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: Sept. 2015
- Percent complete: on going

Budget

- Total project funding:
  - $1.3M in FY13
  - $1.2M in FY14

Barriers

- Cost: Reduce manufacturing costs with advanced processing methods
- Performance: Process selection and optimization for maximum performance

Partners

- Scaling materials for:
  - Jet Propulsion Laboratory (UT-Austin)
  - Argonne's Applied R&D Group
  - Sharp Laboratories of America (ARPA-E)
- Provided materials to:
  - ITN Energy Systems
  - Jet Propulsion Laboratory
    - Coatings study
    - Full cells to be made by SAFT
  - Argonne National Laboratory
    - Materials Screening Group
    - CAMP's Cell Fabrication Facility
    - Applied R&D Group
    - ALD Group

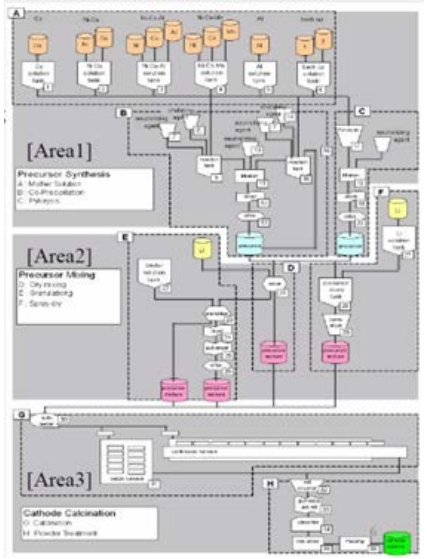
Objectives - Relevance

- 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 specifications for industrial evaluation or further research.
  - To evaluate emerging manufacturing technologies for the production of these materials.

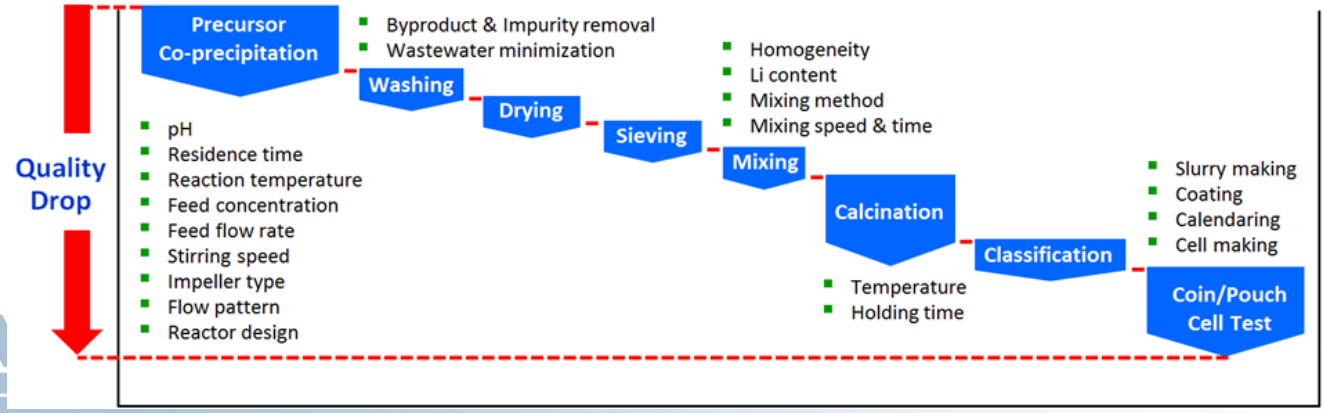
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing
    - Reducing the risk associated with the commercialization of new battery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

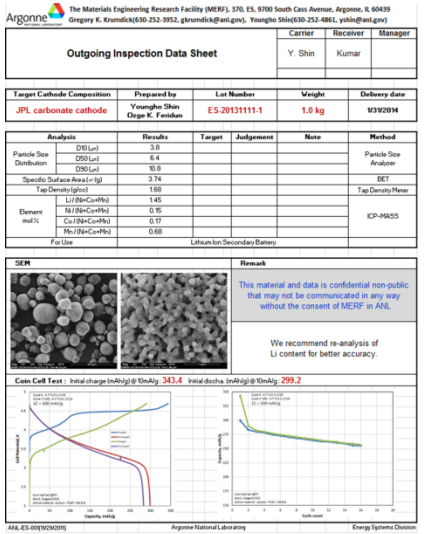
Approach

- Define target specification with discovery R&D group.
  - Evaluate bench-scale samples from discovery R&D group.
- Explore various synthesis routes.
  - Develop customized process for candidate material.
  - Solve scale-up challenges.
  - Evaluate emerging manufacturing technologies.
  - Evaluate preliminary product with discovery R&D group.
- Process optimization to maximize cathode performance.
- Kilogram quantity production.
  - Final product inspection and delivery.
- Feedback from collaborators for improvement.



Actual performance is dropped without optimization of the each process variable



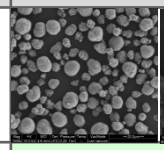
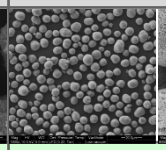


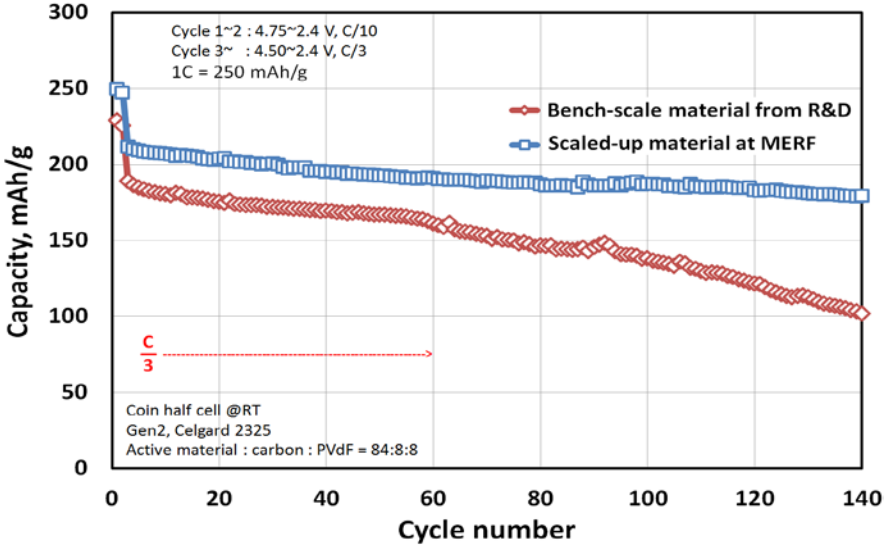
Approach - Milestones

- FY13
  - **Target material #1 ($Li_{1.37}Ni_{0.33}Mn_{0.67}O_y$)**
    - Process development to understand carbonate particle cracking issue **(beyond program scope)**
    - Complete hydroxide process assessment **(completed)**
  - **Target material #2 ($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$) – JPL/UT-Austin**
    - Identify target material, complete preliminary assessment **(completed)**
    - Complete precursor optimization, provide samples for evaluation **(completed)**
    - Complete post treatment optimization **(completed)**
- 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)**
  - **Target material #3 (layered layered spinel)**
    - Identify target material, complete preliminary assessment **(completed)**
    - Complete precursor optimization, provide samples for evaluation **(ongoing)**
    - Complete post treatment optimization **(ongoing)**
    - Complete scale-up at kilogram quantity
  - **Target material #4 (to be determined)**
    - Identify target material, complete preliminary assessment
    - Complete precursor optimization for material, provide samples for evaluation

