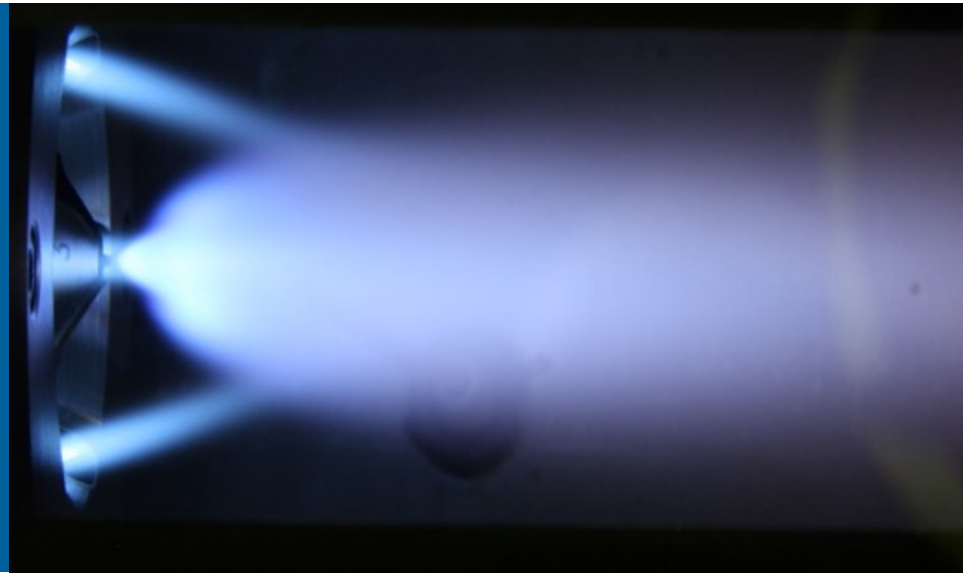
PROCESS R&D FOR DROPLET-PRODUCED POWDERED MATERIALS



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Project ID: BAT315

2020 DOE Vehicle Technologies Office Virtual Annual Merit Review (AMR),
June 1-4, 2020,

Overview

Timeline

- Project Start Date: September 2016
- Project End Date: September 2020

Partners

- Cabot Corporation
- ORNL

Budget

- Total project funding:
  - $490K in FY19

Supporting battery research for:

- DOE Battery Research Community

Barriers

- **Cost of high-energy Li-ion**
- **Life**

Objectives - Relevance

- To produce customized and optimized LLZO for the basic battery community and to produce large crystal-domain cathode powders.

- The relevance of this task to the DOE Vehicle Technologies Program is:
  - This synthesis technique has the potential to provide large cost reduction through continuous high-volume production methods.
  - The high purity and crystallinity of FSP materials has the potential to improve performance for the same materials synthesized by other means.

Approach and Strategy

- Flame Spray (combustion synthesis) is a proven industrial technology for commodity scale production of numerous simple compounds (TiO_2, C black, SiO_2). The ANL FSP facility provides a highly instrumented pre-pilot powder production facility for the development and optimization of aerosol production of powders. This heavily instrumented facility provides in-operando scientific feedback to enable rapid materials development and fundamental understanding of this complex manufacturing process.

- Spray Pyrolysis and Spray Drying have been added to compliment the aerosol synthesis capability. They provide a complimentary perspective and greatly aid in the understanding of the challenges each new material brings.

- Maintain a close relationship with our industrial partners to assure we follow sensible routes for potential commercialization.

