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/end dates: Oct. 2010 / Sept.2025
- Percent complete: On-going

Budget

- Funding for FY2024 = $1,475,000

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 storage-life issues

Partners

- Feng Wang (ANL) and Jianming Bai (BNL)(BAT183), Pallab Barai and Venkat Srinivasan (ANL) (BAT402),
- Prof. Corie Cobb (University of Washington)
- Prof. Stanley Whittingham (Binghamton University)
- Prof. Sahar Vahabzadeh (Northern Illinois University)
- Jacob Jin (Austin Elements)
- EaCAM
- Joe Libera (ANL) (BAT315)

OBJECTIVES AND RELEVANCE

- The objective of this project is to provide a systematic research approach to:
  - Develop continuous and scalable processes for the manufacturing of advanced cathode materials that are not commercially available
  - Implement advanced synthesis technologies that can reduce the time and cost of manufacturing
  - Provide high quality, custom-made cathode precursors & cathodes that are not commercially available
  - Scale up promising chemistries up to kg quantities for large scale evaluation
  - Tailor particle properties based on the requests by collaborators
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - To sustain development and scalable synthesis of “hard-to-make” and on-demand materials which are essential for accelerating innovation in battery technologies.
  - To support the battery research community by advancing process engineering strategies to improve accessibility and reproducibility of these next-generation materials

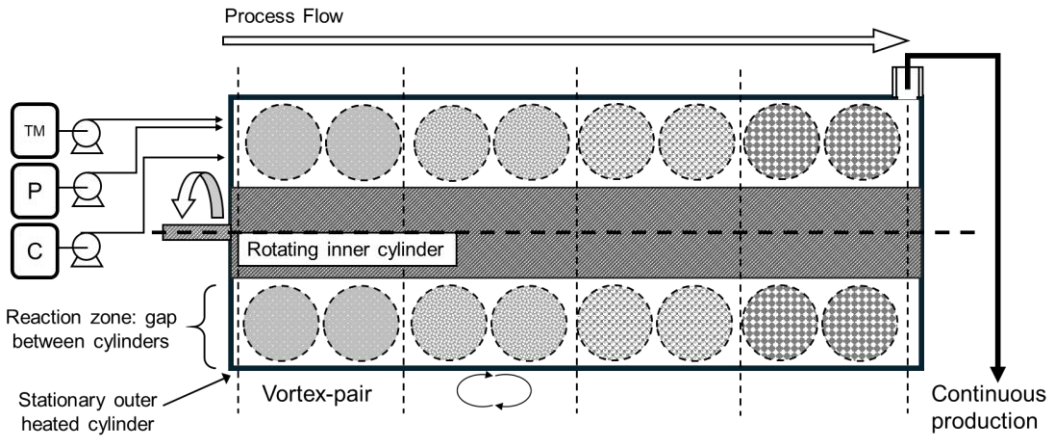
MILESTONES

Description of Tasks/Milestones	Planned End Date	Type	Status
Task 1. Investigate low-waste and greener domestic pCAM production M1.1. Ammonium free co-precipitation of Co-free cathode pCAM using Taylor Vortex Reactor. Screening compatible complexing agent is selected from non-hazardous chemicals. M1.2. pCAM optimization that meets performance metrics matching industry standard pCAM materials. M1.3. Calcination optimization of earth abundant CAMs.	**12/31/2025**	Annual	In progress Completed In progress Completed
Task 2. Explore co-precipitation processes utilizing other than sodium hydroxide and sulfate-based salts for pCAM production M2.1. Asses the applicability of the reactants other than sulfates for the pCAM production process. M2.2. Improve pCAM particle morphology	**12/31/2025**	Annual	In progress Completed In progress
Task 3. Explore advanced heating technologies for calcination process. M3.1. Asses the feasibility of induction heating technologies for calcination of next generation CAMs -Establishment of benchtop low&medium frequency induction heating equipment.	12/31/2025	Annual	In progress Completed Future work
Task 4. Address needs for experimental materials for domestic battery research community	12/31/2026	Annual	In progress

APPROACH - STRATEGY

- Develop scalable processes by implementing emerging synthesis technologies

Taylor Vortex Reactor (TVR) – pCAM Synthesis



Adjustable particle sizes: 3 – 15 µm
Production rate: ~20g/h (1L) & ~200g/h (10L)

Main synthesis platform to synthesize pCAMs since 2015

Conventional hydroxide co-precipitation process

$$M^{2+} + \boldsymbol{n}\mathbf{NH_4OH} \rightarrow [M(NH_3)_n]^{2+} + 2H_2O$$

$$M(NH_3)_n]^{2+} + 2OH^- + nH_2O \rightarrow M(OH)_2 + 2H_2O + \boldsymbol{n}\mathbf{NH_4OH}\uparrow$$

$$[MSO_4 + 2NaOH \rightarrow M(OH)_2 + \mathbf{Na_2SO_4}]\downarrow$$

Low-Waste pCAM Production Approach

Task 1 / Strategy 1: Ammonium-free reactions

Task 2 / Strategy 2: Sulfate-free reactions

Task 3 : Alternative heating technologies – High frequency induction heating process
High frequency alternating current → electromagnetic field to induce eddy current flow into material for rapid heating

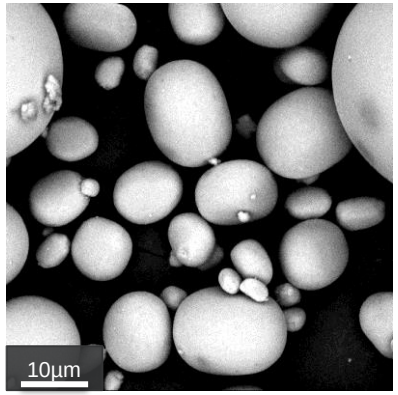
Task 4: Address needs for experimental materials for domestic battery research community

