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Project ID: BAT402



#### IMPROVING BATTERY PERFORMANCE THROUGH STRUCTURE-MORPHOLOGY OPTIMIZATION



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Date: 21<sup>st</sup> – 25<sup>th</sup> June 2021 Location: Online

#### **OVERVIEW**

	Timeline	Barriers
•	Start date: October 2018 End date: September 2022 Percent complete: 66%	<ul> <li>Limited control on particle structure/morphology during synthesis of NMC cathodes</li> <li>High cost of sintering and calcination</li> <li>Low density and conductivity during sintering of solid electrolytes</li> </ul>
•	Budget \$500k/year > 1.5 FTE Scientist > 1.0 FTE Postdoc	<ul> <li>Partners</li> <li>Joseph Libera (MERF, ANL), Project ID: BAT315</li> <li>Ozge Kahvecioglu (MERF, ANL), Project ID: BAT167</li> <li>Jason Croy (CSE, ANL), Project ID: BAT049</li> <li>Feng Wang (BNL), Project ID: BAT183</li> <li>Joanne Stubbs and Peter Eng. (U. Chicago, APS)</li> <li>Jeff Sakamoto (Univ. of Michigan, Ann Arbor)</li> </ul>
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# **MILESTONES**

Serial no.	Milestone description	Completion date	Status
1	Compare reaction temperatures and rates during calcination of NMC811 and NMC111 with lithium carbonate and lithium hydroxide. Correlate changes with primary and secondary particle morphology. Study the properties of the 811 intermediate and final cathodes by XAS, XRD, and SEM.	31 <sup>st</sup> December 2020	Completed
2	Investigate the mechanism of lithiation of the NiO rock-salt intermediates during LiNiO <sub>2</sub> synthesis using atomistic modeling approaches and Ab-initio molecular dynamics. Also, incorporate the information into the macroscopic model.	31 <sup>st</sup> March 2021	Completed
3	Understand the combined influence of pressure and temperature on the densification experienced by the LLZO solid electrolytes from both experimental and computational standpoint. Also, explore dopants segregation to surfaces and effect on phase stability using atomistic modeling.	30 <sup>th</sup> June 2021	In progress
4	Develop mesoscale based computational scheme to capture the calcination of precursors, and compare the model predictions with experimental observations.	30 <sup>th</sup> September 2021	In progress





#### COPRECIPITATION OF Ni-Mn-Co-CARBONATE PRECURSORS

- MnCO<sub>3</sub>
- CoCO<sub>3</sub>
- NiCO<sub>3</sub>

Ni<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>CO<sub>3</sub> (NMC111 CARBONATE)



#### PRIMARY PARTICLE MORPHOLOGY FOR TRANSITION METAL CARBONATE PRECIPITATES

Coprecipitation in "batch" reactors:  $[NH_4HCO_3] / [TMSO_4] \sim 40$ ,  $[TMSO_4] \sim 4.5 \text{ mM}$ 



Investigation of NiCO<sub>3</sub> primary particle morphology is underway



Primary particle morphology:

- **1. MnCO**<sub>3</sub>  $\rightarrow$  Large single crystals
- **2.**  $CoCO_3 \rightarrow Rod$ -like primary particles
- Ni<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>CO<sub>3</sub> → Slightly elongated primaries with surface growth

# Type of transition metal being precipitated influences the primary particle morphology.



#### COMPUTATIONAL MODELING TO DECIPHER THE PRIMARY PARTICLE MORPHOLOGY



#### SECONDARY PARTICLE MORPHOLOGY FOR CARBONATE PRECURSORS



#### **RELATIVE AMOUNT OF Ni, Mn AND Co IN NMC-CARBONATE PRECURSORS**



# CALCINATION OF HYDROXIDE PRECURSORS ▷ PRECURSOR TYPE: Ni<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>(OH)<sub>2</sub> (NMC811 HYDROXIDE) ▷ OXIDATION (ENVIRONMENT: OXYGEN, AIR) ▷ LITHIATION (SOURCE: LIOH, LI<sub>2</sub>CO<sub>3</sub>)



# $\label{eq:pre-conversion} \begin{array}{l} \mathsf{PRE-CONVERSION} \ \mathsf{OF} \ \mathsf{Ni}_{0.8}\mathsf{Mn}_{0.1}\mathsf{Co}_{0.1}(\mathsf{OH})_2 \ \mathsf{TO} \ \mathsf{CUBIC} \\ \mathsf{Ni}_{0.8}\mathsf{Mn}_{0.1}\mathsf{Co}_{0.1}\mathsf{O} \ \mathsf{PROMOTES} \ \mathsf{LAYERED} \ \mathsf{CATHODE} \ \mathsf{PHASE} \end{array}$

Calcination of  $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$  with LiOH is characterized using *in situ* X-Ray diffraction. Two different cases are investigated: a) Pre-converted  $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ , b) Conventional

Pre-conversion: Heating Ni<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>(OH)<sub>2</sub> precursors at 350°C for 4 hours without Li source, then calcination with LiOH at elevated temperatures.

**Conventional:** Heating  $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$  precursors with LiOH at elevated temperature.



In X-Ray diffraction:

- (003) peak  $\rightarrow$  Layered phase
- (104) peak → Rock-salt phase
- Area(003) / Area(104) → Extent of layering within the cathode particles.

