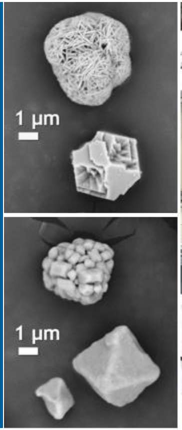
Process R&D Using Supercritical Fluid Reactors



Youngho Shin (PI)
Carrie Siu

Argonne National Laboratory
Project ID: BAT470

June 2021
Virtual

Overview

Timeline

- Project start date: Oct. 2019
- Project end date: Sept. 2021
- Percent complete: On-going

Budget

- Total project funding:
  - $ 600K in FY21

Barriers

- Advanced synthesis processes and materials are needed to improve battery performance.
- New active battery materials with desired particle size, morphology, and composition distribution are not commercially available.

Partners

- Battery material process R&D:
  - Brookhaven National Laboratory
    - 3D XRF tomography
    - XANES and EXAFS
  - University of Wisconsin
    - Nano-indentation
    - Particle elasticity
  - University of California, Irvine
    - HRTEM
  - Argonne Post-Test Facility
    - Cross-sectional SEM of cycled cathode electrode
    - XPS analysis

Relevance

- The relevance of this program to the DOE Vehicle Technologies Program is:
  - Emerging synthesis processes need to be explored to enable rapid robust reproducible manufacturing of active battery materials.
  - This program is a key missing link between the discovery of advanced battery materials, market evaluation of these materials, and high-volume manufacturing.
  - It reduces the risk associated with the synthesis process development and scale-up of new battery materials.

- The objective of this program is to establish flexible R&D capability of supercritical fluid reactions as an emerging manufacturing process for active battery materials:
  - Develop a robust and reproducible hydro-solvothermal (HYST) synthesis process to assure economic feasibility and scale-up strategies.
  - Produce and provide single-crystal battery materials with desired particle size, morphology, and composition distribution to support fundamental research.
  - Characterize single-crystal battery materials and improve their high-rate capability and long-term cyclability by synthesis process optimization.

Approach : Milestones

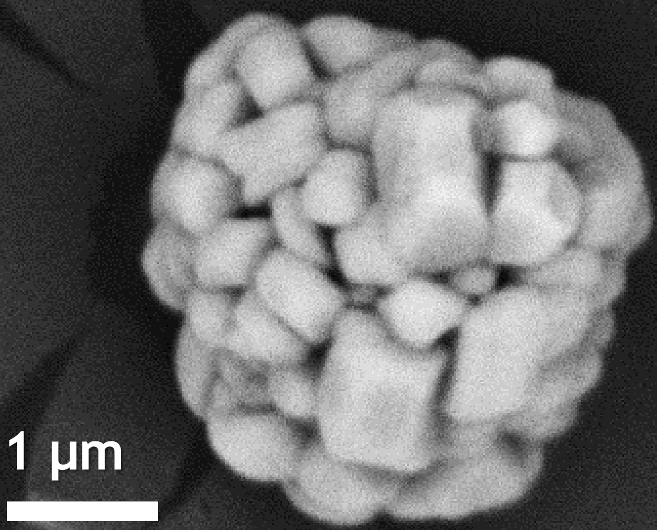
2020	Hydrothermal synthesis process set-up ▪ System adjustment to produce single-crystal NMC96-2-2 precursor ▪ Synthesis process tuning and reaction chemistry confirmation ▪ Preliminary material synthesis and evaluation for feedback to synthesis process	*Completed*	Q4
2021	Production of single-crystal NMC96-2-2 cathode ▪ Derivation of process parameters and understanding of their impacts ▪ Particle size and morphology control of single-crystal NMC96-2-2 precursor ▪ Lithiation and heat treatment optimization ▪ Material characterization and electrochemical performance evaluation ▪ Provide produced materials to collaborators	*Completed*	Q1
	Preliminary synthesis of Al/Zr-doped single-crystal NMC96-2-2 cathodes ▪ Synthesis process tuning ▪ Preliminary synthesis of Al/Zr-doped single-crystal NMC96-2-2 precursors and cathodes ▪ Preliminary material characterization and electrochemical test	*In-progress*	Q2
	Production of Al/Zr-doped single-crystal NMC96-2-2 cathodes ▪ Optimize the size and morphology of Al/Zr-doped single-crystal NMC96-2-2 cathodes ▪ Evaluate the effect of Al/Zr-doping amount ▪ Material characterization and electrochemical performance evaluation ▪ Provide produced materials to collaborators	*go/no-go*	Q3

Approach : Strategy

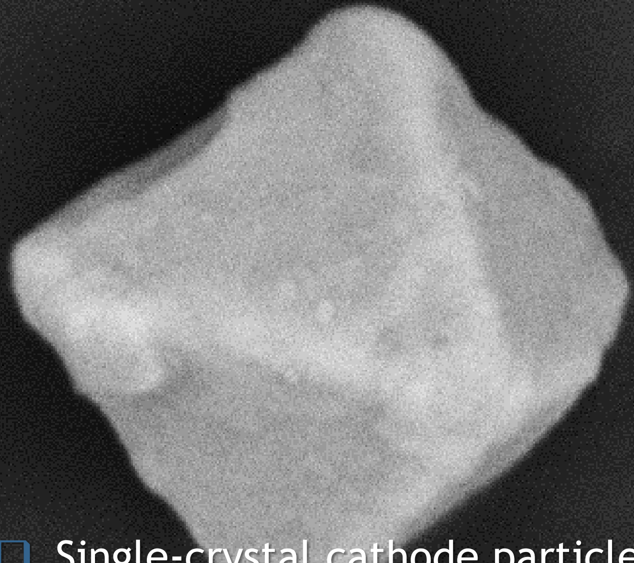
- Commercializable hydro-solvothermal process is one of the most important synthesis routes to produce single-crystal particle.
- Hydro-solvothermal process can tailor the morphology of single-crystal particle by changing the reactant, concentration, pressure, temperature, and mineralizer.
- Establish a flexible hydro-solvothermal synthesis platform to produce advanced single-crystal battery materials with desired particle size, morphology, and composition distribution.
- Provide single-crystal battery materials with advanced features to support basic researchers and to facilitate industrial evaluation:
  - 1~3 micron single-crystal particle without internal void fraction to enhance electrode density
  - Longer cycle life with robust particle structure by suppressing particle crack during cycling
  - Reduced surface area without internal grain boundary to mitigate side reaction
  - Facet-controlled particle morphology to enable faster lithium transport

Approach : Polycrystalline vs Single-crystal Cathodes

- Polycrystalline cathode particle
  - Secondary particle composed of primary particles having a size of several hundred nanometers

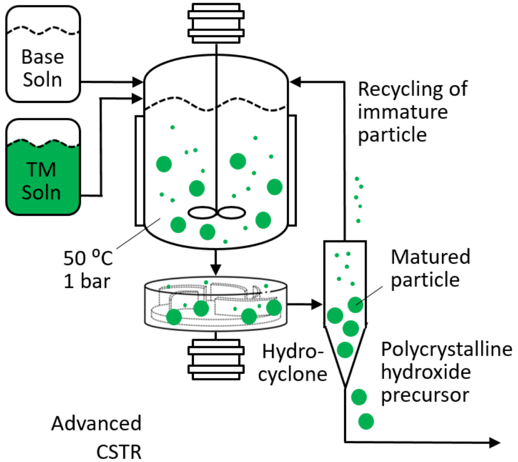


VS



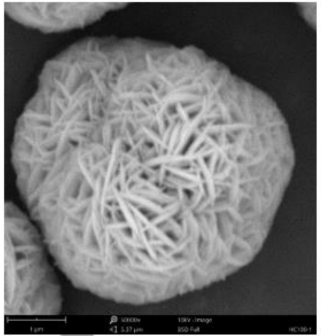
- Single-crystal cathode particle
  - Micron-sized robust structure w/o particle crack
  - High electrode density w/o internal void fraction
  - Reduced surface area mitigating side reaction
  - Facet-controlled morphology for faster Li transport
  - Improved surface coating effect

