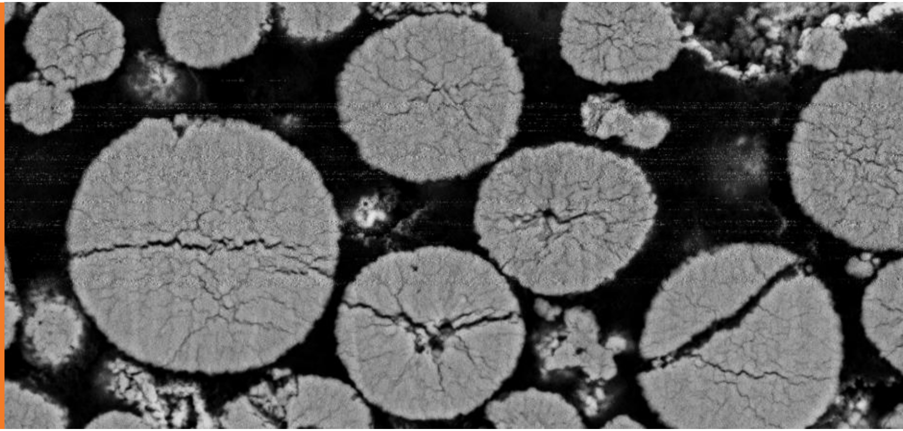
BAT 463
U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

EFFECTS OF EXTREME FAST CHARGING ON LITHIUM-ION BATTERY CATHODE



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June 21-25, 2021
Web conference

INL/CON-21-62664

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 94%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

- Funding for FY-20: $5.6M

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab
- Oak Ridge National Lab

RELEVANCE

Impact:

- Increase electric vehicle adoption by decreasing charge time
- Identify cycle-life issues arising from cathode degradation when charging above 4C
- Refine understanding on cathode cracking and other cathode-aging mechanisms with respect to C-rate and SOC
- Explore pathways to mitigate cathode issues during extreme fast charging (XFC)

Objective:

- Using full cells to identify and quantify cathode-failure modes and mechanisms; provide insights into cell to material degradation under XFC
- Map cathode issues and provide clearer understanding on particle cracking and its evolution
- Develop complementary and aligned advanced analytical methods and modeling tool sets
- Guide future R&D efforts on mitigation and/or elimination of cathode issues

MILESTONES

Milestone	End Date	Lead	Status
Aging-mode identification of gr/NMC811 R1 cells at different C-rates and SOC and compare with gr/NMC532*	3/31/2021	INL, Argonne	90%
Understanding of the relation between particle architecture and cracking*	3/31/2021	NREL	80%
Aging mode identification in next builds	3/31/2021	INL, Argonne	60%
Improvement verification and aging-modes and mechanisms identification and validation in next builds with improved charging protocols	9/30/2021	INL, Argonne	60%
In-plane and through-plane aging heterogeneity evaluation in NMC532 and NMC811*	9/30/2021	Argonne, SLAC	60%
Demonstration of performance improvement in modified particle architecture and morphology in coin cells under fast-charge conditions*	9/30/2021	LBNL	60%
Advanced cathode cracking modeling	9/30/2021	NREL	60%
Finalization of review article on cathode thrust	9/30/2021	INL	25%

*Impacted by Covid-19

APPROACH

Impacts of high-rate charging

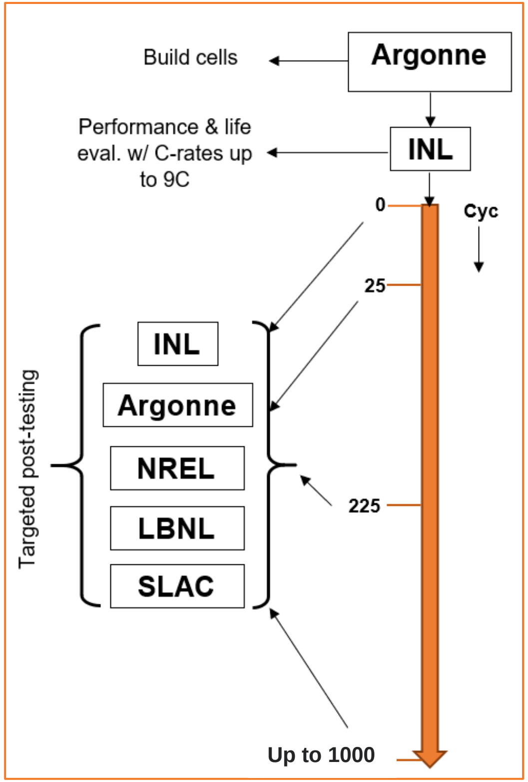
- Identify charge-acceptance limitations
- Design experiments with respect to charging rates and SOC
- Analyze electrochemistry with targeted post-testing to evaluate changes in aging parameters as function of cycling

Identify key barriers as different charge conditions are used

- Focus clearly on identifying cathode-aging mechanisms which were not investigated before for XFC conditions

Evaluate heterogeneity of performance and aging at different length scales

Explore particle microstructure modification for performance improvement during XFC

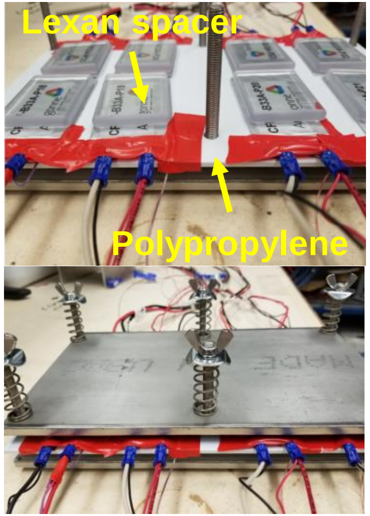


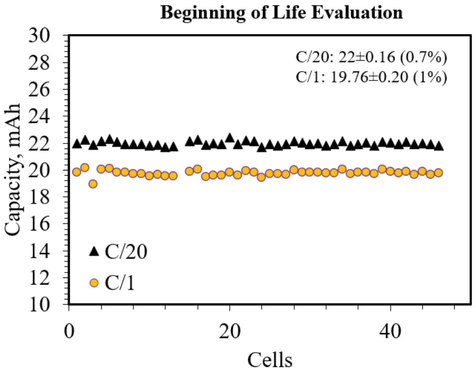
Develop complementary and aligned advanced analytical methods and modeling toolsets

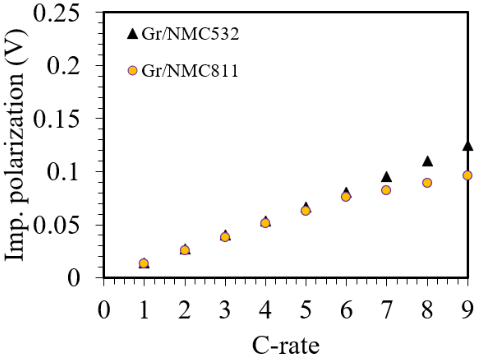
VARIABILITY AND POLARIZATION BEHAVIOR

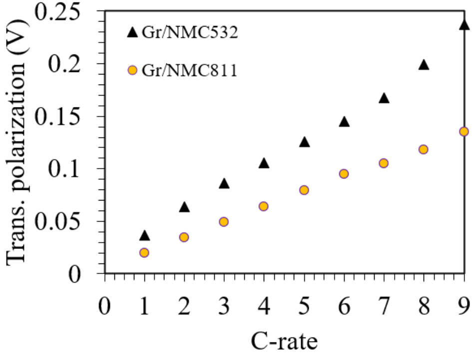
Cell design, test set up, initial characterization, cycling

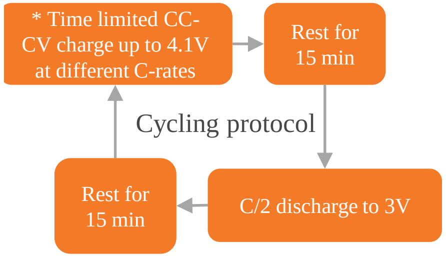
- Used ~19 mAh **gr/NMC532** and **gr/NMC811** SLPCs with 11 and 9 mg/cm^2 cathode loadings, res., and N:P ratio ~ 1.1. ~90% active material and porosity ~33%. **Gen2 electrolyte**.
- 60+ cells tested at 30°C. Includes charging rates up to 9C and voltage between 3 and 4.1V. Targeted post-testing at different cycling interval.
- Low initial variability. NMC811 cells have lower polarization. Used time-constrained CC-CV charging protocols.











