RECELL: WORKING TO ADVANCE BATTERY RECYCLING

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

ReCell ADVANCED BATTERY RECYCLING

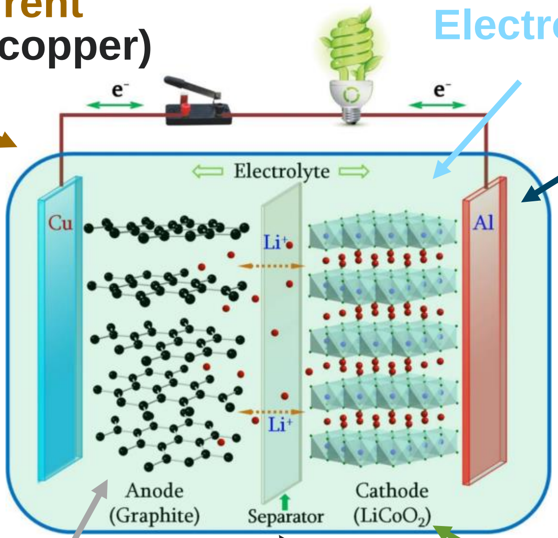
ANATOMY OF LI-ION BATTERIES

Recycling Technologies Recover at Least the Co and Ni in the Cathode

Anode current collector (copper)

Electrolyte (lithium salt in organic solvent)

Cathode current collector (aluminum)



Positive half-reaction $LiTMO_2 \leftrightarrow Li_{1-x}TMO_2 + xLi^+ + xe^-$

Negative half-reaction $C_y + xLi^+ + xe^- \leftrightarrow + C_yLi_x$

Total reaction $LiTMO_2 + C_y \leftrightarrow Li_{1-x}TMO_2 + C_yLi_x$

Liu, C. et. al. *Mater. Today* **2016**, *19* (2), 109–123.

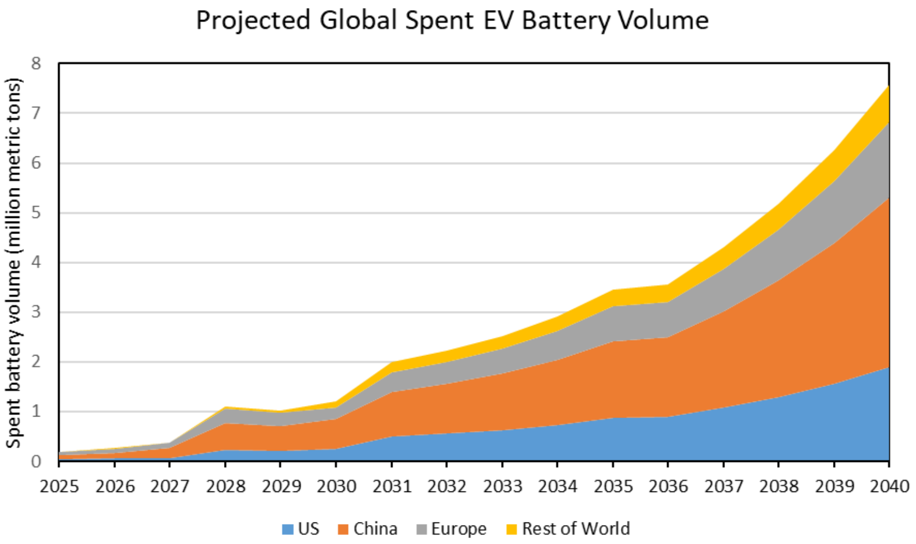
Anode (graphite and binder)

Separator (polyolefin)

Cathode (lithiated transition metal oxide, binder, and carbon black)

NEED FOR BATTERY RECYCLING

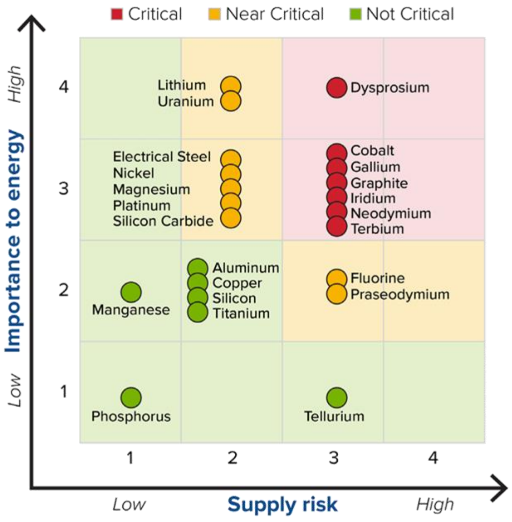
- Collection of consumer electronics is poor
- Electric vehicles have not reached their end-of-life yet
- Stationary storage is even further out
- Lithium-ion batteries in electric vehicles and stationary applications typically cost money to recycle



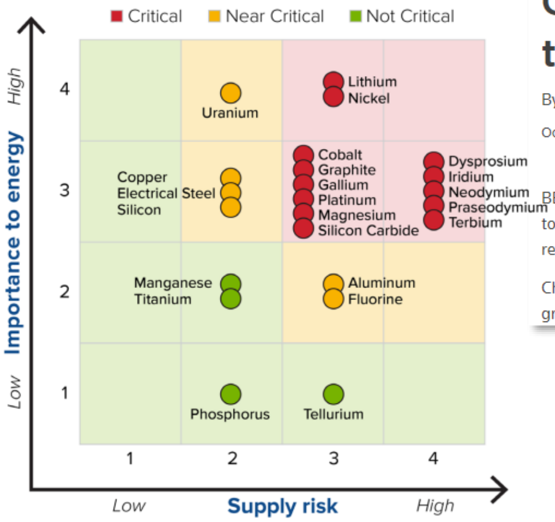
(ANL projection based on IEA global PEV projection)