Approach - Milestones

	Phase 1 - FSP Facility Construction and Commissioning		
FY16	Project start and Completion of Flame Spray Pyrolysis System Design	*Completed*	
FY17	Completed construction and commissioning of FSP Facility	*Completed*	
	Phase 2 - FSP Research for Battery Materials		
FY18	Completed First year of materials research, discovered low temperature c-LLZO and completed addition of advanced diagnostics including scanning mobility particle sizing, laser PLIF, and optical emission spectroscopy	*Completed*	
FY 19	Added Spray Pyrolysis and Spray Drying to aerosol synthesis portfolio	*Completed*	Oct-2019
	Upgraded OES with medium resolution spectrograph; Added in-situ Raman spectroscopy for FSP	*Completed*	Mar-2020
	Discovered new routes for c-LLZO using spray pyrolysis and spray drying	*Completed*	Jan-2020
	Completed broad comparative survey of NCM cathode active phase materials using FSP and SP	*Completed*	Jan 2020
	Commercialize c-LLZO production	*ongoing*	Sep-2020

Technical Accomplishments And Progress Overview

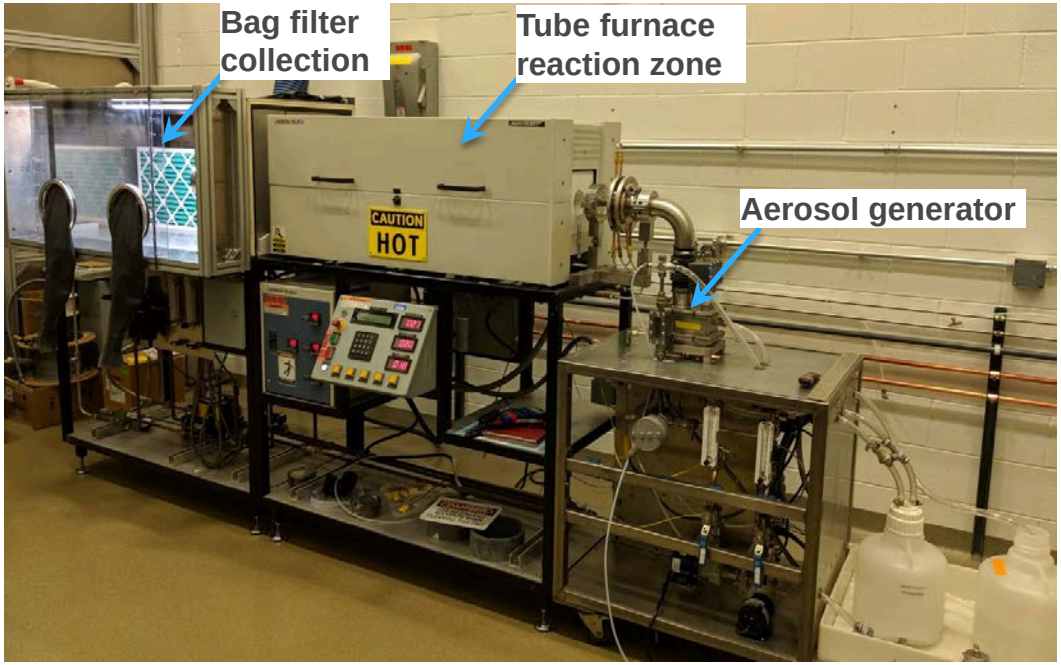
Accomplishment Summary Aerosol Synthesis Facility

- Added Spray Pyrolysis and Spray Drying as additional Aerosol synthetic routes for c-LLZO and cathode active phases.
- Added In-Situ Raman Spectroscopy for FSP.
- Added a medium resolution spectrograph for Flame Emission Spectroscopy
- Added an improved burner design for FSP with a motorized air-gap control for the atomizing nozzle and cooling for the burner body.

Technical Accomplishments And Progress Overview

Facility Expansion and Improvement

- Received and recommissioned Nomad VIII spray pyrolysis system donated to ANL by Cabot Corp.
  - Ultrasonic nebulization
  - 500 g/hour solution processing rate.
  - 50 g/hour powder production rate
  - Material collection in bag filter.
  - Added glove panel PPE for rapid collection and turnover.