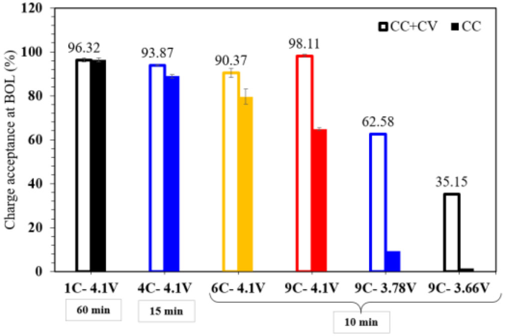
*Charge time for 1C charge=60 min, 4C=15 min, and 6C and 9C =10 min

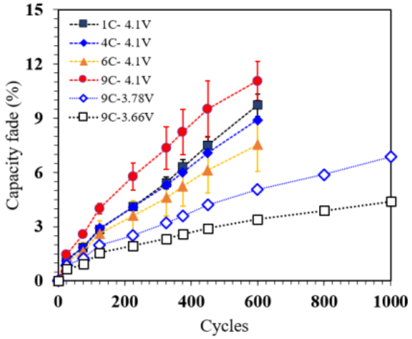
Polarizations obtained from constant current rate capability test. See details in Tanim et al., JES, 166(10) (2019) p.A1926

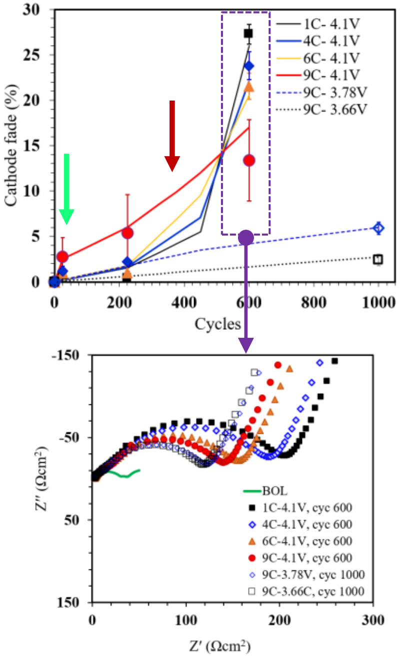
FAST CHARGE AND AGING MODES IN NMC532

Aging mode identification and quantification

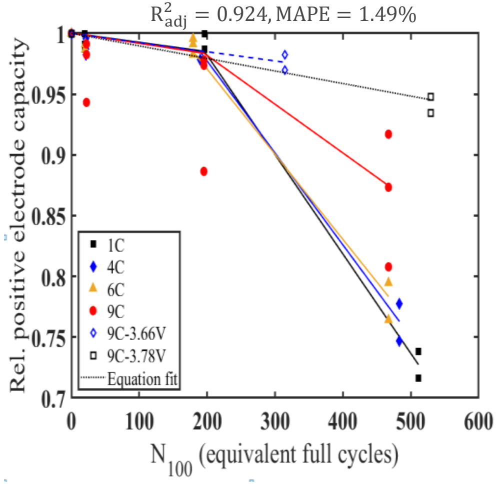
- 90%+ charge acceptance
- Dominating aging modes are loss of lithium inventory (LLI) in anode and loss of active material in cathode (LAM_{PE})
- Early break-in (↓) and later fatigue mechanism (↓) in cathode
- Break-in dominated by charge rate and fatigue dominated by depth of charge in CC
- Distinct increase in charge transfer resistance in cathode
- Constrained voltage even at 9C minimizes cathode issues







Machine-learned reduced order model (ROM) vs data



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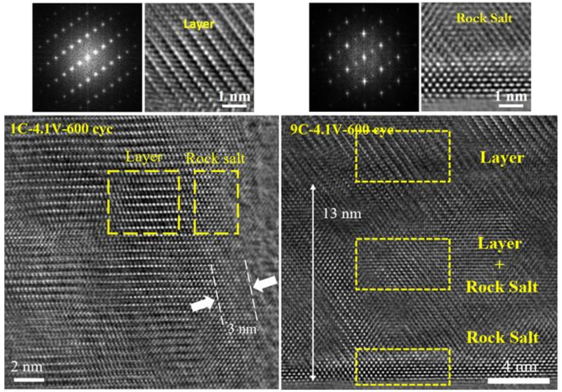
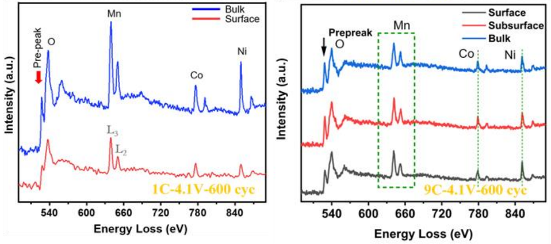
Tanim et al., publication submitted, May 2021

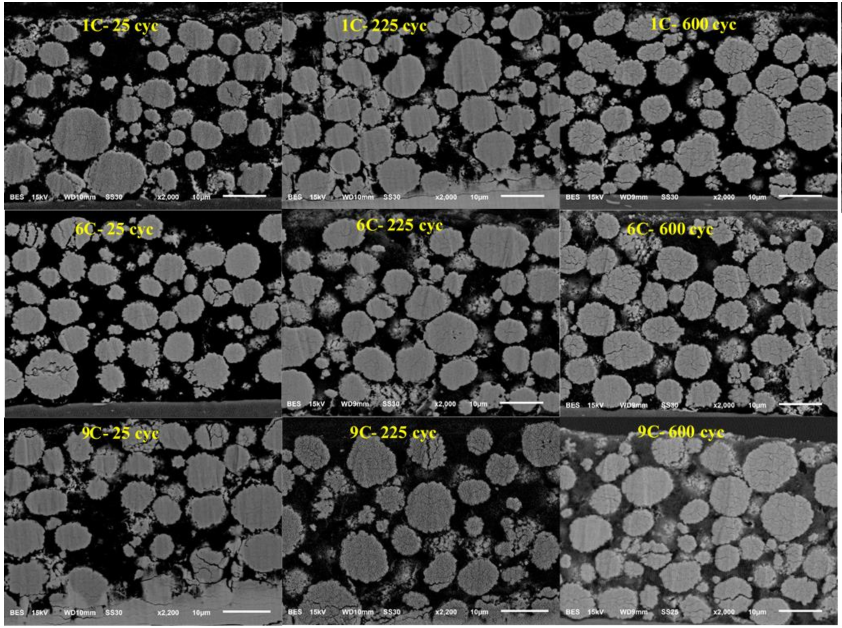
FAST CHARGE AND AGING MECHANISMS IN NMC532

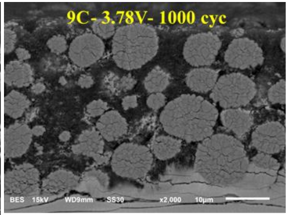
NMC532 post-test: Aging mechanisms

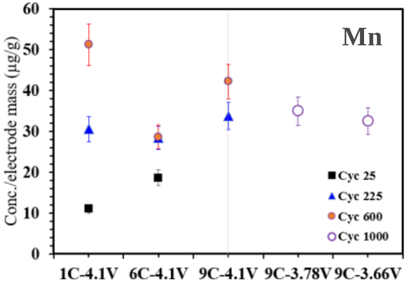
- Interprimary particle separation (IPPS or cracking) with distinct evolution. Particles can retain performance even with evident IPPS.
- Bulk structure remained layered. More surface reconstruction at higher C-rates.
- More extent of Mn dissolution than Co and Ni. No drastic change in TM increase for XFC conditions.

