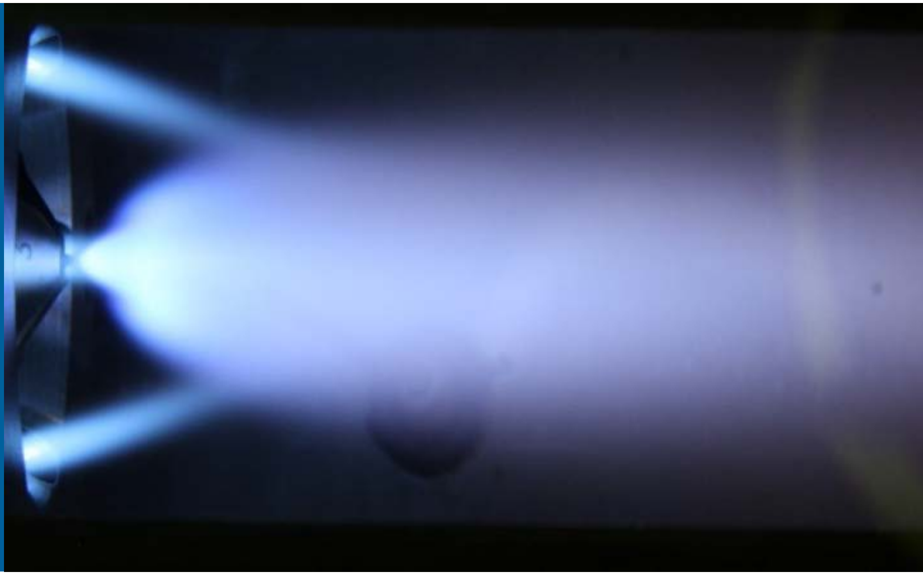
PROCESS R&D FOR DROPLET-PRODUCED POWDERED MATERIALS



JOSEPH LIBERA (PI) **YUJIA LIANG**

Project ID: BAT315

2019 DOE VTO Annual Merit Review
June 2019, Washington, D.C.

Overview

Timeline

- Start date: Jan. 2016
- End date: Sept. 2019
- Percent complete: 80%

Budget

- Total project funding:
  - $500K in FY18

Barriers

Cost of Li-ion batteries
Performance of Li-ion batteries

Industrial Partners

- Cabot Corporation

Supporting battery research for:

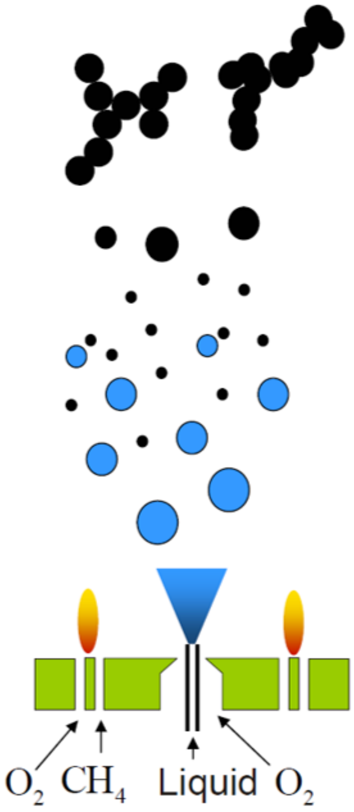
- DOE Battery Research Community

Objectives - Relevance

- The objective of this task is to establish a flexible R&D capability in the MERF for developing Flame Spray Pyrolysis (FSP) as a synthesis method for battery materials
  - Develop FSP battery materials with industrial partner guidance to assure relevance to sensible scale-up strategies.
  - Provide quantities of high quality materials sufficient for industrial evaluation.
  - Explore simplification of battery manufacturing by eliminating of calcination, combining cathode powder and carbon matrix, direct deposition of cathode/carbon material onto electrode substrates (roll-to-roll schemes)
- 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).
- R&D using flame spray for battery materials is ongoing around the world in academic and industrial settings showing the potential promise of this approach.
- This effort will specifically follow the guidance of our industrial partners to assure sensible approaches to achieve scalability and low cost.



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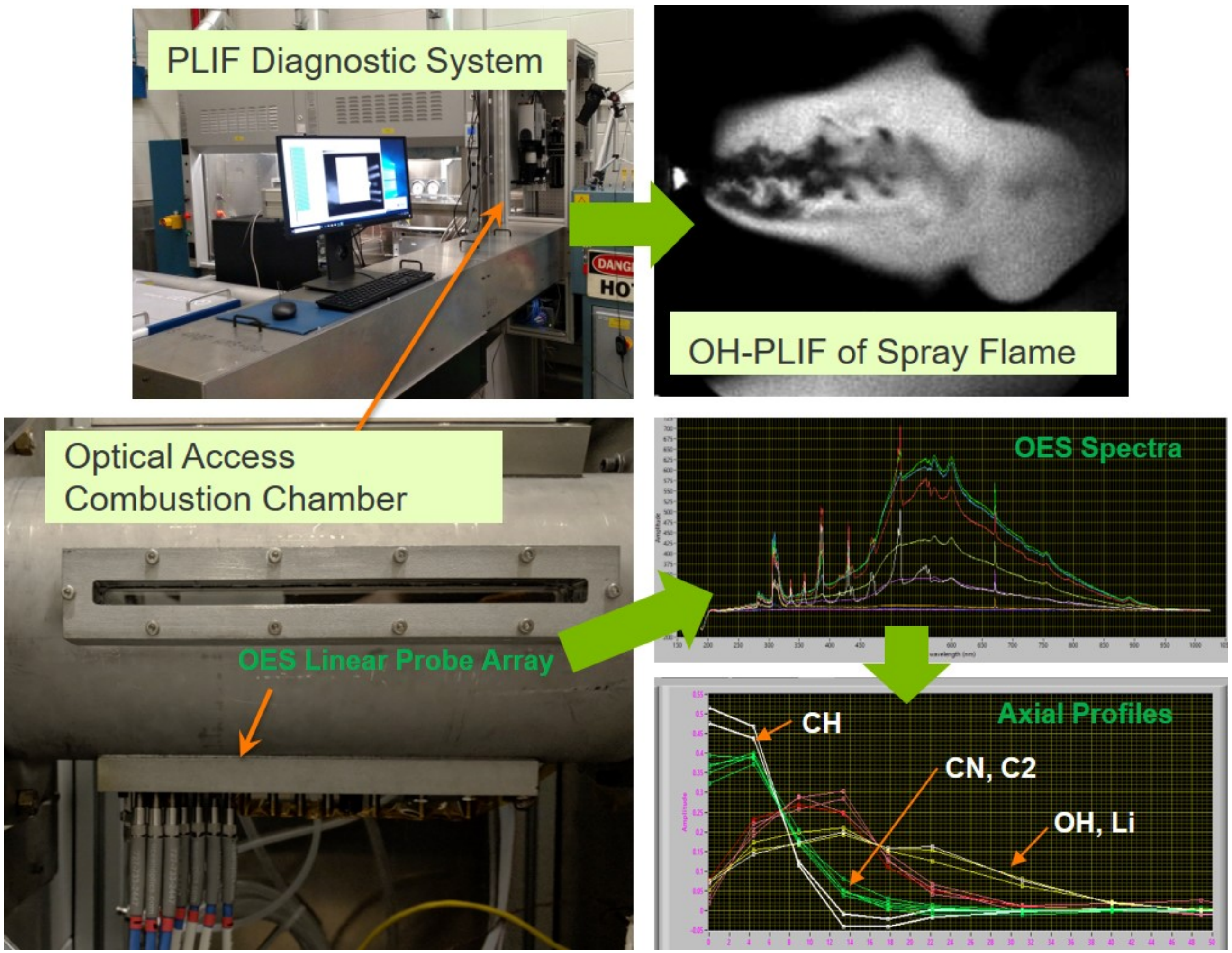
Approach and Strategy – In-Situ Diagnostics