Single-crystal Material via Hydrothermal Synthesis

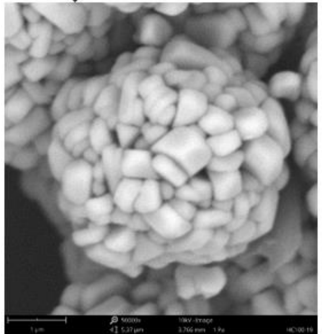


US. Patent 9,446,967
US. 2020/0099045 A1

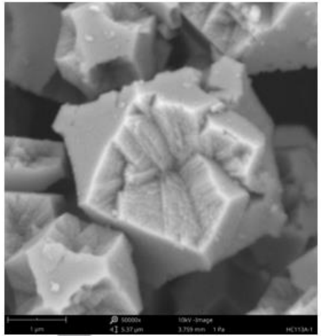
$Ni_{0.96}Co_{0.02}Mn_{0.02}(OH)_2$
co-precipitated precursor



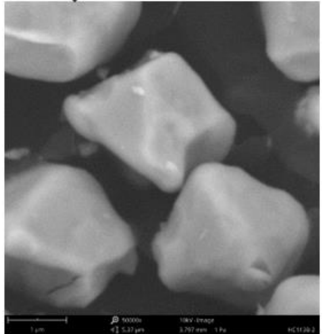
Lithiation
Calcination

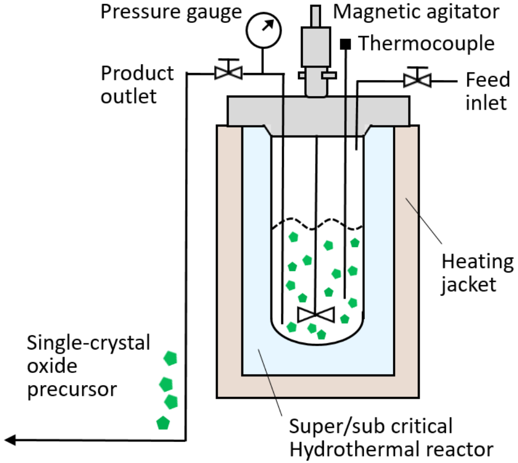


$Ni_{0.96}Co_{0.02}Mn_{0.02}O$
hydrothermal precursor



Lithiation
Calcination





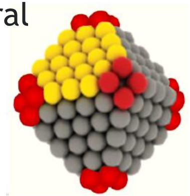
Patent filed

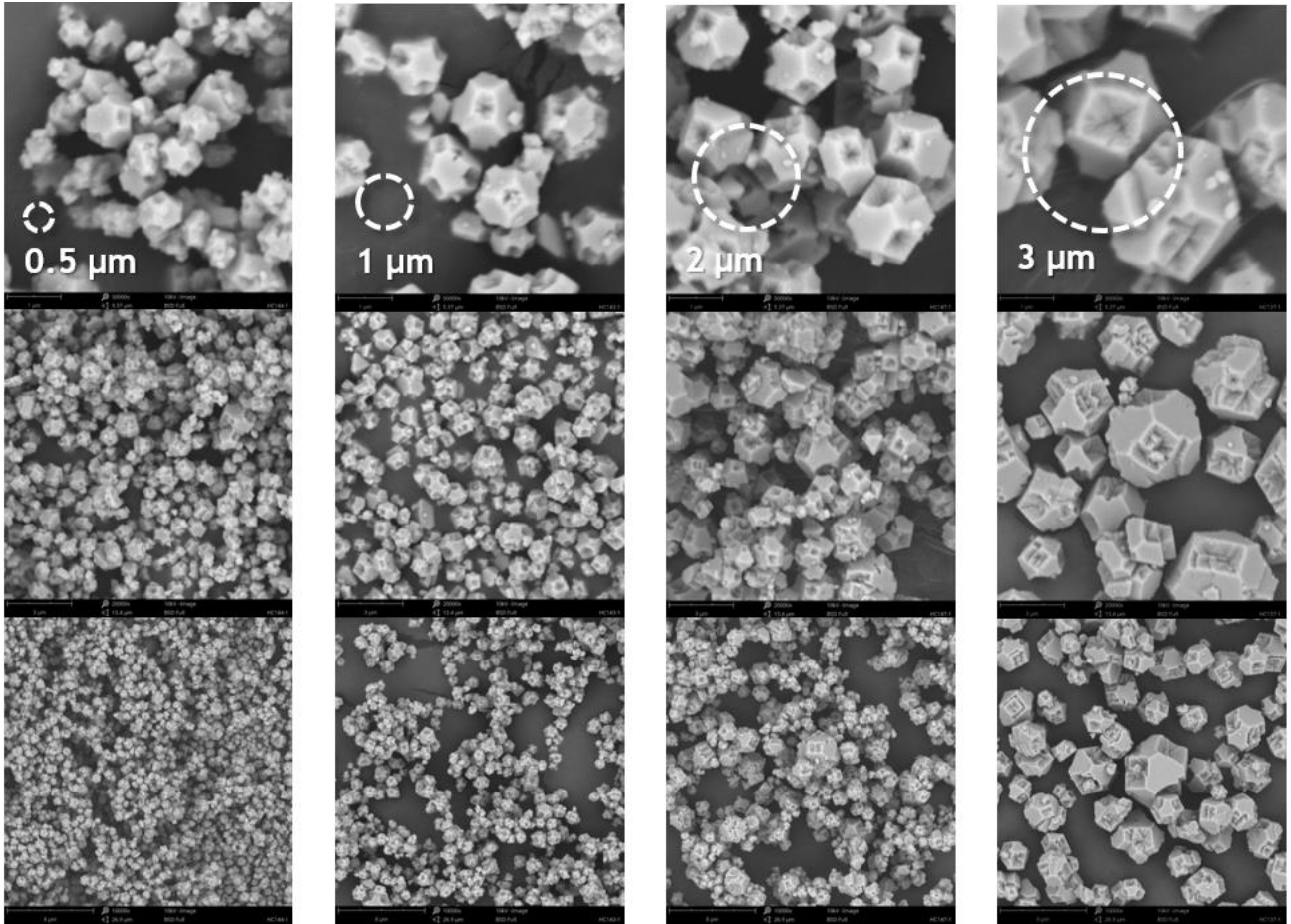
- Super/sub-critical hydrothermal process can tailor crystallization by adjusting the reactant, concentration, pressure, temperature, and mineralizer.

Single-crystal Hydrothermal Precursor

❑ Size-controlled NMC96-2-2 oxide precursor

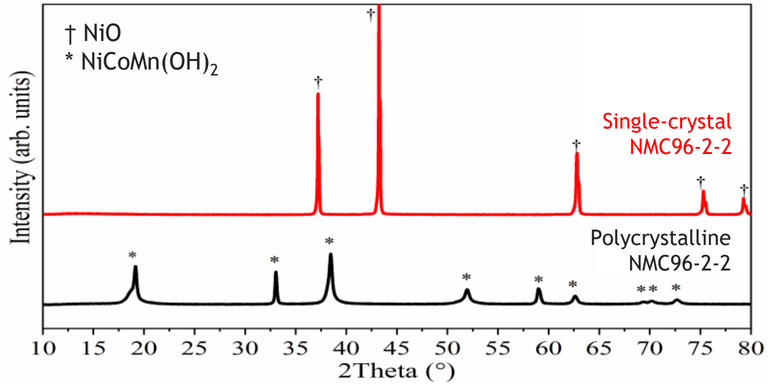
- Single crystals with size ranging from 0.5 μm to 3 μm were produced.
- Truncated octahedral shape is obtained regardless of size.
- Particle shape evolution can be controlled by adjusting growth rates along the [100] and [111] facet directions.