Scale-up of 1st Target Material (previously reported)

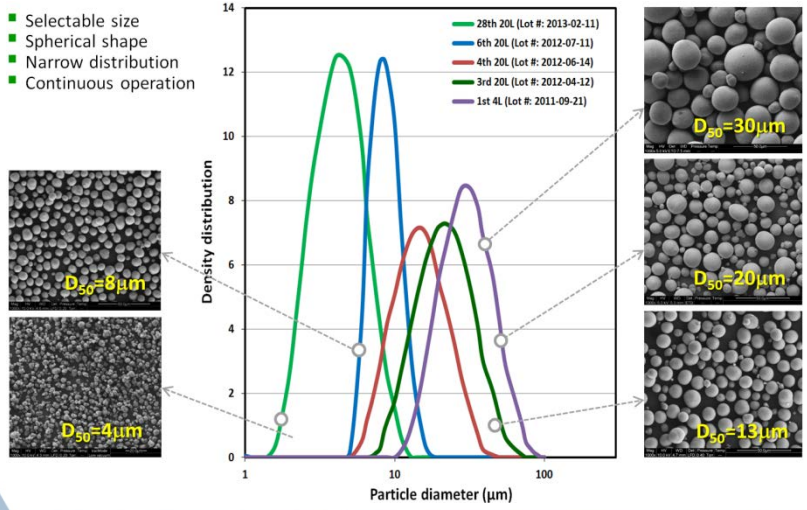
- Co-free lithium- and manganese rich cathode was selected as the 1st candidate material for process development and scale-up.
  - Tailored 20L continuous synthesis system (CSTR) was developed for 1st candidate material.
  - Particle growth problem was solved by the invention of size-controllable CSTR system.
  - Particle cracking of carbonate cathode was identified during pouch cell evaluation.
  - Small, dense spherical particle was targeted to get improved quality and performance.

1st candidate	Bench-scale material (101217B)	Scaled-up material (ES120905)
SEM X1000, x8000		
ICP analysis	$Li_{1.35}Ni_{0.32}Mn_{0.68}O_y$	$Li_{1.37}Ni_{0.33}Mn_{0.67}O_y$
$D_{10}/D_{50}/D_{90}$ [μm]	7.6/12.7/21.0	6.9/11.1/18.4
Tap density [g/cc]	**1.41**	**1.70**



- Kilogram quantities were delivered for further R&D.
- In discussions with commercial manufacturer to evaluate particle size control technology at larger scale.

- Advanced 20L CSTR was developed for size control.
  - Selectable size
  - Spherical shape
  - Narrow distribution
  - Continuous operation

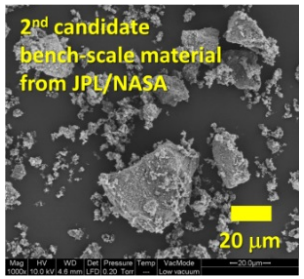


Scale-up of 2nd Target Material ($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$)

Jet Propulsion Laboratory

- JPL/UT-Austin high energy LMR-NMC cathode was selected as the 2nd target material.

  Reasons: High energy material that can be applied for electric vehicles.
  Process research and development applicable to other LMR-NMC materials.
  Coatings study by JPL and full cell evaluation to be carried out by Saft.



Target specification:

Composition: $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$
Tap density: > 1.5 g/cc
1st discharge capacity: ~ 240 mAh/g
Cycle life: ~ 200 cycles
Uniform spherical morphology for surface coating application

- JPL/UT-Austin development history.
  - UTA 18 month results (bench-scale): 95 % initial discharge capacity and 113 % tap density to target specification.
  - Commercial cathode manufacturer (pre-pilot scale-up): Failed to scale up with target specification.

✓ **Issues:** - UT-Austin process was a *batch* process – scaling decreased material performance.
- Commercial scale-up met performance specs on small scale (batch) but not at kilogram scale

- At Argonne, process development and scale-up was carried out via two synthesis methods for the development of a *continuous* process.
  - Hydroxide co-precipitation: Bench-scale synthesis method by JPL/UT-Austin.
  - Carbonate co-precipitation: To attempt to achieve higher material performance.

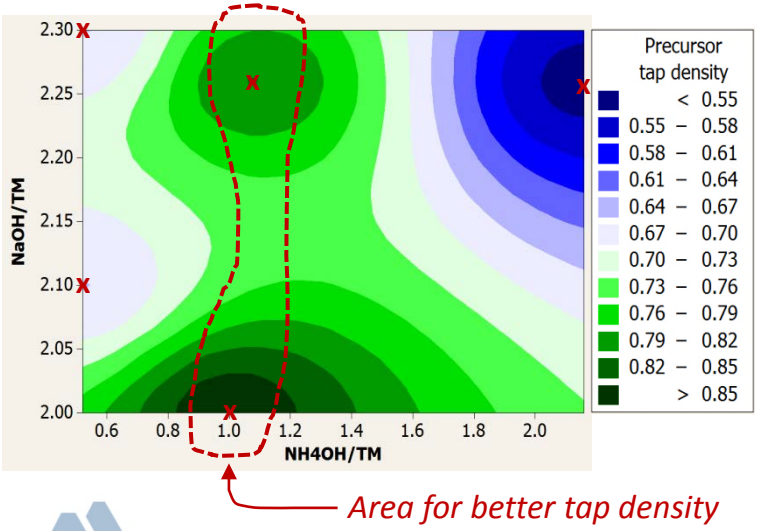
Hydroxide Precursor Synthesis

- Evaluated hydroxide co-precipitation process to meet performance specifications.