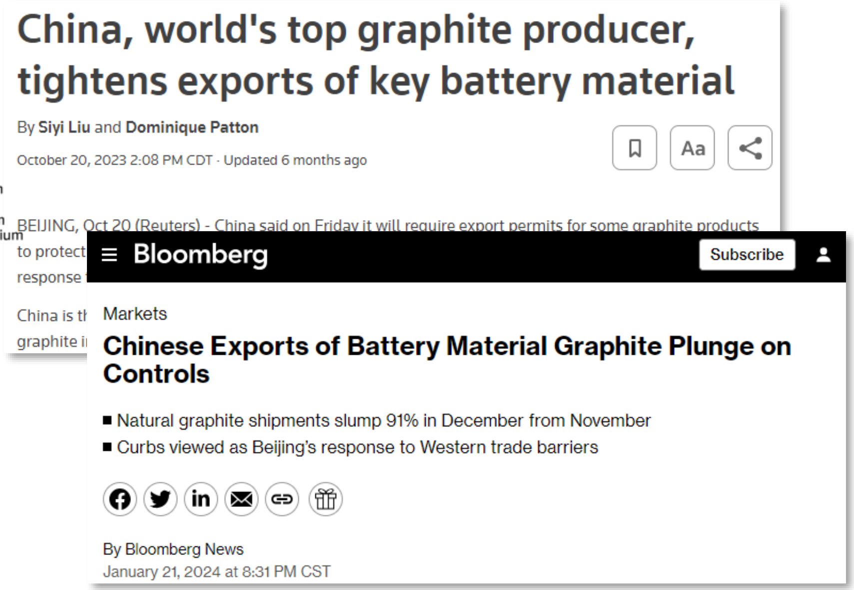
CRITICAL MATERIALS FOR BATTERY PRODUCTION

SHORT TERM 2020-2025



MEDIUM TERM 2025-2035





China, world's top graphite producer, tightens exports of key battery material

By Siyi Liu and Dominique Patton

October 20, 2023 2:08 PM CDT · Updated 6 months ago

Aa

BEIJING, Oct 20 (Reuters) - China said on Friday it will require export permits for some graphite products
to protect
response
China is th
graphite i

Bloomberg

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Markets

Chinese Exports of Battery Material Graphite Plunge on Controls

- Natural graphite shipments slump 91% in December from November
- Curbs viewed as Beijing's response to Western trade barriers

By Bloomberg News

January 21, 2024 at 8:31 PM CST

www.energy.gov/sites/default/files/2023-07/doe-critical-material-assessment_07312023.pdf

WHY RECYCLE BATTERIES?

Keep Batteries out of Landfills

Reduce Reliance on Foreign Countries

Reduce Environmental Impact

WHERE WILL BATTERY MATERIALS FOR RECYCLING COME FROM?

ELECTRONIC DEVICES

Nearly 152 million cell phones are thrown away in the U.S. every year, with the rest ending up in drawers

Source: USA Today

MANUFACTURING SCRAP

Waste from the battery industry is expected to supply nearly 80% of the material for recycling by 2025

Source: Benchmark Minerals

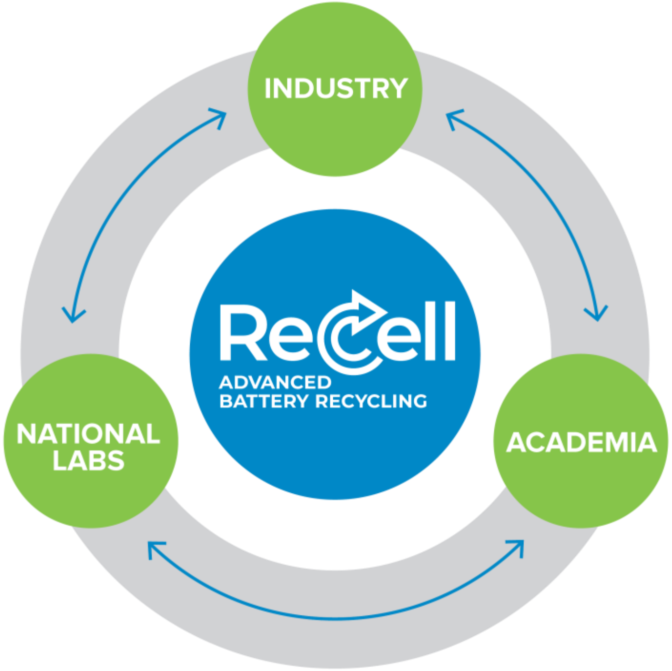
ELECTRIC VEHICLES EVs

Over 1 million vehicles on the road today will become 8 million tons of battery scrap by 2040

Source: Reuters

ARGONNE AND BATTERY RECYCLING

- Argonne brings together battery development, process optimization, scale-up, recycling, and modeling expertise
- Argonne leads DOE's ReCell Center for Advanced Battery Recycling
- We work in other areas of recycling:
  - Critical materials
  - Plastics
  - Electronics waste
- We work closely with industry and our goal is to help industry succeed



THE RECELL CENTER

The center develops cost-effective, flexible processing techniques to extract as much value as possible from current and future batteries chemistries making recycling economically viable.

