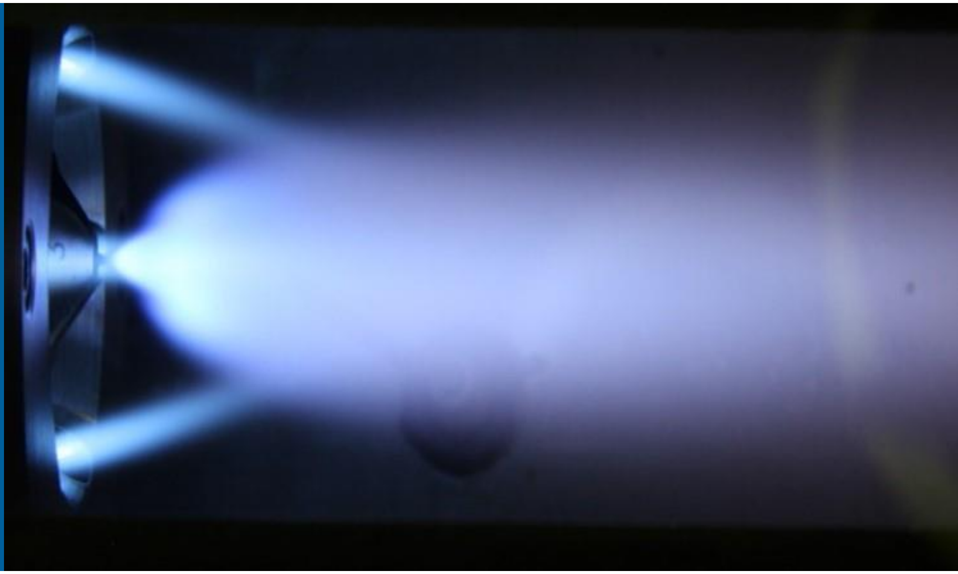
DEVELOPING FLAME-SPRAY PRODUCTION LEVEL PROCESS FOR ACTIVE MATERIALS



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Project ID: BAT315

2017 DOE VTO Annual Merit Review
June 2018, Washington, D.C.

Overview

Timeline

- Phase 1 start date: Jan. 2016
- Phase 1 end date: Sept. 2017
- Percent complete: 100%
- Phase 2 start date Oct 2017

Budget

- Total project funding:
  - $500K in FY16

Barriers

- 2.1.1 A: Cost of Li-ion batteries
- 2.1.1 C: Performance of Li-ion batteries

Industrial Partners

- Cabot Corporation
- Fiskers Inc.

Supporting battery research for:

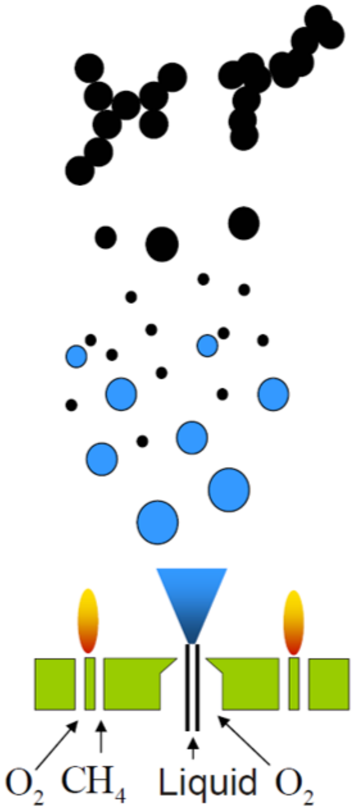
- DOE Battery Research Community

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.



Approach - Milestones

	Phase 1 - FSP Facility Construction		
FY16	Project start	*Completed*	Feb-16
	Facility Specification	*Completed*	May-16
	Facility Design	*Completed*	Aug-16
	Place major Equipment orders	*Completed*	Aug-16
	Burner Design	*Completed*	Sep-16
	Control System Design	*Completed*	Sep-16
FY17	NFPA 86 Burner Control Panel	*Completed*	Oct-16
	Spencer Blower for Filter Box	*Completed*	Nov-16
	Installation of fume hoods and ventilation	*Completed*	Jan-17
	Construction of facility	*Completed*	Sept-17
	Phase 2 - FSP Research for Battery Materials		
FY18	Pilot/Spray Burner Design Optimization	*Completed*	Dec-17
	Commence materials production	*Completed*	Feb-18
	Commissioning of scanning mobility particle sizer	*Completed*	Feb-18
	Synthesize FSP Al-LLZO solid electrolyte by published recipe	*Completed*	Mar-18
	Synthesize FSP Al-LLZO solid electrolyte by original recipe	*Completed*	Mar-18
	Optimize Al-LLZO solid electrolyte by original recipe	*In-progress*	Jul-18
	Provide FSP Al-LLZO solid electrolyte to Battery500 partners	*In-progress*	Aug-18

