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# Aerosol Manufacturing Technology for Production of Low-Cobalt Li-ion Battery Cathodes

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**Project ID# bat411**

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# Overview

## Timeline

- Project start date: 10/01/2018
- Project end date: 12/31/2021
- Percent complete: 15%

## Budget

- Total project funding: $3,749,057
  - DOE share: $2,989,057
  - Contractor share: $ 760,000
- Funding for FY 2019: $1,397,139
- Funding for FY 2020: $1,198,369
- Funding for FY 2021: $1,153,549

## Barriers and Technical Targets

- Performance: cell chemistries that provide higher energy have life and performance issues
- Life: next gen technologies still suffer major cycle and calendar life issues.
- Cost: main drivers are the high cost of raw materials and materials processing, the cost of cell and module packaging, and manufacturing costs

## Partners

- ANL: Joseph Libera – Flame Spray Pyrolysis development, Eungje Lee-cathode development
- SAFT: Joong Sun Park – cell fabrication and testing

# Relevance - Project Objectives

## Impact:

- Address both cost and performance challenges for the next generation Li-ion batteries (LIB). If successful, the project will have significant impact on cost reduction of Li-ion battery towards the $100/kWh target
- Flexibility to produce all key Low-Cobalt cathode compositions

## Objective:

Research, develop, and demonstrate Reactive Spray Technology (RST) and Flame Spray Pyrolysis (FSP) for production of low-Cobalt active cathode materials for use in next-generation Li-ion batteries (LIB) capable of achieving the following performance targets:

| Beginning of Life Characteristics at 30°C | Cell Level | Cathode Level |
|---|---|---|
| Useable Specific Energy @ C/3 | | ≥600 Wh/kg |
| Calendar Life (< energy fade) | 15 Years | |
| Cycle Life (C/3 deep discharge with <20% energy fade) | 1,000 | |
| Cobalt Loading | ≤ 50mg/Wh | |
| Cost | ≤ $100/kWh | |

# Milestones

| Date | Milestone | Type | Description | Status |
|---|---|---|---|---|
| **FY 2019** | | | | |
| Jun. | Optimize and Setup RST System | Technical | RST system operational for Battery Materials | On-track |
| Nov. | Synthesize RST Battery Materials | Technical | First material produced | On-track |
| Oct. | Synthesize FSP Battery Material | Technical | Low Co cathode materials produced | On-track |
| Dec. | Material evaluation in coin cell | Go/No Go | (1) tap density > 2g/cm$^3$, (2) Voltage window from ≤2.3 to > 4.25 V vs. Li/Li+, (3) specific capacity > 185 mAh/g | On-track |
| Dec. | Pouch Cell Build and Test | Technical | 31 PPCs completed. 6 PPCs retained by recipient in accordance with DOE Cell Testing Protocol prior to shipment of the deliverable cells to DOE | Not started |
| **FY 2020** | | | | |
| Jun. | Produce RST and FSP cathodes for pouch cells | Technical | Determine most promising route forward for either RST, FSP, or both produced powders | |
| Jun. | Cell design optimization | Technical | Low-Co cathode electrode design selected, optimization of inactive components, anode and electrolyte completed | |
| Dec. | Pouch Cell Build and Test | Go/No Go | Interim pouch cells on test, maintaining 600 Wh/kg at 80% SoC after 300 cycles | |
| **FY 2021** | | | | |
| Jul. | Optimize low-Co compositions | Technical | Final refinement of FSP and RST cathodes and production for pouch cells | |
| Jul. | Optimize electrode formulation and architecture | Technical | Finalize the design of cathode and selection of anode, electrolyte and inactive components | |
| Sep. | PCC Pouch Cell build and test | Technical | Fully optimized final battery design used for building of PPCs | |
| Nov. | Delivery of 31 PCC to DOE along with testing data | Technical | Delivery and testing PCCs in accordance with DOE Cell Testing Protocol | |
| Dec. | End of Project Goal | | Better than 600 Wh/kg at 80% SoC after 1000 cycles for a ACM/graphite pouch cell with ≤ 50 $mg_{Cobalt}$/ Wh | |