An advanced suite of in-situ diagnostics developed in an LDRD project is used help guide materials discovery and optimization. Temperature and chemical species distributions in the flames are probed by laser based diagnostics and flame emission spectroscopy. Flame properties are correlated to materials properties and adjusted to achieve optimal results.



Milestones

FY19	LLZO process optimization for sintered wafers - Optimized LLZO for press sintered wafers. -	*Completed*	Jan-19
	Radiation shielding to control particle size - Deploy radiation shielding for combustion zone particle condensation control and complete characterization of radiation shielding control of particle size	*Completed*	Feb-19
	Large Crystal-domain Cathode Powders - Demonstrate large domain cathode powders for LMO and NCM811. - 6/30/2019	*In-Progress*	June-19
	LLZO production - Optimized LLZO for Battery 500 partner applications and produce kg quantities of LLZO for Battery 500 partners. - 9/30/2019	*In-Progress*	Sept 19

Technical Accomplishments And Progress Overview

Accomplishment Summary

Synthesis of cubic-LLZO at <800ºC from arbitrary precursor solutions

- Discovered process conditions to synthesize LLZO powders by FSP that anneal to the cubic phase at low temperature using any metal-organic precursors and solvent combination.
- Discovered process conditions to synthesize LLZO powders by FSP that anneal to the cubic phase using low cost inorganic precursors.
- Performed synchrotron studies of FSP LLZO in-situ annealing
- Investigated the procedures to press LLZO pellets without hot-pressing

Breakthroughs achieved of using LLZO powders in electrochemical applications

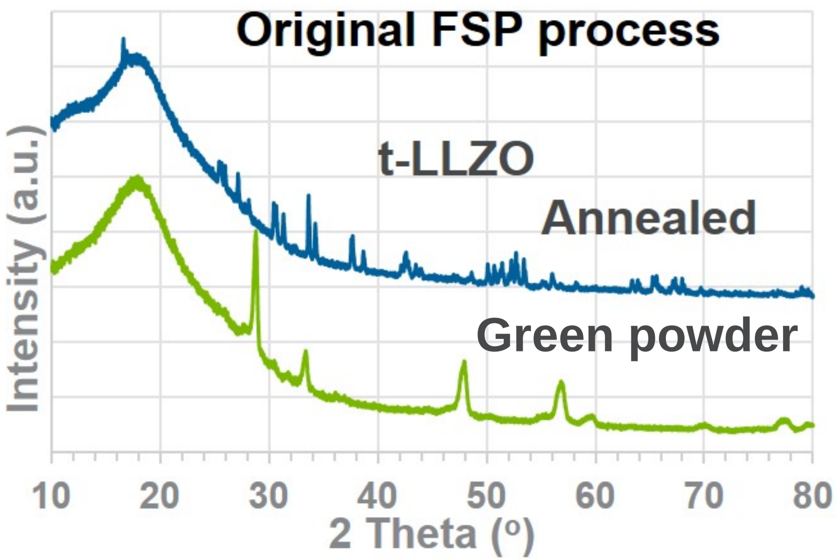
- Performed co-sintering studies of FSP green powders with LCO.
- Discovered cathode stabilization benefit in conventional Li-ion batteries by using c-LLZO as an additive to NCM622 cathode powder prior to cathode calcination.

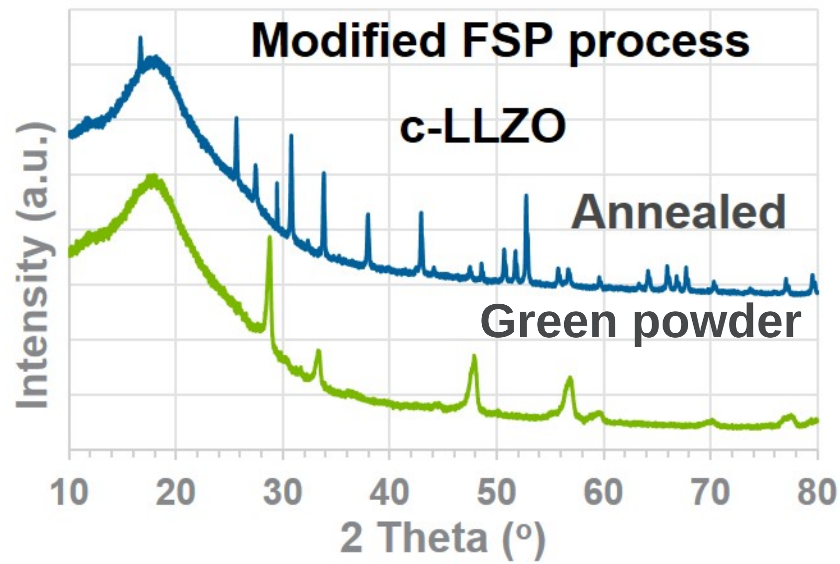
Active material synthesis with FSP

- Attained good performance in NCM111 and NCM811
- Demonstrated route to synthesize disordered rock salt phases.