EARTH ABUNDANT CATHODE ACTIVE MATERIALS

Progresses in Process R&D and Scale-up

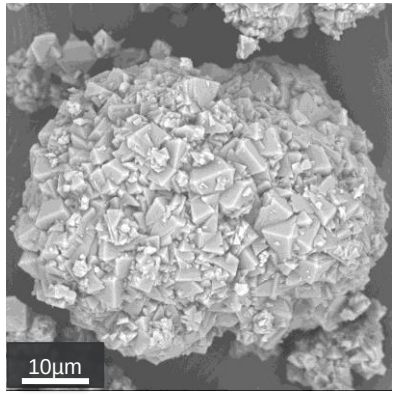
2022 → 2023 - 2024 → 2024 - 2025

Carbonate-route



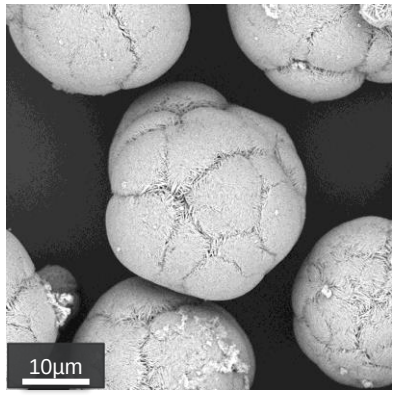
- × Severe particle cracking
- ✓ Smooth surface morphology
- × Challenging for cont. process
- × Low density pCAM
- ✓ High density CAM
- × High ASI
- ✓ High capacity

Oxalate-route



- × Poor morphology
- × Low production rate
- × Low density
- ✓ Na&NH_3-free, fast rxns at RT
- ✓ Superior storage stability
- ✓ High capacity

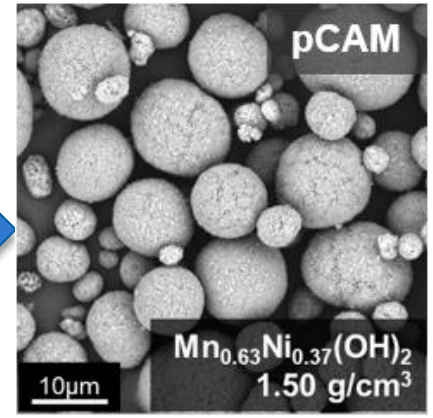
Hydroxide-route



- × pCAM oxidation
- × Ni-loss at low pH
- ✓ High density
- ✓ Suitable for cont. process
- ✓ High capacity

Optimization @1L TVR

Scale up @10L TVR



- ✓ Spherical morphology
- ✓ Bi-modal PSD (packing density)
- ✓ Avg. particle size at 13.5µm
- ➢ Higher densities with higher pH (≥10.8) → nodular morphology

Key parameters
pH ≤ 10.8
NH_3/TM ≤ 1
Res. Time ~ 6 h

~2.2kg product

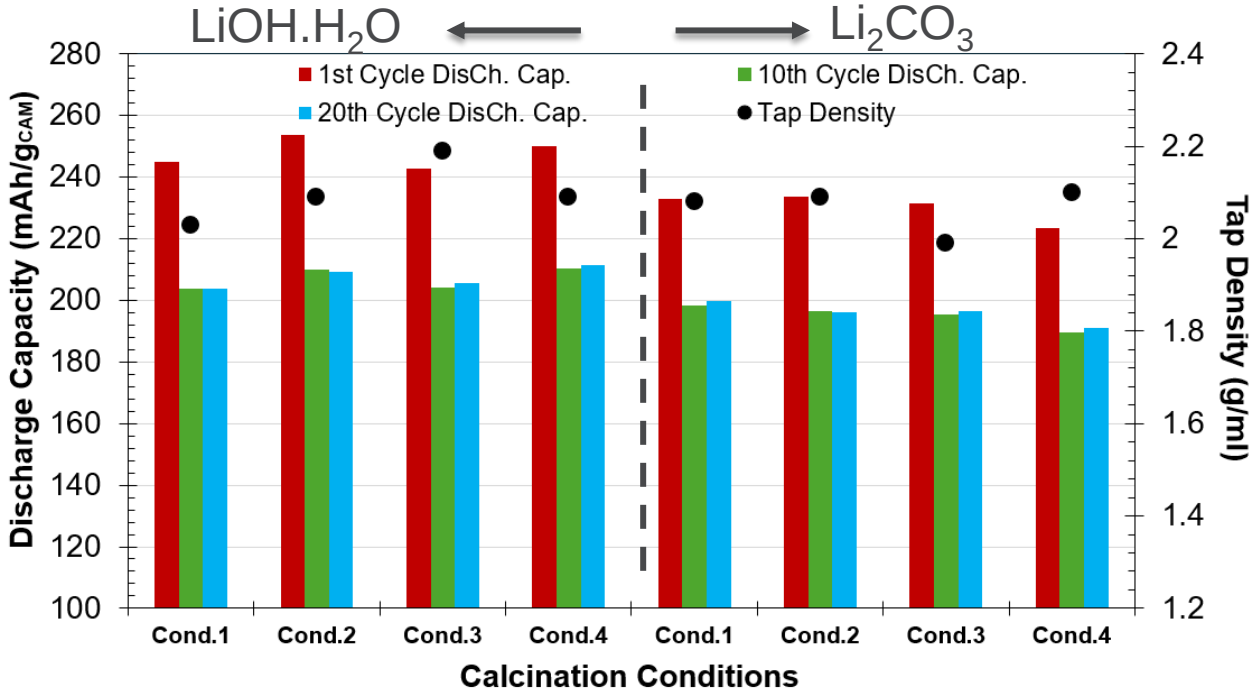
- ➢ Selection of synthesis route is critical for obtaining optimal quality pCAMs
- ➢ Large quantities are needed to eliminate batch-to-batch variability for calcination screening

Manuscript in preparation

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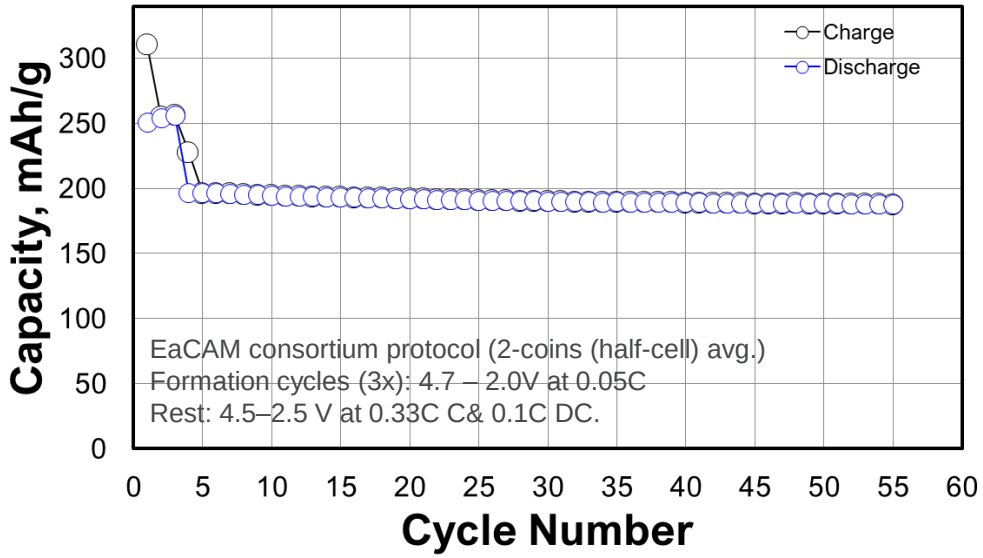
DIFFERENCES IN LMR MATERIALS BASED ON CALCINATION PROTOCOLS

