Process Development and Scale-Up of Advanced Active Battery Materials

Ozge Kahvecioglu (PI)

Argonne National Laboratory
Project ID: BAT167

June 2, 2020

OVERVIEW

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2020
- Percent complete: on going

Budget

- Total project funding:
  - $900K in FY19

Barriers

- Cost: Reduce manufacturing costs with scalable continuous processes
- Availability: Advanced cathode materials needed for research are not commercially available with the desired composition or morphology
- Performance & Life: High energy density advanced cathode materials have major performance and life issues

Partners

- Collaborators in Deep-Dive into Next-Generation Cathode Materials (BAT375, BAT252)
  - ANL, ORNL, NREL, BNL, PNNL
- Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing (BAT164)
  - Jianlin Li, David Wood, ORNL
- Improving Battery Performance through Structure-Morphology Optimization (BAT402)
  - Venkat Srinivasan, ANL
- In Situ Spectroscopy of Solvothermal Synthesis of Next-Generation Cathode Materials (BAT183)
  - Feng Wang, BNL
- Suppressing Phase Transition by Graphene Coating on LNO
  - Kyu-Young Park, Northwestern University

OBJECTIVES AND RELEVANCE

- The objective of this program is to provide a systematic research approach to:
  - Produce and provide **sufficient quantities of high quality** battery materials for industrial evaluation and to support further research
  - Evaluate **emerging synthesis technologies** for the production of experimental battery materials
  - Develop **cost-effective, scalable** processes for manufacturing of advance materials that are not commercially available
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between invention of new 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 and prototyping in large format cells
  - To allow battery community access to new materials and advance further research

MILESTONES

Month/Year	Description of Milestones and Go/No-Go decision	Status
	Deep-Dive into Next-Generation Cathode Materials (BAT375, BAT252) Collaboration	**On track**
July 2019	Screening of LNO-based materials (LNO and 90%Ni) at 1L TVR	Complete
October 2019	Scaling up of promising candidates at 10L TVR	Complete
December 2019	Introducing new LNO-based materials (95%Ni) at 1L TVR	Complete
March 2020	Scaling up of promising candidates and baseline NCM622 material at 10L TVR	On Track
April 2020	Milestone: Feedback from participants were retrieved and some are being reported in AMR 2020	Complete
	(Journal publications are in preparation)	On track
	Ex-situ XAS Experiments to Understand Differential Effects of Mn and Co on LNO-Based Materials	**On track**
February 2020	Ex-situ XAS and S-XRD experiments for pristine and cycled cathodes at ANL's APS	Complete
April 2020	Data interpretation (requires laboratory computer access; closed due to COVID-19)	On track
	Improving Battery Performance through Structure-Morphology Optimization (BAT402) and In Situ Spectroscopy of Solvothermal Synthesis of Next-Generation Cathode Materials (BAT183) Collaboration	**Complete**
September 2019	$Ni(OH)_2$ and $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor materials synthesized at 10L TVR were used at in-situ calcination studies using x-ray diffraction (at BNL) and small angle x-ray scattering at ANL's APS facility	Complete
April 2020	Milestone: Feedback from collaborators were received and are being reported in AMR 2020	Complete
	Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing (BAT164) Collaboration	**On track**
(May 2019)	TVR-made small size NCM811 (6-7µm) were delivered to ORNL @ 1kg scale	Complete
November 2019	Feedback from ORNL was received: TVR-made small particles showed fewer cracks compared to large commercial cathode materials	Complete
March 2020	Same electrodes were used for XFC studies at ORNL	On track
April 2020	Milestone and Go/No-Go: Future collaborations on XFC rate capability research	On-going
	Collaboration with Northwestern University	**On track**
June'19 & February'20	LNO materials (3 and 10 µm particle sizes) were delivered to NU for graphene coating	Complete
April 2020	Milestone: Journal publication is in preparation	On track

APPROACH AND STRATEGY

- Basic science researchers invent new materials, synthesize small amounts and evaluate electrochemical performance in small cell formats
- Materials Engineering Research Facility (MERF) collects information about new materials, prioritizes them based on level of interest, validates performance and scale up feasibility
- MERF evaluates new emerging manufacturing technologies, conducts process R&D, develops and validates optimal process parameters for production of new materials
- Proof of concept in stages from 10g to 100g to kg's
- Make new materials available to assist basic researchers and to facilitate industrial evaluation
- Provide feedback to discovery scientists helping promote future research
- The program evaluates emerging synthesis techniques that can reduce costs

TECHNICAL ACCOMPLISHMENTS

Several Different Cathode Materials: Synthesis, Scale up and Delivery

- Synthesized and scaled up commercially unavailable cathode materials/structures
  - Materials synthesized using 1L Taylor Vortex Reactor (TVR) in **FY19**, were scaled up using 10L TVR in **FY20**:
    - $Ni(OH)_2$, $Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2$, $Ni_{0.90}Co_{0.10}(OH)_2$, $Ni_{0.90}Mn_{0.10}(OH)_2$, $Ni_{0.80}Co_{0.10}Mn_{0.10}(OH)_2$
    - Calcination studies focusing on optimal Li ratio and optimal temperature were done
    - Materials were delivered to collaborators and are being reported in FY20 (BAT402, BAT375, BAT183, BAT164)
  - New materials were introduced to the BAT375 program using 1L TVR in FY20:
    - $Ni_{0.95}Co_{0.05}(OH)_2$, $Ni_{0.95}Mn_{0.05}(OH)_2$, $Ni_{0.95}Mg_{0.05}(OH)_2$ (under optimization)
  - Baseline material (NCM622) was scaled up at 10L TVR (BAT375) (under optimization)
  - NCM811 and $LiNiO_2$ at different particle sizes (Northwestern University)
- Investigate the local structure and oxidation state change on pristine and cycled LNO-based materials in full-cells:
  - Ex-situ XAS of pristine and cycled LNO-based materials in full-cell
  - Ex-situ synchrotron XRD: new phase formation on cycled LNO-based materials
- Post treatment of cathode materials after calcination
  - Surface impurity removal by washing & drying & re-calcining, using different conditions

TECHNICAL ACCOMPLISHMENT

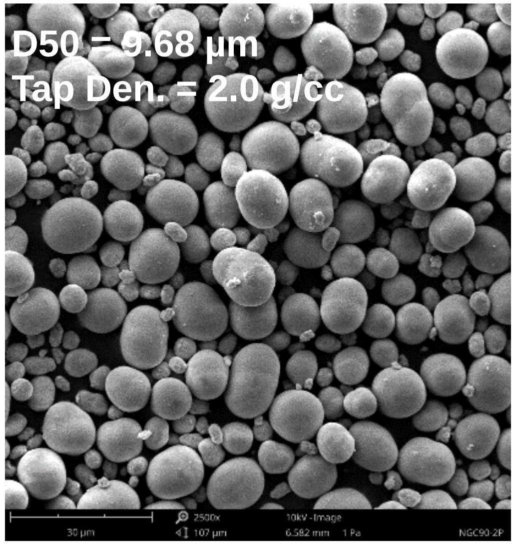
Synthesis of LNO-Based Cathode Active Materials

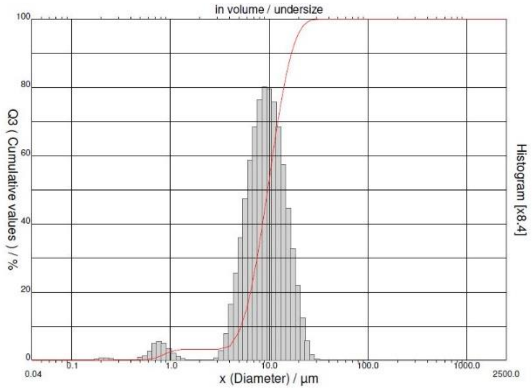
- A typical feature of continuous co-precipitation operation introduces smaller particles as a consequence of applying high pH conditions (e.g.; pH ≥ 11.7) along with extended reaction time.
- While precursor particles have bi-modal particle size distribution, PSD, (4-6% of particles are ≤ 1µm); those converted to narrow PSD after calcination at high temperature.
- Secondary particle morphologies appear dense and spherical in general, with closely packed primaries, having ~0.3 m^2/g surface area.
- Surface Li_2CO_3 impurity presents at all screened Li ratios and calcination temperatures → requiring post treatment