*** This effort for this work was performed jointly with project "Aerosol Manufacturing Technology for the Production of Low Cobalt Li ion Battery Cathodes". See bat411**

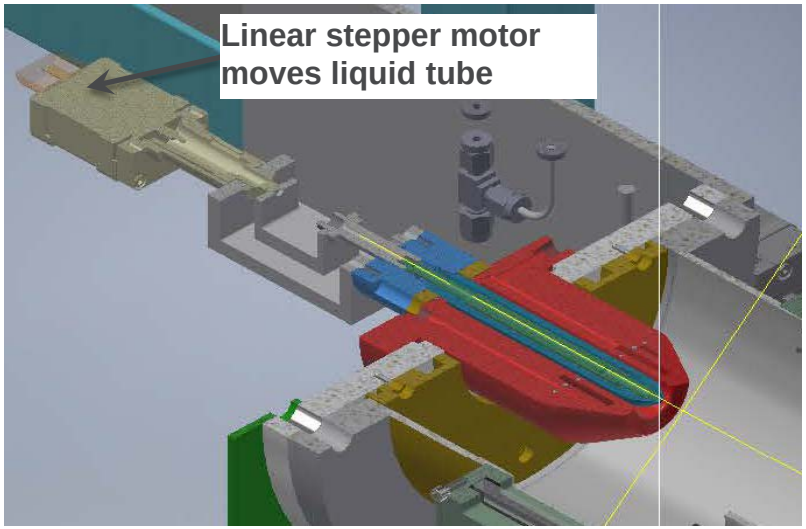
Technical Accomplishments And Progress Overview

Facility Expansion and Improvement

- Added In-Situ UV-Raman spectroscopy for FSP.
  - **266,355,512, and 633 nm excitation**
  - **FSP powder sample accumulated onto a sample window in <5 min. Measurement 5-15 minutes.**

- Upgraded burner for FSP
  - **Motorized nozzle air-gap for dynamic atomization adjustment and optimization.**
  - **Added burner body cooling to improve process consistency for short duration collections.**

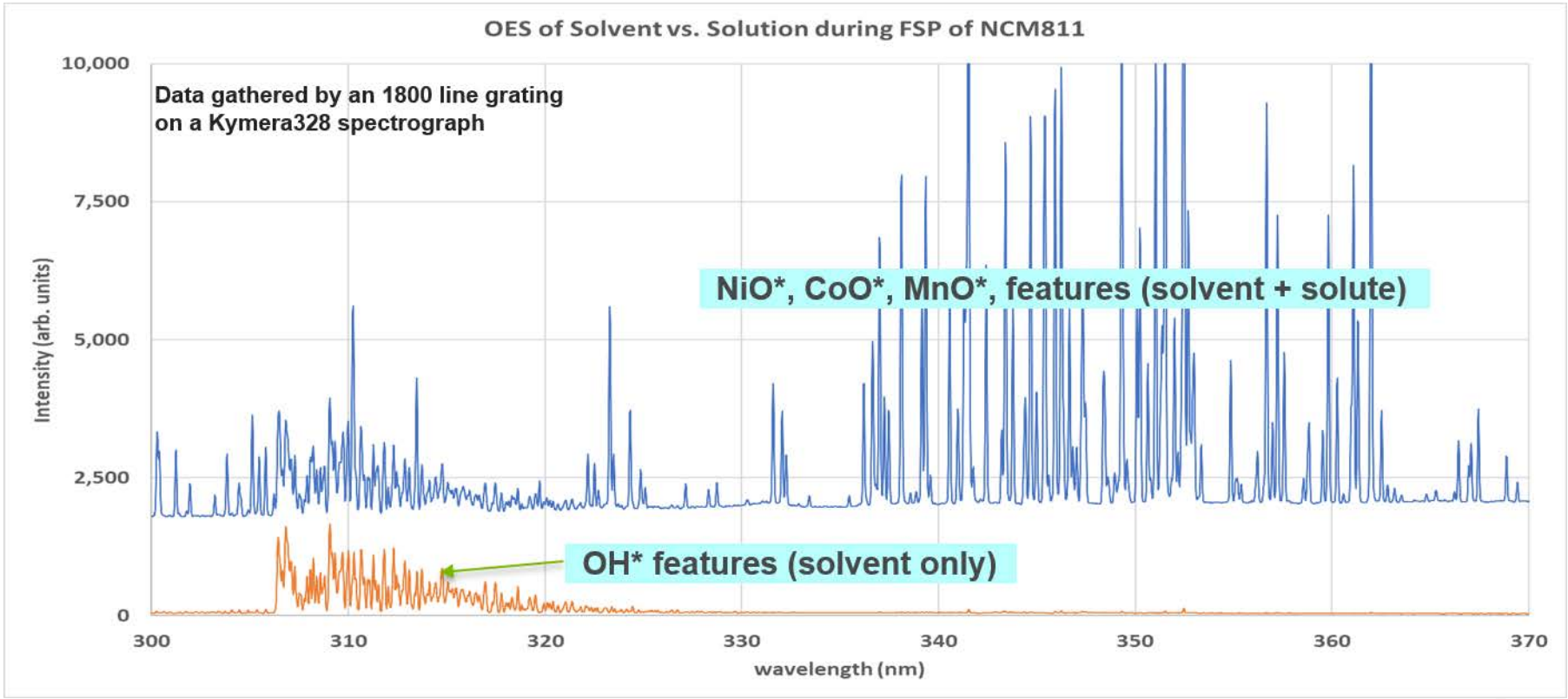
- Added medium resolution spectrograph for monitoring flame chemistry by optical emission spectroscopy.



