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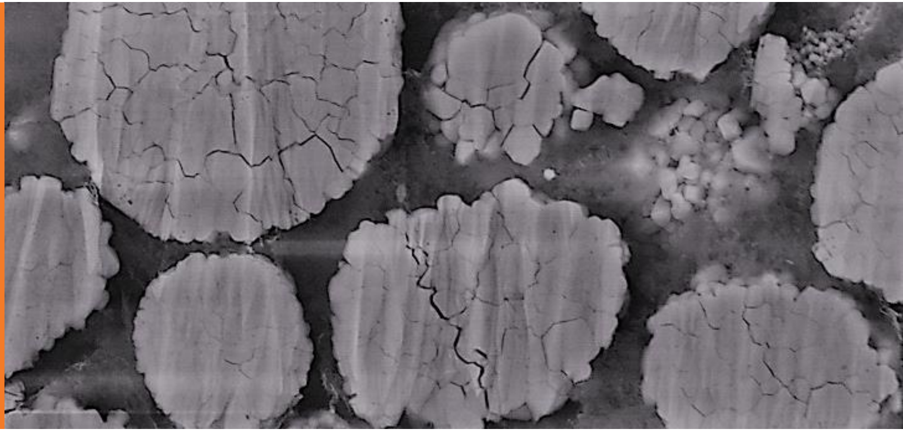
BAT 463
U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW

eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

EFFECTS OF EXTREME FAST CHARGING ON LITHIUM-ION BATTERY CATHODE



TANVIR R. TANIM

Idaho National Laboratory (INL)

CO-AUTHORS:

INL: Eric Dufek

Argonne: Kamila Wiaderek , Harry Charalambous, Stephen Trask, Zhenzhen Yang, Ira Bloom

NREL: Kandler Smith, Donal Finegan

LBNL: Guoying Chen

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

June 1-4, 2020
Web conference

INL/CON-20-58136

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 60%

Budget

- Funding for FY20 – 5.6M

Barriers

- Cell degradation during fast charge
- Full suites of cathode issues during fast charge is unknown
- Low energy density and high cost of fast charge cells

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 due to cathode degradation when charging above 4C
- Refine understanding on cathode cracking and other cathode aging mechanisms with respect to C-rate and SOC
- Use understanding to mitigate cathode issues during XFC

Objective:

- Using full cells to identify and quantify cathode failure modes/mechanisms, provide insights into materials degradation and other dominating mechanisms after cycling
- Map out cathode issues with respect to charging rate and more clear understanding of particle cracking and its evolution
- Develop complementary and aligned advanced analytical methods and modeling toolsets
- Guide future R&D efforts on mitigation and/or elimination of cathode issues

MILESTONES

Milestone	End Date	Lead	Status
Cell testing, provide assorted samples to other institutions. Identify aging mode at different C-rates	3/31/2020	INL	90%
Investigate in-operando heterogeneity of reaction and correlate with cracking	6/30/2020	Argonne	60%
Coordinate findings on additional aging mechanisms and report		INL	50%
Develop algorithm for defining critical crack size		NREL	50%
Quantify heterogeneity of aging and correlate with cracking	9/30/2020	SLAC	30%
Evaluate the effects of XFC on particles and micro-structures, identify improvement needs, and explore synthesis approaches to produce cathode particles w/ different microstructures	9/30/2020	LBNL	50%
Advanced cathode modeling	9/30/2020	NREL	60%

Covid-19 related work curtailment may delay some of the milestones

APPROACH

Impacts of high rate charging

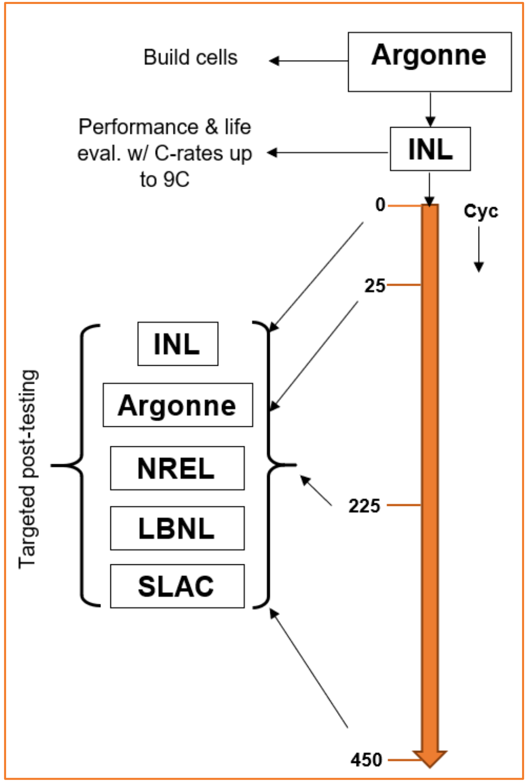
- Identify charge acceptance limitations
- Design of experiments with respect to charging rates and SOC
- Electrochemical analyses followed by targeted post-testing to evaluate changes in aging parameters as function of cycling