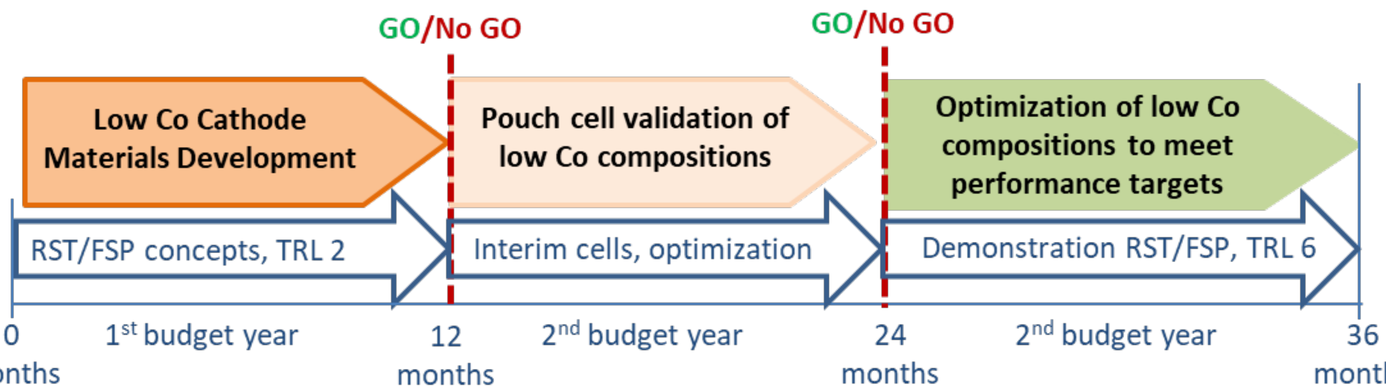
# Approach/Strategy

**How to enable low/free Cobalt cathodes and improve cost and performance?**

1. Materials supply chain optimization
   - Access to metals, strategic collaborations
2. Materials Improvements
   - Compositional modifications (less Co, cheaper raw materials)
   - Surface modifications (coatings, core/shell)
3. Improved synthesis process
   - Often as important as composition
   - Industry needs new ideas and approaches

## Approach

- Develop Low-Cobalt cathode materials via Reactive Spray Technology (RST) and Flame Spray Pyrolysis (FSP) targeting < 50 $mg_{Cobalt}$/Wh
- Implement structural and morphological modifications through aerosol particle production process
- Synthesize high Ni content NCM and disordered rock-salt materials
- Optimize conductive additive formulations for Low/free Co active material

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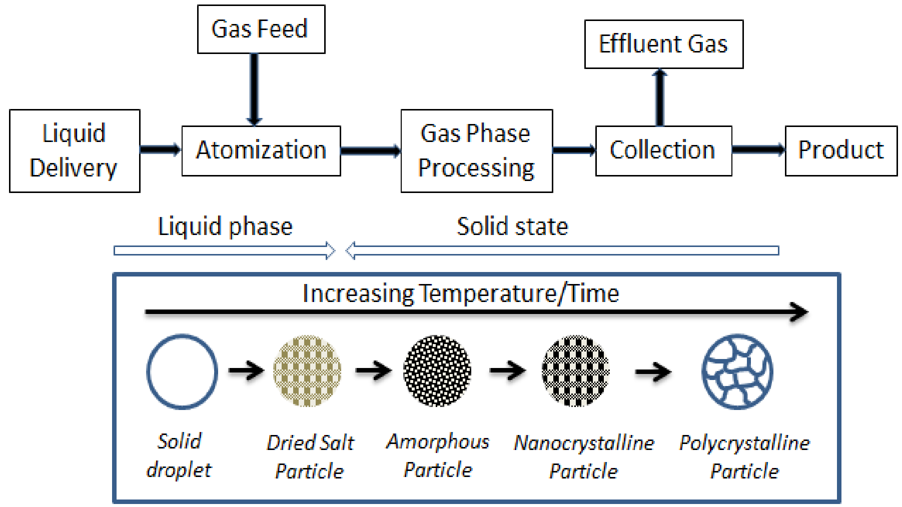
# Task 1.1 Optimize and Setup RST System for Battery Materials

## Reactive Spray Technology (RST) System

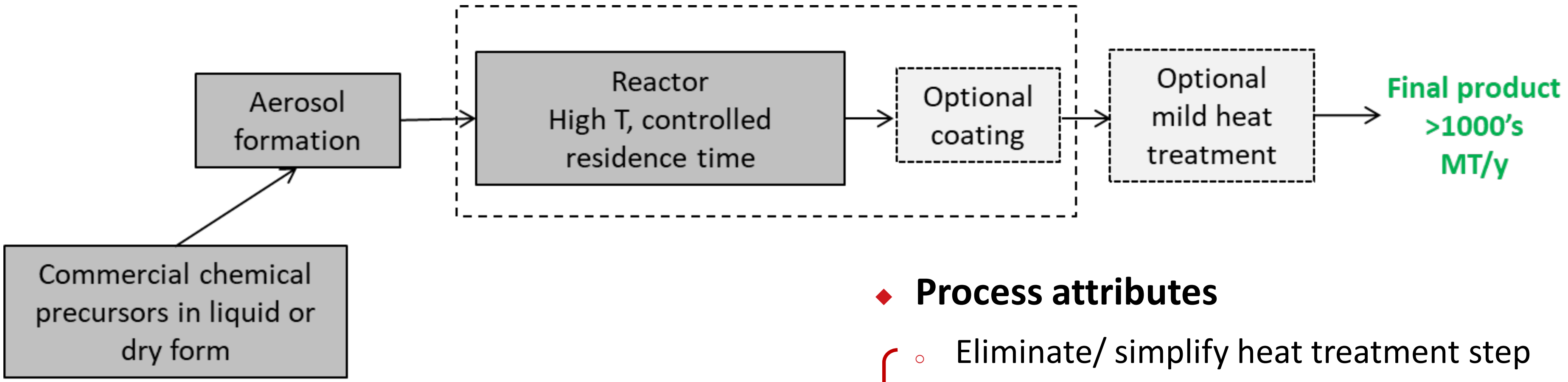
- Cabot has developed an aerosol process to synthesize LIB cathode active materials at large scale with improved properties and lower cost
- RST is a flexible platform for production of LIB cathode particles
- The Cabot RST experimental system optimized for battery research has been relocated to ANL's Material Engineering Research Facility (MERF)

