Process Development and Scale-Up of Advanced Active Battery Materials



OZGE KAHVECIOGLU (PI) **CARRIE SIU** **MATEUSZ ZUBA** **ISIKSU BUYUKER**

Argonne National Laboratory
Project ID: BAT167

June 4, 2024

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2024
- Percent complete: On-going

Budget

- Funding for FY2024 = $1,475,000
- Funding for FY2023 = $1,475,000

Barriers

- Cost: Reduce manufacturing costs with scalable continuous processes
- Performance & Life: High energy density advanced cathode materials have major performance and life issues

Partners

- EaCAM consortium
- CatSE Program
- ReCELL subgroups
- University of Washington
- Feng Wang (ANL), and Jianming Bai (BNL)
- Pallab Barai and Venkat Srinivasan (ANL)

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 precursors of cathode materials (pre-CAMs) and CAMs.
  - Develop **cost-effective, scalable** processes for manufacturing of advance materials that are not commercially available
- The program plays a crucial role within the DOE Vehicle Technologies Program by:
  - Bridging the gap between the development of innovative cathode materials, their assessment in the market, and the transition to large-scale manufacturing.
  - Facilitating comprehensive evaluation by multiple R&D groups, enabling a thorough understanding of the materials' potential at full scale.
- This program provides large quantities of materials with consistent quality in order to:
  - Facilitate prototyping in large format cells
  - Provide access to new materials for the battery community to advance further research

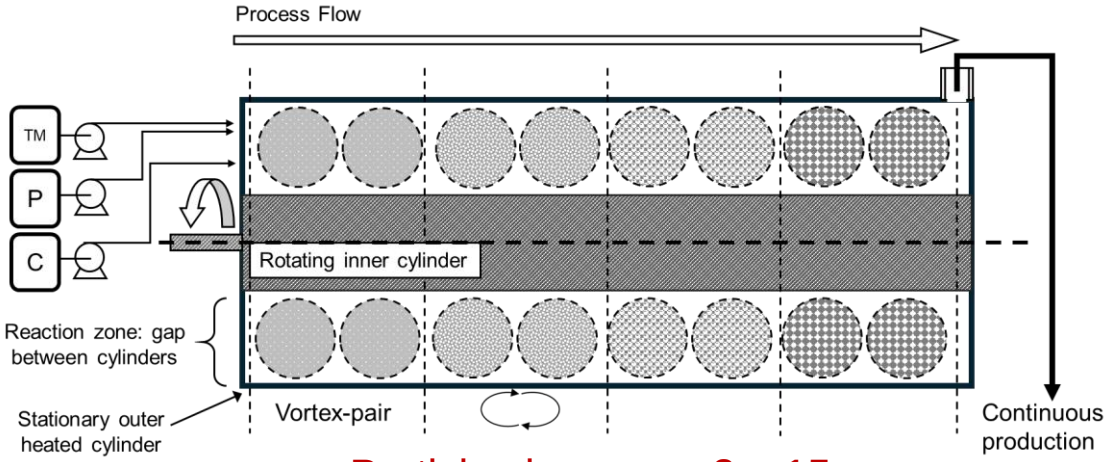
MILESTONES

Description of Tasks/Milestones	Planned End Date	Type	Status
Mn-Based Earth Abundant Cathode Active Materials M.1: Development of continuous co-precipitation processes M.2: Screening different synthesis routes using green chemistries	**09/30/2025**	**Annual (Regular)**	**On-going**
Taylor Vortex Reactor (TVR) – process control M.3: Investigate process parameters to produce desired materials morphology for various precursors using Taylor Vortex reactors	**09/30/2025**	**Annual (Regular)**	**On-going**
Single Crystal Precursor Development M.4:Co-precipitation process for producing monocrystalline precursors	**09/30/2025**	**Annual (Regular)**	**On going**
Scale-up and Optimization M.5:Conduct process R&D to establish relationship between calcination parameters and material performance M.6: Develop optimized calcination parameters for high Ni and high Mn materials and assess scalability of the process through advanced characterization	**09/30/2026**	**Annual (Stretch)**	**On-going**
Beyond Li-Ion Battery Materials (Preliminary)	**09/30/2027**	**Annual (Regular)**	**Planning**
Material Support for US Battery Community M.7: Ni-rich pre-CAMS and final CAMs M.8: Size specific CAMs M.9: CAMs with different morphologies at scale	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

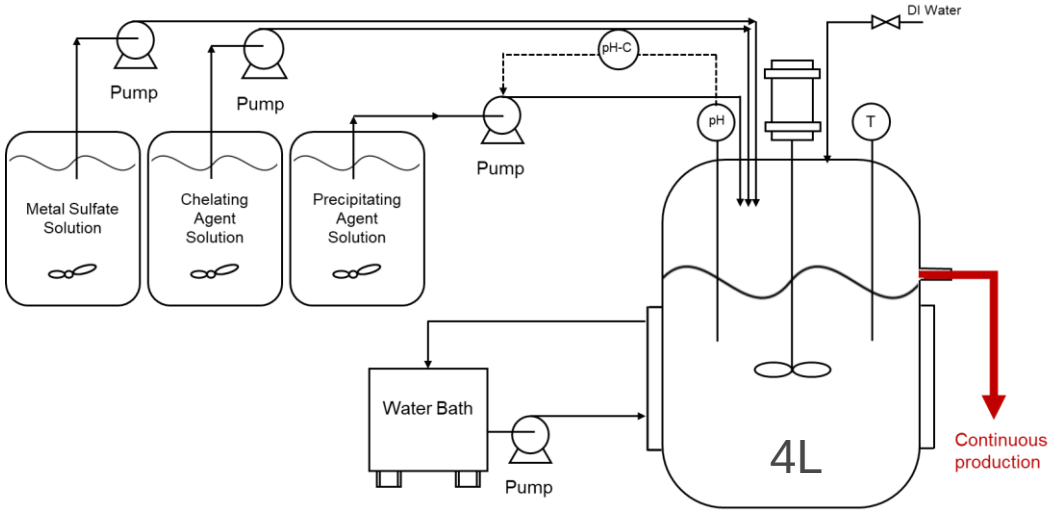
Taylor Vortex Reactor (TVR)



Particle size range 3 – 15 µm

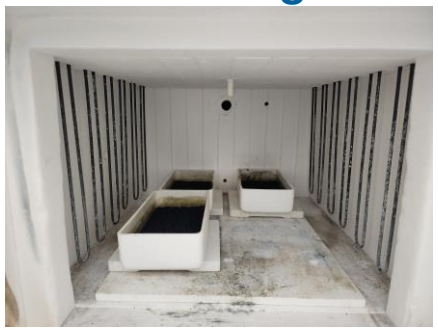
Main synthesis platform to synthesize pre-CAMs since 2015

Continuous Stirred Tank Reactor (CSTR)



Particle size range 10 – 20+ µm

Large Commercial Box Furnaces





5.0L O_2 flow rate → 2.5kPa

1 kg/batch in atmosphere controlled (O_2 or O_2/N_2)

To quickly address the material needs of the US battery community, we can:

- Supply high-quality cathode precursors and cathodes that are commercially unavailable.
- Scale up promising chemistries to kilogram quantities for extensive large-scale evaluation.