Identify key barriers as different charge conditions are used

- Focus clearly on identifying cathode aging mechanisms which weren't investigated before at XFC conditions

Quantify heterogeneity of aging and correlate with cracking

Particle microstructure modification for performance improvement during XFC

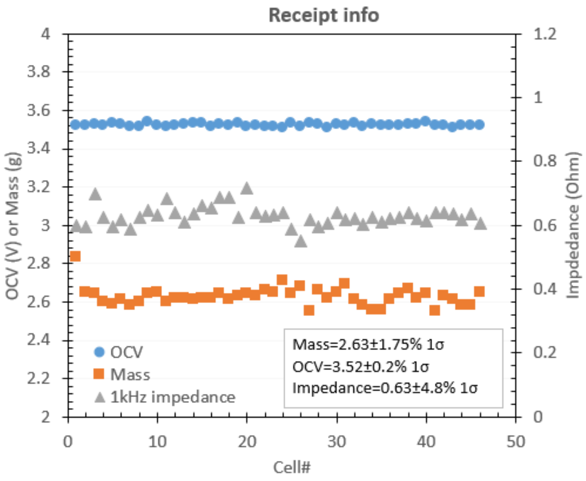


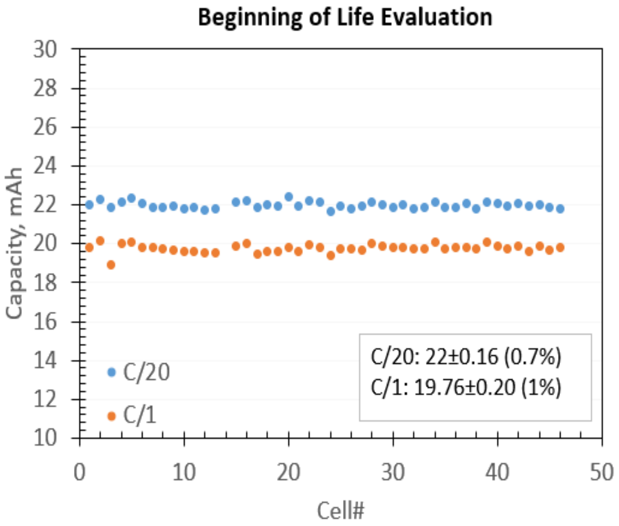
Develop complementary and aligned advanced analytical methods and modeling toolsets

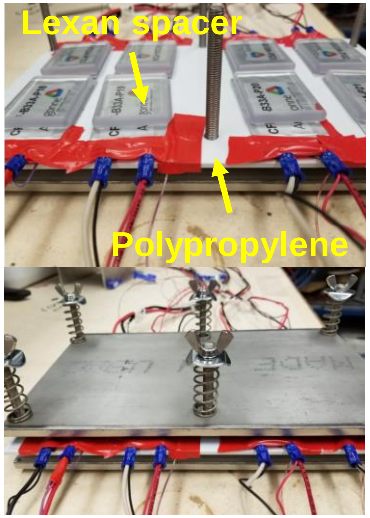
LOW VARIABILITY FOR AS RECEIVED CELLS

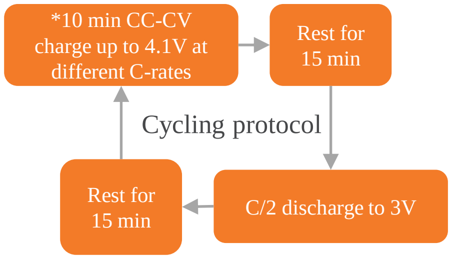
Test set up and design

- Used 19.8 mAh R1 gr/NMC532 CAMP cells with 1.9 mAh/cm^2 anodes.
- 40+ cells testing. Includes charging rates up to 9C.
- Testing at 30˚C.
- Targeted post-testing at different cycling interval, e.g., 0, 25, 225 and EOT.









*Charge time for 1C charge=60 min and 4C=15 min

FAST CHARGE AND AGING MODES

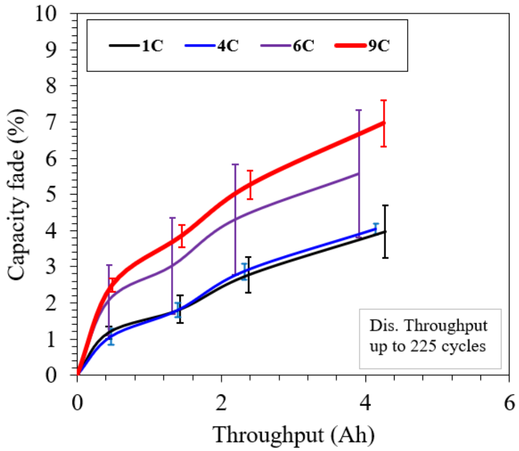
Electrochemical identification of aging modes using RPT and cycle-by-cycle data and IC analysis