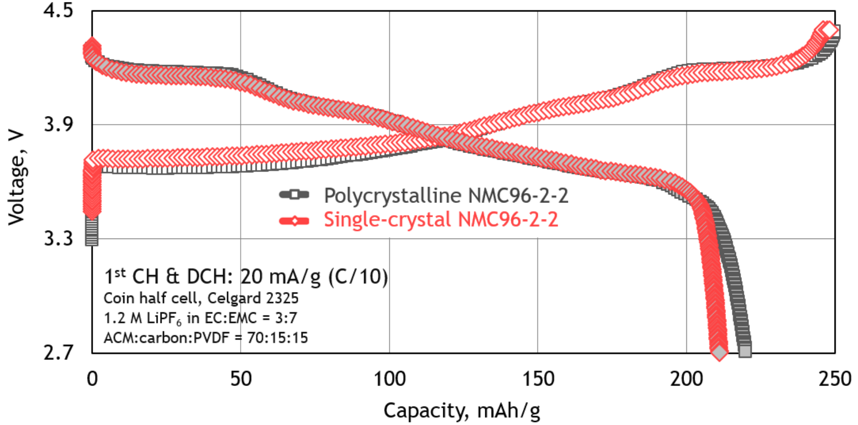


XRD and Electrochemical Performance

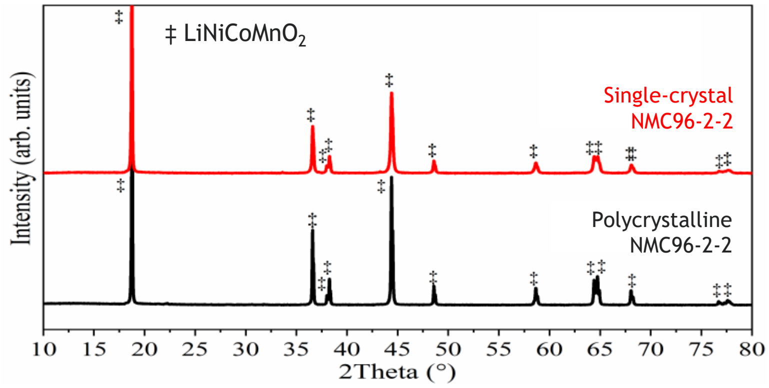
- Polycrystalline & single-crystal precursors

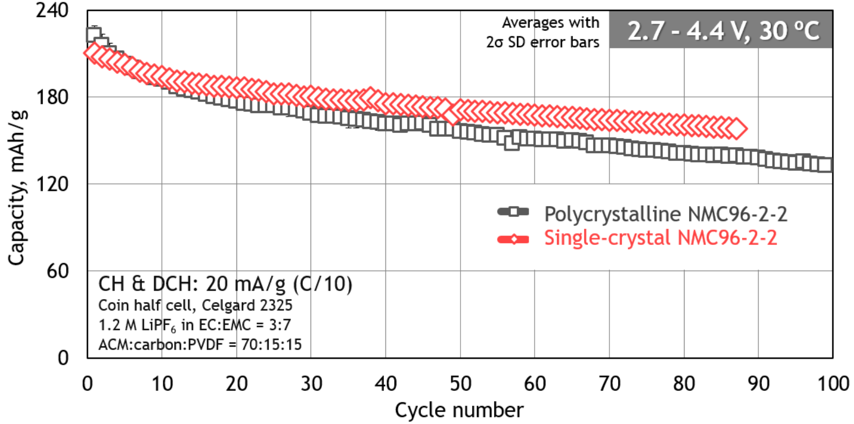


- Coin half-cell evaluation



- Polycrystalline & single-crystal cathodes





Diagnosis at ANL Post-Test Facility

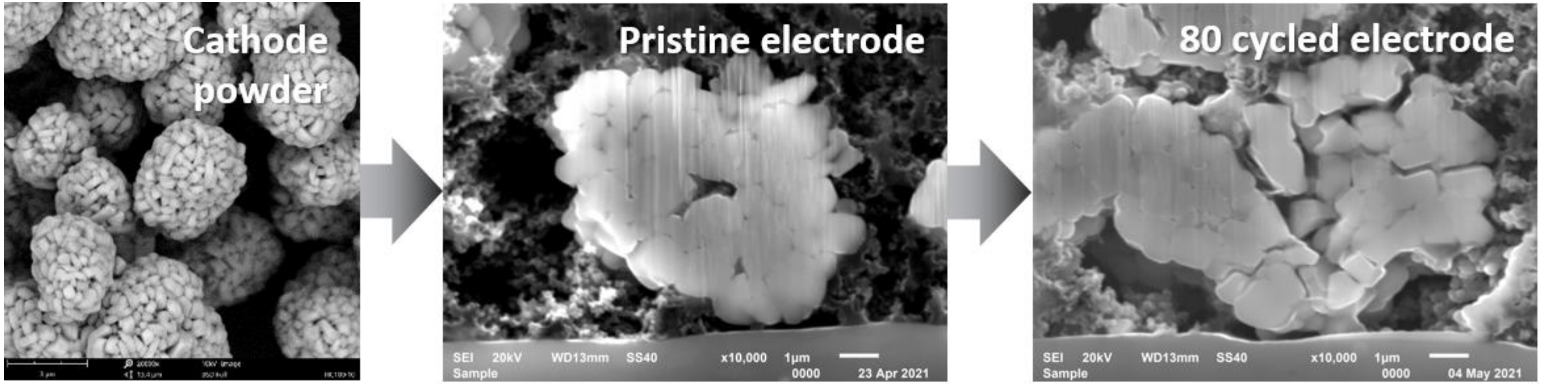
Argonne NATIONAL LABORATORY | 75 1946–2021

Dr. Seoung-Bum Son & Dr. Ira Bloom

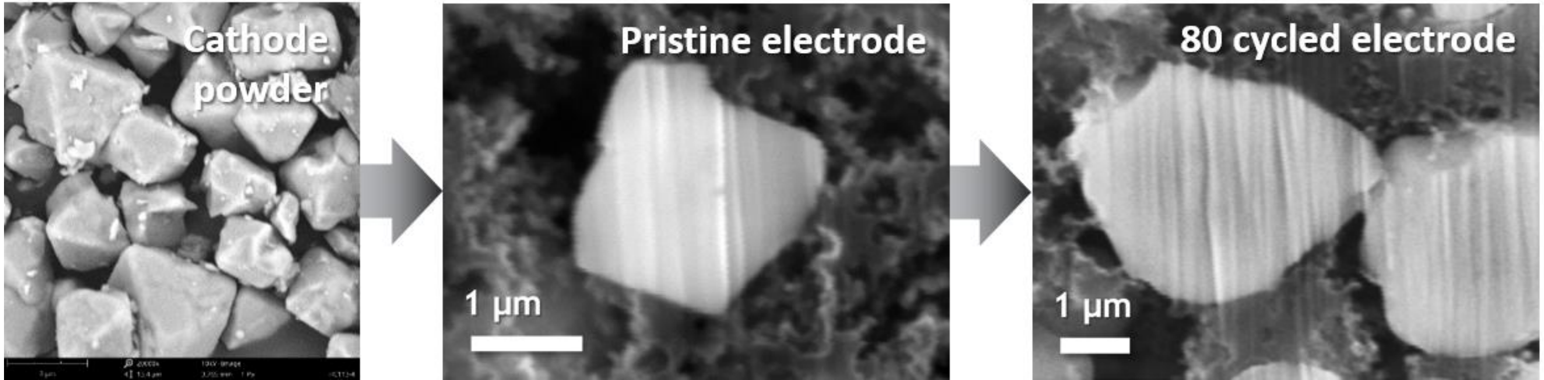
- Cross-sectional SEM observation of cathode electrodes