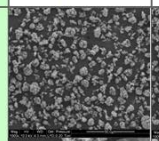
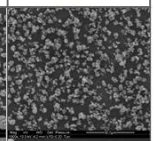
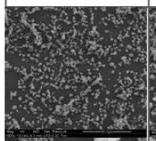
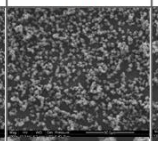
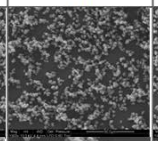
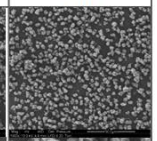
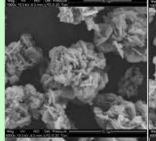
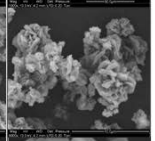
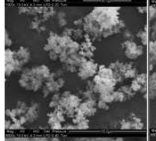
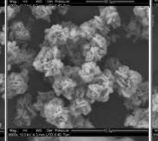
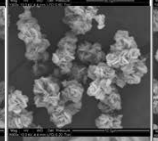
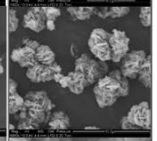
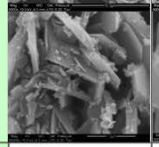
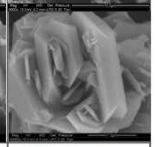
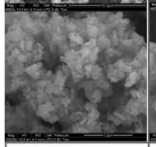
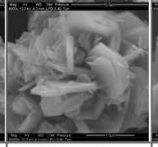
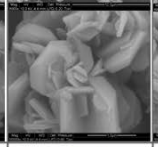
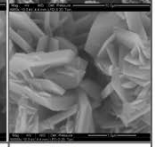
- Process variables for co-precipitation
  - Reactor type = 20L CSTR (fixed)
  - N_2 atmosphere (fixed)
  - Stirring speed = 3000 rpm (fixed)
  - Residence time = 3hr (fixed)
  - TM feed concentration = 1M (fixed)
  - pH = 11.68 ~ 12.56 (varied)
  - Reaction temperature = 35 ~ 52 °C
  - NaOH/TM ratio = 2 ~ 2.3
  - NH_4OH/TM ratio = 0.52 ~ 2.16

- Contour graph of precursor tap density

  x : Experimental points at 36 °C



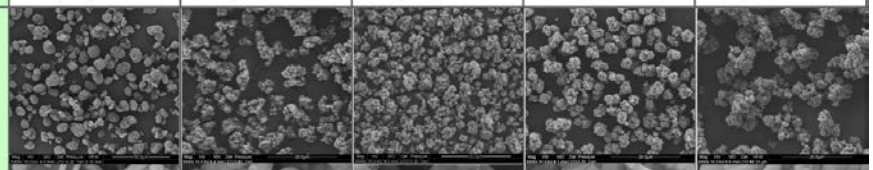
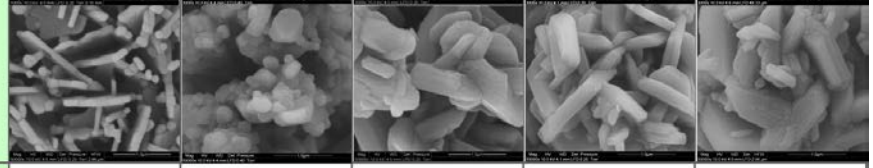
Area for better tap density

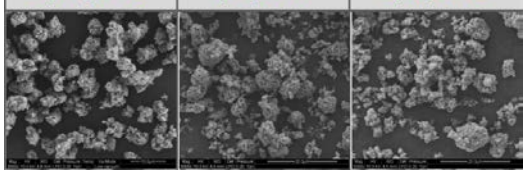
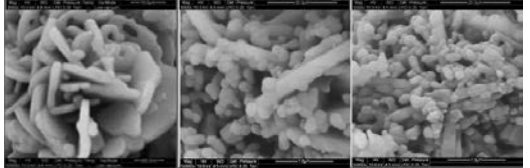
PRECURSOR	Production #	ES20130920	ES20130923	ES20130927	ES20131001	ES20131002	ES20131004
	Variable change	Only reaction temperature		Only the ratios of NaOH/TM and NH_4OH/TM			
	Rxn temp. [°C]	52.1	35.6	36.5	35.4	37.1	35.6
	NaOH/TM ratio	2.26	2.26	2.26	2.10	2.30	2.00
	NH_4OH/TM ratio	1.08	1.08	2.16	0.52	0.52	1.00
	Reaction pH	12.00	12.17	12.56	11.87	11.68	11.83
	SEM x1,000						
	SEM x8,000						
	SEM x50,000						
	$D_{10}/D_{50}/D_{90}$ [μm]	3.1/5.3/9.2	1.1/3.8/6.3	0.1/2.0/3.8	0.1/2.9/5.1	0.1/3.1/5.0	0.4/4.6/6.8
	Tap density [g/cc]	**0.68**	**0.82**	**0.54**	**0.67**	**0.67**	**0.87**

- ✓ *Lower reaction temperature gives better precursor tap density.*
- ✓ *NH_4OH/TM ratio of 1.0 shows better precursor tap density.*
- ✓ *Desired reaction pH is between 11.8 and 12.2.*
- ✓ *Further research is necessary to get better results.*

Hydroxide Cathode Synthesis

- Comparison of morphology, size, tap density and capacity of hydroxide cathode.

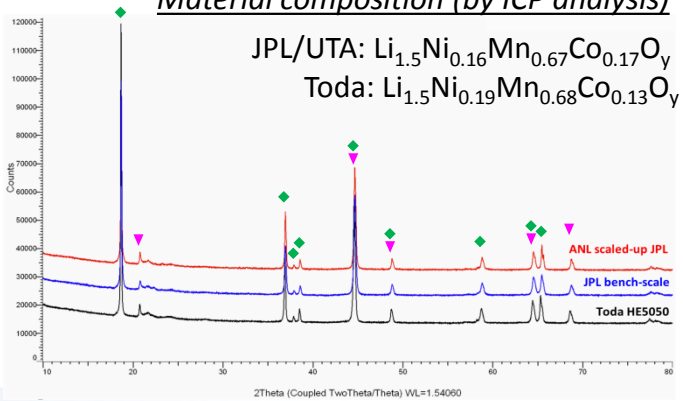
	Manufacturer	ANL ES20130715	ANL ES20130805	ANL ES20130923	ANL ES20131004	ANL ES20131105
	Scale / Status	Pre-pilot				
	Production date	7/15/2013	8/05/2013	9/23/2013	10/04/2013	11/05/2013
CATHODE	SEM x3,000					
	SEM x50,000					
	$D_{10}/D_{50}/D_{90}$ [µm]	5.2/9.5/17.4	3.0/5.4/9.9	3.3/6.5/12.1	3.0/5.1/9.0	3.1/5.5/9.8
	Tap density [g/cc]	0.66	0.99	1.06	1.23	1.21
	1st disch. cap. [mAh/g]	263.6	249.8	227.6	237.7	218.6

Toda- HE5050 5-P767	Toda- HE5050 5-P1407	Toda- HE5050 P2564
Commercial		
4/10/2009	1/18/2012	3/18/2013
		