Pre-conversion at 350°C helps in the formation of layered phase and delays the Li/Ni mixing at higher temperatures.

Hypothesis: Surface oxygen during preconversion helps in enhanced lithiation and layered phase formation

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#### LITHIATION OF INTERMEDIATE CUBIC PHASE MEDIATED BY SURFACE OXYGEN

Atomistic (AIMD) simulation of reaction between NiO and LiOH at elevated temperatures



- 1 Oxygen adsorbs to NiO surface
- 2 Ni migrates to the new oxygen surface as Ni
- 3 Simultaneously, Li enters vacancies to balance charge, forming a full layer
- 4 More oxygen adsorbs to the fresh surface, restarting the cycle.

# Presence of oxygen (O) at the surface of NiO (or Ni-vacancy) is necessary to start lithiation.



#### FORMATION OF LAYERED PHASE WITHIN LITHIATED CATHODE PARTICLES

AIMD simulation of layering within lithiated NiO



Gliding between the Li and Ni layers is necessary for the formation of layered phase from rocksalt. Gliding for plastic deformation is a possibility.



#### SINTERING OF NMC CATHODE PRECURSORS DURING CALCINATION

During calcination of Ni<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>(OH)<sub>2</sub> with LiOH at high temperature, sintering of the particle occur.

Particle size (domain size) extracted from the width of the X-ray diffraction peaks.



#### SURFACE OXYGEN COVERAGE GOVERNS SINTERING AT INTERMEDIATE TEMPERATURE

Mesoscale computational model of particle sintering, lithiation, oxygen diffusion and volume expansion.



Enhanced lithiation of pre-converted particles:

- 1. Better surface oxygen coverage
- 2. Shorter Li diffusion length

For computational modeling of sintering of NMC811 cathode particles, see BAT183. Argonne

#### SUMMARIZING THE IMPORTANCE OF PRE-CONVERSION IN THE LITHIATION PROCESS



17 Smaller particle → More lithiation Argonne ▲

# LLZO DENSIFICATION \* EXPERIMENTAL CHARACTERIZATION AND COMPUTATIONAL MODELING



#### **MODELING THE DENSIFICATION OF LLZO** SOLID-STATE-ELECTROLYTES



#### **INFLUENCE OF TEMPERATURE AND PRESSURE ON RELATIVE DENSITY DURING SINTERING**

Mesoscale modeling of LLZO particle densification under elevated temperature and pressure.



#### RELATIVE DENSITY OBTAINED AFTER SINTERING UNDER EXTERNAL PRESSURE



# COMBINED INFLUENCE OF TEMPERATURE AND PRESSURE ON THE DENSIFICATION OF LLZO



# IN SITU DENSIFICATION

#### LLZO at high pressure, high temperature

- Large volume press (APS, 13BM-D) used to map changes in morphology and crystal structure of LLZO
   P = 0 - 5 GPa, T = 0 - 2000C
- Experiments studied variable temperature, pressure, and starting material as well as kinetics of densification.
  - Transition to cubic LLZO and lithium loss occurs at lower temperature (400C) during operation at GPa pressures.





#### **RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS**

This project was not reviewed last year.



# **COLLABORATION AND COORDINATION**

- Argonne National Laboratory (ANL)
  - Gregory Krumdick and Joseph Libera (MERF), Project ID: BAT315
  - Jason Croy and Arturo Gutierrez (CSE), Project ID: BAT049
  - Ozge Kahvecioglu and Shankar Aryal (MERF), Project ID: BAT167
  - Jianguo Wen and Ilke Arslan (CNM)
  - Vincent De Andrade (APS)
- University of Chicago
  - Joanne Stubbs and Peter Eng. (APS, ANL)
  - Tony Yu and Yanbin Wang (APS)
- University of Michigan (Ann Arbor)
  - Jeff Sakamoto
  - Alexandra Moy
- Brookhaven National Laboratory (BNL)
  - Feng Wang and Jianming Bai, Project ID: BAT183
- DOE User Facility
  - Advanced Photon Source (APS), located in ANL
  - Center for Nanophase Materials (CNM), located at ANL
  - Laboratory Computing Resource Center (LCRC), located at ANL



#### **REMAINING CHALLENGES AND BARRIERS**

- □ Understanding the coprecipitation of NMC-hydroxide cathode precursors with gradient in transition metal concentration.
- $\Box$  Elucidation of the growth process of Ni<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>(OH)<sub>2</sub> precursor primary particles.
- □ Calcination of NMC-carbonate cathode precursors.
- Investigation regarding lowering the calcination temperature by using different source of lithium.
- Understanding the influence of lithium loss at higher temperatures during the densification process of LLZO.



# **FUTURE WORK PLANS**

Formation of disk shaped primary particle morphology within NMC-hydroxide precursors during coprecipitation.



Feng et al., JES (2018) 165 13 A3077 – A3083

Eutectics: Lowering the calcination temperature through the usage of low melting point lithium salts.

Modeling lithium loss from the LLZO surface at the time of high temperature sintering.



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### SUMMARY

Precipitated NMC-carbonate cathode precursors and developed computational models to understand their growth process.





Characterized calcination of NMC-hydroxide cathode precursors and analyzed the importance of surface oxygen coverage on the overall lithiation process.

Developed computational model to understand the influence of pressure and temperature on the densification experienced by LLZO solid electrolytes.