Before cycling | After cycling

Polycrystalline NMC96-2-2 cathode



Single-crystal NMC96-2-2 cathode



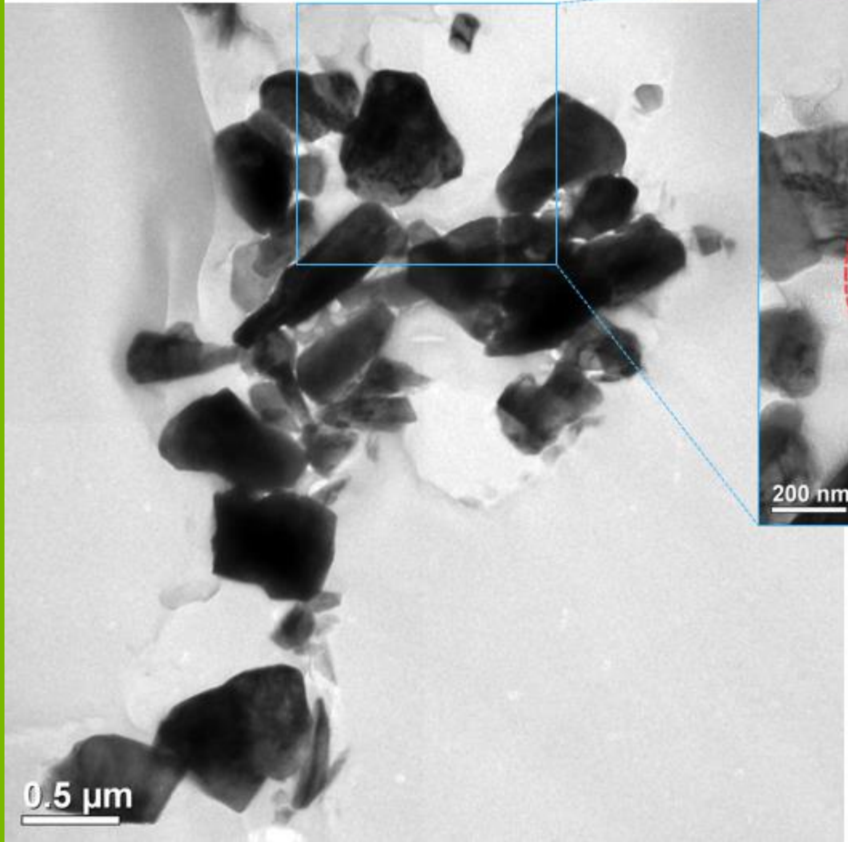
TEM of Single-crystal NMC96-2-2 Cathode

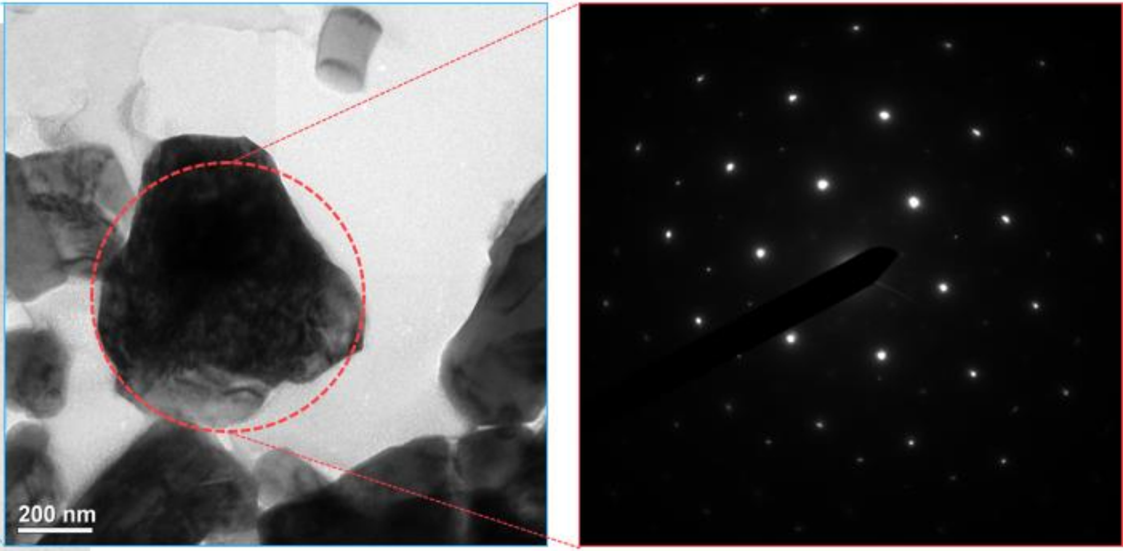
BROOKHAVEN NATIONAL LABORATORY

Dr. Feng Wang

- Bright-field TEM imaging

Electron-diffraction



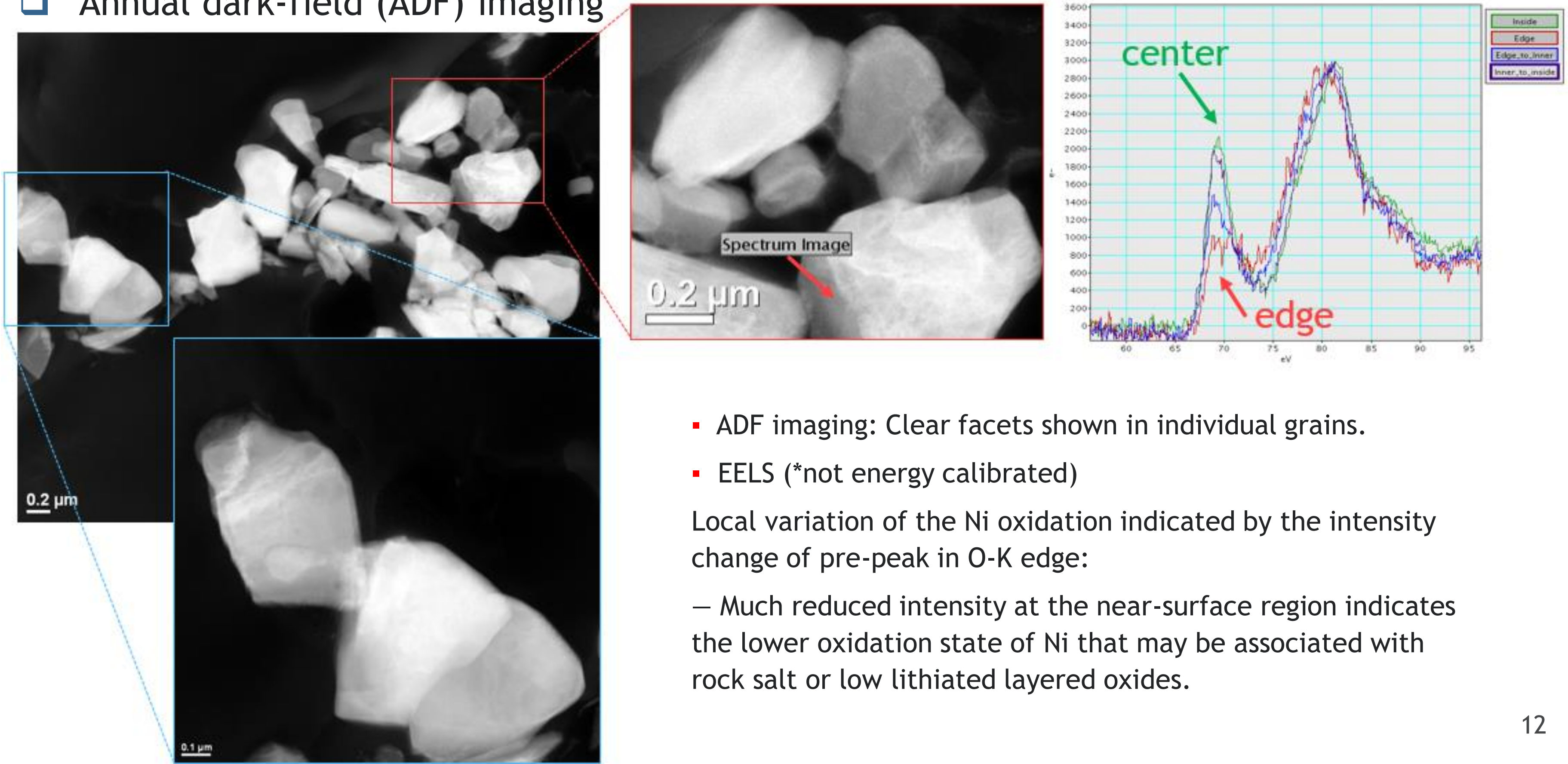


- Diffraction spots dominantly arising from scattering from the same set of lattice planes (i.e. 001). (*less intense spots may come from broken particle around the large particle.)
- Electron-diffraction result shows single-crystal nature of the large-sized particles.

