An Integrated Flame Spray Process for Low Cost Production of Battery Materials

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Project ID#: bat269

Overview

Timeline

- Start: January 1, 2016
- End: December 31, 2019

Budget

- Total project funding
  - DOE share: $2,215,556
  - Contractor share: $310,694
- Funding received in FY 2017

  - $616,797.52
- Funding for FY 2018

  - No-cost extension

Barriers

- Low cost target of battery $125/kWh
- Lost of materials and componenets
- Energy density target of $250 Wh/kg

Partners

- Project lead - University of Missouri
- Collaborator - EaglePicher Technologies

Relevance

Overall objective

The overall objective of this project is to develop an advanced manufacturing technology for battery materials production at low cost and in a green chemical process using glycerol as solvent to replace water.

Specific objectives

- To reduce material cost by at least 25% to $34/kg or less as compared to a baseline $45/kg;
- To achieve a lab scale production rate of 3 kg/day and a pilot scale production rate of 4 metric tons per year of cathode powders.
- To demonstrate battery cells with 250 Wh/kg energy density.

Objectives for the review period

1. Upgrade the flame spray reactor
2. Resolve lithium loss in powder formation process
3. Control flame spray process
4. Optimize powder morphology and size
5. Improve electrochemical performance of active material

Milestones (1)

FY17/FY18 Milestones and Work Status

Schedule	Milestone Descriptions	Type	Status
12/31/2017	Demonstrate five (5) cells of 250Wh/kg energy density.	Tech	On-going
12/31/2017	Demonstrate a production capacity of 3 kg/day with the high throughput spray technology.	**GNG***	Completed
06/30/2018	Demonstrate control of active material powder sizes to around 10 microns on average.	Tech	On-going
06/30/2018	Cell design including matching anode and suitable electrolytes.	Tech	On-going
09/30/2018	Select an in situ or semi-in situ coating process.	Tech	On-going

* Although the Go/No-go milestone in production rate has been achieved in 2017, battery performance of the cathode powders has not met expectations. This challenge has made it necessary to have a no-cost extension period, which is focused on improving the properties of the powders.

Milestones (2)

FY18/FY19 Milestones and Work Status

Schedule	Milestone Descriptions	Type	Status
12/31/2018	Demonstrate five (5) cells of 250Wh/kg energy density.	Tech	On-going
12/31/2018	Demonstrate a production capacity of 3 kg/day with the high throughput spray technology.	**GNG****	On-going
03/31/2019	Materials processing method using either a flow process or a stationary process will be selected.	Tech	To start
06/30/2019	Pilot production line construction.	Tech	To start
09/30/2019	Cost reduction of at least 25% to $34/kg or less for active material NMC demonstrated.	Tech	To start

** The Go/No-go decision will have to be made again, given that there was a major change in the flame reactor, aimed at making powders with satisfied performance.

Approach

The **overall approach** is to develop a new flame spray process to make active cathode powders with new chemistry. Glycerol, as a cheap industrial byproduct, is used as solvent to replace water and as a fuel to process transition metal oxide powders to reduce energy consumption. The process also uses natural gas through combustion to provide energy to anneal the powders during the synthesis to lower material cost.

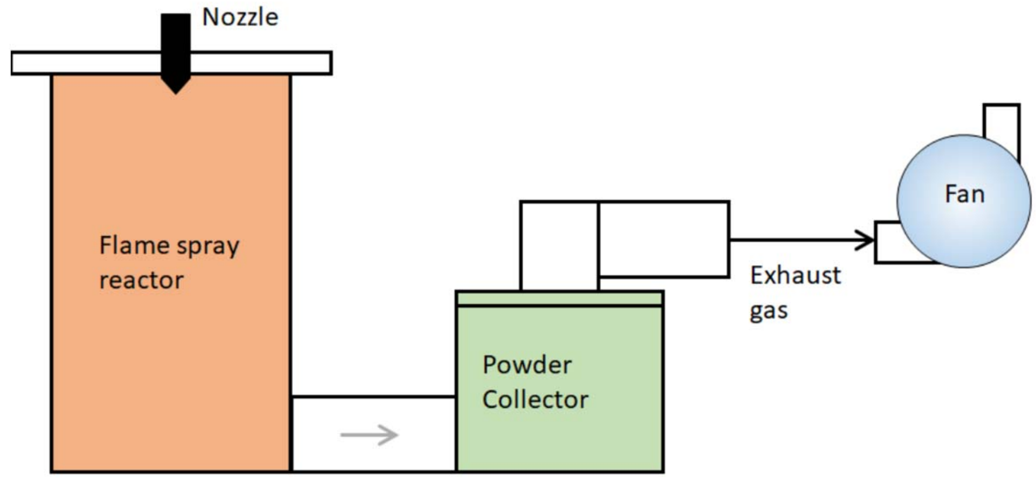
Approaches to technical barriers:

- ❑ A new Gen 3.0 reactor has been constructed to address the production rate (completed);
- ❑ Change in precursor chemistry has been made to address the loss of lithium during powder formation (completed);
- ❑ Control powder of morphology and size is being addressed through flow field control and temperature distribution in the reactor (on-going);
- ❑ Battery charge-discharge performance is being addressed through material processing parameters, such as processing temperatures and powder morphology, size and tap density (on-going).

Technical Accomplishments and Progress (1)

1. Upgrade of flame spray reactor

- Compared to last review period, the flame spray reactor has been upgraded from Gen 2.0 to Gen 3.0. The new reactor has allowed new nozzle design to increase production rate and it also allows flexibility in process control of the properties of the produced powders.



Schematic experimental set-up
(for illustration only)

- A new design change in the spray nozzle improved the nozzle characteristics to have reduced droplet and powder sizes. This improvement made it possible to control powder morphology and sizes.

- A larger fan has been purchased and installed for more powder collection.

Technical Accomplishments and Progress (2)

2. Li loss resolved

- Since last review, the loss of Li in the powder formation process has been resolved by adding more Li in the precursor. As shown in the table below, the stoichiometric ratio of Li in the expected $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder has been raised to its assumed stoichiometric ratio (i.e., 1.0), when a 30% more Li was used (temperature dependent).

ICP-MS analysis results on powder stoichiometry

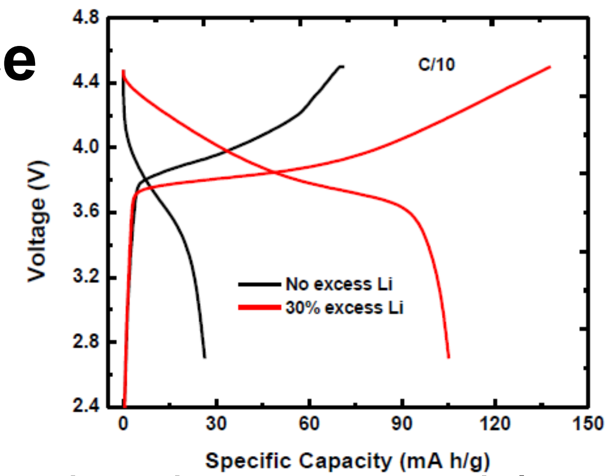
Elements	Li	Mn	Co	Ni
Old powders	0.791	0.346	0.320	0.334
New powders	1.048	0.337	0.335	0.328

- Li_2O has a high vapor pressure at temperatures above 800 °C. As a result, when the processing temperatures are above that, there is a loss of Li. A concern is that the extra Li added would lead to a cost increase in the final powders. This barrier is currently being addressed by collecting Li_2O down stream of the exhaust system where temperature is low (e.g., 300 °C) enough to condense it. Recovered Li_2O powders can be reused.

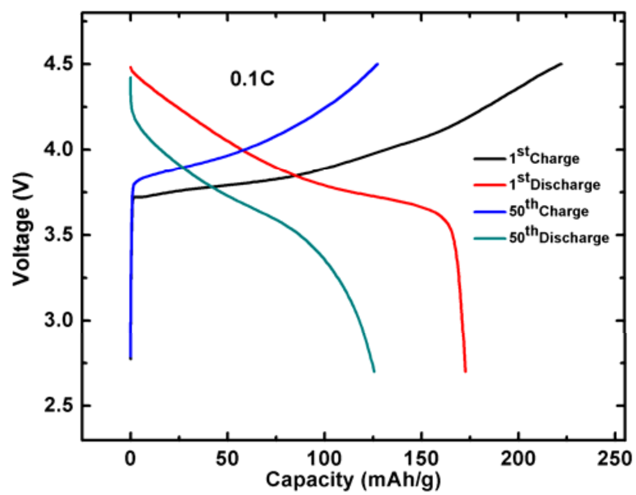
Technical Accomplishments and Progress (3)

