Design of Safer High-Energy Density Materials for Lithium-Ion Cells

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Argonne National Laboratory

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Project ID es163

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Overview

Timeline

- Start – January 2011
- Finish – October 2014
- Percent complete – 25%

Barriers

- Energy density of available Li-ion battery technologies
  - Weight, volume, and affordability
- Abuse tolerance
  - Energy storage systems that must be intrinsically tolerant of abusive conditions

Budget

- Total project funding in FY11 and FY 12: $250K + $300K
- Funding in FY12: $300K
- Funding in FY11: $250K

Partners

- Collaboration:
  - Binghamton University
  - Washington University in Saint Louis
  - Pacific Northwestern National Laboratory
  - Energy Systems Division, Argonne
- Support: G. Koenig, D. Wang, X. Zhang, B. Polzin, W. Lu, A. Jansen, G. Krumdick, K. Takeya, K. Amine.
- Project lead: Ilias Belharouak

Objectives of this Study

We aim to correlate the electrochemical properties of materials (ANL-composite cathodes) to their structural, morphological, and physical properties by coordinating the science of synthesis with the science of function, in order to enable the use of these compounds in vehicle technologies.

$xLi_2MnO_3.(1-x)LiMO_2$ (M = Ni, Co) will be written $Li_{1+x}(Ni_aCo_bMn_c)O_{2+d}$

(1+x)/(a+b+c) > 1, c>(a+b), a>b, d is for balance

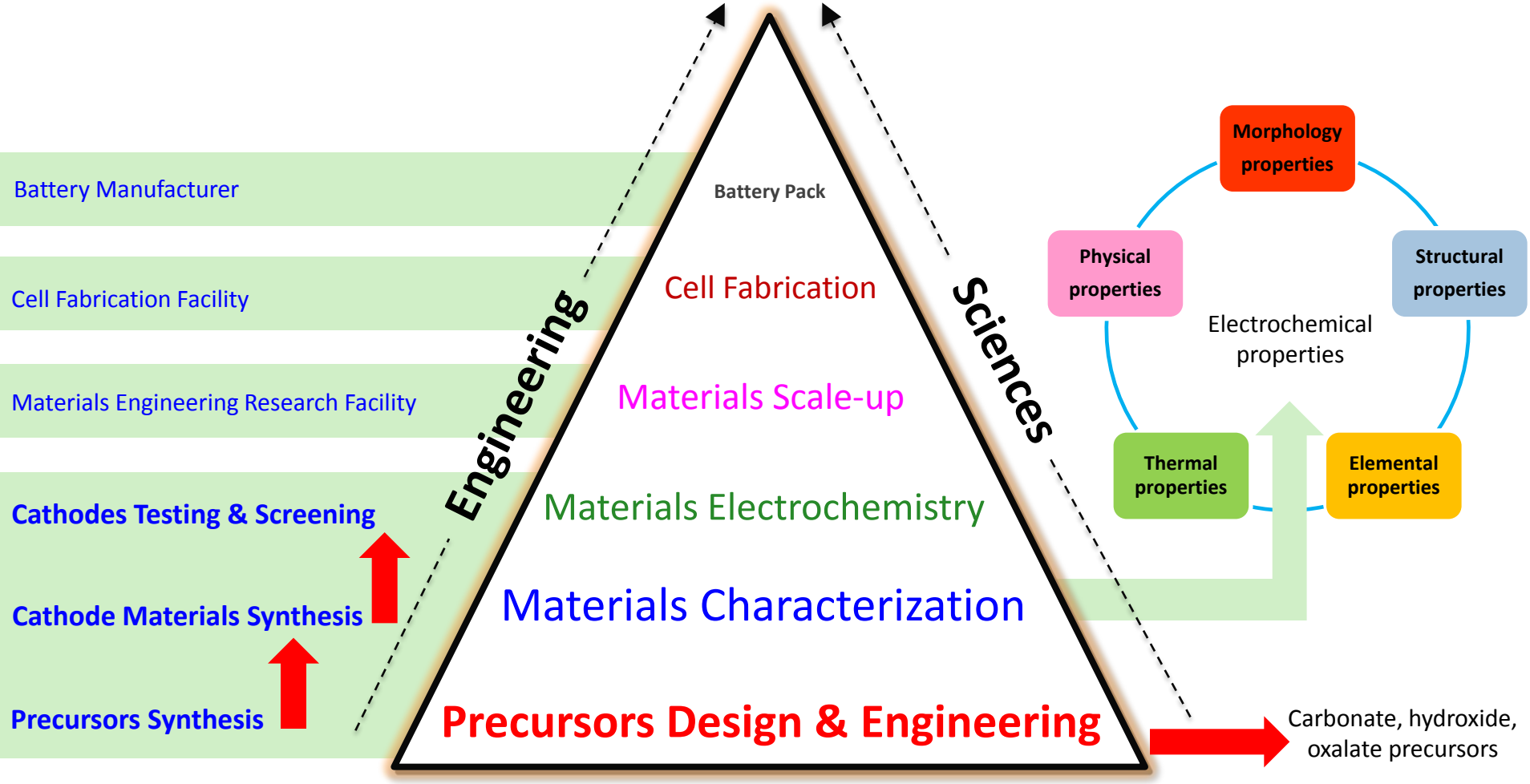
In this study b = 0

Milestones for FY12

- **Design of 4L-CSTR reactor to produce Ni/Co/Mn carbonate and hydroxide, and transfer of materials scale up technology to Energy System Division at Argonne.** (completed).
- **Characterize and understand (correlation approach) both the precursors and their lithiated materials using structural, physical, chemical, and electrochemical tools** (75% completed for carbonate, 50% for hydroxide, 10% for oxalate).
- **Investigate the origin of voltage fade observed in Li- and Mn-rich cathode materials using a material synthesis approach** (initiated).

Approach

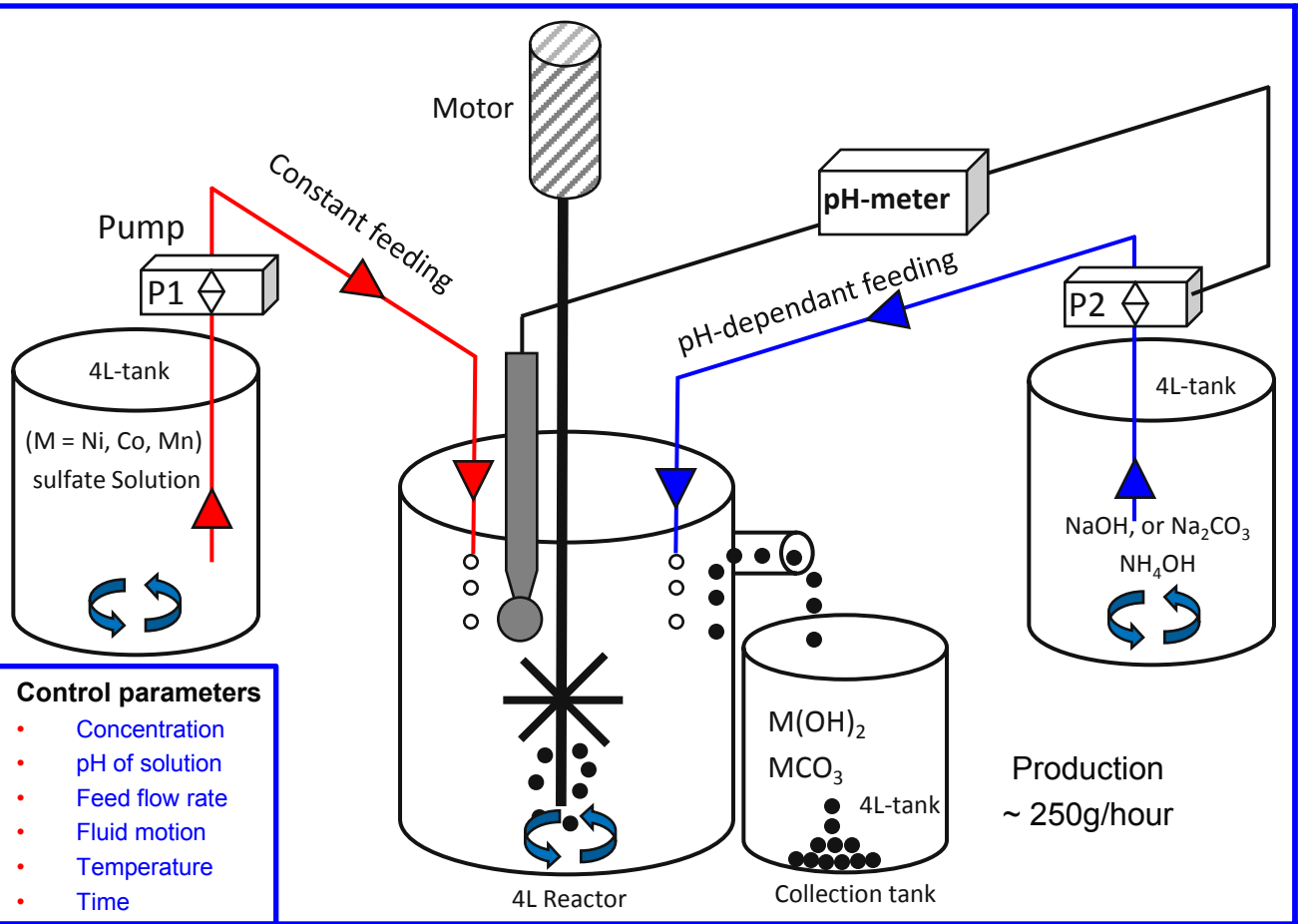
Coordinating the science of synthesis with the science of function*