Argonne NATIONAL LABORATORY

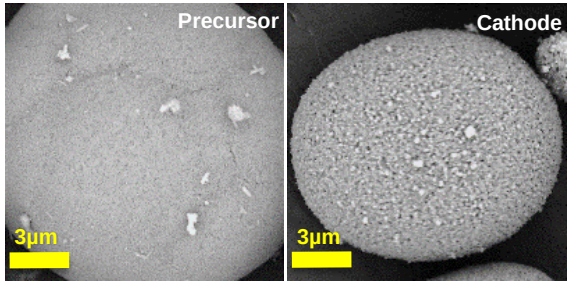
EARTH ABUNDANT CATHODE ACTIVE MATERIALS CONSORTIUM

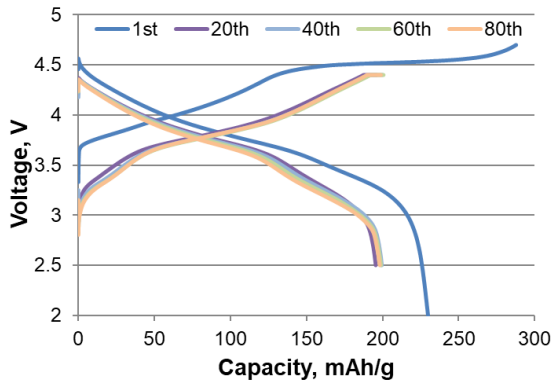
Development of Mn-based precursor chemistries through different continuous coprecipitation

- Advanced synthesis process R&D to address issues which are intrinsic to conventional processes
  - Develop and optimize new continuous synthesis procedures
    - Investigate particle architecture design through synthesis route and process parameters
  - Substitute Ni with earth-abundant elements (e.g.: Fe), to improve structural stability

Carbonate

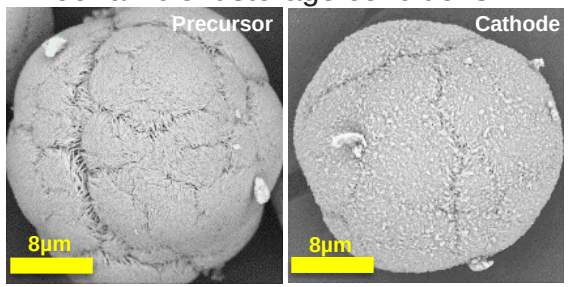
- ✓ Shorter RT give higher capacity
- ✓ Highest tap density (>2 g/cm^3)
- – Peeling and cracking particles
- – Challenging for continuous process

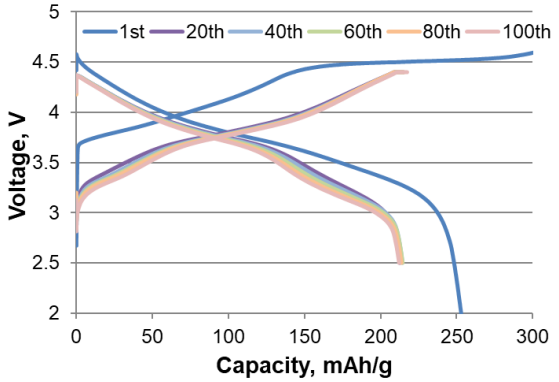




Hydroxide

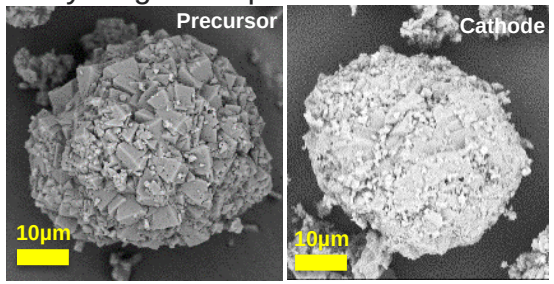
- ✓ Suitable for continuous-process
- ✓ Highest capacity (>200 mAh/g)
- – Delicate balance in synthesis parameters
- – Poor ambient storage conditions

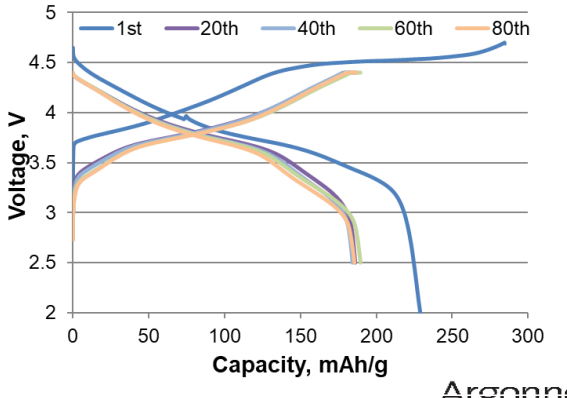




Oxalate

- ✓ Superior storage stability
- ✓ Fast reaction time (≤15 min)
- ✓ Room temperature reaction
- – Early stages of optimization



