Process Development and Scale up of Advanced Active Battery Materials

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Project ID: ES167

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2016
- Percent complete: on going

Budget

- Total project funding:
  - $1.2M in FY14
  - $1.2M in FY15
    ($86K for equipment)

Barriers

- Cost: Reduce manufacturing costs with advanced processing methods
- Performance: Selection of synthesis route and process and its optimization for maximum performance

Partners

- Active material process R&D:
  - Argonne's Applied R&D Group
    - Material synthesis and scale-up
  - Sharp Laboratories of America (ARPA-E)
    - Material synthesis and scale-up
  - Jet Propulsion Lab
    - Coating study
  - PPG Industries
    - Modified cathode materials for binder study
  - Global Battery Solutions
    - Active material recovery process development
- Provided materials to:
  - University of Illinois
  - NanoResearch, Inc.
  - Argonne National Laboratory
    - Materials Screening Group
    - CAMP Facility
    - Applied R&D Group

Objectives - Relevance

- The objective of this program is to provide a systematic engineering research approach to:
  - Identify and resolve constraints for the scale-up of advanced battery cathode materials, from the bench to pre-pilot scale with the development of cost-effective process technology.
  - To provide sufficient quantities of these materials produced under rigorous quality control and process optimization for industrial evaluation or further research.
  - To evaluate emerging manufacturing technologies for the production of target material.

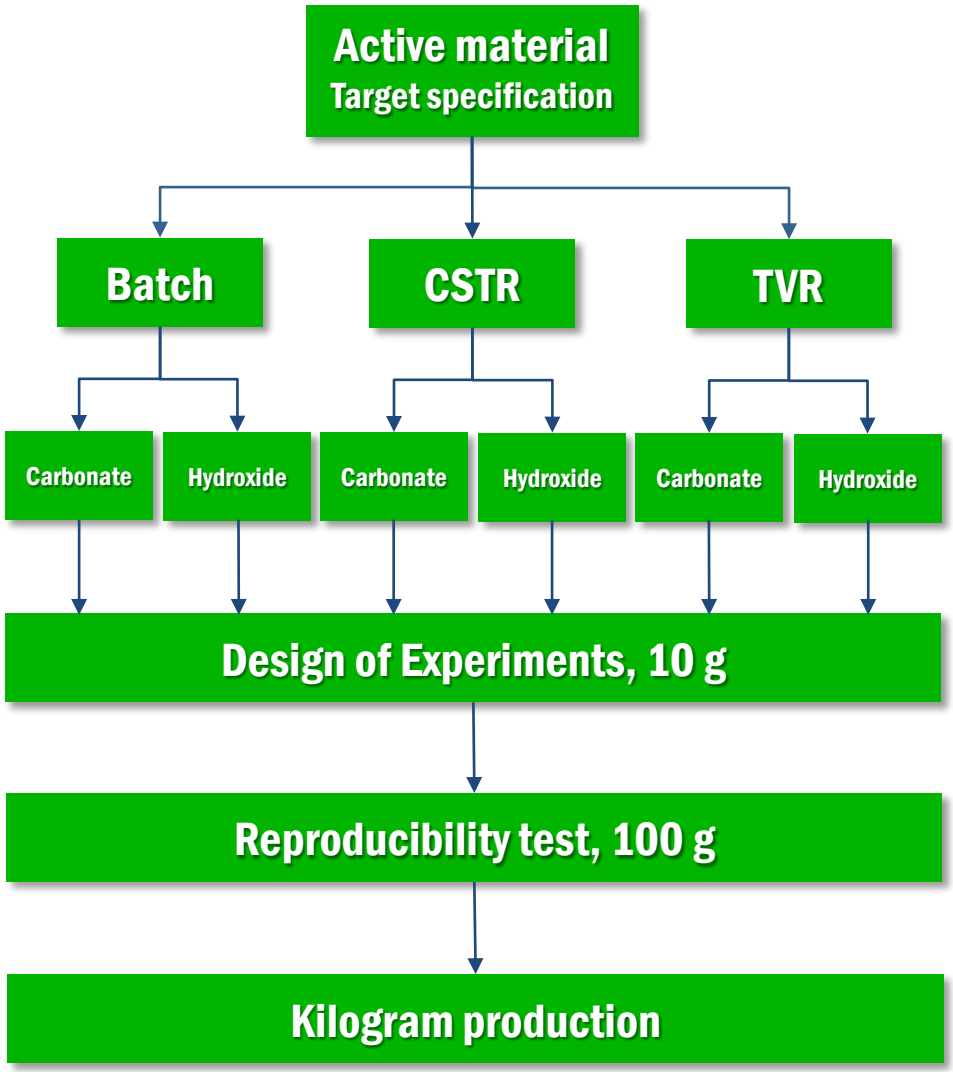
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing.
    - Reducing the risk associated with the commercialization of new battery materials.
  - This program provides large quantities of materials with consistent quality.
    - For industrial validation in large format prototype cells.
    - For further research on the advanced materials.

Milestones

- FY14
  - **Target material #2 ($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$) – JPL/UT-Austin**
    - Complete scale-up of JPL material at kilogram quantity **(completed – Previously reported)**
  - **Target material #3 (layered layered spinel: $Li_{1.14}Ni_{0.28}Mn_{0.53}Co_{0.19}O_y$)**
    - Identify target material, complete preliminary assessment **(completed)**
    - Material production and delivery **(completed)**
  - **Target material #4 (layered layered: $Li_{1.067}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$)**
    - Identify target material, complete preliminary assessment **(completed)**
    - Determine accurate composition by reproducibility test of ICP-MS and coin cell **(completed)**
- FY15
  - **Target material #4 (layered layered: $Li_{1.067}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$)**
    - Complete precursor optimization, provide samples for evaluation **(completed)**
    - Complete the comparison of synthesis technologies **(completed)**
    - Complete scale-up at kilogram quantity **(ongoing)**
  - **Target material #2 ($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$) – JPL/UT-Austin**
    - Complete the assessment of AlF_3 surface coating on the scale-up material **(completed)**
  - **Target material #5 (gradient cathode material)**
    - Identify target composition, complete preliminary assessment
    - Complete precursor optimization