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Approach and Strategy

- Establish a flexible flame spray pyrolysis R&D synthesis facility for evaluation scale materials production of 200 g/day with daily turnover capability.
  - 4x 20 g samples/day samples from unique processing condition or 1x 200 g sample/day for industrial testing
  - High temperature residence time section up to 900 deg C for tuning particle size and phase purity.
  - Clean-in-place design for rapid clean-up and minimization of run-to-run drag out.
  - Modular engineering for quick interchange of alternate burner designs including loaner units from our industrial partners. First deployment: Cabot Spray Pyrolysis (aqueous solvent) or Flame Spray Pyrolysis (organic solvent)
  - Robust engineering controls for safe facility operation and nanomaterial control.
- Advanced Diagnostic Capability
    - In-situ Laser-Induced Fluorescence Flame Diagnostic
    - In-situ Scanning Mobility Particle Sizer
    - Ex-situ APS and CNM x-ray and TEM microscopy

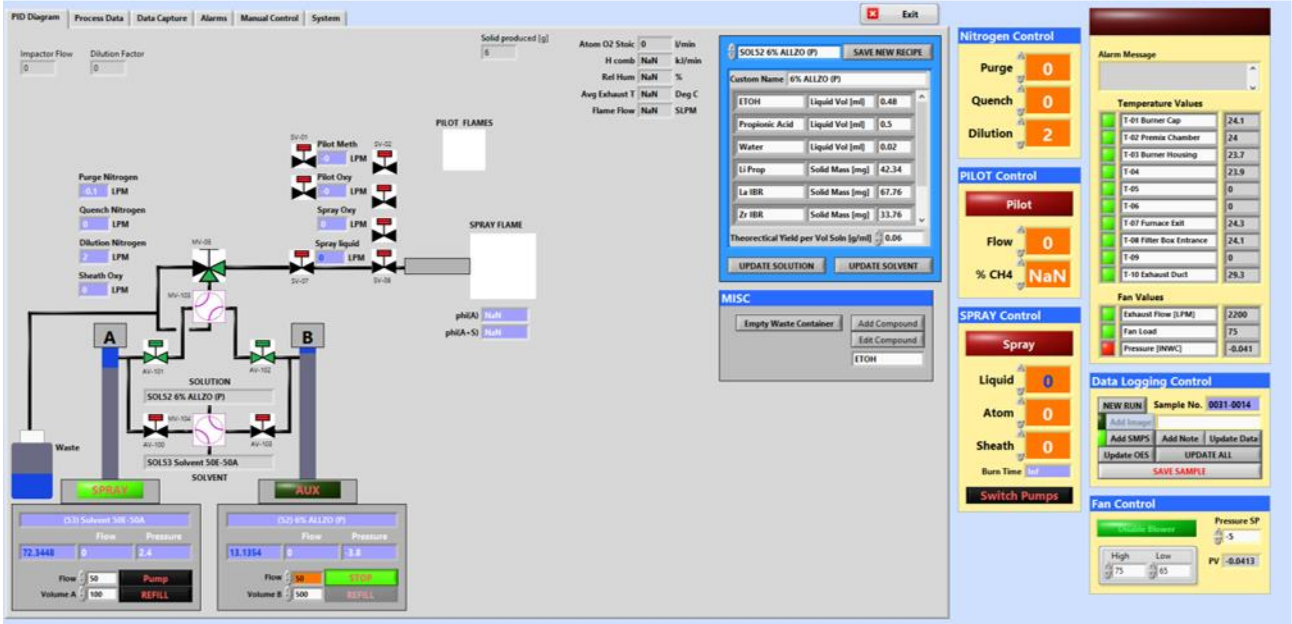
Technical Accomplishments and Progress Overview

Completion of Core FSP facility:– Automated Solution Handling

- Fully automated PC control of dual syringe pump handling
  - Continuous solution delivery for long burns.
  - Pre- and Post-solvent/solution switching for solution flushing
  - System cleanout

Syringe Pump
with actuated valves

Labview Control Software



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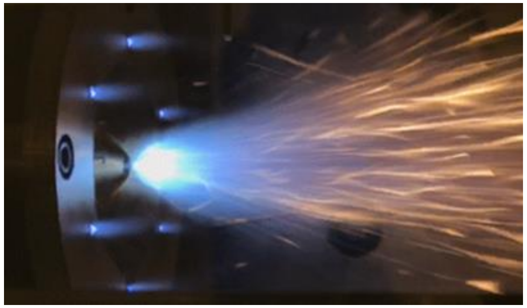
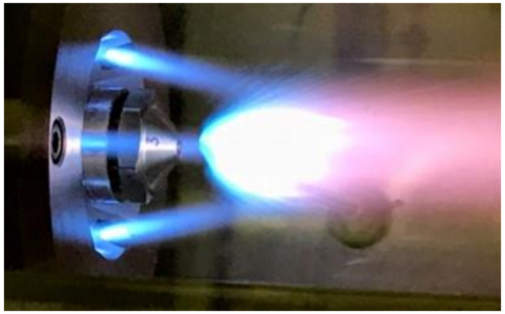
Technical Accomplishments And Progress Overview