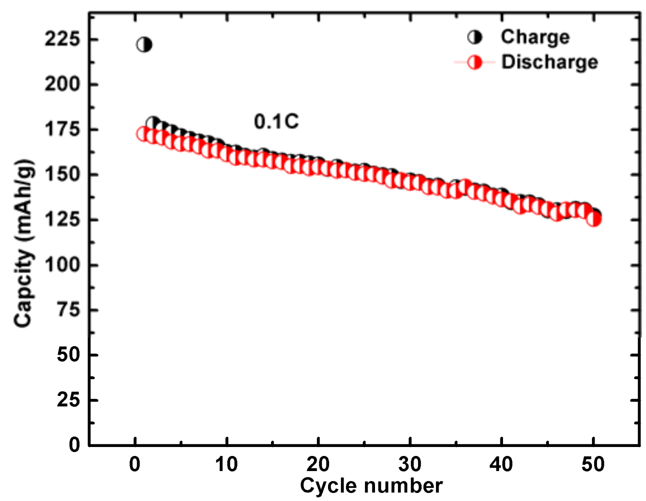
3. Improved NMC performance

- At the last review the powders had not shown expected charge-discharge characteristics. A previous result is shown in the figure on the right.



- Since the last review, efforts have been made to improve material properties. The figures below show charge-discharge of a recently made powder. The charge-discharge performances have been much improved. We expect to continue to improve the charge-discharge performances.

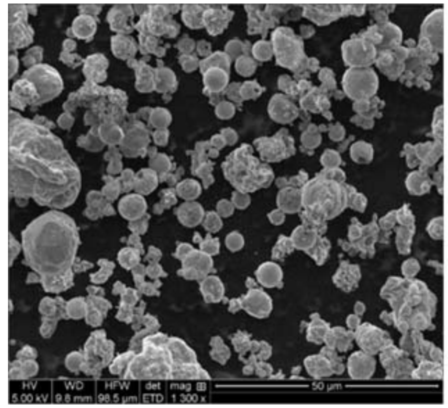


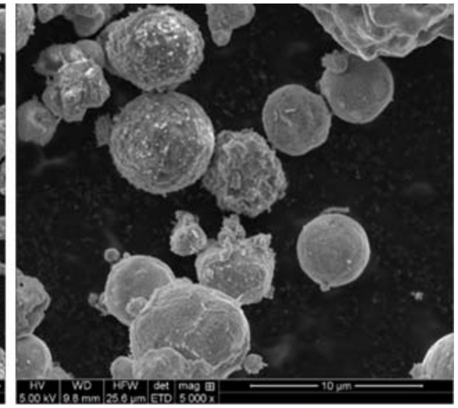


Technical Accomplishments and Progress (4)