Optimization Studies to Determine Process Parameters



- ✓ Process conditions can impact the performance
- ✓ Selection of Li-source is critical per pCAM chemistry

Electrochemical Evaluation (Feedback by Dr. Anh Vu EaCAM)



- ✓ High tapping & pressing densities = 2.2 & 3.0 g/cc
- ✓ Stable cycling performance = 96% C.R.

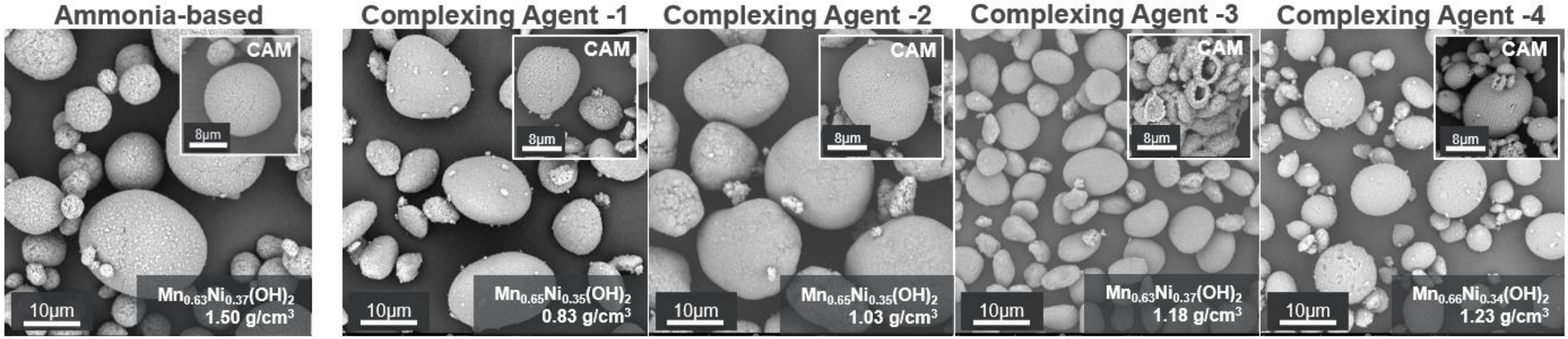
- Lab-source *ex situ* (Cu Kα) and *in situ* X-ray spectroscopy investigations at Brookhaven National Laboratory (NSLS-II, 7BM): to understand the structure evolution and to identify the optimal calcination protocols.

➢ Advanced analysis techniques are critical and help linking structure-performance relationship for optimal performance

AMMONIUM-FREE HYDROXIDE COPRECIPITATION

Patent pending

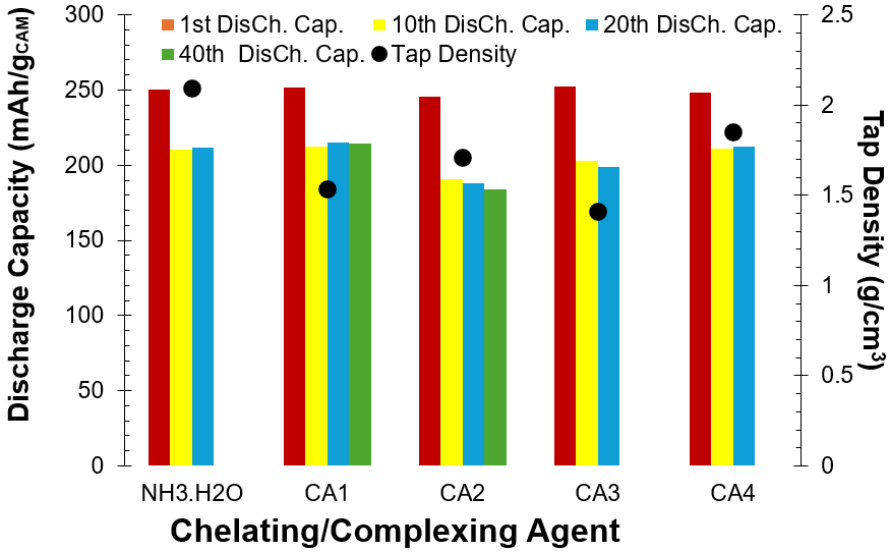
Screening non-toxic complexing agents for $Mn_{0.65}Ni_{0.35}(OH)_2$ synthesis



CAM TD: 2.03 g/cm³ | CAM TD: 1.53 g/cm³ | CAM TD: 1.71 g/cm³ | CAM TD: 1.41 g/cm³ | CAM TD: 1.85 g/cm³

pCAM: Bi-modal, spherical secondary, plate-like primaries

pCAMs have smooth surface texture, round secondaries, nano-size grain-like primaries; PSD is ranging between ~8 – 12 µm (inset SEMs show the cathode morphologies)



Lab-scale cost comparison/100g product

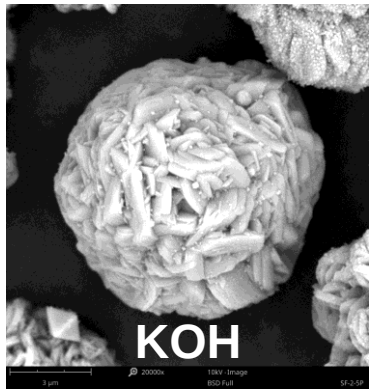
Complexing Agent***	$/unit (purity, ≥99%)	Price/ Experiment (1L TVR for 24 h)
$NH_3.H_2O$	$93.90/L	$ 51.69
CA1	$125/kg	$ 18.79
CA2	$144.40/kg	$ 36.41
CA3	$51.40/kg	$ 19.75
CA4	$30.00/kg	$ 8.05