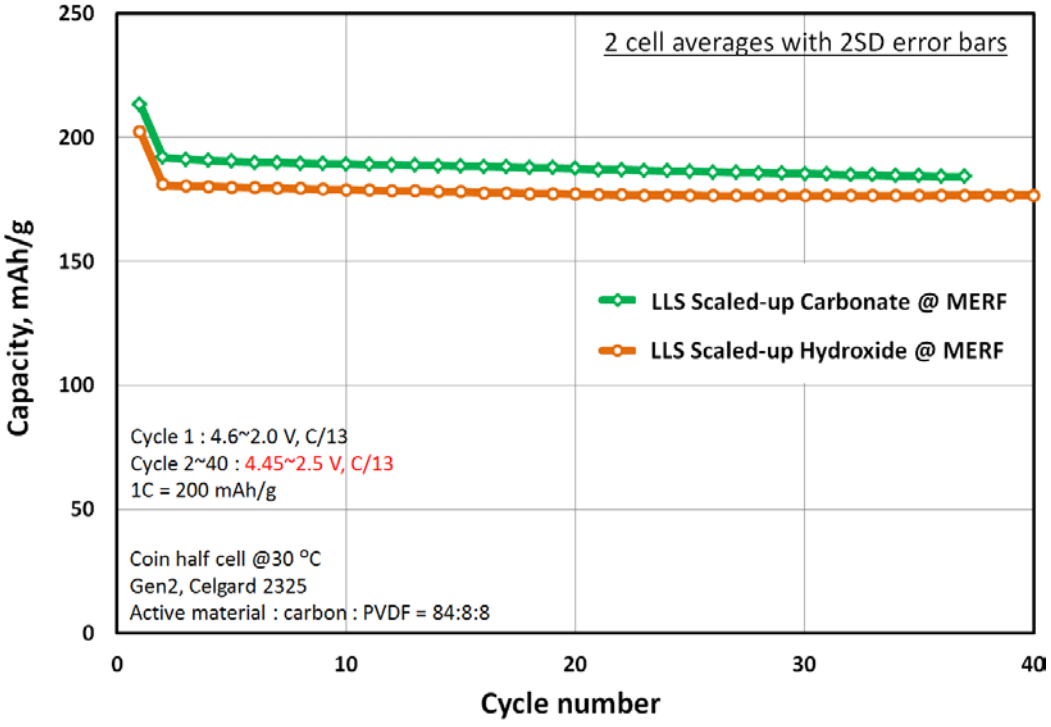
Approach - Strategy

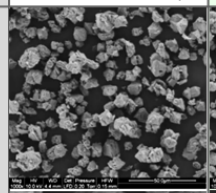
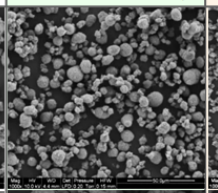
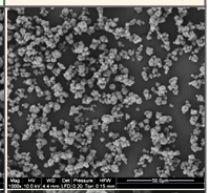
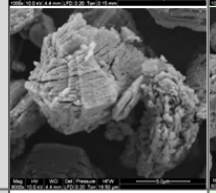
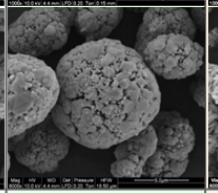
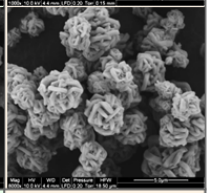
- Define target material to be scaled
  - Evaluate bench-scale samples from R&D group
- Select synthesis process and technologies
  - Batch system
  - CSTR (Continuous Stirred Tank Reactor) system
  - TVR (Taylor Vortex Reactor) system
- Select synthesis route
  - Carbonate and hydroxide co-precipitation
- Optimize synthesis condition by DoE
  - Maximize cathode quality and performance
- Produce 100 g intermediate cathode
  - Material evaluation and reproducibility check
- Kilogram production and delivery
  - Feedback from collaborators for improvement



Layered-Layered Spinel Material Synthesis

- Target composition: 0.85 [0.25 Li_2MnO_3●0.75 $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$]● 0.15 $Li_{0.5}M'O_2$

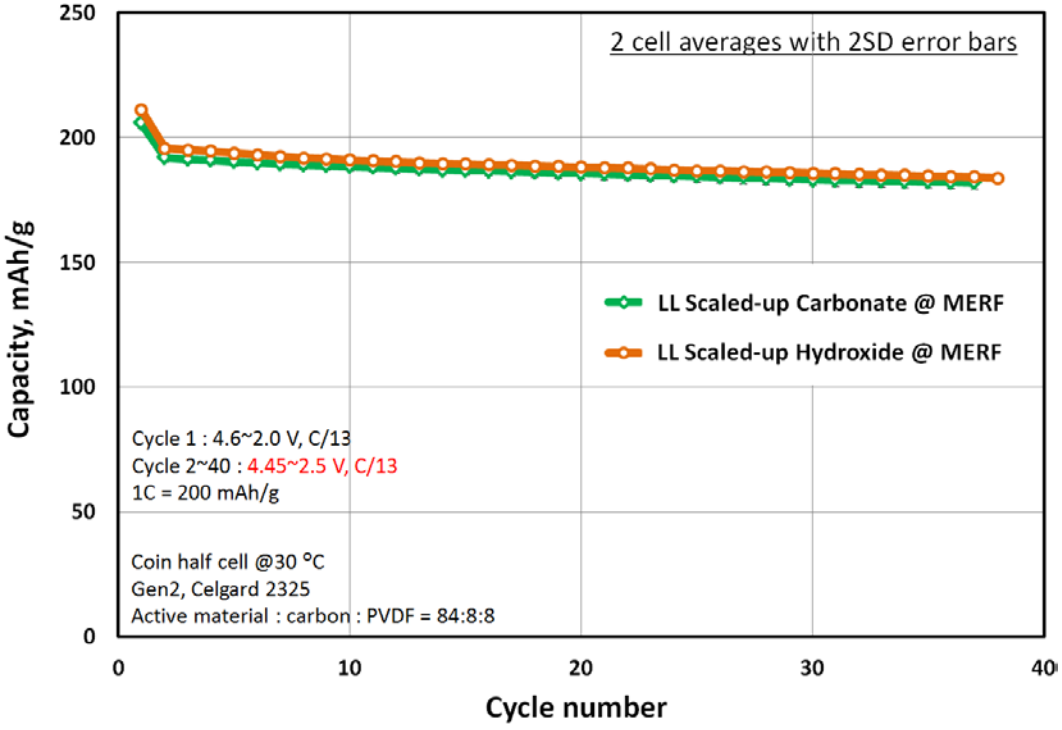


	Bench-scale Oxalate	ES20140402 Scale-up Carbonate 1st	ES20140710 Scale-up Hydroxide 1st
	Target composition	Pre-pilot Preliminary	Pre-pilot Preliminary
Composition (by ICP-MS)	$Li_{1.14}Ni_{0.28}Mn_{0.53}Co_{0.19}O_y$	$Li_{1.063}Ni_{0.265}Mn_{0.542}Co_{0.193}O_y$	$Li_{1.206}Ni_{0.274}Mn_{0.534}Co_{0.191}O_y$
SEM x1,000			
SEM x8,000			
$D_{10}/D_{50}/D_{90}$ [µm]	6.3 / 12.3 / 22.3	5.2 / 9.6 / 16.8	2.4 / 4.8 / 8.8
Tap density [g/cc]	1.70	1.80	1.51
Initial disch. cap. @15mA/g [mAh/g]	193	218	202

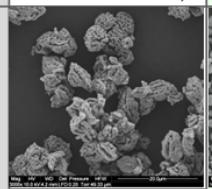
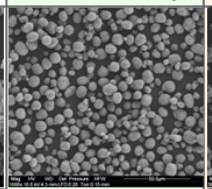
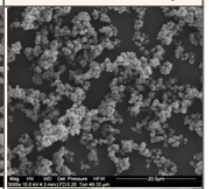
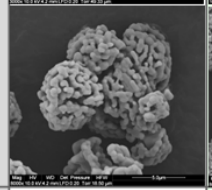
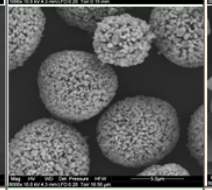
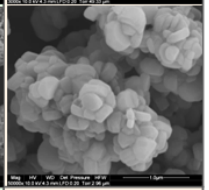
- ✓ *LLS material was requested for basic materials research.*
- ✓ *Carbonate material shows better tap density and discharge capacity than hydroxide material.*
- ✓ *Multiple batches were synthesized and delivered to M. Thackeray's research group for stability studies and surface coating research.*
- ✓ *Additional samples have been requested and may be synthesized upon approval.*

Layered-Layered Material Synthesis

- Target composition: $Li_{1.05}Ni_{0.5225}Mn_{0.43}Co_{0.0475}O_y$



Preliminary synthesis route comparison

	BL140804 Bench-scale Oxalate	ES20140929 Pre-pilot Carbonate 1st	ES20140925 Pre-pilot Hydroxide 1st
	Target composition	Preliminary scaled-up	Preliminary scaled-up
Composition (by ICP-MS)	$Li_{1.05}Ni_{0.52}Mn_{0.43}Co_{0.05}O_y$	$Li_{1.07}Ni_{0.52}Mn_{0.43}Co_{0.05}O_y$	$Li_{1.03}Ni_{0.52}Mn_{0.44}Co_{0.05}O_y$
SEM x1,000			
SEM x8,000			
$D_{10}/D_{50}/D_{90}$ [μm]	4.5 / 8.8 / 16.9	4.8 / 8.0 / 13.5	1.9 / 3.4 / 6.1
Tap density [g/cc]	1.04	1.39	0.97
Initial disch. cap. @15mA/g [mAh/g]	201.4	209.7	213.4