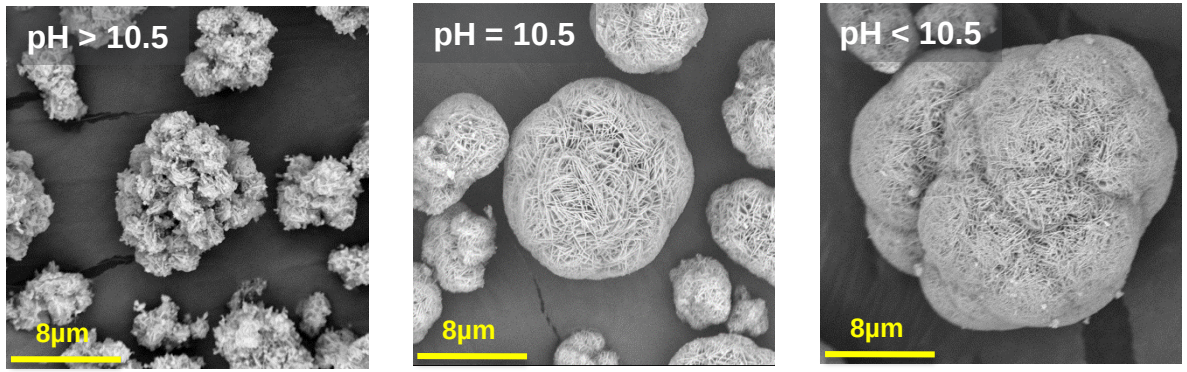


Argonne NATIONAL LABORATORY

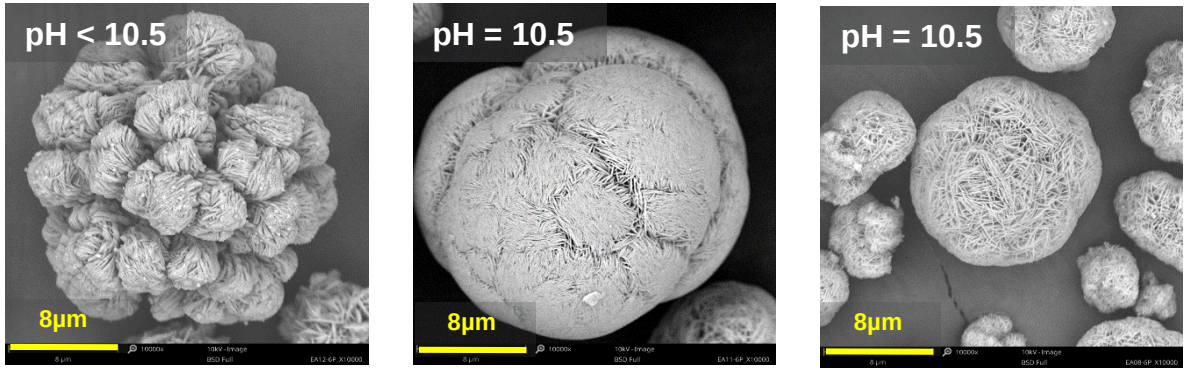
EARTH ABUNDANT CATHODE ACTIVE MATERIALS CONSORTIUM

Optimization Studies: Co-precipitation

pH Control (τ = 1 hour)



Residence Time (τ) & pH Control

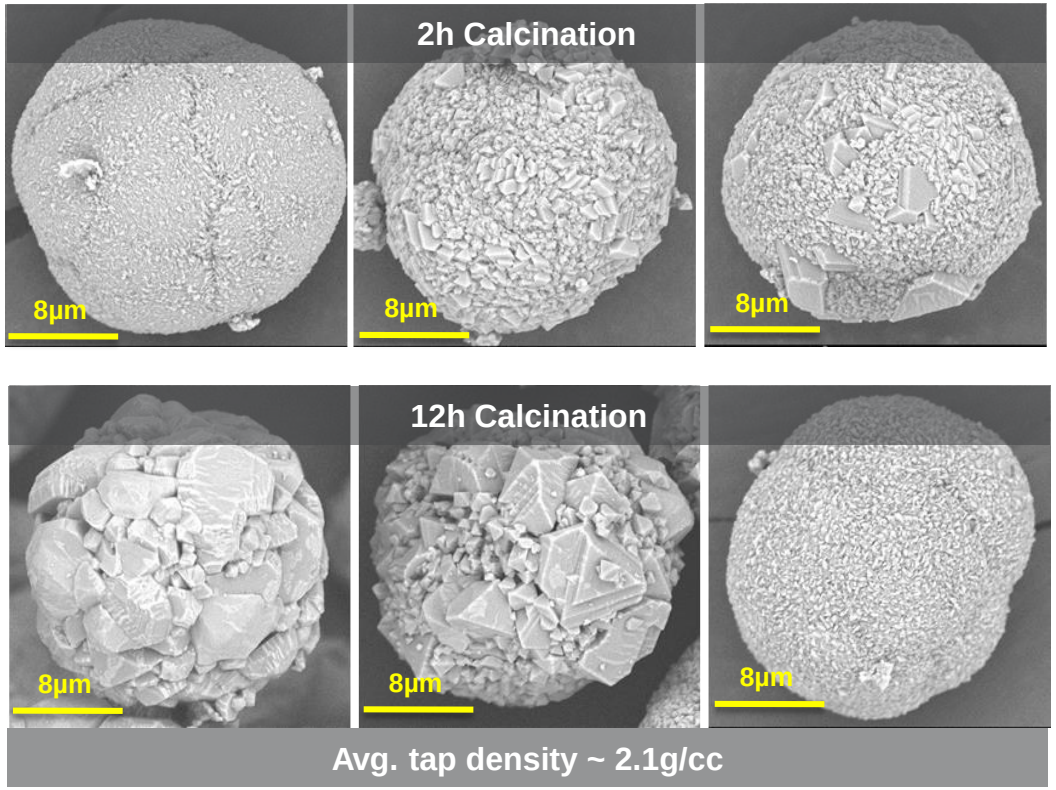


τ = 4 hours τ = 1 hour

- Delicate balance between the reaction conditions can produce high density and spherical particles in continuous hydroxide coprecipitation.