		
3.1/5.3/9.2	1.1/5.2/11.3	2.0/4.9/10.4
1.03	1.16	1.07
255.3	261.8	254.5

Material composition (by ICP analysis)

JPL/UTA: $Li_{1.5}Ni_{0.16}Mn_{0.67}Co_{0.17}O_y$

Toda: $Li_{1.5}Ni_{0.19}Mn_{0.68}Co_{0.13}O_y$



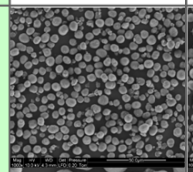
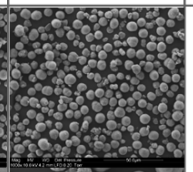
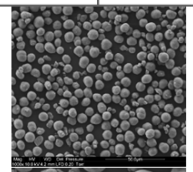
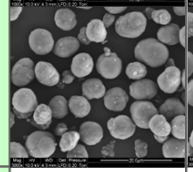
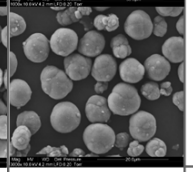
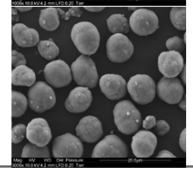
- ✓ *Increasing tap density resulted in a decrease in capacity.*
- ✓ *Toda HE5050 has similar composition, morphology and performance.*
- ✓ *None of these materials met JPL's target specifications.*
- ✓ *Materials were distributed for basic R&D use.*

Carbonate Precursor Synthesis

- Carbonate co-precipitation enabled higher precursor tap density.

- Process variables for co-precipitation
  - Reactor type = 20L CSTR (fixed)
  - N_2 atmosphere (fixed)
  - Stirring speed = 3000 rpm (fixed)
  - Residence time = 3hr (fixed)
  - TM feed concentration = 1M (fixed)
  - pH = 7.7 ~ 8.5 (varied)
  - Reaction temperature = 35 °C (fixed)
  - Na_2CO_3/TM ratio = 1.05 (fixed)
  - NH4OH/TM ratio = 0.1 ~ 0.03

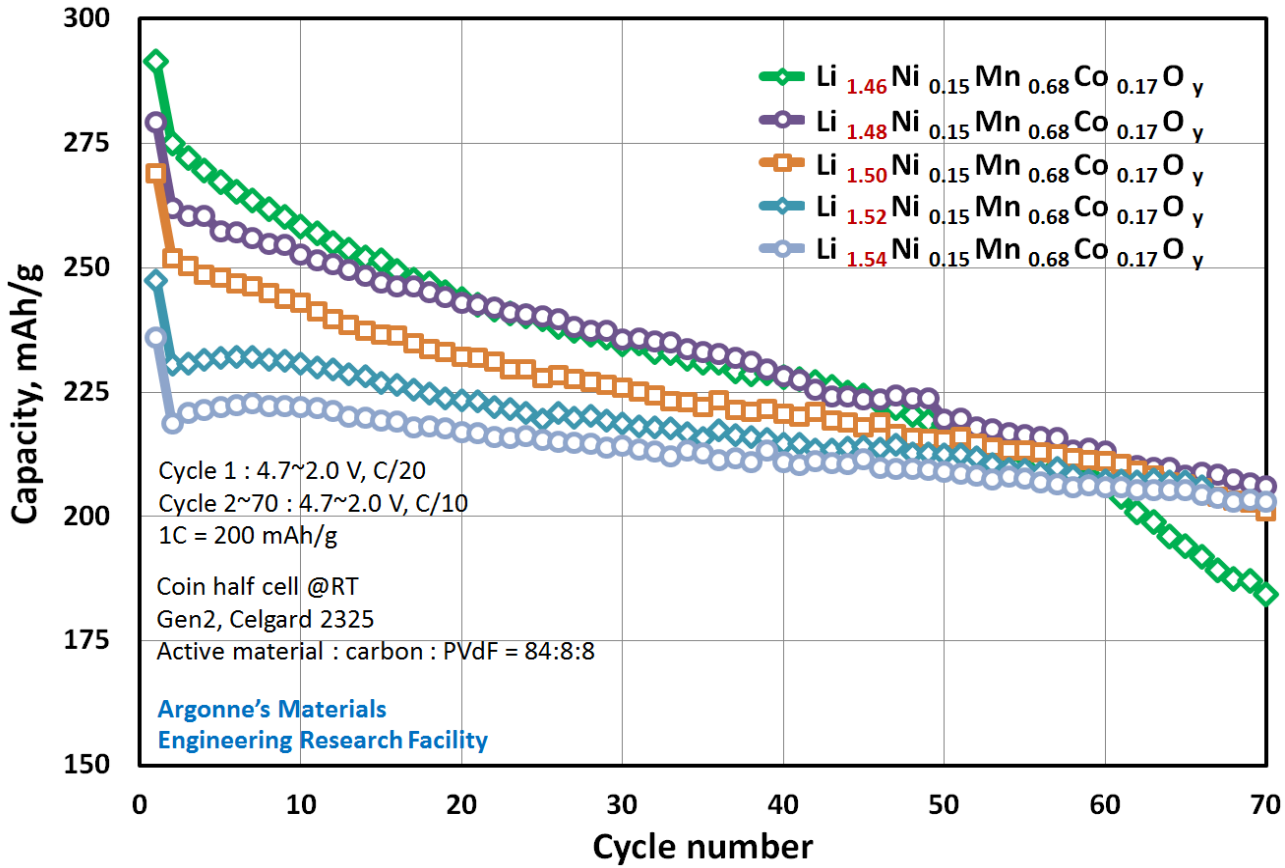
* Process scale-up of the 1st target material accelerated the scale-up work of 2nd target material – however, process was not fully optimized.

PRECURSOR	Production #	ES20130924	ES20131106	ES20131111	ES20131114
	Variable change	Preliminary experiment	Lower NH_4OH/TM	5kg precursor production	
	Rxn temp. [°C]	35.2	35.2	36.0	37.4
	Na_2CO_3/TM ratio	1.05	1.05	1.05	1.05
	NH_4OH/TM ratio	0.1	0.03	0.03	0.03
	Reaction pH	8.5	7.7	7.8	7.9
	Operation time	12 hour	24 hour	30 hour	30 hour
	SEM x1,000				
	SEM x3,000				
	$D_{10}/D_{50}/D_{90}$ [μm]	0.2/7.0/10.5	0.2/7.9/11.8	3.2/7.0/10.7	
	Tap density [g/cc]	**1.50**	**1.52**	**1.60**	

- ✓ *Lower reaction temperature was applied according to hydroxide co-precipitation result.*
- ✓ *Lower NH_4OH/TM ratio shows better tap density.*
- ✓ *Desired reaction pH is between 7.7 and 7.9.*
- ✓ *Carbonate precursor has better morphology and higher tap density than hydroxide precursor.*

Effect of Li Ratio on Capacity and Cyclability

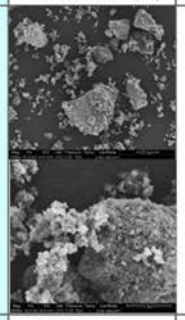
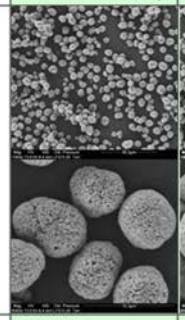
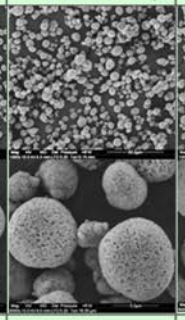
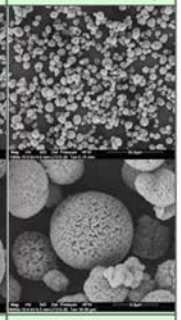
- Determination of optimal lithium content.