Exemplary scaled up cathode material: $LiNiO_2$

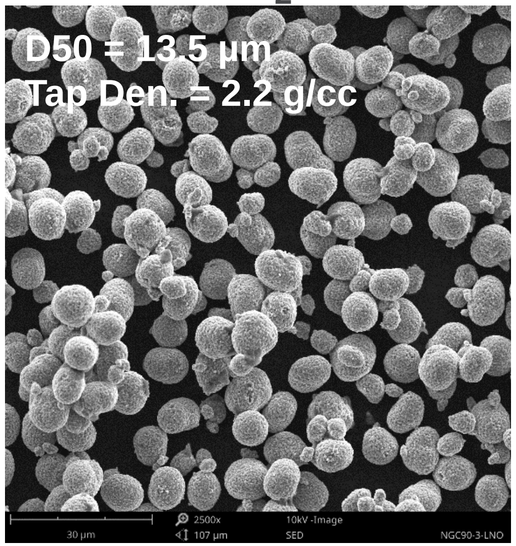
SEM images and PSD analysis

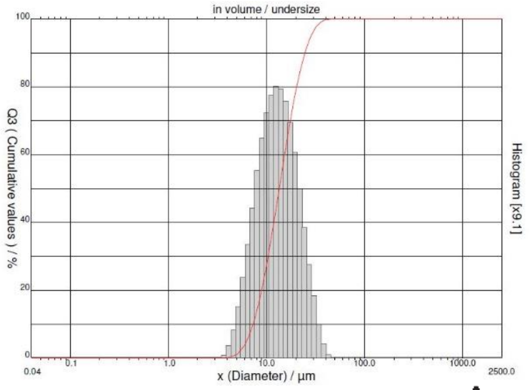
$Ni(OH)_2$





$LiNiO_2$



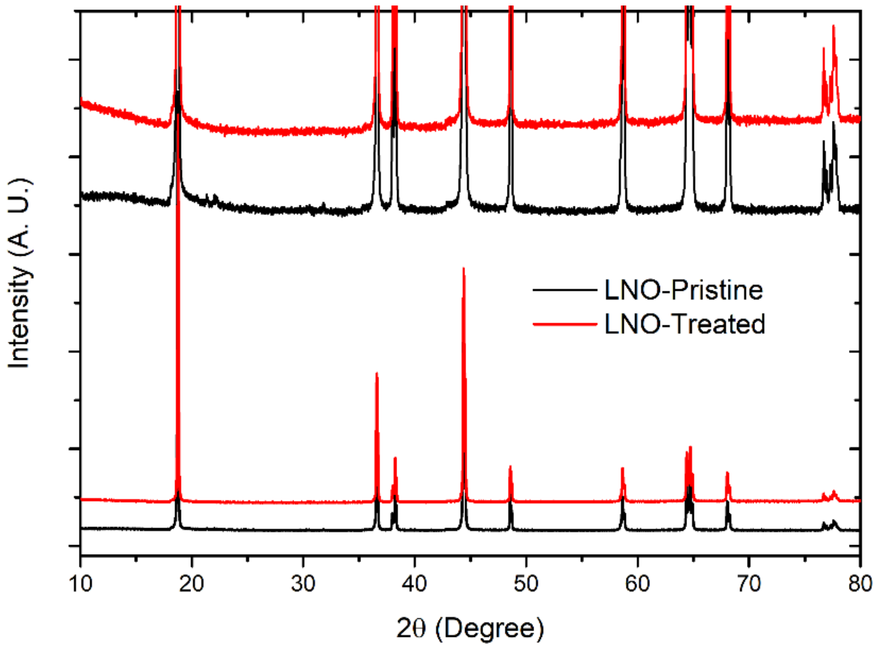


TECHNICAL ACCOMPLISHMENT

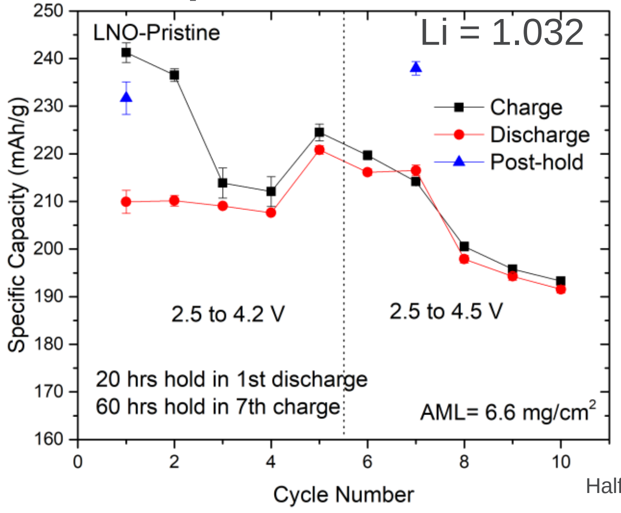
Post Treatment of Cathodes

- An attempt to remove the Li_2CO_3 surface impurity, which causes post-processing problems (e.g.; high pH of the cathode slurries, gelation, and etc.), was achieved by washing, vacuum drying and re-calcining of the cathode particles.

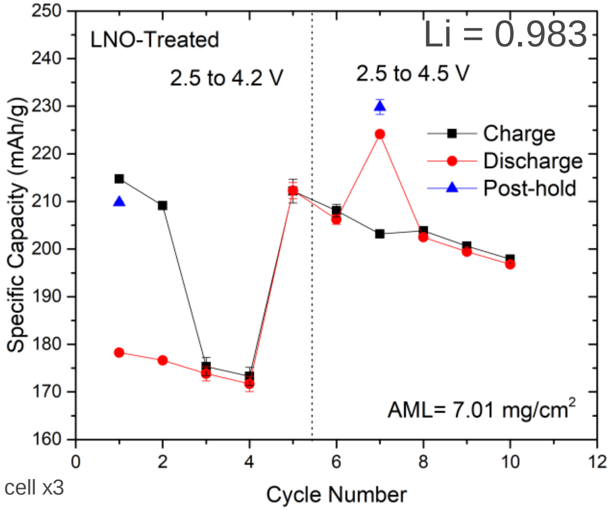
XRD Profiles of Pristine and Treated LNO

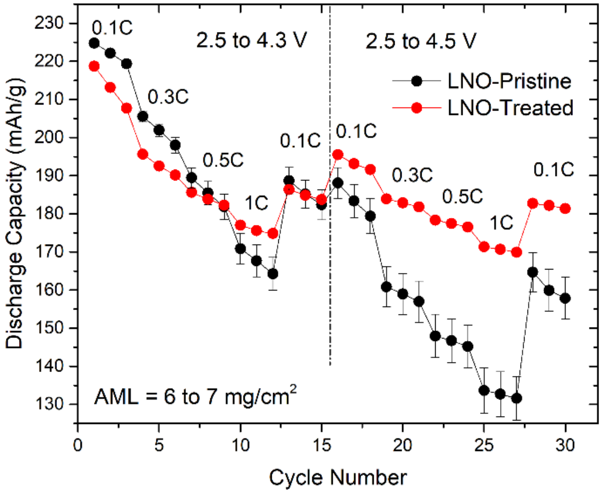


RNGC Specific Protocols for Pristine and Treated LNO Cathode



Half coin cell x3





- The Li_2CO_3 impurity was washed off, as is evident by the XRD profile.
- Due to different surface properties and amount of active Li, the nature of capacity trend of pristine and treated cathode is different.
- Detailed electrochemical characterization results are reported in multiple projects (BAT375, BAT252)

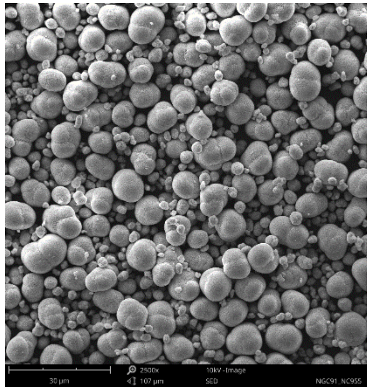
TECHNICAL ACCOMPLISHMENTS

MERF-Synthesized Low-Co Precursors Used in RNGC (BAT375, BAT252)

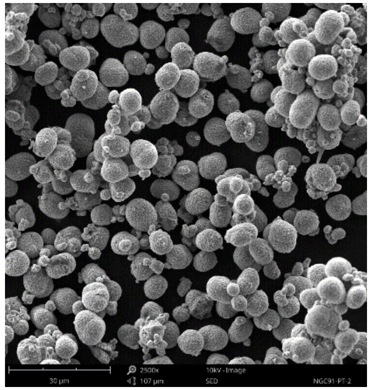
- An exemplary feedback from RNGC collaborators → Typical data from $LiNi_{0.95}Co_{0.05}O_2$ shown below

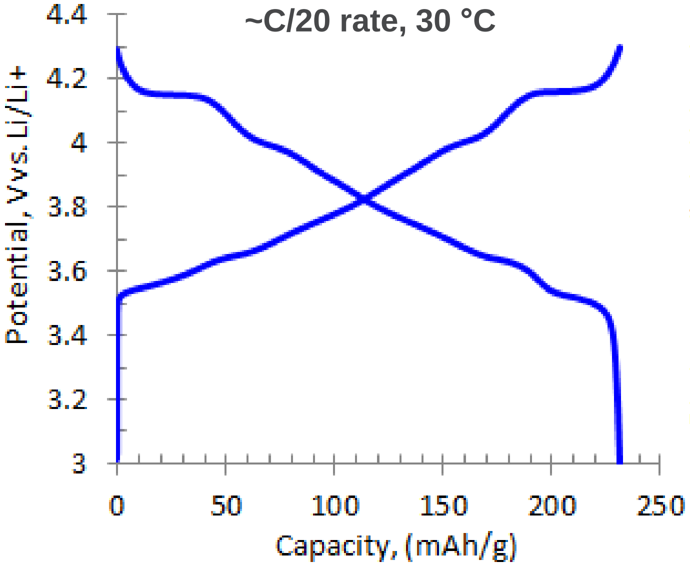
SEM | **Voltage Profile** | **Full cell, 1 HEHV protocol, 3-4.2 V, 30°C**