Optimization Studies: Calcination

Short vs Long Duration Calcination



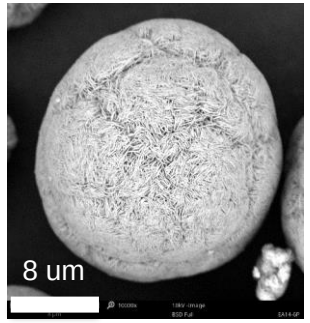
- Ensuring lithiation homogeneity is imperative!
- Reaction parameters that control primary and secondary **particle architectures** must be better understood for Mn-rich cathodes in order to achieve optimal performance

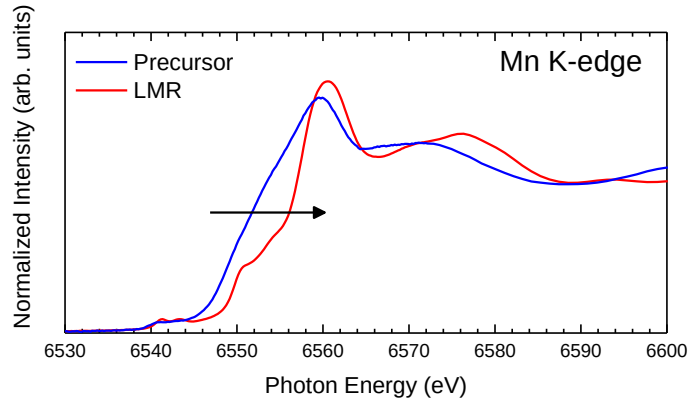
Argonne NATIONAL LABORATORY

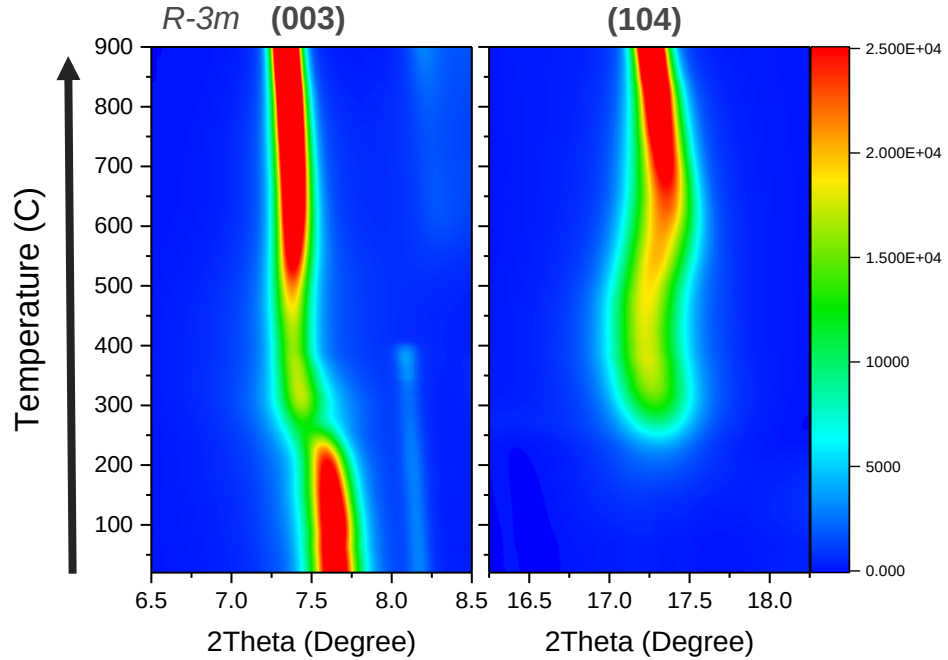
ADVANCED CHARACTERIZATION TO SUPPORT CALCINATION OPTIMIZATION STUDIES

Synchrotron Studies to Understand the Calcination Kinetics for Optimal Processing

- Several EACAM precursors (Mn:Ni = 0.65:0.35) hydroxides, oxalates, and carbonates:
  - Ex/In-situ XRD Calcinations
    - To understand the crystallographic evolution during calcination.
    - Identification of optimal calcination temperatures. Linked to stoichiometry, morphology, and density properties.
  - Ex-situ XAS Studies
    - To better understand Mn-rich precursors (in)stability.
    - Determining Mn/Ni oxidation and local geometry pre/post-calcination.
  - Ex-situ 2D/3D Tomography Measurements
    - Identify material oxidation gradients and lithiation (in)homogeneity on secondary particle level through Mn/Ni valence dynamics
- Pretreatment/storage conditions of precursors (analysis on going)