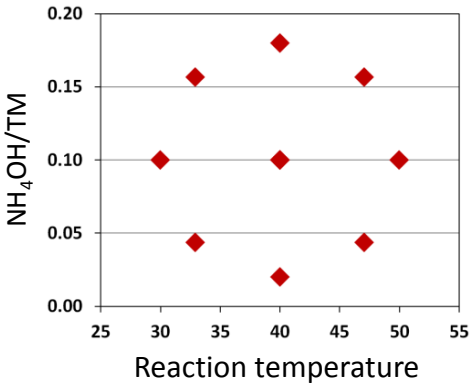
- ✓ *LL material was requested to support HE/HV program.*
- ✓ *Design of Experiments (DoE) was used for synthesis condition optimization.*
- ✓ *Process comparison was conducted via batch, continuous and emerging manufacturing technology – vortex flow reactor.*

Optimization by Design of Experiments (DoE)

Statistical design of experiments (DoE)

- To evaluate process stability and effect of key variables
- 13-time experiments by Response Surface Modeling
- 12hr continuous operation using 20L CSTR (steady-state)

RunOrder	TEMP	NH_4OH/TM
1	40.0	0.10
2	40.0	0.10
3	32.9	0.16
4	40.0	0.10
5	32.9	0.04
6	30.0	0.10
7	47.1	0.04
8	40.0	0.02
9	47.1	0.16
10	40.0	0.10
11	40.0	0.18
12	50.0	0.10
13	40.0	0.10



Response surface regression and ANOVA

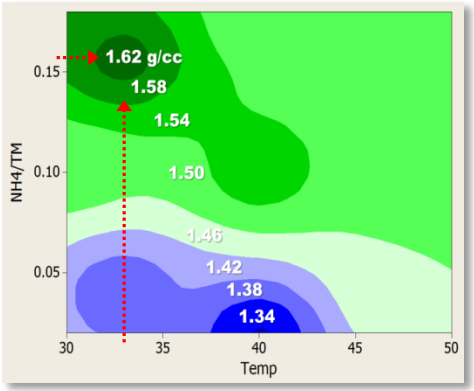
Response Surface Regression: Tap Density vs. Temp, NH4/TM

R-Sq = 94.55% R-Sq(pred) = 69.78% R-Sq(adj) = 90.65%

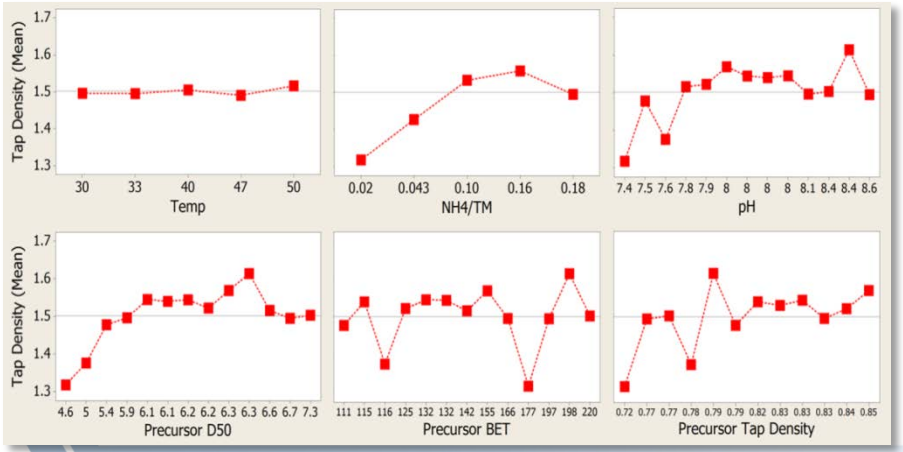
Analysis of variance for tap density

Source	F	P
Regression	24.28	0.000
Linear	28.97	0.000
Temp	0.08	0.783
NH4/TM	57.87	0.000
Square	21.75	0.001
Temp*Temp	1.19	0.311
NH4/TM*NH4/TM	43.45	0.000
Interaction	19.93	0.003
Temp*NH4/TM	19.93	0.003
Residual Error		
Lack-of-Fit	3.38	0.135

Contour plot of cathode tap density



Main effects plot of variables



- ✓ *A 2-way interaction between temperature and NH_4OH/TM ratio was identified.*
- ✓ *NH_4OH/TM ratio of 0.16 shows best cathode tap density.*
- ✓ *Cathode density increases if precursor density increases.*
- ✓ *Regression model accurately fits the experimental data.*
- ✓ *ANOVA shows statistically significant terms.*

Process comparison at 33°C and 0.16 ratio

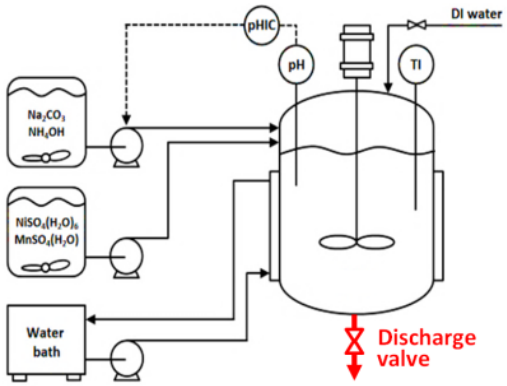
40L Batch 24hr operation → **20L CSTR** 24hr operation → **1L TVR** 24hr operation

Process Comparison: Batch, CSTR and TVR

- Features of co-precipitation processes (concept drawing)

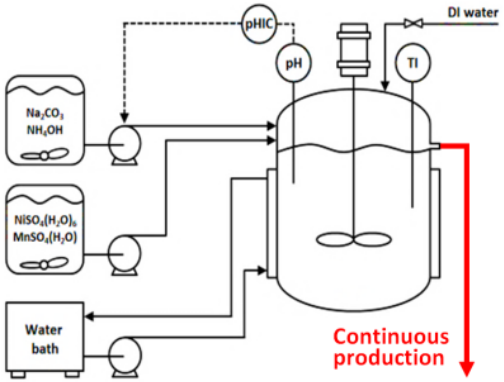
Batch

- Labor intensive operation
- Batch to batch variability
- Longer reaction time



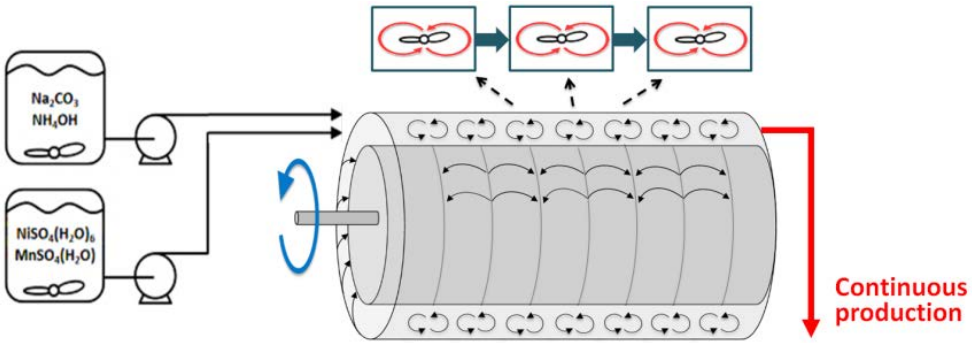
CSTR

- Product uniformity
- Process complexity
- Longer residence time



TVR

- Simplified operation
- Product uniformity
- Shorter residence time

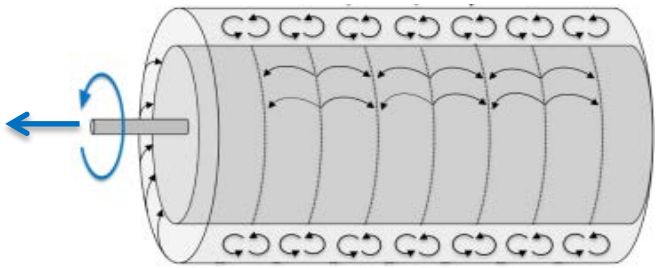


– **TVR provides a homogeneous intense micro-mixing zone and produces spherical precursors with narrow size distribution.**

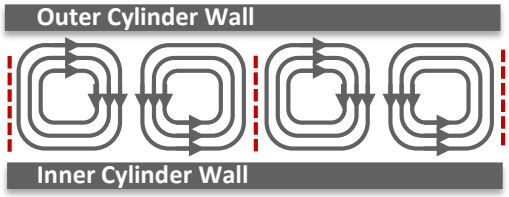
Emerging Manufacturing Process: Taylor Vortex Reactor

- A novel reactor for the continuous production of cathode precursors
  - Homogeneous micro-mixing
  - High mass and heat transfer enabling a high degree of uniform super saturation
  - Faster reaction kinetics and denser particles
  - Uniform spherical morphology and sharp particle size distribution
  - Shorter processing time
- A continuous process with higher reproducibility and lower cost than conventional material manufacturing.