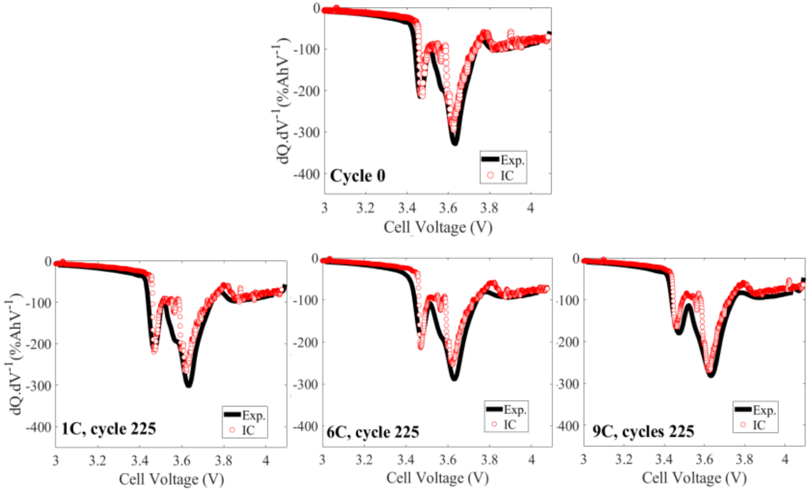
Lower C-rates: 1C

- SEI growth due to parasitic side reactions at Anode (LLI) dominates aging
- Loss of active material (LAM) in Cathode remains minimal

Higher C-rates: 4C to 9C

- Up to 6C: LLI dominates in Anode with some LAM in Cathode.
- > 6C: LAM overtakes LLI above 6C rates



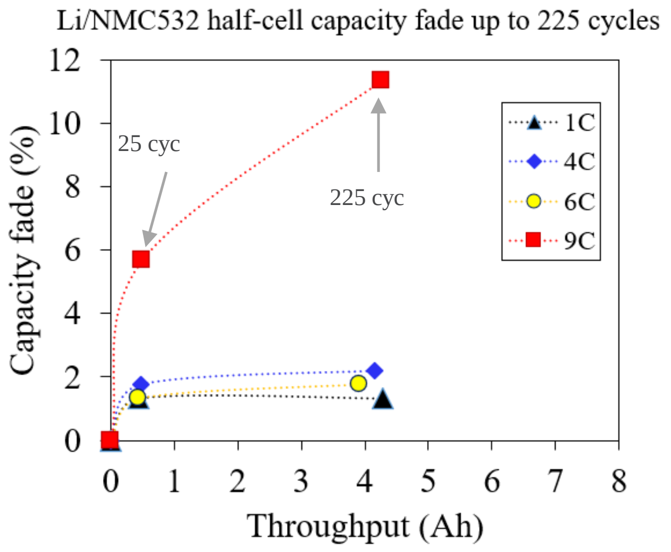


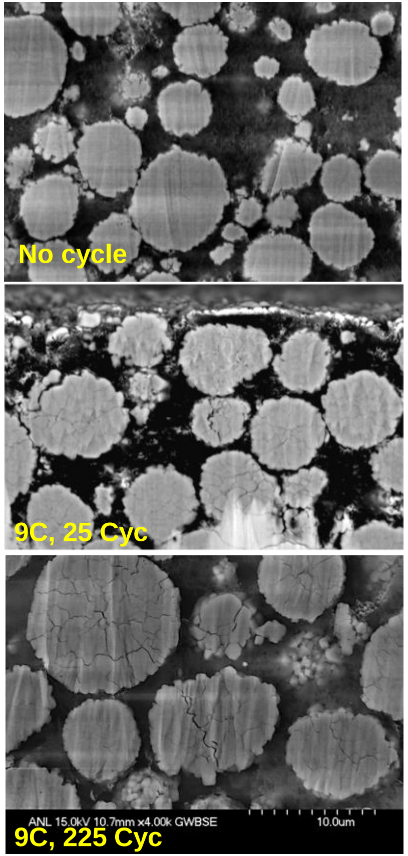
Results show good match between experimental and incremental capacity (IC) signatures with identified dominating aging modes.

FAST CHARGE AND AGING MECHANISMS

Aging modes verification with targeted post-testing

- LAM in cathode remains low up to 6C rates- *inline with prior EC analysis*. LAM increased drastically at 9C rate.
- Non-uniform rate of LAM in Cathode with cycles.
- SEM images of Cathode x-section show clear evidence of cracking at 9C: starting as early as 25 cycles, but not many, and then increases as cycling continued.