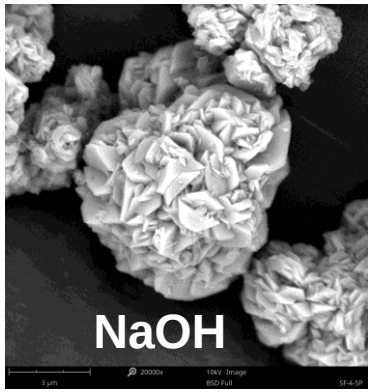
*** Vendor prices

- Demonstrated the feasibility of non-toxic complexing agents
- Alternative complexing agents offer comparable performance while reducing both cost and environmental impact
- Process optimization is required for increasing density of the materials

SULFATE-FREE HYDROXIDE COPRECIPITATION

Production of every 1 kg of $M(OH)_2$ pCAM produces 1.3 kg of Na_2SO_4 in process waters





$Mn_{0.65}Ni_{0.35}(OH)_2$

T.D. = 1.95 g/cc
9.7/14.2/20.1 (µm)

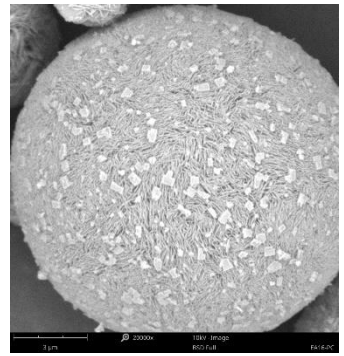
T.D. = 1.7 g/cc
4.1 /7.8 / 13.3 (µm)

Sulfate-based $MSO_4 + 2NaOH \rightarrow M(OH)_2 + \mathbf{Na_2SO_4}$

Nitrate-based

$M(NO_3)_2 + 2\,KOH \rightarrow M(OH)_2 + 2\,\mathbf{KNO_3}$

$M(NO_3)_2 + 2\,NaOH \rightarrow M(OH)_2 + 2\,\mathbf{NaNO_3}$



$Mn_{0.65}Ni_{0.35}(OH)_2$

T.D.= 1.5 g/cc
6.3 /13.5/ 21.7 (µm)

Key observations:

- ✓ 15 - 30% increase in particle density depending on precipitating agent
- ✓ Faster reaction kinetics: short residence time, high throughput
- ✓ Compatible with Ni-based NMC pCAMs with process optimization (on-going effort)
- ✓ Process waters: $NaNO_3$ / KNO_3 + NH_4NO_3 solution (primary fertilizer components)
- × Large/thick primary particle morphology & nodular particle morphology with rough surfaces

Key challenge: Lithium diffusion limitations due to the dense packing of primaries

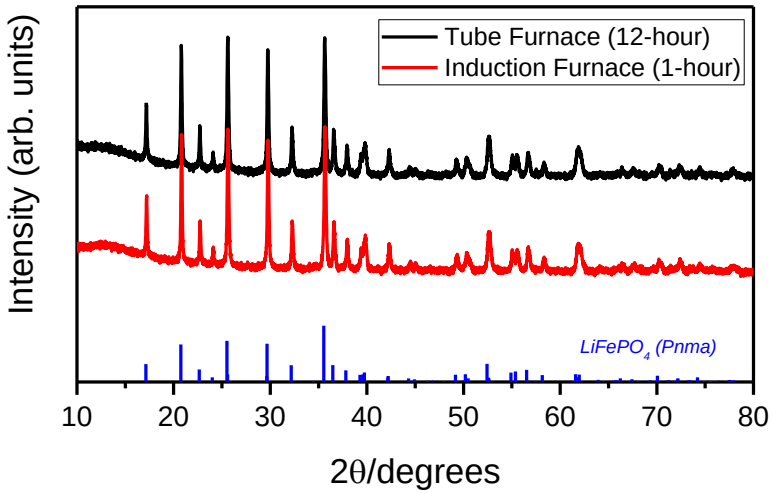
- ➢ Process research will focus on particle engineering: Implement findings from NH_3 free reactions (Task 1) to control the primary and secondary particle morphologies for optimal pCAM properties

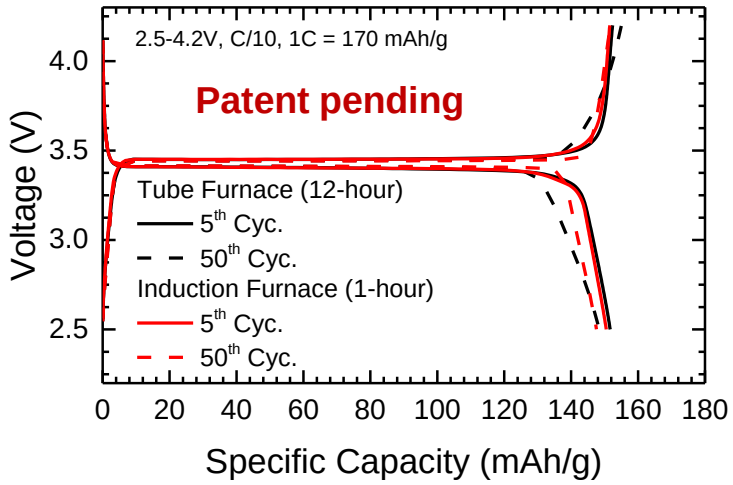
EXPLORE ADVANCED HEATING TECHNOLOGIES FOR RAPID CALCINATION PROCESS

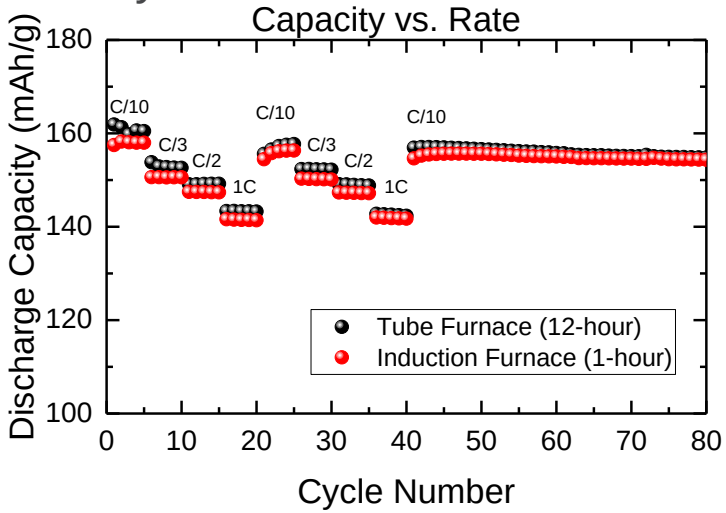
Collaboration with Industry-Startup (New)