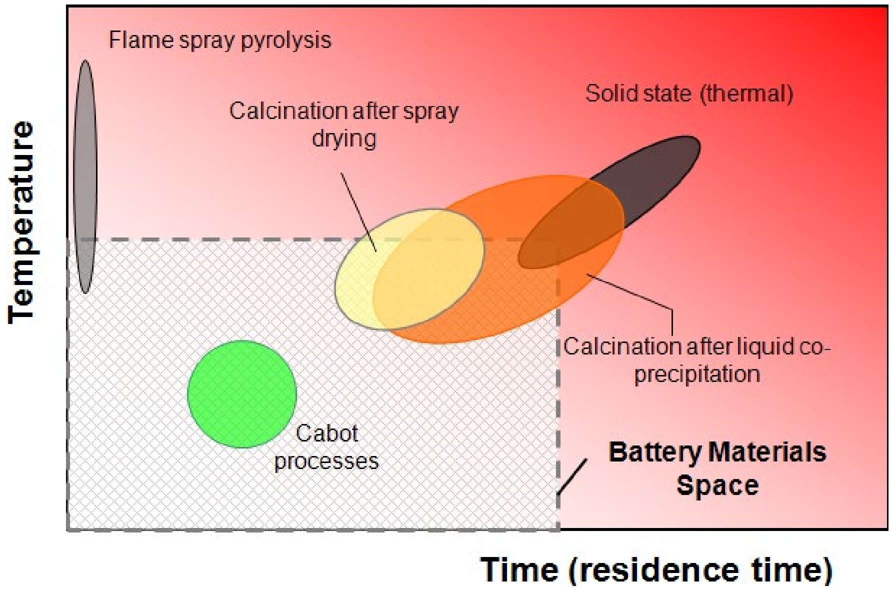
RST system diagram




Reactive Spray Technology System

# RST process offers cost and scale benefits




- **Process attributes**

Cost
- Eliminate/ simplify heat treatment step
- Continuous process
- Internally heated reactor to enable scale and reduce cost
- Integrated precursor production
- No/less liquid waste

Performance
- Fine spray or dry feed for small and controllable particle size
- Liquid precursors enables compositional flexibility and homogeneity
- Means to control particle density (chemical/physical)

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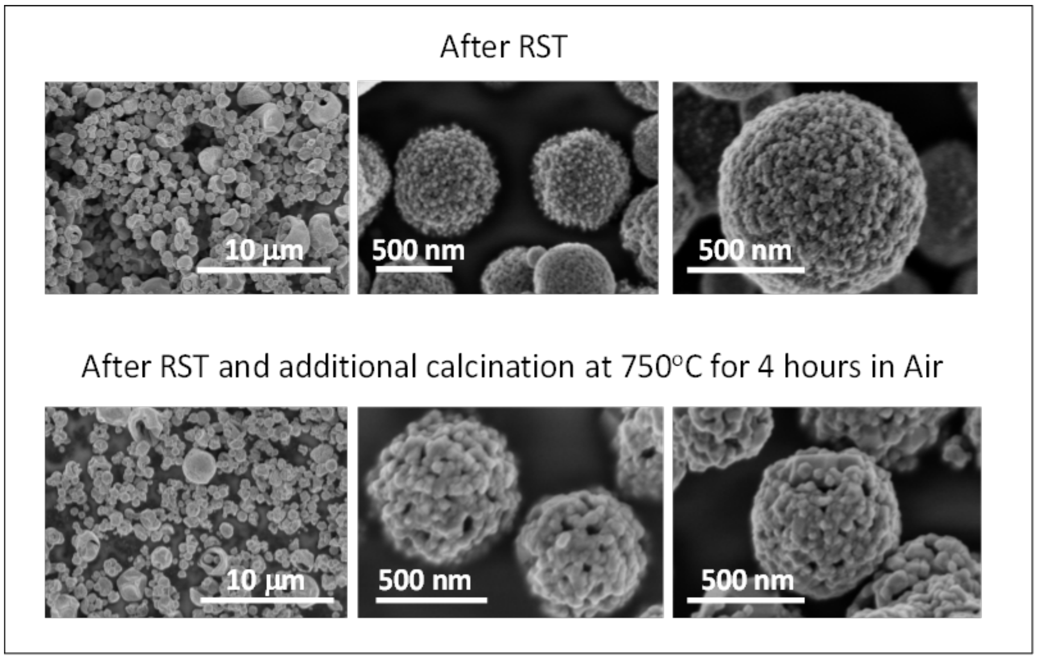
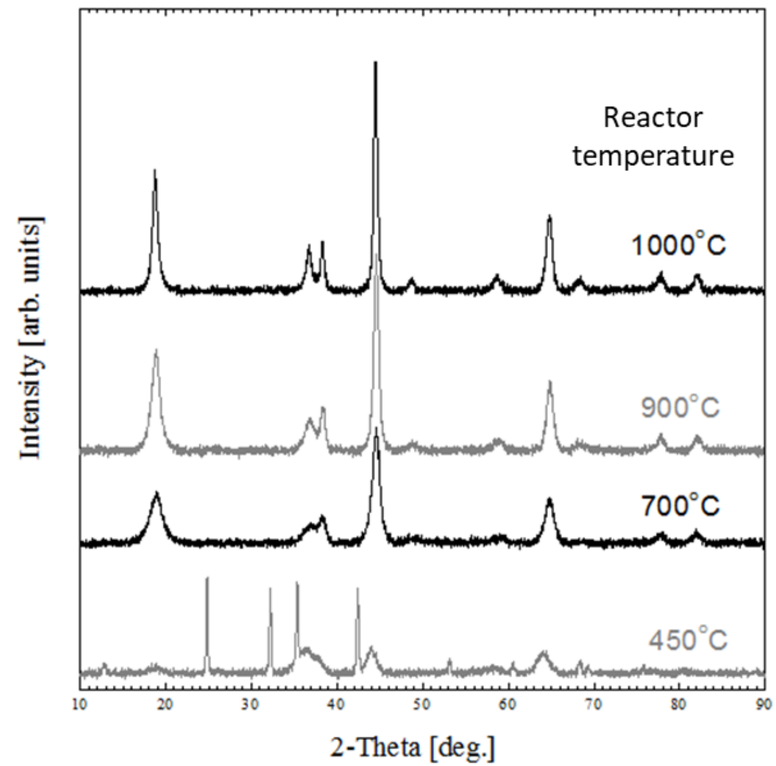
# Task 1.2. Synthesize and Optimize RST Battery Materials

