Process Development and Scale-up of Advanced Cathode Materials

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Project ID: ES167

Overview

- **Timeline**
  - Project start date : Oct 2010
  - Project end date : Sep 2014
  - Percent complete : on going

- **Budget**
  - Total project funding :
    - $1.5M in FY12
    - $1.3M in FY13
      ($780K received, $520K expected)

- **Barriers**
  - Complex linking of process variables affecting product quality
  - Trade-off between capacity, cycle life, rate performance and tap density
  - Scale-up challenges
  - Manufacturing costs

- **Partners**
  - Argonne National Laboratory
    - Materials Screening Group
    - Cell Fabrication Facility
    - Applied R&D Group
  - Jet Propulsion Laboratory

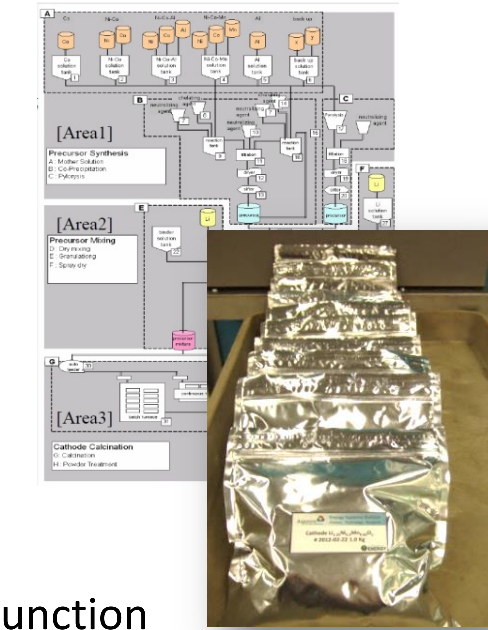
Objectives - Relevance

- 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 specifications for industrial evaluation or further research.

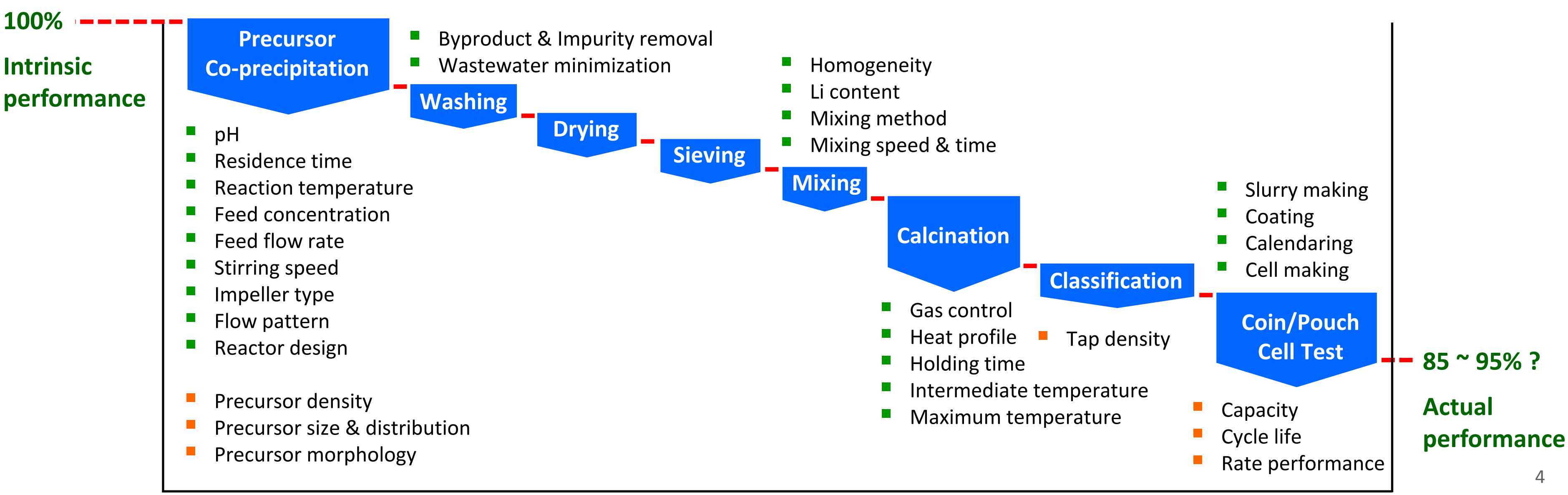
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing
    - Reducing the risk associated with the commercialization of new battery 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.

Approach - Strategy and Deliverables

- For the target lab-scale candidate material we will:
  - Develop a scalable manufacturing process
    - Process development to overcome engineering challenges
  - Achieve performance specifications of the target material
    - Understand performance trade-offs and process optimization to minimize quality drop
  - Produce kilogram quantities of the target candidate
    - With batch to batch reproducibility



- Evaluation and optimization of each process variables in conjunction with desired performance specifications:



Milestones

- FY12
  - Scale-up synthesis of $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$ using the carbonate process
    - Process development for pre-pilot scale production
      - Particle growth issue (completed)
      - Particle cracking issue (ongoing)
    - Optimize process variables for performance targets (completed)
    - Produce kilogram quantities of materials (2 batches delivered)
  - Synthesize $MnCO_3$ and Li_2MnO_3 for ion exchange research (completed)
  - Relocate interim labs to the Materials Engineering Research Facility (completed)

- FY13
  - Process development to resolve carbonate particle cracking issue
    - Determine effect of particle size on cracking (completed)
    - Understand tradeoff between particle cracking and performance (ongoing)
  - Scale-up synthesis of $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$ using the hydroxide process
    - Compare results of carbonate and hydroxide processes (completed)
    - Optimize process variables for performance targets (ongoing)
  - Begin scale-up synthesis of new material
    - Specific material and process is under discussion

Relocation of Interim Labs to the MERF

Wet processing area
(located next to the MERF)

- 4L and 20L transparent CSTR
- Washing equipment
- Microscope

Dry processing area

- Powders hood
- GL Filtration filter washer dryer
- Spray dryer & Air classifier
- Vertical and shaker mixer
- Shaker sieve, crusher, mill
- Calcination furnace

Characterization lab

- ICP
- XRD
- BET
- PSA
- TGA-DSC
- Tap density

Coin cell fabrication

- VAC glove box
- Maccor cycler
- Coating equipment
- Drying equipment
- Calendaring equipment
- Coin making equipment

The Materials Engineering Research Facility (MERF)

- 10,000 sq. ft. high hazard facility
- Contains electrolyte and cathode scale-up programs

Over 1,200 coin cells
were tested to optimize process variables and check reproducibility

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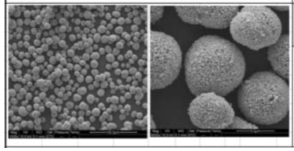
Outgoing Inspection Data Sheet	Carrier	Receiver	Manager

Target Cathode Composition	Prepared by	Lot Number	Weight	Delivery date
$Li_{1.33}Ni_{0.33}Mn_{0.67}O_{2.35}$	Young Ho Shin	#2012-07-09&11	1.0 Kg	9/10/2012

Analysis		Target Spec.	Results	Judgement	Note	Method
Particle Size Distribution	D10 (μm)	> 10.0	4.8			Particle Size Analyzer
	D50 (μm)	20.0 ± 3.0	7.8			
	D90 (μm)	< 30.0	12.9			
Specific Surface Area (m/g)			5.56			BET
Tap Density (g/cc)			1.49			Tap Density Meter
Element Wt %	Li		9.49			ICP-MASS
	Ni		19.09			
	Mn		35.90			
	Na		0.38			
For Use		Lithium Ion Secondary Battery				

SEM



Remark

This material and data is confidential non-public that may not be communicated in any way without the consent of Energy Systems Division

1) To minimize cathode fracture during calendar process, 7.8μm spherical cathode with narrow particle size distribution was prepared.