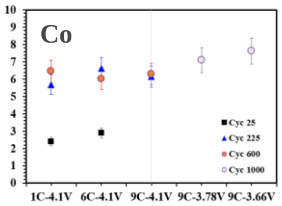


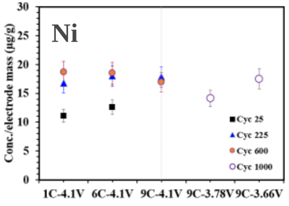










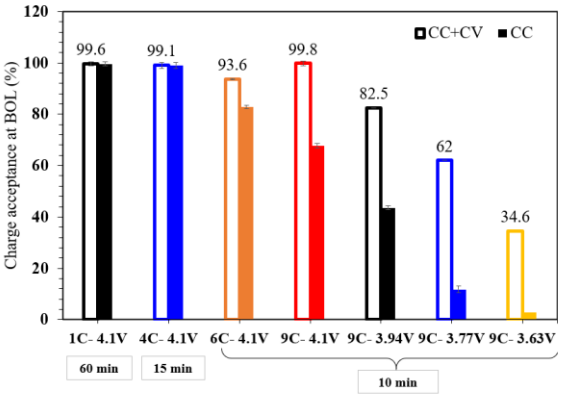


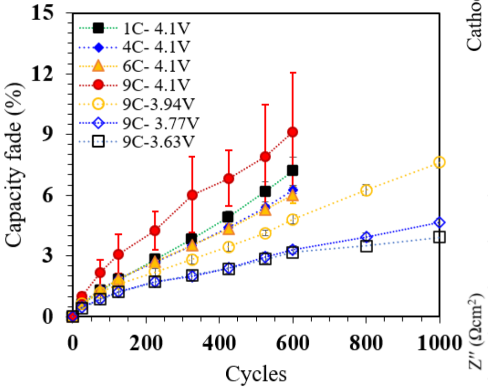
Post-tests were performed at Argonne. Error bars show experimental uncertainty.

FAST CHARGE AND AGING MODES IN NMC811

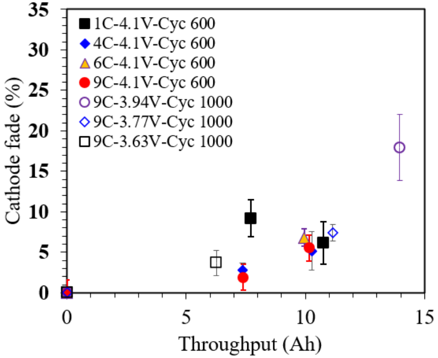
Aging-mode identification and quantification

- Better rate acceptance than NMC532 cells
- Reduced cell aging in NMC811 cells—trends remain comparable to NMC532 cells
- Less-aggressive cathode issues in NMC811

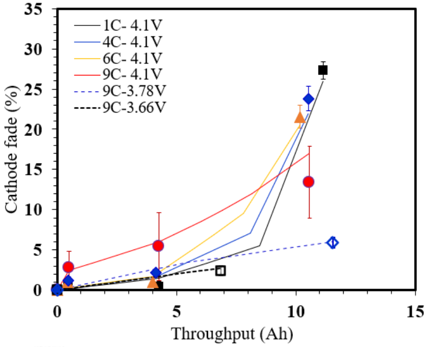


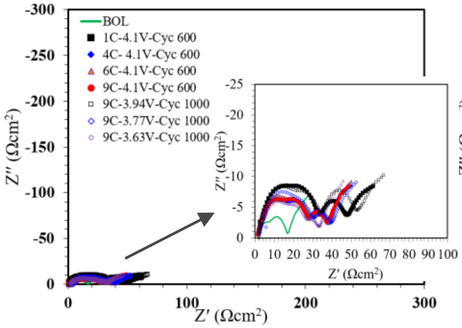


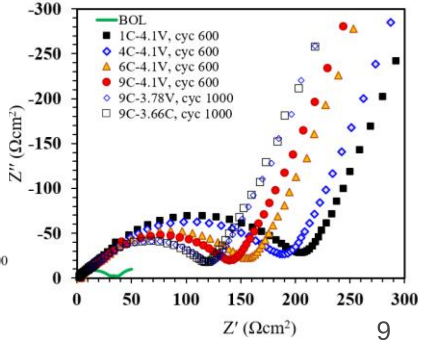
NMC811



NMC532







Cathode fade was measured from harvested electrodes in Li/NMC coin cells@C/20.

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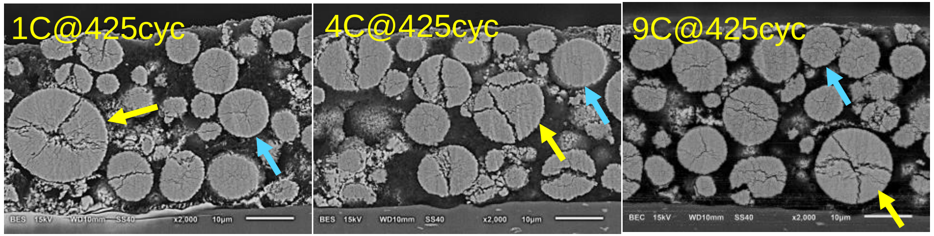
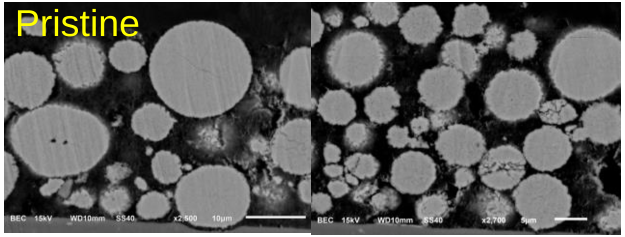
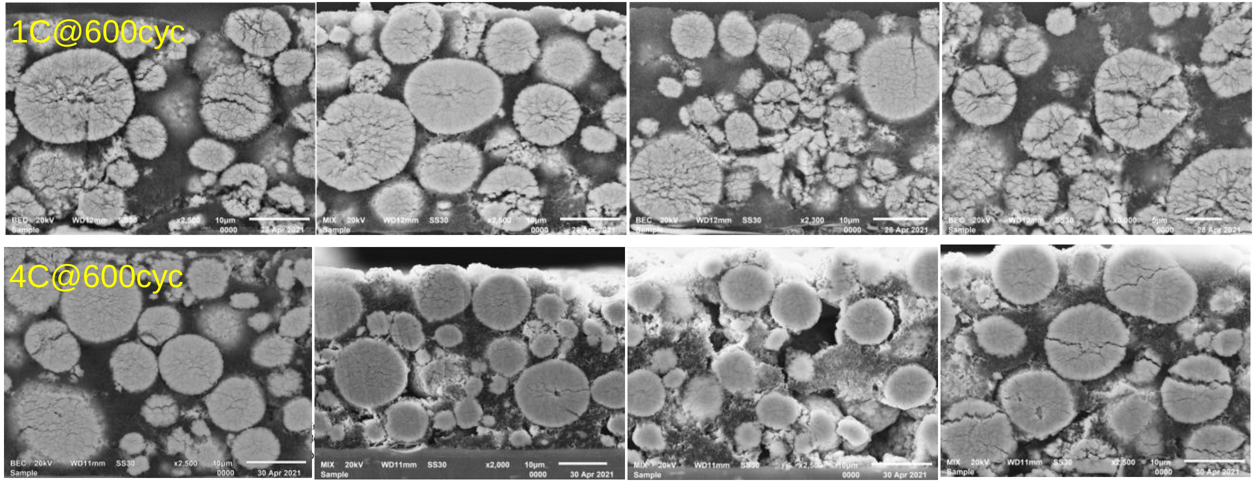
FAST CHARGE AND AGING MECHANISMS IN NMC811