Completion of Core FSP facility: Burner Optimization/Characterization

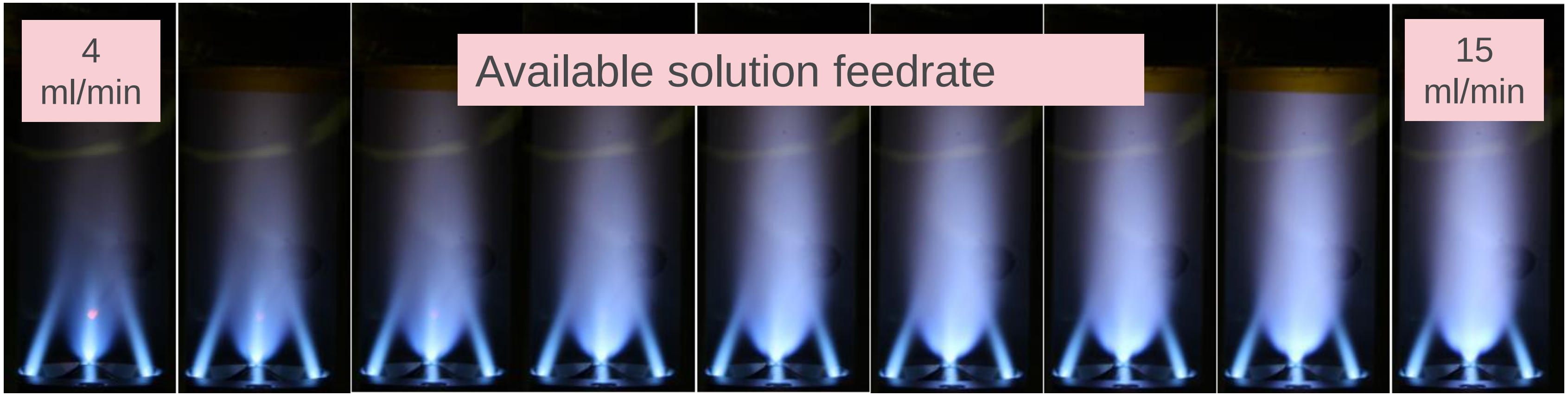
- Tested all commonly used solvents: xylene, ethanol, acetonitrile, methanol, ethanol/water/acetic acid, 2-ethylhexanoic acid/xylene
  - Optimized pilot and spray design

Initial Design





Final Design

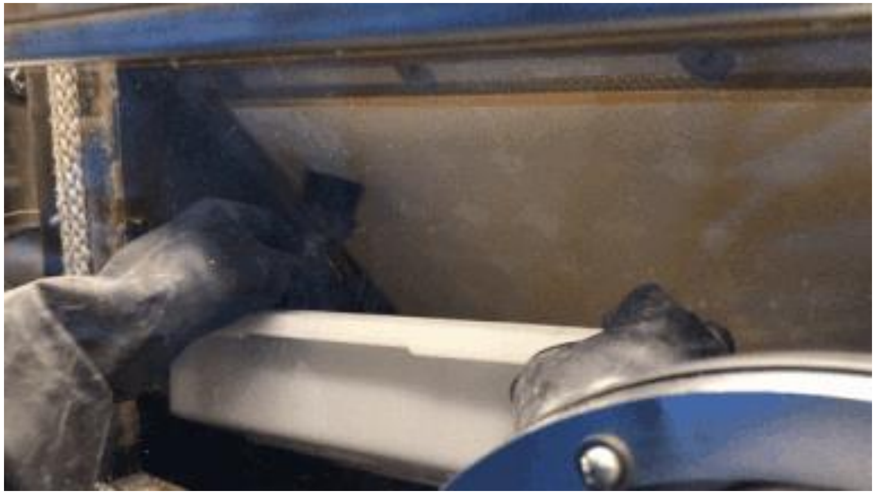


Technical Accomplishments And Progress Overview

Completion of FSP facility – System Features for High Sample Productivity

- Clean-In-Place Fixture allows for tube cleaning without dismantling the system
- Filter Box product collection enabled using glove box protection
- 4 x 20 g sample per day are possible with these features
- Day-to-day switch of material system are possible with these features

CIP Fixture in Operation



Test Sample Material Collection

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Technical Accomplishments And Progress Overview

Expansion of Capability – Addition of Advanced Diagnostics

- Several advanced diagnostic tools have been furnished to the MERF FSP by an LDRD project focused on flame-synthesized catalyst materials.

- Scanning Mobility Particle Sizer
  - TSI 3938 SMPS
  - 5-1000 nm size range
  - ~1 minute scan time

- Planar Laser Induced Fluorescence System
  - Filtered Rayleigh Scattering Temperature
  - Laser Induced Fluorescence imaging of multiple chemical species (OH, CH, Li)