4L bench-scale vs. 20L pre-pilot-scale (previously reported)

- **4L bench-scale (Optimized)**

  Lot #: ES-110921 $Li_{1.35}Ni_{1/3}Mn_{2/3}O_y$

  Batch operation → Particle growth issue

  100g production

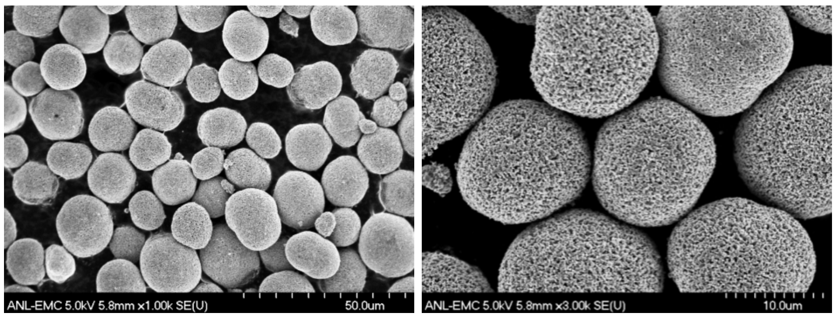
- **20L pre-pilot-scale (Preliminary)**

  Lot #: ES-120222 $Li_{1.35}Ni_{1/3}Mn_{2/3}O_y$

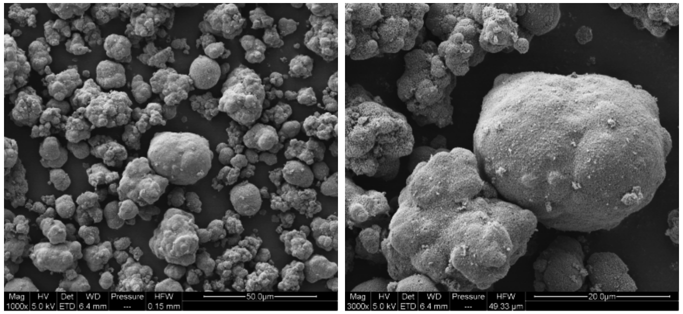
  Continuous operation → Shape & density issue

  5kg production

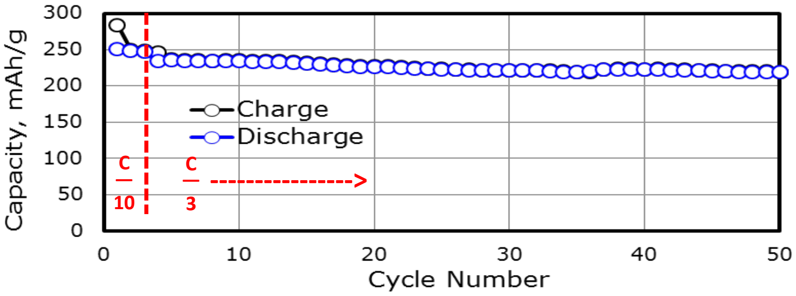
  1st delivery to Cell Fabrication Facility (1.0kg)

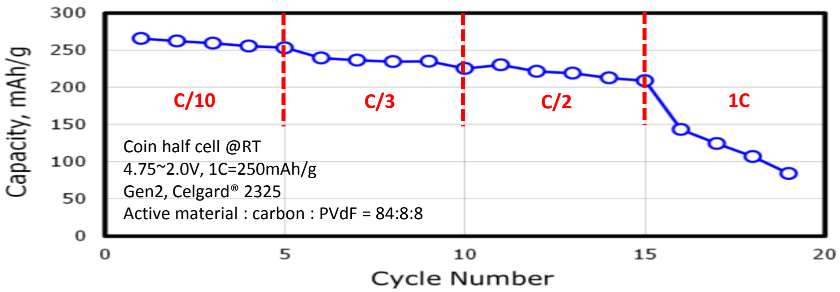


D50 = 17 μm, Tap density = 1.61 g/cc



D50 = 15 μm, Tap density = 1.36 g/cc





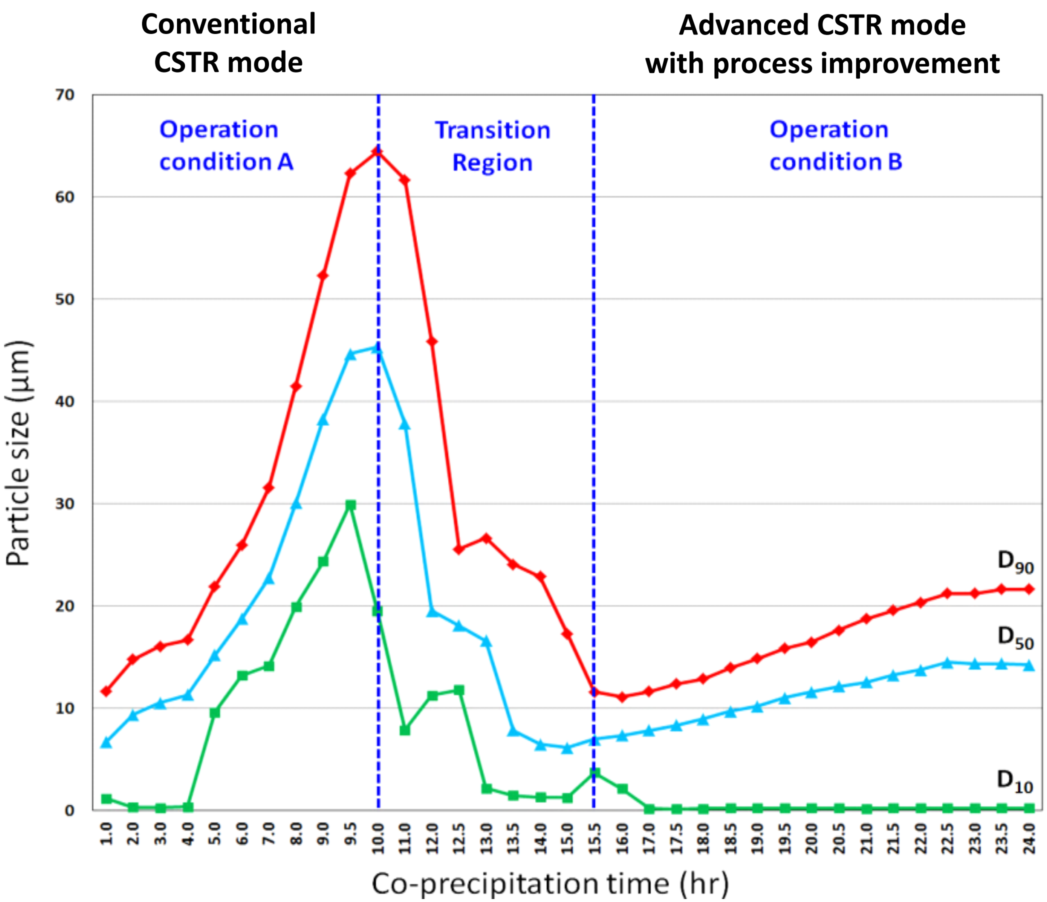
✓ ***4L Bench scale (batch process) product showed good morphology, capacity and cycle life.***

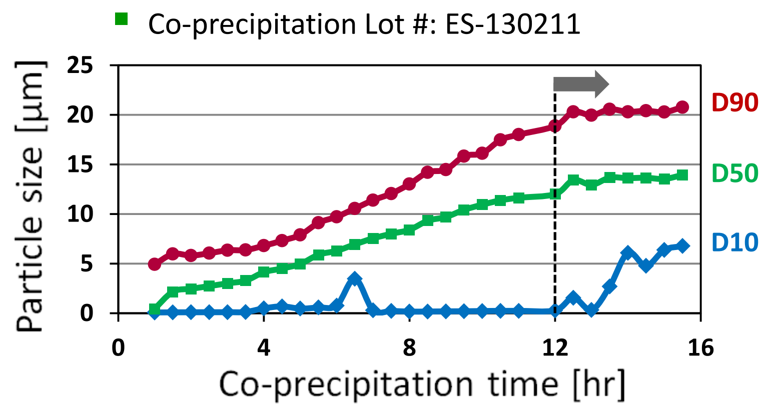
✓ ***20L pre-pilot scale (continuous process) product had good capacity but poor morphology and cycle life.***

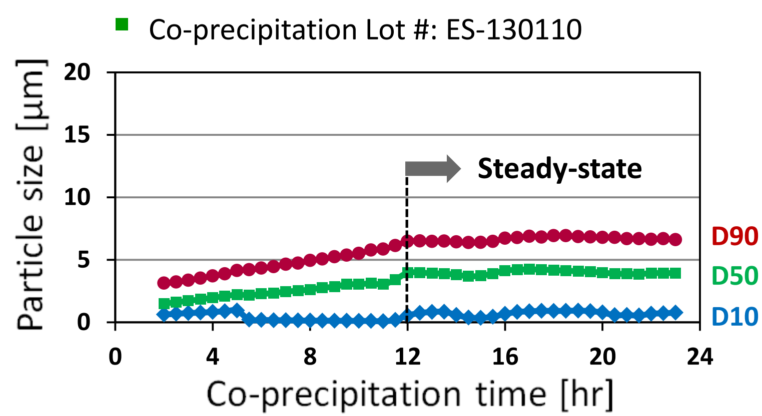
Improvement for Continuous Particle Growth Control