TEM of Single-crystal NMC96-2-2 Cathode

BROOKHAVEN NATIONAL LABORATORY
Dr. Feng Wang

- Annual dark-field (ADF) imaging



- ADF imaging: Clear facets shown in individual grains.
- EELS (*not energy calibrated)

Local variation of the Ni oxidation indicated by the intensity change of pre-peak in O-K edge:

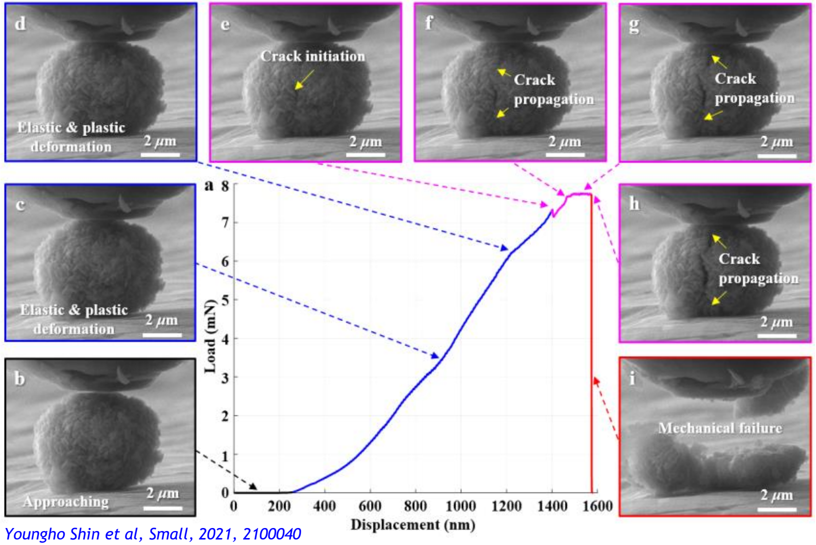
— Much reduced intensity at the near-surface region indicates the lower oxidation state of Ni that may be associated with rock salt or low lithiated layered oxides.

Particle Crack Analysis by Nano-indentation

WISCONSIN
UNIVERSITY OF WISCONSIN–MADISON
Prof. Sangkee Min

❑ Indentation measurement

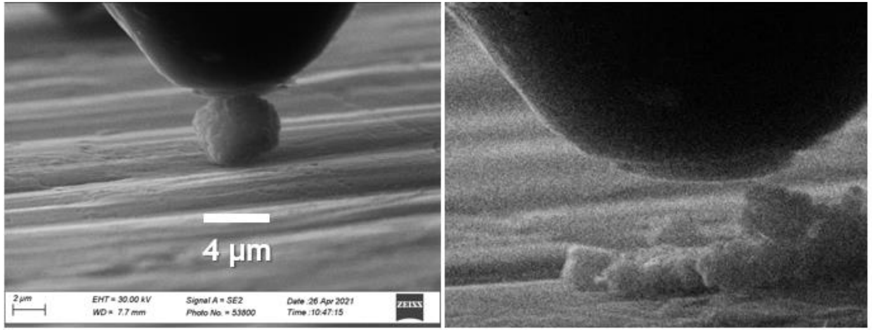
- a) example of L–D curve for polycrystalline NMC622;
- b) the indenter tip is approaching the particle;
- c-d) the particle is elastically and plastically deformed;
- e) the crack initiates;
- f-h) the crack propagates;
- i) the particle is totally shattered

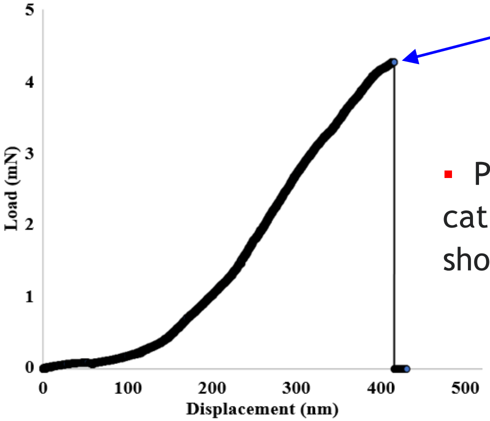


Youngho Shin et al, Small, 2021, 2100040

❑ Indentation of polycrystalline NMC96-2-2

Before indenting　　After indenting



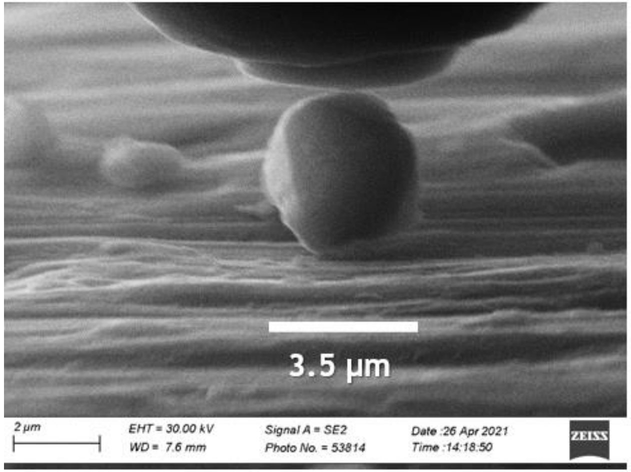


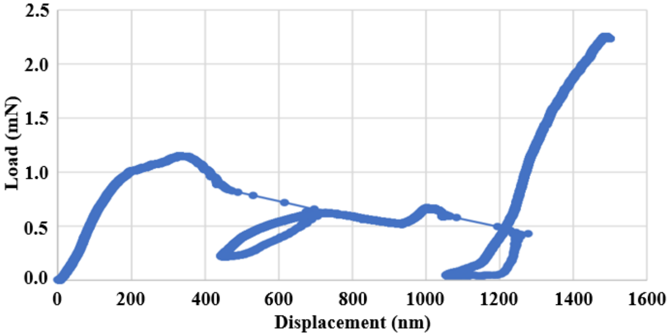
- Polycrystalline NMC96-2-2 cathode particle with 4μm size shows breaking force of 4.3mN.

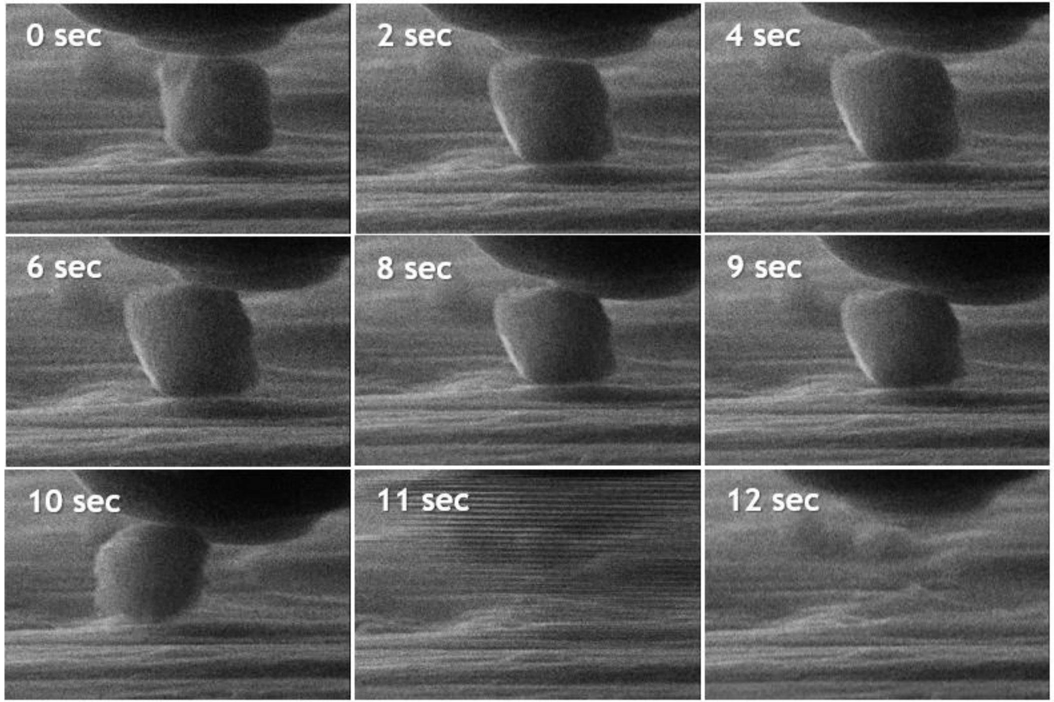
Particle Crack Analysis by Nano-indentation