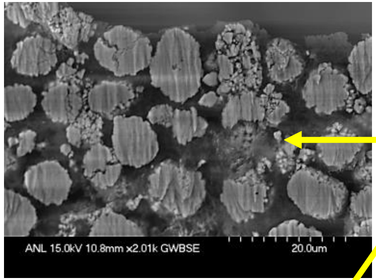


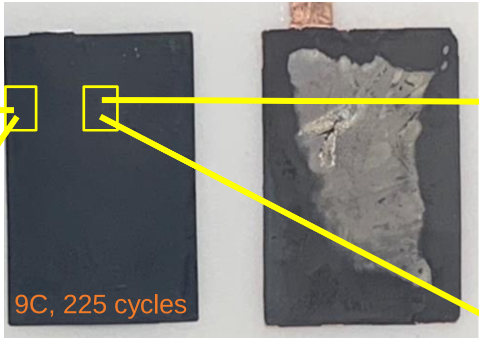
FAST CHARGE AND AGING MECHANISMS

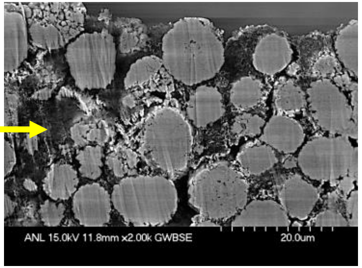
Evaluation of aging mechanisms and heterogeneity with targeted post-testing

Preliminary qualitative results do not show heterogeneity in cracking between center and edges

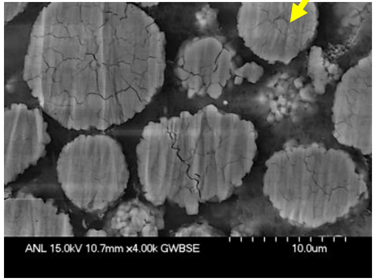
electrode surface

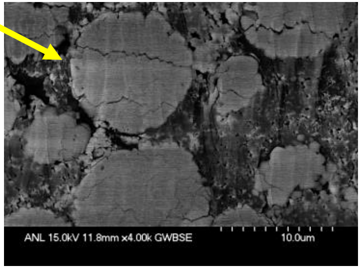






Electrode bulk



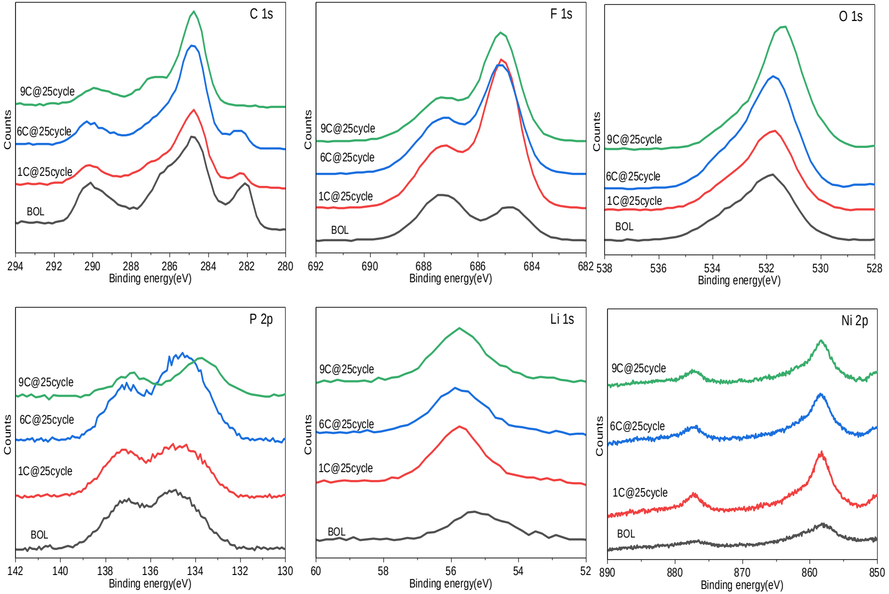


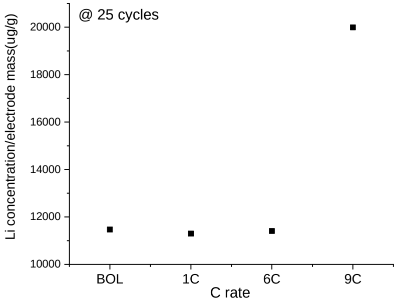
- Preliminary qualitative results of cross section of SEM showed both cathode edge (matched anode without Li plating) and in the center(matched anode with Li plating) displayed similar cracks.
- SEM images will be used to develop crack identification and quantification algorithms.