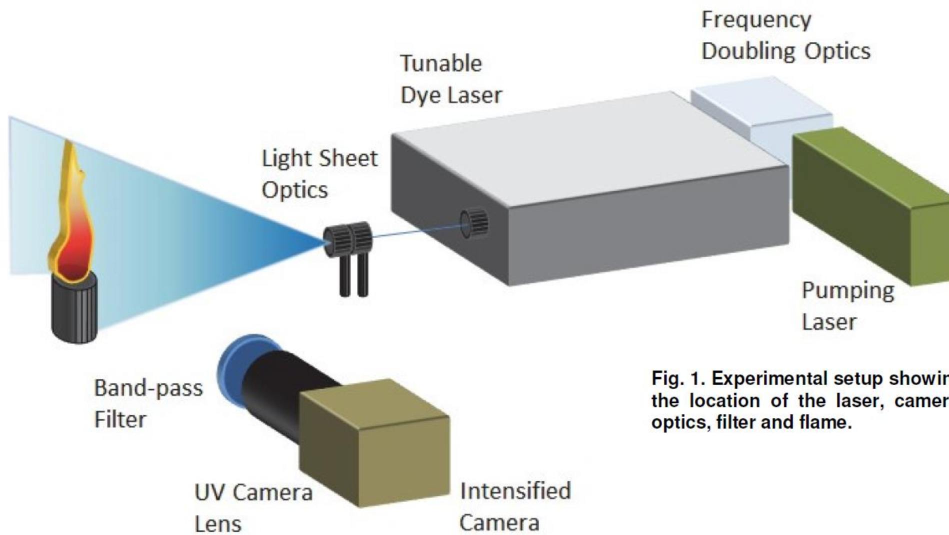
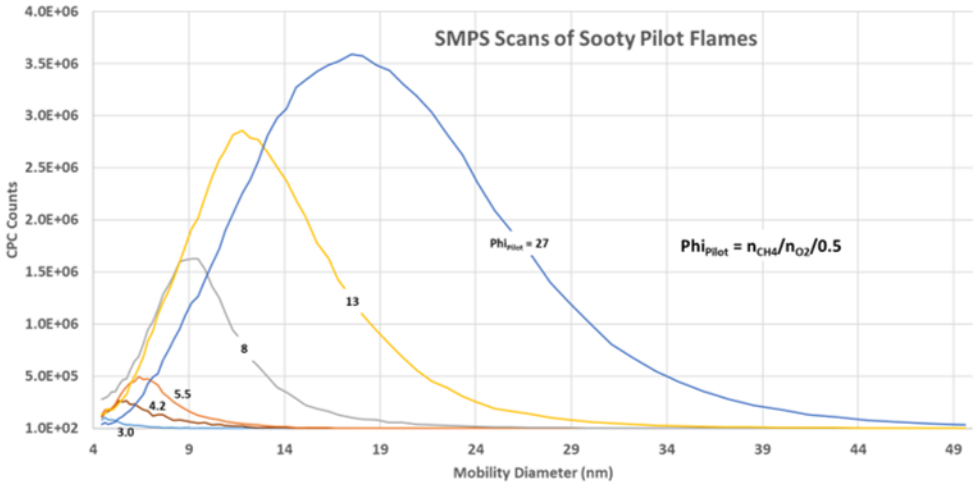


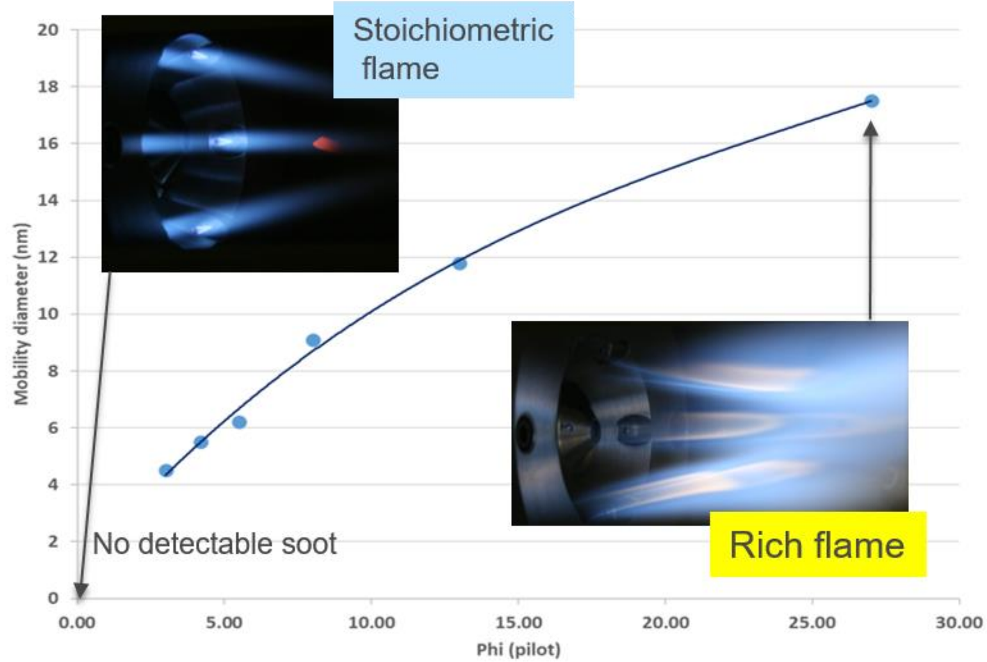
Fig. 1. Experimental setup showing the location of the laser, camera, optics, filter and flame.