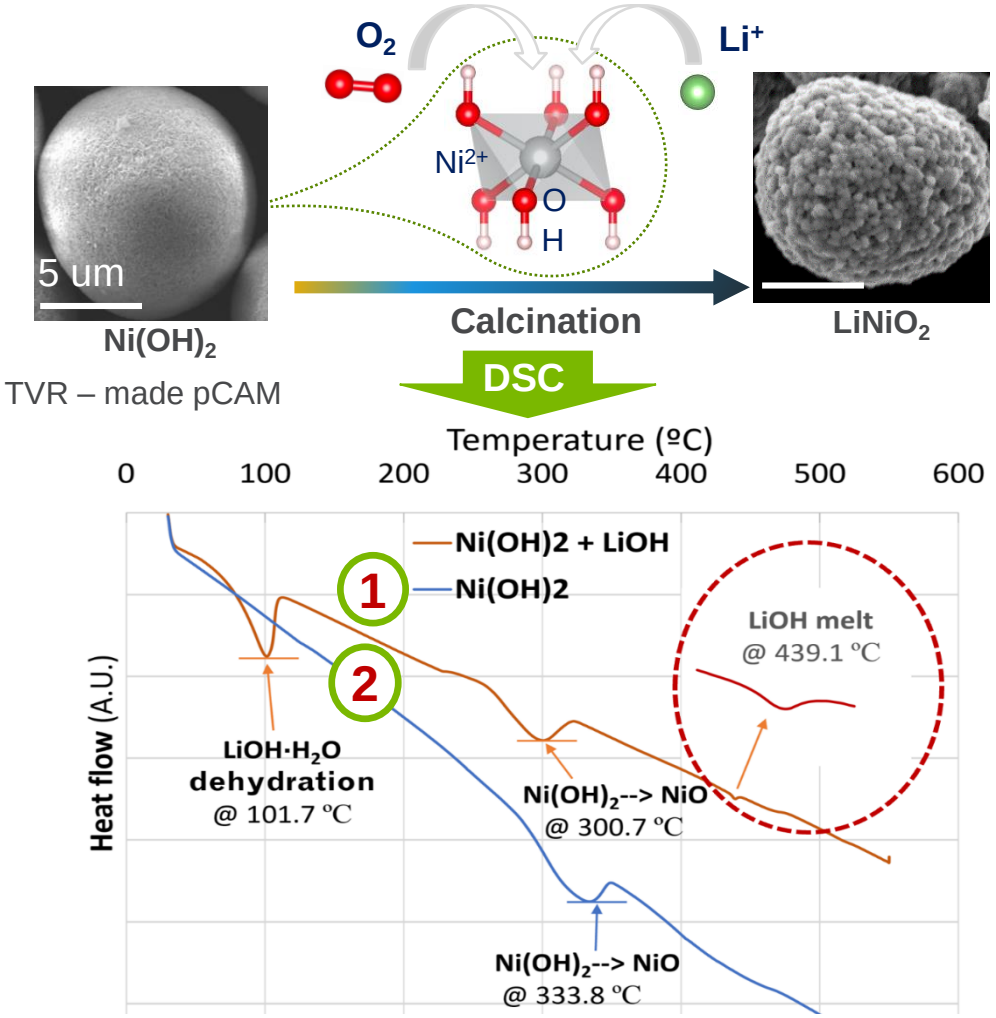


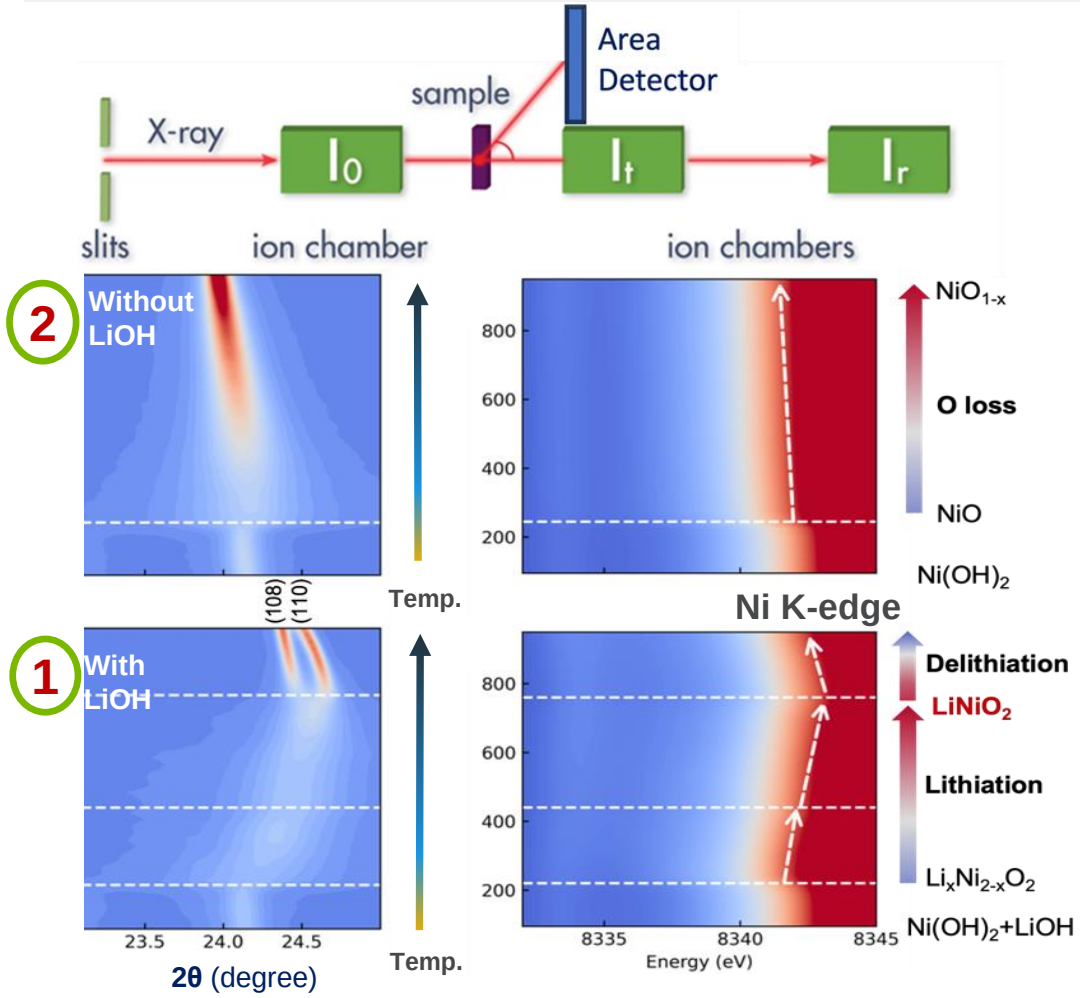


Synchrotron studies by Mateusz Zuba, Isiksu Buyuker, in collaboration with Eva Allen and Feng Wang (BAT183)

LITHIUM-STOICHIOMETRY CONTROL: *IN SITU* INSIGHTS

Calcination: $LiNiO_2$ from $Ni(OH)_2$ ⟷ **In situ:** correlating structure evolution with lithiation





Collaboration W/ NSLS-II, BNL; Bai/Wang (BAT183), Barai/Srinivasan (BAT402)

➢ Calcination is a *lithiation-driven* kinetic phase propagation and crystallization process

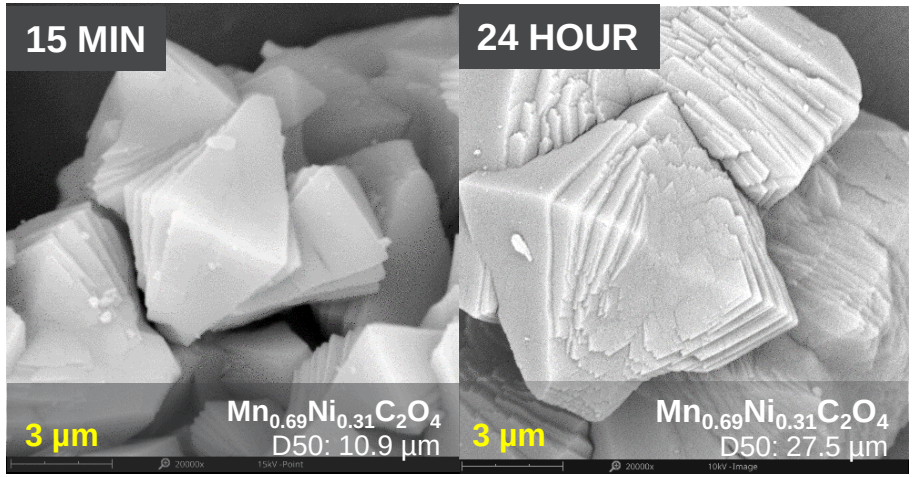
A. Tayal, *et al.*, "In situ Insights into Cathode Calcination for Predictive Synthesis of $LiNiO_2$" (Adv. Mater.; https://doi.org/10.1002/adma.202312027)