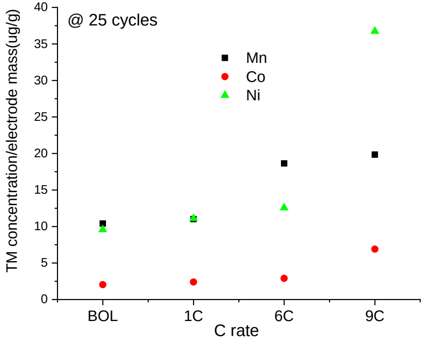
FAST CHARGE AND AGING MECHANISMS

XPS and ICP-MS of Anode for evaluating crosstalk and TM dissolution

- XPS of Anode shows surface compositions (C, F, O, P, Li) change at different C rates.
- Ni dissolution was found, but no Mn and Co detected by XPS at the surface (up to~10nm thick), indicating Co and Mn segregation at the cathode surface.
- Bulk measurements such as ICP-MS confirms increased presence of TM (particularly Ni and Mn) on Anodes with increased charge rate.





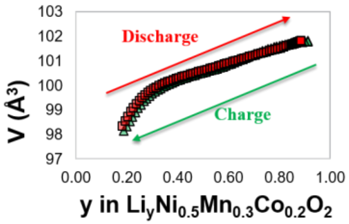


Preliminary results at 25 cycles

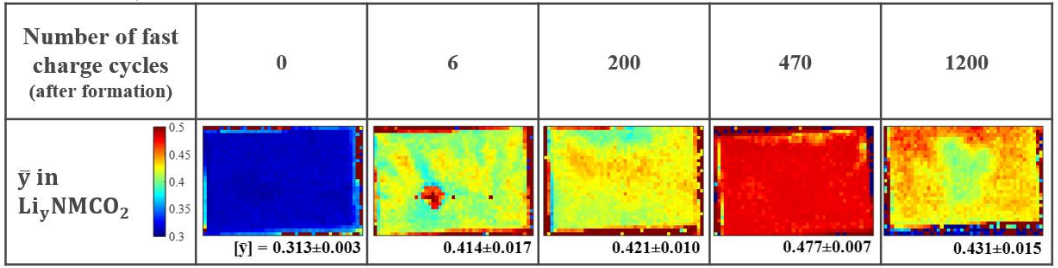
IN-OPERANDO RXN HETEROGENEITY

Identified the evolution of reaction heterogeneity in space and time

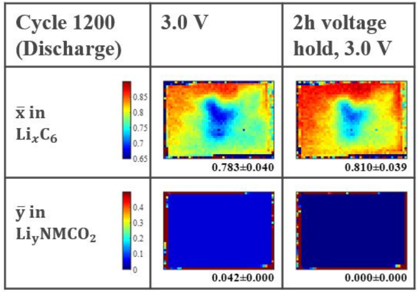
- Fast charge rate lowers charge efficiency, induces spatial heterogeneity across cathode.
- Residual cell outgassing temporarily lowers local area cycling efficiency, does not affect long term performance of region.
- Throughout mid-life of cell higher edge delithiation, at end-of-life higher center delithiation observed. Is it better performance or lithium loss?



Used (003) and (105) for lattice parameter and volume calc.



Spatial maps of lithium concentration within NMC lattice at 6C fast charge (4.1V, CCCV)



- Despite uniform delithiation of remaining lithium in graphite lattice after discharge, the cathode lithium concentration remains highly heterogeneous, suggesting permanent lattice-lithium loss from the cell center or ability of NMC532 to store lithium.

XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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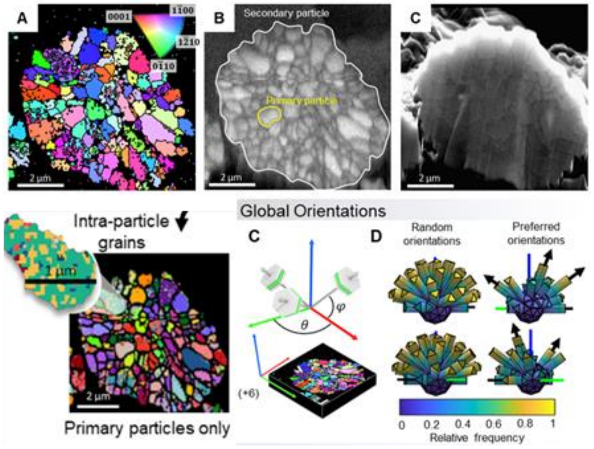
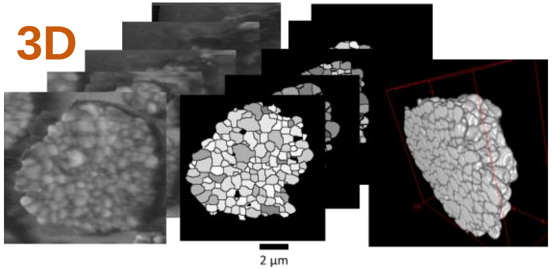
3D MAPPING OF CATHODE PARTICLE GRAINS

Developed process for quantifying properties to understand sub-particle Li transport