*** Function means a capacity of 200-plus mAh/g @ 1C, better cycle life, and no significant voltage fade during extended cycling**

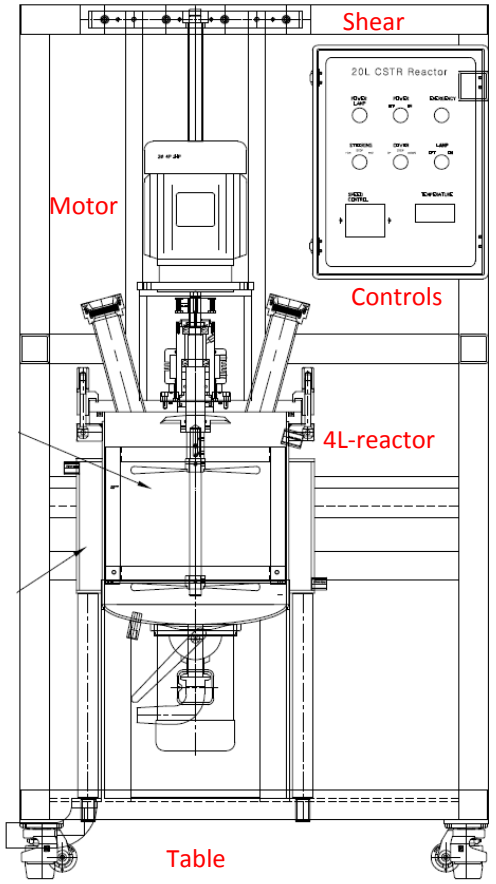
Technical Accomplishments

Design of Continuous Stirred Tank Reactor for 1Kg Precursor Production

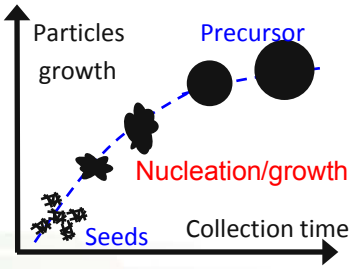


Control parameters

- Concentration
- pH of solution
- Feed flow rate
- Fluid motion
- Temperature
- Time

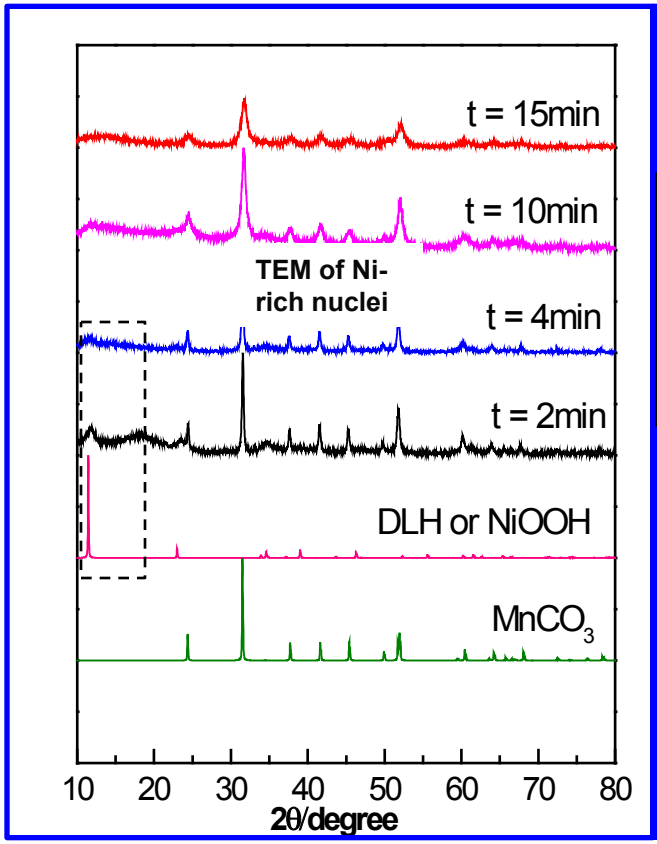


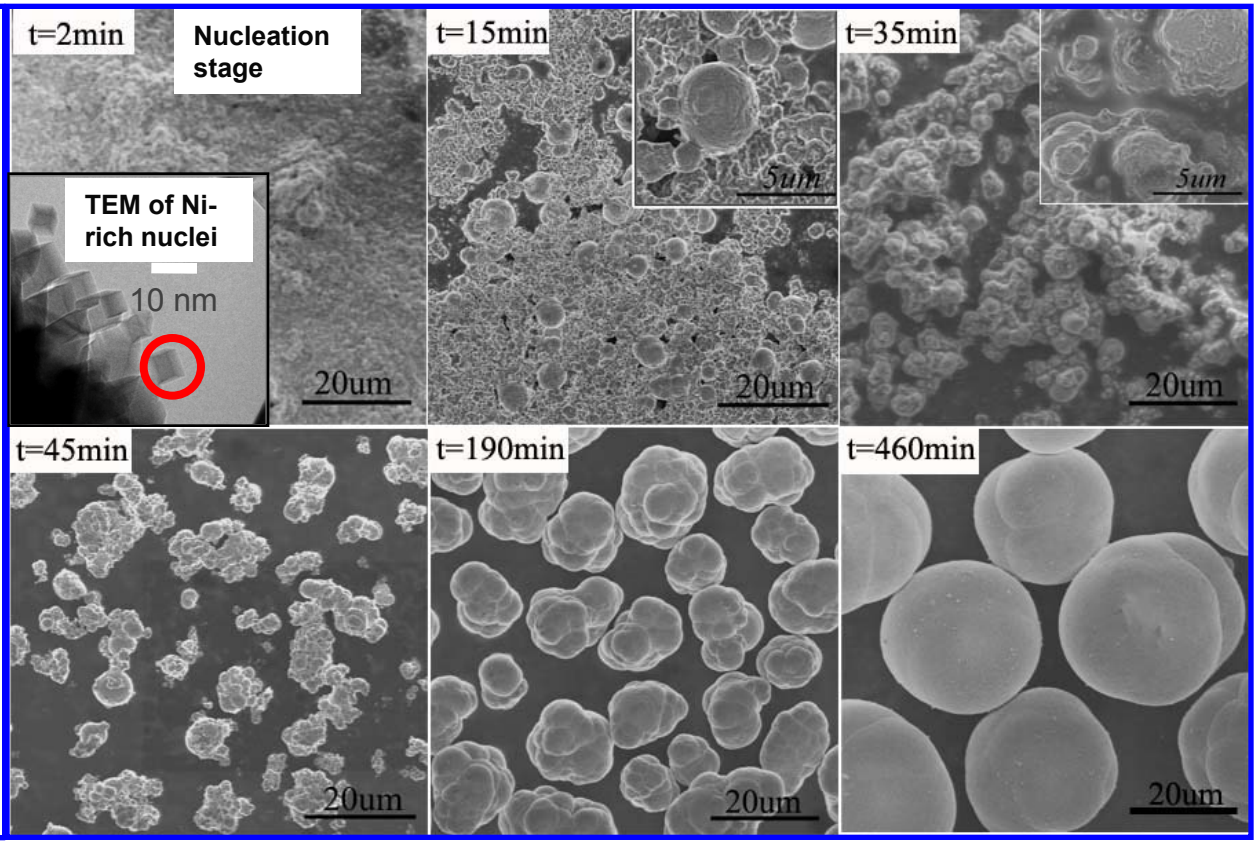
We developed 4L-CSTR reactor to produce Ni/Co/Mn carbonate, hydroxide, oxalate precursors. Basic design was transferred to ES division at Argonne for scale up.