Austin Elements

- **Request:** Evaluation of recycled battery materials as alternative precursors for $LiFePO_4$ production
- **Approach:** Utilizing an induction heating system as an alternative calcination method
- **Materials :** High purity $FePO_4.2H_2O$ and Li_2CO_3 recycled feedstock materials by Austin Elements







- Single phase LFP is achieved in 1h
- Comparable performance with conventional heating

Key takeaways

- Recycled domestic feedstocks from the EoL batteries, are appropriate precursors for LFP production → alternative way for energy-savings and reduction in chemical costs
- Rapid calcination process is developed and will support VTO-funded projects at request

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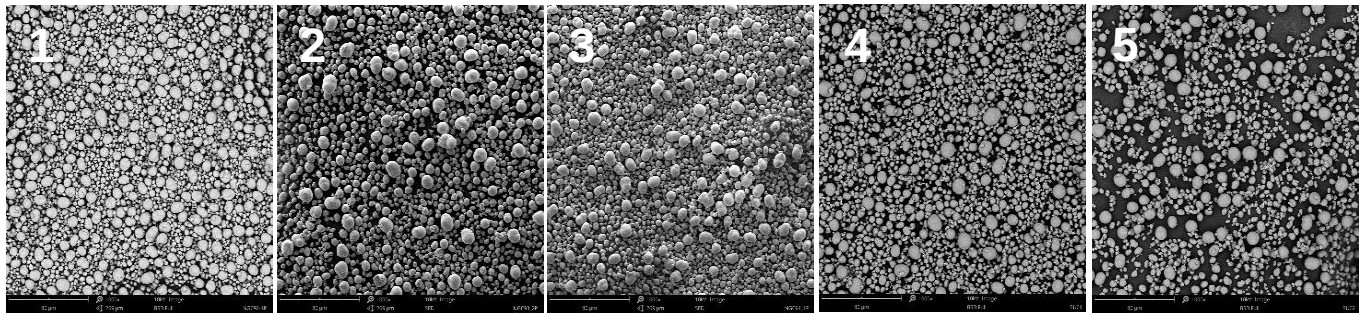
SUPPORT FOR BATTERY COMMUNITY

Collaboration with Binghamton University (New)

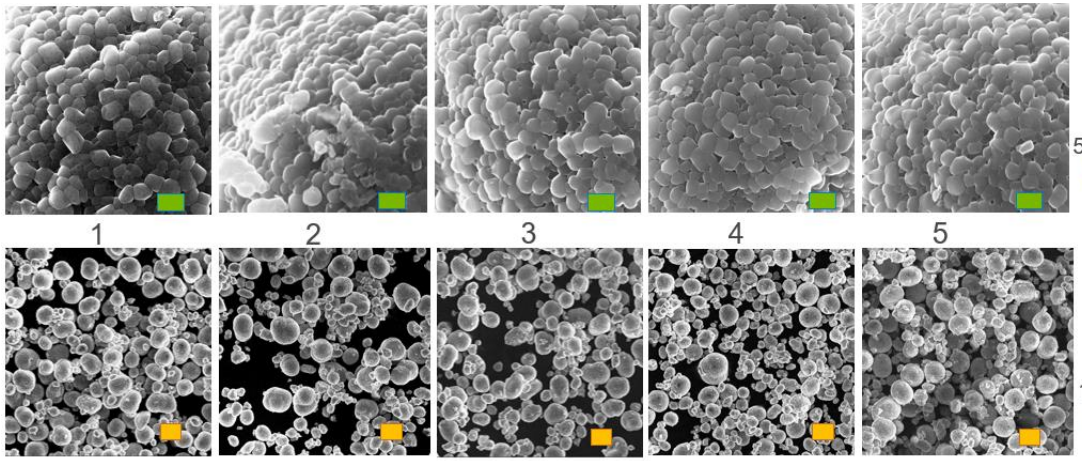
BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

- **Request:** Size specific (bi-modal) and dense $Ni_{0.9}Mn_{0.05}Co_{0.05}(OH)_2$ pCAM with spherical morphology; **Step 1**: Distribution of experimental pCAM (~200 g) and performance feedback, **Step 2**: Scale up to 2 kg

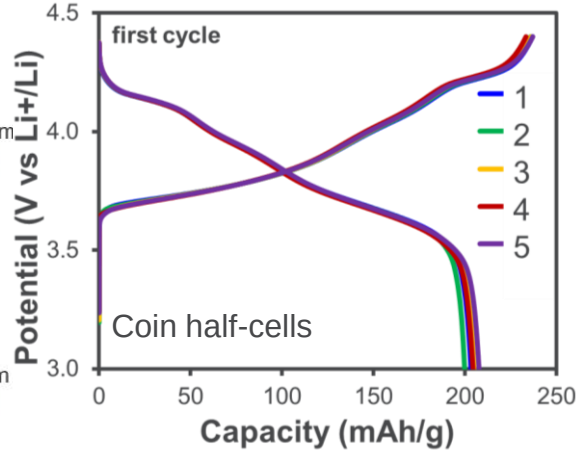
#	T (°C)	pH @ T °C	T.D. g/cc	(D90-D10)/D50
1	45	11.5	2.01	1.03
2	50	11.1	1.90	1.15
3	50	11.2	1.94	1.22
4	48	11.1	1.86	**1.43**
5	48	11.6	1.93	1.30



- **Nb - coating/substitution at Binghamton University:** To identify all forms degradation, including gassing



TM-hydroxide, Nb-precursor, Li-source are mixed and calcined at 750°C



- 5 × 250g custom-made materials were provided for calcination and preliminary electrochemical analysis.
- pCAM process optimization studies will continue.
- Final deliverable: 2kg optimized material

➢ This program can make the non-commercial materials available in support for domestic battery community

RESPONSES TO PREVIOUS REVIEWER COMMENTS

Reviewer comments:

- Approach:
  - "…the project was thoughtfully designed, encompassing clear objectives that addressed both technical and financial aspects."
  - "…remarked on the project's successful alignment with its defined objectives and the prevailing challenges in this sector. The organized and effective approach towards achieving specific targets was commended."
- Technical Accomplishments:
  - "…. There has been a clear demonstration of progress and tangible outcomes across all the research projects under his/her leadership. One of the significant highlights being that the discharge capacity of most of the CAMs developed by the PI is on par, if not superior to, the current state of the art."
- Collaborations:
  - "…These achievements underscore the PI's cooperative and collaborative spirit. Her commitment to supporting various projects, ensuring their success, stands out prominently."
  - "…commended the collaborative nature of the project, showcasing a synergistic relationship between the project and the broader battery research communities."
- Proposed Future research:
  - "…A significant milestone would be the team's development of procedures that eliminate the use of ammonia in pre-CAM production."
  - "…The idea of replacing other metal ions for Co was also flagged as noteworthy, with a call to delve into the implications of introducing different non-transition metal ions on both structural and electrochemical performance."