- ✓ *Lithium ratio has strong effect on initial capacity and capacity loss.*
- ✓ *Kilogram production of two grades of carbonate cathode was completed.*
  - *High initial capacity (ES20131111-1): for surface coating application.*
  - *Good initial capacity and less capacity loss (ES20131111-2): for pouch cell evaluation.*

Carbonate Cathode Synthesis - Kilogram Production

- Comparison of scaled-up JPL/UTA carbonate cathodes (delivered)

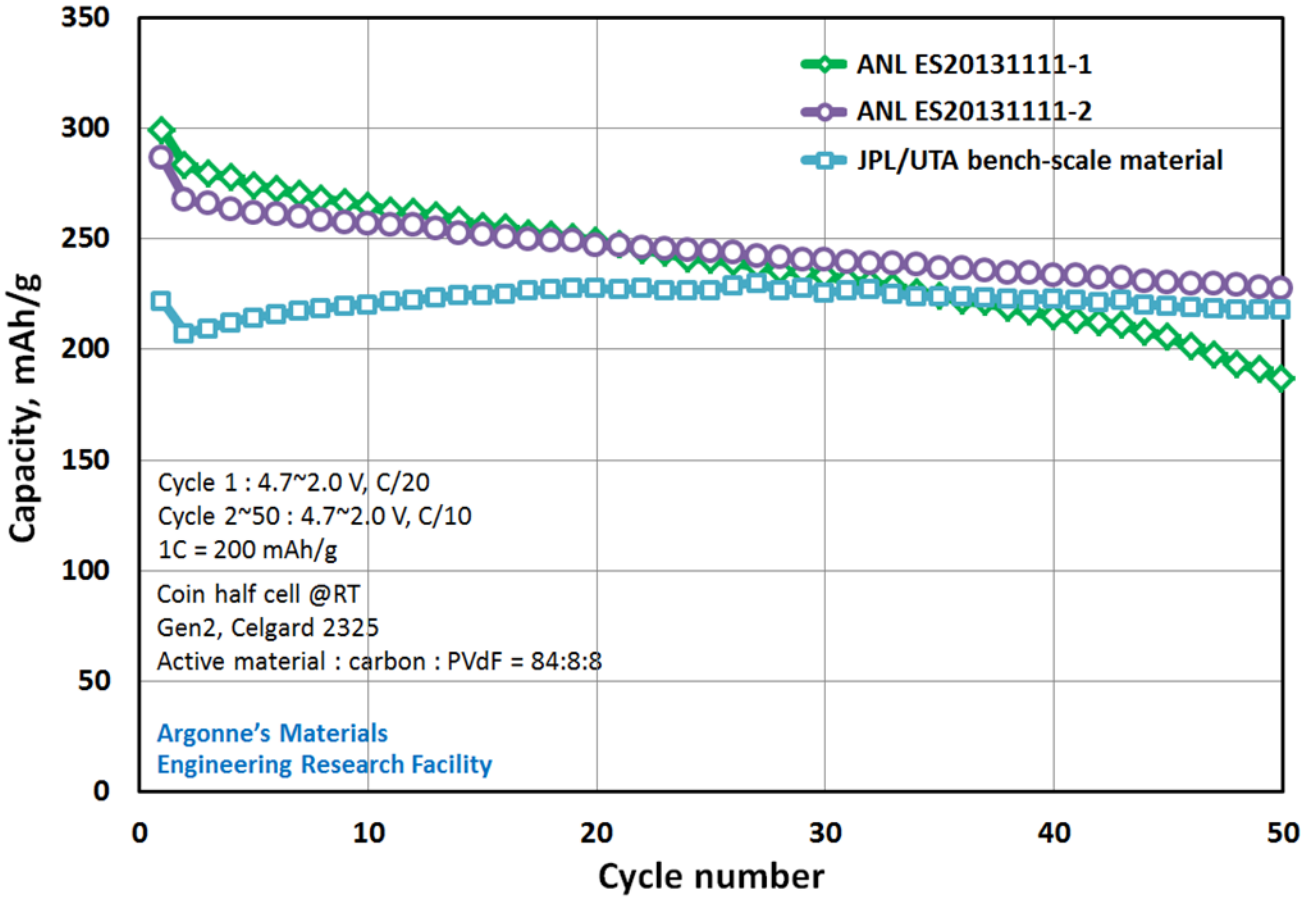
	JPL/UTA Target Specification	UTA(18 mo.) uncoated	Commercial Scale-up	ES20130924 Scale-up carbonate	ES20131111-1 Scale-up carbonate	ES20131111-2 Scale-up carbonate
		Bench scale	Pre-pilot	Pre-pilot Preliminary 100g delivered	Pre-pilot Production 1 kg delivered	Pre-pilot Production 2 kg delivered
Composition (by ICP)	$Li_{1.5}Ni_{0.1625}Mn_{0.675}Co_{0.1625}O_{2.5}$	$Li_{1.6}Ni_{0.14}Mn_{0.68}Co_{0.18}O_y$	x	$Li_{1.48}Ni_{0.15}Mn_{0.68}Co_{0.17}O_y$	$Li_{1.45}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$	$Li_{1.47}Ni_{0.16}Mn_{0.67}Co_{0.16}O_y$
SEM x1,000 SEM x8,000	Uniform spherical morphology		x			
$D_{10}/D_{50}/D_{90}$ [µm]	x	1.2/11.1/29.3	x	4.0/6.7/11.4	3.8/6.4/10.8	3.8/6.3/10.7
Tap density [g/cc]	> 1.50	1.70	1.45 +	1.84	1.68	1.81
Initial disch. gravi. capacity [mAh/g]	> 240	228	223 +	289	299	288
Initial disch. vol. capacity [mAh/cc] **	> 360	388	323	532	503	521