- Orientation of crystals in anode/cathode materials determine how Li moves throughout particles during operation
- Electron backscatter diffraction (EBSD) used to map NMC532 sub-particle grain morphologies and orientations
- Deep learning neural network method used to identify and segment grains from EBSD data
- Grains distinctly labelled for analysis
- Not all grains have single crystal orientations, some have sub-grain defects (crystal twins)
- Extension to 3D achieved via FIB-EBSD (slice by slice)
  - Multi-detector use and slice-wise sample realignment
  - Errors in sample realignment corrected post-process



3D

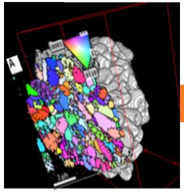


Quinn et al.; The application of electron backscatter diffraction for investigating intra-particle grain architectures and boundaries in lithium-ion electrodes, ***submitted***

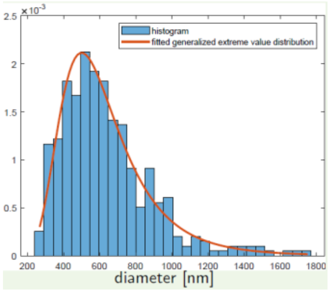
QUANTIFYING TRANSPORT-RELEVANT GRAIN PROPERTIES

Statistics of sub-particle grain characteristics

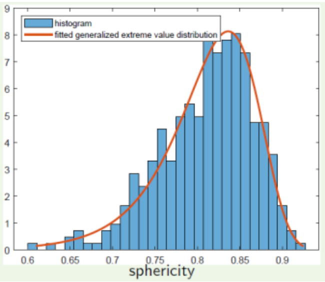
Processed 3D EBSD data



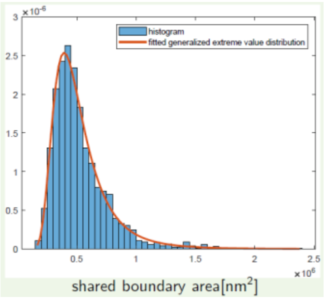
Equivalent diameter distribution



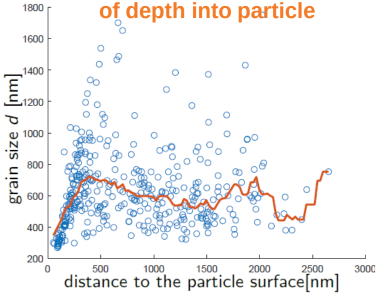
Grain sphericity distribution



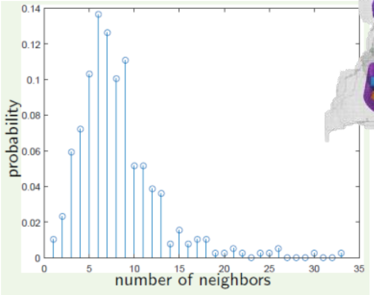
Shared boundary area between grains



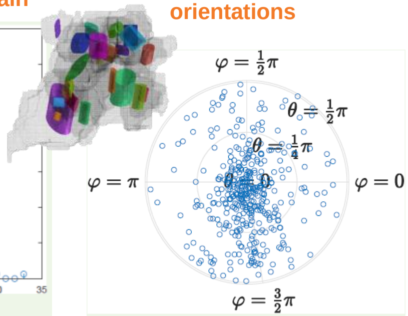
Grain size as a function of depth into particle



Distribution of the number of connecting neighbors per grain



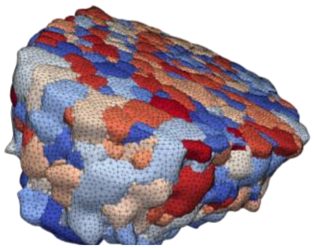
Distribution of grain orientations



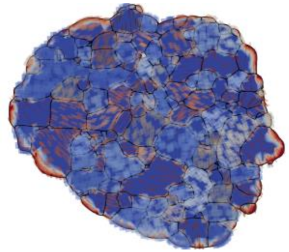
COHESIVE ZONE MODEL OF NMC532 INTERGRANULAR TRANSPORT/FRACTURE

- Model simulates multiple CC-CV cycles using
  - Butler-Volmer boundary conditions (non-uniform flux)
  - Anisotropic diffusivity
  - Coupled diffusion and solid mechanics
- Intergranular contact treated with cohesive zone element
  - Grain-to-grain delamination when failure threshold exceeded
  - Further intergranular Li transport impeded due to delamination
- Presently validating model
  - Fracture criteria
  - Mechanical boundary cond.
  - Capacity fade
  - Damage pattern
- Next steps
  - 3D simulations
  - Recommendations for NMC architectures & charge protocols