(Patent filing pending)

- Enables particle size control
- Enables production of specific size particles





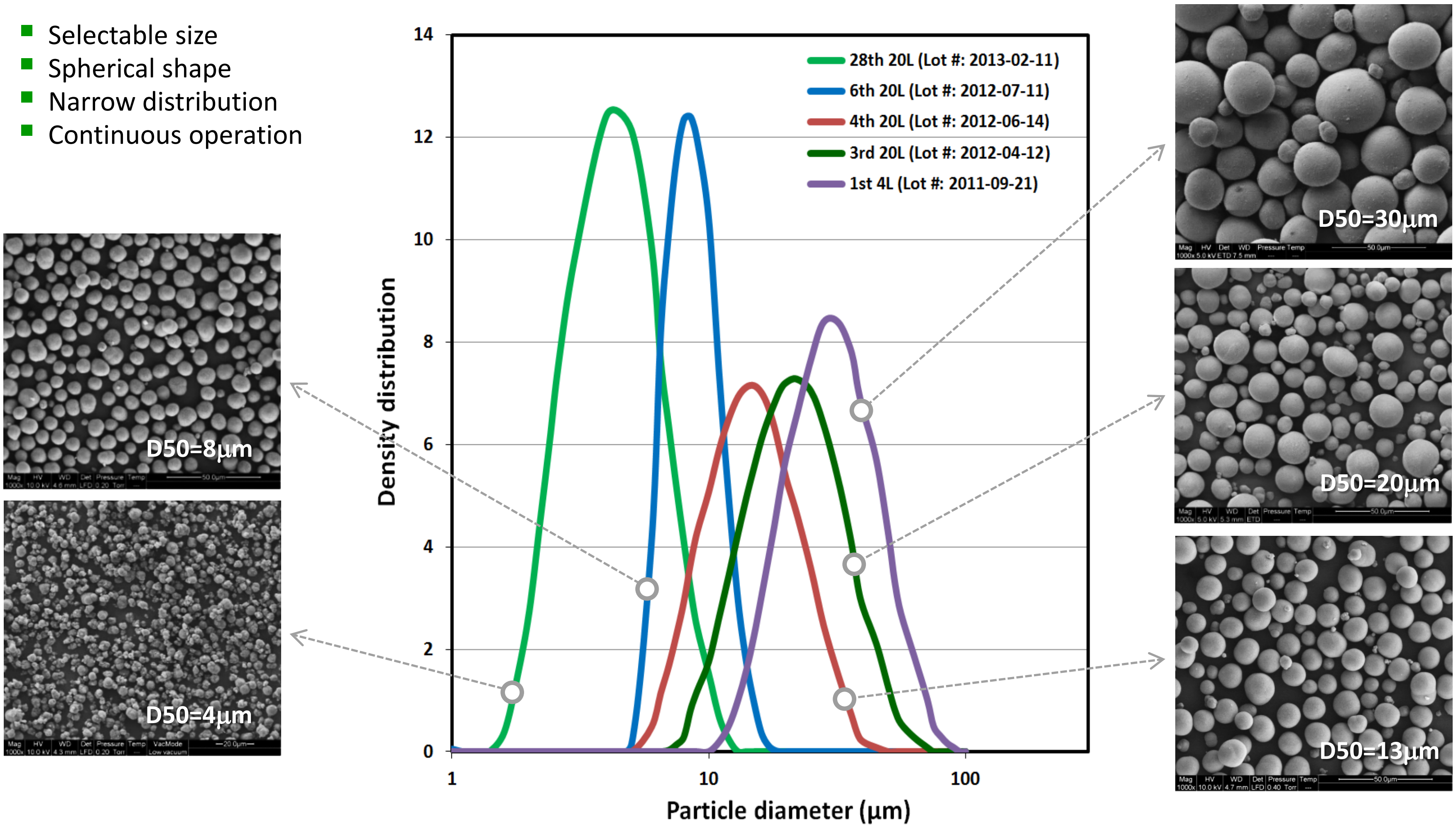


✓ ***Specific-size precursors can be produced continuously.***

Improvement for Continuous Particle Growth Control

- Enables improved precursor formation

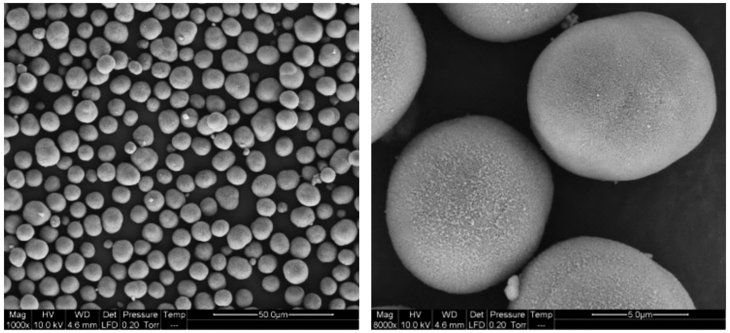
  - Selectable size
  - Spherical shape
  - Narrow distribution
  - Continuous operation



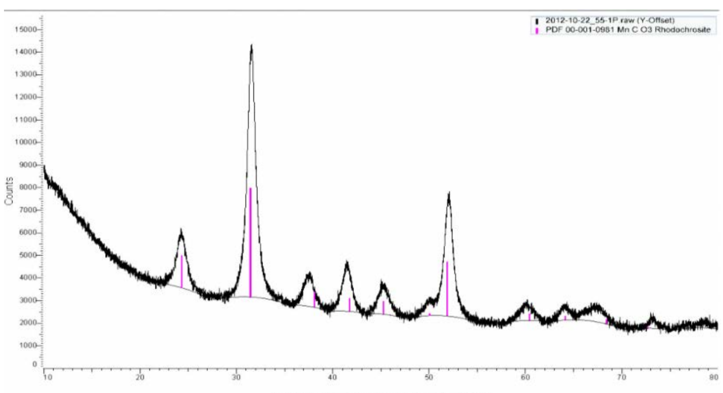
✓ ***Precursor size, shape and distribution are controllable.***

Precursor and Cathode Production

- ES-120709+11 $Ni_{1/3}Mn_{2/3}CO_3$ precursor

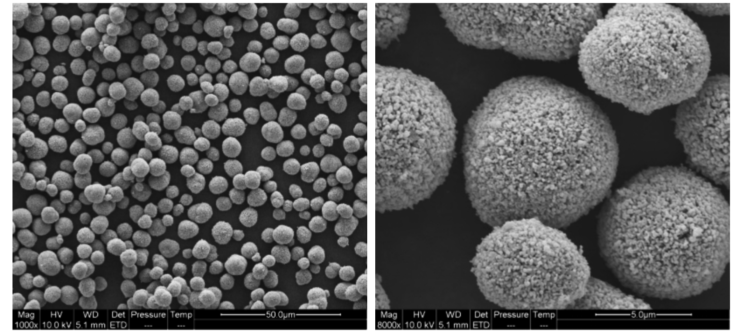


Lot #	ES-120709+11 precursor 3.2kg
PSA	D10/D50/D90 = 4.5/8.1/11.9 µm
ICP	Ni:Mn = 0.332:0.668
Tap density	1.40 g/cc

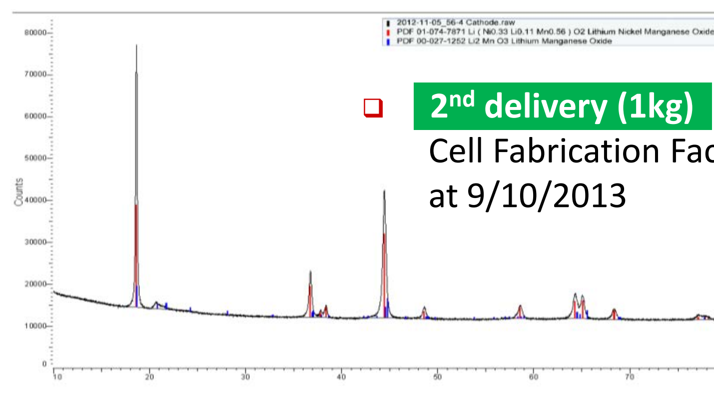


Post processing

- ES-120709+11 $Li_{1.39}Ni_{1/3}Mn_{2/3}O_y$ cathode



Lot #	ES-120709+11 cathode 1.2kg
PSA	D10/D50/D90 = 4.8/7.8/12.9 µm
ICP	Li:Ni:Mn = 1.392:0.332:0.668
Tap density	1.49 g/cc