✓ Rotating inner cylinder: enabling macro-mixing

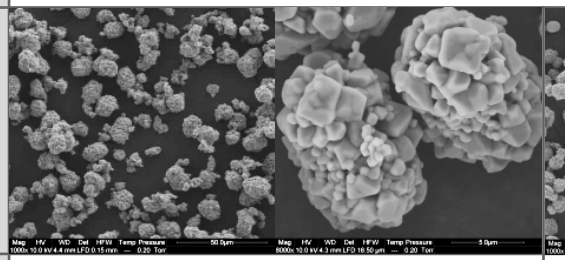
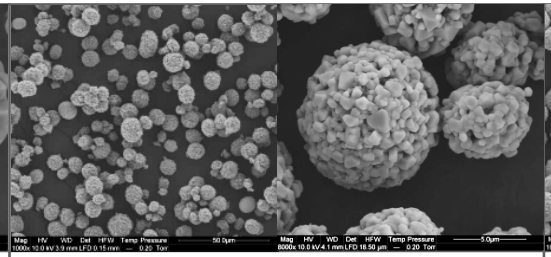
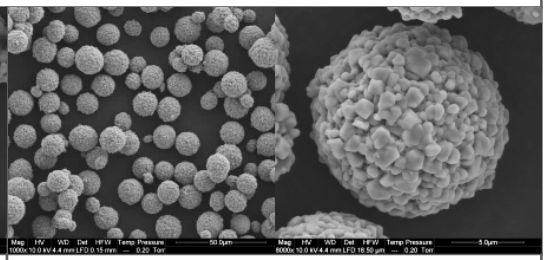


✓ Each unitary vortex cell : enabling micro-mixing



Material Production: Batch, CSTR and TVR

- Final target composition = $Li_{1.067}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$

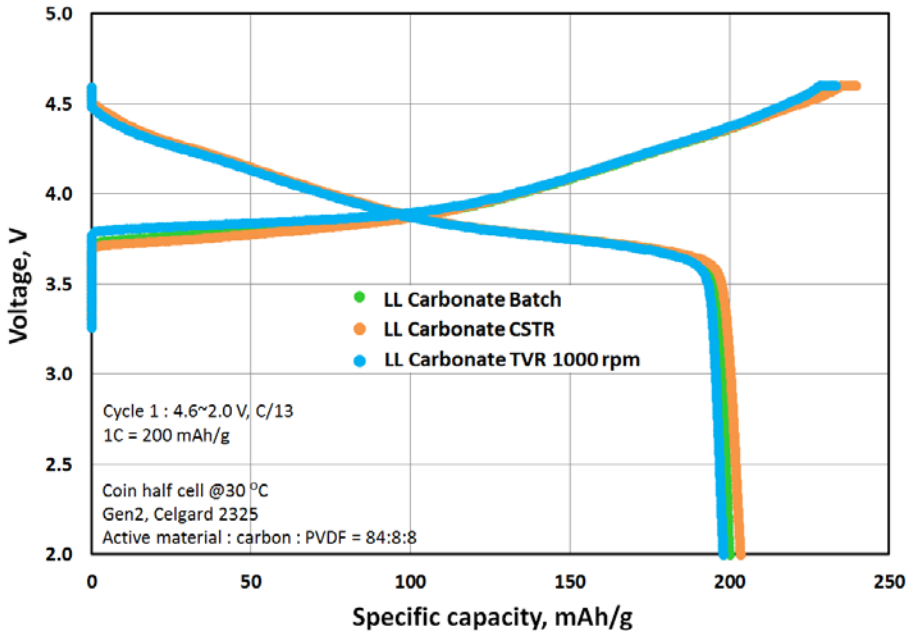
Process	Conventional 40L Batch	Advanced 20L CSTR	1L TVR (Taylor Vortex Reactor)
Synthesis condition	Precursors were obtained after 24hr operation at reaction temp. = 33°C and NH_4OH/TM = 0.16		
Calcined material SEM x1000, x8000			
ICP-MS analysis	$Li_{1.067}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$	$Li_{1.065}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$	$Li_{1.073}Ni_{0.60}Mn_{0.34}Co_{0.06}O_y$
$D_{10}/D_{50}/D_{90}$ [µm]	3.9 / 13.0 / 19.9	6.4 / 11.2 / 19.7	8.9 / 15.1 / 25.9
BET [m^2/g]	0.71	0.53	0.46
Tap density [g/cc]	**1.73**	**2.06**	**2.04**
*Press density [g/cc]	**2.92**	**2.95**	**2.88**
Initial disch. gravi. capacity [mAh/g]	**200.0**	**203.4**	**198.0**
**Initial disch. vol. capacity [mAh/cc]	**584.0**	**600.0**	**570.2**

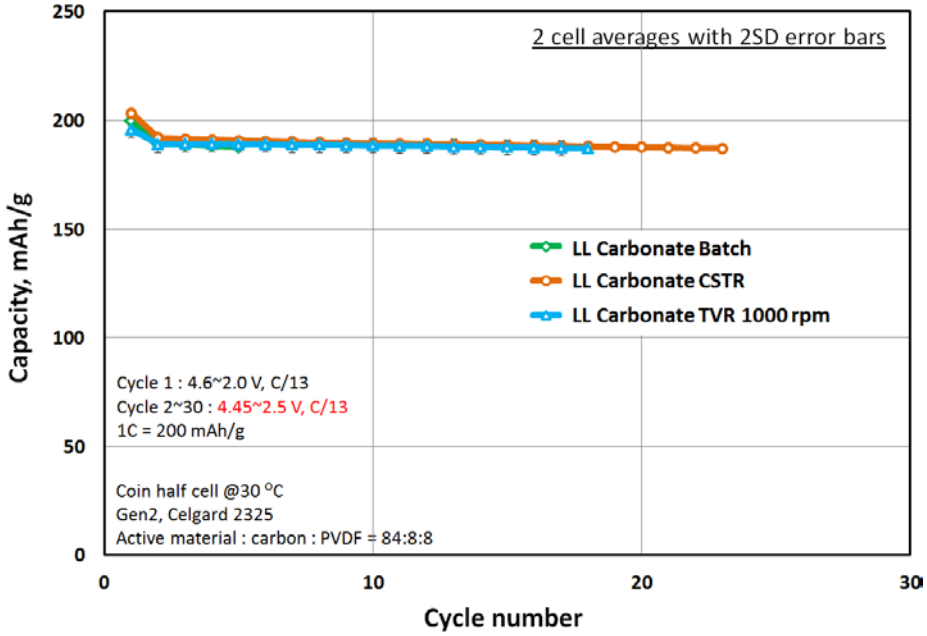
* Press density was measured at 2.5 t/cm² ** Calculated based on press density

- ✓ *Target composition was successfully synthesized using Batch, CSTR and TVR processes.*
- ✓ *DoE resulted in a 48 % increase in tap density compared to preliminary synthesized material.*
- ✓ *Physical properties (morphology, size, density, …) depend on synthesis process.*
- ✓ *TVR shows good material quality on our first attempt. Process optimization will be carried out to understand system capabilities.*

Coin Cell Result: Batch, CSTR and TVR

- Voltage profile and cyclability of produced LL materials





- ✓ *Initial discharge capacity and cycling performance look similar.*
- ✓ *Samples were delivered for material evaluation.*
- ✓ *Kilogram scaled-up is in progress for use in HE/HV Program.*

Developing Coating Process for Scaled Materials

For maximum coating performance

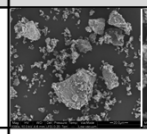
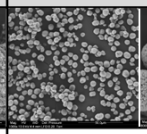
- Active materials need to be customized.
- Numerous pilot scale coating processes should be compared.
- Scalability and reproducibility are critical.

