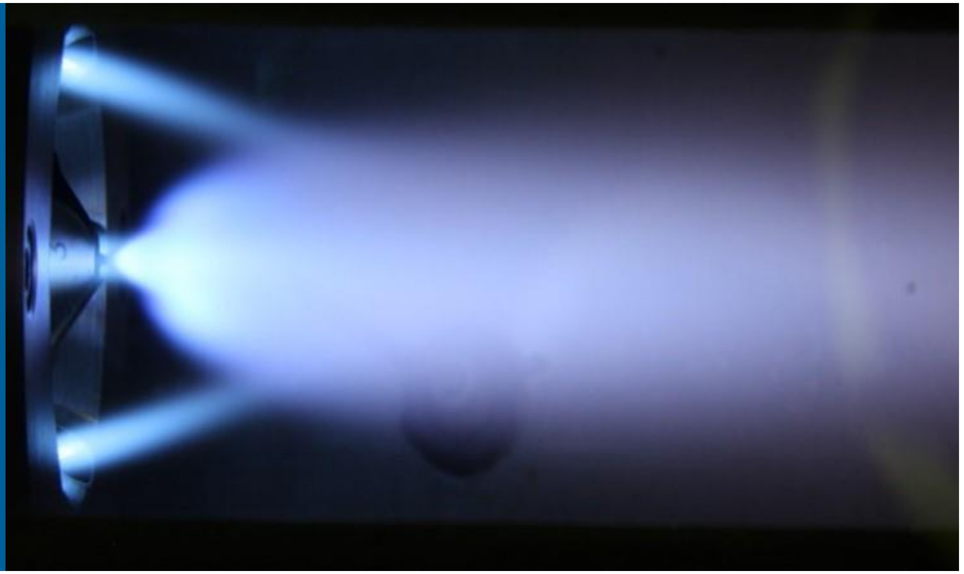
PROCESS R&D FOR DROPLET-PRODUCED POWDERED MATERIALS



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Project ID: bat315

2021 DOE Vehicle Technologies Office Virtual Annual Merit Review (AMR),
June 23, 2021

Overview

Timeline

- Project Start Date: September 2016
- Project End Date: September 2021

Budget

- Total project funding:
  - $300K in FY20
  - $400K in FY21 estimate

Barriers

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

Partners

- Cabot Corporation
- ORNL, LBNL
- Purdue University

Supporting battery research for:

- DOE Battery Research Community

Objectives - Relevance

- To produce customized and optimized LLZO for the basic battery community and to explore single crystal cathode powder synthesis.

- 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 aerosol materials has the potential to improve performance for the same materials synthesized by other means.

Approach and Strategy

- Flame Spray Pyrolysis 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.

- Alternative aerosol techniques: (a) Spray Pyrolysis, (b) Slurry Flame Spray Pyrolysis, (b) Slurry Spray Pyrolysis.

- 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 (FSP) 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 (SP) 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
FY 20	Supplied LLZO research samples to ORNL and LBNL.	*ongoing*	Sep-2021
	Opened collaboration with Purdue University for using Al-LLZO and LLBZO for polymer composite SSE	*Ongoing*	
	Discovered process conditions for one step synthesis to layered phase in FSP.	*Completed*	Feb 2021
	Added SFSP (slurry FSP) and SSP (slurry SP) to techniques portfolio	*completed*	June 2021
	Developed new concept for all ceramic cathode using LLZO green powder.	*ongoing*	Sept-2021

Technical Accomplishments And Progress Overview

Al-doped LLZO research samples

- Al-doped LLZO is produce by first synthesizing a green powder consisting of LZO and lithium carbonate or lithium hydroxide. The green powder is converted to cubic LLZO by a calcination step at 700-1000^oC. The key to enabling the low limit of required calcination temperature is the atomic mixing SP and FSP provide.

- The green powder can be produced by FSP or SP but in both cases, the green powder particle morphology is erased by the sintering that occurs during the transformation to the cubic LLZO phase. Post-calcination milling is then performed to produced the particle size distribution specified by utilization schemes for the SSE.