Technical Accomplishments And Progress Overview

FSP Process Adjustment for cubic-LLZO <800ºC





	Last year (left)	This year (right)
Green powders	Main: $La_2Zr_2O_7$ (cubic,01-070-5602)	$La_2Zr_2O_7$ (cubic, 01-070-5602)
Annealed	t-LLZO (01-078-6708)	c-LLZO (01-080-9103)
Improvement	1. Ability to adjust FSP process settings to obtain the cubic LLZO phase after annealing to 700-800ºC for any solvent and solute combination	

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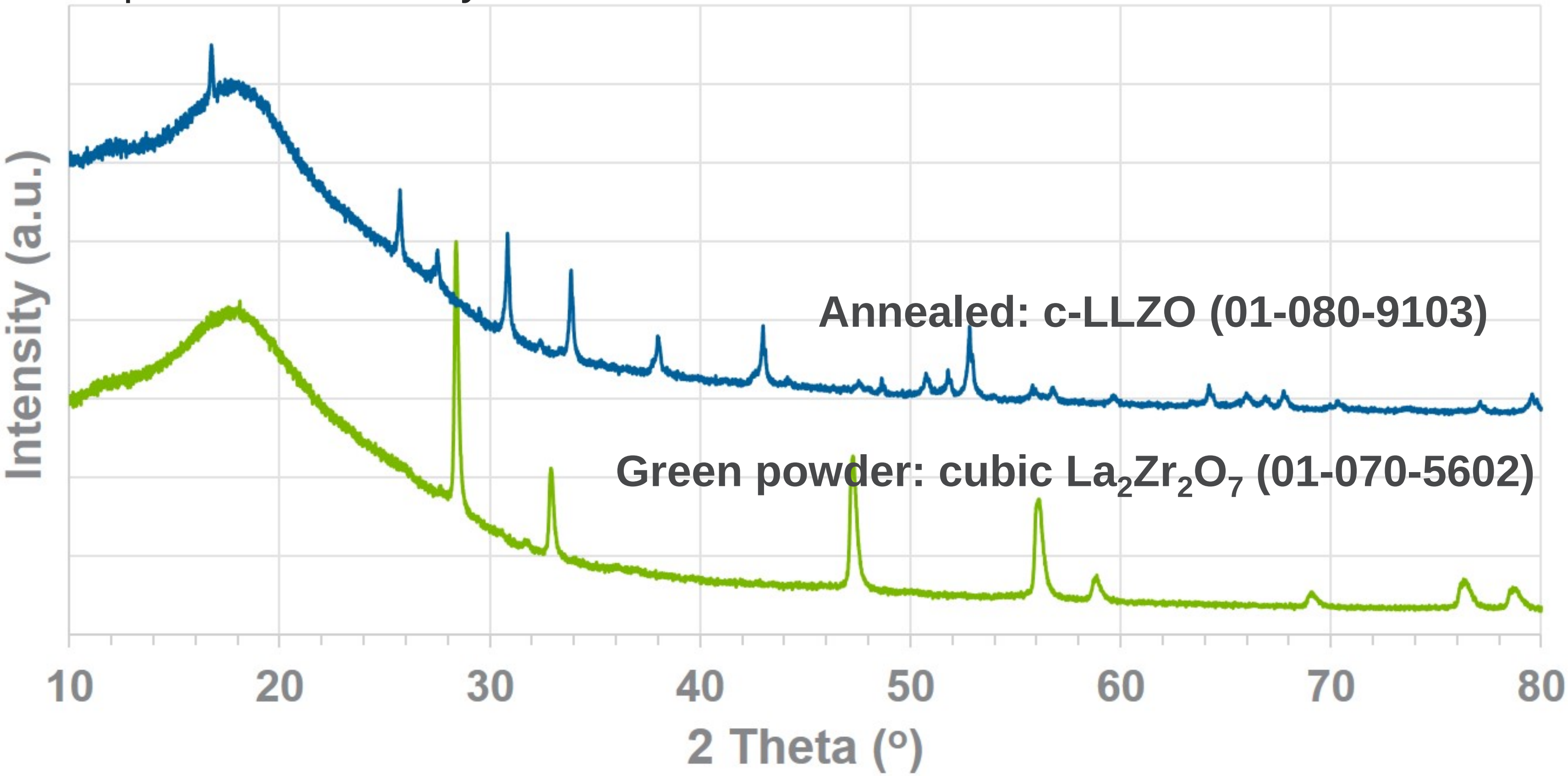
Technical Accomplishments And Progress Overview

Cubic-LLZO from low-cost inorganic precursors

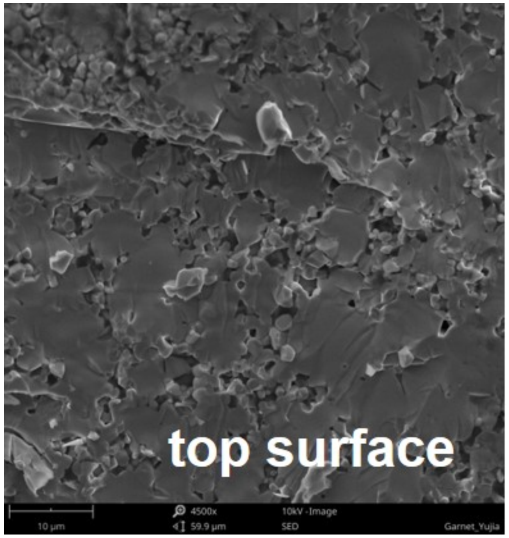
- We then targeted at making c-LLZO powders from economic precursor solutions, e.g., low-cost inorganic metal compounds instead of organometallic salts which are expensive but widely used in FSP.