** *Calculated value based on tap density*
+ *Data from SPS Battery KDP meeting (June 25, 2012)*

- ✓ *20 % increased tap density compared to target specification.*
- ✓ *20 % increased initial discharge capacity.*
- ✓ *Spherical morphology was obtained.*
- ✓ *3 kg product (two grades) was delivered to JPL/NASA.*

Carbonate Cathode Cyclability

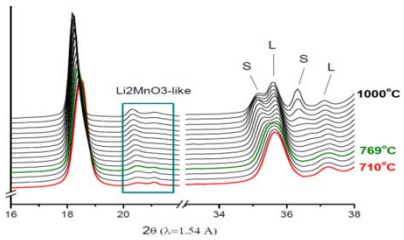
- Cycle life comparison of scaled-up JPL/UTA carbonate cathodes



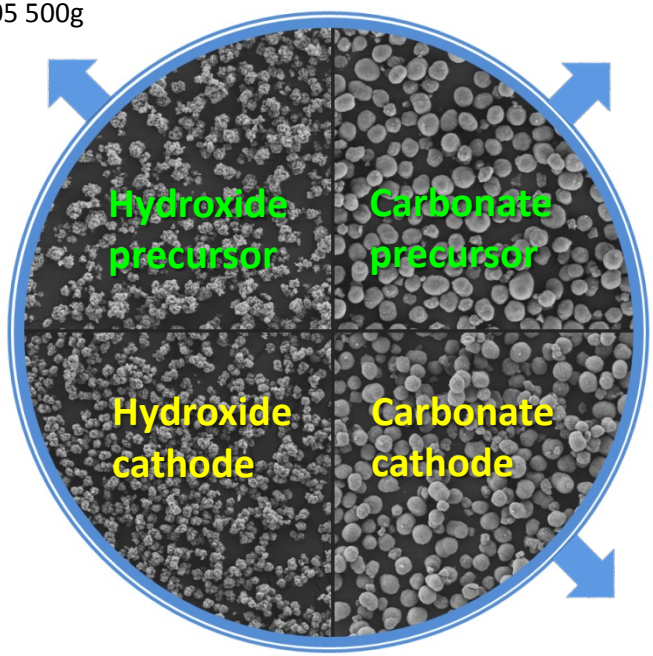
- ✓ *ES20131111-1 shows high initial capacity (designed for surface coating application).*
- ✓ *ES20131111-2 shows better capacity than bench-scale material for 50 cycles.*
- ✓ *Program objective for 2nd candidate material was achieved.*

Synthesized Materials – A Critical Bridge for R&D

- Domain size / formation mechanism study at Argonne
  - Hydroxide precursor ES20131004 5g
  - Hydroxide precursor ES20131105 500g



JPL/UTA material scaled at the MERF



- Ion exchange research to mitigate voltage fade problem at Argonne
  - Carbonate precursor ES20130924 100g

- ALD surface coating at Argonne
  - Carbonate cathode 600g
- Material evaluation at NASA
  - Carbonate cathode ES20130924 100g
  - Carbonate cathode ES20131111-1 1kg
  - Carbonate cathode ES20131111-2 2kg
- Material screening group at Argonne
  - Carbonate cathode ES20131111-2 50g
- Pouch cell evaluation at Argonne CAMP
  - Carbonate cathode ES20131111-2 400g
- Basic research ITN Energy Systems
  - Carbonate cathode ES20131111-1 50g
  - Carbonate cathode ES20131111-2 25g

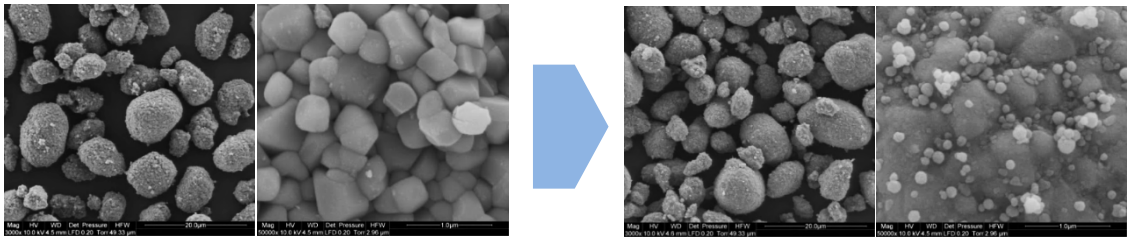
- ✓ *Many research groups and companies need advanced cathode material for their further research and application.*
- ✓ *Advanced materials are hard to get as commercial products.*
- ✓ *High quality, advanced precursors and cathode materials are needed for basic R&D.*
- ✓ *Evaluation results are being collected and discussed with collaborators to design better cathode performance.*

Dry Particle Coating

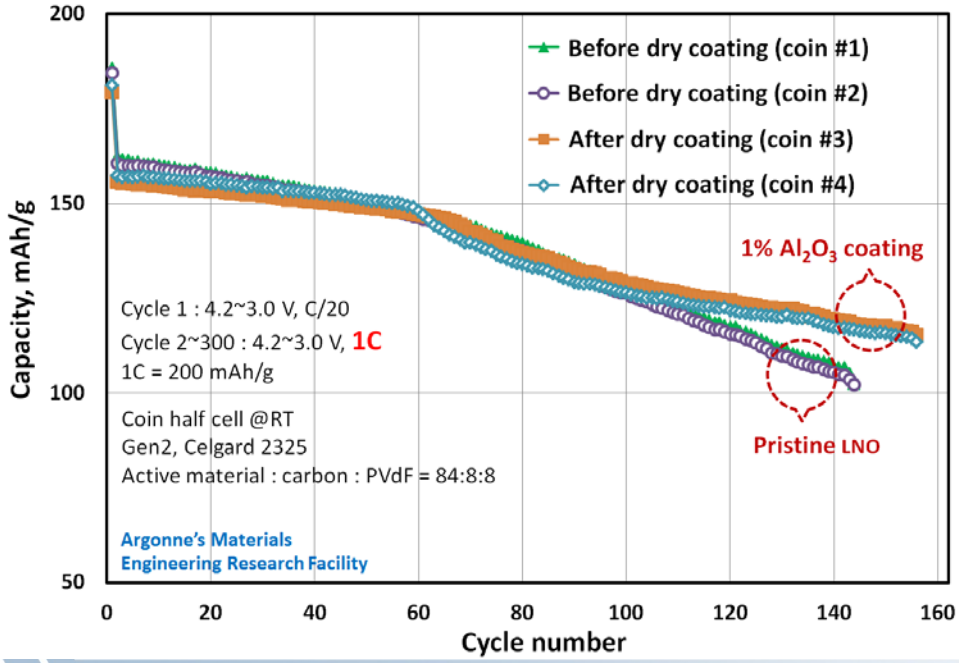
- Dry surface coating to improve performance

Before dry coating
Commercial lithium nickel oxide
D_{50} = 8.2 μm
Tap density = 2.58 g/cc