THE RECELL CENTER’S FOCUS AREAS

Overview

DIRECT RECYCLING

Recycling materials back to their original purpose without destroying their chemical structure.

26 Projects

ADVANCED RESOURCE RECOVERY

Recapturing materials for reuse in batteries or other applications through chemical conversion.

13 Projects

DESIGN FOR SUSTAINABILITY

Working toward more sustainable batteries by improving material choice, battery design, and second life opportunities.

8 Projects

MODELING AND ANALYSIS

Developing tools to provide a deep materials/ process understanding and evaluate economic and environmental impacts.

11 Projects

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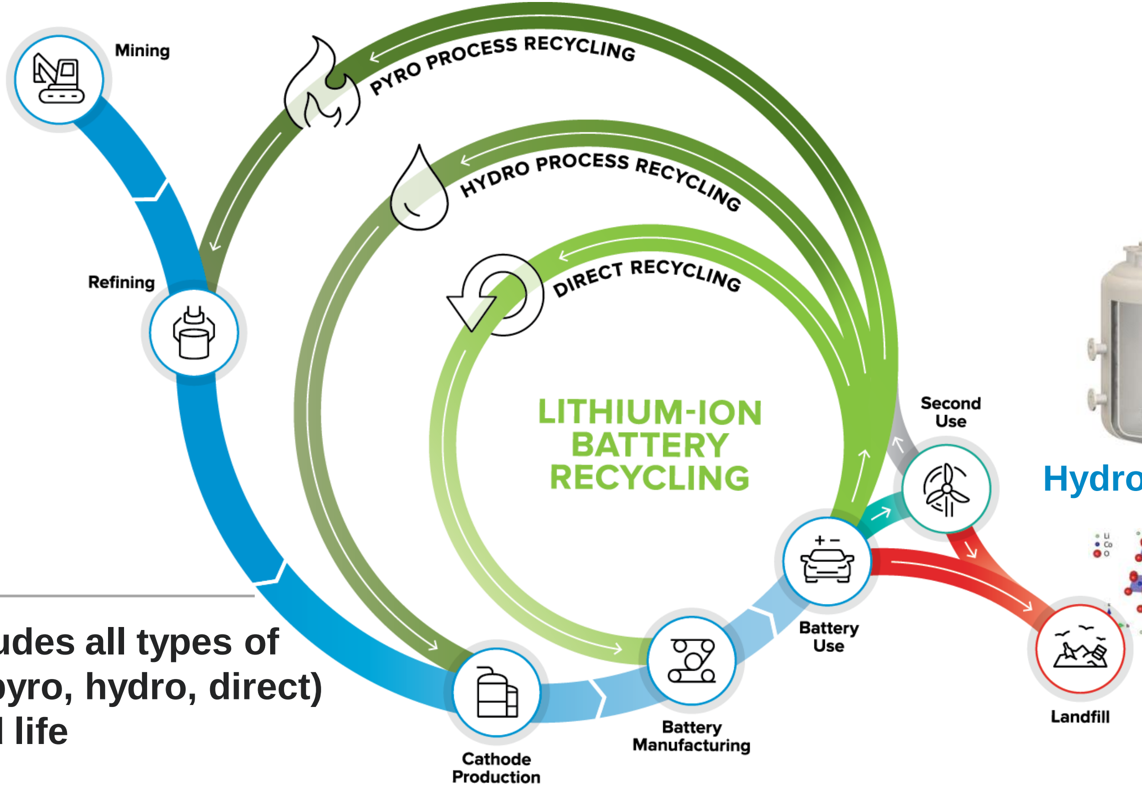
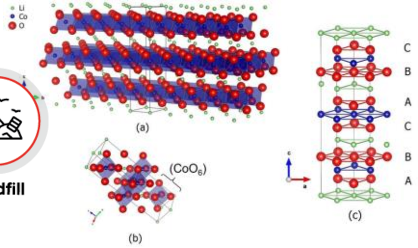
LITHIUM-ION BATTERY RECYCLING



ReCell includes all types of recycling (pyro, hydro, direct) and second life

Pyrometallurgical Processing

Hydrometallurgical Processing



Direct Recycling

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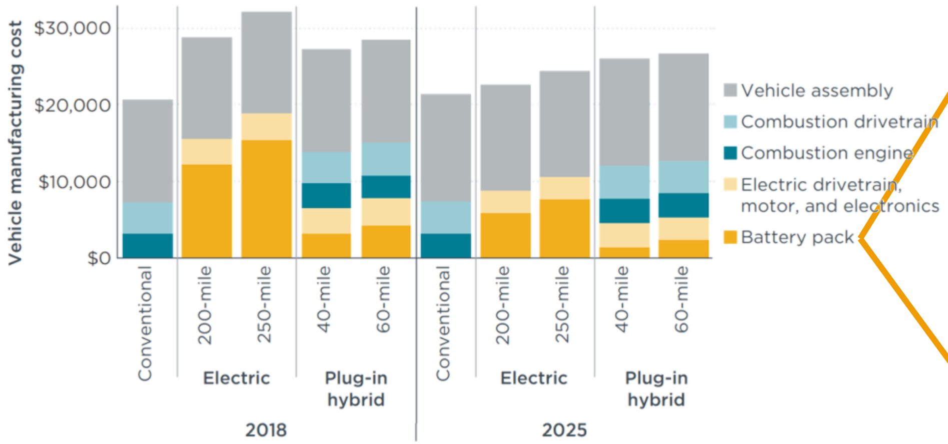
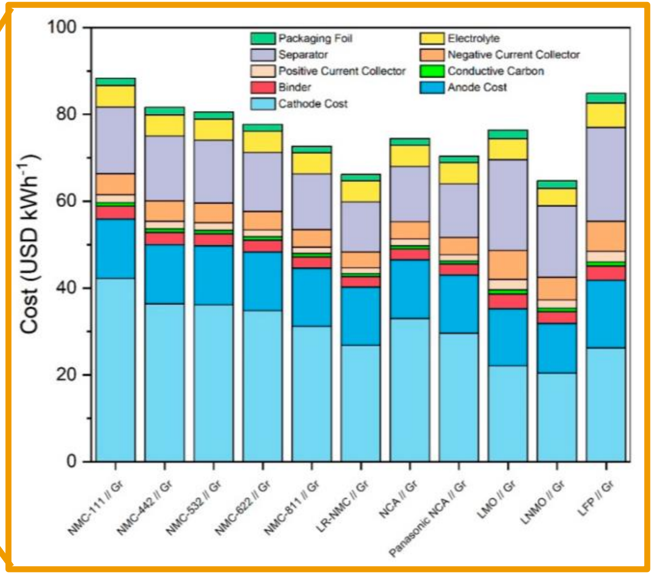
COMPARISON OF EV PRODUCTION COST