Surface coating capability at the MERF

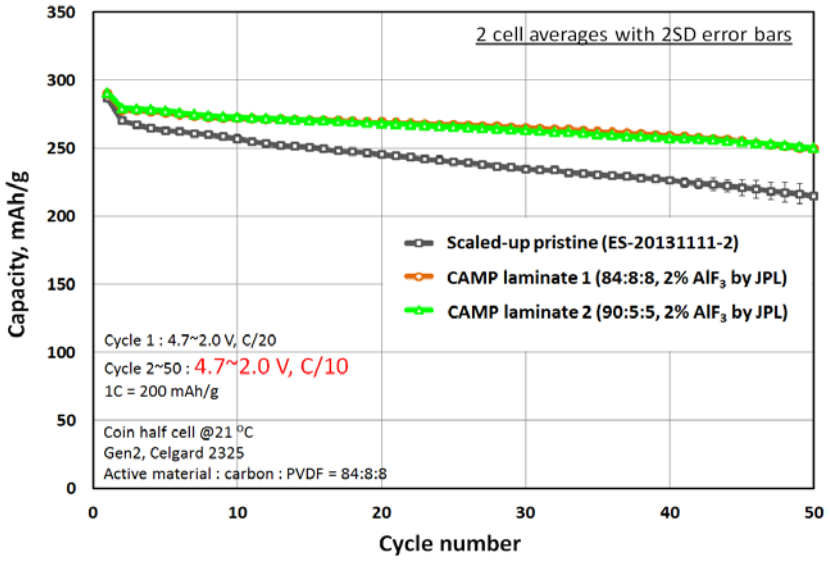
- Pilot scale mechanofusion dry coater (500g/batch)
- Pilot scale spray drying coater (200 ~ 500g/hour)
- Bench scale wet coater
- Pilot scale wet coater (future)

1L and 4L bench scale wet coating system was set up to carry out systematic scale-up research

- **To optimize material performance**
- **To assist HE/HV program**
- **Industrial collaborations on material coatings**

2nd cathode	JPL/NASA	Scaled-up material
SEM X1000, x8000		
ICP analysis	$Li_{1.6}Ni_{0.14}Mn_{0.68}Co_{0.18}O_y$	$Li_{1.47}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$
$D_{10}/D_{50}/D_{90}$ [µm]	1.2/11.1/29.3	3.8/6.3/10.7
Tap density [g/cc]	**1.70**	**1.81**

3kg scaled-up JPL material → JPL → 2 wt.% AlF_3 Coating by JPL → ANL → **Laminates @ CAMP**



✓ *Preliminary AlF_3 coating by JPL was evaluated.*

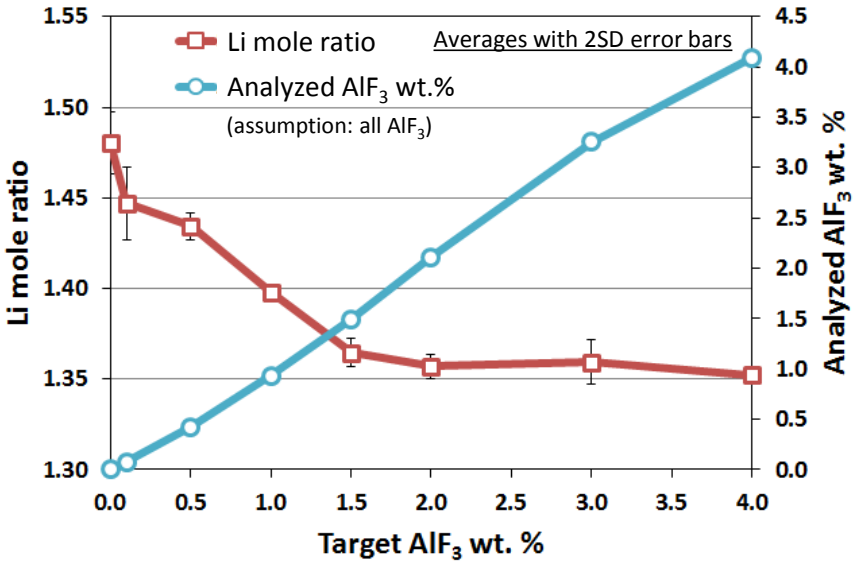
✓ *Optimization study for AlF_3 coating was conducted.*

0.1 ~ 4 wt.% AlF_3 Wet Coating

Wet surface coating procedure

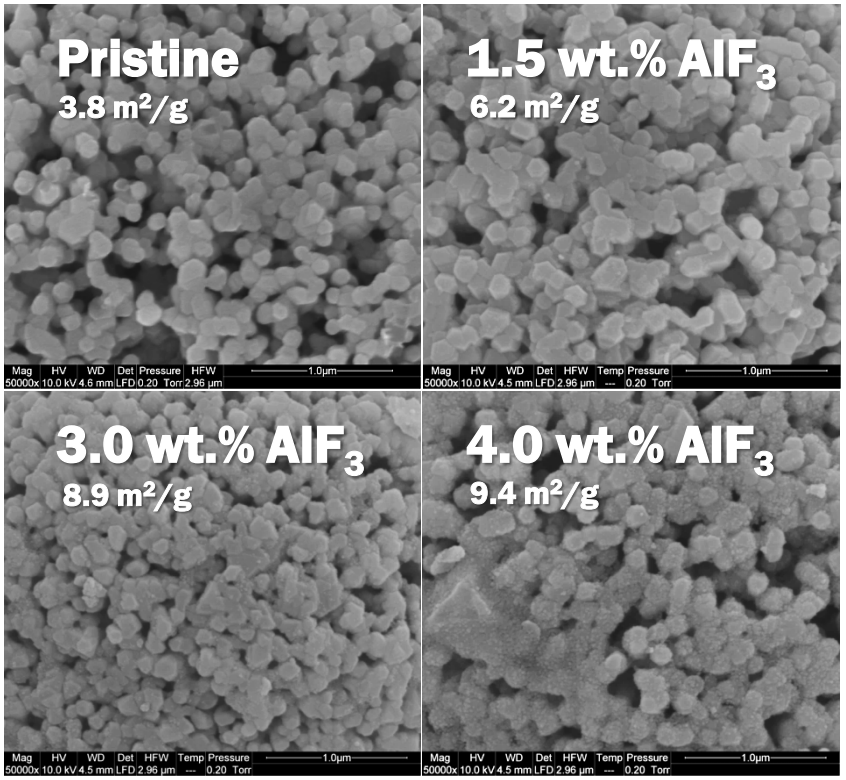
- Charge cathode powder into reactor with DI water
- Feed aluminum nitrate and ammonium fluoride solutions into reactor separately
- Keep reaction at 70 ^{O}C with stirring
- Powder filtration and drying after reaction completion
- Post heat treatment with N_2 condition

ICP-MS analysis of AlF_3-coated materials.



SEM of pristine and AlF_3-coated materials.