DEVELOPMENT OF SINGLE CRSYTAL PRECURSORS

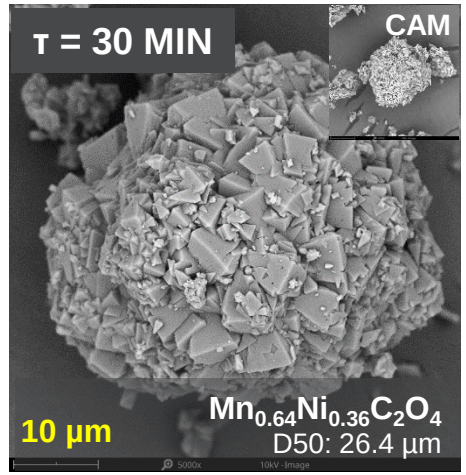
Preliminary Co-precipitation Reactions in Batch and Continuous Methods

- ✓ Room temperature co-precipitation (T= 20°C ± 1°C); reduces energy consumption
- ✓ Environmentally friendly approach: 16 x reduction in ammonium usage in the reaction; decreased emission of toxic gases
- ✓ Easy application to wide range of chemistries consisting of Fe
- ✓ Excellent air & storage stability (after weeks of exposure)
- ❑ For improved performance, optimal calcination conditions are being investigated

BATCH



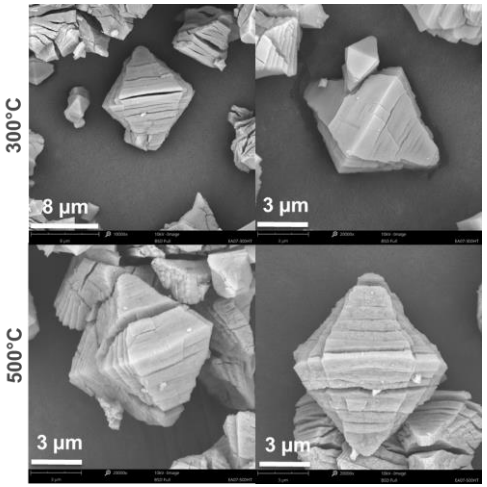
CONTINUOUS (TVR)



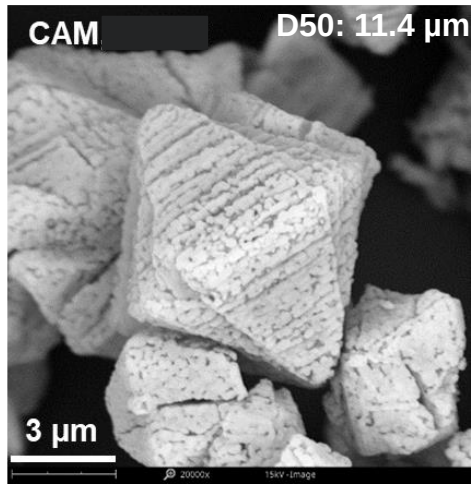


The precursor maintained its integrity after several months of exposure to air and humidity.

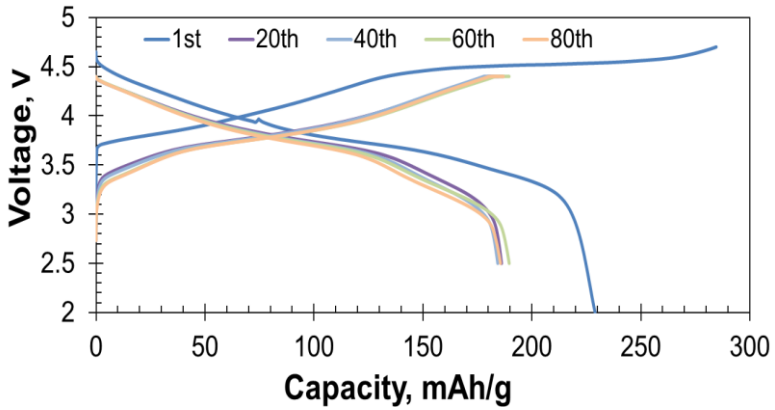
Pretreatment



Calcination



E-chem Performance

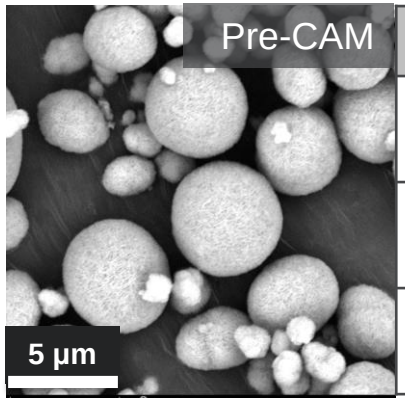


Formation: 4.7 – 2.0V, C/20 (1x), 4.4 – 2.5V, C/5 (3x).

Argonne NATIONAL LABORATORY

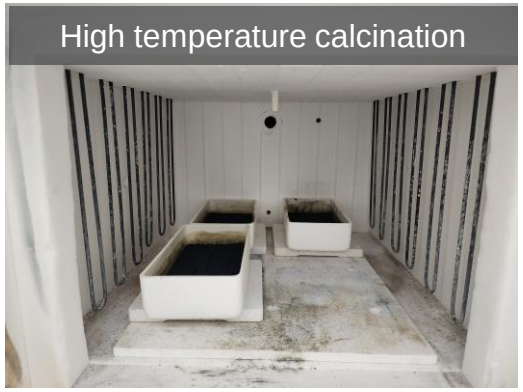
MATERIAL SUPPORT FOR BATTERY COMMUNITY

The US-German CatSE (Cathode Solid Electrolyte) Project

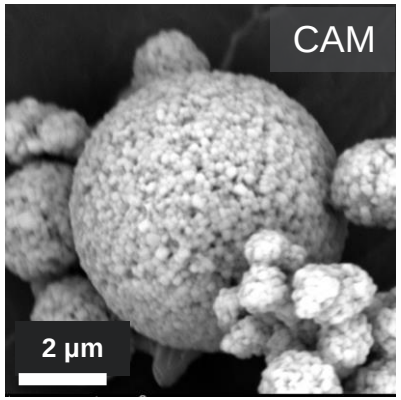


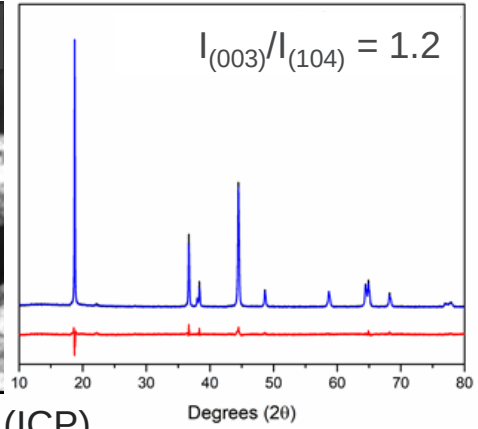
PSD
D10 = 1.77 µm
D50 = 3.17 µm
D90 = 5.73 µm