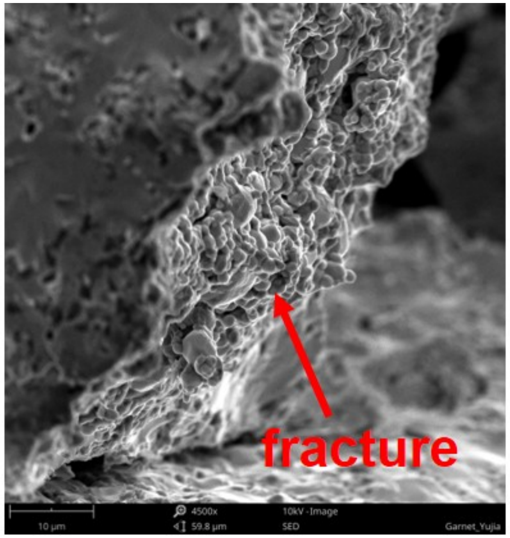


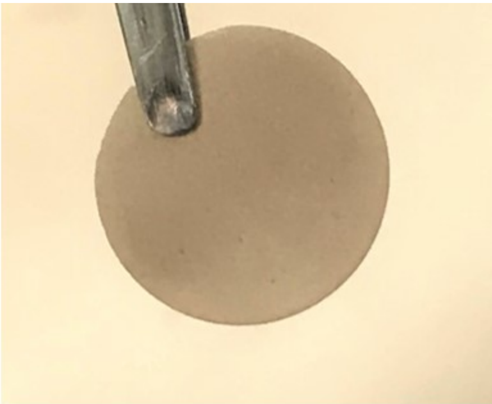
Technical Accomplishments And Progress Overview

LLZO Pellet from COLD pressing

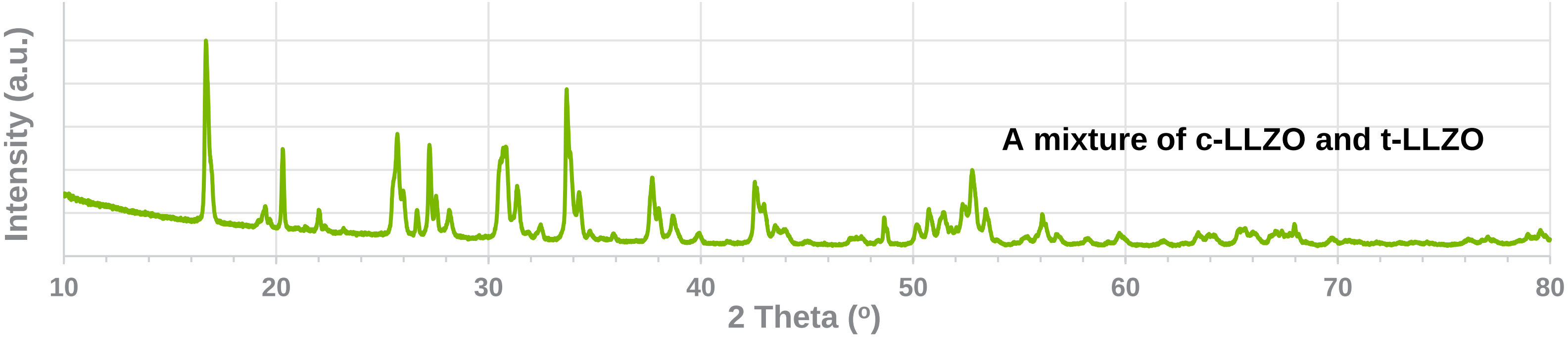
- LLZO pellets were successfully obtained from c-LLZO powders by COLD pressing, followed by another annealing step
- The pellet had a high density (please see SEM images)







Thickness: 0.5 mm
Diameter: 12.7 mm



Technical Accomplishments And Progress Overview - Collaborations

- FSP green powders were provided to P. Barai and T. Fister (see BAT_402. for details) Reaction pathways were revealed and grain growth dependencies on annealing rates were revealed.

- Annealed powders were provided to Z. Chen for in-situ APS electrochemical and co-sintering experiments (see BAT_418 for details). Compatibility with NMC622 was observed during co-sintering with Al-LLZO. Potential for improved stability in NMC622 and LCO were observed (see below)