Pristine scaled-up JPL material:
$Li_{1.47}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$

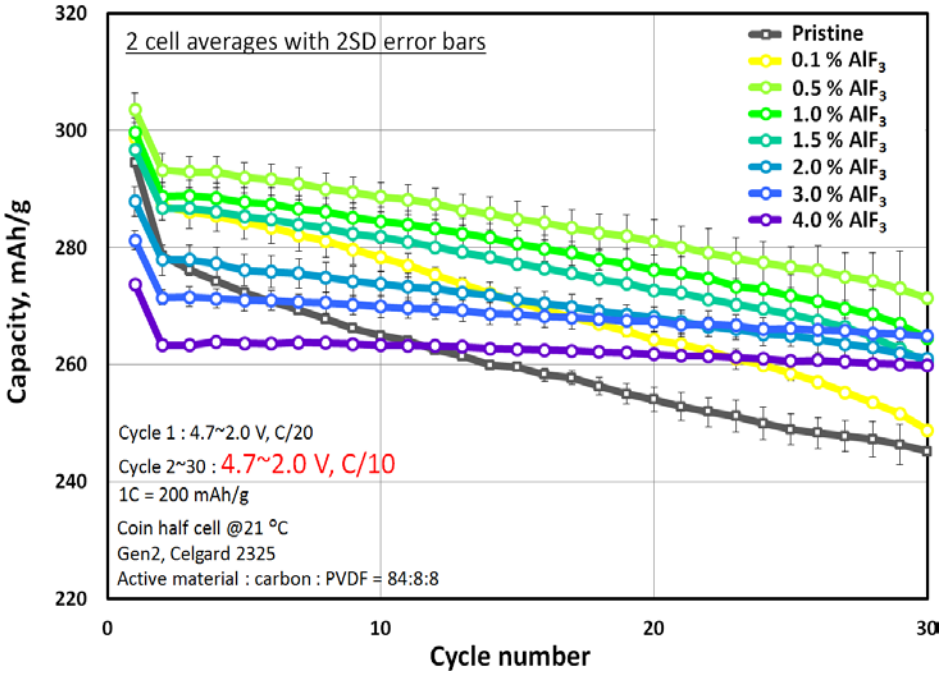


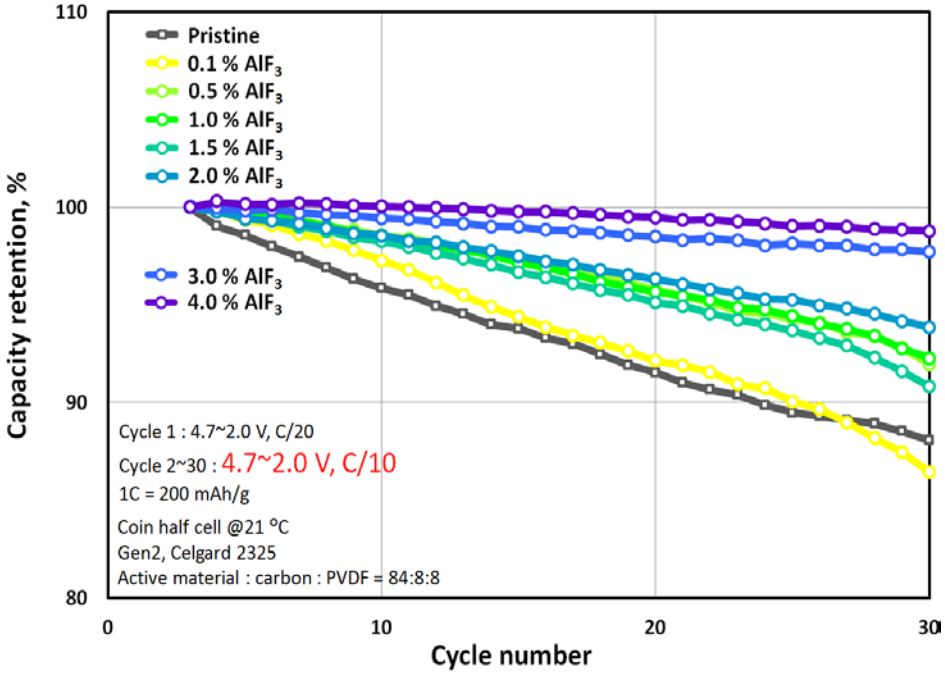
✓ *Li dissolution increases when AlF_3 coating amount increases but Ni, Mn and Co mole ratio remains the same.*

✓ *Surface area (BET) increases according to AlF_3 amount.*

0.1 ~ 4 wt.% AlF_3 Wet Coating

- Cycle performance of AlF_3-coated material





- ✓ *Pristine scaled-up JPL material shows 12 % capacity drop after 30 cycles.*
- ✓ *4 wt.% AlF_3-coated material shows only 1 % capacity drop after 30 cycles.*
- ✓ *0.5 wt.% AlF_3 coating shows the highest 1st discharge capacity (304 mAh/g).*
- ✓ *Increased AlF_3 amount increases capacity retention but decreases the discharge capacity.*

For more details: Y. Shin et al, "Effect of AlF_3 surface coating on high energy LMR-NMC material", 227th ECS Meeting, May 24-28, 2015.

Responses to Previous Year Reviewers' Comments

- "The reviewer recommended the design of experiments methods should be used for experiments involving a large number of parameters."
  - *Response: A Design of Experiments approach was used to optimize process variables (temperature and NH_4OH to TM ratio) and to maximize tap density. We have also developed a DoE model for the optimal coating material and method.*
- "The reviewer reported that this team looked to be progressing at just behind their proposed rate of two materials per year. … with optimization there be inherent scope limitations to maintain this rate until there is greater certainty in the selection of cathode materials."
  - *Response: Agreed. Material optimization is highly dependent on its composition, synthesis route, condition and process. We discuss the degree of optimization required for a requested material and can vary our approach depending on the purpose of the synthesized material.*
- "The reviewer said that the planning should have a more transparent process. … it is key that the broader industry has a stake in what is being scaled up to maximize impact of the large quantities of material that will be available as an output to this research."
  - *Response: A new center has recently been established at Argonne referred to as the Argonne Collaborative Center for Energy Storage Sciences (ACCESS). ACCESS will integrate the battery and energy storage work at Argonne through an internal research, development and commercialization team and an external advisory board, composed of experienced members from other national labs, academia and industry. We intend to work through ACCESS to have stakeholders help us gauge and advise on materials selected to scale, resulting in a more robust and transparent process.*

Collaborations

- Active materials process R&D:
  - Jet Propulsion Lab (Kumar Bugga)
    - Coating optimization
  - Argonne National Lab (Michael Thackeray)
    - Material synthesis
  - Sharp Labs of America - CRADA (Jong-Jan Lee)
    - ARPA-E developed material
  - PPG Industries - CRADA (Stuart Hellring)
    - Custom cathode materials for a binder study
  - Global Battery Solutions – CRADA (Jennifer Sierra)
    - Active materials recovery

- Materials provided for further research:
  - University of Illinois at Chicago (Prof. Jordi Cabana)
  - NanoResearch Inc. (David Noye)
  - Argonne National Lab (various researchers)

- Electrochemical evaluation of scaled materials:
  - Argonne's Materials Screening Group (Wenquan Lu)
  - Argonne's CAMP facility (Andrew Jansen)

Open to working with any group developing advanced cathode materials that will be beneficial for the ABR program.

Remaining Challenges and Barriers

- New battery materials are continually being discovered and developed.
- There is a strong demand from the research community for high quality experimental materials in quantities exceeding bench scale synthesis.
- Production of high performance cathode materials is extremely complex. A detailed understanding of how process variables effect performance is critical to fully understand material cost and capability.
- Emerging manufacturing technologies need to be evaluated to further reduce production costs and increase performance of battery materials.
- Development and scale-up of surface coating technology is challenging but has great promise to improve the performance of battery materials.