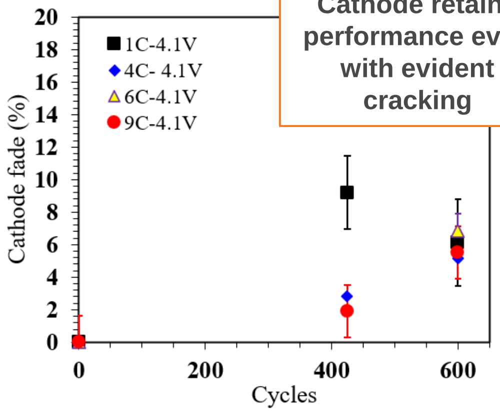
NMC811 Post-Test: Early post-test results

- After 425 cycles- Cracking observed irrespective of C-rates, particularly in larger size particles (≥20μm). Less cracking in smaller size particles.
- After 600 cycles- Cracking is more evident in both larger and smaller particles. Quantification in progress.









Cathode retains performance even with evident cracking

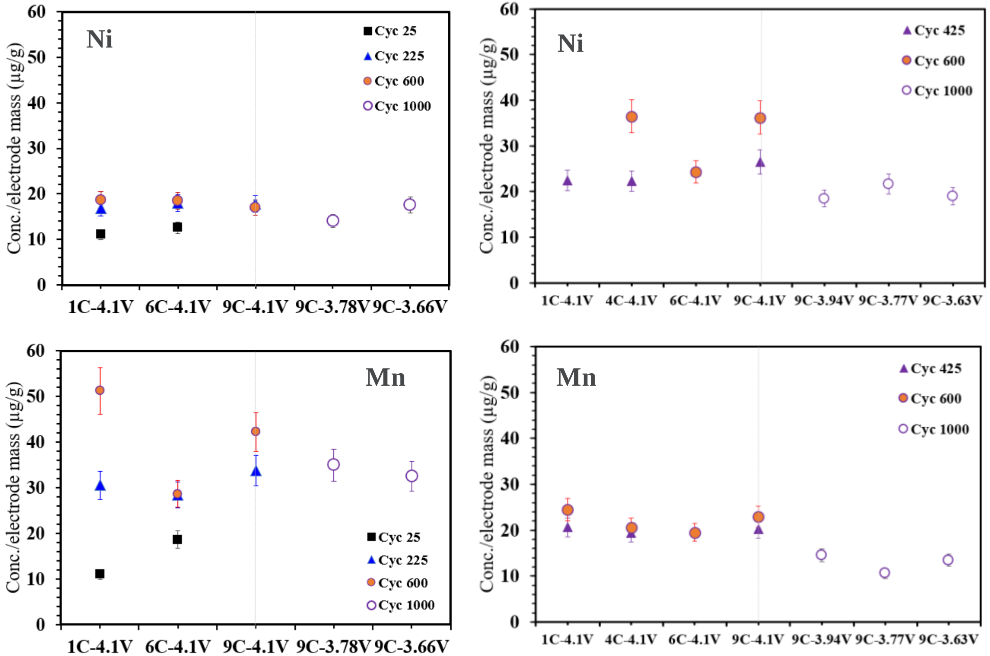
Post-tests were performed at Argonne.

FAST CHARGE AND AGING MECHANISMS IN NMC811

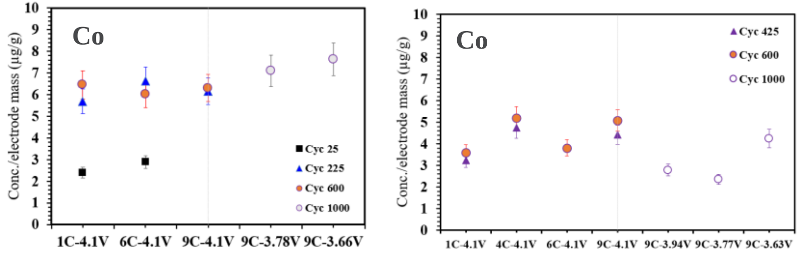
NMC811 Post-Test: Early post-test results

- ICP-MS data show the presence of more Ni in the anode than Mn and Co due to relative contents in NMC 811

NMC532 NMC811



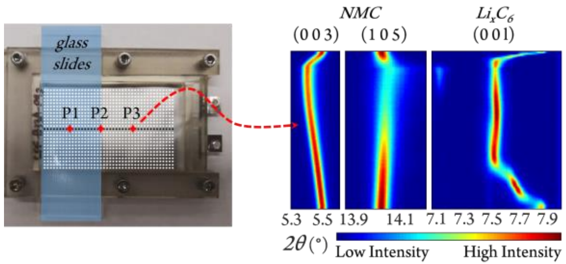
NMC532 NMC811



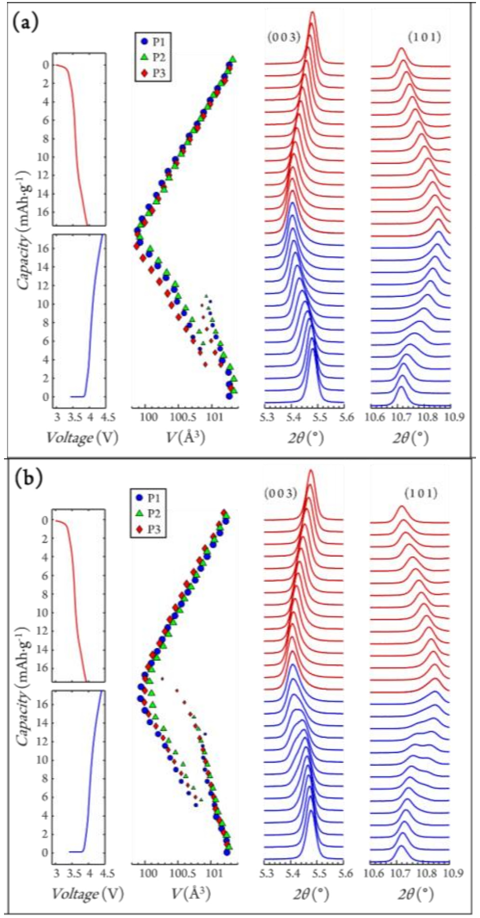
Post-tests were performed at Argonne. Error bars show experimental uncertainty.