Conventional and electric vehicle manufacturing cost for 2018 and 2025

Lutsey, N.; Nicholas, M. et. al.*Int. Counc. Clean Transp.* **2019**, 1–12.

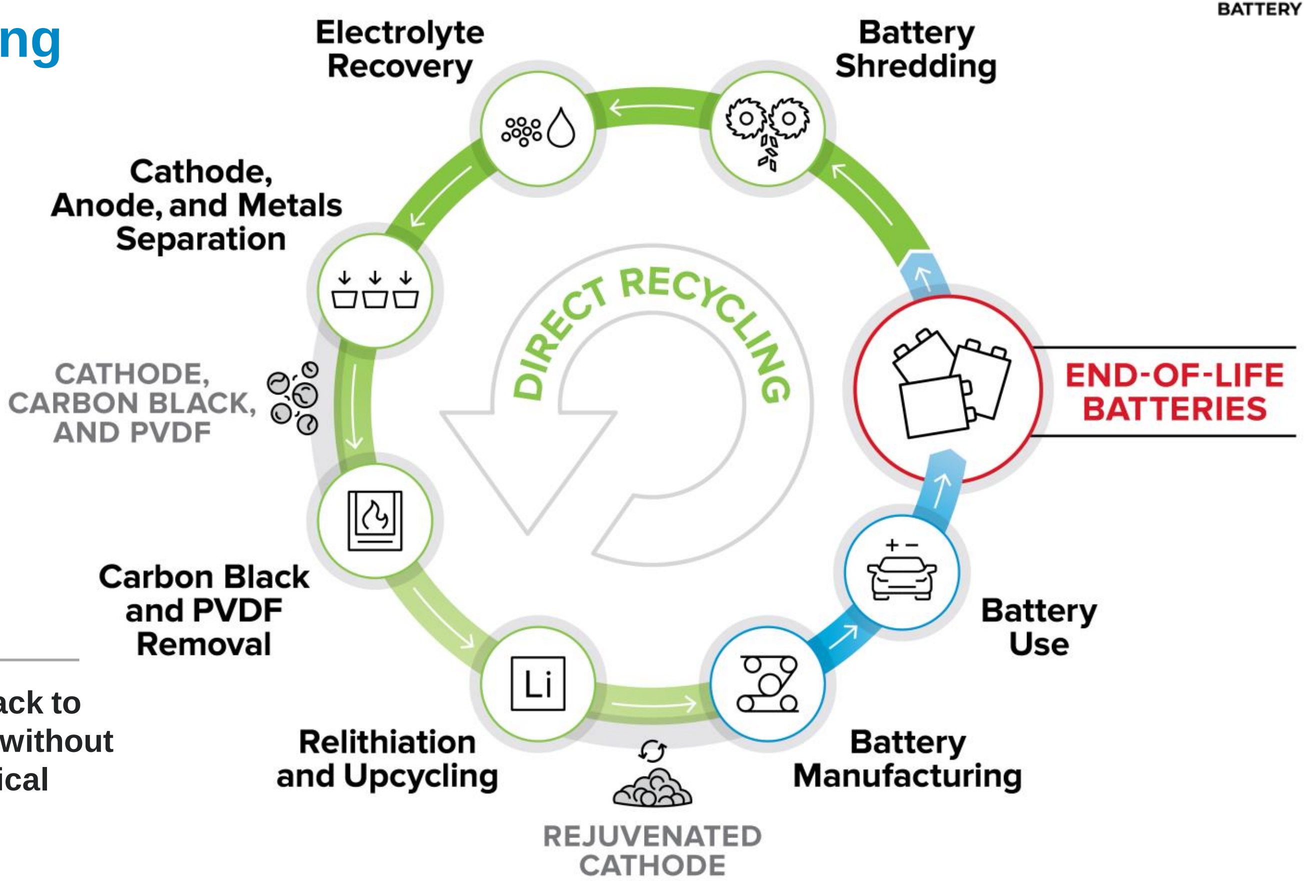


Battery cost by component

Qian, G.; et. al. *Cell Reports Phys. Sci.* **2022**, *3* (2), 100741.