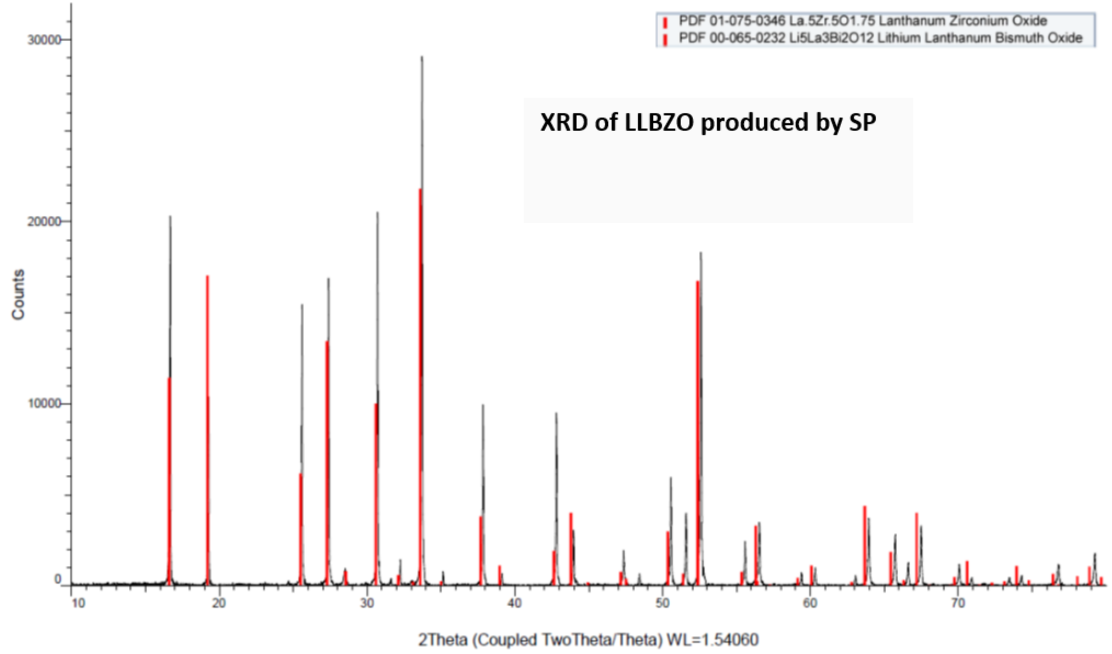
- When a cubic LLZO finished prescribed PSD is needed, SP is the better choice as it is produced at lower cost than FSP green powder. However, the nano-form of FSP green powder makes it ideal for schemes that perform c-LLZO formation during composite cathode manufacture.

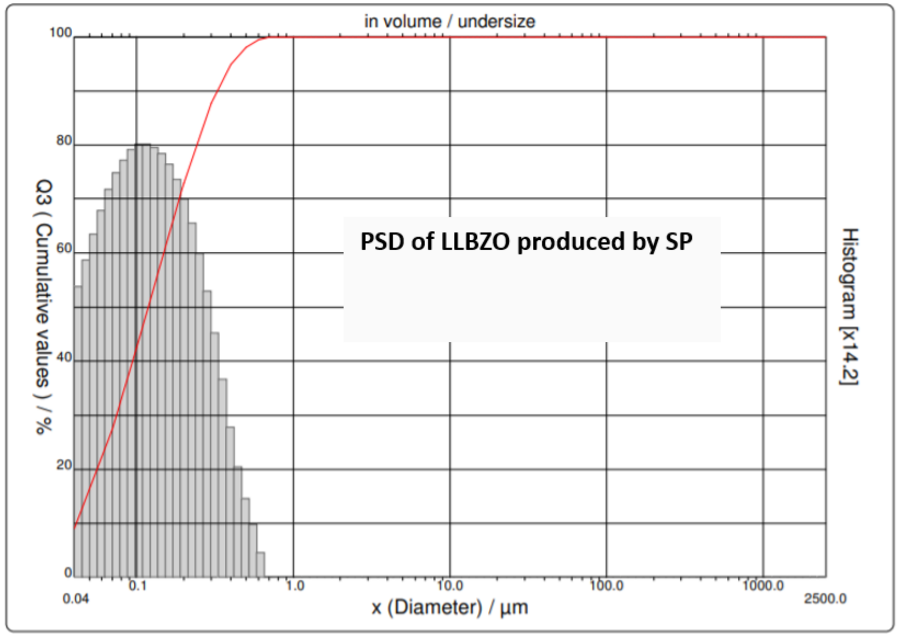
- Upon request, provided Al-doped LLZO to ORNL and LBNL.
- Upon request, provided non-lithiated LLZO green powder to ORNL.