Response: We thank the reviewers for their positive feedback and suggestions.

COLLABORATIONS AND COORDINATION

- Pallab Barai, Xiaoping Wang, Venkat Srinivasan (BAT 402, ANL) and Jiangming Bai (BNL), Feng Wang (ANL) (BAT183) – continued collaborative work with TVR-made materials (Ni-rich)
- Anh Vu (EaCAM Consortium): material evaluation, MERF-analysis support
- Prof. Sahar Vahabzadeh (Northern Illinois University): calcination screening work for EaCAM
- Jacob Jin (Austin Elements) for providing recycled chemicals for LFP production and performance evaluation
- Fengxia Xin, Nichakarn Anansuksawat and Prof. Stanley Whittingham (Binghamton University) in support for their BAT500 project: different lots of size specific Ni-rich pCAM (5 x 250g)
- Prof. Feng Lin (Virginia Tech): using the TVR-made pCAMs to synthesize layered CAM materials to investigate how different electrolyte chemistries change the surface reactivity, with a goal to mitigate interfacial degradation and prolong cycle life
- Emilee Armstrong, Prof. Corrie Cobb (UW) and Eva Allen (ANL-ReCell) → NMC622 cathodes for “Enabling UW’s acoustophoretic additive manufacturing for scalable 3D battery electrodes” (AMMTO)
- CatSE Program (US-German Cathode Solid Electrolyte Project): supported size-specific NMC811 cathodes (1kg) to ORNL
- BTMS (NREL-led) & CAMP (ANL): supported with NMC9055 pCAM/recent publication
- Beihai Ma (ANL): for high-frequency induction heating support
- Joe Libera (BAT315): Large-scale calcination collaboration using in-house developed “glovebox integrated pilot scale tube furnace”

REMAINING CHALLENGES AND BARRIERS

- High quality next generation cathode materials are needed for real-cell validations, but they are not commercially available.
- Material processing and manufacturing costs remain as barrier, when new cathode chemistries are developed.
  - New chemistries necessitate process developments through systematic synthesis approach
  - Emerging synthesis technologies can address “fast process parameter screening”
  - Economic feasibility of a new process requires thorough experimental data input (time constraint validation)
  - Domestic battery manufacturers prefer established technologies, and proven at large scale
- Large scale calcinations remain challenging, especially for air/humid sensitive next generation cathode materials. New heating technologies are needed.

PROPOSED FUTURE RESEARCH

- **Continue exploring low-cost pCAM synthesis**
  - Improve particle densities with low-cost complexing agent through optimization
  - Exploring coprecipitation of earth abundant dopants (i.e. Zn, Fe)
  - Imaging techniques and X-ray spectroscopy to examine the effect of primary particle size on the lithiation mechanisms
  - Control primary particle growth of pCAMs from sulfate-free coprecipitation reactions through non-toxic complexing agents
- **Establishment of low and medium frequency induction heating units**
  - Advance the process development for calcination and surface treatment of next generation CAMs
- **Continue supporting battery research community by providing customized materials**
  - Commercially unavailable pCAMs & CAMs (e.g.; Ni-based hydroxides, LNO-based cathodes, Mn-based, Ni-low and Co-free cathodes)
  - Commercially unavailable cathode particle sizes (e.g.; small particles, bi-modal PSD)
  - Process design for synthesis by multiscale characterization (correlated with modelling) (e.g.; in-situ calcination for calcination optimization (BAT183, BAT315, BAT402)
- **Suggestions are welcome for scaling up newly invented, promising battery materials**

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

SUMMARY

- **Mn-Based Earth Abundant Cathode Active Materials**
  - Hydroxide based coprecipitation process is optimized followed by scaling up to >2.0kg
    - It is imperative to use the same lot of pCAM in calcination optimization to eliminate batch-to batch variability
    - Delivered high capacity, high density, high stability CAMs evaluated by EaCAM partners
  - Ammonium hydroxide free coprecipitation
    - at least one chelating/complexing agent delivers physical characteristics of the pCAM similar to ammonia-based process
    - compatible complexing agent is selected from non-hazardous chemicals
  - Sodium hydroxide and sulfate free coprecipitation
    - Short residence time, high throughput: high density pCAMs - lithiation challenges for the CAM
- **Calcination Screening and Optimization**
  - Conducted process R&D to establish relationship between calcination parameters and material performance (EaCAM baseline materials)
  - Conducted in-situ XRD using BNL's NSLS-II to determine suitable calcination parameters for best performances
  - Optimized calcination conditions for EaCAM cathodes using optimal $TM(OH)_2$
  - Designing surface stabilization process for Ni-based materials and assessment of the process scalability in collaboration with BAT183 and BAT315
- **Asses the feasibility of induction heating technologies for calcination of next generation CAMs**
  - Demonstrated rapid calcination of LFP from recycled feedstocks using high frequency induction heating
- **Material Support for US battery community:** Universities, National Laboratories, VTO-funded Consortia and Programs, Start-up.