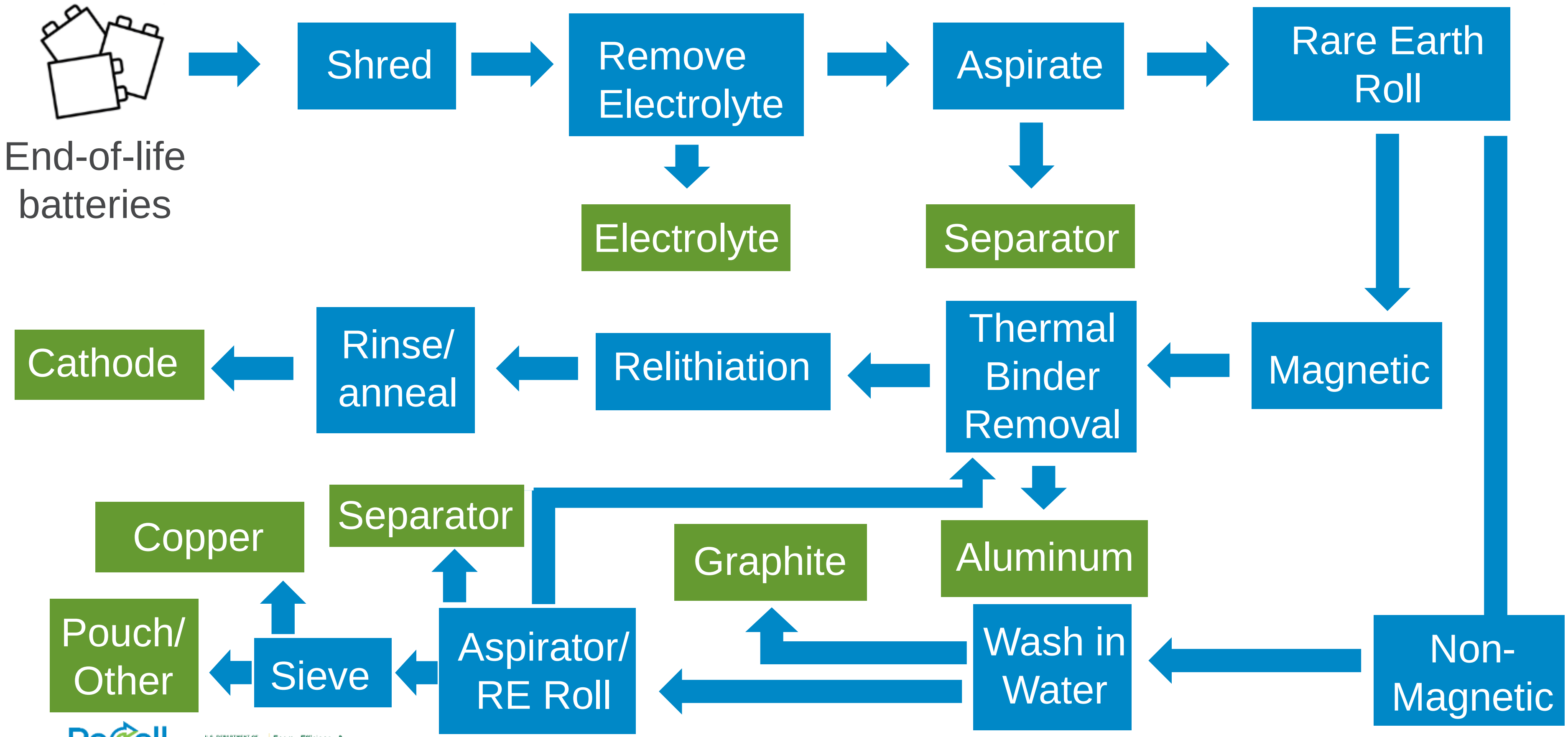
LITHIUM-ION BATTERY RECYCLING

Direct Recycling



Recycling materials back to their original purpose without destroying their chemical structure

PROCESS BLOCK DIAGRAM



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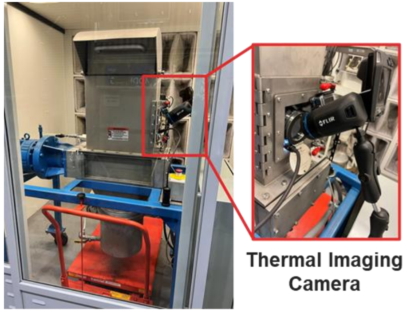
BATTERY RECYCLING FACILITIES

- ReCell currently occupies:
  - 3,000 ft^2 of highbay space
  - Bench and pilot scale labs in the MERF
- Equipment includes:
  - Shredding
  - Size separation
  - Magnetic separators
  - Froth columns
  - High-temperature furnaces
  - Rotary kiln
  - Optical sorter
  - Sink/float separation
  - Electrochemical separation
  - Aspirator
  - Sheer mixers



Shredding
Safely break down lithium-ion batteries

Froth Flotation
Separation of battery materials (anode and cathode powders)

Optical Sorter
Color, shape, and size separation

Rotary Kiln
Thermal binder removal and relithiation

OTHER MATERIALS RECYCLING CAPABILITIES

MATERIALS SEPARATION

Large Wet Separation System

Wet Separation Systems	Processing Capability
Small (55 gallons)	100 lbs/hr
Medium (250 gallons)	500 lbs/hr
Large (1,000 gallons)	4,000 lbs/hr (~2 tons/hr)

- Process and separate plastics and metals from various sources (electronics waste, toner cartridges, vehicles, household appliances, etc.)
- Produce clean feedstocks for plastics or metals recycling processes
- FY22 ANL Lab-to-Market (L2M) funding
  - E-waste material from 2 companies
  - Processed 10-15 tons material each