FAST CHARGE AND HETEROGENEITY

Bimodal cathode delithiation identified



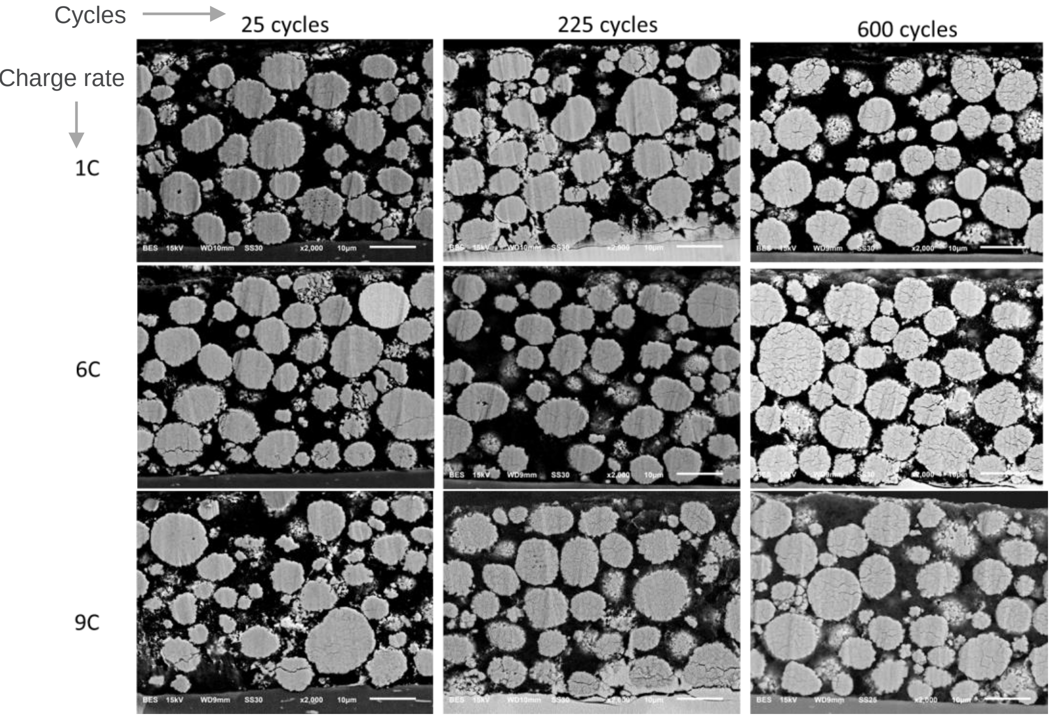
- Fast charge (6C), slow discharge (C/2), 3–4.4 V. Part of cell under pressure to study pressure effects.
- **Bimodal cathode delithiation** (peak splitting) observed in early cycles, **no clear pressure influence**.
- **Bimodal distribution deepens** at different rates for each position after several cycles.
- **Potential mechanisms**
  - Electrolyte diffusion limited (tortuosity and loading thickness)
  - Bulk diffusion limited (particle size)
  - Surface reaction limited (surface contamination or cathode electrolyte interphase [CEI])
  - Particle cracking (anisotropic strain in secondary particles).



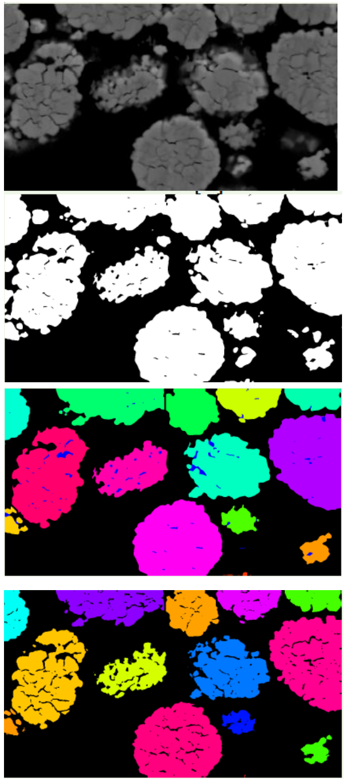
XRD performed at APS, Argonne.

QUANTIFYING CRACKS AND LINKING TO PARTICLE ARCHITECTURE

Identify, segment, and quantify cracks in NMC particles with various cycle histories from SEM images



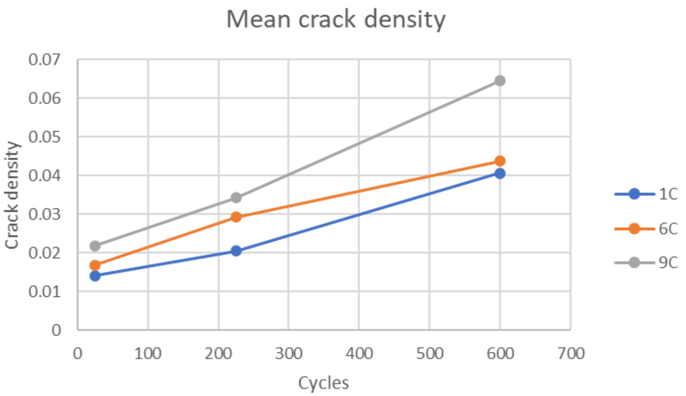
SEM images provided by Zhenzhen Yang (Argonne).



Data processing led by Okun Furat and Volker Schmidt at Uni. Of Ulm.

QUANTIFYING CRACKS AND LINKING TO PARTICLE ARCHITECTURE

- The **mean crack density** is calculated by dividing the number of pixels associated with cracks by total number of pixels in particle

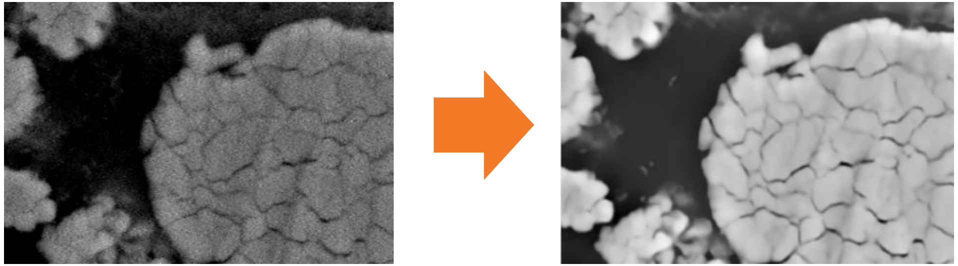


Challenge:

- Higher-resolution images are needed to quantify features of cracks, such as crack width and spatial distributions of cracks, within particles

Solution:

- Enhancing resolution using generative adversarial networks (GANs)



Next steps:

- Used enhanced images to quantify the properties of cracks in more detail and build a statistical description of the evolution of cracks with cycling and C-rate during charging

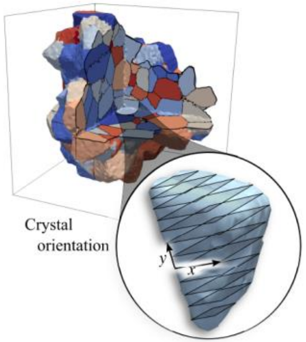
Data processing led by Orkun Furat and Volker Schmidt at Uni. Of Ulm.

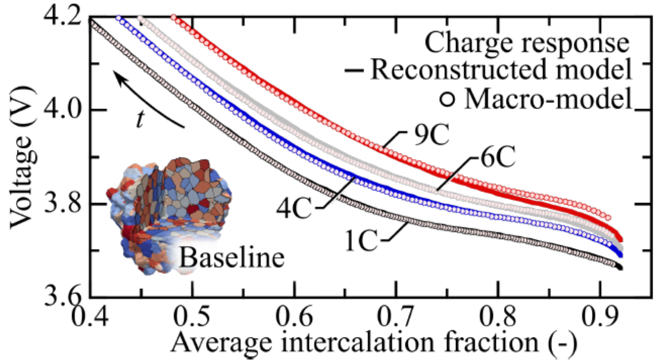
3D CONTINUUM DAMAGE MODEL

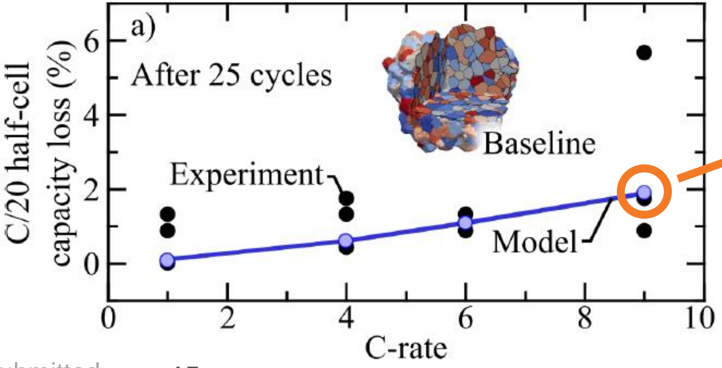
Tracks cracking over multiple cycles, based on material properties and 3D polycrystalline architecture