Technical Accomplishments And Progress Overview

Pilot Flame Characterization Soot Study

- Pilot flame quality was established using soot characterization as a function of equivalence ratio
- Stable and clean operation was found for stoichiometric premixed methane-oxygen pilot flames
- Dilution sampling of particle flame particulate allowing for continuous online particle size measurement using the SMPS. Measurement interval ~2-5 min.





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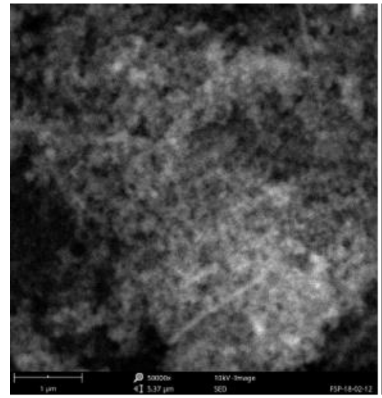
Technical Accomplishments And Progress Overview

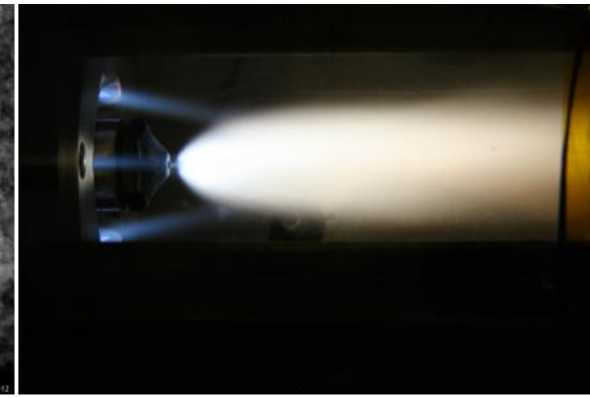
First Material System Validation: Silica Synthesis

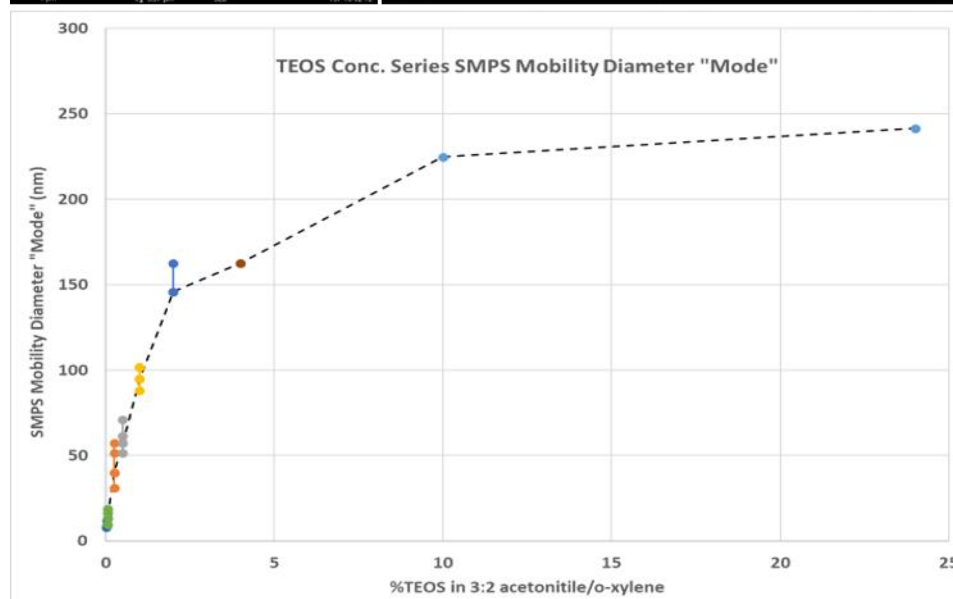
- FSP material synthesis was commissioned using TEOS/ethanol solutions to synthesize silica

- Spray flame operation was optimized using this test system as well as the online particle size measuring system – TSI scanning mobility particle sizer (SMPS)

- A particle size vs precursor concentration series was performed over 3 orders of magnitude solution concentration (0.03 – 24% TEOS)