Rare-Earth Magnetic Drum

Remove and separate ferrous metals

Eddy Current

Remove and separate non-ferrous metals

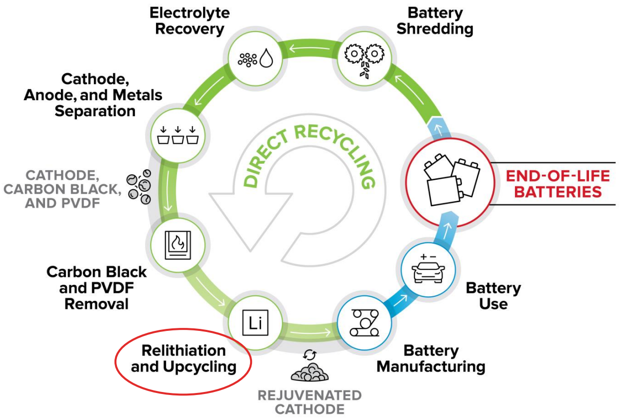
Aspirator/Cyclone

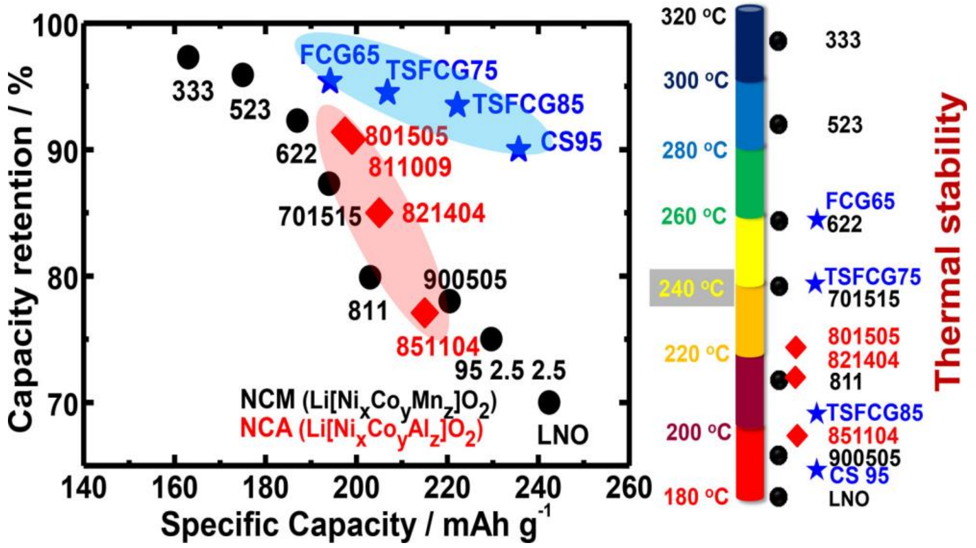
Remove light materials (foam, thin plastics)

RELITHIATION AND UPCYCLING

NEED FOR UPCYCLING PROCESSES

- Cathode materials recovered from vehicles that are about 15 years old are likely to be of lower nickel composition
  - Lower capacity
- Adding nickel to these compositions can increase capacity





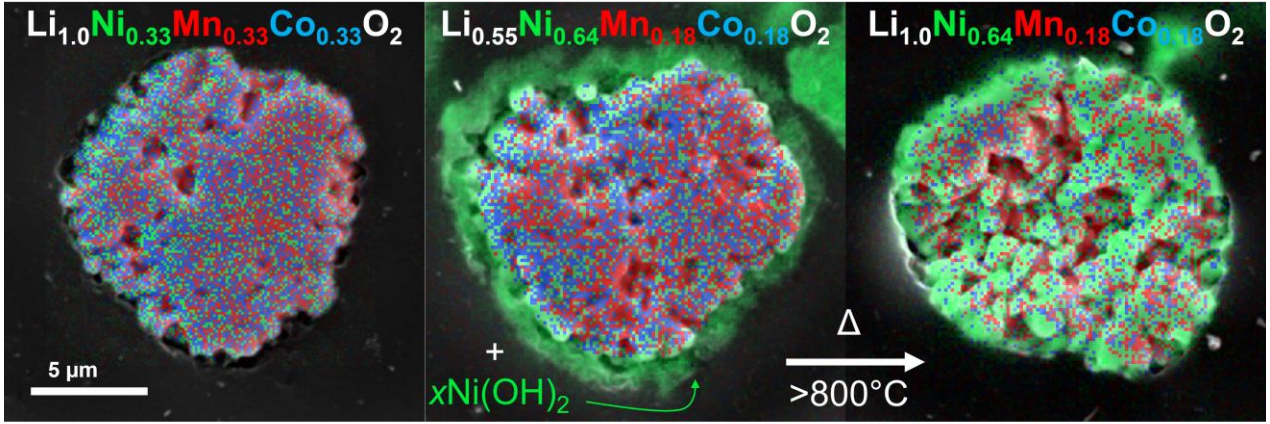
Chong S. Yoon, et. al. *Chemistry of Materials* **2017** *29* (24), 10436-10445 DOI: 10.1021/acs.chemmater.7b04047

CATHODE UPCYCLING

Increasing energy density of directly recycled cathodes

Rapid Coprecipitation Advantages:

- Low capital cost:
  - Minimal inputs of additional chemicals and equipment
- Fast reaction: ~1.5 h
- Ambient pressure and aqueous environment