Technical Accomplishments

Nucleation and growth mechanism of precursor particles were investigated during CSTR co-precipitation of $Ni_{0.3}Mn_{0.7}CO_3$ precursor



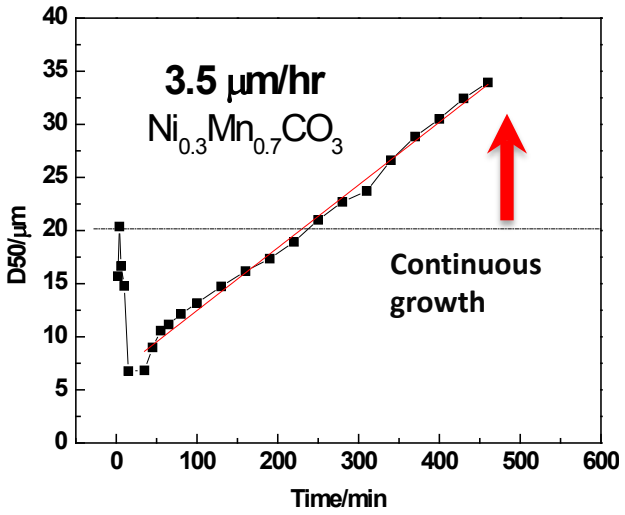


The following observations could be made:

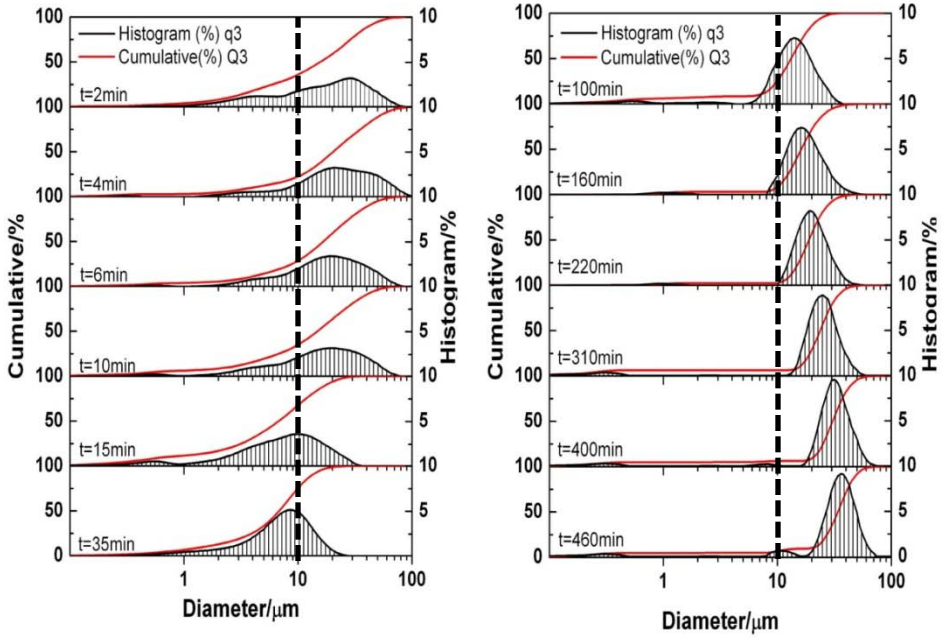
- Seed particles were rich in nickel during the nucleation stage.
- Spherical carbonate particles were obtained after few hours of co-precipitation.
- Packing density was in the range of 1.6-1.8 g/cm^3
- Particles growth was continuous.

Technical Accomplishments

$Ni_{0.3}Mn_{0.7}CO_3$ Particle size distribution and growth during CSTR co-precipitation



Individual particles grew in mass and volume during the co-precipitation

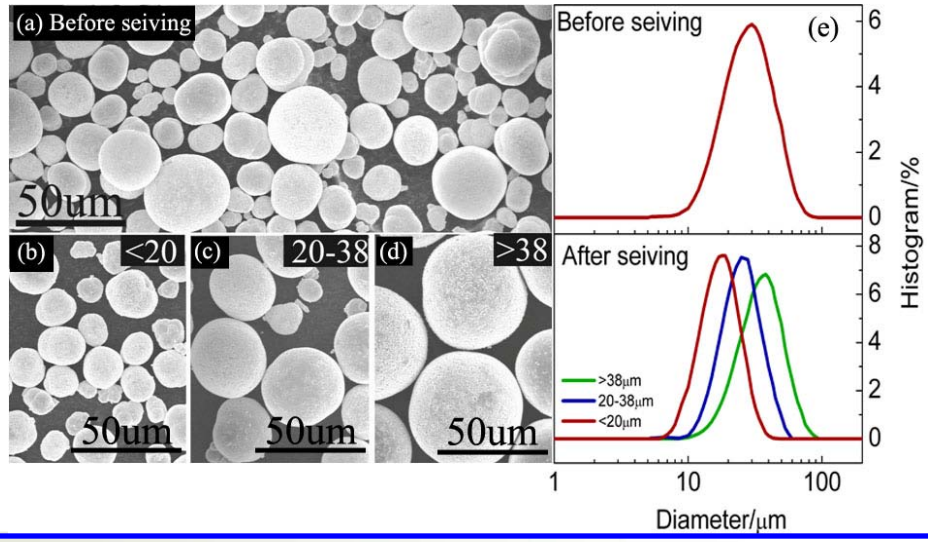


Solution: particle Selection

- **Particles below 20μm**
- **Particles between 20 and 38μm**
- **Particles above 38μm**

Continuous growth of particles for the carbonate process will have an impact on:

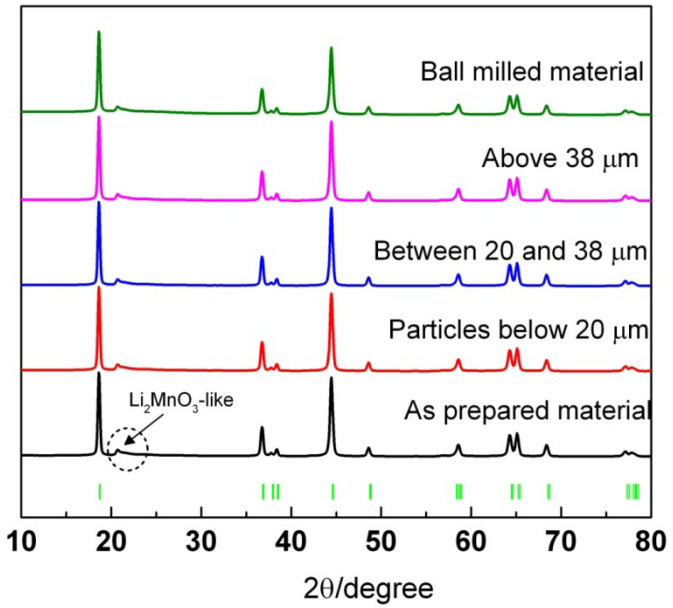
- **results consistency.**
- **lithium diffusion.**
- **engineering of electrodes.**
- **issue shared with ES materials scale up staff.**



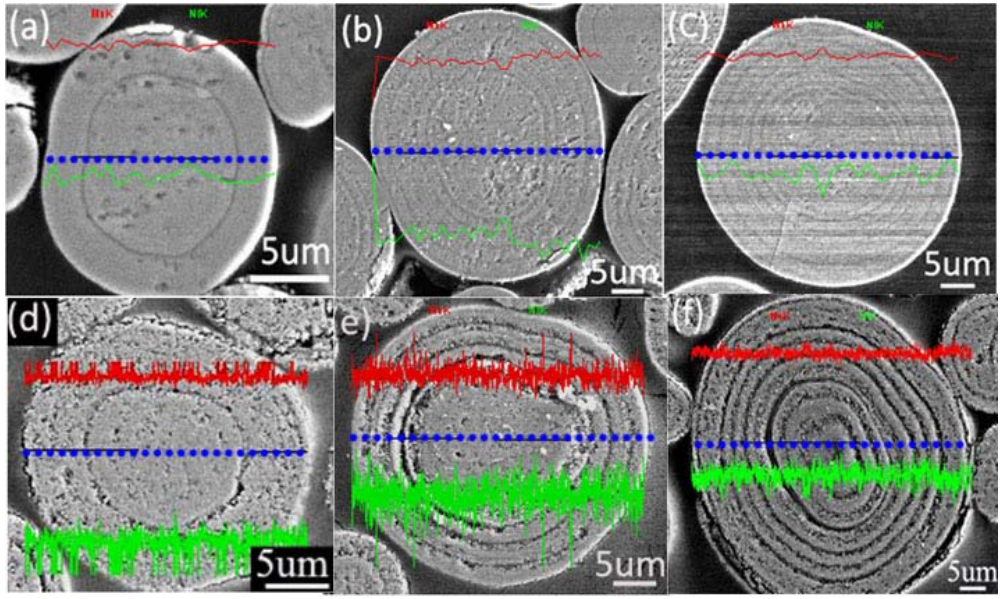
Technical Accomplishments

No noticeable structural or compositional differences between the size selected particles

X-ray diffraction analysis



Particle cross section and EDXS analysis



Particles < 20μm | 20μm <P< 38μm | P>38μm

Structural refinement

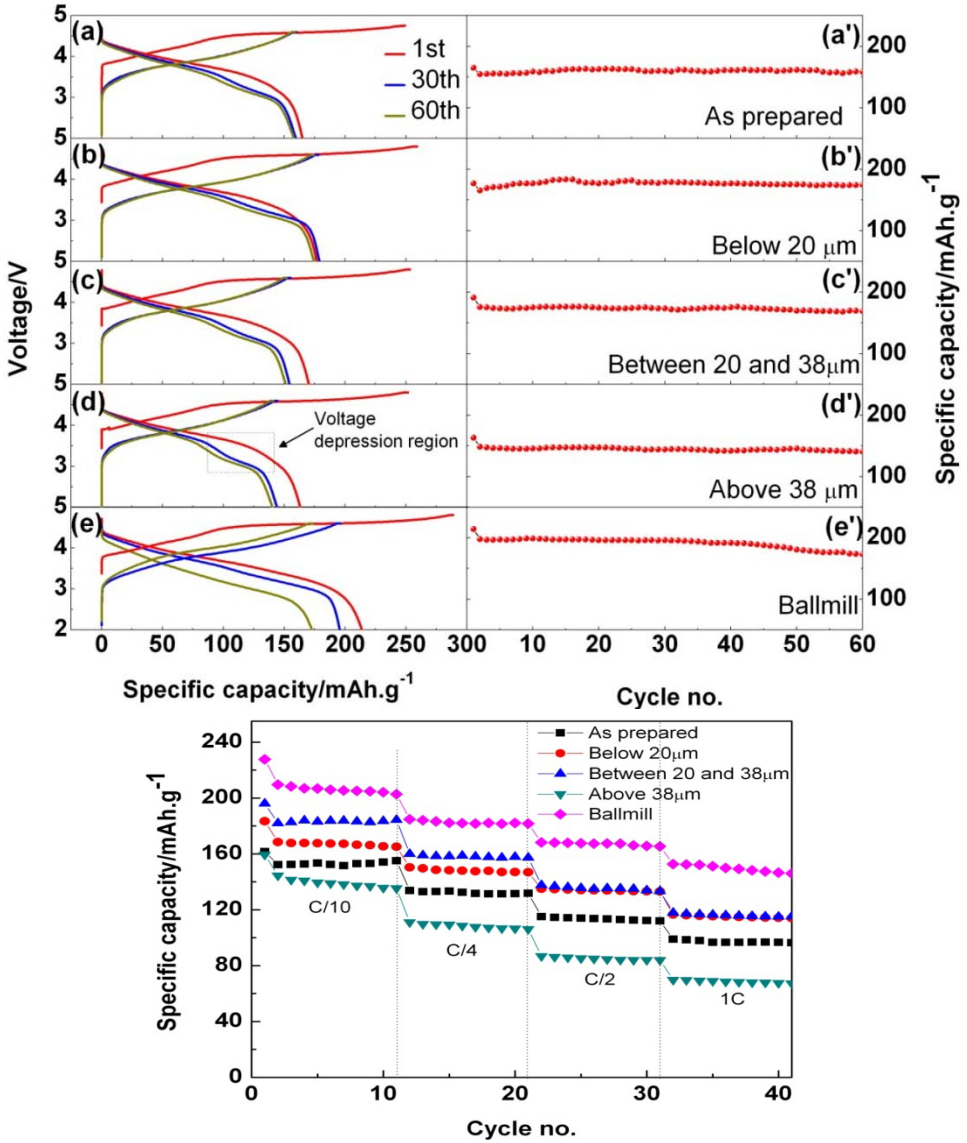
Sample	a (Å)	b (Å)	c (Å)	V(Å³)	c/a
Pristine	2.862	2.862	14.267	101.260	4.98
>38um	2.862	2.862	14.266	101.250	4.98
20-38um	2.862	2.862	14.268	101.27	4.98
<20um	2.862	2.862	14.268	101.27	4.98

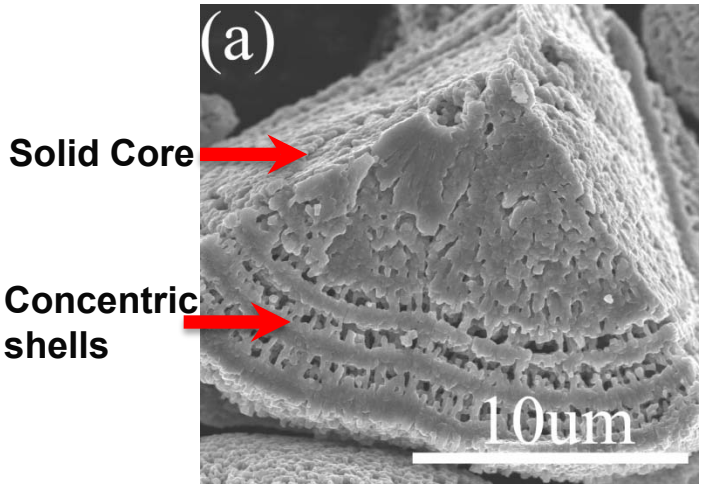
ICP analysis

Sample	Mn (atomic %)	Ni (atomic%)	Mn/Ni (atomic)	Li/(Mn+Ni) (atomic)
<20um	75.620	24.380	3.1017	1.49
20-38um	75.889	24.111	3.1475	1.52
>38um	75.935	24.065	3.1554	1.51