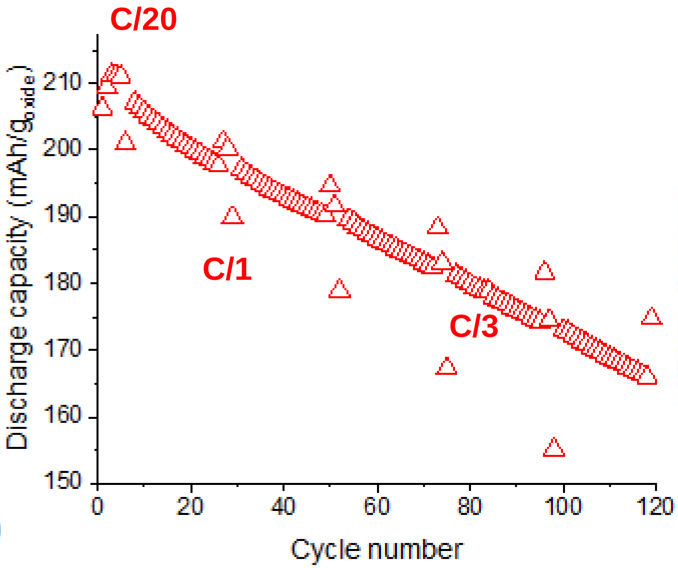
Hydroxide precursor

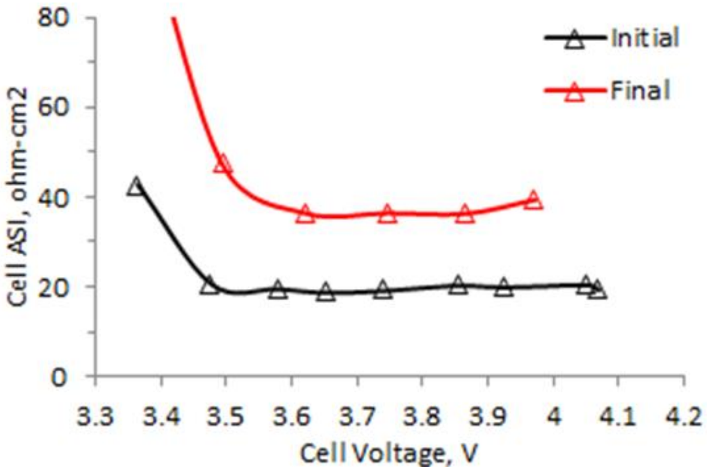


Oxide particles









- Metal hydroxide precursor showed bi-modal PSD
- Tests in half-cells (vs. Li) show excellent capacity
- Data from full-cells (vs. graphite anode) show expected capacity fade and impedance rise

✓ Other oxides prepared include $LiNiO_2$, $LiNi_{0.90}Mn_{0.10}O_2$ & $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$

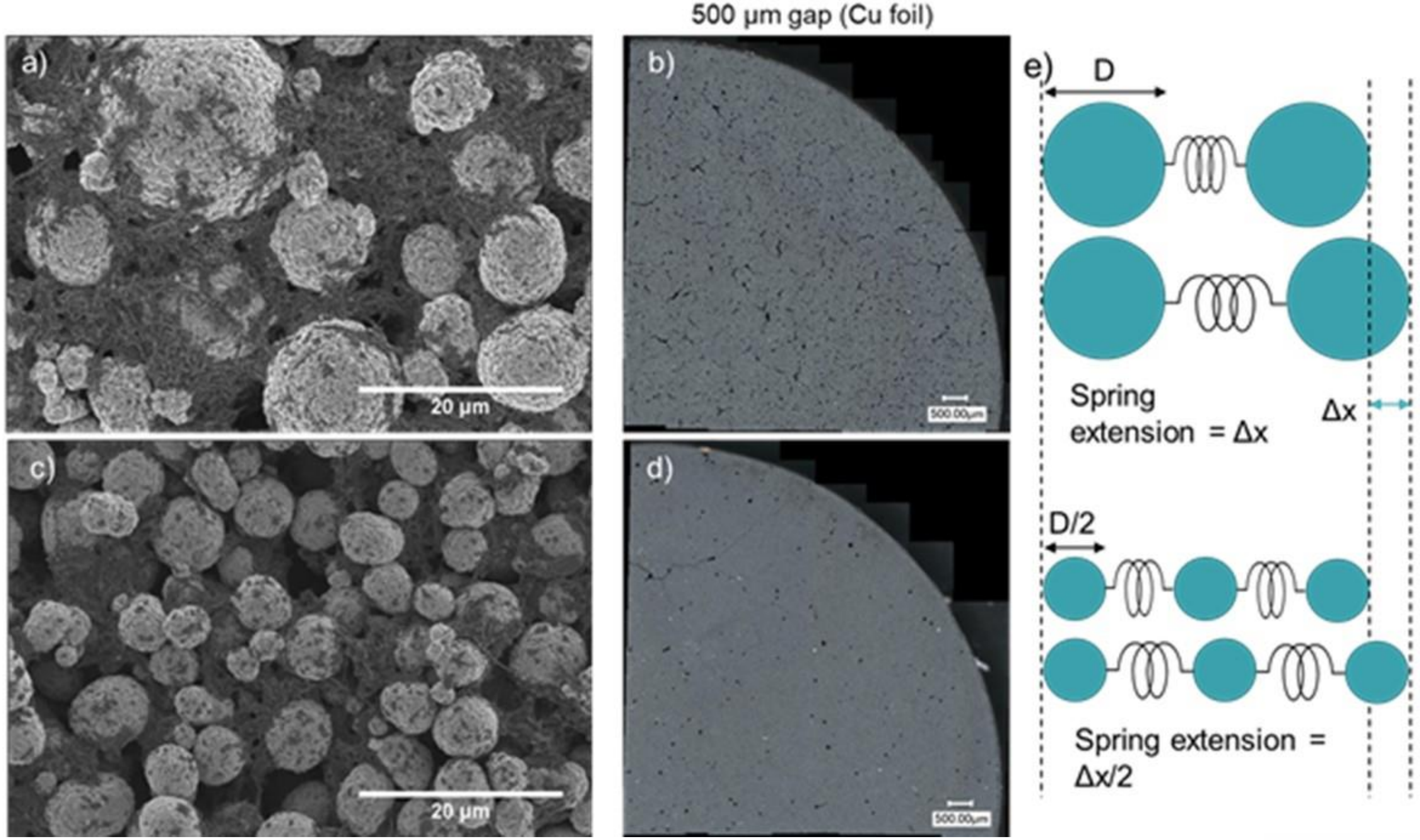
Data Courtesy: Daniel Abraham, Adam Tornheim (ANL)

Also see BAT252

TECHNICAL ACCOMPLISHMENTS

ANL-ORNL Collaboration: In support for “Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing (BAT164)”

- Small, dense, spherical, secondary NCM particles between 5 – 8 µm are not commercially available:
  - $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material delivery @ 1kg scale to ORNL



NCM811 by TVR, material properties:
$Li_{1.021}Ni_{0.793}Co_{0.105}Mn_{0.103}O_2$
D_{50} = 7.4 µm
Tap density = 1.93 g/cc

Figure comparing particle size effect on electrode cracking. Top row (a,b) shows commercial NCM811 material, bottom row (c,d) shows TVR-made NCM811 which shows fewer cracks.

Image Courtesy: Jianlin Li, ORNL

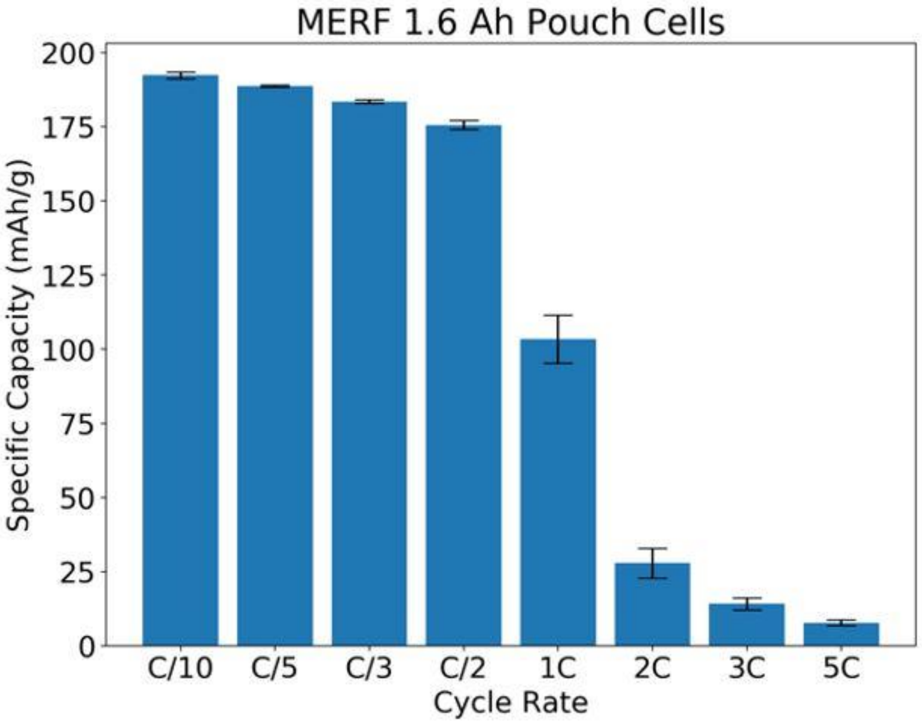
Ritu Sahore et.al, *ACS Sustainable Chem. Eng*. 2020, 8, 3162 – 3169.

TECHNICAL ACCOMPLISHMENTS

ANL-ORNL Collaboration: MERF's Materials (ANL) Built in Thick Electrodes (ORNL, BAT164) Tested for Extreme Fast Charging, XFC (ORNL)

- Scaled up NCM811 cathode particles (D_{50} = 7.4 µm) with low surface area (BET = 0.392 m^2/g) has been used in BAT164 for thick bilayer electrode manufacturing at ORNL. These electrodes were tested under XFC protocols.

Rate Capability of Graded-Cells



- 3 V Tap → 3 C/10 Formation Cycles → Rate Capability → 6C – 1C long term cycling.