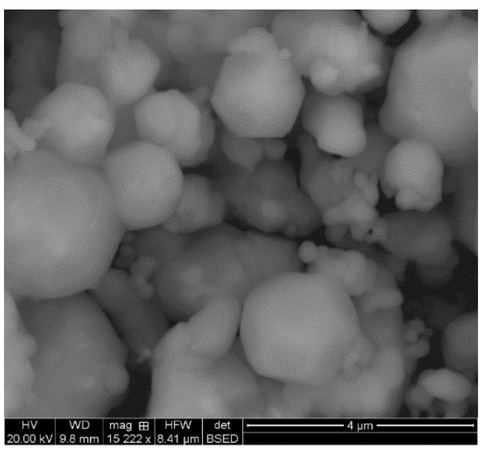
4. NMC powder morphology

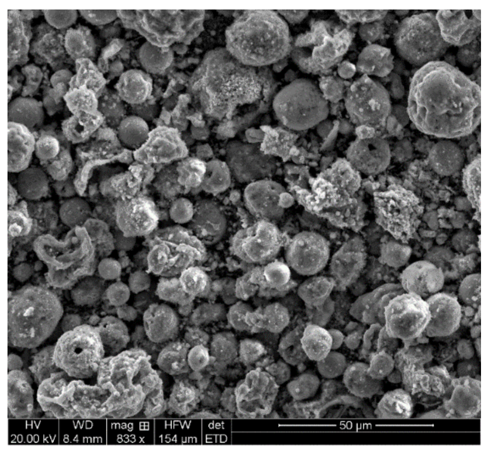
Previous powders produced from the Gen 2.0 reactor, showing average size of 3 microns, much smaller than those obtained previously. The powders also appear to be solid, not porous as before.

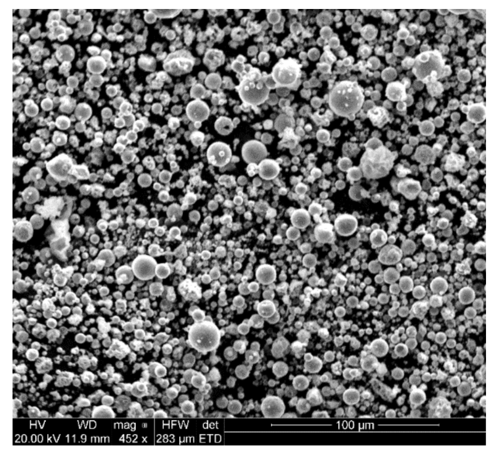




The new NMC powders produced in Gen 3.0 reactor, showing a flexibility of making powders of a range of sizes, from sub-microns to tens of microns. The work is still going on to control the flow field in the reactor and temperatures to obtain optimized powder morphology and size.







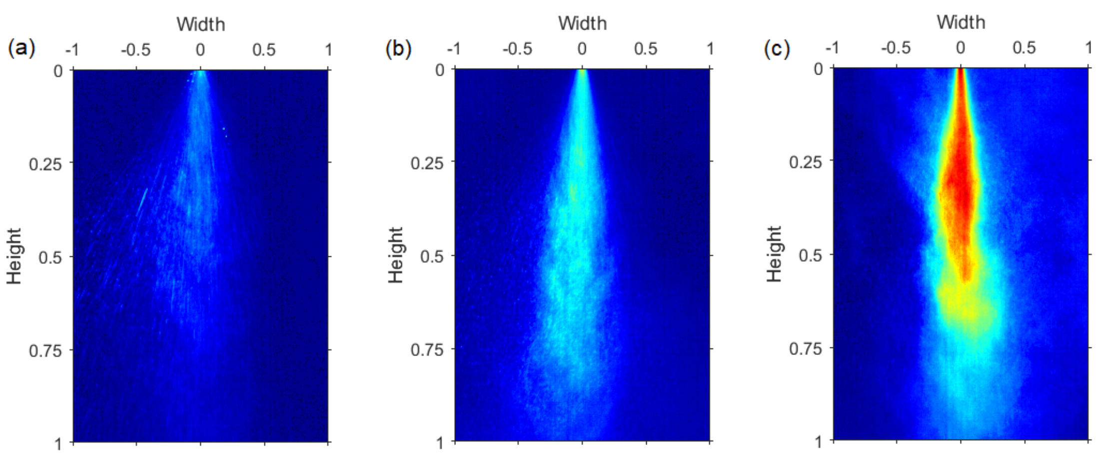
Samples of prepared powders in Gen 3.0 reactor.

Technical Accomplishments and Progress (5)

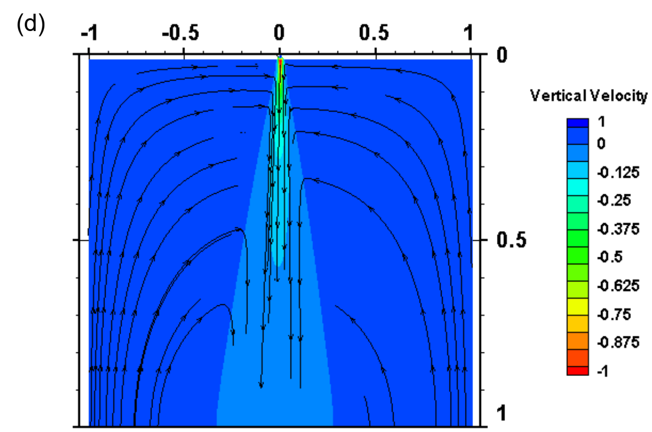
(5) Process engineering

We have started a study on understanding the processes in the reactor. This study is to guide selection of experimental conditions in the control of flows and temperature distributions in the reactor. The following figures are some preliminary results. Going forward, we expect to get a better understanding of the reactor and thus to have a better control of it to produce the expected powders with further optimized morphology and size.