Technical Accomplishments And Progress Overview

Exploration of Aerosol Techniques for LLBZO synthesis

- Synthesized LLBZO ($Li_6La_3Zr_{1.25}Bi_{0.75}O_{12}$) using Flame Spray Pyrolysis and Spray Pyrolysis.
  - Aqueous nitrate based Spray Pyrolysis synthesis
  - Achieves cubic phase at 700^{o}C
  - Provides an alternative LLZO garnet phase for polymer composite SSE (Villa, A., Verduzco, J.C., Libera, J.A. et al. Ionic conductivity optimization of composite polymer electrolytes through filler particle chemical modification. Ionics (2021))





Technical Accomplishments And Progress Overview

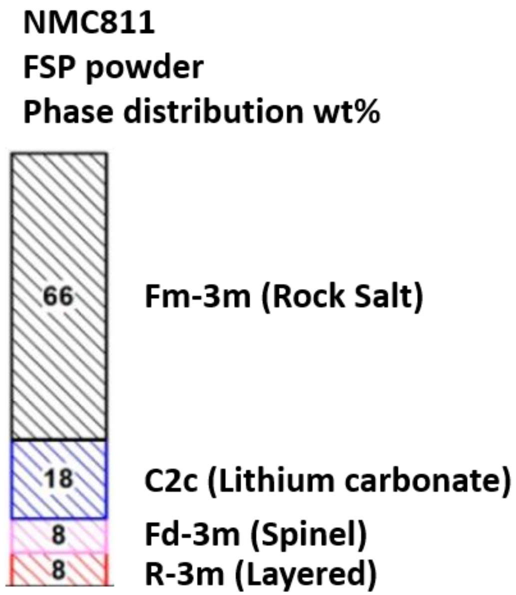
Cathode Active materials: One-step Synthesis to layered phase using Flame Spray Pyrolysis

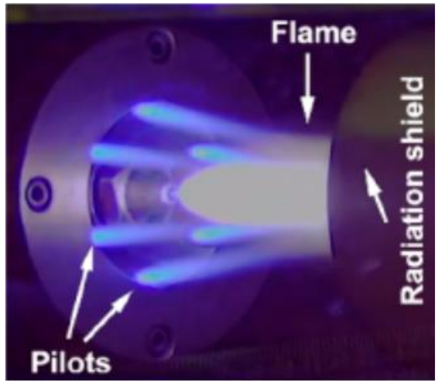
- Goal: One-step synthesis to the layered phase using FSP would eliminate calcination in belt furnaces and greatly simplify cathode manufacture.

- Flame Spray Pyrolysis was used to produce up to 8wt% of the layered Fd-3m phase in immediate products of FSP synthesis (so-called green powder) demonstrating the potential to produce the required phase entirely by an aerosol route.

- The observed trend was increasing layered phase with solution enthalpy (i.e, flame temperature)

- Published in: “Process Engineering to Increase the Layered Phase Concentration in the Immediate Products of Flame Spray Pyrolysis”, accepted to ACS Applied Materials and Interfaces, April 2021.





Remaining challenges:

1. **Complete conversion to layered phase**
2. **Attain dense larger particles (1-2 microns**)