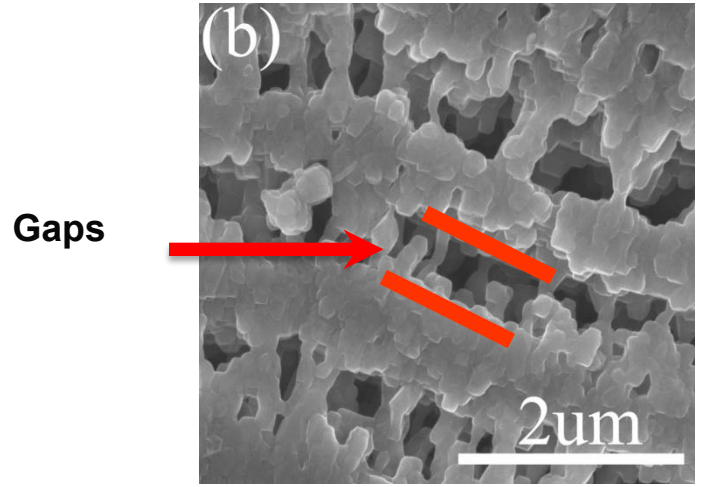
Technical Accomplishments

The capacity and rate performance of the material depends upon the size of particles





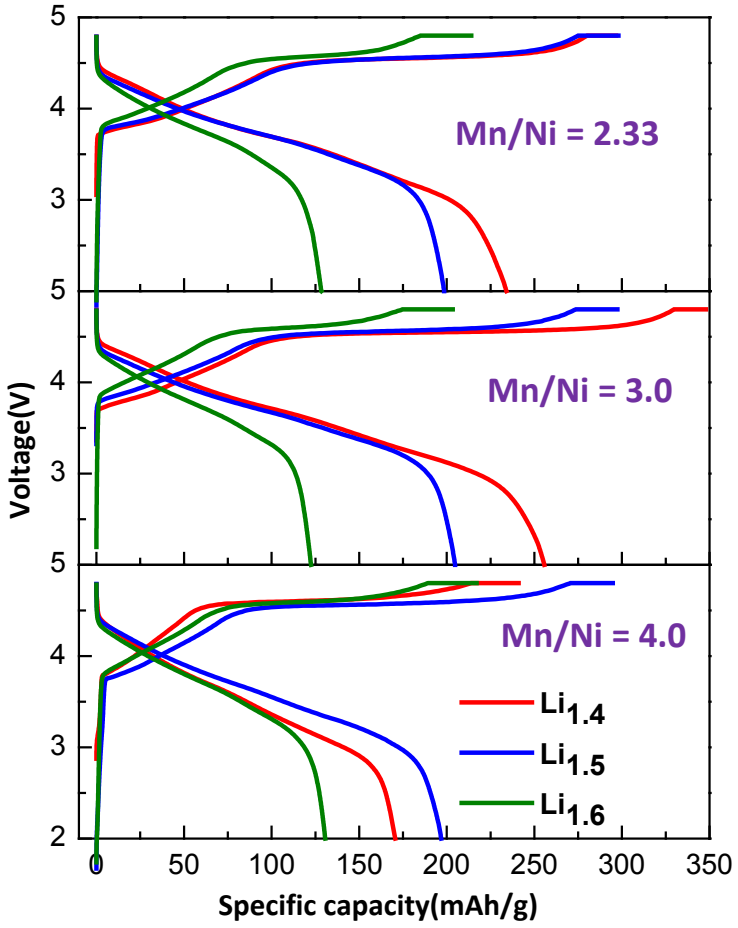
This morphology could make the particle fragile during electrode calendaring

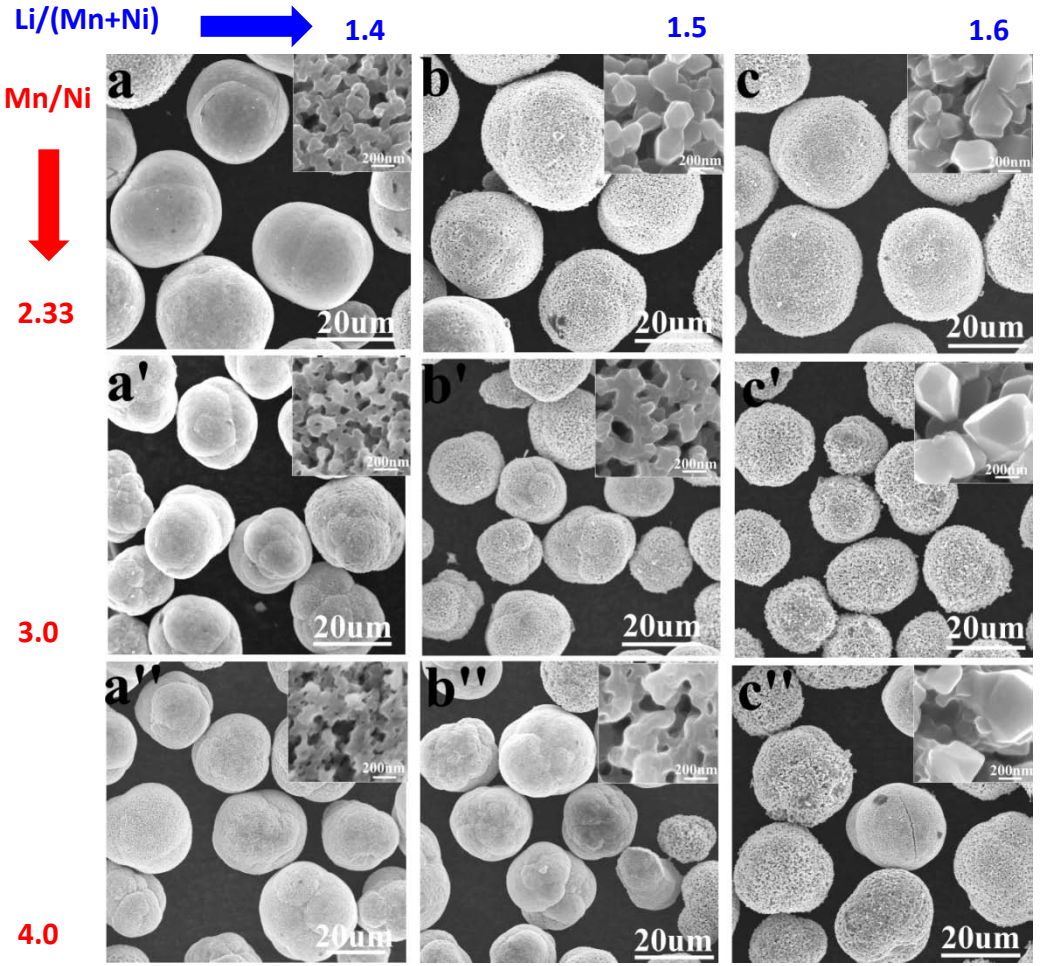


The gaps could make lithium diffusion difficult

Technical Accomplishments

Continuous growth of particles has been observed for different compositions $Ni_xMn_yCO_3$