Images of glycerol sprays showing the effect of different atomizing gas flow rates.



Reactor simulation showing flow field profiles.

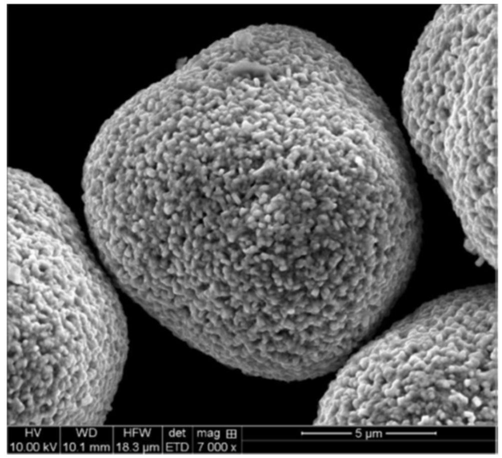


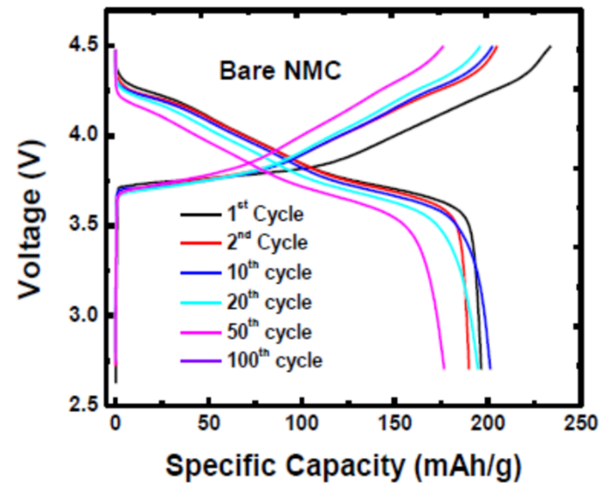
Technical Accomplishments and Progress (6)

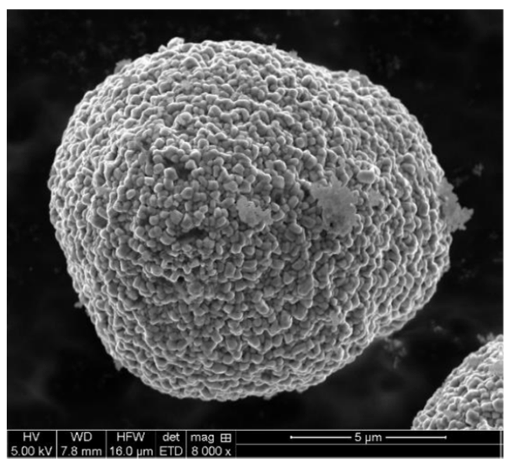
(6) Powder surface coating

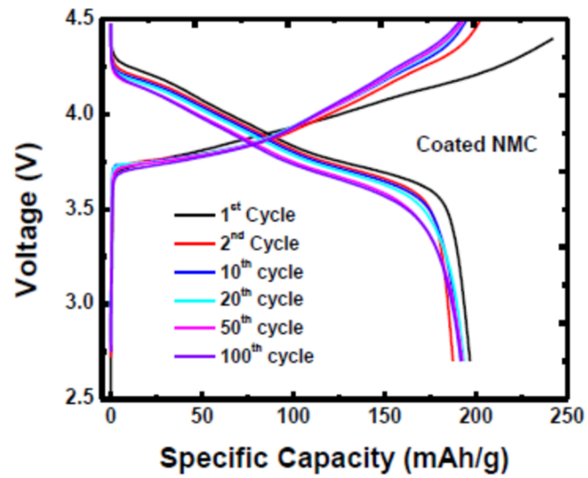
We have started work on powder surface coating. Initial study was focused on coating powder materials with a metal oxide. A new coating process has been developed and will be explored to integrate with the reactor system. The preliminary results showed much improved stability after an NMC powder (produced by precipitation) were coated.