Electrode Processing Details (ORNL)

- Cathodes were double-side coated using a dual-pass process for both sides (3.0 mAh/cm^2 per pass):
- Small (D_{50} = 7.4 µm) MERF NMC 811 particles on top (against separator)
- Large (D_{50} = 12 µm) Commercial NMC 811 particles on bottom (against Al current collector)
- More details can be found in BAT164

Preliminary Conclusions (ORNL)

- Structured NMP-processed cathodes have improved high discharge-rate capability

Image & Data Courtesy: Jianlin Li, David Wood Alexander Kukay (ORNL)

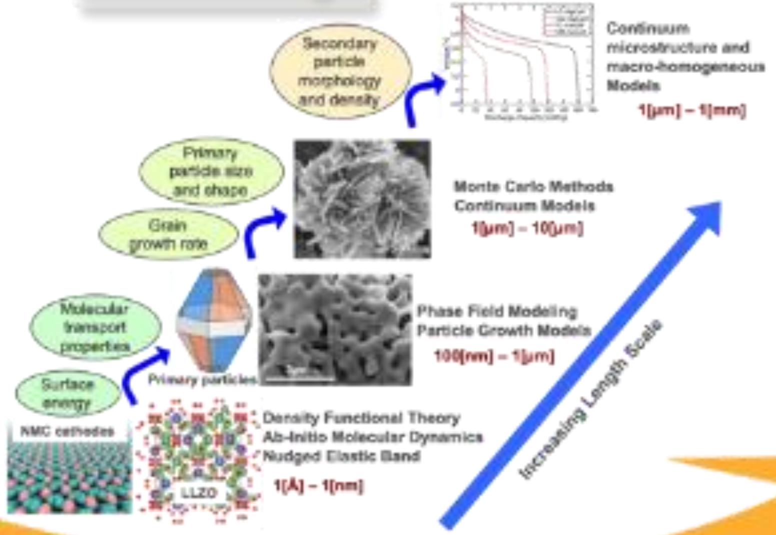
TECHNICAL ACCOMPLISHMENT

ANL-BNL Collaboration Established under the Processing Science & Engineering Program

Lab-scale Processing

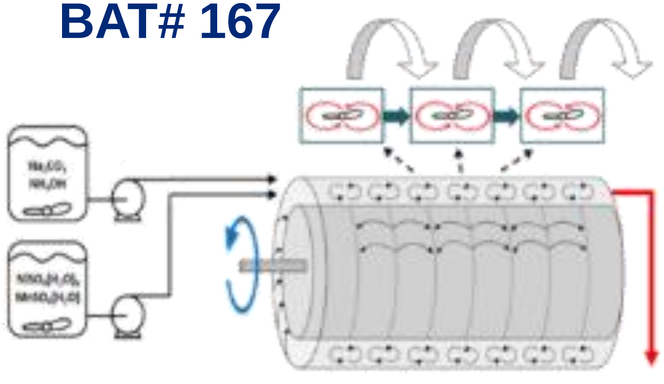
“Black box”

Modeling **BAT# 402**



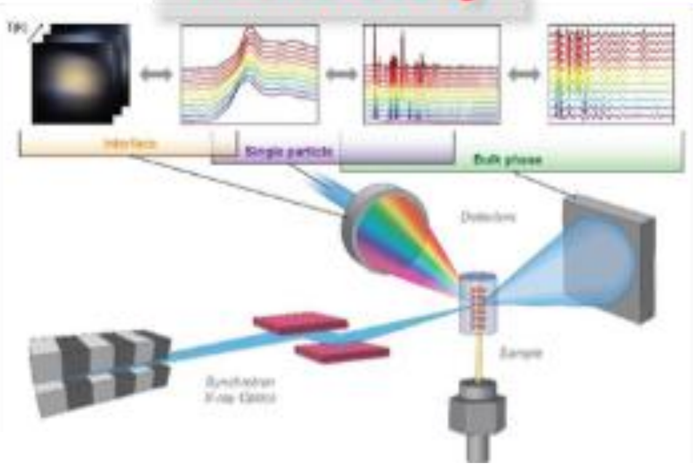
Scaled-up Processing

BAT# 167



Taylor vortex reactor

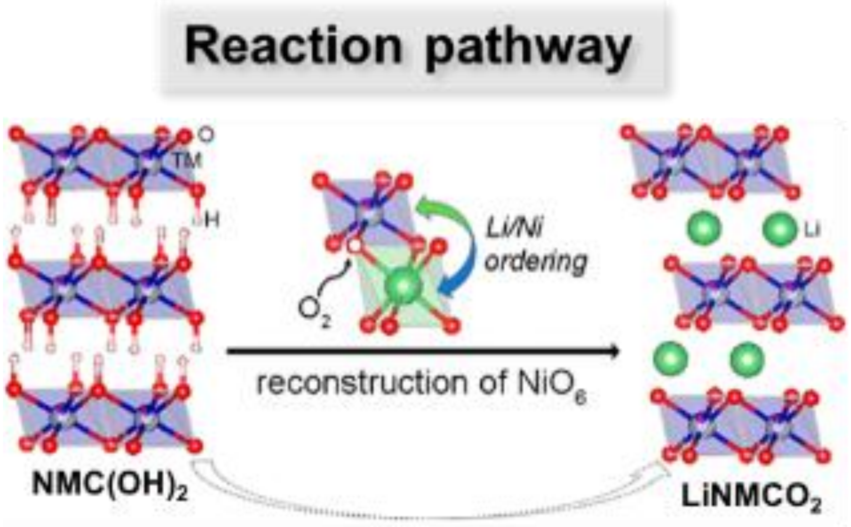
***In situ* Study**



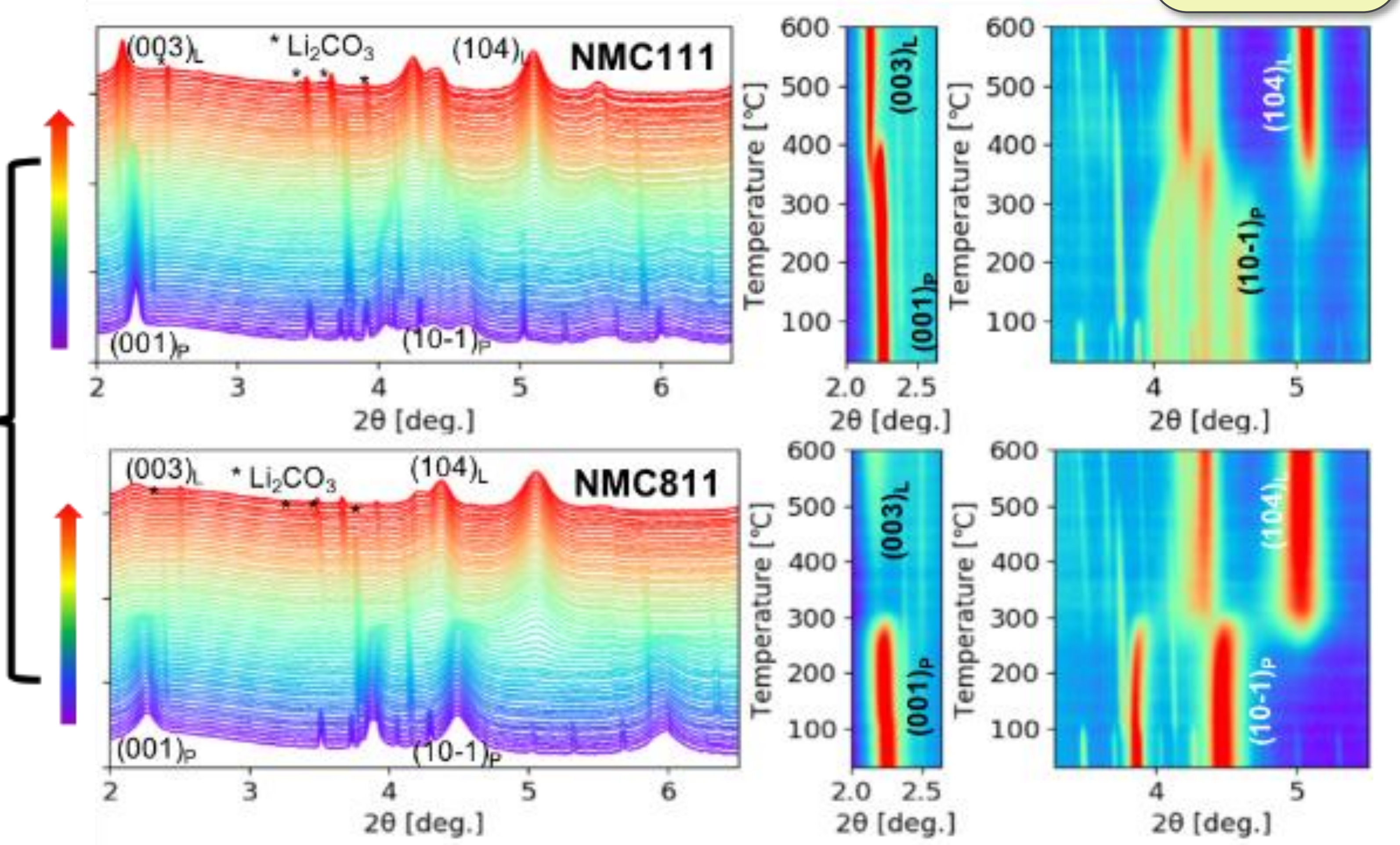
- **Traditional synthesis:** *trial & error*
- ➢ **Synthesis by design:** modeling, *in situ* study in synergy with scaled-up processing.