ACKNOWLEDGEMENTS AND CONTRIBUTORS

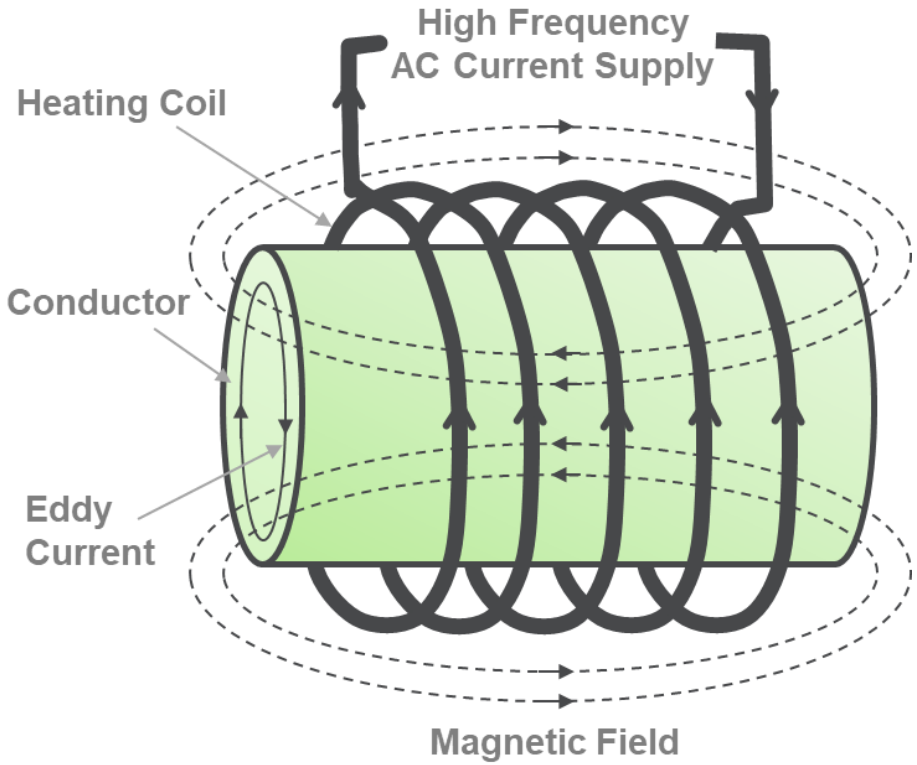
Continuous support from Haiyan Croft, and Brian Cunningham of the U.S. Department of Energy's Office of Vehicle Technologies is greatly appreciated.

- **Project Team:** Carrie Siu, Mateusz Zuba and Isik Su Buyuker, are acknowledged for their contributions in synthesis, characterization and synchrotron studies. Jason Aranda is acknowledged for his support and assist in the experimental work.
- EACAM: Anh Vu (ANL-CSE) is acknowledged for his contributions for the evaluation of TVR-made EaCAM materials.
- Northern Illinois University: Prof. Vahabzadeh for her effort in screening calcination conditions for EaCAM material
- Austin Elements: Jacob Jin for providing high purity recycled $FePO_4.2H_2O$ and Li_2CO_3
- ANL: Feng Wang is acknowledged for the NSLS-II beamtime. Eva Allen is acknowledged for her contributions in NMC622 pCAM synthesis,. Beihai Ma is acknowledged for his contributions for the induction heating application
- ANL-MERF Analytical Lab: Gerald Jeka is acknowledged for his support in ICP analysis.

TECHNICAL BACKUP

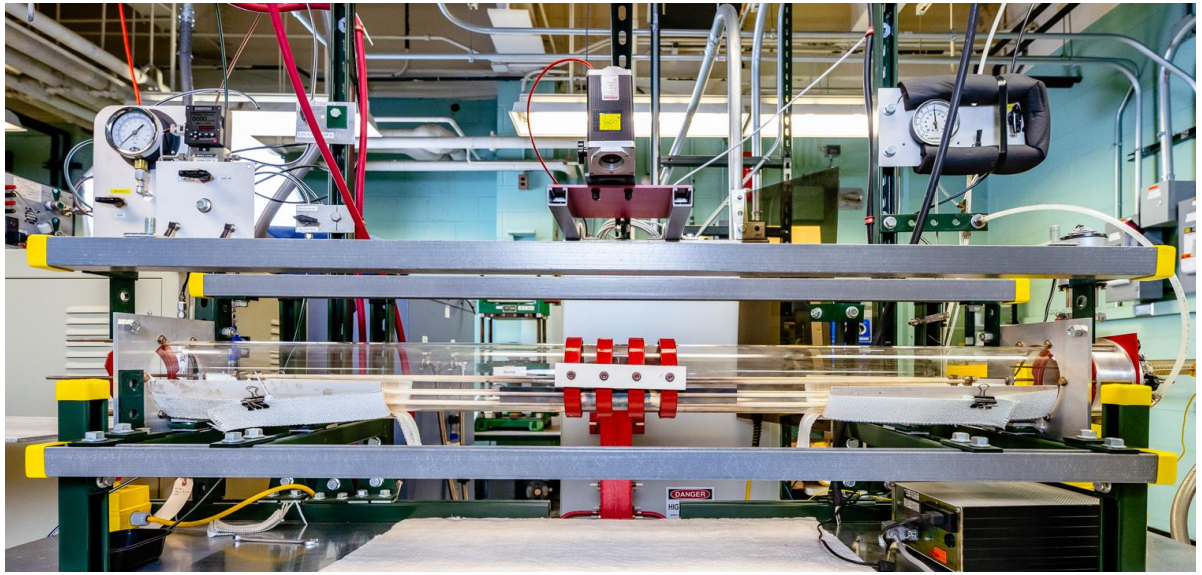
HIGH FREQUENCY INDUCTION HEATING

Non-contact, rapid heating



Induction Coil: to generate an alternating electromagnetic field, powered by a high-frequency alternating current (AC).
Electromagnetic Field: created by the AC passing through the coil
Induced Currents: electromagnetic field induces eddy currents within the material.

Setup at ANL



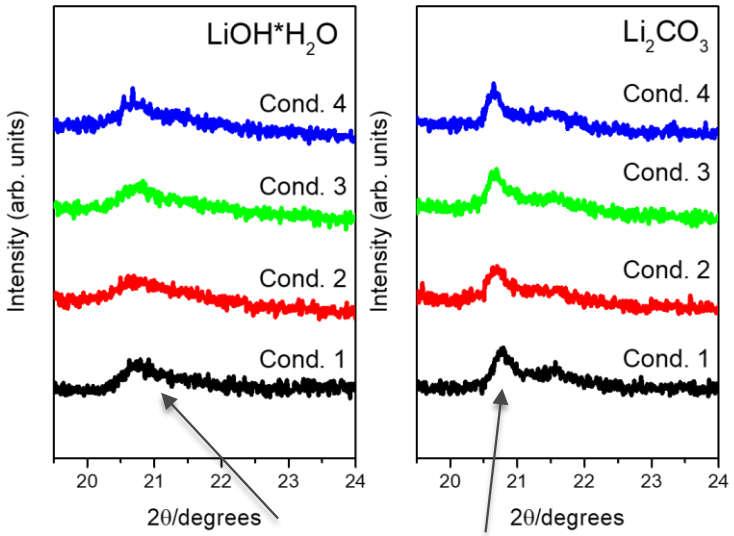
High Frequency Induction Heating

- Process that uses electromagnetic induction to heat electrically conductive materials