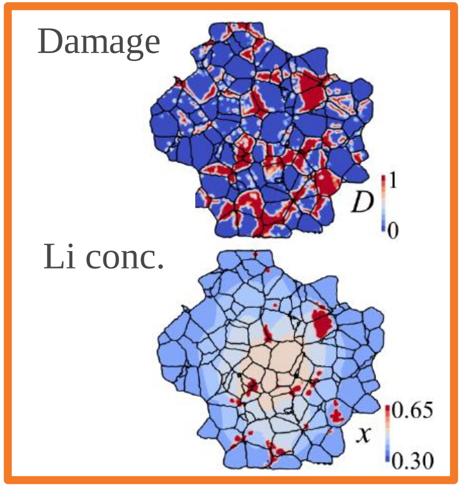
NMC532 validation

- **Electrochemistry**
  - Anisotropic solid diffusion
  - Butler-Volmer boundary condition (variable surface flux)
- **Solid mechanics**
  - Anisotropic expansion and stiffness
- **Damage**
  - Irreversible, when equivalent strain threshold exceeded
  - Impacts local diffusivity and mechanical stiffness









J. Allen et al., submitted.

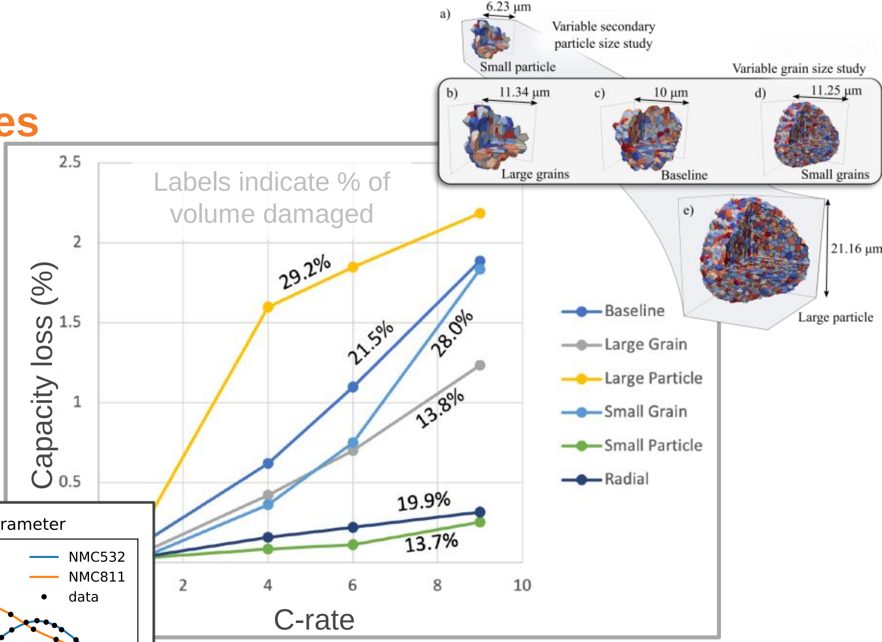
MODEL PROJECTIONS

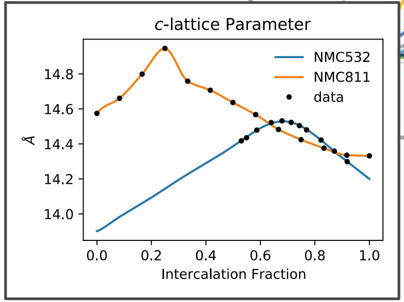
for various architectures, chemistries, & electrodes

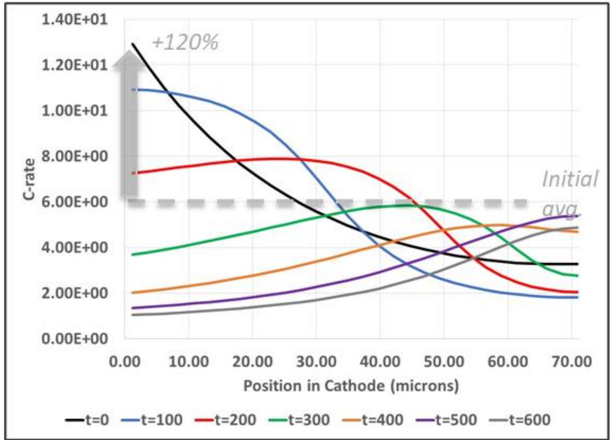
- **Preferred 3D architectures (NMC532)**
  - Small particles (smaller concentration gradients)
  - Radially oriented (little mechanical damage, as with small particle, but with benefit of low surface area for good chemical stability)
  - Large or single grain (fewer misoriented grain/grain boundaries)

- **NMC811 vs. NMC 532**
  - Higher C-rate capability due to faster diffusion
  - Damage caused by volume expansion (ΔSOC) rather than C-rate
  - Retains higher capacity despite more damage

- **C-rate heterogeneity across thick electrodes**
  - Round 1 electrodes experience 50% higher C-rate at front
  - Round 2 electrodes experience 120% higher C-rate at front

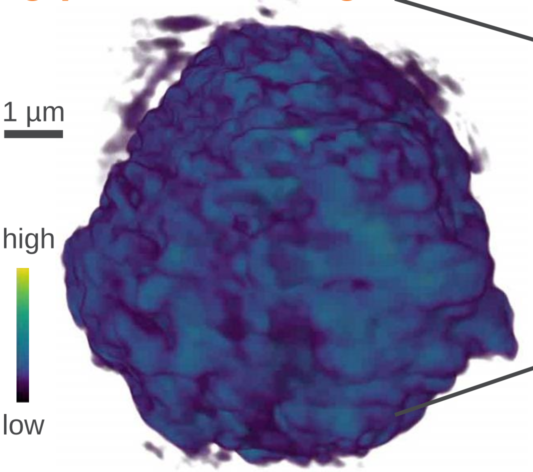


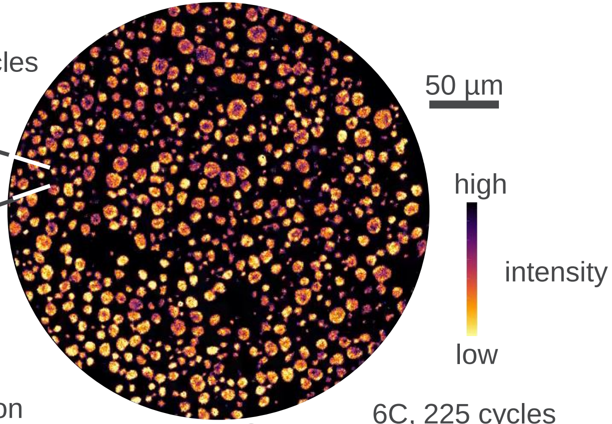




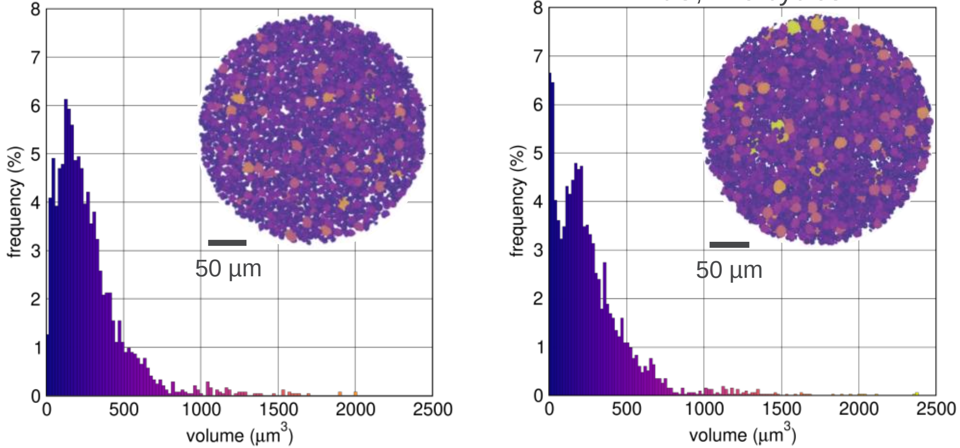
3D MULTI-LENGTH SCALE APPROACH

Quantifying particle damage as a result of cycling using TXM and µCT





- TXM gives insight into transition-metal concentration in relation to cracks within single particles
- From µCT data, particle volume distribution changes upon extended cycling at 6C rate, with much higher frequency of small particles, which could suggest particle pulverization