## Key earlier technical accomplishments

- Cabot has synthesized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode material using its RST system

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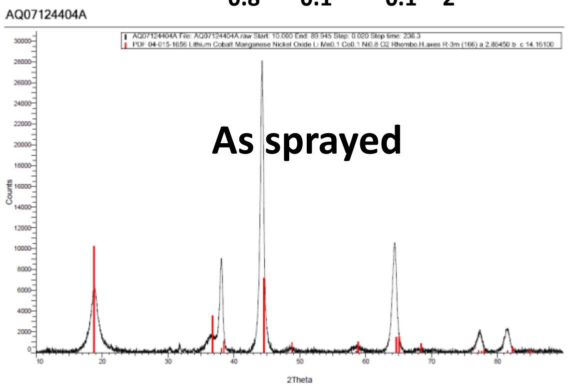
# Task 1.2. Synthesize and Optimize RST Battery Materials

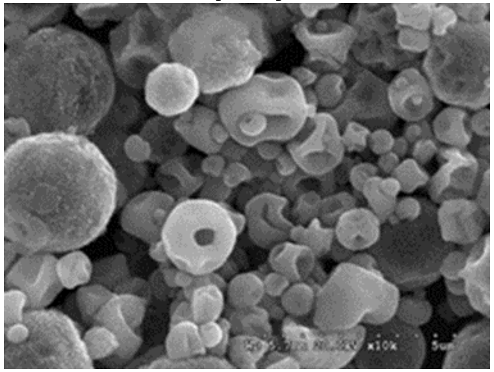
## Key earlier technical accomplishments

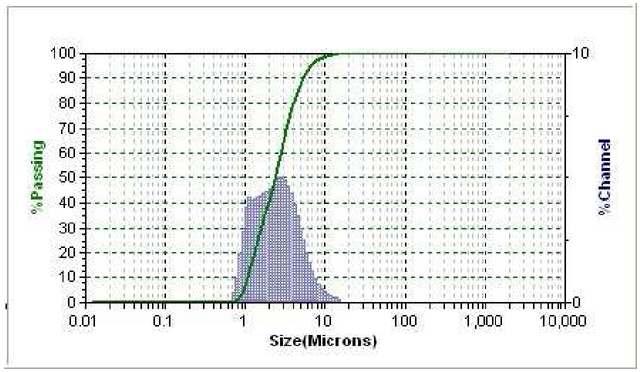
- We also have demonstrated the synthesis of $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$ via RST

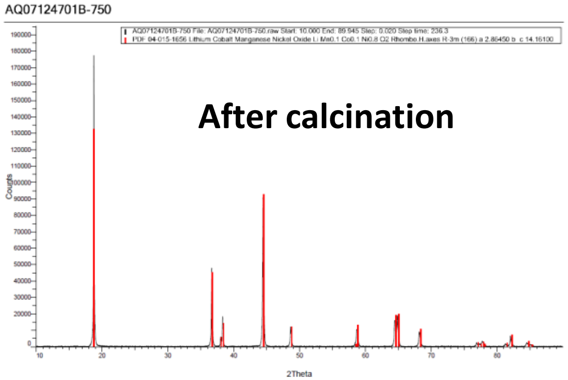
$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$