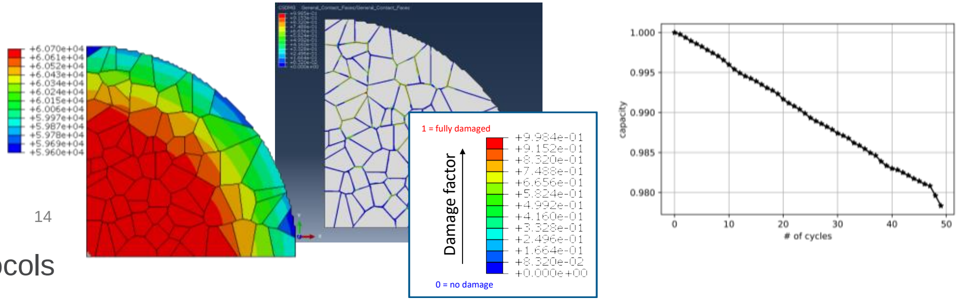
Geometry from 3D EBSD mapping



Anisotropic diffusivity in grains



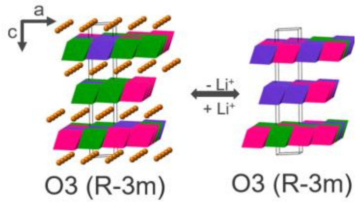
Evolution of concentration/transport, damage pattern and capacity fade over multiple cycles



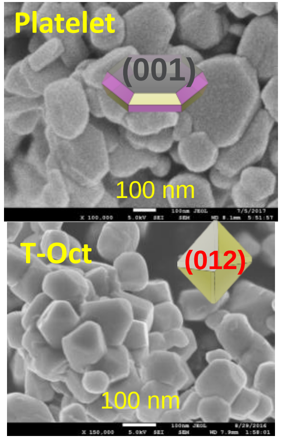
PARTICLE MICROSTRUCTURE MODIFICATION FOR PERFORMANCE IMPROVEMENT

Effect of primary particle morphology on rate

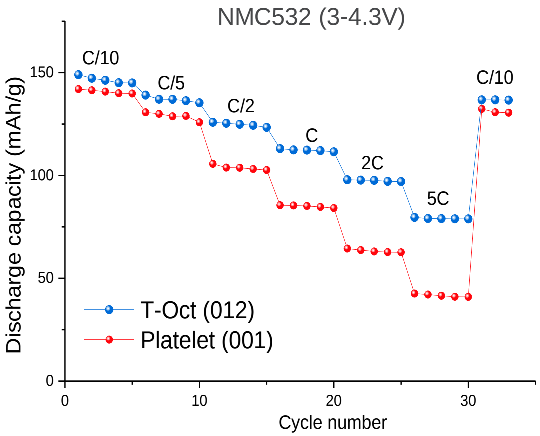
- XFC exacerbates strain caused by anisotropic expansion/contraction.
- Microstructures of current NMC particles are not optimized for XFC
- Primary particle morphology matters – T-Oct particles with (012) surface have better rate capability than platelet particles with (001) surface.

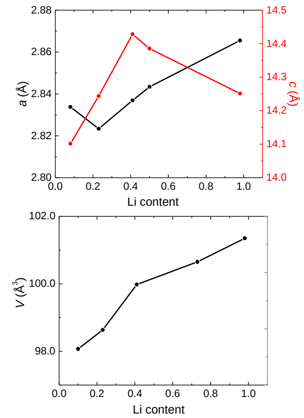


SC-NMC532 (LBNL)



Single crystals ~200-300 nm in size synthesized with different surface orientation



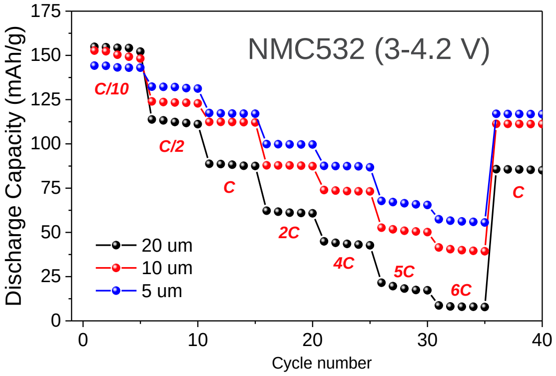


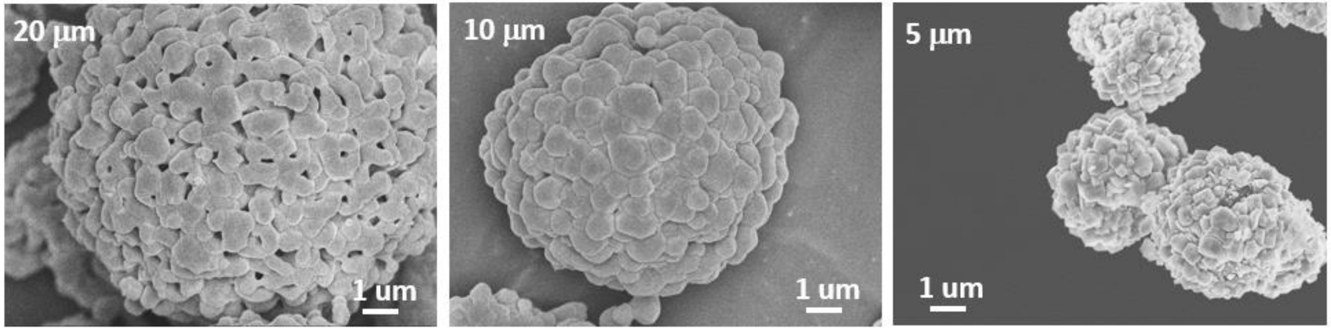
G. Chen et al, *J. Electrochem. Soc.* **159** (9), A1543 (2012)