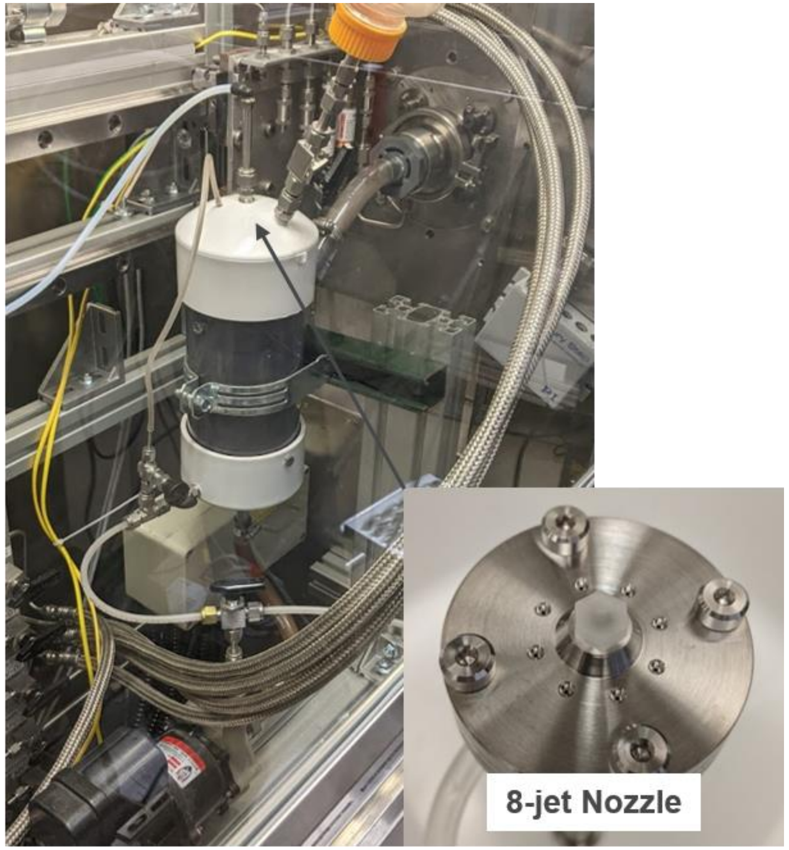
Argonne NATIONAL LABORATORY

Technical Accomplishments And Progress Overview

Slurry Flame Spray Pyrolysis (SFSP) and Slurry Spray Pyrolysis (SSP)

- Slurry aerosols can increase the particle density and facilitate contactless sintering for one-step to single crystal particle synthesis.
- Slurry droplets can be solids-only or combined solid and soluble component mixtures.

ISCO slurry syringe pump for flammable (FSP) slurry aerosol generation

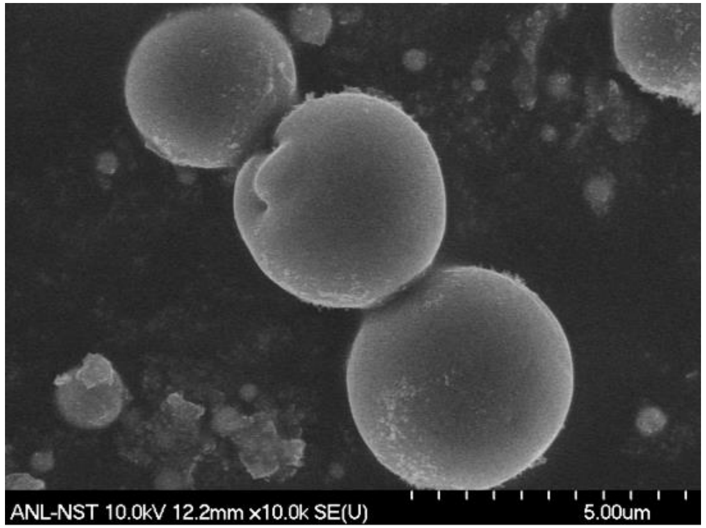


Slurry Aerosol Generator for non-flammable spray pyrolysis aerosol generation based on Collison technology.

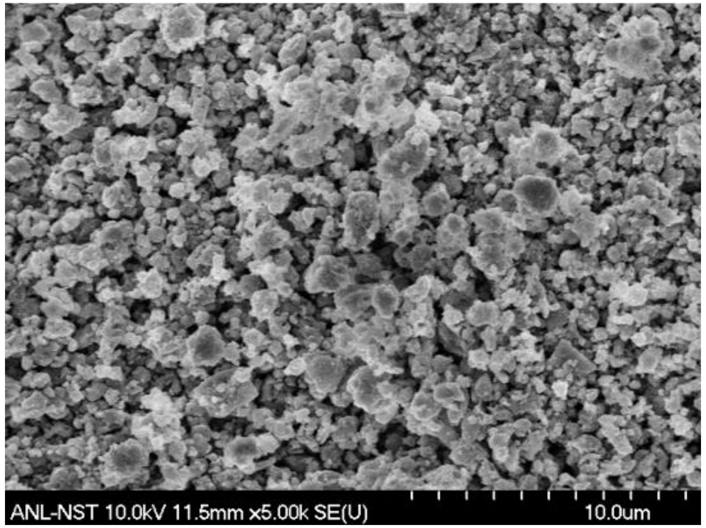
Technical Accomplishments And Progress Overview