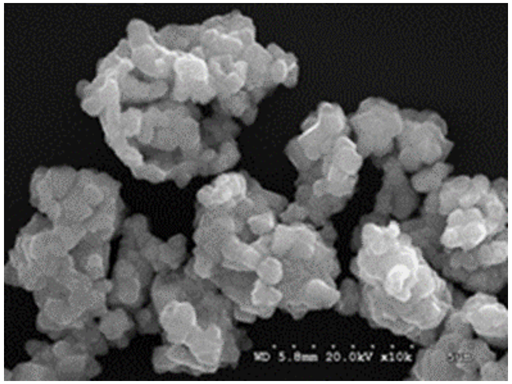

As sprayed





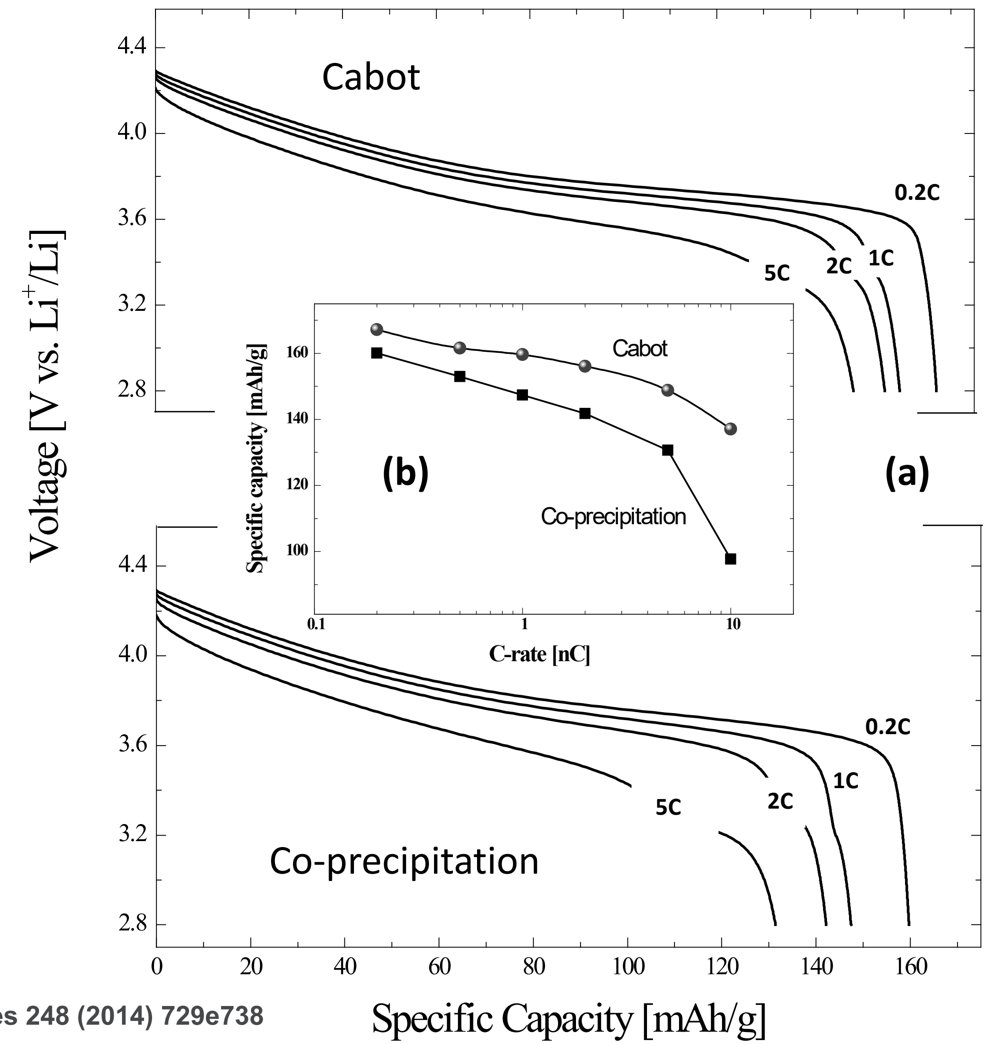

After calcination



| % metal by ICP | Result |
| --- | --- |
| Li/Co Ratio | 9.7 |
| Li/Mn Ratio | 9.3 |
| Li/Ni Ratio | 1.2 |
| Formula | $LiNi_{0.83}Co_{0.083}Mn_{0.0775}$ |

# Rate capability performance for RST-made NCM111

- Cells fabricated with RST-made NCM11 showed higher power performance compared to co-precipitation-made cathode material
- Half coin cell configuration:
  - Cathode: 94 wt.% NCM:3 wt.% CCA :3 wt.% PVDF
  - Li metal counter electrode
  - Loading: 1.5 mAh/cm$^2$
  - Voltage range: 2.8-4.3 V vs. Li/Li$^+$