After dry coating
LNO coated with 1% Al_2O_3 (45 nm)
D_{50} = 8.3 μm
Tap density = 2.74 g/cc



Kilogram quantity mechanofusion dry coater



- ✓ *Better capacity retention after 100 cycles.*
- ✓ *No particle cracking during dry coating process.*
- ✓ *Tap density increase due to surface grinding.*

- **Preliminary result shows positive effect on capacity retention.**
- **Scaled-up advanced materials will be tested.**
- **Collaboration with Chris Johnson's research group**

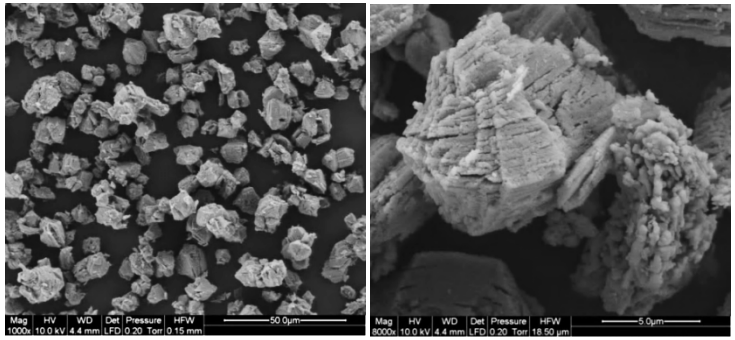
Scale-up of 3rd Target Material: Started

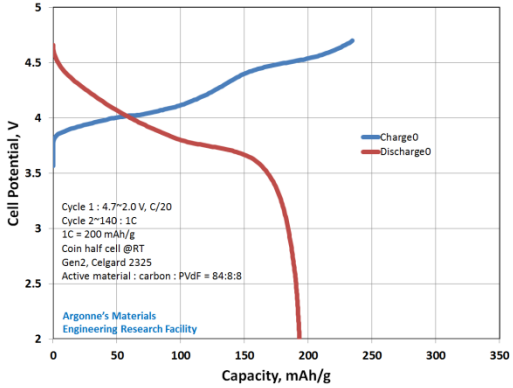
- Scale-up of layered-layered spinel material (Collaboration with Michael Thackeray's group)

  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 material
Obtained from basic R&D
2L glassware
Oxalate co-precipitation

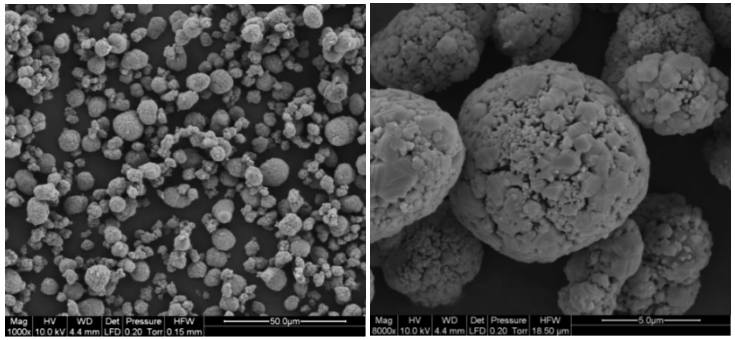
Particle size:
$D_{10}/D_{50}/D_{90}$ = 6.3/12.3/22.3 µm
Tap density = 1.7 g/cc
1st disch. capacity = 193 mAh/g

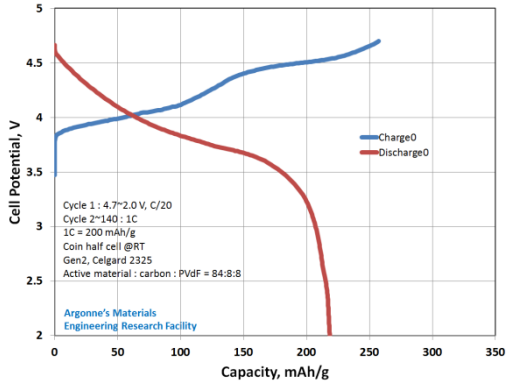




Pre-pilot (scale-up) material
Preliminary result
20L continuous reactor
Carbonate co-precipitation

Particle size:
$D_{10}/D_{50}/D_{90}$ = 5.2/9.6/16.8 µm
Tap density = 1.8 g/cc
1st disch. capacity = 218 mAh/g

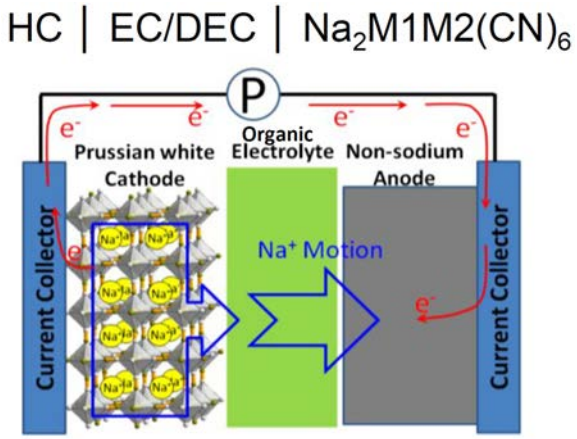


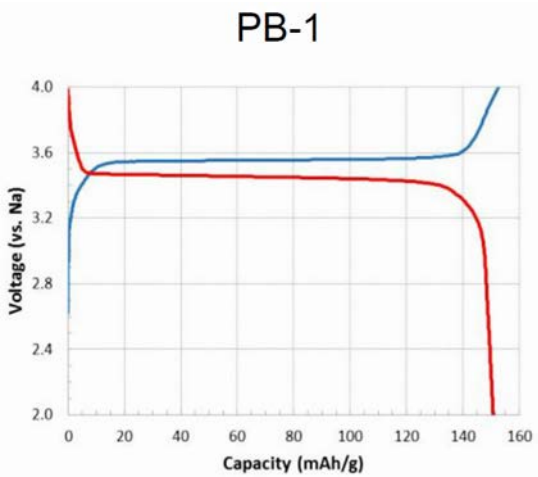


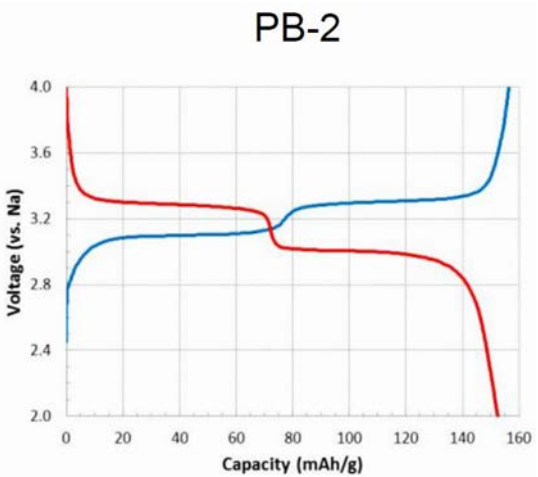
✓ *Objective is to develop continuous process to synthesize multiple kilograms of high purity material for basic R&D and full cell evaluation.*