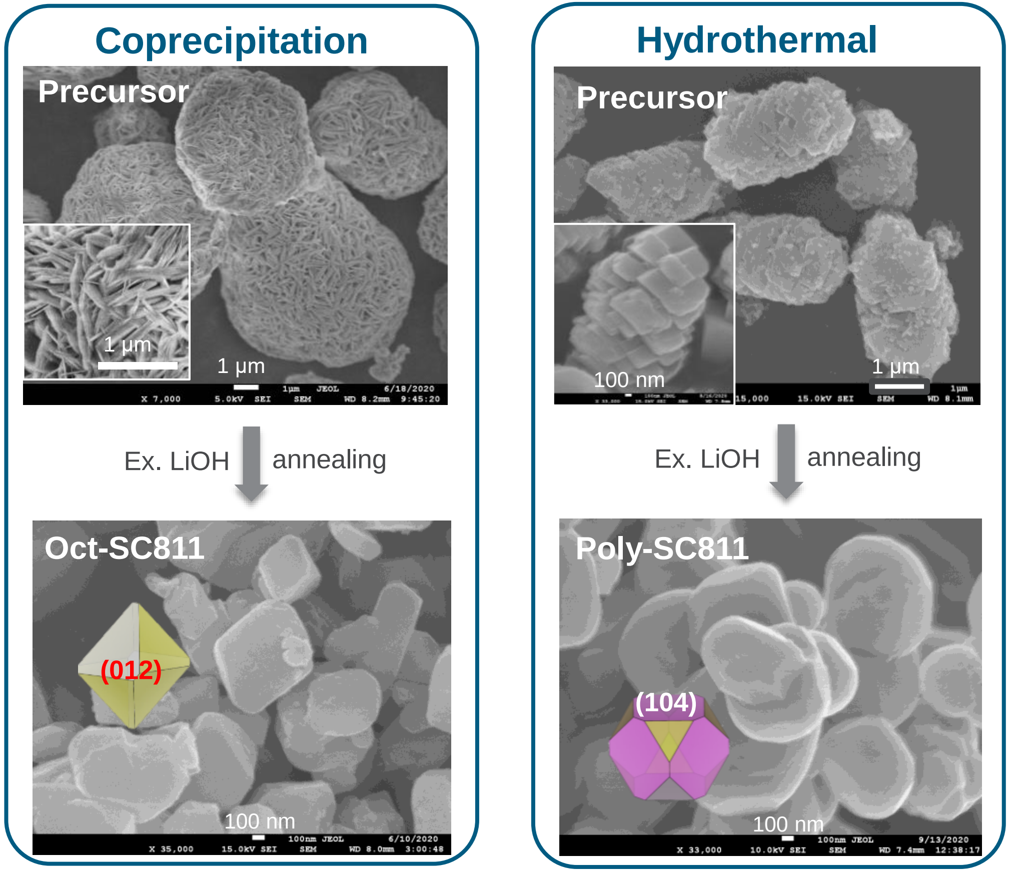


DEVELOPING SINGLE-CRYSTAL CATHODES FOR FAST CHARGE

Synthesis and properties of single-crystalline (SC) NMC811s

Two synthesis methods developed

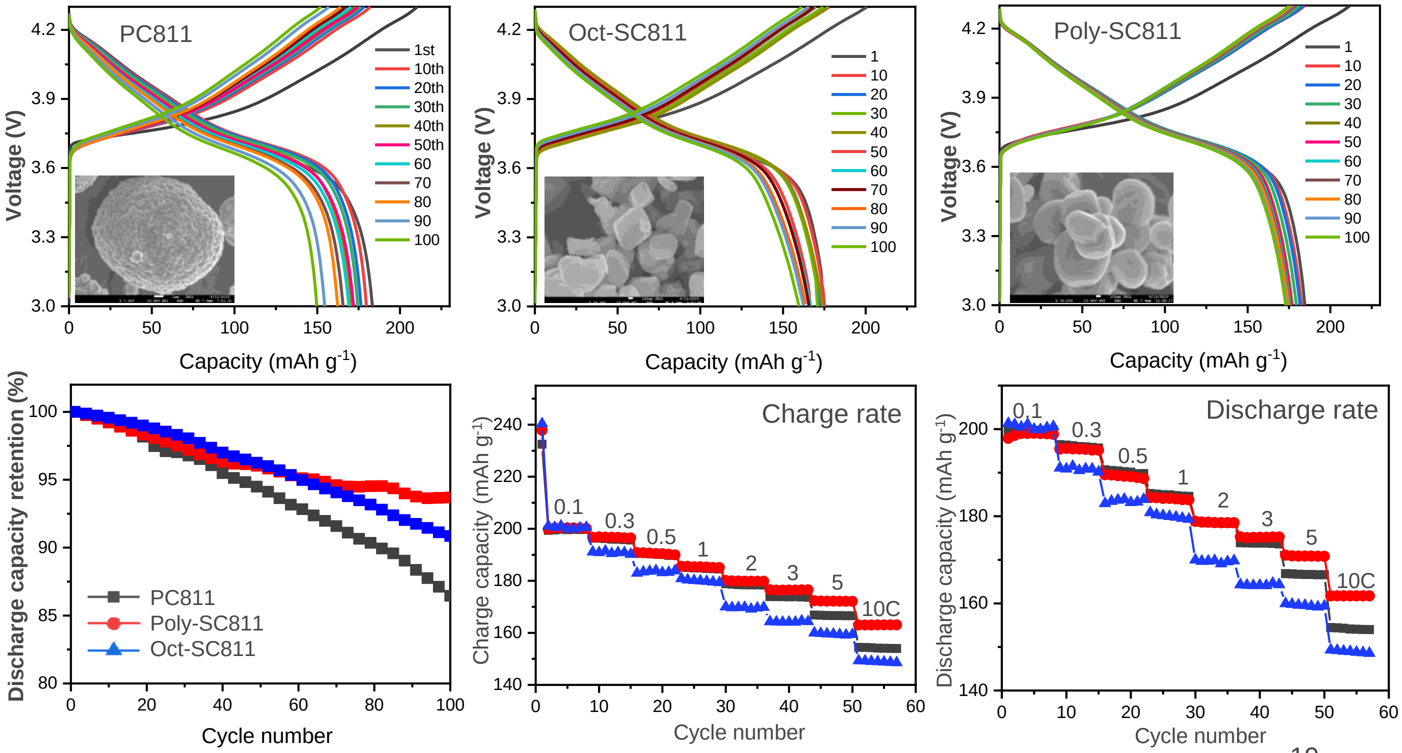
- Coprecipitation method
  - Precursor prepared by coprecipitation. Large secondary particles with submicron-sized primary particles in needle shape.
  - Octahedron-shaped SC-NMC811 particles with predominant (012)-family surface obtained.
- Hydrothermal method
  - Precursor made by hydrothermal method. Secondary particles with submicron-sized primary particles in diamond shape.
  - Polyhedron-shaped SC-NMC811 particles with predominant (104)-family surface obtained.