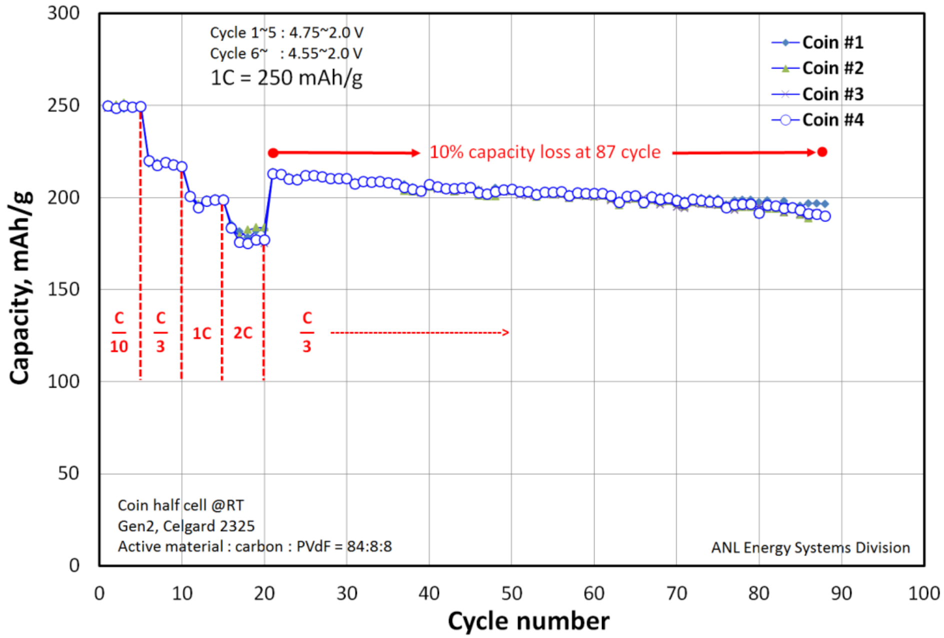
- 2nd delivery (1kg) to Cell Fabrication Facility at 9/10/2013

✓ ***7.8µm-size spherical cathode material was produced in kilogram quantity.***

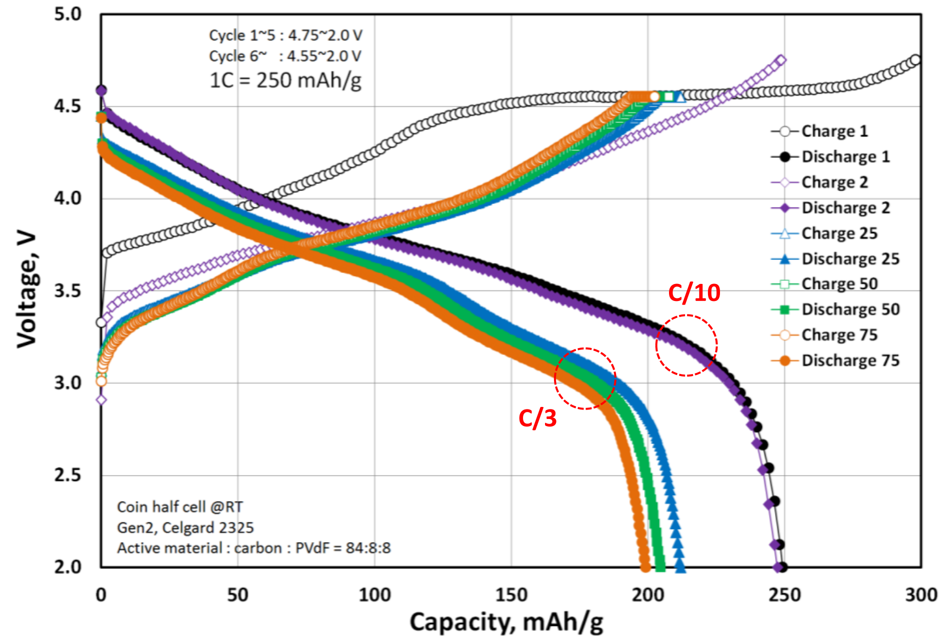
Electrochemical performance

- **2nd CFF delivery** ES-120709+11 $Li_{1.39}Ni_{1/3}Mn_{2/3}O_y$

- Rate performance, cycle life (C/3) and reproducibility check



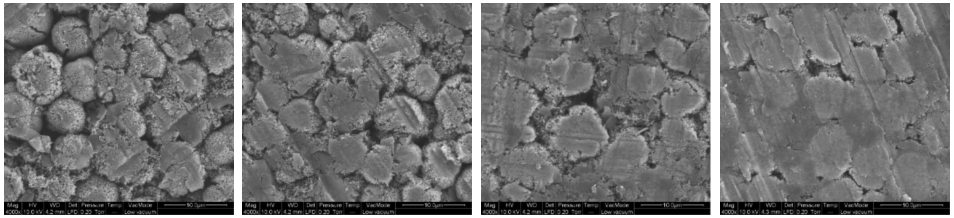
- Voltage profile (coin #1)



✓ ***2nd CFF delivery product shows high capacity (~250mAh) and good cycle life (~100 cycle).***
✓ ***However, particles were found to cracking during calendaring.***

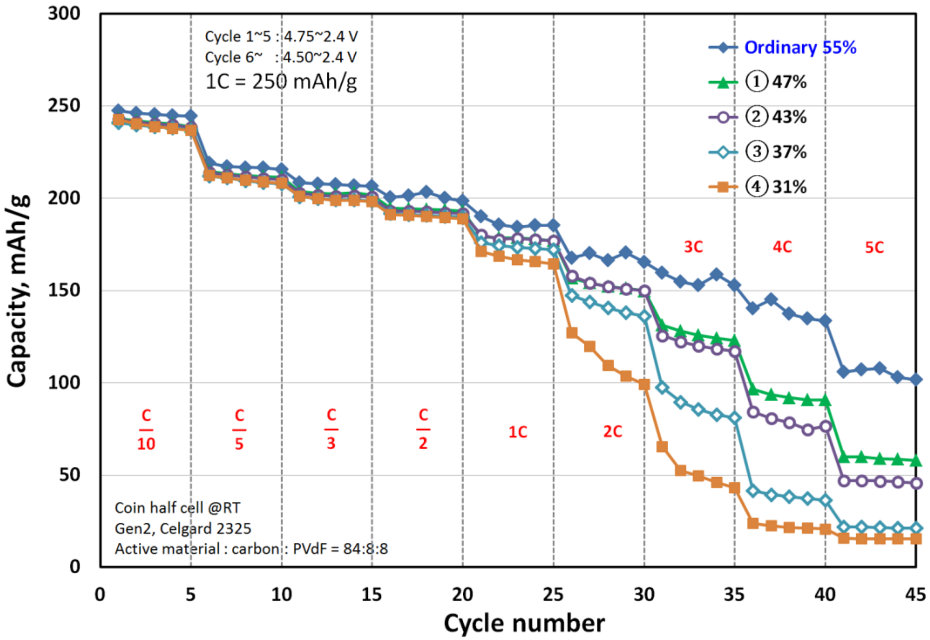
Effect of Electrode Porosity on Performance