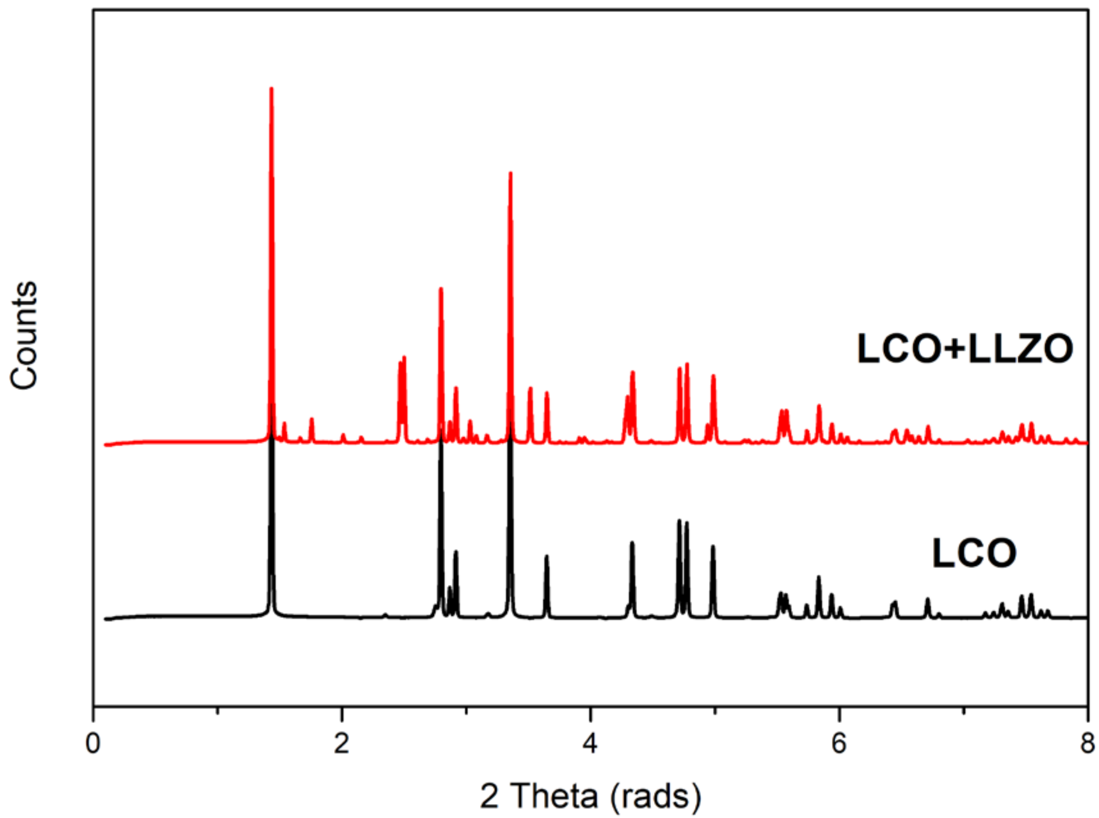
- LLZO materials provided to CAMP for active material additive studies

- LLZO materials provided to M. Doeff(LBNL) for SSE application evaluation

Technical Accomplishments And Progress Overview

Co-sintering experiments with LCO and LLZO

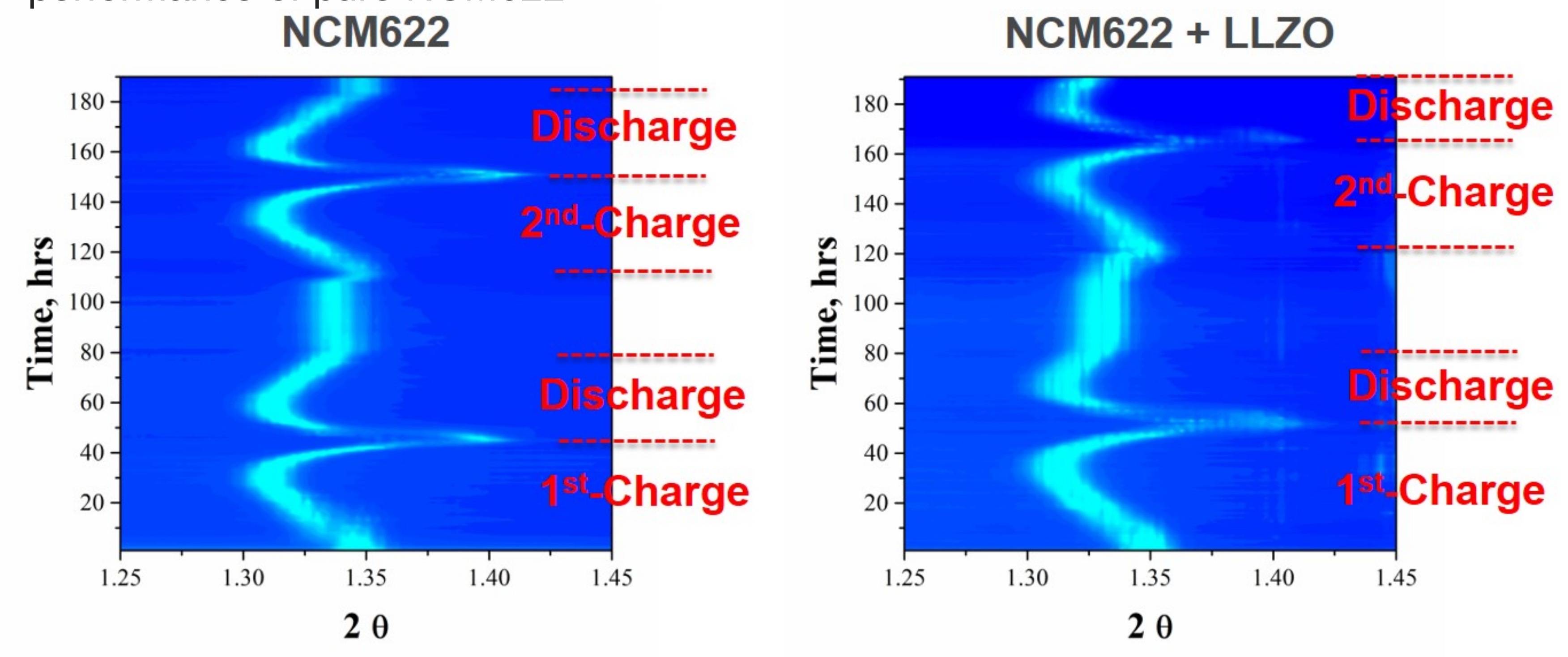
- Compatibility of LLZO particles was tested by ex-situ calcination process
- A mixture of LCO and LLZO (1:1 in weight) green powders were co-sintered to 1100 ^{o}C
- As a comparison, LCO powders were sintered under the same conditions
- LCO kept its own structure when co-sintered with LLZO particles
- The LCO did not react with LLZO powders