DIFFERENCES IN LMR MATERIALS BASED ON CALCINATION PROTOCOLS

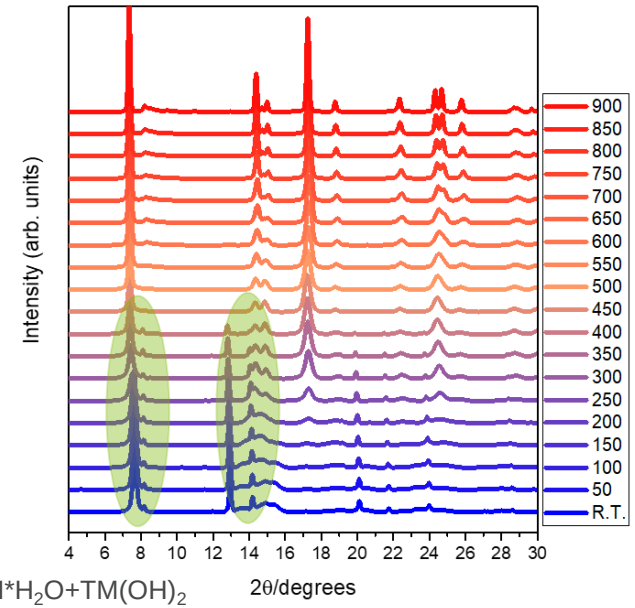
X-ray Spectroscopy Investigations to Determine Process Parameters

Lab-source, Ex-situ, *Cu k-alpha*

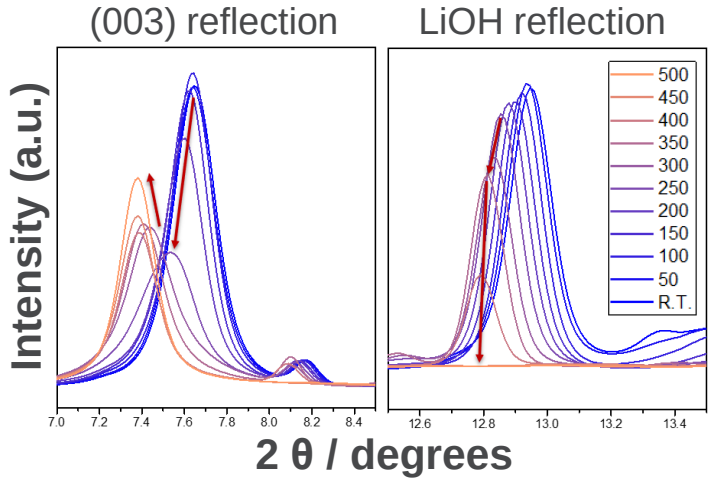


Super lattice reflections (SLRs)

NSLS-II (7BM) In-situ Heating



$LiOH*H_2O+TM(OH)_2$



$Mn_{0.65}Ni_{0.35}(OH)_x + LiOH*H_2O$
"Solid-liquid lithiation"

Observations

- Super lattice reflections (SLR) – associated with monoclinic character of the material (i.e. Li_2MnO_3-like domains)
- Pronounced SLRs with Li_2CO_3 but broader peak with LiOH; suggesting LiOH with a low-T hold enables homogeneous lithiation resulting in more elementally uniform final-CAM
- LiOH peaks disappears in tandem with 003 peak evolution (topotactic) - vs non-topotactic reaction with Li_2CO_3 (literature)*

Manuscript in preparation

Designing Scalable Processes for Surface Stabilization

Collaborative Work under Processing Science and Engineering Projects

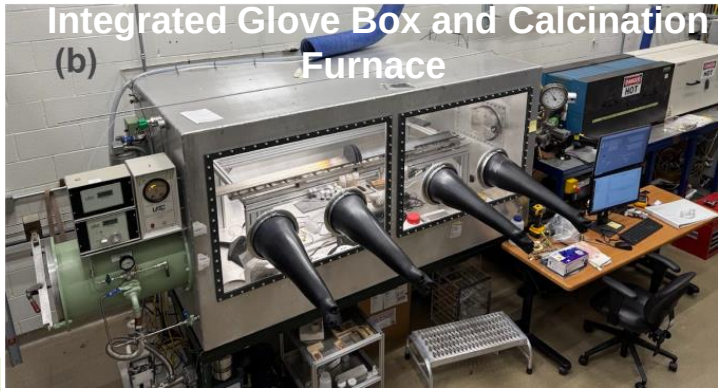
Approach: process design for synthesis by multiscale characterization (correlated with modelling)



Large scale pCAM production

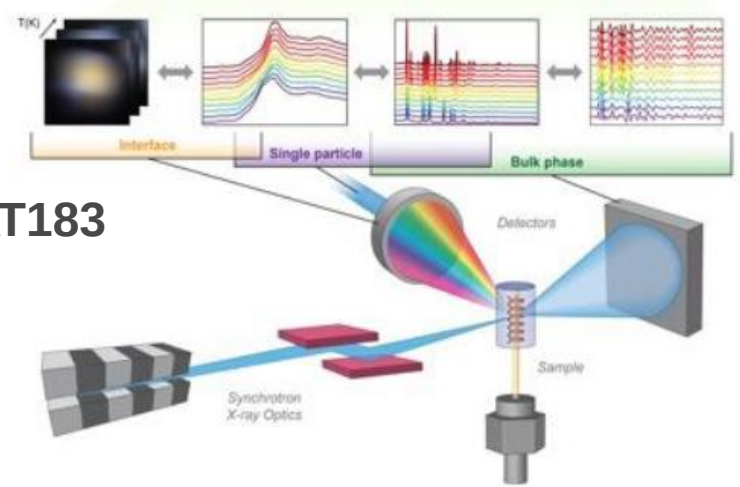


Large scale nano materials



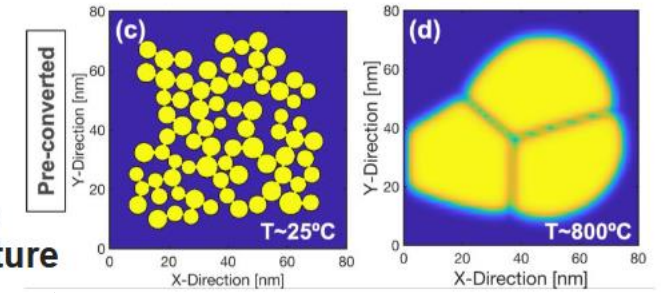
Inert handling pre- and post- calcination

BAT183



Particle microstructure

BAT402



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