Technical Accomplishments And Progress Overview

Optical Emission Spectroscopy for FSP Synthesis Diagnostic

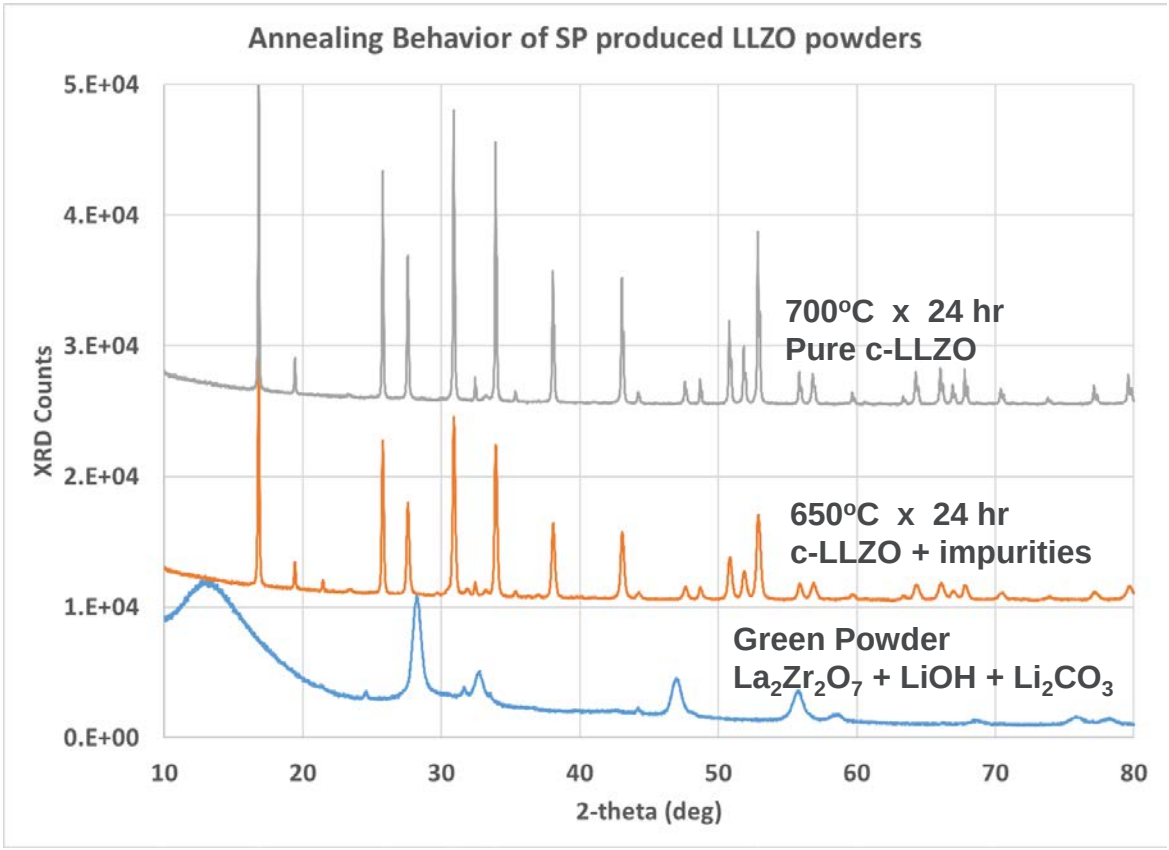
- **OES provides chemical mapping of pre-condensation gas phase radicals which informs us about the processes leading to the formation of target material phases**
- **Artificial Intelligence(AI) and Machine Learning (ML) tools are being applied to help manage and interpret the vast amount of data gathered.**
- **A flame-axis probe array provides a linear mapping of flame chemistry**



