO project
- Prof. Feng Lin → material support for basic R&D

REMAINING CHALLENGES AND BARRIERS

- Synthesis of cobalt-free, manganese–rich pre-CAMs thru a continuous co-precipitation is challenging:
  - Maintaining steady-state conditions in continuous carbonate co-precipitation with P&ID vs fixed flow rates → pH fluctuation (phase-segregation, compromised morphology) vs slow pH rise (onion peel like layering)
  - Small and loose particle formation in continuous hydroxide co-precipitation (for fast reactions at high pH); incomparable results with “batch” reactions in tank reactors with the same pH and NH_3:TM mol ratios.
- TM-hydroxides with Mn content are not stable and degrade (oxidize) during washing/filtration/drying process right after the co-precipitation reaction
- LMR-NMCs with small particle sizes (≤1 µm plates having <100nm thicknesses), low density and, high surface areas outperform industry standard sizes (15-20 µm) and morphologies (spherical)
- Calcination scale-up for next generation cathode chemistries (Ni-based) is slowly improving
  - Requires multiple batch operations to obtain 1 kg of final CAM using lab scale box furnaces
  - Lab scale tube furnace has a lower batch size compared to box furnaces
  - New heating technologies are needed
- Material requests (pre-CAMs, CAMs, different compositions, morphologies and/or particle sizes) are diverse and the needs are urgent
  - Requires using different process technologies to address the US battery community needs

PROPOSED FUTURE RESEARCH

- Material synthesis on a wide range of Mn-high, Ni-low cathodes with and w/o Co, (0.00≤[Co]≤0.05) polycrystalline baseline cathode materials (for EaCAM consortium);
  - Varying Ni:Mn molar ratios → started
  - Replacing cobalt with an element of interest (e.g.; Al, Mg, Zn, Sn and etc.) → planned
  - Selection of co-precipitation route (chelating agent) per varying Ni:Mn molar ratios → started
  - The effect of particle size and morphology on the electrochemical performance → started
- In depth research activities for the selection of atmosphere controlled lab scale calcination furnace-types for CAM synthesis → planned
- Continue supporting battery research community by providing and making available advanced cathode material → continued effort
  - Commercially unavailable precursor materials (e.g.; NMC hydroxides and/or carbonates)
  - Commercially unavailable cathode compositions (e.g.; LNO-based cathodes, Co-free cathodes, DRX cathodes)
  - Commercially unavailable cathode particle sizes/morphologies (e.g.; small particles (D_{50}= 3-8 µm),and/or large particles
  - Continue on synthesis of CAMs by design (e.g.; in-situ calcination → modelling)
- Suggestions are welcome for scaling up newly invented, promising battery materials

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

SUMMARY

Several Different Cathode Materials: Synthesis, Scale up and Delivery

- Synthesized and/or scaled up commercially unavailable cathode and/or precursor materials for process development studies and for US battery community
  - LMR-NMC materials ($Li_{1+a}Mn_{0.65}Ni_{0.35}O_2$) – fast co-precipitation using carbonate & hydroxide synthetic routes using TVRs → process flaws in maintaining steady state conditions (carbonate) & small particle formation (hydroxide)
  - High Mn, low Ni NMCs (with low cobalt; ≤0.05)
    - Varying Ni:Mn molar ratios via continuous co-precipitation syntheses using TVRs
    - Calcination optimization (Li:TM ratio, temperature (↓), time (↓), atmosphere, heating profile and furnace type)
  - Calcination studies for LNO-based cathodes via modifications for efficient gas flow
    - Increased the batch size from 5-10 g scale to 200 g single batch operation → improved capacity retentions
  - $Ni_{0.95}Mn_{0.05}(OH)_2$ – Reproduced using TVR → continued material support for BNL
  - $Ni(OH)_2$ and $Ni_{0.90}Mn_{0.10}(OH)_2$ → reproduction (2kg/pre-CAM) using TVRs for continuous support to different groups
    - MERF, Low/No Cobalt Deep-Dive, CAMP, BTMS
    - ReCELL subgroups
  - Size specific, $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ CAMs periodic production using 4L CSTR-products to enable 3D acoustic electrode manufacturing technology → material support for University of Washington (AMMTO)
  - DRX GEN1 baseline material → scaled up (3-5 g scale to 200 g scale) using HE-BM route for DRX consortium
    - Eliminated the need for pelletizing (time consuming) and scaled up calcination at 50 g scale for single batch
  - Surface clean LNO cathode materials (size specific; ~8 µm) for exploring environmental degradation of Ni-based layered oxides and for surface impurity removal studies (NU & Volexion) → continued support

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- Seong-Bum Son
- Venkat Srinivasan

External

- DRX partners (LBL,PNNL,ORNL,UC Berkeley)
- BTMS (NREL)
- Jianming Bai and Ke Chen (BNL)
- Prof. Sahar Vahabzadeh (NIU)
- Prof. Feng Lin (VT)
- Emilee Armstrong and Prof. Corrie Cobb (UW)
- Prof. Zheng Chen, Hongpeng Gao (UCSD)
- Prof. Mark Hersam (NU)
- Damien Despinoy (Volexion)

TECHNICAL BACKUP

STRATEGY

- Define target cathode active material (CAM)
  - Evaluate bench-scale samples from material development groups
- Select synthesis technology and process
  - Taylor Vortex Reactor (TVR) or Continuous Stirred Tank Reactor (CSTR)
    - Carbonate and hydroxide co-precipitation
  - High Energy Ball Mill (HE-BM)
  - Calcination - Solid-State (SS)
    - Atmosphere controlled/modified box furnaces
    - Tube furnaces (electric and/or alternating magnetic field)
- Optimize synthesis condition
  - Tailoring particle properties & compositions
- Produce 100s g intermediate materials
  - Product validation
  - Synthesis improvement & optimization based on feedback
- Reproduction and scale-up
  - Material characterization and reproducibility check
  - Large scale production (when needed)
- Feedback from the collaborators and recipients