Slurry Flame Spray Pyrolysis (SFSP) and Slurry Spray Pyrolysis (SSP)

- Example of SFSP particles using P25 titania slurry in xylene/acetonitrile solvent/suspension fluid. P25 30 nm slurry particles are assembled and sintered into large micron sized spherical particles.



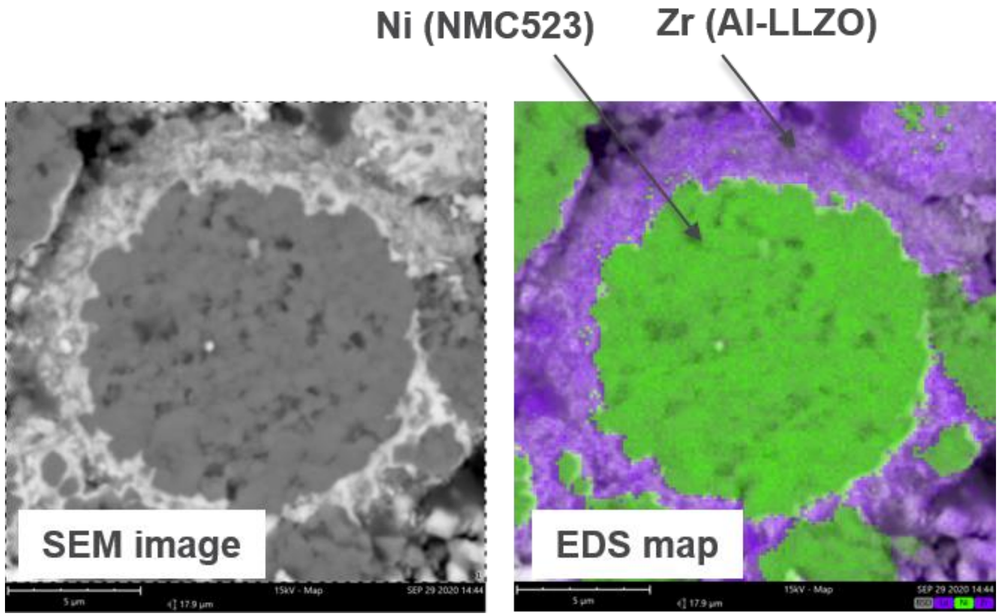
- Example of powder produced by SSP using 150 nm NCM111 precursor TM oxides solid particles + dissolved lithium nitrate. Some droplet explosion creates the smaller particles in this example. Ongoing efforts will utilize lithiated TM solids.