Technical Accomplishments And Progress Overview

Additional manufacturing routes to low-temperature c-LLZO

- Spray Pyrolysis was used to produce c-LLZO through low-temperature calcination
- Potentially the most economic route for large scale production.
- c-LLZO was also produced using Spray Drying but a higher calcination temperature of 900°Cwas required since the emergent phase was tetragonal LLZO.



Technical Accomplishments And Progress Overview

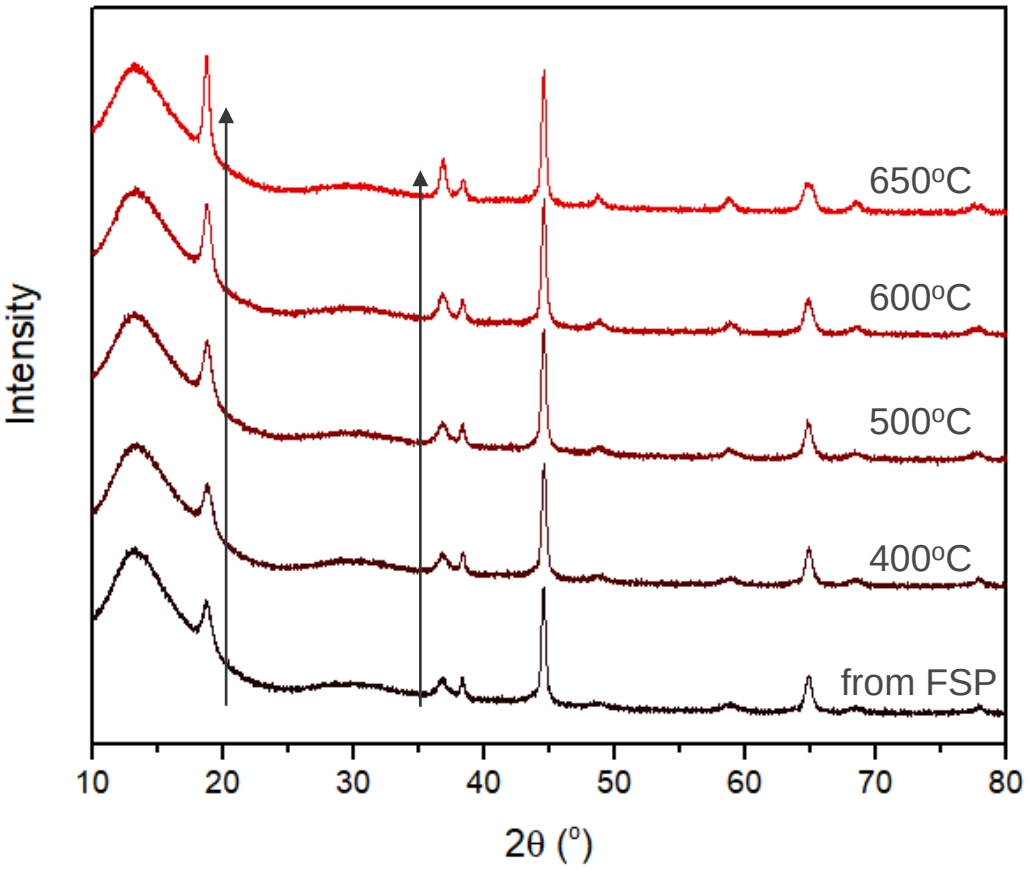
Accomplishment Summary Cathode Active Phase