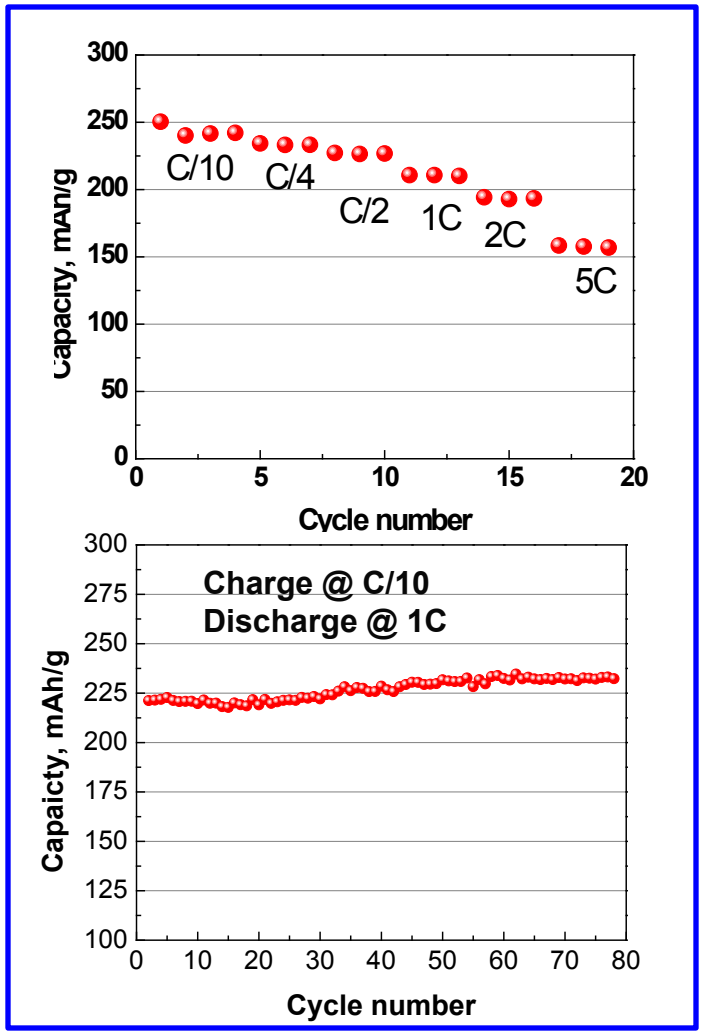


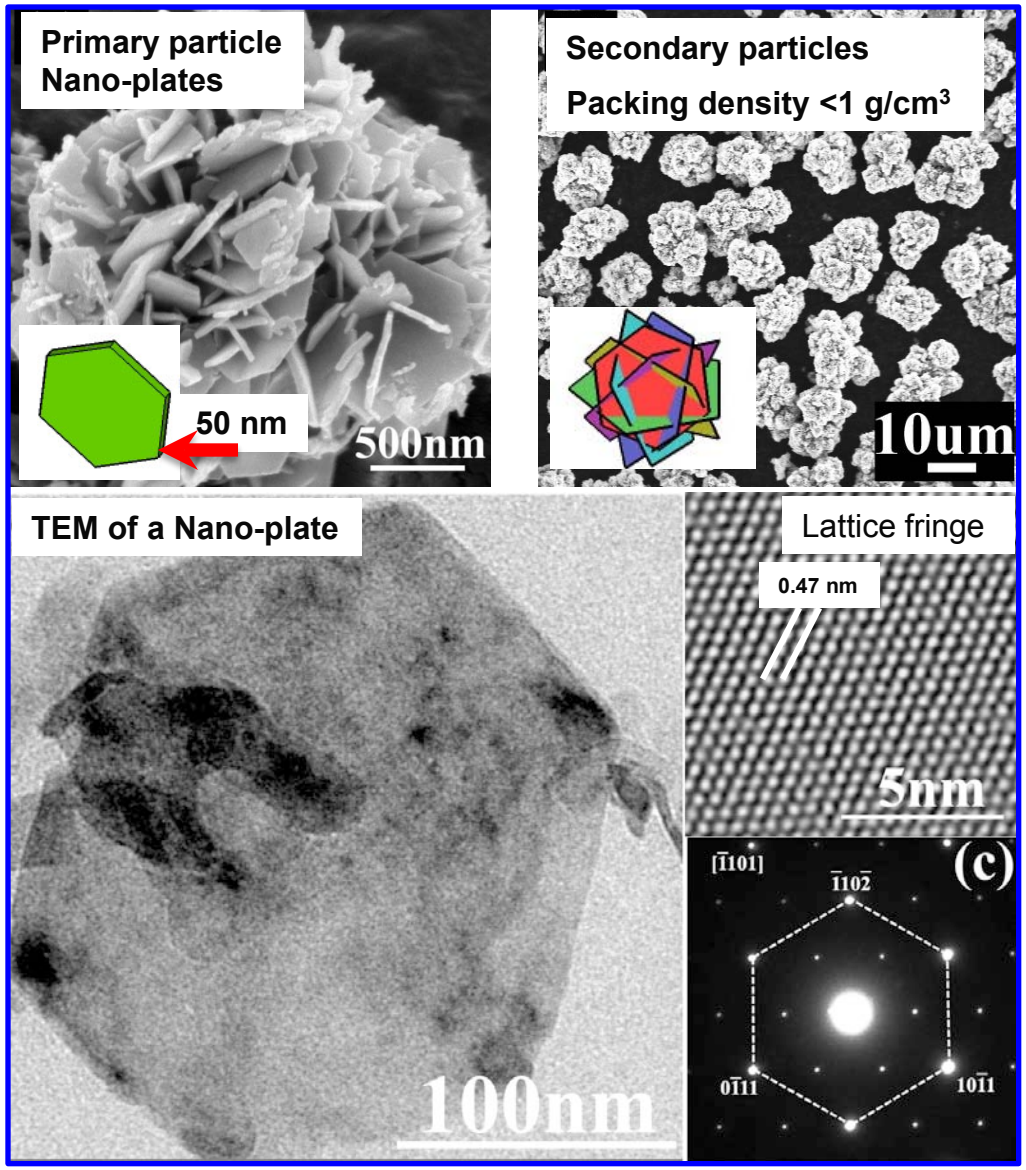
The capacity is higher for Mn/Ni = 3.0 and Li/(Ni+Mn) = 1.4

$Ni_xMn_yCO_3$ (y/x = 2.33, 3, and 4) particles were selected below 20 µm

Technical Accomplishments

Synthesis of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ using $Ni_{0.25}Mn_{0.75}(OH)_2$ nano-plates