~1.7% submicron size hydroxide pCAM

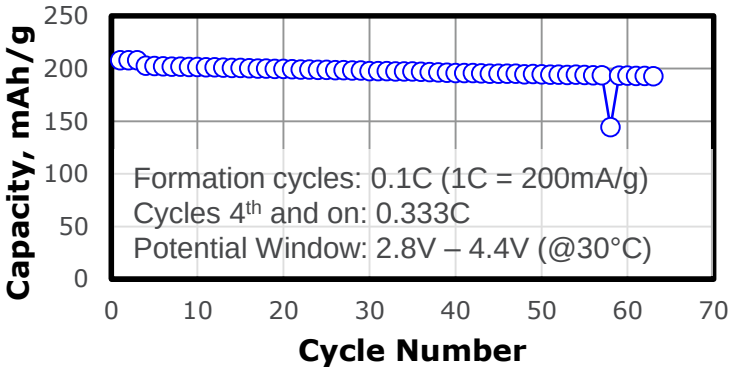


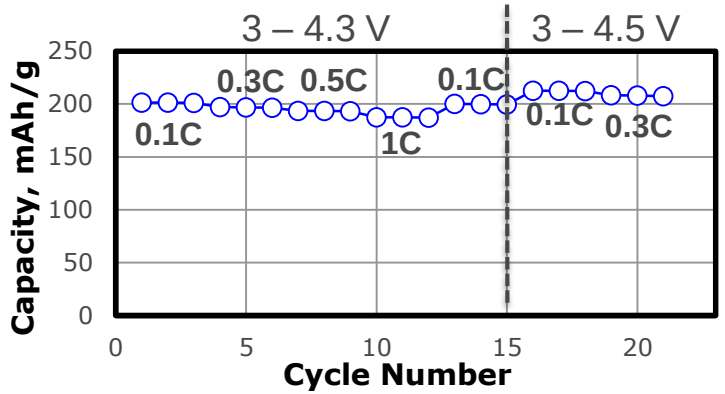
2 × 1 kg/batch calcinations

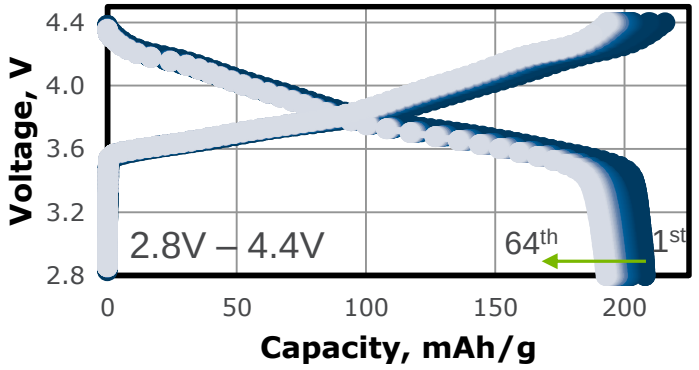




Li/TM mol ratio = 1.03 (ICP)







Request: 2-5 µm NMC811 cathodes for all-solid state battery research

- ☑ Achieved ~3 µm pre-CAM particle with narrow PSD using TVR
- ☑ Continuous operation (~180g/h) with consistent product quality over several hours
- ☑ 2 kg NMC811 cathode active material delivered to ORNL

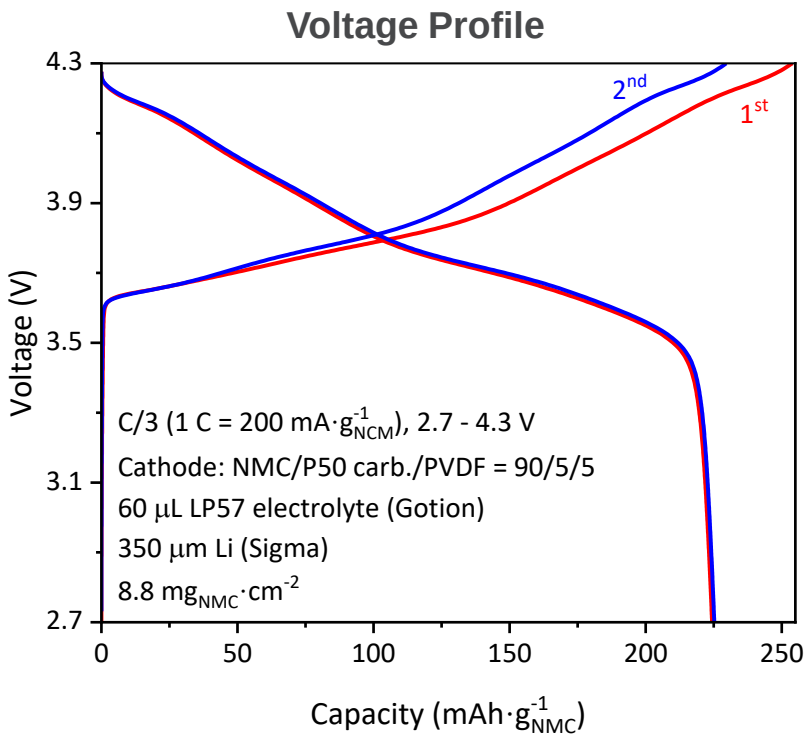
MATERIAL SUPPORT FOR BATTERY COMMUNITY

The US-German CatSE (Cathode Solid Electrolyte) Project

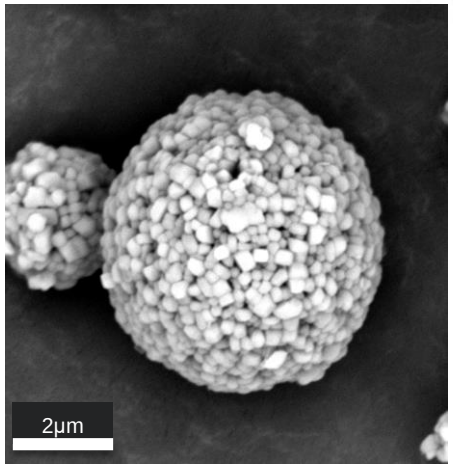
- Focus on understanding interface between NMC811 and LLZO or Argyrodite solid electrolytes

✓ MERF successfully delivered 2 kg of size-specific NMC811 to ORNL in the smallest feasible size.