TECHNICAL ACCOMPLISHMENT

ANL-BNL Collaboration: Composition-dependent reaction pathways (1): NMC811 *vs* NMC111



(J. Am. Chem. Soc. 140, 12484 (2018))

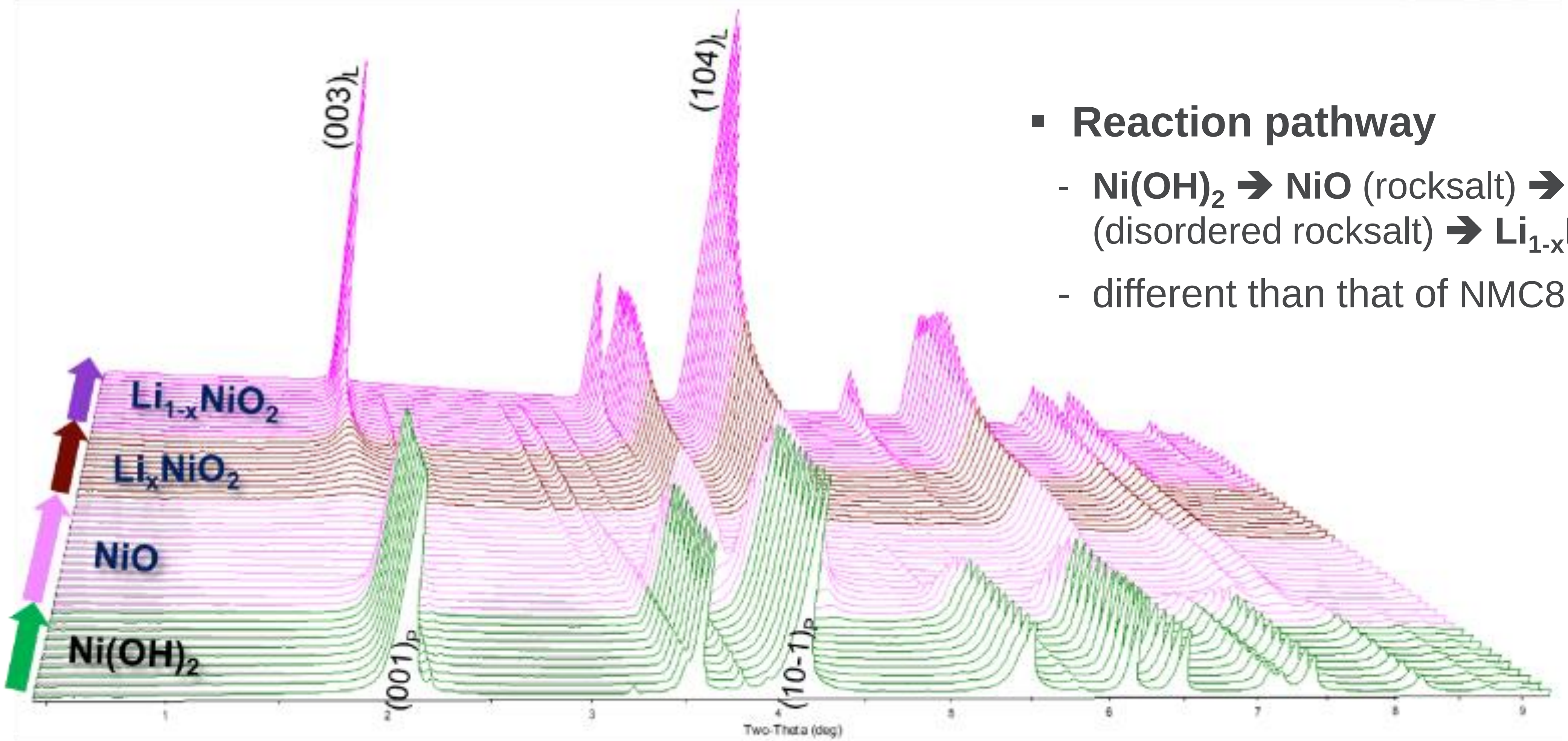


- **NMC111**: gradual transformation into layered oxides with high ordering; **NMC811:** abrupt transformation/ low ordering.

Also see BAT183

TECHNICAL ACCOMPLISHMENT

ANL-BNL Collaboration: Composition-dependent reaction pathways (2): $LiNiO_2$



- **Reaction pathway**
  - **$Ni(OH)_2$** ➔ **NiO** (rocksalt) ➔ **Li_xNiO_2** (disordered rocksalt) ➔ **$Li_{1-x}NiO_2$** (layered)
  - different than that of NMC811/NMC333

- **Insights into synthesis:** i) role of Mn/Co in tuning the reaction pathways; ii) design of procedures/parameters for synthesizing high-Ni NMC: balancing lithiation *vs.* Li/O loss.

Data and Image Courtesy: Feng Wang, Jianming Bai, BNL

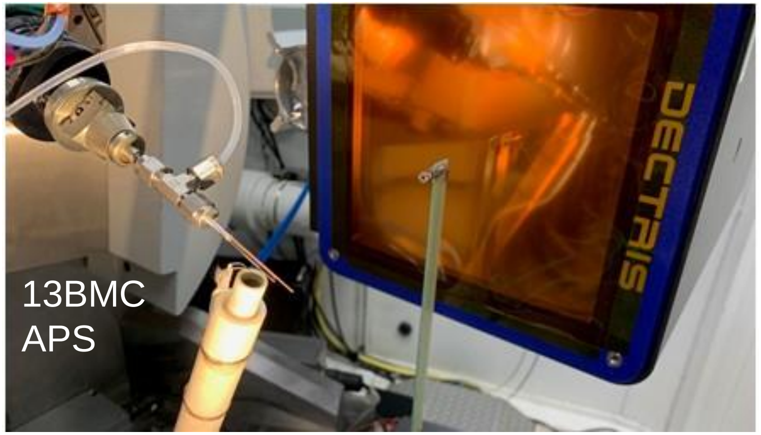
Also see BAT183

TECHNICAL ACCOMPLISHMENTS

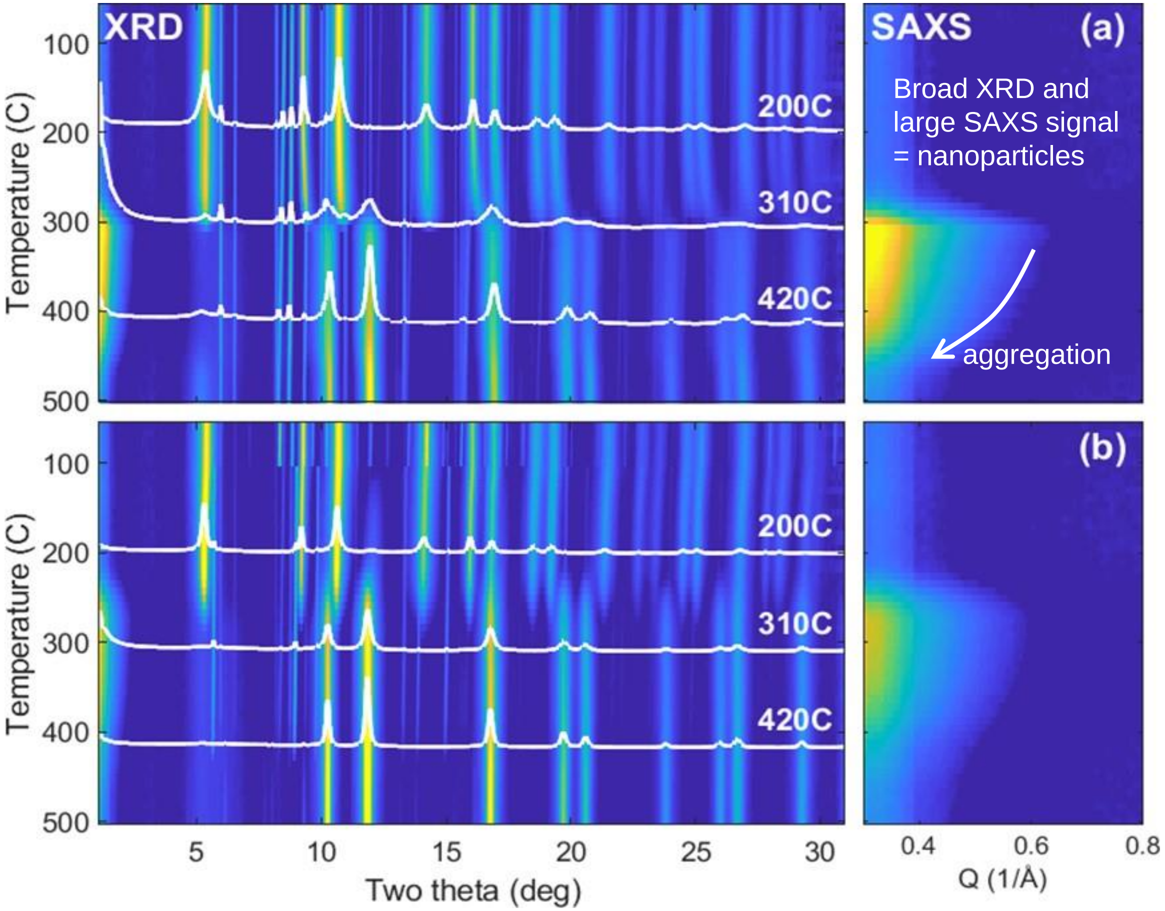
In support for “Improving Battery Performance through Structure-Morphology Optimization (BAT402)

- Comparing the sintering behavior of TVR made $Ni(OH)_2$, NMC811 and NMC111 hydroxide precursors with different Li source in different atmosphere

Studying calcination with x-rays: NCM811 by TVR



Example data taken from NMC811 with (a) Li_2CO_3 and (b) $LiOH.H_2O$ salts.