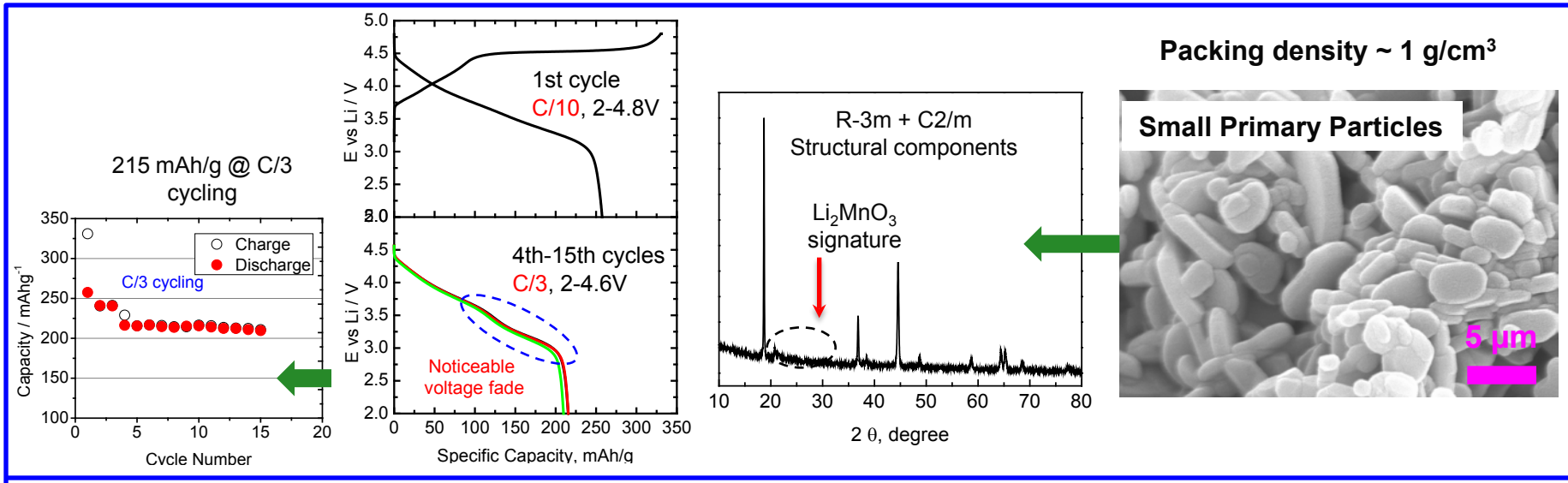


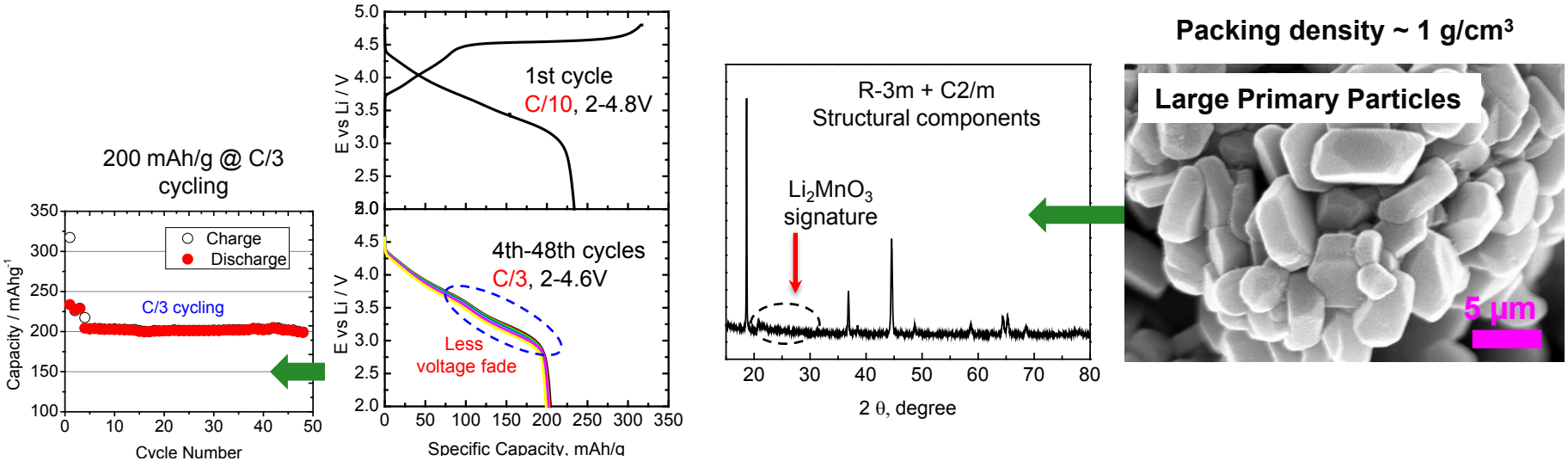


Nano-plates morphology improved the rate capability of the material

Technical Accomplishments

$Li_{1+x}(Ni_{0.25}Mn_{0.75})O_{2+d}$ made of $Ni_{0.25}Mn_{0.75}(OH)_2$: effect of primary particles

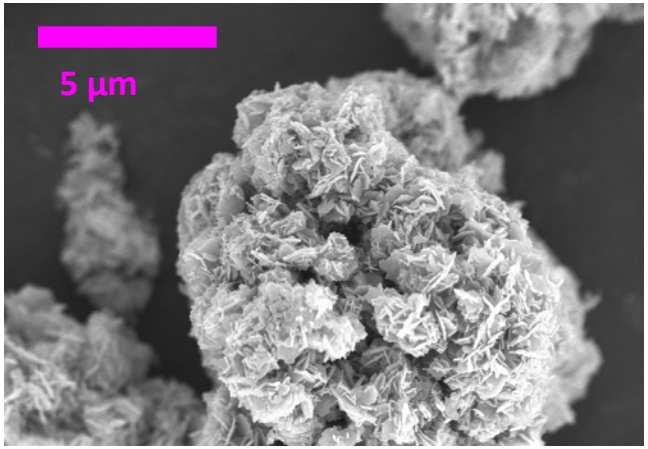




Technical Accomplishments

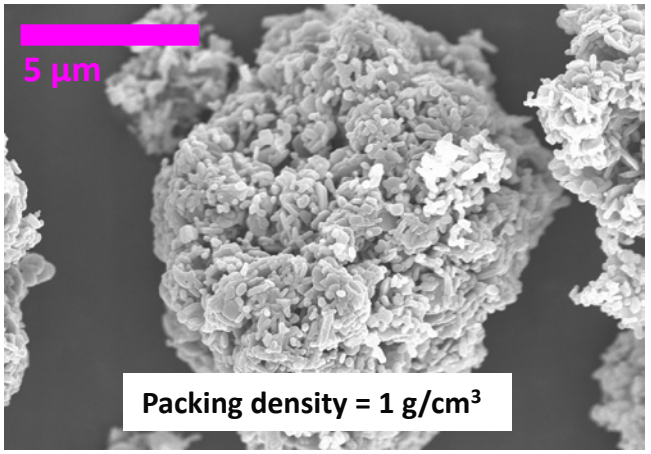
Recent development on materials made from hydroxide process

$Ni_{0.25}Mn_{0.75}(OH)_2$ Precursor

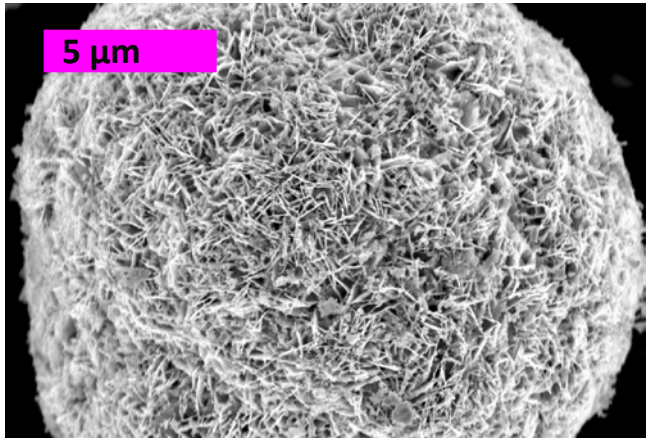


Li_2CO_3

Lithiated cathode material

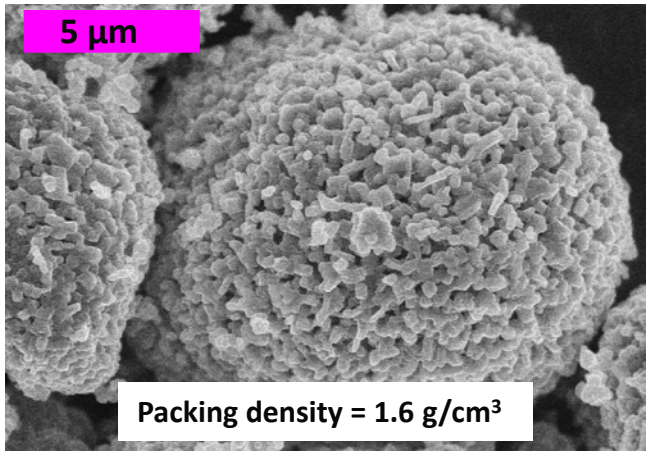


$Ni_{0.25}Mn_{0.75}(OH)_2$ Precursor



Li_2CO_3

Lithiated cathode material



Tuning of both experimental and engineering conditions during CTRS co-precipitation have led to obtaining spherical particles and higher packing density $Ni_{0.25}Mn_{0.75}(OH)_2$

Collaborations

Energy Systems Division, Argonne

Collaboration to assist the scale up of high capacity cathode materials via the transfer of the carbonate co-precipatiation technology.