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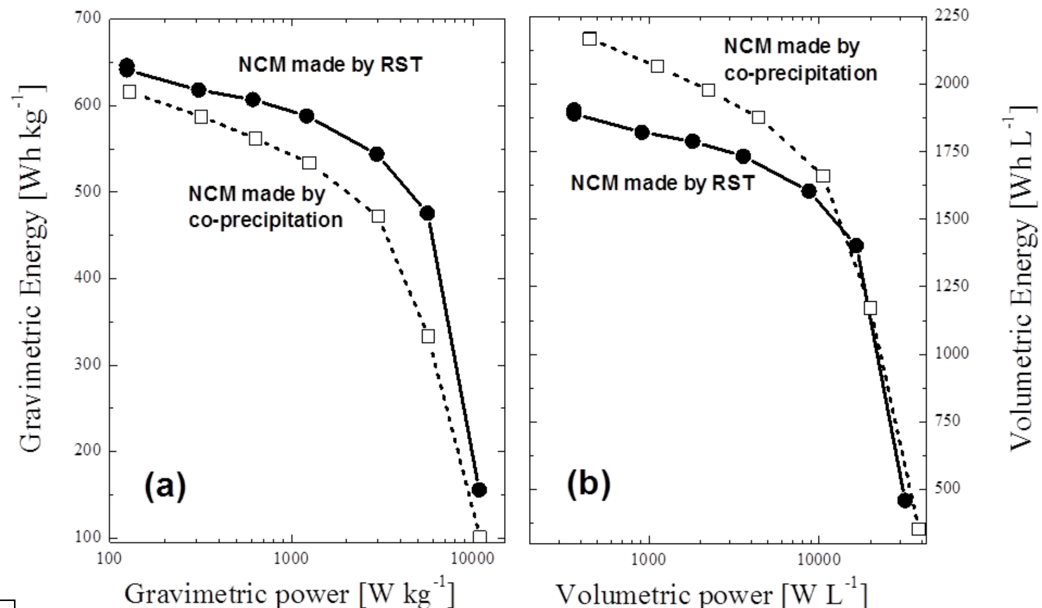
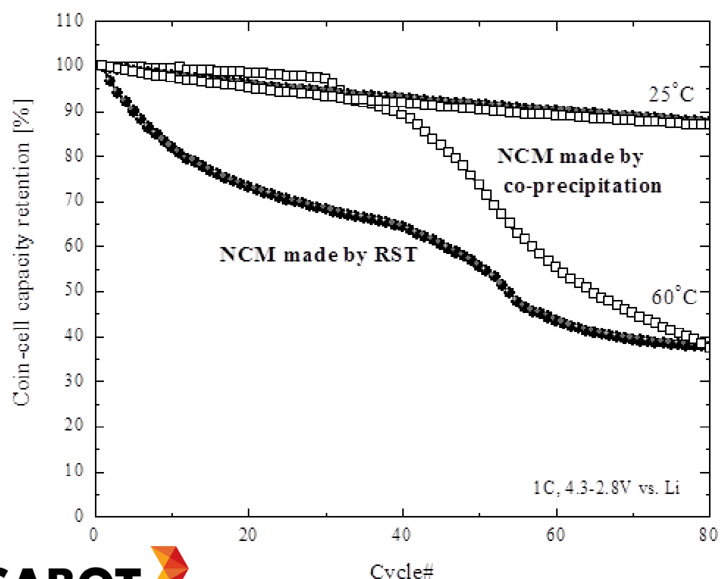
# Packing density and cycle stability needs improvement

- Volume normalize Ragone plots shows the penalty of low electrode density in the case of RST-made NCM111
- At high discharge power improvement in rate capability of small particles compensates for lower packing density




- Cycle performance at 25°C RST-made NCM is similar to its co-precipitation counterpart
- Under accelerated conditions (60°C), high surface area NCM (RST) suffers from rapid capacity fade

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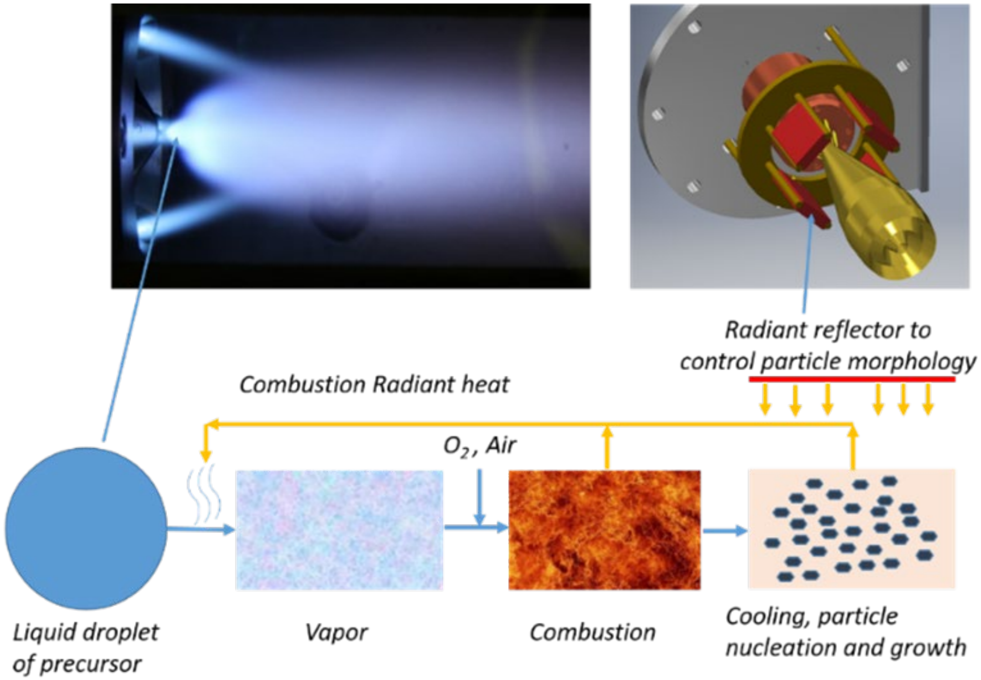
# Task 1.3. Synthesize and Optimize FSP Battery Materials

## Flame Spray Pyrolysis (FSP) System

- Flame Spray Pyrolysis is a subtype of aerosol synthesis techniques
- Utilize Aerosol Manufacturing processes for high-volume continuous manufacturing of battery cathode powders and solid state electrolyte
- ANL has recently built and commissioned a process development unit for developing FSP materials

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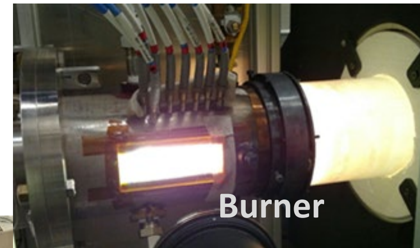
# ANL Combustion Synthesis Research Facility