WISCONSIN
UNIVERSITY OF WISCONSIN–MADISON
Prof. Sangkee Min

- Indentation of single-crystal NMC96-2-2 cathode

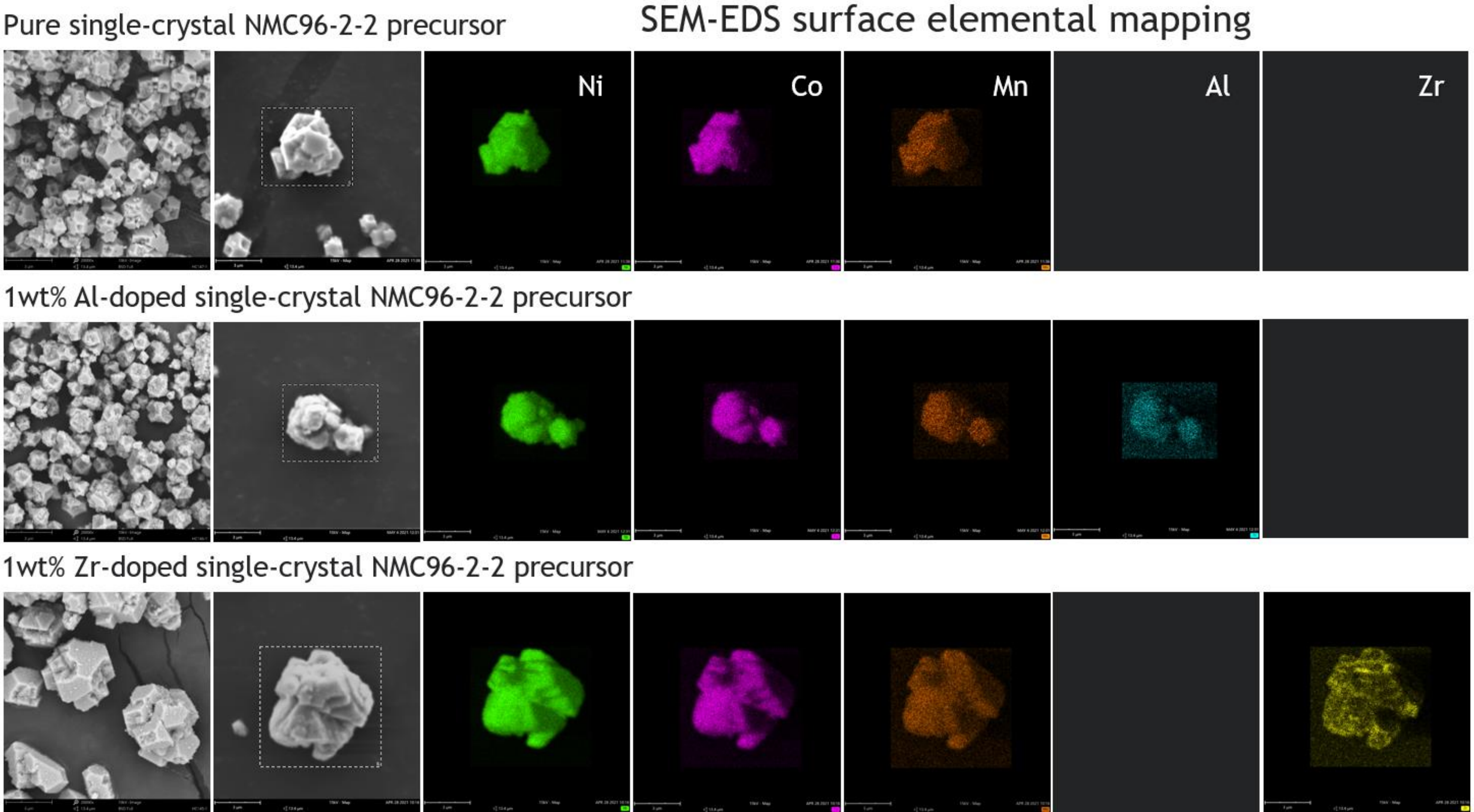






- Larger indenter and/or dimpled surface may bring particle to rest at an equilibrium position.

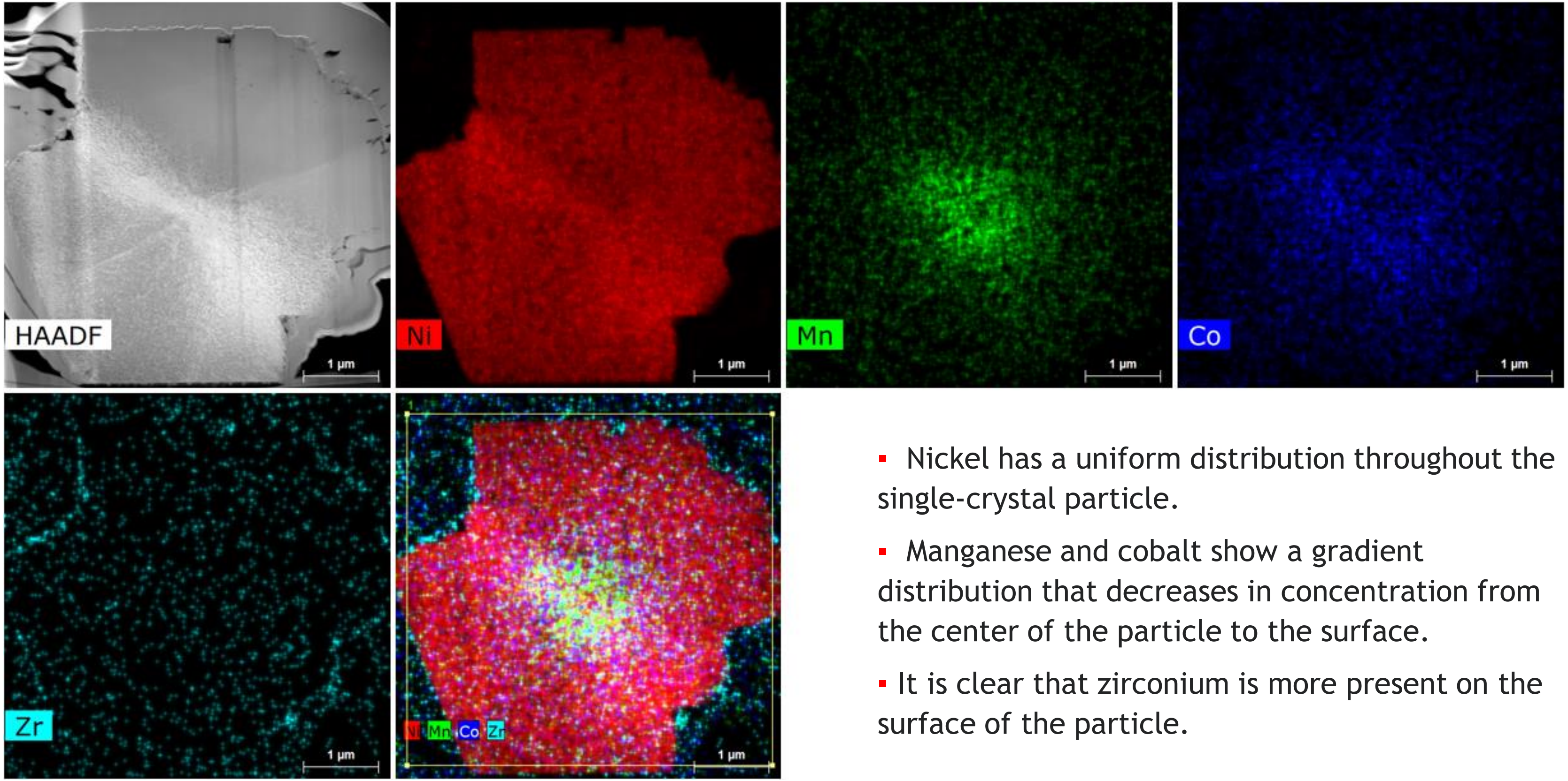
Al/Zr-doped Hydrothermal NMC96-2-2 Precursors