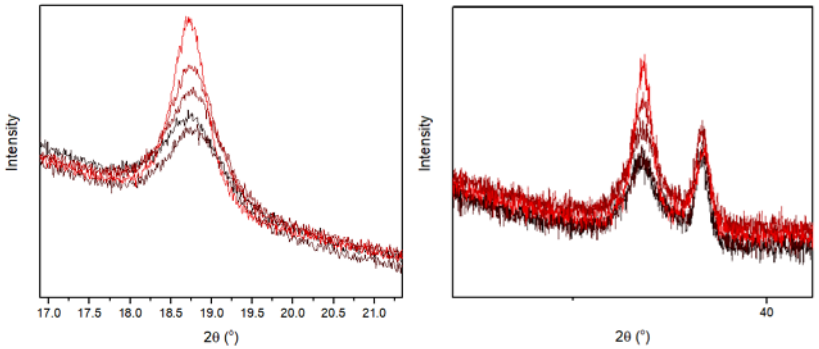
- Explored NCM 111, 622, and 811, 9055, and NCA by FSP and SP synthesis to obtain a broad perspective of material potential across a broad spectrum of TM oxide active phases*.
- Discovered NCM 111 spinel active phase using FSP.
- Discovered route to large single crystal NCM phase from FSP nano green powder.

- **Note: low-Co candidates in this list were produced under project “Aerosol Manufacturing Technology for the Production of Low Cobalt Li ion Battery Cathodes”. See bat411**

Technical Accomplishments And Progress Overview

FSP NCM111 powders exhibit a composite rock salt/spinel structure





- 111, 311 peaks increase with increasing annealing temperature, indicating the ordering formation
- Anneal at 650ºC produced lithiated spinel NCM111 for the first time
- This material has an initial EC capacity of 150 mA/g.

*** This work was performed in collaboration with E.J. Lee. See BAT251**

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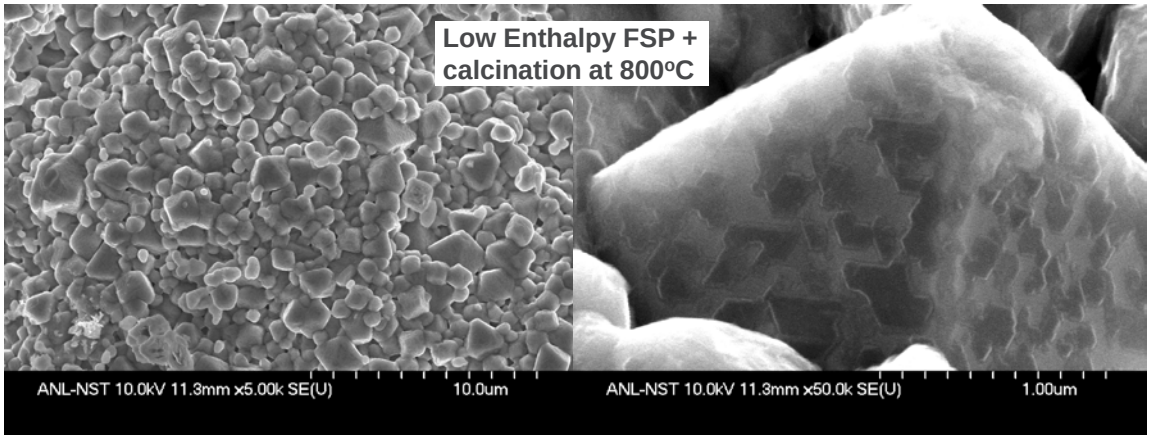
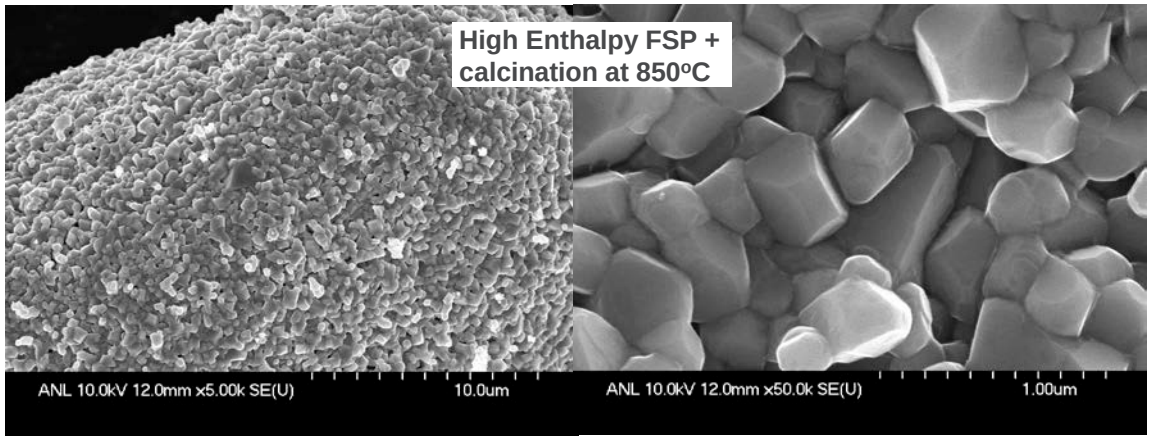
Technical Accomplishments And Progress Overview