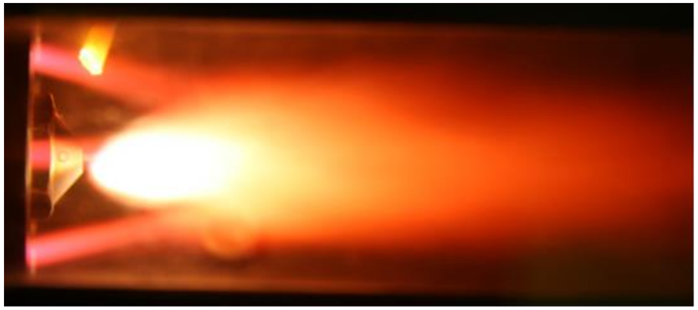


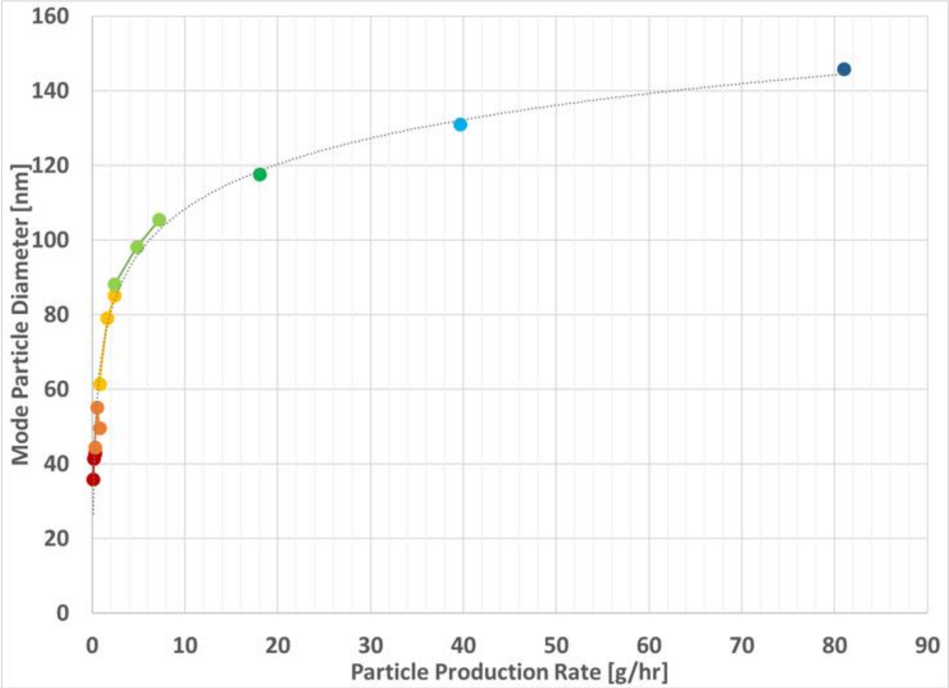
Technical Accomplishments And Progress Overview

Synthesis Milestone – LLZO Synthesis

- Al-doped LLZO was synthesized using U of Michigan (**E. Li 2017 Ph.D Thesis**) recipe based on Li propionate, La isobutyrate, Zr isobutyrate and Alumatrane (Triethanolamine Al) with an ethanolic based solvent.

- The published behavior of this system was reproduced using a 3% ceramic yield solution. In