- **2nd CFF delivery** ES-120709+11 $Li_{1.39}Ni_{1/3}Mn_{2/3}O_y$

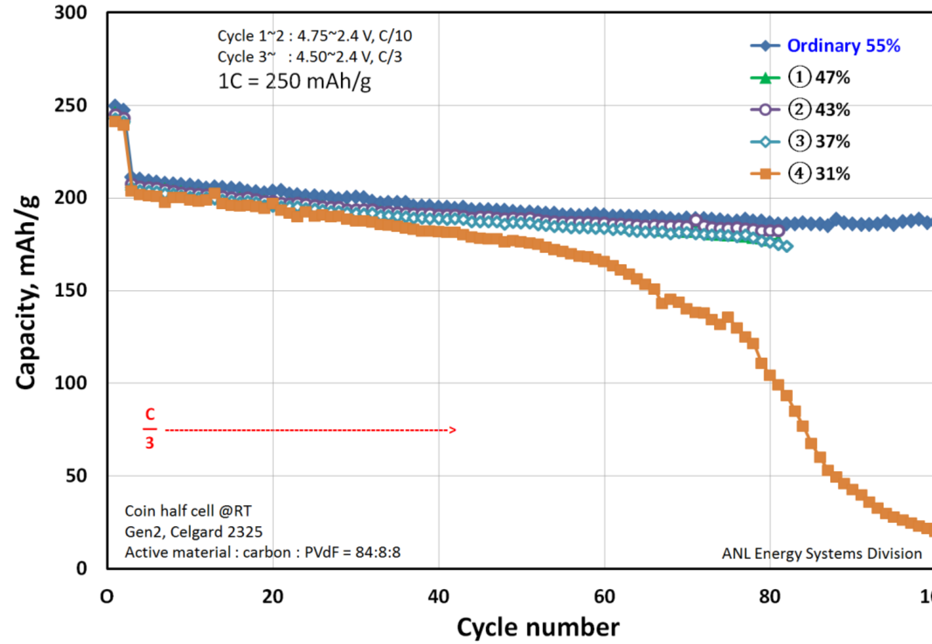


① Porosity=47% ② Porosity=43% ③ Porosity=37% ④ Porosity=31%

- Rate performance comparison



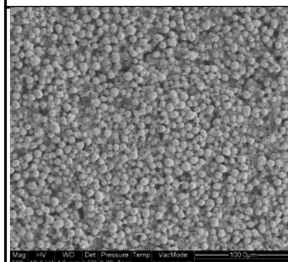
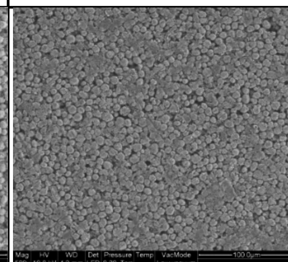
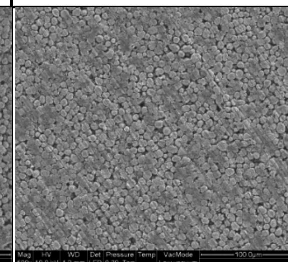
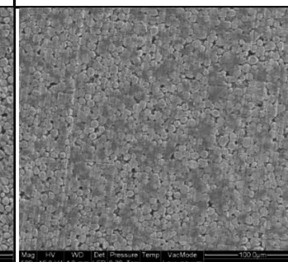
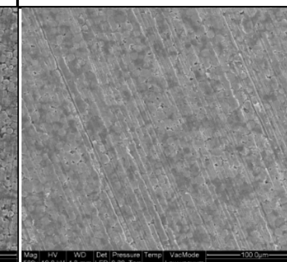
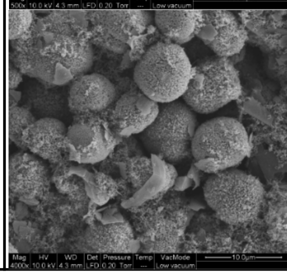
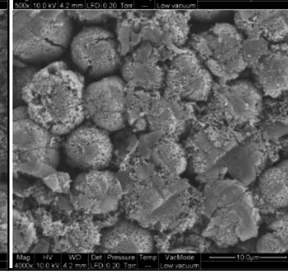
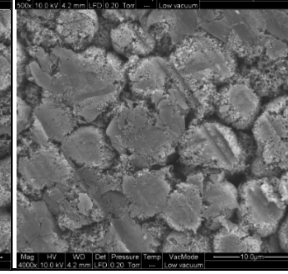
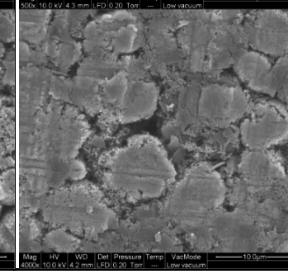
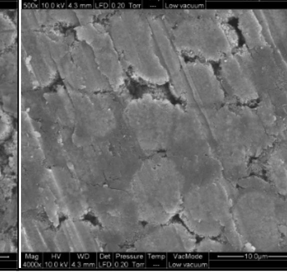
- Cycle life (C/3) comparison



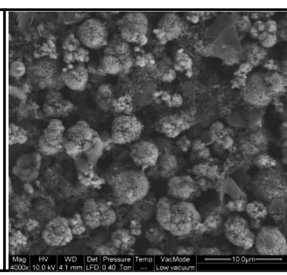
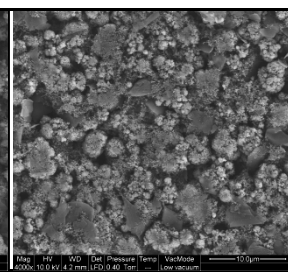
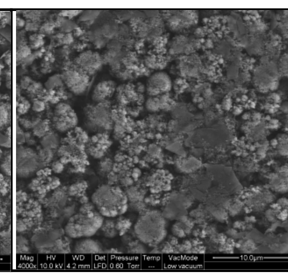
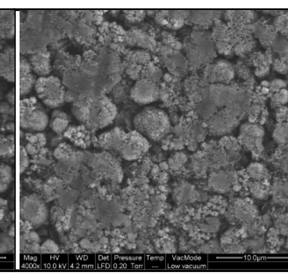
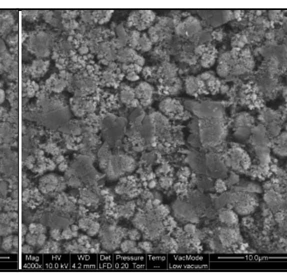
✓ ***Electrode porosity has minimal effect on initial capacity.***

✓ ***However, rate performance and cycle life decrease as electrode porosity is reduced.***

Particle Cracking Issue During Calendaring

	Without calendaring	With calendaring			
Porosity	**62 %**	**47 %**	**43 %**	**37 %**	**31 %**
Coating layer w/o Al foil	84 μm (100%)	47 μm (72%)	44 μm (67%)	40 μm (59%)	36 μm (55%)
SEM x500					
2nd CFF delivery ES-120709+11 **D50=7.8μm TD=1.49g/cc** SEM x4000					

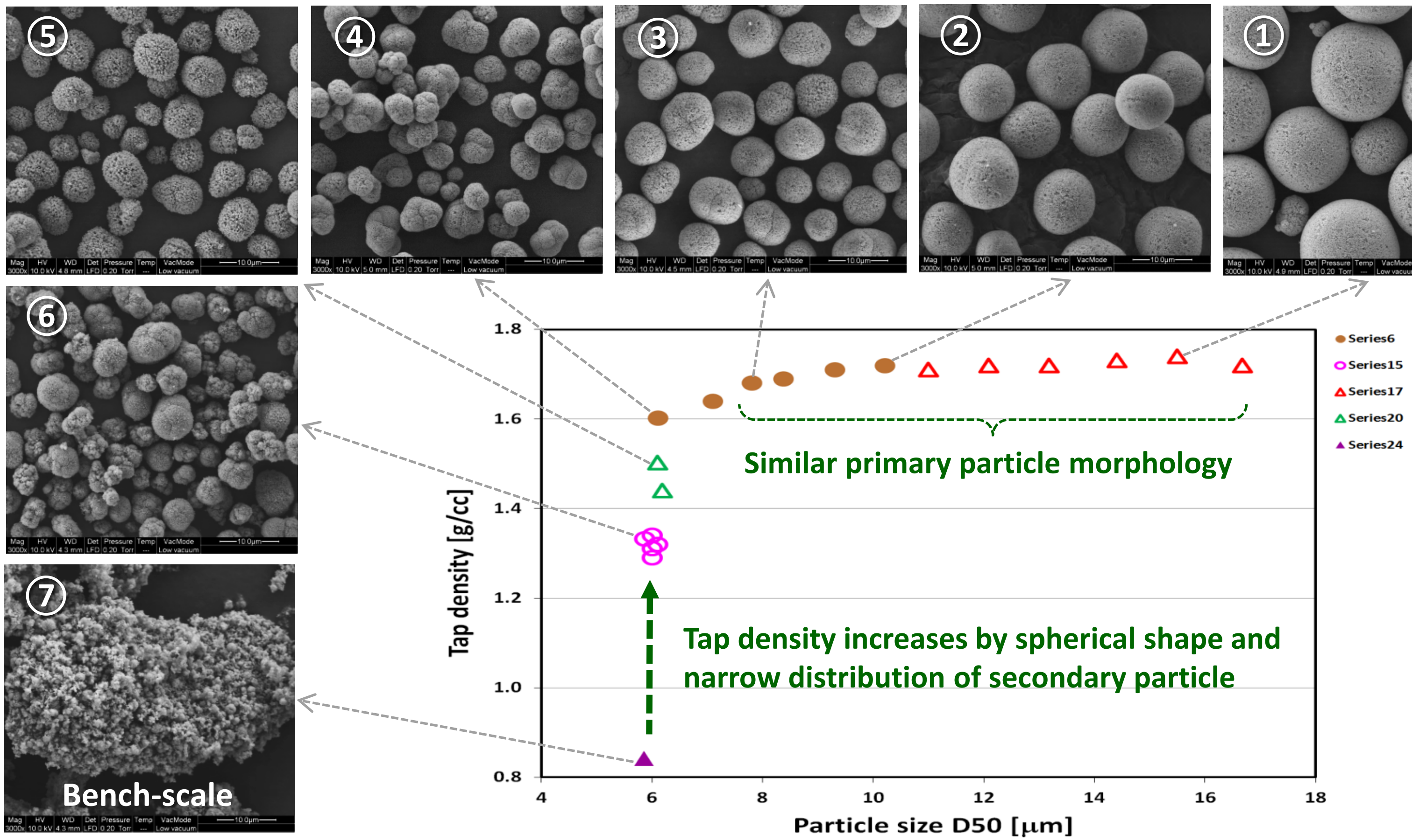
Effect of particle size on cracking

ES-130211-4 **D50=4.0μm TD=1.12g/cc** SEM x4000					

- ✓ ***Smaller particles resulted in less cracking.***
- ✓ ***However, smaller particles resulted in lower tap density.***