- Calcination of various MERF precursors was studied at APS using x-ray diffraction and small angle x-ray scattering.

- Both Li-sources shows strong SAXS signals → a dramatic change in NMC primary particle size at $T_{m.p.}$
- With $LiOH.H_2O$, this phase change occurs at lower temperature and proceeds more slowly

Images & Data Courtesy: Tim Fister, ANL

TECHNICAL ACCOMPLISHMENTS

TVR-made LNO (ANL) Coated with Graphene at Northwestern University

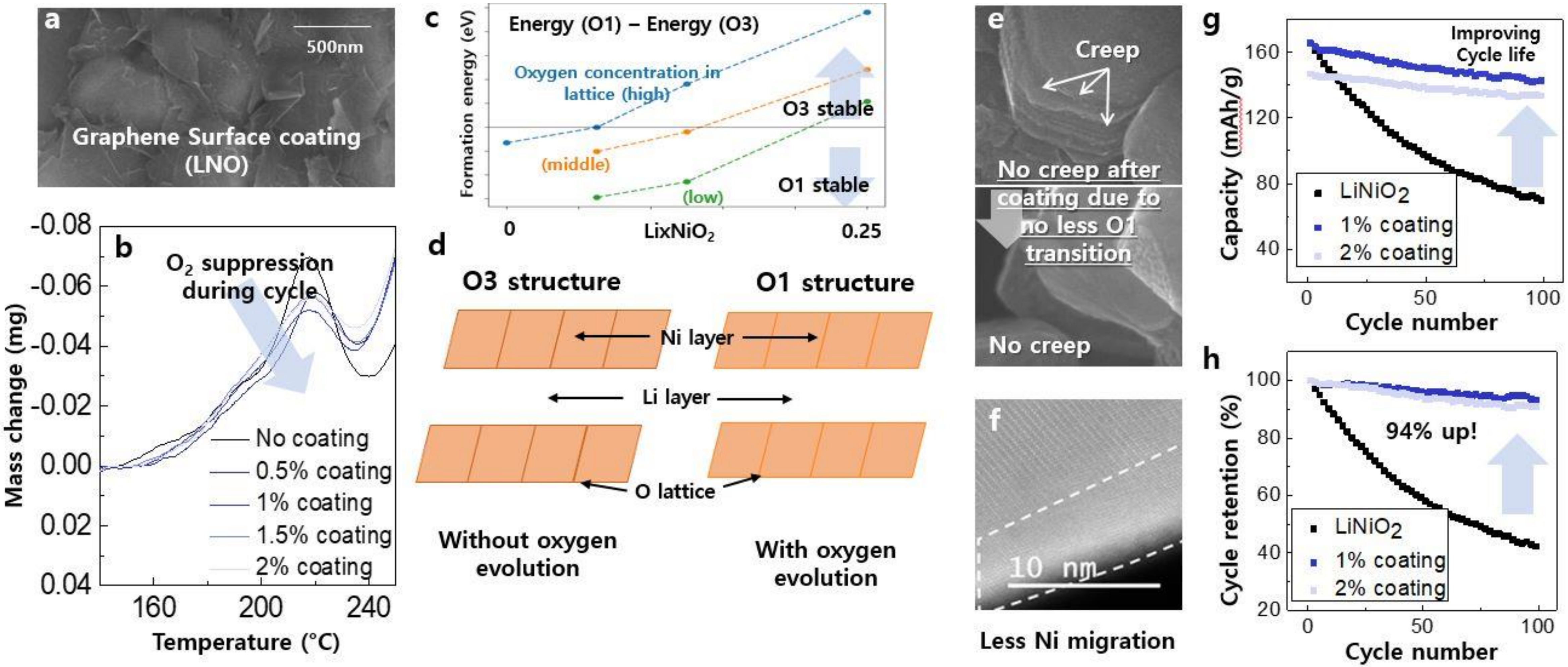


Image & Data Courtesy: Dr. Kyu-Young Park, Mark Hersam Group at Northwestern University

- Graphene coated $LiNiO_2$ shows a suppression of O1-O3 stacking faults at H3 phase
- Oxygen gas evolution and Ni-migration are efficiently suppressed

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project was not reviewed last year

COLLABORATIONS

- Deep-Dive into Next-Generation Cathode Materials (2A): Realizing the Potential of Layered Transition-Metal Oxide (BAT375 & BAT252)
- Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing (BAT164)
  - Jianlin Li and David Wood (ORNL) → Electrode cracking studies using scaled up ~7µm NCM811 cathode particles (synthesized at 10L TVR) and XFC rate capability research
- Improving Battery Performance through Structure-Morphology Optimization (BAT402)
  - Venkat Srinivasan, Tim Fister, Xiaoping Wang, Pallab Barai (ANL) → In-situ characterization and modelling (LNO, NCM811, NCM111)
- In Situ Spectroscopy of Solvothermal Synthesis of Next-Generation Cathode Materials (BAT183)
  - Feng Wang, Jiangming Bai (BNL) → In-situ calcination of LNO, NCM811
- Northwestern University, Prof. Mark Hersam group
  - Kyu-Young Park → various particle sizes of LNO and NCM811 for the development of graphene coating to suppress H2-H3 transition

PROPOSED FUTURE RESEARCH

- Optimization of the calcination processes by utilizing different techniques to create higher quality cathode materials
  - Sealed tubular furnaces (optimizing oxygen partial pressure for calcination)
  - Rotary furnaces (in-situ mixing during calcination)
  - Roller heart kiln (homogeneous heat dissipation during calcination)
  - Microwave sintering (monolithic ceramic oxides, single crystals)
  - Dopants/Coatings/Single Crystals: High frequency induction heating (rapid consolidation of components for conformal coating)
- Continue supporting battery research community (National Laboratories, Universities, Companies) by providing and making available advanced cathode materials
  - Commercially unavailable hydroxide precursor materials
  - Commercially unavailable cathode compositions (e.g.; LNO-based cathodes)
  - Commercially unavailable cathode morphologies (e.g.; good performing small particles (D_{50}= 4-8 µm))
  - Continue on synthesis of high-Ni NMC by design (e.g.; in-situ calcination → ANL-BNL collaboration)
- Scale up and process optimization of promising new cathode materials
  - Suggestions are welcome for scaling up newly invented, promising battery materials

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

SUMMARY

- **Eight** different LNO-based cathode materials made at 1 L TVR and **scaled up** at 10 L TVR were delivered to several R&D groups at National Laboratories **(internal and external)**
- **Two different chemistries (LNO, NCM811)** at different particle sizes were delivered to **Northwestern University** for enabling a graphene technology
- NCM622 were scaled up as **baseline material** (for performance metrics) at 10 L TVR
- **Ex-situ XAS experiments** to understand differential effects of Mn and Co on LNO using ANL's APS facility were done; requiring access to the facilities for data interpretation
- **Scalability evaluation of Taylor Vortex Reactors** were continued for different chemistries
- TVR is the preferred platform for **rapidly** making advanced cathode materials with desired morphologies and compositions

TECHNICAL BACK-UP

SYNTHESIS OF CATHODE PRECURSORS

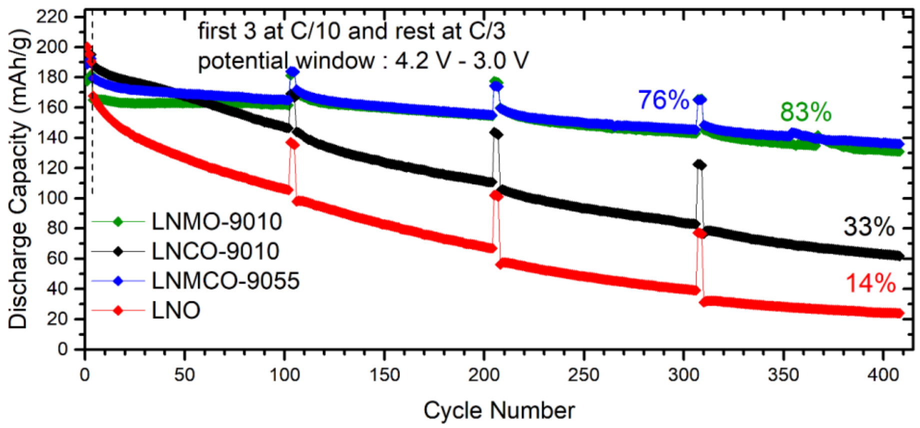
LNO-Based Cathodes: Synthesis using Taylor Vortex Reactors (TVRs)

- Taylor Vortex Reactors (TVRs) were used for rapid process development and scale up (1 & 10 L TVR) for the synthesis of LNO-based cathode precursors.
- Synthesis conditions were controlled at fixed residence time (4h) for all compositions at 2 scales in continuous mode:
  - high pH → 11.7 - 12.4
  - moderate reaction temperature → 40 - 50°C
  - moderate rotation speed → 600 - 900 rpm
  - varying NH_3:Me^{2+} mol ratio → 0.8 - 1.2
- Scaled up materials from FY19:
  - $Ni(OH)_2$, $Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2$, $Ni_{0.90}Co_{0.10}(OH)_2$, $Ni_{0.90}Mn_{0.10}(OH)_2$, $Ni_{0.80}Co_{0.10}Mn_{0.10}(OH)_2$
- New materials in FY20:
  - $Ni_{0.95}Co_{0.05}(OH)_2$, $Ni_{0.95}Mn_{0.05}(OH)_2$, $Ni_{0.95}Mg_{0.05}(OH)_2$ (under optimization)
  - $Ni_{0.60}Co_{0.20}Mn_{0.20}(OH)_2$ (as baseline control sample)
- All precursors were calcined mixing with $LiOH.H_2O$ to form cathodes at different Li-ratios and calcination temperatures and evaluated at half coin cells.