addition we observed the same behavior for 6% and 9% ceramic yield solutions.
- This system produces a green powder consisting of Lanthanum Zirconium Oxide and Lithium Carbonate that requires annealing to produce the desired cubic phase





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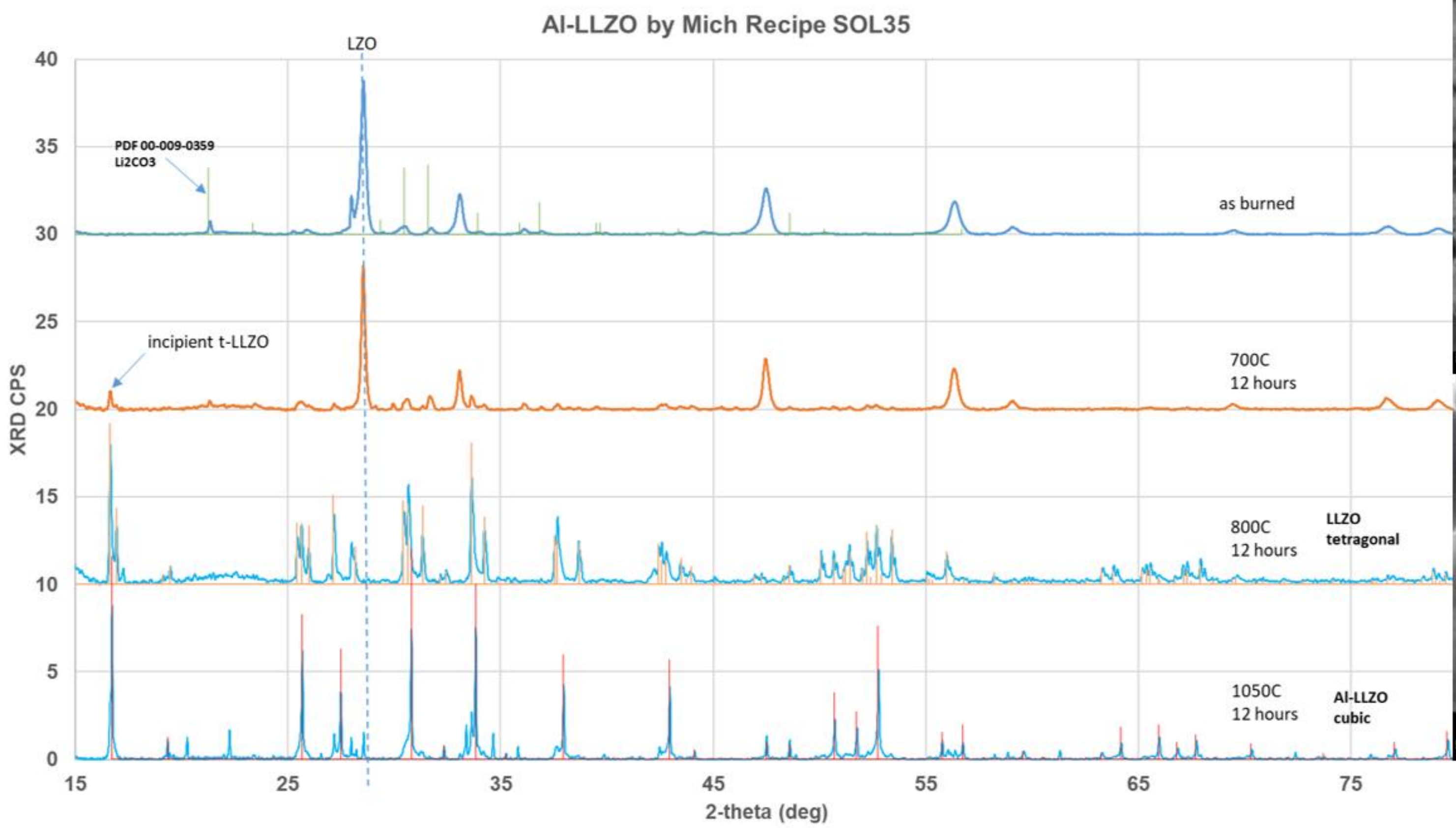
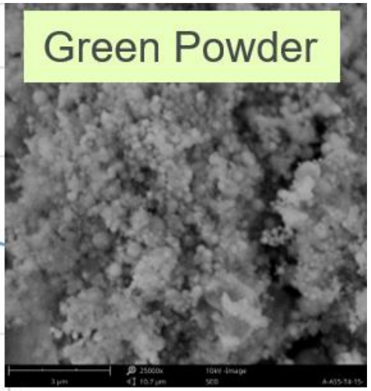
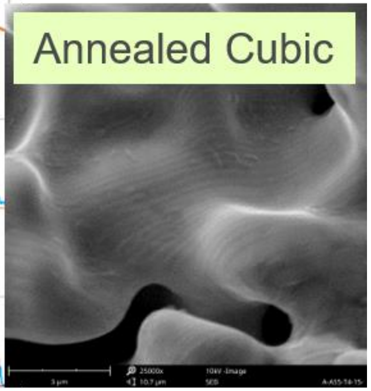
Technical Accomplishments And Progress Overview