Technical Accomplishments And Progress Overview

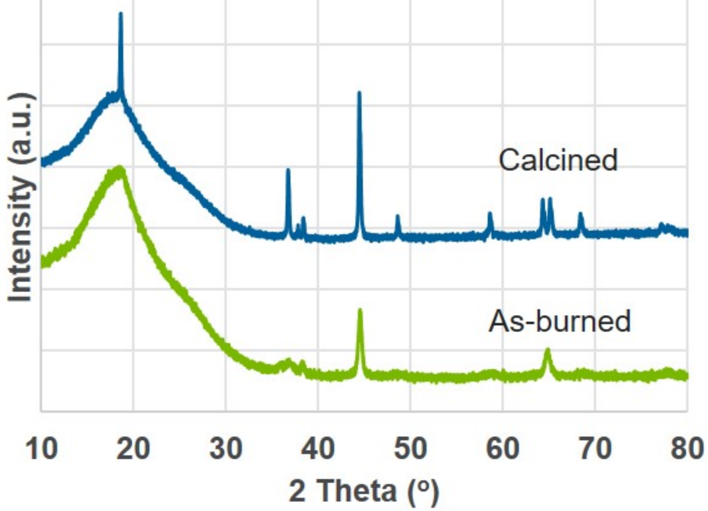
Electrochemical in-situ testing of co-sintered NCM622 and LLZO

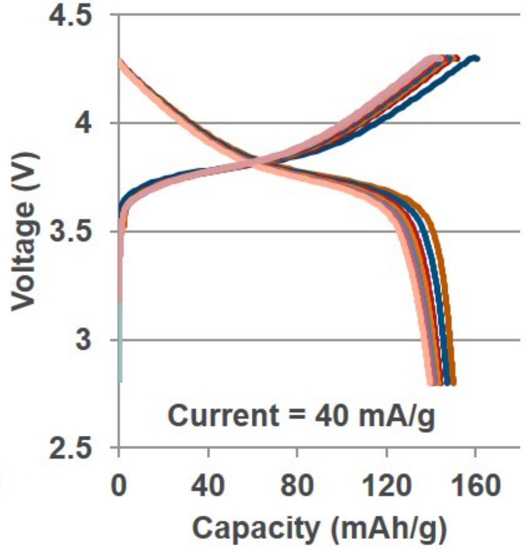
- The mixture of NCM622 and LLZO green powders were calcined at 900 ^oC
- In-situ lattice change while cycling; Voltage range: 3 - 4.6 V; Current: 0.1 C
- W/O LLZO, the NCM622 cathode had significant lattice changes in both cycles.
- For NCM622+LLZO, the lattice change in 2nd cycle was less than the 1st cycle or the performance of pure NCM622

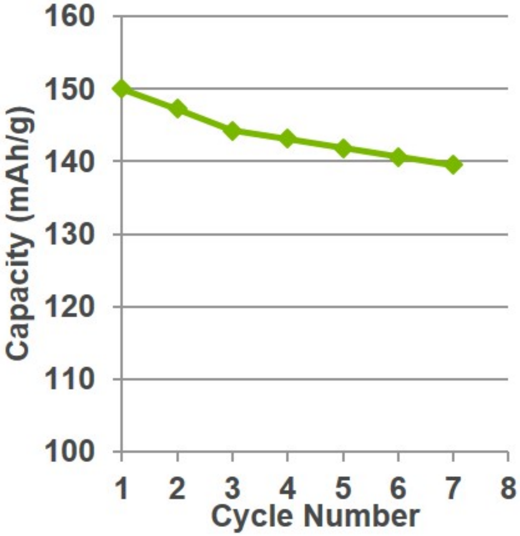


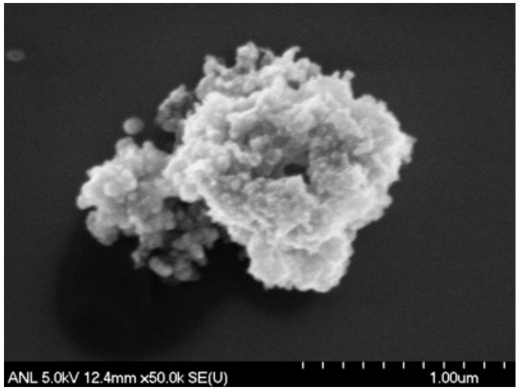
Technical Accomplishments And Progress Overview