Activities for Next Fiscal Year

- Complete work on target material #4 (layered layered)
  - Complete scale-up at kilogram quantity
  - Coating scale-up work by design of experiments (DoE)
- Begin work on target material #5 (gradient cathode)
  - Develop continuous process to synthesize multiple kilograms of high purity material for basic R&D and full cell evaluation
- Evaluate emerging manufacturing and surface coating technologies
  - Advanced reaction technology candidates:
    - Spray pyrolysis
    - Supercritical hydrothermal
  - Advanced mixing technology
    - Acoustic mixing
  - Surface coating technology candidates:
    - Wet coater
    - Spray dryer
    - Fluidized bed coater
    - Mechanofusion dry coater

Summary

- 3rd Target Material (layered layered spinel)
  - Material synthesis and delivery have been completed.
- 4th Target Material (layered layered)
  - Synthesis route and preliminary material assessment have been completed.
  - Complete precursor optimization.
  - Produce 100g intermediate material - material exceeds performance specifications.
  - Complete the comparison of 3 synthesis technologies (Batch, CSTR and TVR).
- 2nd Target Material (JPL/UT-Austin)
  - Develop scalable wet surface coating process.
  - Complete the optimization of AlF_3 surface coating on the scaled material.
- Sharp ARPA-E Material (CRADA)
  - First material was scaled to the kilogram level.
  - Total 36 samples (1,339 g) were delivered for electrochemical testing.
  - Work was started on a 2nd material; but proved to be not as scalable as the first material.
- PPG (CRADA) – Customizing cathode materials for a binder study.
- Global Battery Solution (CRADA) – Active material recovery.

Acknowledgements and Contributors

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- Argonne National Laboratory
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  - Kumar Bugga
- Sharp Labs of America
  - Jong-Jan Lee
- PPG Industries INC.
  - Stuart Hellring

Technical Backup Slides

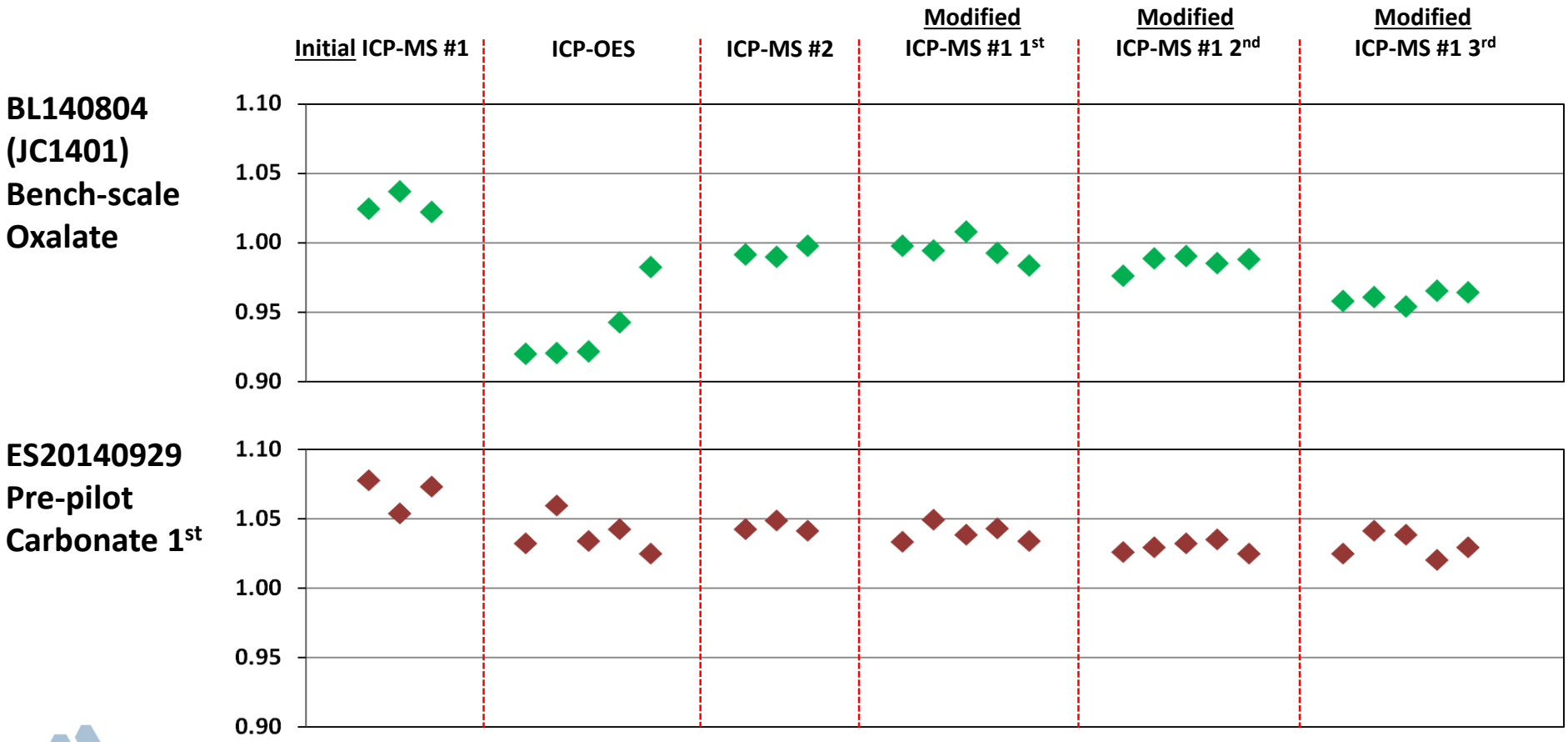
ICP Comparison of LL Oxalate and Carbonate

- LL target composition: $Li_{1.05}Ni_{0.5225}Mn_{0.43}Co_{0.0475}O_y$

3 or 5-time Analysis (x_1, x_2, x_3, x_4, x_5) $\sigma = \sqrt{\frac{\sum(x_i-\bar{x})^2}{(n-1)}}$	BL140804 (JC1401) Bench-scale Oxalate Mole Ratio Average, $\bar{x}$ / StDev, σ				ES20140929 Pre-pilot Carbonate 1st Mole Ratio Average, $\bar{x}$ / StDev, σ			
	Li	Ni	Mn	Co	Li	Ni	Mn	Co
Initial ICP-MS #1	1.027/0.007	0.606/0.001	0.335/0.001	0.059/0.000	1.068/0.012	0.522/0.002	0.428/0.002	0.050/0.000
ICP-OES	0.937/0.027	0.618/0.005	0.324/0.004	0.058/0.000	1.039/0.013	0.535/0.004	0.416/0.005	0.049/0.001
ICP-MS #2	0.993/0.004	0.609/0.004	0.341/0.002	0.057/0.001	1.043/0.004	0.497/0.002	0.413/0.002	0.047/0.000
Modified ICP-MS #1 Average of 1st 2nd 3rd	0.980	0.611	0.331	0.058	1.033	0.526	0.424	0.050
Modified ICP-MS #1 1st reproducibility test	0.995/0.008	0.611/0.001	0.331/0.001	0.058/0.000	1.039/0.007	0.526/0.002	0.424/0.002	0.050/0.000
Modified ICP-MS #1 2nd reproducibility test	0.985/0.005	0.611/0.000	0.331/0.000	0.058/0.000	1.029/0.004	0.525/0.001	0.425/0.001	0.050/0.000
Modified ICP-MS #1 3rd reproducibility test	0.960/0.004	0.611/0.001	0.331/0.001	0.058/0.000	1.031/0.009	0.527/0.001	0.423/0.001	0.050/0.000

Improved Lithium Analysis by Statistical Approach

- ✓ Exact analysis of material composition is challenging especially for lithium.
- ✓ 3 equipment (ICP-MS #1, ICP-OES and ICP-MS #2) were tested.
- ✓ By statistical approach, analysis protocol was modified.
- ✓ Modified ICP-MS analysis protocol generates improved Li analysis accuracy.