Mapped NCM 811 Single Crystal Formation from FSP powders

- Single Crystal primary particle morphology is prevalent from FSP produced NCM precursor powders
- FSP was used to produce pre-lithiated NCM811 nano-powders from various solvent/precursor combinations.
- Produced powders are a mixture of LiOH, Li2CO3, and NCM rock salt phases with small incipient quantities of active phases (spinel and layered)
- The average single crystallite size depends on the FSP solution enthalpy – hotter flames result in smaller single crystallite size





Responses to Previous Year Comments

No reviewer comments were received from the 2019 AMR review.

Collaboration and Coordination with Other Institutions

- Cabot Corp. is a continuing partner in low-Co cathode active phase development. Cabot has also joined with ANL on 2020 TCF proposal to commercialize c-LLZO production.

- ANL is sponsoring a CRI Innovator with Northwestern University for the development of novel graphene-active material composite cathode architectures.

- ANL is supplying ORNL with aerosol-produced c-LLZO for evaluation in SSB manufacturing.

Remaining Challenges and Barriers

- Optimize c-LLZO for manufacturing processes that take advantage of the low-temperature route to cubic LLZO
- Improve product quality through advanced FSP burner optimization.
- Optimize spray pyrolysis and/or spray drying for commercial scale production of c-LLZO
- One-step synthesis in FSP to the layered phase NCM materials.

Proposed Future Research

- Optimize blends of c-LLZO made by SP and FSP for SSB manufacturing.

- Reduce carbon use in FSP solutions to promote direct synthesis of target phases that are competitive with carbonate phases.

- Optimize FSP synthesis for direct production of ready to use battery cathode phases.
  - Follow the guidance of in-situ Raman for rapid process optimization.
  - Explore post-flame annealing for battery active phases and LLZO

- Continue exploration of emerging disordered rock-salt type cathode materials

Summary Slide

- Spray Pyrolysis and Spray Drying were added to the ANL aerosol synthesis capability.
- In-situ Raman spectroscopy and medium resolution flame spectroscopy was added the advanced diagnostics suite for the FSP system.
- High purity c-LLZO attained at a calcination temperature of 700 deg C was produced in the new Spray Pyrolysis reactor.
- Completed a broad survey of NCM active phases ranging from traditional NCM111 to current low-Co candidate.
- Established plan to commercialize c-LLZO production with Cabot Corp.