## Flame Spray Pyrolysis (FSP) System

Flammable cabinets for pilot gases and burn solutions

Dual syringe pumps for solvent/solution delivery




Gas quench section


Laser based Flame Diagnostics

Tube furnace for post-flame HTRT (1000 C)

SMPS Particle size analyzer

Nanomaterial collection filter box

Clean-In-Place fixture

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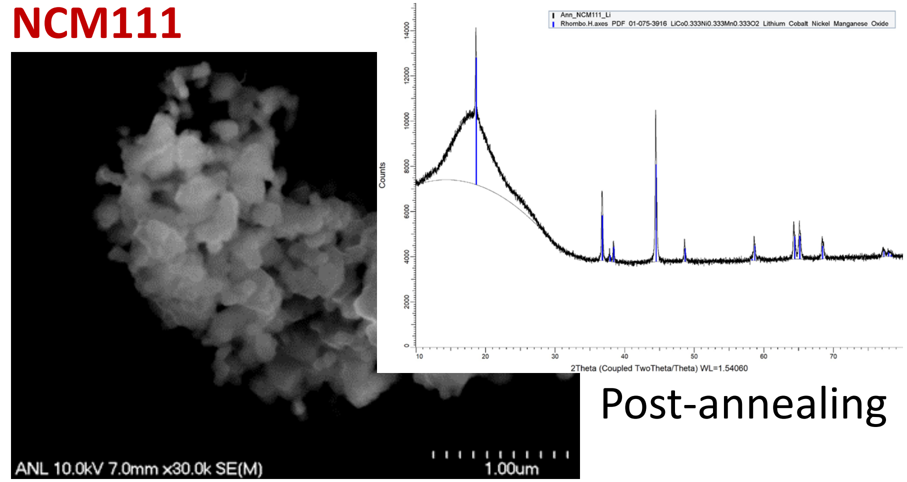
# Task 1.3. Synthesize and Optimize FSP Battery Materials

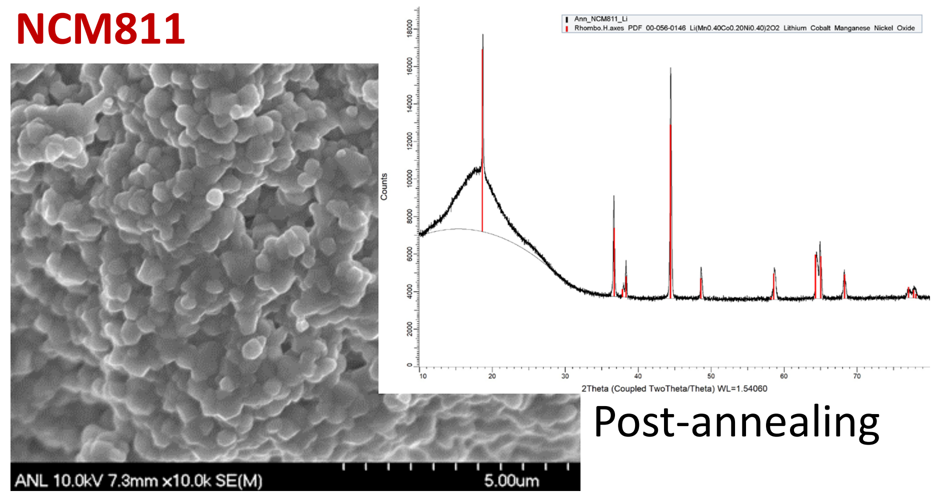
- NCM 111 and NCM 811 powders have been synthesized using the FSP system
- The primary particles of the as-prepared material ranges between 20 and 200 nm
- Larger size particles are achieved by primary particle coalescence and growth in post-flame in-situ annealing
- The as-prepared material forms a disorder rock salt type phase
- A layered structure is obtained after annealing at temperatures above 750°C