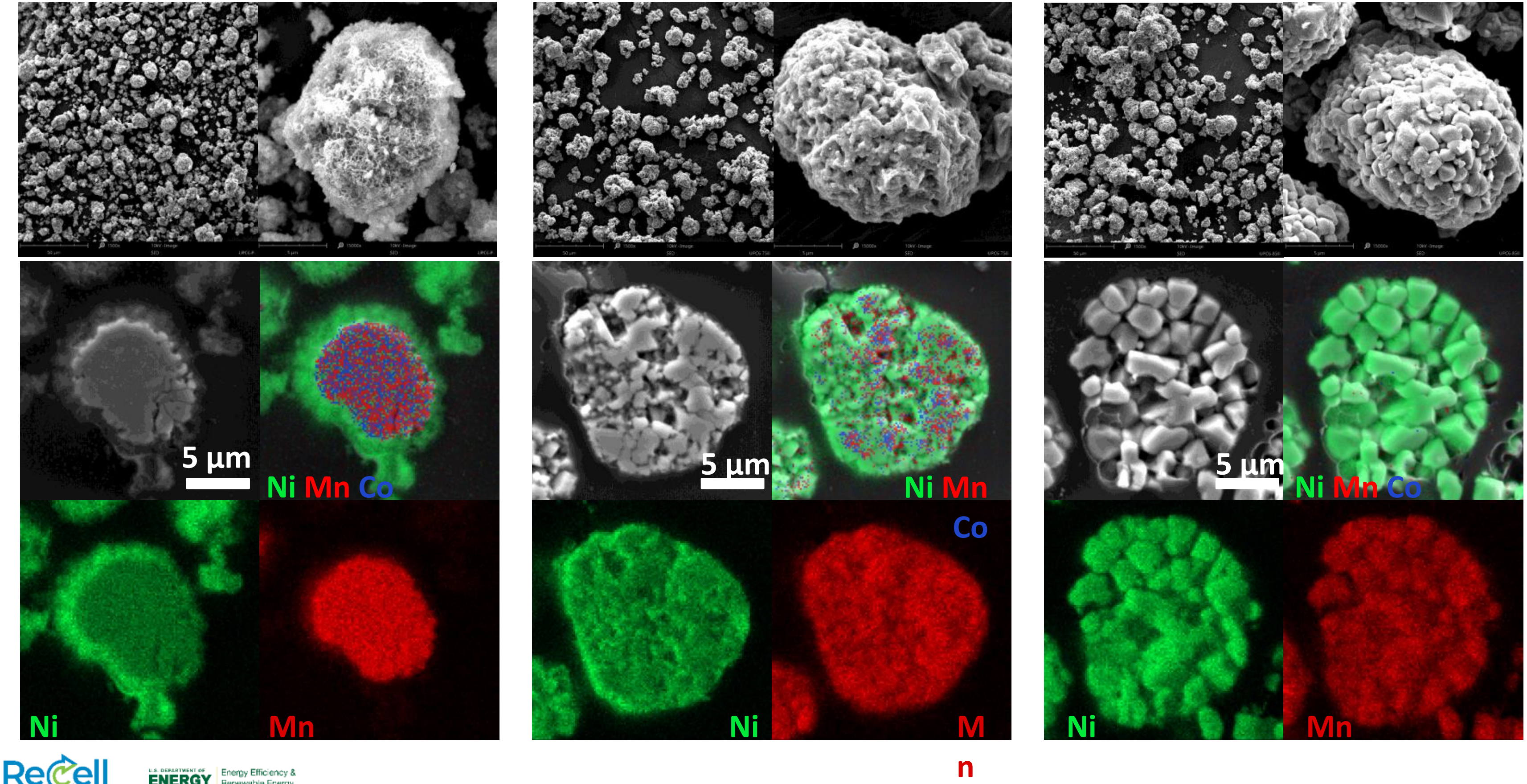


Recycled Cathode → Coating with Nickel Hydroxide → Relithiation at High Temperatures