Particle Morphology, Size and Density

- Same composition ($Li_{1.39}Ni_{1/3}Mn_{2/3}O_y$) by carbonate process (20L CSTR)

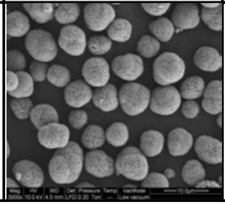
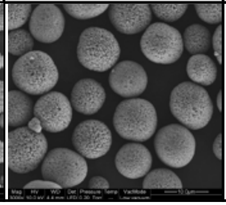
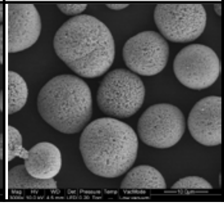
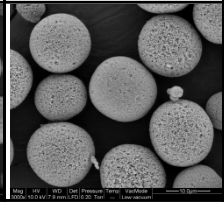
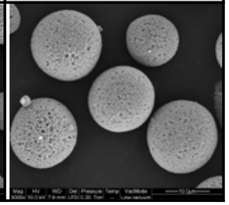


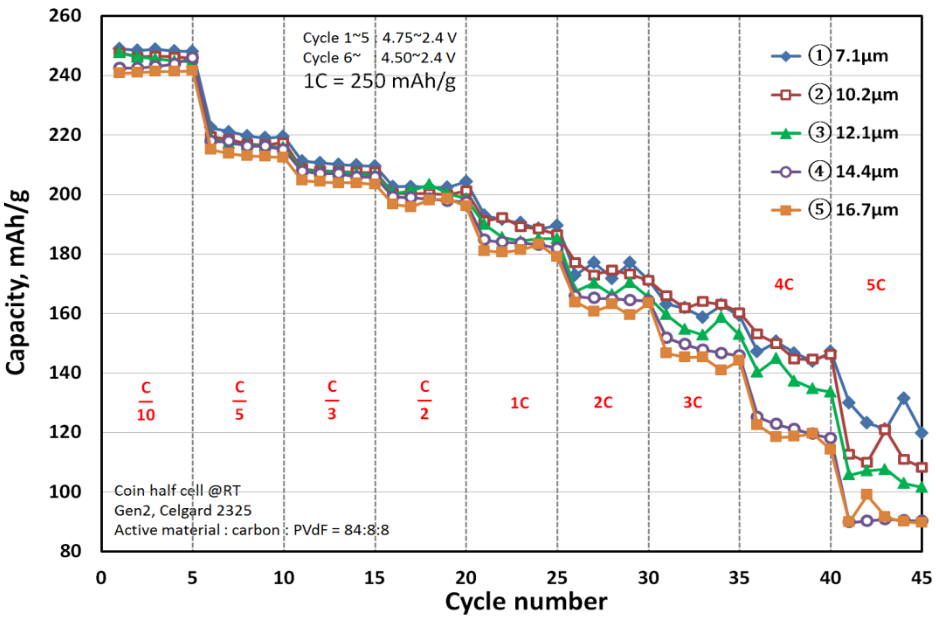
✓ ***Particle morphology has a greater effect on tap density than particle size.***

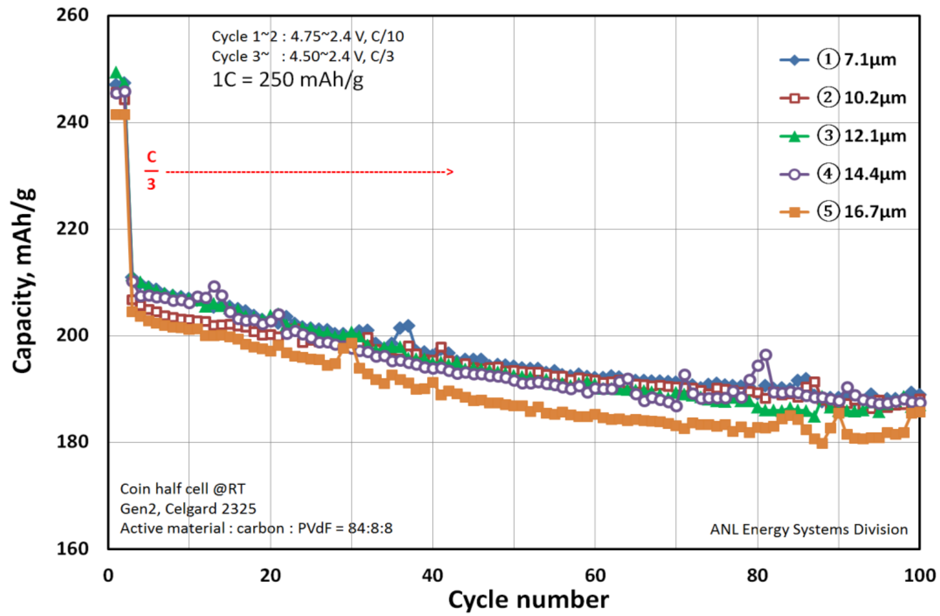
✓ ***If spherical, small secondary particles have similar tap density.***

Size Effect on Electrochemical Performance

- Effect of secondary particle size on rate performance and cycle life

Sample	① 7.1μm	② 10.2μm	③ 12.1μm	④ 14.4μm	⑤ 16.7μm
SEM x3000					





✓ ***Small particles have higher rate capability.***

✓ ***Large particles have minimal effect on initial capacity, but have a reduction of rate capability.***

Comparison of Carbonate Produced Materials, Start of Hydroxide Process Work

Carbonate process

	ANL optimized pre-pilot-scale	Commercial manufacturer A	Commercial manufacturer B
Composition	$Li_{1.39}Ni_{1/3}Mn_{2/3}O_y$	$Li_aNi_bCo_cMn_dO_y$	$Li_aNi_bCo_cMn_dO_y$
Capacity @ C/10 (mAh/g)	**250**	**170**	**165**
Density (g/cc)	**1.7**	**2.8**	**2.0**
BET (m^2/g)	**4.0**	**0.3**	**0.5**
D50 (µm)	**11**	**11**	**11**
Calendaring	**Particles crack**	**No cracking**	**No cracking**

✓ ***Density increase can minimize cracking.***
✓ ***Trade-off between density and performance.***

● **For high performance, carbonate produced particles that don't crack, you need:**

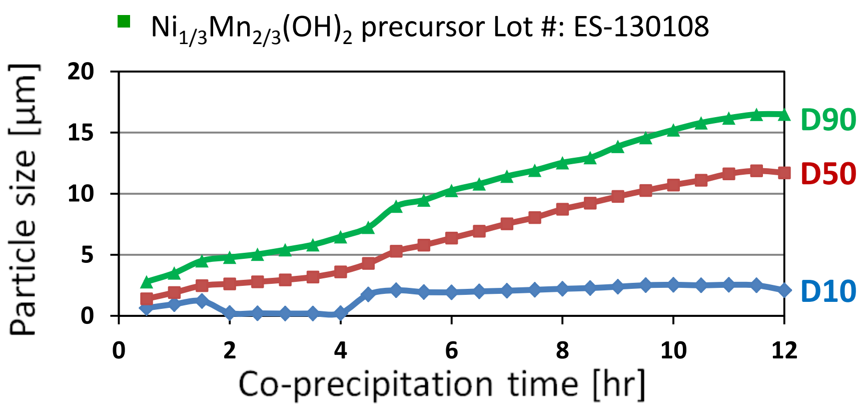
✓ ***Spherical secondary particles.***
✓ ***Small secondary particles.***
✓ ***Increased particle density.***