DEVELOPING SINGLE-CRYSTAL CATHODES FOR FAST CHARGE

Better electrochemical performance with SCs

- Cycling conditions: 3–4.3 V at 1C, Gen2 electrolyte
- Improved cycling stability on SC samples as compared to the polycrystalline (PC) baseline
- Best cycling stability and rate capability obtained on poly-SC811 with (104) surface.



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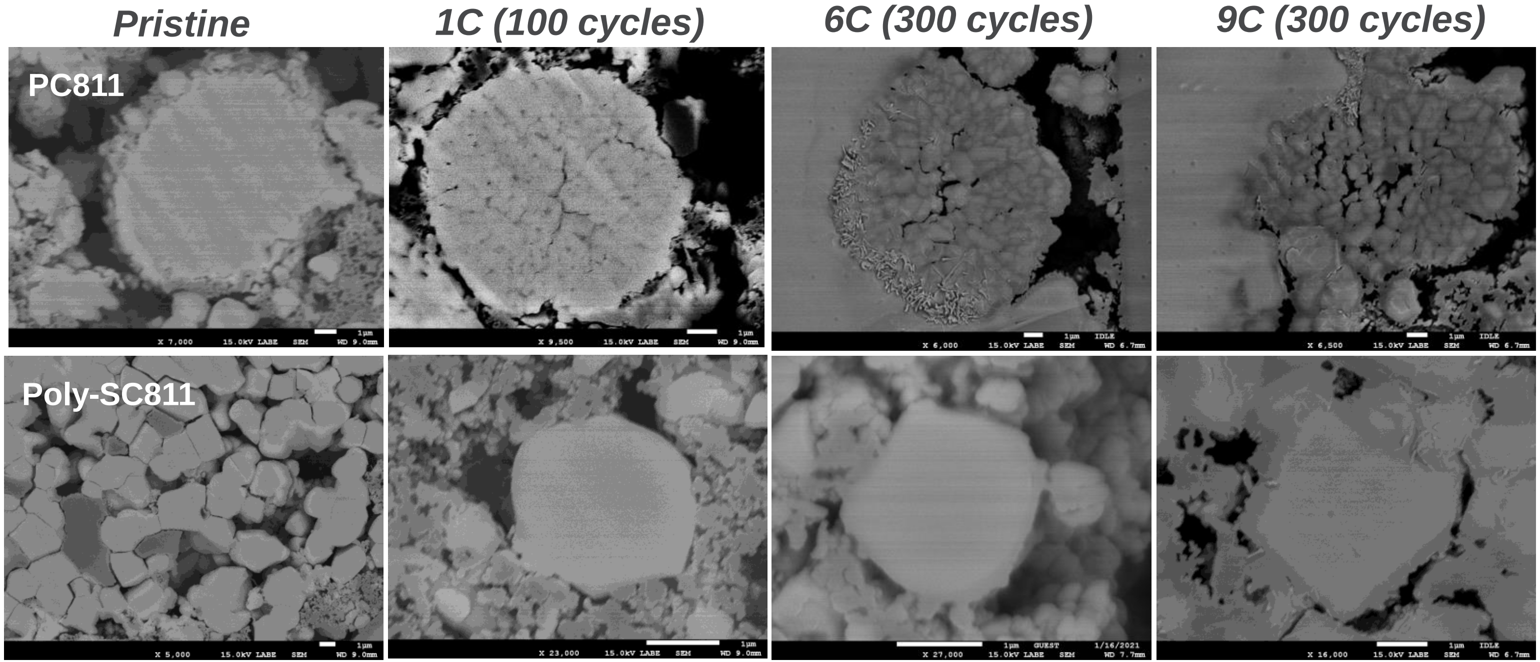
DEVELOPING SINGLE-CRYSTAL CATHODES FOR FAST CHARGE

Cycling-induced particle cracking

- Cross-sectional SEM images show severe cracking in PC811 cycled to 4.3 V
- No cracking observed on Poly-SC811 cycled under the same conditions



SUMMARY

- Elevated charging rates enhance cathode aging
  - Higher rates increase spatial heterogeneity in use
  - Fewer aging effects during early cycles, but failure modes accelerate during later cycling.
  - Cracking dominant aging mechanism for NMC532 cathode. Besides cracking, distinct presence of rock-salt at XFC conditions even with lower voltage cutoff.
  - Early data show fewer aging issues in NMC811 than NMC532 when cycled between 3 and 4.1 V. Cracking is still an issue.
  - Partial charging up to 80% SOC have shown to reduce cathode aging issues.
- Works in progress to develop methods for crack quantification
  - Advanced methods and algorithm to quantify crack is underway in electrode level—2D (SEM image based) and 3D (μ-CT based)—and particle level—TXM.
- Developed and validated modeling tools including sub-particle information
  - Tracks cracking over multiple cycles, based on materials properties and 3D polycrystalline architecture.
  - Performed experimental validation with NMC532 data. Extension to NMC811 is underway.
  - Providing fundamental understanding behind different aging mechanisms, guidance on cathode aging agnostic 3D particle architectures and charging protocols.
- Explored performance improvement with alternate particle architecture
  - Early results on SC-NMC811 show promise. Need more data for mapping out full performance spectrum.
  - Exploring radially oriented PC-NMCs

NEXT STEPS

- Generate full understanding of NMC811 aging mechanisms
  - Cracking, surface reconstruction issues, bimodal multiparticle effects, electrode swelling, and tortuosity
  - Workflow and synergy among different teams for quick evaluation is in place
- How cathode issues change with next iterations of designs
  - Loading, carbon-binder domain, electrolyte change, Vmax, advanced charging protocols, different source of NMCs, coating, etc.
- Develop quantitative methods for quantify particle cracking and correlate with electrochemical data
- Obtain more understanding on the spatial distribution of utilization and cracking
- Continue to develop and refine advance analytical methods and modeling tools with cycled cell data
  - Validate 532 and 811 models versus crack density and other diagnostic microscopy data
  - Calibrate NMC811 3D model versus capacity-fade data
  - Beyond initial break-in, isolate physics that cause long-term damage
  - Scale particle-damage model to electrode level, incorporate findings to design charge protocols and cathodes with improved life
- Continue the optimization effort of NMC particles for XFC
  - Not all SCs are equal. Optimized SCs for XFC application and explore radially oriented PCs.

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

RESPONSE TO PREVIOUS YEARS REVIEWS

- Not reviewed in Fiscal Year 2020

COLLABORATION ACROSS LABS AND UNIVERSITIES

Argonne National Laboratory	Cell and electrode design and building, performance characterization, post-test, cell and atomistic modeling, cost modeling
INL Idaho National Laboratory	Performance characterization, failure analysis, electrolyte modeling and characterization, Li detection, charging protocols
Berkeley Lab	Li detection, electrode architecture, diagnostics
NREL National Renewable Energy Laboratory	Thermal characterization, life modeling, micro and macro scale modeling, electrolyte modeling and characterization
Oak Ridge National Laboratory	Detailed Li plating kinetic models, SEI modeling
SLAC National Accelerator Laboratory	Li detection, novel separators, diagnostics

BYU ESRF UCL Purdue University

XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

U.S. Department of Energy | Energy Efficiency & Renewable Energy
Vehicle Technologies Office

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Michael Evans
Michael Toney
Molleigh Preefer
Nancy Dietz Rago
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Support for this work from the Vehicle Technologies Office, DOE-EERE: Samuel Gillard, Steven Boyd, and David Howell