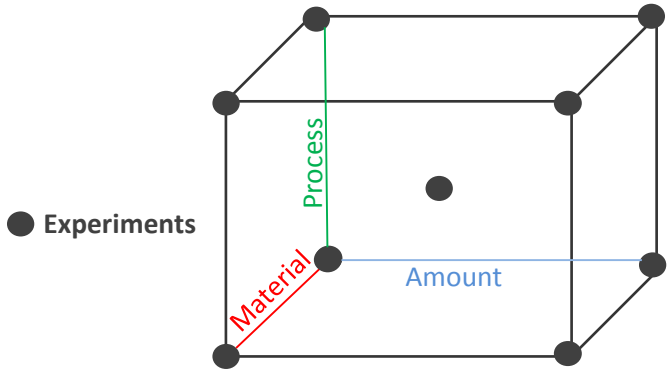


Material Delivery to R&D Group and Industry

FY	Date	Material	To	Purpose
14	10/30/2013	$Ni_{0.16}Mn_{0.67}Co_{0.16}(OH)_2$	ANL- CSE Division	Domain size study
	10/31/2013	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	NASA-JPL	Material Evaluation
	11/11/2013	$Ni_{0.16}Mn_{0.67}Co_{0.16}(OH)_2$	ANL- CSE Division	Domain size study
	01/17/2014	$Ni_{0.16}Mn_{0.67}Co_{0.16}CO_3$	ANL- CSE Division	Ion exchange-VF study
	01/20/2014	$Li_{1.37}Ni_{0.33}Mn_{0.67}O_y$	ANL-ES	ALD Coating
	01/21/2014	$Li_{1.37}Ni_{0.33}Mn_{0.67}O_y$	ANL-ES	ALD Coating
	01/30/2014	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	NASA-JPL	Material Evaluation
	0/31/2014	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	NASA-JPL	Material Evaluation
	02/03/2014	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	CSE-Material Screening	Material Evaluation
	02/03/2014	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	CSE-CAMP	Material Evaluation
	03/17/2014	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	ITN Energy Systems, Inc.	F-doping
	03/18/2014	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	ITN Energy Systems, Inc.	F-doping
	04/14/2014	$Na_2MnFe(CN)_6$	Sharp laboratories	Material Evaluation
	05/16/2014	$Na_2MnFe(CN)_6$	Sharp laboratories	Material Evaluation
	06/26/2014	$Na_2MnFe(CN)_6$	Sharp laboratories	Material Evaluation
	07/11/2014	$Na_2Fe_2(CN)_6$	Sharp laboratories	Material Evaluation
	05/20/2014	$Li_{1.37}Ni_{0.33}Mn_{0.67}O_y$	ANL- CSE Division	Material Evaluation
	08/05/2014	$Ni_{0.60}Mn_{0.34}Co_{0.06}CO_3$	ANL- CSE Division	Material Evaluation
	09/04/2014	Modified NMC 532	AAA Machine, Inc.	Particle classification
	09/26/2014	$Li_{1.37}Ni_{0.33}Mn_{0.67}O_y$	NanoResearch, Inc.	Material Evaluation
15	10/13/2014	$Mn_{0.67}Ni_{0.33}CO_3$	UIC	Material Evaluation
	10/13/2014	$Li_{1.38}Mn_{0.67}Ni_{0.33}O_y$	UIC	Material Evaluation
	10/13/2014	$Ni_{0.27}Mn_{0.54}Co_{0.19}CO_3$	UIC	Material Evaluation
	10/13/2014	$Li_{1.14}Ni_{0.27}Mn_{0.54}Co_{0.19}O_y$	UIC	Material Evaluation
	10/24/2014	Modified NMC 532	Microfluidics Int. Corp.	Particle separation
	12/01/2014	$Li_{1.05}Ni_{0.52}Mn_{0.43}Co_{0.05}O_y$	ANL- CSE Division	HE/HV research
	12/01/2014	$Li_{1.14}Ni_{0.28}Mn_{0.53}Co_{0.19}O_y$	ANL- CSE Division	HE/HV research
	02/04/2015	Modified NMC 532	ANL- CSE Division	Pouch cell evaluation
	02/10/2015	Modified NMC 532	ANL- CSE Division	Pouch cell evaluation
	04/03/2015	$Li_{1.14}Ni_{0.28}Mn_{0.53}Co_{0.19}O_y$	ANL- CSE Division	Surface coating study
	04/24/2015	$Li_{1.07}Ni_{0.60}Mn_{0.34}Co_{0.06}O_y$	ANL- CSE Division	HE/HV research

Cathode Coating Optimization Using Design of Experiments

- Objectives:
  - Choosing coating material and method among many candidates.
  - Finding a response to measure quality of coating that is meaningful.
- Approach:
  - Start with a broad study and work inward to optimize.
  - Statistically prove that results are meaningful.



- JMP Software
- Screening Design
  - Popular design for industrial experimentation.
  - Examine many factors to identify most important.
  - Identified factors are then used in more sensitive designs.
- Studying effects of processes and coating materials simultaneously

Screening Design of Experiments Matrix

Coating Amount	Coating Process	Coating Material	Response Capacity Retention After Rate Testing
0	Dry	$AlPO_4$	0.9662
0	Wet Aq	Al_2O_3	0.9662
0	Wet EtOH	$AlPO_4$	0.9662
0.25	Dry	Al_2O_3	0.9692
0.25	Wet Aq	$AlPO_4$	0.9380
0.25	Wet EtOH	Al_2O_3	0.9542
1	Dry	$AlPO_4$	0.9505
1	Wet Aq	$AlPO_4$	0.9361
1	Wet EtOH	Al_2O_3	0.9561
2	Dry	Al_2O_3	0.9622
2	Wet EtOH	$AlPO_4$	0.9517

Cathode Coating Optimization Using Design of Experiments

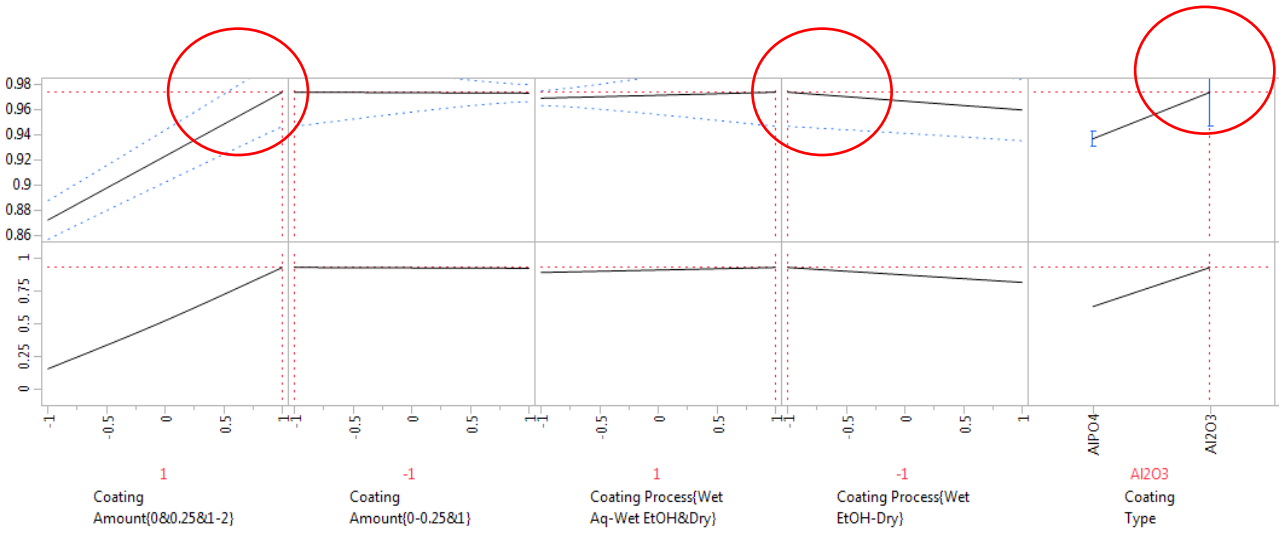
- Example of DoE result
  - Data was fit to a model R-squared = 0.9995, model P *value* =0.0019.
  - Promising coating selection based on electrochemical response.

Optimal Condition

Based on maximizing the Capacity Retention after rate of coin cells

Response is the capacity retention after rate.

Desirability is to maximize capacity retention.



- Aluminum oxide coating by Wet Solvent Process at 2 wt% on cathode is the best combination for increasing capacity retention predicted by model.
- Future work is to optimize aluminum oxide coating by wet solvent process.