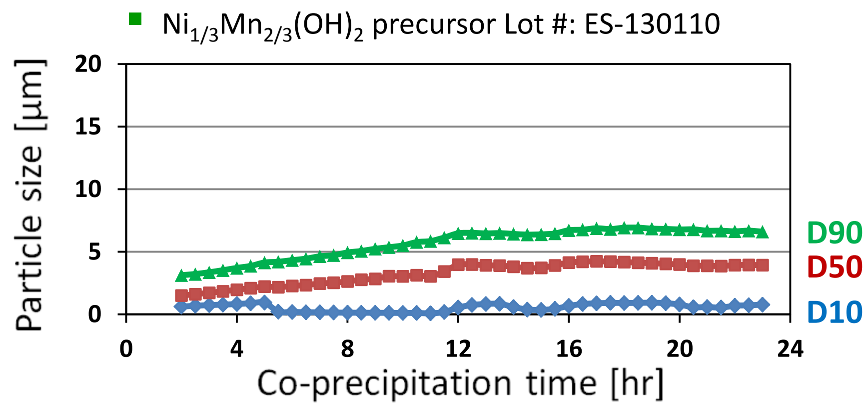
Hydroxide process

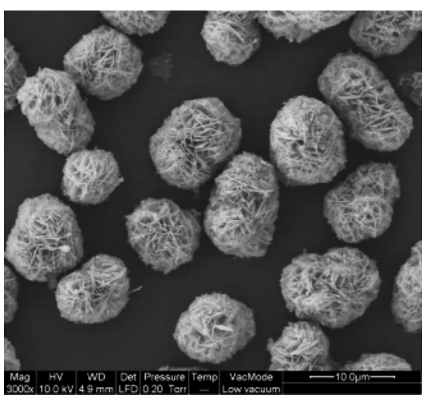
- The hydroxide process can produce crack free material, although typically has much lower tap density.
  - Established pre-pilot-scale hydroxide process.
  - Preliminary size-controlled hydroxide precursors were produced continuously.
  - Electrochemical performance of hydroxide and carbonate materials was compared.

Hydroxide precursor synthesis : $Ni_{1/3}Mn_{2/3}(OH)_2$

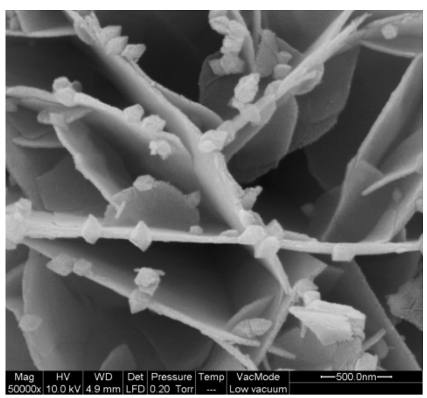
- 2013-01-07 : Set-up completion of 20L hydroxide co-precipitation CSTR
  01-08 : 1st hydroxide synthesis during 12hr (Lot #: ES-130108)
  01-10 : 2nd hydroxide synthesis during 24hr (Lot #: ES-130110)



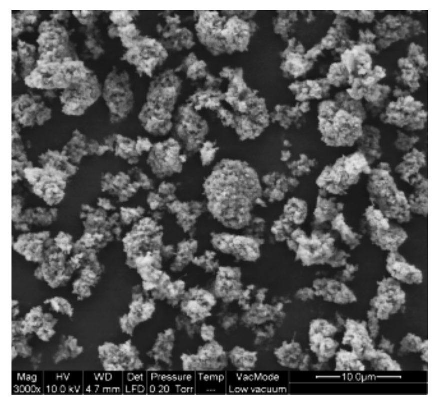




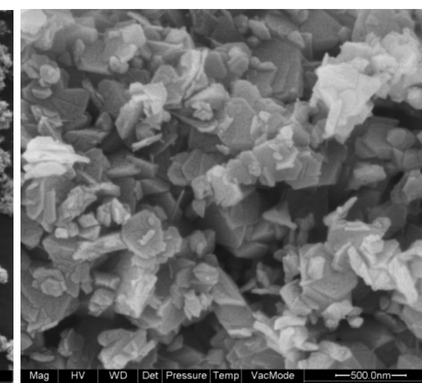
SEM x3,000



SEM x50,000



SEM x3,000

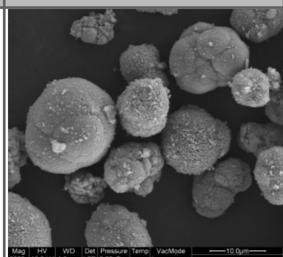
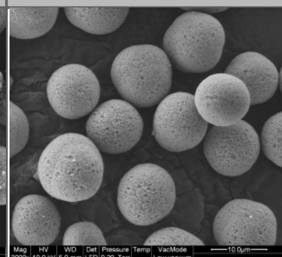
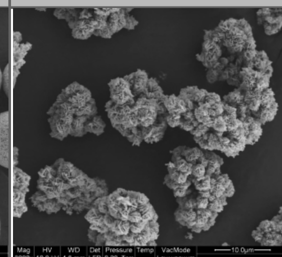
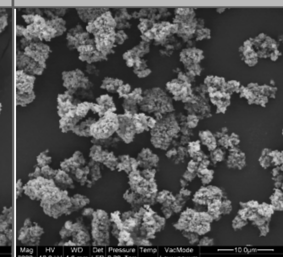
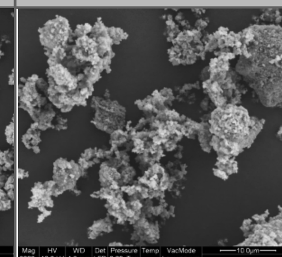
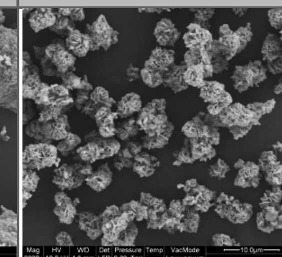
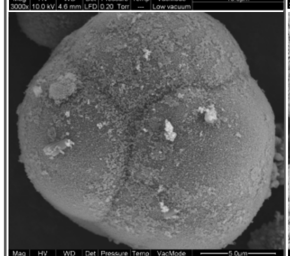
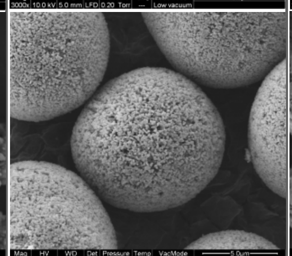
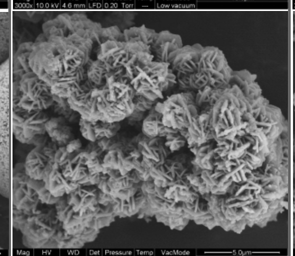
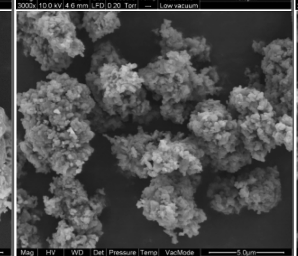
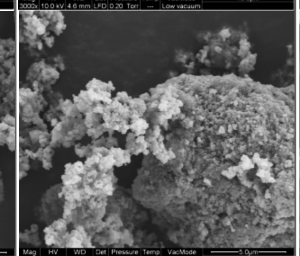
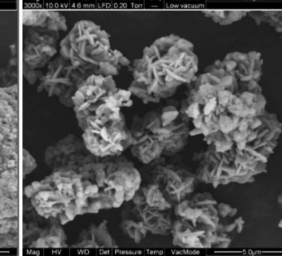


SEM x50,000

✓ ***Size-controlled hydroxide precursors (preliminary pre-pilot-scale) were produced continuously.***