Synthesis Milestone: LLZO-Mich 9% Ceramic Yield Annealing

- As-synthesized material consists of 146 nm particle with a BET SA = 5.8 m^2/g
- Green powder anneals to tetragonal at 800^{o}C, to cubic at 1050^{o}C.



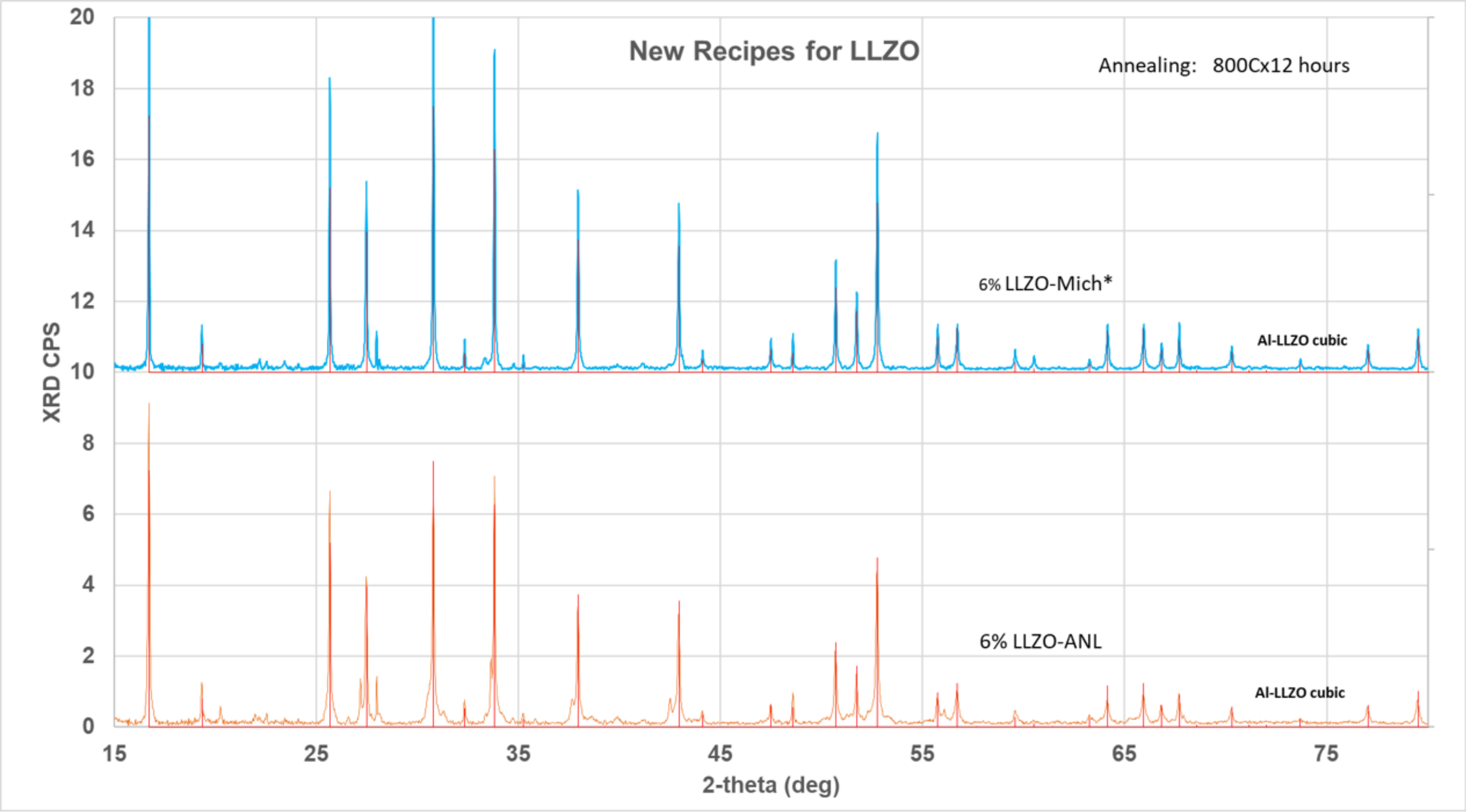




Technical Accomplishments And Progress Overview

Synthesis Milestone: Improved LLZO with New ANL Recipe and Modified U of Michigan Recipe

- A variant of the U of Michigan recipe was discovered giving cubic LLZO at 800 C
- An original recipe based on alternate precursors was discovered also giving cubic LLZO at 800 C



Responses to Previous Year Comments

Comment from 2017 AMR	Response
"The reviewer acknowledged that the project team set up the equipment, but it was difficult to assess project success. The reviewer commented that there is no analytical data or performance data on the materials produced by the flame spray analysis, and that analytical and performance data should be part of the quantifiable milestones"	Materials synthesis is in full operation as of 2/18 starting with Al-doped LLZO. The analysis of the material performance was performed and process improvements made so that the improved material exceeds published performance. Further evaluation of material performance will be obtained through distribution of samples to our collaborators and industrial partners.
"This reviewer expressed interest in more convincing details or evidence that flame spray pyrolysis can deliver the claimed benefits (e.g., reduced cost, better purity, crystallinity, etc.). One of the key needs in active materials is uniformity in particle size, and yet having particles large enough to be easily handled. It was not convincingly demonstrated to this reviewer how this work would do on this metric."	The addition of advanced diagnostic tools, especially the scanning mobility particle sizer informs on the particle size during operation including the effectiveness of the high temperature residence time section on particle growth. Additionally novel process strategies are being explored to increase the particle size beyond the norms typically reported in the literature.
"The reviewer noted a reasonable approach to reduce cost by eliminating the calcination step and combining the cathode and carbon matrix during the flame spray synthesis. It was recommended by this reviewer that the project team provide a cost model and show how the flame spray process can reduce cost versus traditional calcination"	Details of the FSP material synthesis cost is provided to our industrial partners who can provide the most realistic cost assessment.

Collaboration and Coordination with Other Institutions

- Cabot Corp. continues to provide engineering guidance for FSP process technology
- Professor S. Pratsinis (ETH)
- Samples of LLZO are provided to the Battery500 consortium for evaluation.
- LBNL is testing FSP synthesized materials.
- Montana State University is testing our Al-LLZO
- A partnership with FISKERS Inc is being negotiated for use of the Al-LLZO material
- ANL is sponsoring a CRI Innovator with Northwestern University for the development of novel graphene-active material composite cathode architectures.

Remaining Challenges and Barriers

- Increase material collection yield
- Apply Laser PLIF diagnostics for material synthesis guidance
- Optimize LLZO for scalable manufacturing; discover one step synthesis to cubic phase directly from combustion step and/or in-situ annealing.
- Discover process conditions and/or formulations that produce materials in the 200-1000 nm size range
- Discover process conditions and/or formulations that use the lowest cost metal salts.

Proposed Future Research

- Optimize solid electrolyte LLZO production for scale-up
  - Explore lowest cost precursor routes
  - Correlate Laser diagnostic measurement of temperature and chemical species with as-burned phase outcome.
  - Search for conditions to directly yield cubic Al-LLZO synthesis.

- Explore active material synthesis (LMO, NCM 523, 622, 811)

- Explore Co-free cathode chemistries

- Explore disordered rock-salt type cathode materials

- Build and commission 5 kg/day pilot scale unit

Summary Slide

- The Phase 1 goal of establishing an FSP capability at the ANL MERF FSP facility has been completed and high sample production capability has been established.

- Advanced online diagnostic instrumentation has been added to the capability of the system (a) scanning mobility particle sizer and (b) Laser PLIF temperature and species distribution measurement in the flame.

- Material synthesis research has begun on LLZO. Literature results have been reproduced and a new formulation was discovered that gives the cubic phase at 800^{o}C.