**NCM111**




Post-annealing

**NCM811**

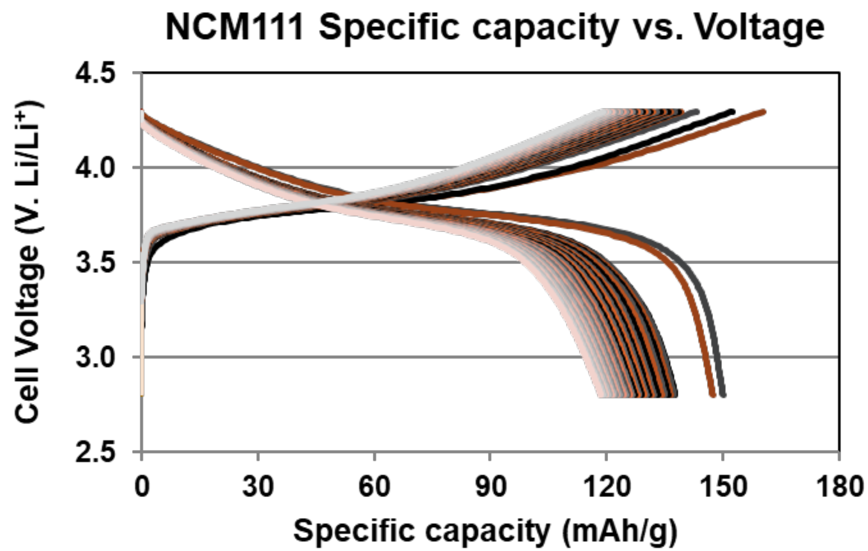


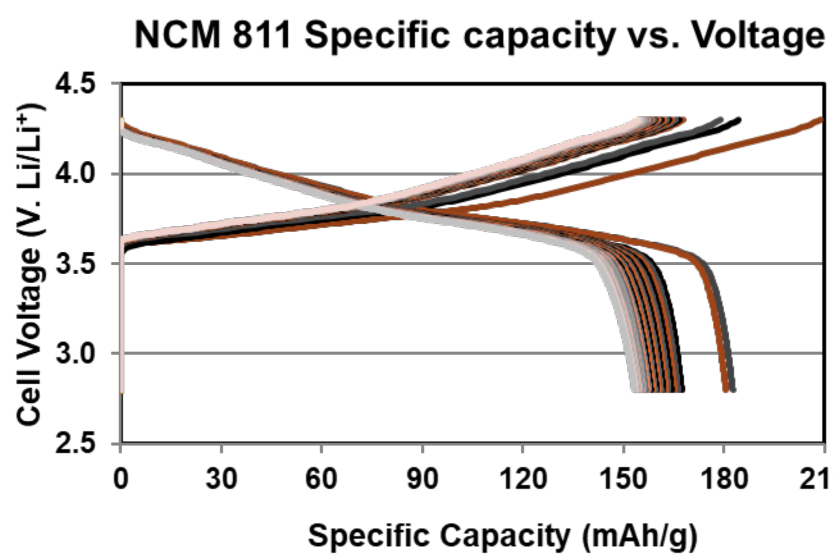

Post-annealing

# Task 1.3. Synthesize and Optimize FSP Battery Materials

## Electrochemical testing

- Half coin cells were build with FSP-made NCM active materials:
  - Two formation cycle at @ 0.1C
  - Cycling at @ 0.33C, voltage range 2.7 to 4.3V
- Electrochemical properties are affected by post-annealing conditions
- Initial reversible capacities were 155 and 185 mAh/g for NCM11 and  811 respectively
- Further optimization is required to increase NCM811 specific capacity and improve stability

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# Response to Previous Year Reviewers' Comments

New Project –No Comments

# Collaborations

- Argonne National Laboratory (ANL): Cathode compositions, cathode synthesis (FSP and RST), synthesis know-how, battery and analytical capabilities
  - ANL team has been working on Li-ion cathodes and other battery materials for more than 15 years. They have extensive understanding of cathode materials, electrodes, and unique facilities for the fabrication, characterization and testing of battery materials.
  - ANL team has developed high performance LIB cathode compositions such as layered-layered high energy materials with extremely high capacity.

- SAFT: Battery design, fabrication and testing; will assist selecting battery component materials
  - World leader in providing Li-ion systems for commercial, defense and space markets.
  - Experience manufacturing pouch cells ranging from 2Ah to 50Ah.

# Remaining Challenges and Barriers

- Reducing or eliminating Co in LiBs is required to reach cost & production targets (< $100/kWh)
- Eliminating Co from cathode while maintaining performance in LiBs is not yet technologically possible
- Increase RST/FSP-made NCM cathode material packing density targeting tap density > 2.0 $g/cm^3$
- Improve RST/FSP-made NCM cathode material structure and composition to reach specific density > 185 mAh/g
- Reduce and control particle agglomeration during heat treatment

# Proposed Future Work

## Remainder of FY19

- Continue with synthesis and optimization of RST/FSP battery materials: improve cathode compositions with initial focus on $Li(Ni_{1-x-y}Co_xMn_y)O_2$ (x, y ≤1) and then Li-excess disordered rock salt (LxDRS)
- Modify precursor chemistry  and utilize fine atomization approaches to improve particle density
- Select cell components and synthesize enough cathode material to fabricate project progress cells (PPC)
- Assemble 31 pouch format PPCs (≥2Ah) for DOE and TARDEC, along with final cell chemistry and internal testing results
- Any proposed future work is subject to change based on funding levels

## Go/No Go (12/2019)

- RST/FSP cathode active material should meet the following requirements (at coin cell level):
  - (1) Tap density > $2g/cm^3$
  - (2) Voltage window from ≤2.3 to > 4.25 V vs. $Li/Li^+$
  - (3) Specific capacity > 185 mAh/g

# Summary

## Relevance

- Address cell cost (≤ \$100/kWh) and cathode performance (≥ 600Wh/kg) challenges for the next generation LIBs
- Flexibility to produce all key low-Cobalt cathode compositions

## Approach

- Develop low-Co cathode materials via RST and FSP targeting < 50 $mg_{Co}$/Wh
- Implement structural/morphological modifications through aerosol particle production process
- Synthesize high Ni content NCM and disordered rock-salt materials
- Optimize conductive additive formulations for Low/free Co active material

## Technical Accomplishments

- RST system optimized for battery research has been relocated to ANL
- Early data showed advantages of making NCM by RST: particle tuneability and improved rate
- Initial experiment with FSP-made NCM111 and 811 show encouraging results:
  - Layered NCM phase has bee obtained
  - Specific capacity: 155 and 185 mAh/g for NCM 111 and 811 respectively

## Future Work

- Synthesis and optimization of RST/FSP Low-Cobalt cathode materials
- Modify precursor chemistry and atomization approaches: to improve particle density
- Manufacture 31 pouch PPCs (≥2Ah)