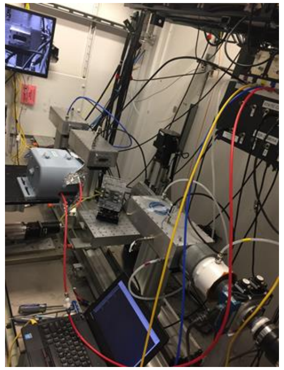
EX-SITU XAS OF LNO-BASED CATHODES IN FULL CELL – 1

- To investigate the local structure and oxidation state change, EXAFS and XANES of pristine cathode (PC) and cycled cathode after 400 cycles (400C) were measured at APS, Argonne National Laboratory.

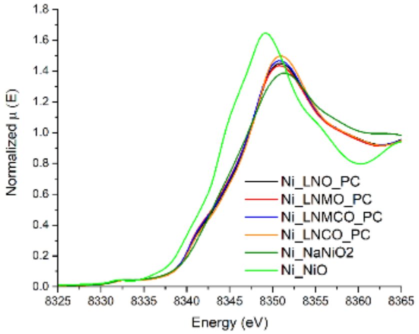
Full cells vs CAMP Gr-anode, n:p = ~1.1



Experimental set up

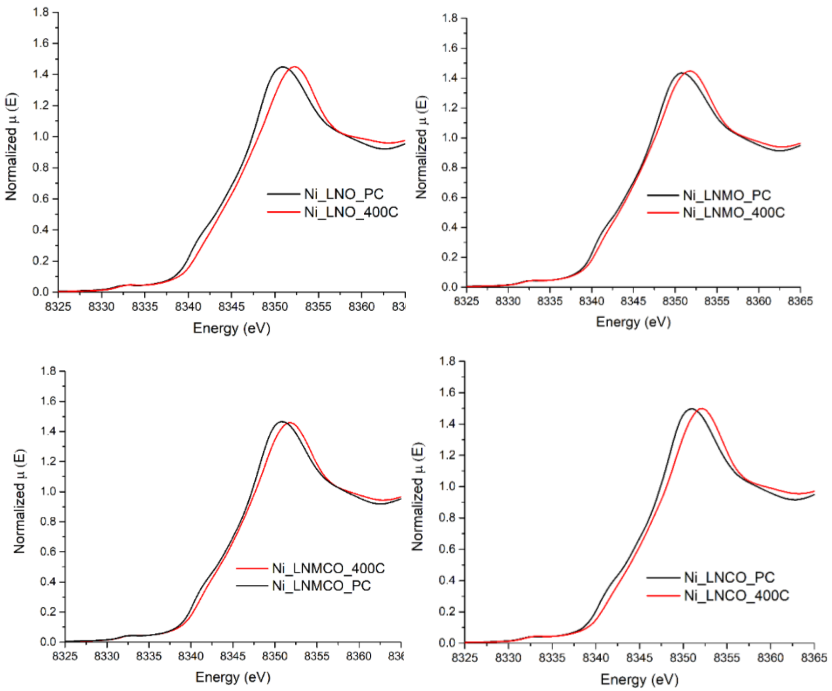


Ni K-edge XANES



$LiNiO_2$ = LNO
$LiNi_{0.9}Co_{0.1}O_2$ = LNCO
$LiNi_{0.9}Mn_{0.1}O_2$ = LNMO
$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ = LNMCO

Ni K-edge XANES (Pristine vs Cycled)



- LNMO and LNMCO showed more stable cyclic performance
- LNMCO showed slightly higher capacity than LNMO in first 100 cycles
- LNO and LNCO both showed similar capacity fading trend

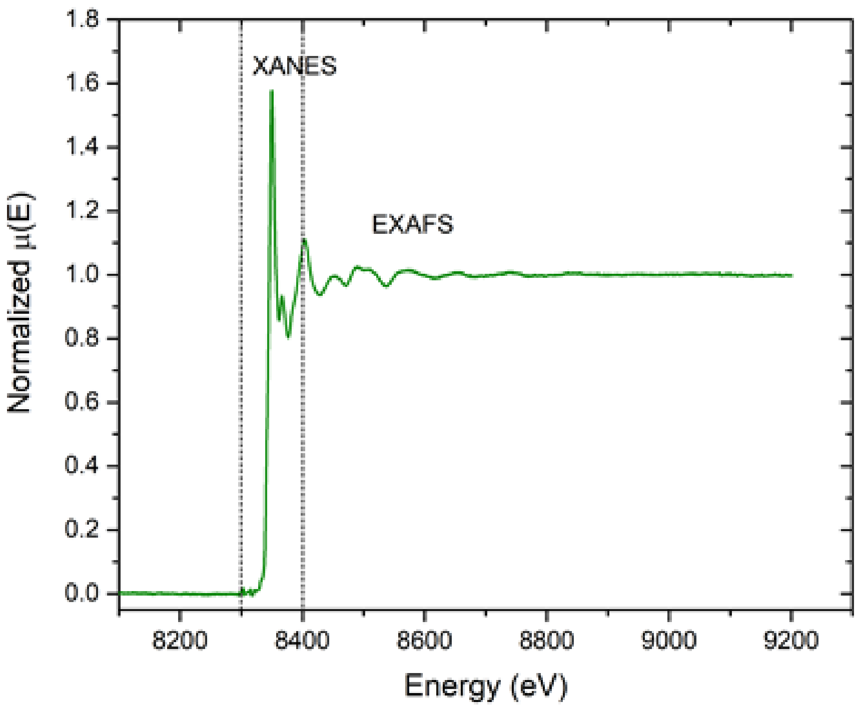
- Ni in pristine cathode is mostly in 3+ oxidation state, LNMO and LNMCO have some Ni^{2+} species
- Ni oxidized partially to Ni^{4+} after 400 cycles in LNO and LNCO

- Further data interpretation requires laboratory computer access (closed due to COVID-19 outbreak)

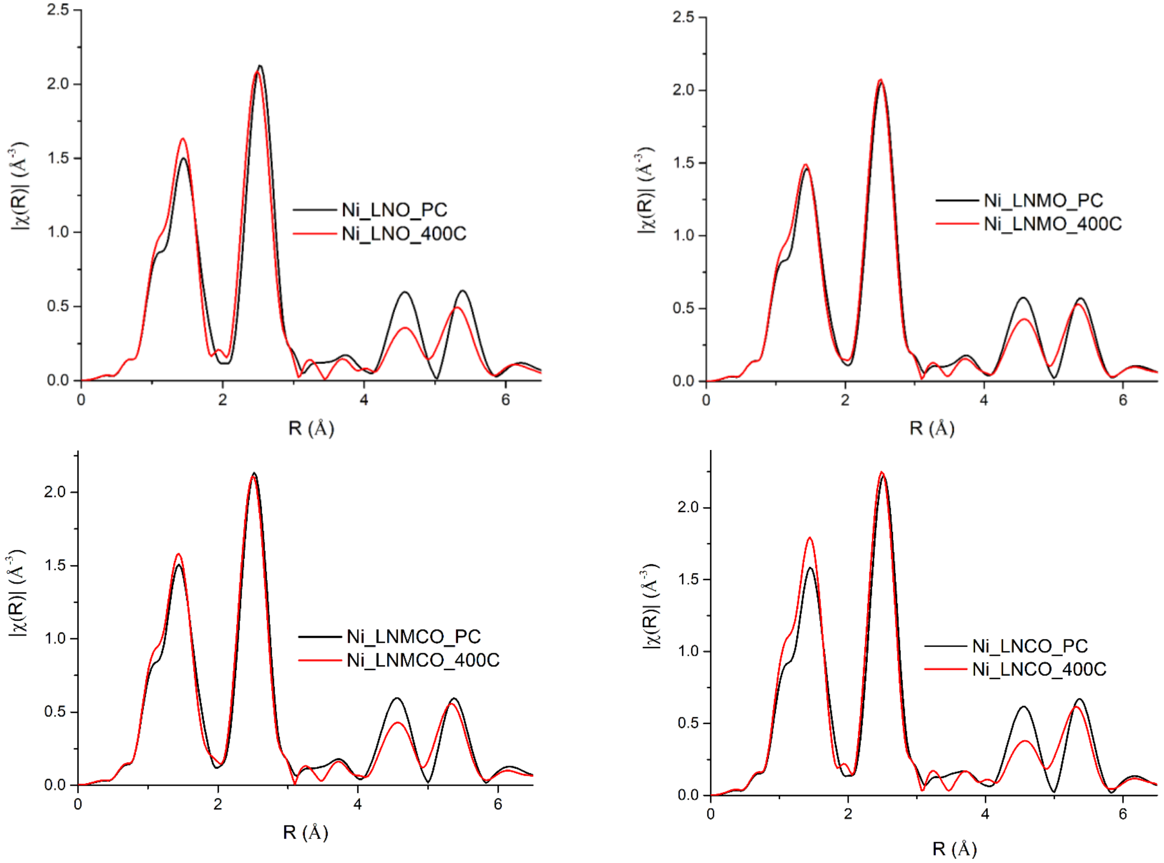
EX-SITU XAS OF LNO-BASED CATHODES IN FULL CELL – 2

- An approach to understand the differential roles of Co vs Mn were studied using pristine and cycled cathodes by advanced characterization tools