✓ MERF-made NMC811 were distributed between January to February with experiments currently in progress



E-chem data feedback: Dr. Gabriel Veith (ORNL)



UCSB

UNIVERSITY OF WATERLOO

Argonne NATIONAL LABORATORY

MERF

OAK RIDGE National Laboratory

Gabriel Veith

UNIVERSITY OF MARYLAND

Germany

JÜLICH Forschungszentrum

JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

ZSW

TUM

☑ 2kg NMC811
☑ Manufactured in the US by MERF
☑ Average particle size: 5.7 µm

Argonne NATIONAL LABORATORY

COLLABORATIONS AND COORDINATION

- EaCAM Consortium (Multi-Lab, VTO): Developing continuous synthesis processes and designing particle architectures
  - Guoying Chen (LBNL):LMR-NMC precursor materials at different particle sizes (Earth Abundant Cathode Active Materials Consortium (EACAM)
- CatSE Program (US-German Cathode Solid Electrolyte Project, VTO): custom size NMC811 cathode material
  - Gabriel Veith (ORNL) and several institutes in US and Germany
- ReCELL Subgroups
  - Eva Allen, Albert Lipson (NMC622 via 4L CSTR)
  - Jessica Durham-Macholz (ANL), Prof. Zheng Chen, Hongpeng Gao, Xiaolu Yu (University of California, SanDiego → NMC811 precursor material support
- Pallab Barai, Venkat Srinivasan (BAT 402, ANL) and Jiangming Bai (BNL), Feng Wang (ANL) (BAT183) (VTO)
  - Collaboration in modelling and advanced characterization
- Prof. Sahar Vahabzadeh (Northern Illinois University) (local university support)
- Prof. Feng Lin (Virginia Tech) → Material support for identifying the optimal electrolyte compositions for LNO materials calcined under different conditions
- Emilee Armstrong (PhD Candidate) and Prof. Corrie Cobb (UW) → Enabling UW's acoustophoretic additive manufacturing for scalable 3D battery electrodes (AMMTO)

REMAINING CHALLENGES AND BARRIERS

- Nickel is still needed for achieving high energy density goals set by the DOE's VTO.
- Material processing and manufacturing costs remain as barrier, when new cathode chemistries are developed.
- Stability issues with Mn-based earth abundant cathode hydroxide precursors and their lithiated cathode active counterparts towards air and humid remain as challenge, often requires delicate and costly storage conditions to be adopted. New synthetic routes, that are scalable, are necessary to overcome these sensitivity issues.
- Nickel free and iron containing cathode chemistries for earth abundant cathode materials are challenging in terms of the operational continuity for the manufacturing; mainly due to the stability issues with transition metal solutions containing Fe
- Large scale calcinations remain challenging. New heating technologies are needed.
- Scarcity of material compositions to optimize or scale up, in the absence of nickel and cobalt: due to the scarcity of new material inventions.

PROPOSED FUTURE RESEARCH

- **Material synthesis on a wide range of Mn-rich, polycrystalline baseline cathode materials**
  - ❑ Reducing nickel and gradually replacing it with an element of interest (e.g.; Fe, Mg, Zn, Sn and etc.)
  - ❑ Selection of co-precipitation route (chelating agent) per varying Mn:TM molar ratios
  - ❑ Process development for stabilizing precursors solutions containing Fe
  - ❑ The effect of particle size and morphology on the electrochemical performance
- **Installation of large-scale atmosphere-controlled tube furnace for sensitive cathode active materials**
- **Continue supporting battery research community by providing and making available advanced cathode material → continued effort**
  - ❑ Commercially unavailable precursor materials (e.g.; NMC hydroxides, carbonates and etc.)
  - ❑ Commercially unavailable cathode compositions (e.g.; LNO-based cathodes, Mn-based, Ni-free and Co-free cathodes)
  - ❑ Commercially unavailable cathode particle sizes/morphologies (e.g.; small particles, poly crystalline or single crystals)
  - ❑ 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

- **Mn-Based Earth Abundant Cathode Active Materials (LMR-NMCs)**
  - Development of continuous co-precipitation processes: influence of synthesis parameters on the precursor particles' morphology and density
    - TVR-made materials exhibited very high capacity with stable cycling performance
  - Screening different synthesis routes using green chemistries
    - Ammonium free co-precipitation at room temperature
- **Taylor Vortex Reactor (TVR) – Process Control**
  - Investigated process parameters to produce desired materials morphology for various precursors using Taylor Vortex Reactors with residence time as short as 30 min to 4 h
- **Single Crystal Precursor Development**
  - Co-precipitation process for producing monocrystalline precursors using batch reactors and TVR
  - Mn-based compositions w/wo Fe were synthesized with octa/polyhedron single crystal precursor particle morphology
- **Calcination Scale-up and Optimization**
  - Conducted process R&D to establish relationship between calcination parameters and material performance
  - 1kg/batch calcinations for NMC811 → delivered 2kg NMC811
  - Continued developing optimal calcination conditions for high Ni and high Mn materials and assessing scalability of the process
- **Beyond Li-Ion Battery Materials**
  - Na-ion precursors and cathode materials (NFM) were scaled up to 100 g
- **Material Support for US battery community:** Universities, National Laboratories, VTO-funded Consortia and Programs.

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.
- ANL Team: Carrie Siu, Mateusz Zuba, Isiksu Buyuker, and Jason Aranda are acknowledged for their contributions in synthesis, characterization and synchrotron studies.
- ANL: Feng Wang, Pallab Barai, Venkat Srinivasan are acknowledged for their contributions in material characterizations and modelling collaborations. Trevor Dzwiniel, and Kris Pupek are acknowledged for their electrolyte support.
- ANL-ReCell: Eva Allen, Albert Lipson are acknowledged for their contributions to the application of CSTR synthesis
- ANL-MERF Team: Gerald Jeka and Jeremy Webb, are acknowledged for their support in material analysis.
- ANL: Scott Lockwood and Mike Furlan are acknowledged for their technical support.

Argonne NATIONAL LABORATORY