PARTICLE MICROSTRUCTURE MODIFICATION FOR PERFORMANCE IMPROVEMENT

Effect of secondary particle size investigated

- Secondary particle size varied by changing the solvent mixture used in NMC precursor synthesis
- Reducing secondary particle size improves rate capability



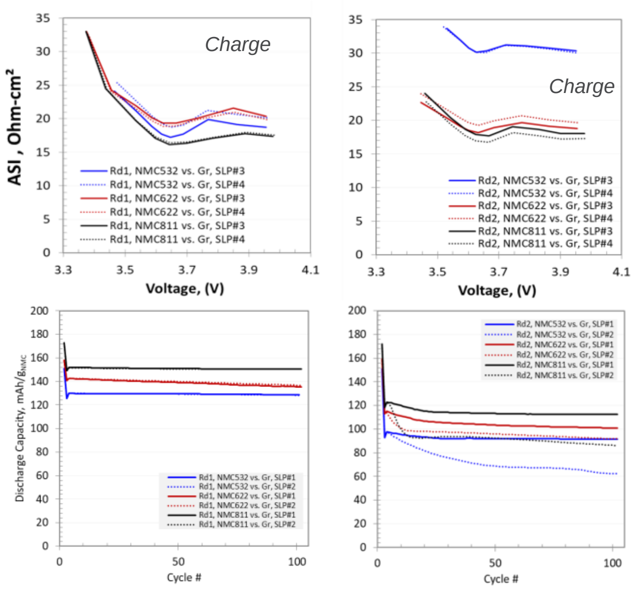


IMPACT OF XFC ON OTHER NMC CHEMISTRY

Quick evaluation of NMC622 & NMC811 and comparison with NMC532 (baseline)

- NMC811 shows the most reduction in HPPC ASI resistance due to thinner electrode design. This could potentially alleviate transport issues during XFC.
- Limited cycling at 6C shows comparable performance of NMC622 and 811 to NMC532. Additional cycling with Gr/NMC811 cells at multiple C-rates will be performed later in the FY and compared with NMC532 (baseline) cell performance.

<u>3.0-4.1V (6C Charging)</u>
2 Cycles of C/10 Charge, C/10 Discharge
100 Cycles of 6C Charge (CCCV with 10 min total time limit), C/2 Discharge (CC) at 30˚C



SUMMARY

- Elevated rates enhance cathode cracking and TM dissolution
  - TM dissolution and cathode cracking could be avoided if charge rate remains at or below 6C.
  - Early to conclude that cracking is the sole mode of LAM in cathode.
- Fast charge rate induces significant spatial heterogeneity in utilization across cathode
  - Advanced algorithm to define critical crack size is underway
  - A correlation between spatial utilization and cracking is being explored
- Full extent of other cathode aging mechanisms is not fully understood at this point of the study
- Developed processes and modeling tools including sub-particle information
  - To quantify properties to understand sub-particle Li transport
  - Understand intergranular transport/fracture at different aging states and charging conditions
  - Pending experimental validation
- Started to see how particle morphological changes improve performance during XFC

NEXT STEPS

- Complete at least 450 fast charge cycles and complete the targeted post-testing
  - See whether the aging modes and mechanisms hold for extended XFC cycling
  - Identify and quantify other aging modes and their relative extents specific to fast charging
- Obtain more understanding of the spatial distribution of utilization and cracking
- Continue developing/refining advance analytical methods and modeling tools with cycled cell data
  - Clarify the impact of sub-particle grain characteristic on electrode performance through image-based electro-mechanical modelling
  - Conduct EBSD on degraded, cracked particles and elucidate the relationship between crack positions and grain orientations. Compare to fresh particles.
  - Use 3D model to understand how damage propagation and aging/performance depend on cycling, charge protocol and NMC architecture
- Continue the optimization effort of NMC particles for XFC

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

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Hansen Wang
Harry Charalambous
Ilya Shkrob
Ira Bloom
James W. Morrissette
Jiayu Wan
Jeffery Allen
Johanna Nelson Weker
Josh Major
John Okasinski
Juan Garcia
Kae Fink
Kandler Smith
Kamila Wiaderek
Kevin Gering
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