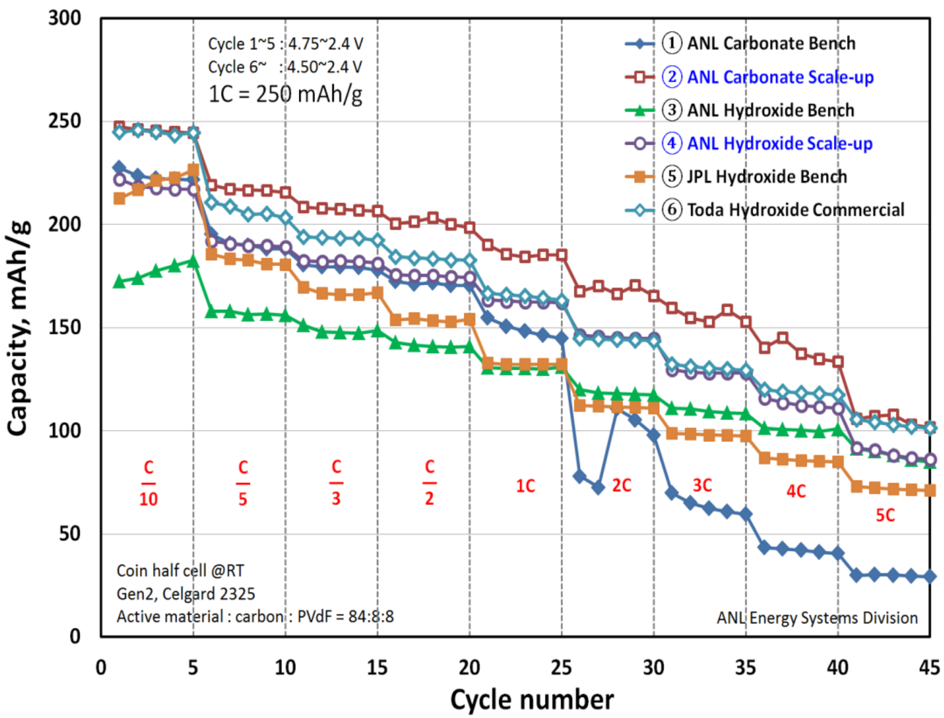
Comparison of Hydroxide and Carbonate Materials

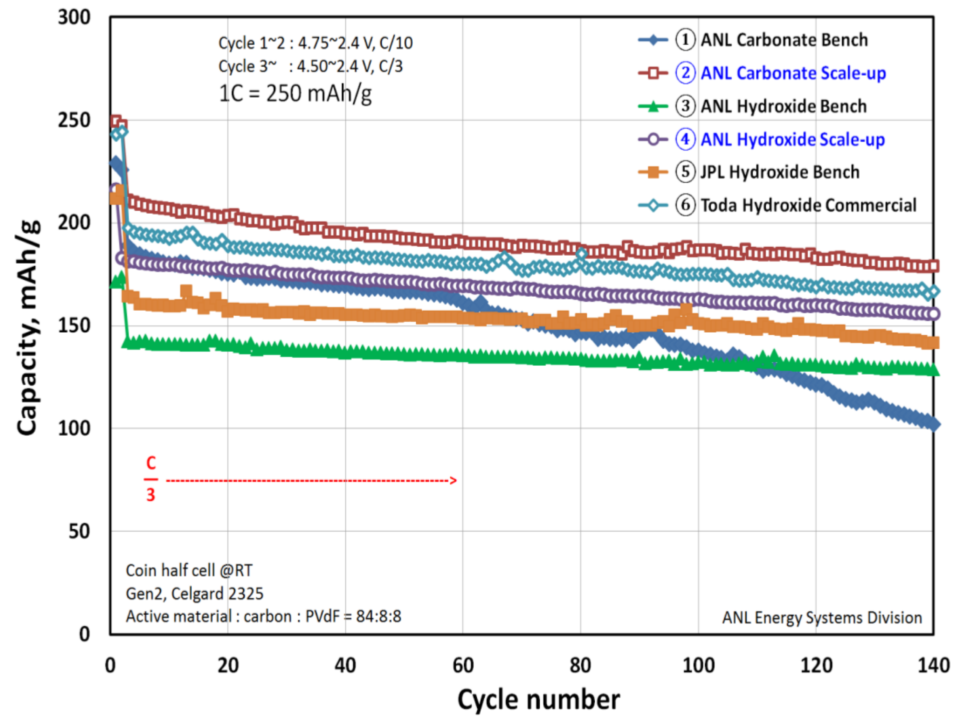
- 6 cathodes : Bench scale carbonate and 2 hydroxide cathodes
  Pre-pilot scale carbonate and hydroxide cathodes
  Commercial hydroxide cathode

	Carbonate cathode		Hydroxide cathode			
Lot #	① ANL-101217B	② ANL-120905	③ ANL-1108102	④ ANL-130110	⑤ JPL	⑥ Toda- HE5050
Scale	Bench scale	Pre-pilot scale Optimized	Bench scale	Pre-pilot scale Preliminary	Bench scale (contains Co)	Commercial (contains Co)
SEM x3,000						
SEM x8,000						
ICP analysis	$Li_{1.35}Ni_{0.32}Mn_{0.68}O_y$	$Li_{1.37}Ni_{1/3}Mn_{2/3}O_y$	$Li_{1.31}Ni_{1/3}Mn_{2/3}O_y$	$Li_{1.35}Ni_{1/3}Mn_{2/3}O_y$	$Li_{1.61}Ni_{0.16}Mn_{0.71}Co_{0.13}O_y$	$Li_{1.52}Ni_{0.16}Mn_{0.71}Co_{0.13}O_y$
$D_{10}/D_{50}/D_{90}$ [μm]	7.6 / 12.7 / 21.0	6.9 / 11.1 / 18.4	7.7 / 13.2 / 22.1	2.4 / 4.7 / 8.9	1.2 / 11.1 / **29.3**	3.1 / 5.3 / 9.2
Tap density [g/cc]	**1.41**	**1.70**	**0.98**	**1.02**	**1.70**	**1.03**

Comparison of Hydroxide and Carbonate Materials

- Rate performance and Cycle life (C/3) comparison between carbonate and hydroxide materials





✓ ***Argonne's scaled carbonate material had the best capacity and rate performance.***
✓ ***Argonne's scaled hydroxide material (not optimized) is close in performance to Toda's HE-5050***

Collaborations

Material Screening Group, Argonne

Screening target lab-scale candidate

Cell Fabrication Facility, Argonne

Pouch cell evaluation

Applied R&D Group, Argonne

Bench-scale sample preparation

Chemical Sciences & Engineering Division, Argonne

Evaluation of material performance

Jet Propulsion Laboratory & NASA

Provided material for comparison

- Delivery of cathode materials

Date	Material / Lot #		Where	Purpose
11/29/2011	LNMO ES-120111	11 g	Argonne – CSE Zonghai Chen	Thermal safety test
03/02/2012	LNMO ES-120111	7 Kg	Bren-Tronics	Performance test
04/05/2012	LNMO ES120222	1 Kg	Argonne Cell Fabrication Facility	Pouch cell evaluation
05/10/2012	LNMO ES-110921	6 g	Argonne – CSE Wenquan Lu	Performance test
09/10/2012	LNMO ES-120709+11	1 Kg	Argonne Cell Fabrication Facility	Pouch cell evaluation
11/26/2012	$MnCO_3$ ES-121009	10 g	Argonne - CSE Jason R. Croy	Material evaluation
11/26/2012	Li_2MnO_3 ES-121009-1	10 g	Argonne - CSE Jason R. Croy	Material evaluation
02/20/2013	Crushed LNMO	0.2 Kg	Argonne Cell Fabrication Facility	Pouch cell evaluation

Activities for Next Fiscal Year

- Minimize cracking issue during calendaring of carbonate synthesized material.
  - Modify process to make denser spherical particles and understand performance trade-off.
  - Produce kilogram quantity of carbonate material for pouch cell evaluation.

- Continue to work on hydroxide candidate material at pre-pilot-scale.
  - Optimize particle size, morphology, density and electrochemical performance.
  - Produce kilogram quantity material for pouch cell evaluation.

- Select and produce new lab-scale candidate material.
  - Candidates :
    - Composition — Layered-layered spinel
    - Process — Lithium ion-exchange reaction
    - Secondary particle structure — Core-shell or gradient material
  - Produce kilogram quantity material for pouch cell evaluation.

Summary

- Interim laboratories were relocated to the MERF.
- Carbonate process at pre-pilot-scale was established and optimized.
  - Advanced 20L CSTR produces size-controlled spherical precursor over 24hr continuous operation.
  - Particle size and morphology were investigated in depth to get high density and performance.
  - 8 μm-size cathode product was delivered to Cell Fabrication Facility (2nd kilogram delivery).
  - Particle cracking and performance was investigated.
- Hydroxide process capability was established and preliminary material was evaluated.
- Synthesized $MnCO_3$ and Li_2MnO_3 for ion exchange research.

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- Argonne National Laboratory
  - Gerald T. Jeka for characterization (MERF)
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