Washington University in Saint Louis & X-Tend Energy

Collaboration to characterize and evaluate the electrochemistry of advanced cathode materials produced by aerosol synthesis process.

Binghamton University

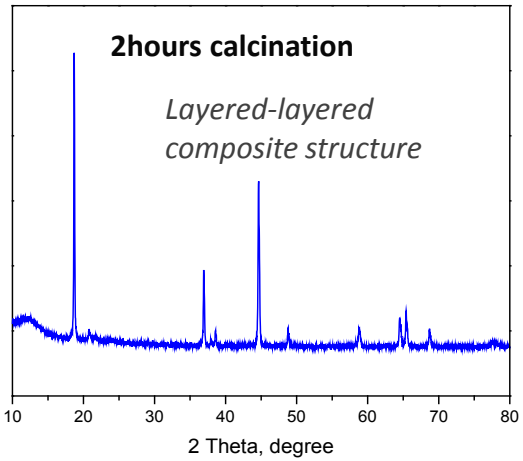
Ph.D. work is being performed at Argonne on the synthesis, structural, and electrochemical characterizations of high capacity materials.

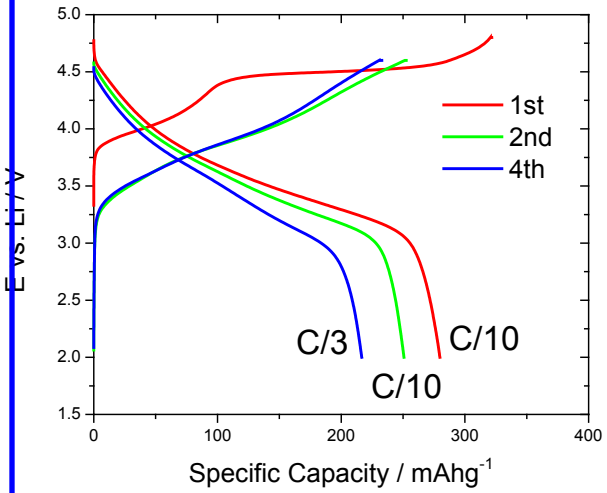
Pacific Northwestern National Laboratory

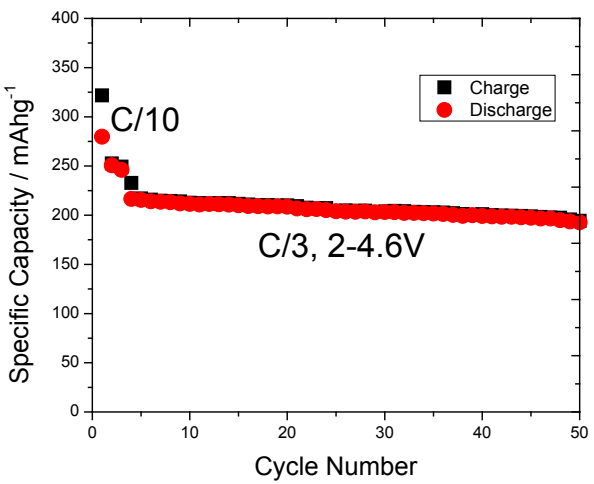
Collaboration on the characterization of high capacity composite materials at atomic scale using aberration corrected STEM imaging and atomic level EELS analysis.

Collaboration

Collaboration to characterize and evaluate the electrochemistry advanced cathode materials produced by aerosol synthesis process.

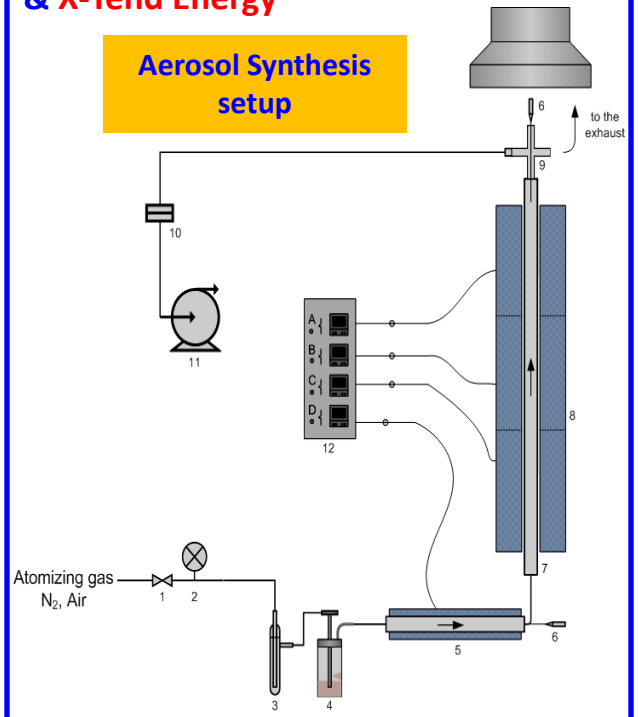






Washington University in Saint Louis & X-Tend Energy

Aerosol Synthesis setup



Advantages:

- **One step process**
- **Consistency in results**
- **Low cost process**
- **Scalable process**

Future Work

- Continue the work on synthesis of high capacity and stable materials via the carbonate co-precipitation method with the focus on: (1) preventing growth of the precursor particles above 20 µm during co-precipitation; (2) optimizing the Li/transition metal ratio because the particles have Ni-hydroxide enriched cores and are sensitive to moisture; and (3) determining the proper balance between porosity and surface area of particles because the former is suited for improving the capacity and rate capability and the latter is unsuited for long life due to parasitic side reactions with electrolytes.

- Continue the work on synthesis of hydroxide and oxalate precursors using the same approach of coordinating the science of synthesis with the science of function. In the case of hydroxide co-precipitation method, the focus will be on further tuning the experimental and engineering condition in order to prepare spherical and high packing density precursors that will serve to prepare variety of cathode including the 5V-spinel and high capacity composite materials.

- Assist the synthesis combinatory (robot assisted) effort recently adopted for ABR program in order to investigate the landscape of cathode materials . Compositions selected by this method will be scaled up using CSTR reactor for electrochemical screening.

- Investigate the origin of voltage fade observed in Li- and Mn-rich cathode materials by benefiting from the accelerated combinatory synthesis approach.

Summary

Carbonate process:

- Systematic investigations including morphological, structural, compositional, and electrochemical characterizations were conducted on cathode materials prepared using co-precipitated carbonate precursors in a CSTR reactor.
- Continuous particle growth has been observed for carbonate precursors regardless of chemical compositions.
- The cathode samples were found to contain secondary particles composed of highly crystalline polyhedral primary particles whose sizes depend upon lithium contents.
- The particles larger than 20 µm developed concentric ring layers within their cores, which compromised the overall electrochemical performance in terms of capacity and rate capability due to the sequential void that separates the inner layers.
- Ball milling improved the electrochemical performance; however, it also accelerated side reactions between the electrode and electrolyte at high operating voltage, leading to gradual capacity loss with cycling.

Hydroxide process:

- Variety of morphologies were obtained using CSTR-hydroxide process.
- Secondary particles (10 µm size) comprising nano-plate primary particles were found to deliver over 200 mAh/g capacity at the 1C rate. However, the packing density was below 1 g/cm^3.
- $Ni_{0.25}Mn_{0.75}(OH)_2$ precursor having spherical particles (15 µm) and high packing density (1.6 g/cm^3) has been obtained by tuning the experimental and engineering conditions during CTRS co-precipitation.