FIB Cross-section of Zr-doped Precursor

UCIrvine
University of California · Irvine
Prof. Huolin Xin

- 1wt% Zr-doped single-crystal NMC96-2-2 precursor

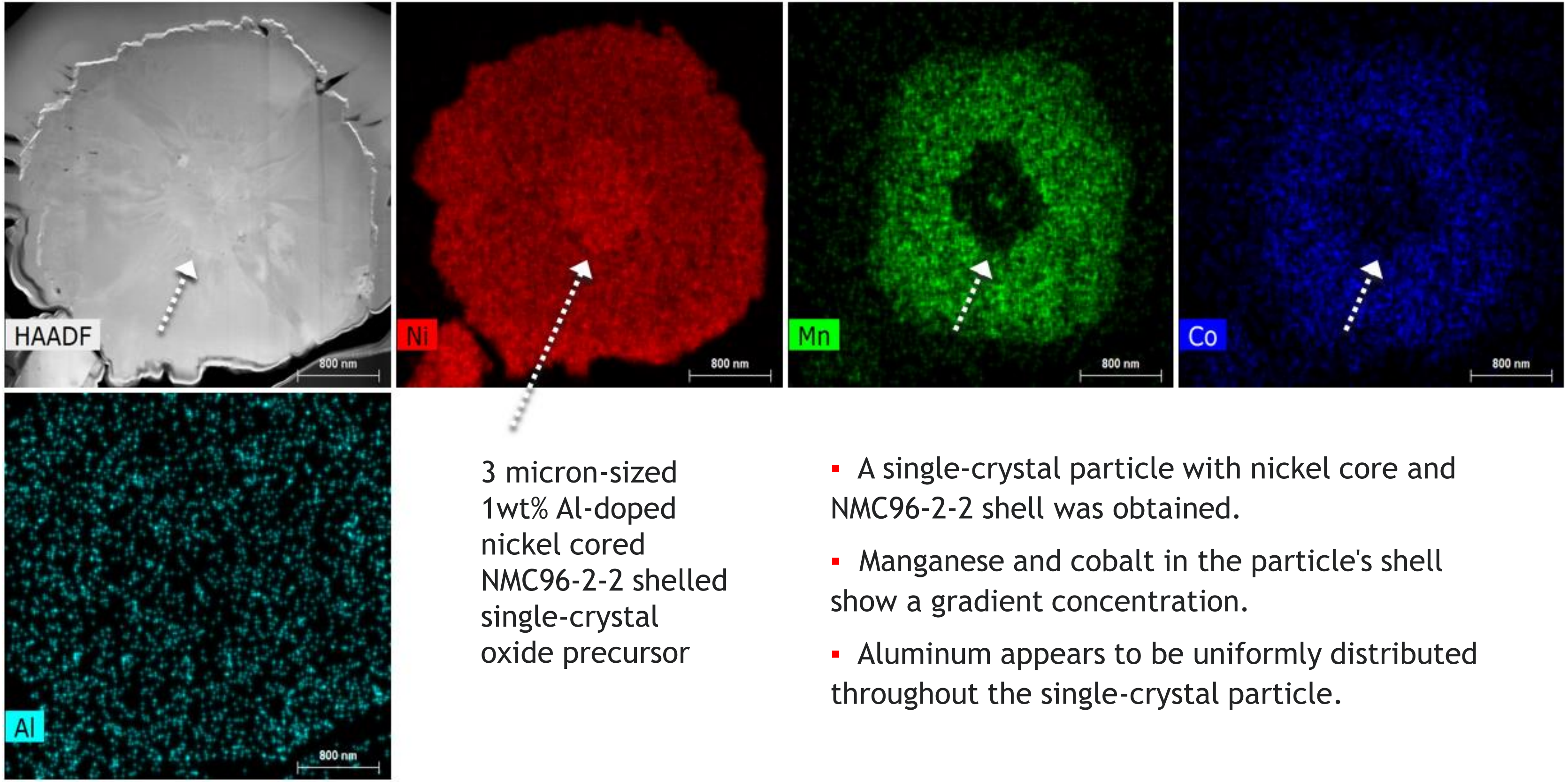


- Nickel has a uniform distribution throughout the single-crystal particle.
- Manganese and cobalt show a gradient distribution that decreases in concentration from the center of the particle to the surface.
- It is clear that zirconium is more present on the surface of the particle.

FIB Cross-section of Al-doped Precursor

UCIrvine
University of California · Irvine
Prof. Huolin Xin

- 1wt% Al-doped single-crystal NMC96-2-2 precursor

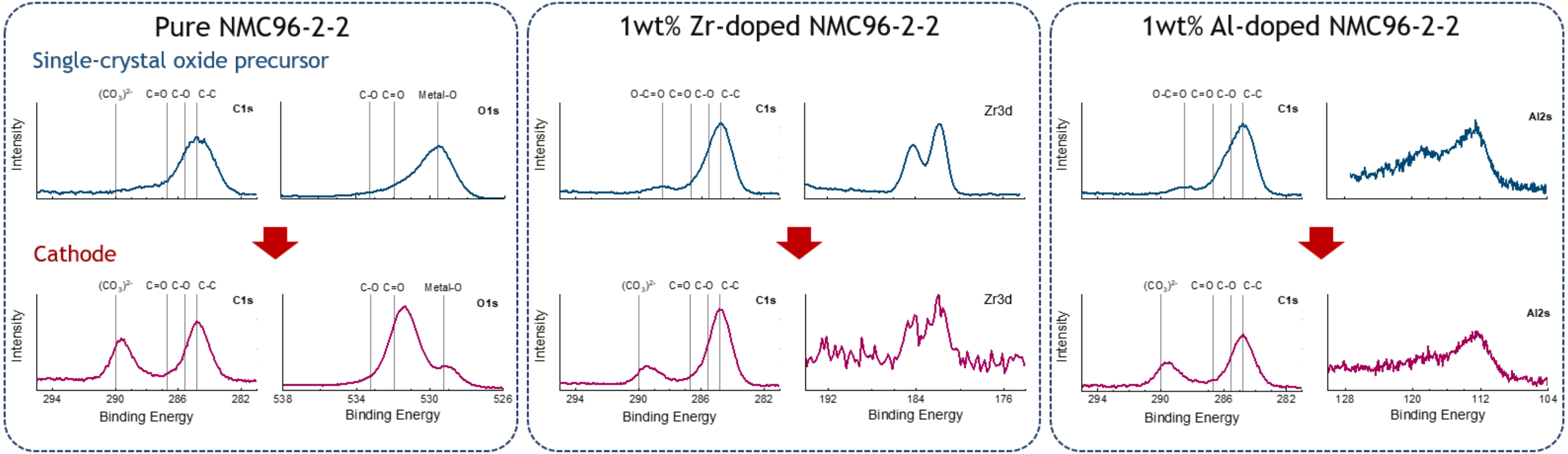


3 micron-sized 1wt% Al-doped nickel cored NMC96-2-2 shelled single-crystal oxide precursor

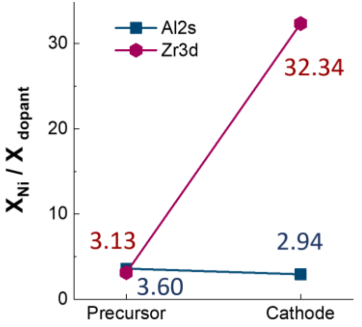
- A single-crystal particle with nickel core and NMC96-2-2 shell was obtained.
- Manganese and cobalt in the particle's shell show a gradient concentration.
- Aluminum appears to be uniformly distributed throughout the single-crystal particle.