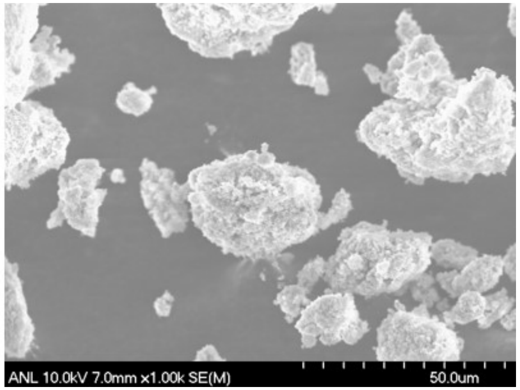
Active Material Synthesis – NCM111







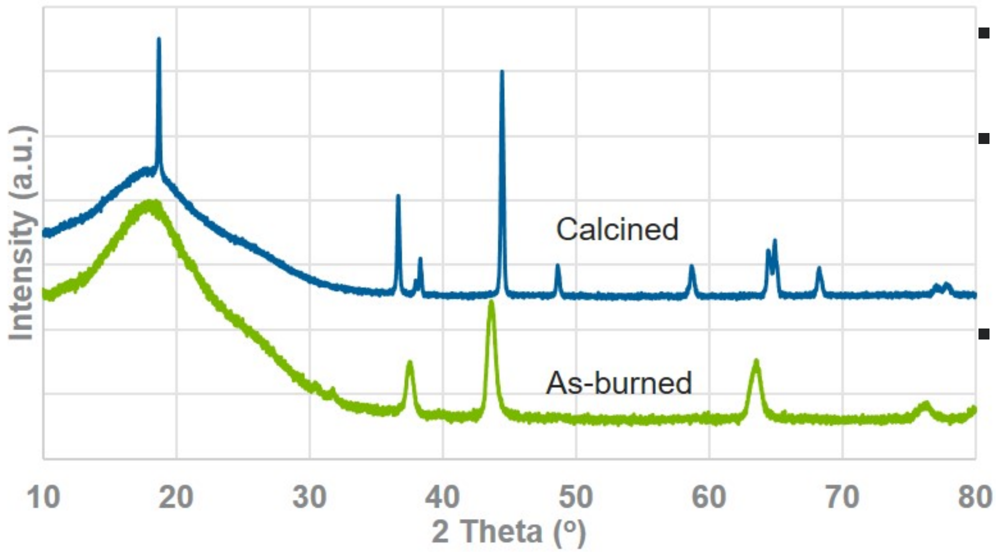




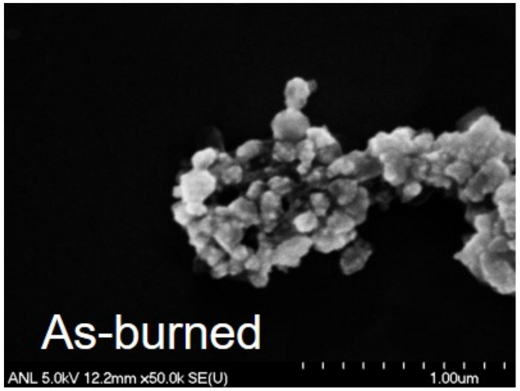
- The green powder has primary particles in nano-regime
- The calcined powder show the phase of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (01-075-3916), nano-sized primary particles in bulk aggregates
- The 1^{st} discharge capacity can achieve ~150 mAh/g when cycled at 40 mA/g

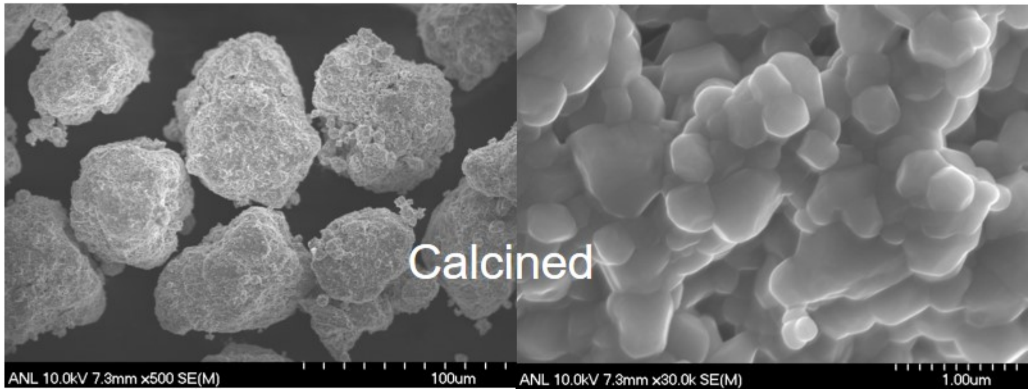
Technical Accomplishments And Progress Overview

Baseline Synthesis of NCM811



- The green powder has primary particles in nano-regime
- The calcined powder show the phase of $LiCo_{0.4}Ni_{0.8}Mn_{0.8}O_2$ (00-056-0146), nano-sized primary particles in micron-sized aggregates
- See BAT_411 for additional detail

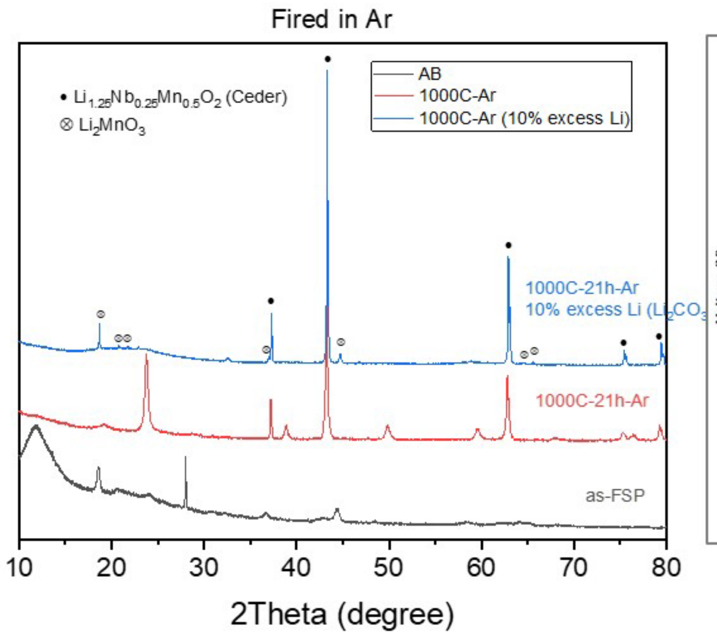


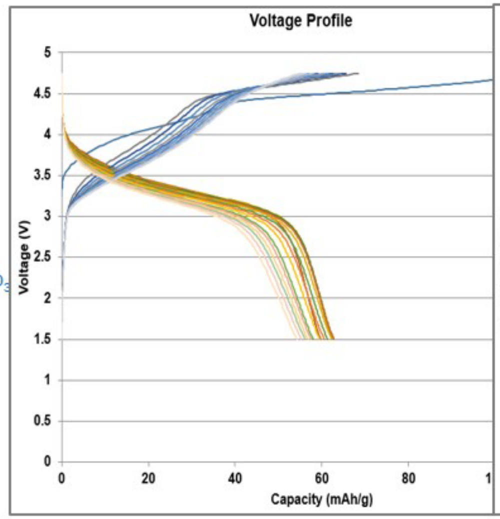


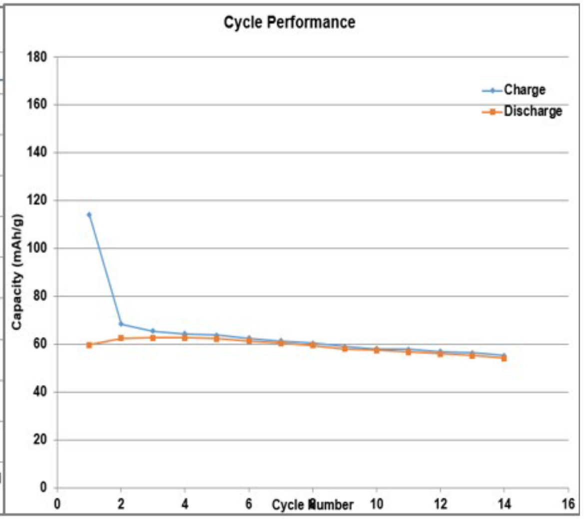
Technical Accomplishments And Progress Overview