We will continue to do research in the surface process.


Uncoated powders.




Coated powders.



Responses to Reviewers' Comments (1)

Some major concerns of the reviewers are addressed below.

Reviewer 2 in Q2, **comment**: "The focus on Ni Mn Co oxide (NMC)111 and NCA may be an acceptable starting point, but neither of these materials are currently being considered for use in "next-generation" batteries for vehicles.

- Response: We agree with the reviewer. We are planning to make other powders, such Ni-rich or Li-rich powders. NMC(111) is as a test material for process control of the flame reactor. Later in FY18, we will explore other formulations to achieve the energy density target.

Reviewer 4 in Q2, **comment**: "The reviewer said that adding 30% excess Li improved, but that would be a significant increase in cost. The reviewer asked how this Li loss will be addressed."

- Response: We agree with the reviewer. If 30% of Li is lost in the production process, it will certainly increase the powder cost significantly. This issue is addressed by collecting Li oxide powders in a downstream collector where low temperature will lead to condensation of the Li oxide vapor. Li oxide recovery will mitigate the issue.

Responses to Reviewers' Comments (2)

Reviewer 2 in Q4, **comment**: "It seems that much more fundamental effort is first needed to address fully characterizing current state-of-the-projects and determining how to address chemistry issues and coating approaches. The reviewer said that the team should rethink milestone events and consider what new roadmaps, economic issues, process and property issues need first to be solved prior to moving ahead with future work."

- Response: Indeed, some fundamental effort is being made since now the project is in a no-cost extension period. Effort is aimed at addressing morphological control through process engineering as well as developing a coating process.

Collaboration with Other Institutions

- EaglePicher Technologies (EPT) is collaborator in the project. EPT as a battery manufacturer and developer has vast capabilities in battery research. The role of EPT in this project is to:

(1) Test the active powders and provide feedback to Mizzou to improve the material properties.
(2) Design and make battery cells to achieve the targeted energy density,
(3) Set-up a pilot production line at EPT as a testbed for the manufacturing technology.

- Future collaborations with National Labs and academic institutions are expected. We expect to send the produced powders for third party testing. We also expect to use the new technology to produce powders with specifications from a user.

Remaining Challenges and Barriers

- While we have made much progress in the past year, morphology and size control remains to be a challenge. We expect to find a solution in the upcoming quarters, with the help of the process engineering study, that will give us a set of conditions to produce powders with good performances.

- It is expected that NMC(111) material will not be meeting the energy density target (250 Wh/kg). As soon as the powder morphology and size are under control, new formulations are expected to be designed and related powders be made (e.g., Ni-rich or Li-rich). While we do not expect a high risk in this regard, we may have some technical barriers. We expect to overcome them going forward.

Proposed Future Research

- To continue studying the spray process in the reactor so that it can be controlled to produce powders with desired characteristics (FY18).
- To obtain a set of operation conditions that will allow to produce powders with high tap density and spherical shape (FY18).
- To control conditions to achieve a range of powder sizes with a specific target at 10 microns (FY18).
- To design and optimize battery cells to achieve the targeted energy density (FY19).
- To design and integrate other processes (e.g., surface coating) (FY19).
- To demonstrate a production capacity of 3 kg/day with produced powders meeting battery performance (Go/No-Go, FY 19).

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

Summary

1. A Gen 3.0 flame spray reactor has been developed that can produce NMC powders at targeted production capacity.

2. Li loss problem has been resolved and NMC powders currently made have stoichiometric ratios.

3. Much progress has been made in material electrochemical performance with charge-discharge capacity improved significantly over previous powders.

4. We continue to get better understanding of the processes in the flame spray reactor and expect to have more control over powder properties.

5. We continue to improve operation conditions and expect to achieve the technical milestones and go/no-go target in the coming quarters.