Scale-up of Sodium-Ion Cathode Material

- Scale-up of Prussian blue-derived cathode material for low-cost sodium-ion battery.
  - Material was developed by Sharp Labs of America for an ARPA-E funded project.
  - Evaluation of scalability and economic feasibility of synthesis route.
  - Kilogram quantity being synthesized for full cell evaluation.
  - Work is being funded by Sharp Labs.







http://arpa-e.energy.gov/?q=arpa-e-projects/sodium-based-energy-storage

Responses to Previous Year Reviewers' Comments

- "Reviewer reported that … the impact can be significant if the project is successful... But there was not enough discussion around how practical various approaches were and what the potential penalties of different approaches were..."
  - *Response: We are in the process of engaging commercial cathode manufacturers to collaborate on the evaluation of emerging manufacturing technologies to determine the technical feasibility and cost impact.*
- "The reviewer thought that it will be important to lay out the target criteria that define success… some significant thought should be put into the issue of whether there is a definable end point to this work"
  - *Response: Agreed. Full process optimization could take years. For target material #2, a set of well defined target specifications were used to determine when the process was optimized enough to produce kilogram quantities of materials for distribution, completing the task.*
- "With the number of variables, there should be some effort to eliminate some of the less sensitive variables from the study."
  - *Response: Agreed. It would take 2-3 times as long to optimize all process variables. Less sensitive variables are fixed using optimal values from prior experiments. Key process variables are then optimized using a statistical approach within the limit of project time frame.*

Collaborations

- Materials process R&D:
  - Jet Propulsion Lab (Kumar Bugga)
    - UT-Austin
  - Argonne National Lab (Michael Thackeray)
  - Sharp Labs of America (Jong-Jan Lee)
    - ARPA-E developed material
- Materials provided for further research:
  - Jet Propulsion Lab (Kumar Bugga)
    - Coatings study
  - ITN Energy Systems (Thomas Kodenkandath)
  - Argonne National Lab
    - Domain size-formation study (Zonghai Chen)
    - Ion exchange research (Chris Johnson)
    - ALD surface coating (Jeff Elam)
    - Dry surface coating (Chris Johnson)
- Electrochemical evaluation of scaled materials
  - Saft (material provided by JPL)
  - 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.

Activities for Next Fiscal Year

- Complete work on target material #3 (layered layered spinel)
  - Develop continuous process to synthesize multiple kilograms of high purity material for basic R&D and full cell evaluation.
- Begin work on target material #4 (to be determined)
  - Develop continuous process to synthesize multiple kilograms of high purity material for basic R&D and full cell evaluation.
- Evaluate Emerging Manufacturing Technologies
  - Complete evaluation of dry coating (mechanofusion) process
  - Advanced reaction technology candidates:
    - Spray pyrolysis
    - Taylor vortex
    - Supercritical hydrothermal

Summary

- 2nd Target Material ($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$)
  - Developed kilogram scale, continuous synthesis process.
    - Improved particle size control technology for better size and morphology control.
  - Process was preliminary optimized - material exceeds performance specifications.
  - Distributed ~ 5 kilograms of high quality precursors and cathode materials.
    - Enabling basic research
- 3rd Target Material (layered layered spinel)
  - Preliminary process assessment has been completed.
  - Preliminary process optimization work has begun.
- Sharp ARPA-E Material
  - Work is well underway and nearing completion
- Emerging Manufacturing Technologies
  - Began evaluation on dry coating (mechanofusion) process

Acknowledgements and Contributors

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- Argonne National Laboratory
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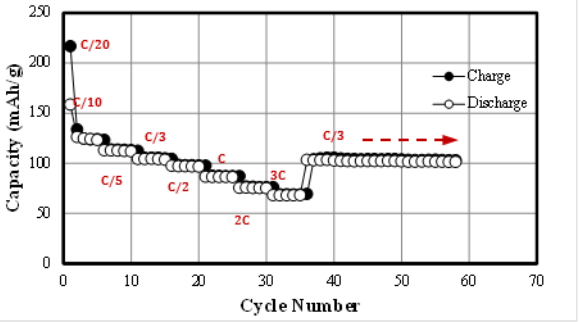
  - Brandon Long
  - Huiming Wu
  - Chris Claxton
  - Carl Shurboff
- Jet Propulsion Laboratory
  - Kumar Bugga
- Sharp Labs of America
  - Jong-Jan Lee
- ITN Energy Systems
  - Thomas Kodenkandath

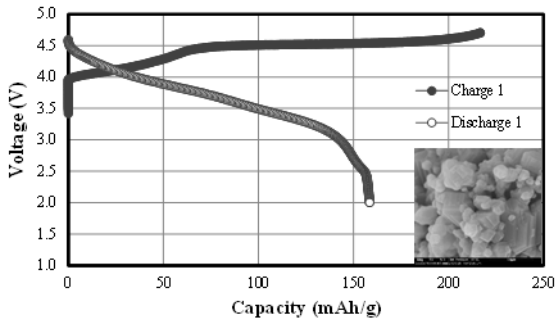
Technical Backup Slides

Rapid Solid State Precursor Synthesis

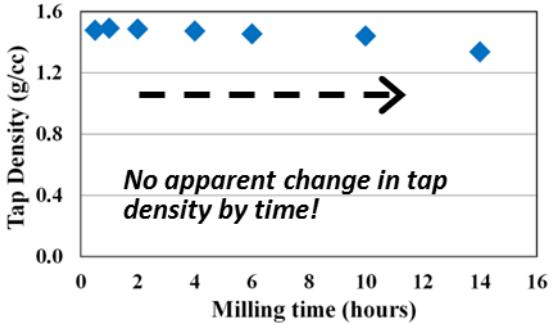
- Planetary ball mill enables the rapid synthesis of 400g quantities of precursors for initial screening and basic R&D use.
  - 30 minute processing time
  - No washing step
- Not a substitute for co-precipitation reactors for quality and material volume production

- Typical rate capability and voltage profile
  (e.g.; prepared from ball milled precursors at 0.5h)





- Effect of milling time



- Typical electrochemical data of selected cathode materials

	1st Charge Capacity* (mAh/g)	1st Disch. Capacity * (mAh/g)	1st Disch. Vol. Capacity** (mAh/cc)
Sample 44 -0.5h	216.72	158.5	232.99
Sample 28 -4h	212.09	157.5	231.53
Sample 42 -14h	218.45	155.3	206.55

* first cycle; 2.0-4.7 V, 10 mA/g
** Calculated based on tap density

- XRD profile – effect of milling time