XPS analysis at ANL Post-Test Facility

Argonne NATIONAL LABORATORY 75 1946–2021
Dr. Seoung-Bum Son & Dr. Ira Bloom

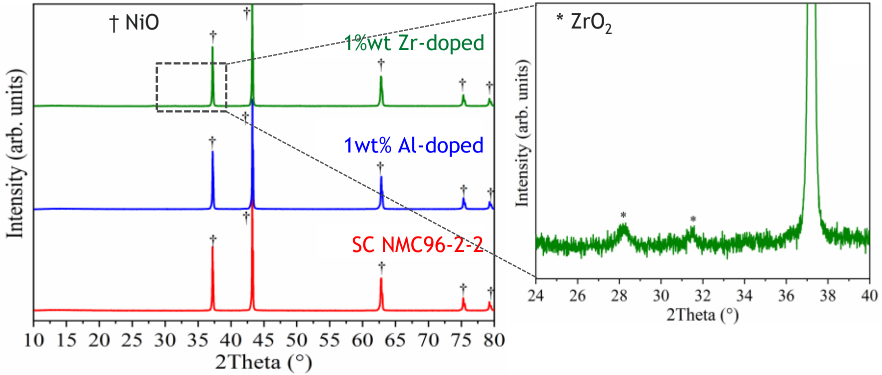


- Pure NMC96-2-2 shows typical XPS spectrums like polycrystalline co-precipitated materials.
- Zr doping: Ni2p/Zr3d ratio is 3.1 for the precursor and 32.3 for the cathode. Zr3d shows notable concentration difference after calcination. The Zr may diffuse into bulk during calcination.
- Al doping: Al2s concentration at surface is higher for its doping level. Ni2p/Al2s ratio is 3.6 for the precursor and 2.9 for the cathode. (Al2p signal overlapped with Ni3p signal.)

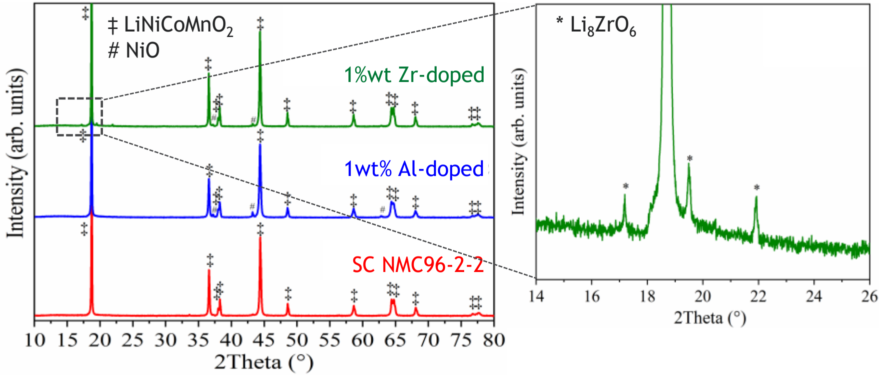


XRD and Electrochemical Performance

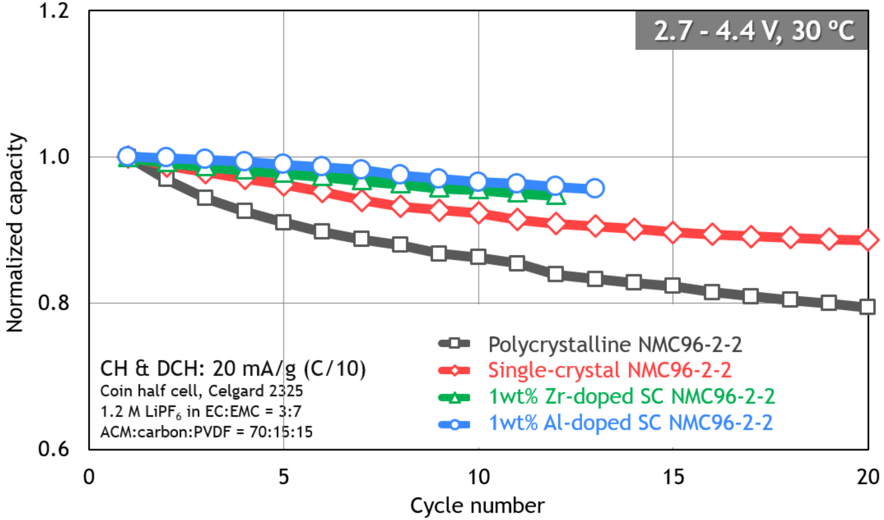
❑ Single-crystal NMC96-2-2 precursors



❑ Single-crystal NMC96-2-2 cathodes



❑ Coin half-cell evaluation



- XRD peaks of Zr oxides were confirmed.
- The capacity reduction of single-crystal NMC96-2-2 is about half of that of polycrystalline NMC96-2-2.
- 1wt% Zr/Al-doping further suppress the capacity reduction of single-crystal NMC96-2-2 cathode.

Responses to Previous Year Reviewers' Comments

- No comments from reviewers last year.

Collaboration and Coordination

- ***Brookhaven National Laboratory***: TEM and EELS analysis of single-crystal NMC96-2-2 precursor and cathode samples
- ***University of Wisconsin***: Nano-indentation of polycrystalline and single-crystal NMC96-2-2 cathode samples
- ***University of California, Irvine***: FIB cross-sectional elemental mapping of Al/Zr-doped single-crystal NMC96-2-2 precursors
- ***Argonne Post-Test Facility***: Electrode cross-sectional SEM and XPS analysis of pristine and cycled electrodes of polycrystalline and single-crystal NMC96-2-2 cathodes, Al/Zr-doped precursors and cathodes
- ***Hunt Energy***: Industrial evaluation of single-crystal NMC811 cathode samples

Remaining Challenges and Barriers

- High quality experimental new active materials are needed for industrial validation and prototyping but they are not commercially available.
- There is a strong demand from the research community and battery industry for high quality, uniform experimental materials.
- Emerging manufacturing technologies need to be developed to address production costs of active battery materials.
- Hydro-solvothermal process can tailor particle size and morphology with robust crystalline structure but needs to be developed as a continuous-flow process for commercialization with economic feasibility.
- For each material composition, systematic synthesis research is needed to enable hydro-solvothermal process to generate single-crystal battery material with controlled size and morphology.

Proposed Future Research (FY21-22)

- Continue working on the synthesis of Al/Zr-doped single-crystal NMC96-2-2 cathodes
  - Optimize the size and morphology of Al/Zr-doped single-crystal NMC96-2-2 cathodes
  - Evaluate the effect of Al/Zr-doping amount
  - Characterization of produced materials
  - Electrochemical performance evaluation of produced materials
  - Provide produced materials to collaborators
- Investigate conductive surface coating of single-crystal NMC96-2-2 cathodes
- Supply produced materials to the research community and industry for their evaluation
- Select and synthesize new compositions for single-crystal battery materials
- This program is open to suggestions in scaling up newly invented, promising active battery materials

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

Summary

- The developed hydro-solvothermal (HYST) system produces 40 grams of single-crystal NMC96-2-2 precursor with size ranging from 0.5 µm to 3 µm per batch operation.
- Single-crystal NMC96-2-2 cathode shows initial discharge capacity of 210 mAh/g and improved capacity retention than polycrystalline NMC96-2-2 cathode.
- It was observed that single-crystal NMC96-2-2 cathode maintains a robust crystal structure without particle crack after cycling.
- Electron-diffraction confirms single-crystal nature of the produced NMC96-2-2 cathode.
- Nano-indentation test platform is being set up to measure particle breaking force.
- 1wt% Zr and Al-doped single-crystal NMC96-2-2 materials were produced and their elemental distributions were investigated by FIB cross-section and XPS analysis.
- 1wt% Zr/Al-doping suppress the capacity reduction of single-crystal NMC96-2-2 cathode.

Acknowledgements and Contributors

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  - Sangkee Min
  - Sangjin Maeng
  - Aditya Nagaraj
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  - Huolin Xin