XANES vs EXAFS



Ni K-edge EXAFS (Pristine vs Cycled)



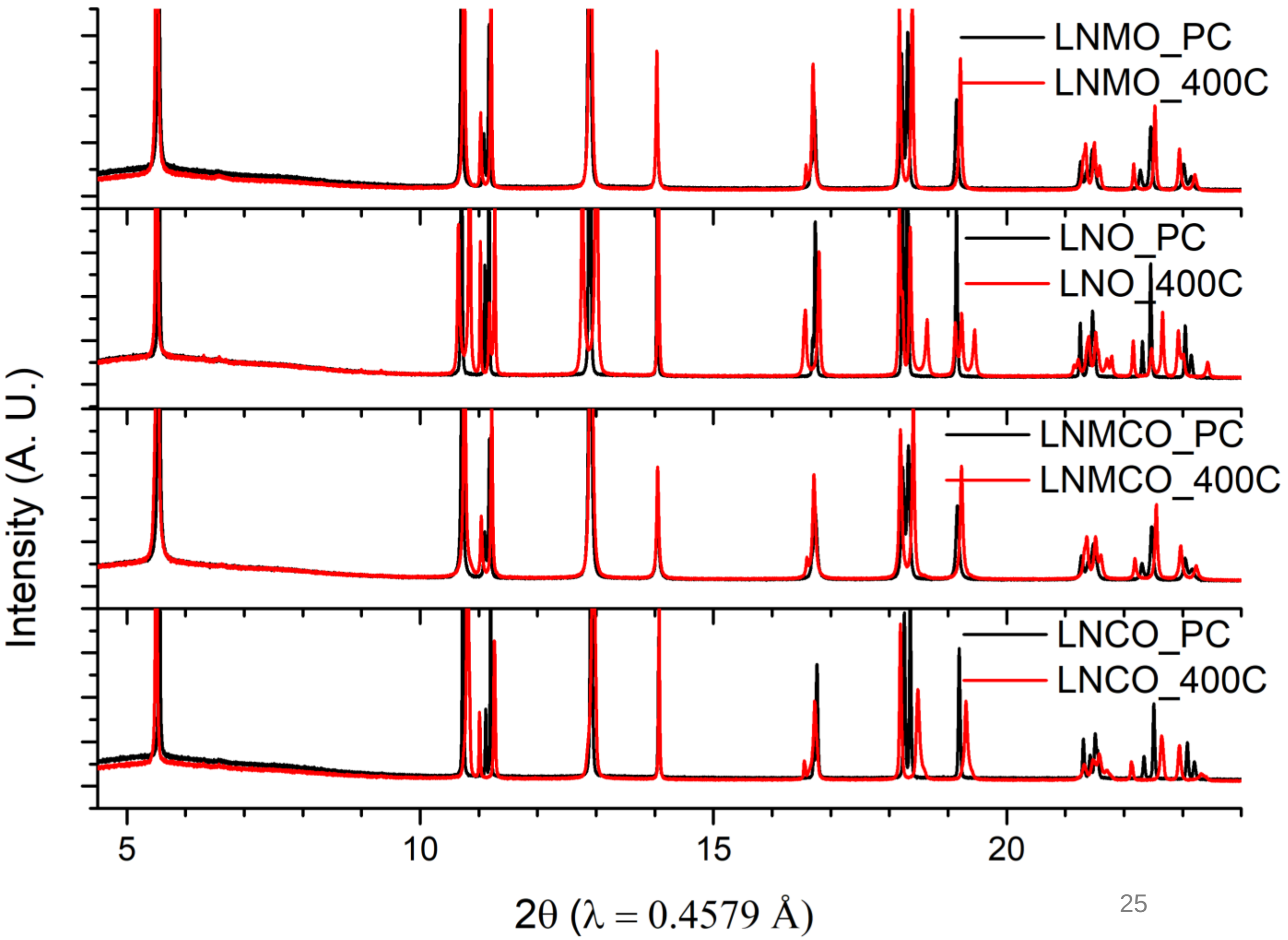
- Ni-Ni bond distance in LNO is shortened after cycling; further data interpretation requires laboratory computer access (closed due to COVID-19 outbreak)

Argonne NATIONAL LABORATORY

EX-SITU SYNCHROTRON X-RAY DIFFRACTION OF LNO-BASED CATHODES

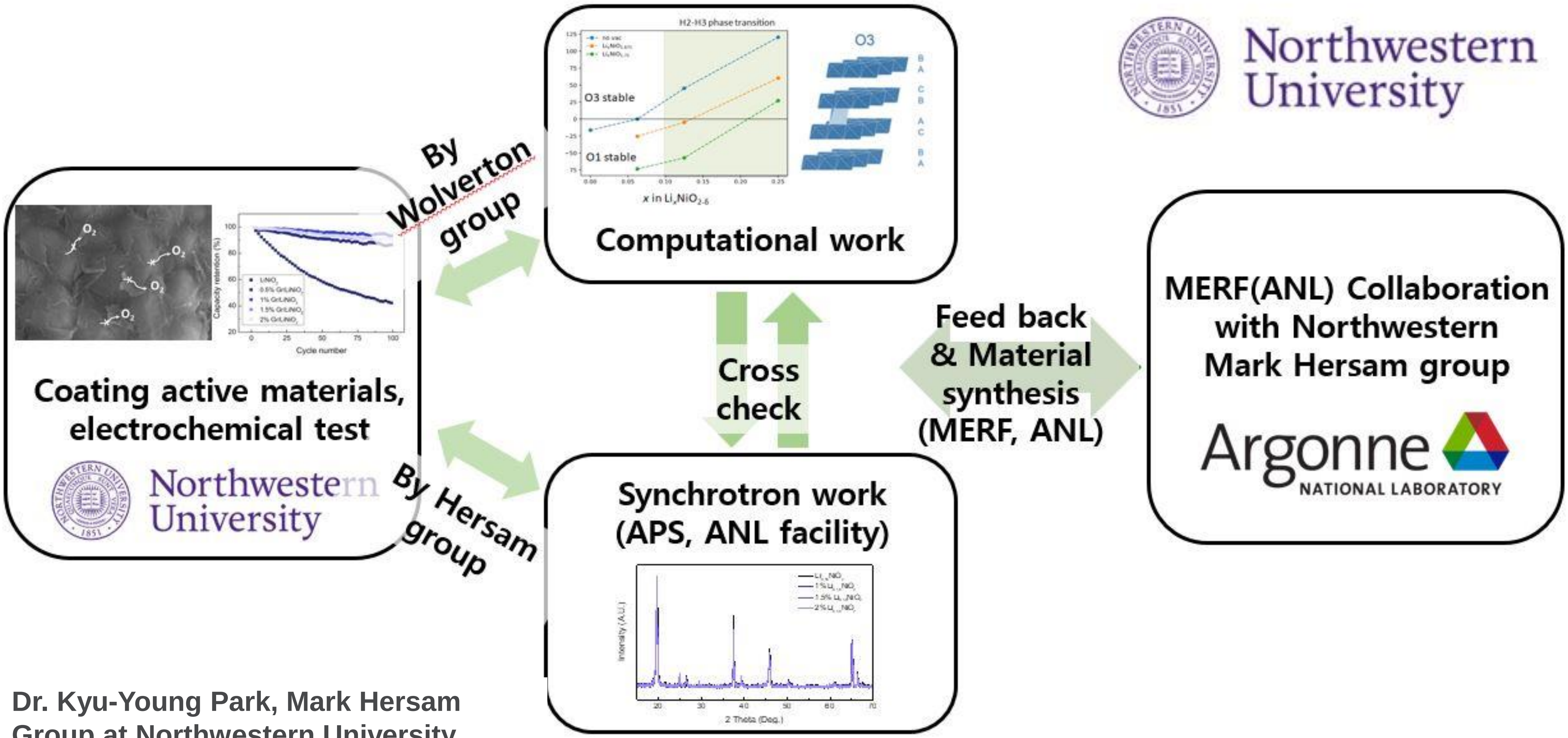
Pristine vs Cycled

- To identify new phase growth and degradation mechanism



- There are new impurity phases in every cathodes after cycling. The new phases are more obvious in LNO and LNCO.
- Rietveld refinement for impurity phase analysis to draw concrete conclusion is underway.
- Further data interpretation requires laboratory computer access (closed due to COVID-19 outbreak)

COLLABORATION WITH NORTHWESTERN UNIVERSITY



Dr. Kyu-Young Park, Mark Hersam Group at Northwestern University

ACKNOWLEDGEMENTS AND CONTRIBUTORS

- Continuous support from Peter Faguy and David Howell of the U.S. Department of Energy's Office of Vehicle Technologies is greatly appreciated.
- Contributors
  - Kris Pupek
  - Shankar Aryal
  - Nick Sovronec
  - Gerald Jeka
  - Andrew Turczynski
  - Jason Croy
  - Jihyeon Gim
  - Adam Tornheim
  - Eungje Lee
  - Venkat Srinivasan
  - Timothy Fister
  - Pallab Barai
  - Xiaoping Wang
  - Andrew Jansen
  - Steve Trask
  - Bryant Polzin
  - Alison Dunlop
  - David Wood (ORNL)
  - Jianlin Li (ORNL)
  - Feng Wang (BNL)
  - Jianming Bai (BNL)
  - Kyu-Young Park (Northwestern University)

Samples request and further information:

www.anl.gov/merf