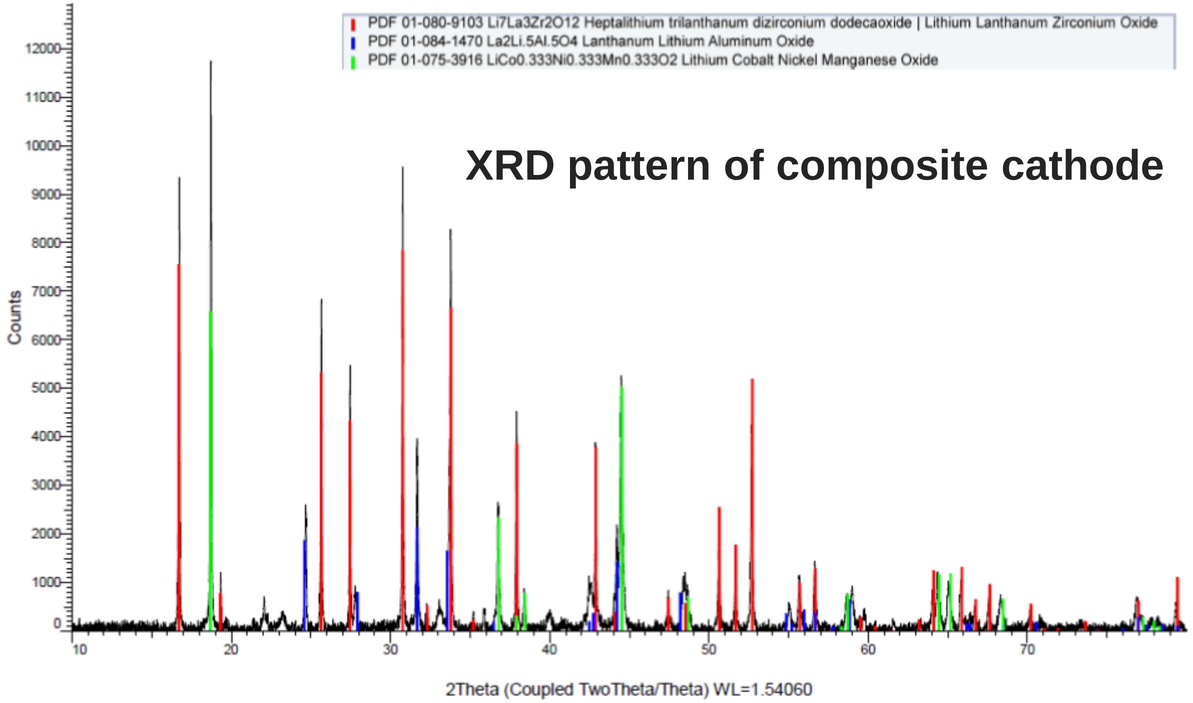
Technical Accomplishments And Progress Overview

LLZO Green Powder as an ingredient in all-ceramic cathode manufacture is enabled by low LLZO formation temperature

- Co-sintering of finished NMC523 cathode particles + LLZO green powder shows that in-situ formation of the cubic LLZO phase occurs and that cubic LLZO phase exhibits a conformal wetting behavior coating the cathode particles with SSE.
- During sintering, the cathode layered phase is preserved while some impurities in the SSE system can occur and need to be minimized



Cross-section of composite cathode



XRD pattern of composite cathode

Collaboration and Coordination with Other Institutions

- Cabot Corp. is a continuing partner in low-Co cathode active phase development and in the design of advanced aerosol processing techniques.
- ANL is sponsoring a CRI Innovator Volexion with Northwestern University for the development of novel graphene-active material composite cathode architectures. This Innovator has been successfully graduated and is moving on to independent start-upstatus.
- ANL is supplying ORNL and LBNL with aerosol-produced c-LLZO for evaluation in SSB manufacturing.
- Purdue University: Synthesis of Al-LLZO and LLBZO for comparative study in polymer composite SSE applications

CABOT

CHAIN REACTION INNOVATIONS
Entrepreneurship at Argonne

Remaining Challenges and Barriers

- Optimize and/or deploy advanced hybrid schemes for one-step to layered phase aerosol synthesis of cathode active materials.

- Develop manufacturing methodology for producing all-ceramic composite cathodes using in-situ calcination for SSE formation and bonding.

- Deploy slurry aerosol processes to attain required particle size and density (possibly single crystal particles)

Proposed Future Research

- Optimize slurry aerosol methods to attain one-step to layered phase synthesis with dense particle in the 1-3 micron range.
- Explore contactless-sintering of high nickel NMC slurry to produce single crystal finished powder. Utilize very high temperatures and controlled temperature gradients to provide the necessary temperature-time profile.
- Explore all-ceramic cathode architectures based on low-T garnet SSE formation during co-sintering of composite cathodes.
- Scale LLZO production to 1 kg/day

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

Summary Slide

- Supplied Al-doped cubic LLZO research samples to ORNL and LBNL.
- Opened collaboration with Purdue University for using aerosol Al-LLZO and LLBZO for polymer composite SSE.
- Discovered process route for one step synthesis to layered phase in FSP.
- Added slurry FSP and slurry SP to techniques portfolio.
- Discovered new pathway for all ceramic cathode using green powder LLZO