FSP Synthesis for lithium excess disordered rocksalt phases

- Synthesized $Li_{1.2}Mn^{3+}_{0.6}Nb^{5+}_{0.2}O_2$ (LMNO)





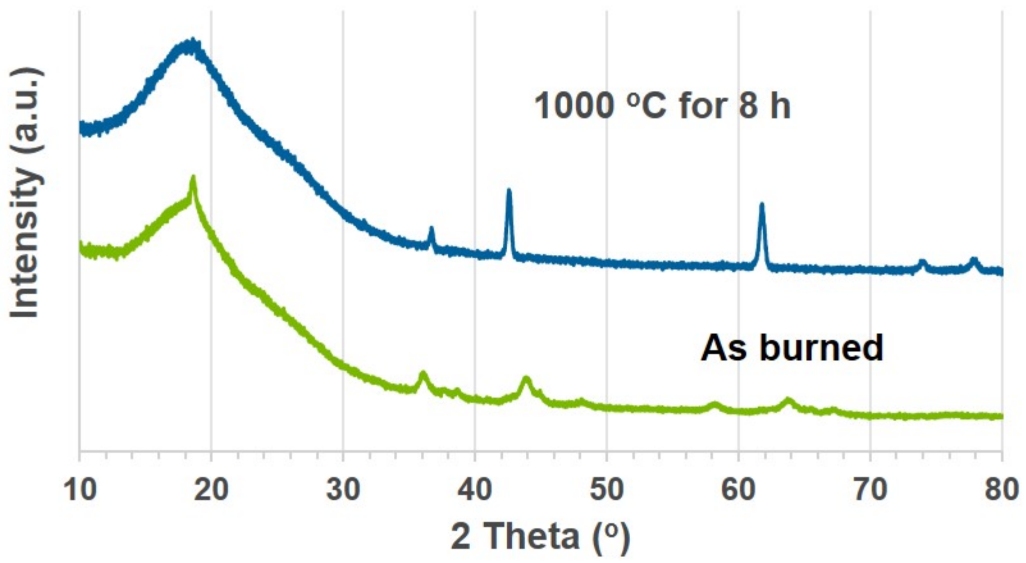


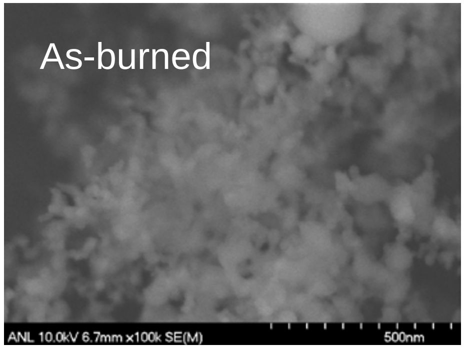
- LxDRS LNMO phase forms when the as-received sample is fired in Ar stream. This phase was first reported in *Electrochemistry Communications 60 (2015): 70-73.*
- But without excess Li, a significant amount of unidentified impurity phases is also observed.
- **With 10% excess Li** (by Li_2CO_3), the unidentified impurity phase is removed, **but small amount of Li_2MnO_3 impurity is formed.**

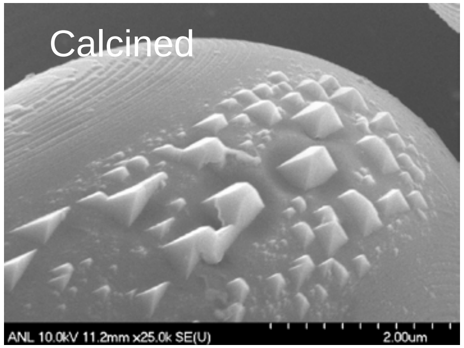
Technical Accomplishments And Progress Overview

FSP Synthesis for F-doped disordered rock-salt phases

- Synthesized $Li_{1.2}Mn^{3+}_{0.625}Nb^{5+}_{0.175}O_{1.95}F_{0.05}$ (LMNOF)
- As-burned powders: crystal phase cubic **$LiMn_2O_4$** (00-035-0782); nanoparticles
- Annealed at 1000 °C for 8 h in Ar: same XRD pattern as reported in *Advanced Energy Materials*, 9, 1802959 (2019); large single crystals were obtained in the annealed product but this gave poor cell performance.







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Responses to Previous Year Comments

No reviewer comments

Collaboration and Coordination with Other Institutions

- Cabot Corp. continues to provide engineering guidance for FSP process technology
- Samples of LLZO are provided to the Battery500 consortium for evaluation.
- LBNL is testing FSP synthesized materials.
- ANL is sponsoring a CRI Innovator with Northwestern University for the development of novel graphene-active material composite cathode architectures.

Remaining Challenges and Barriers

- Optimize LLZO for co-sintering with active material phases
- Optimize LLZO produced by low-cost inorganic material sources
- Optimize radiation shield process control for single crystal particle production and particle size control.
- Optimize for production rate synthesis

Proposed Future Research

- Deploy LLZO from low-cost inorganic precursor sources for all applicat*ions*
- Explore active material synthesis (LMO, NCM 523, 622, 811, 90-5-5)
- Explore further FSP combustion zone process variation for direct access to final target electrolyte and active phases
- Explore disordered rock-salt type cathode materials
- Build and commission 5 kg/day pilot scale unit

Summary Slide

- Advanced online diagnostic instrumentation was used to aid in understanding the FSP flame structure and resulted in improved material synthesis control leading to the general ability to synthesis LLZO with a low temperature path to the desired cubic phase for any precursor inputs.

- Synthesis of cubic-LLZO by annealing green powders at 700-800^{o}C for any input metal-organic precursor was achieved by FSP process control discoveries.

- A synthesis path to cubic-LLZO required annealing below 800^{o}C using low-cost inorganic precursors was discovered

- Lithium excess disordered rock-salt phases were synthesized by the FSP route

- Active cathode material NCM111 and NCM811 were synthesized with good initial electrochemical performance