WHOLE AND CROSS-SECTIONAL SEM EDS

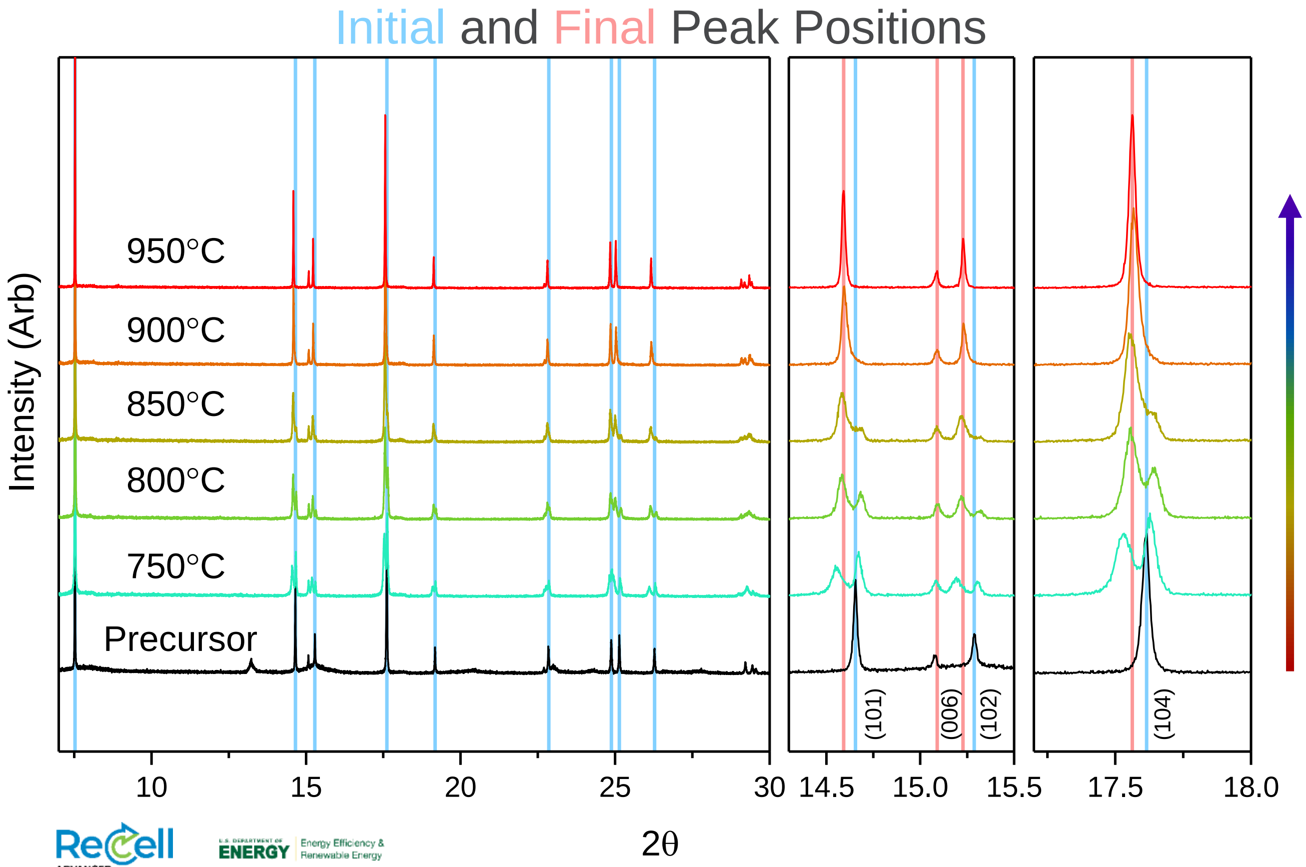
ICP ratio of Ni : Mn : Co after upcycling → 0.64 : 0.18 : 0.18

NMC111 with Ni-rich Hydroxide Coating | NMC622 Cathode - 750°C | NMC622 Cathode - 900°C



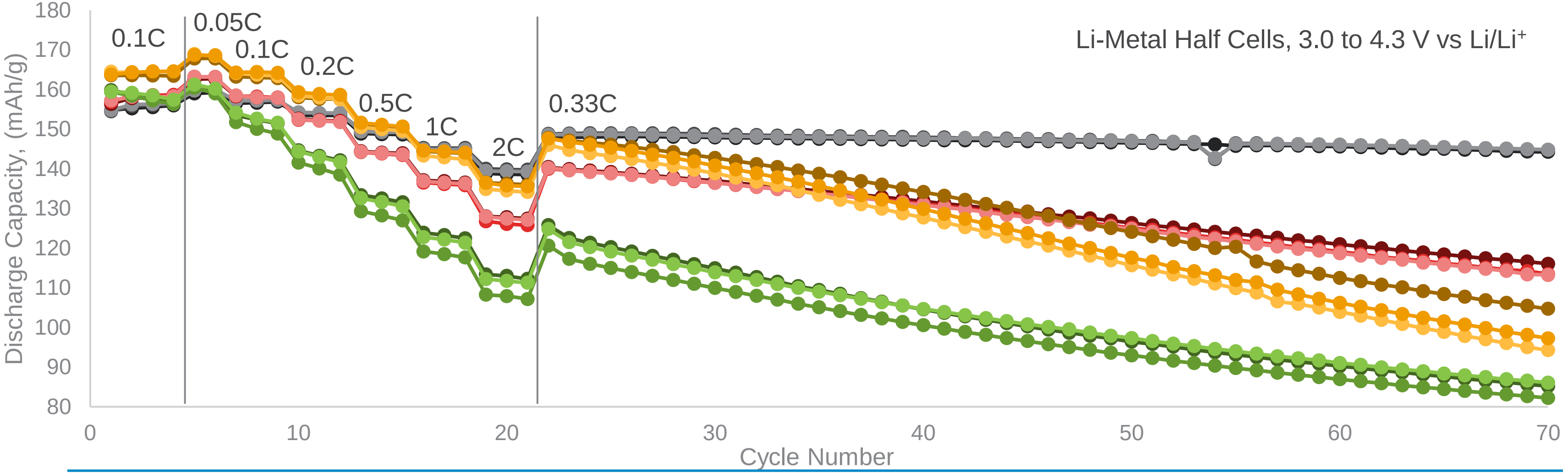
EX-SITU HIGH-RESOLUTION XRD OF CALCINATION

Collected at 5-BMC at the APS



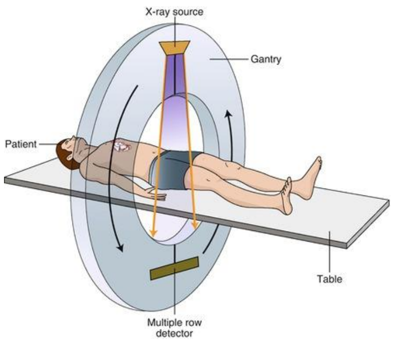
As calcination temperature is increased, pXRD peaks combine and shift to lower 2θ positions indicative of NMC622

ELECTROCHEMICAL PERFORMANCE OF UPCYCLED NMC622

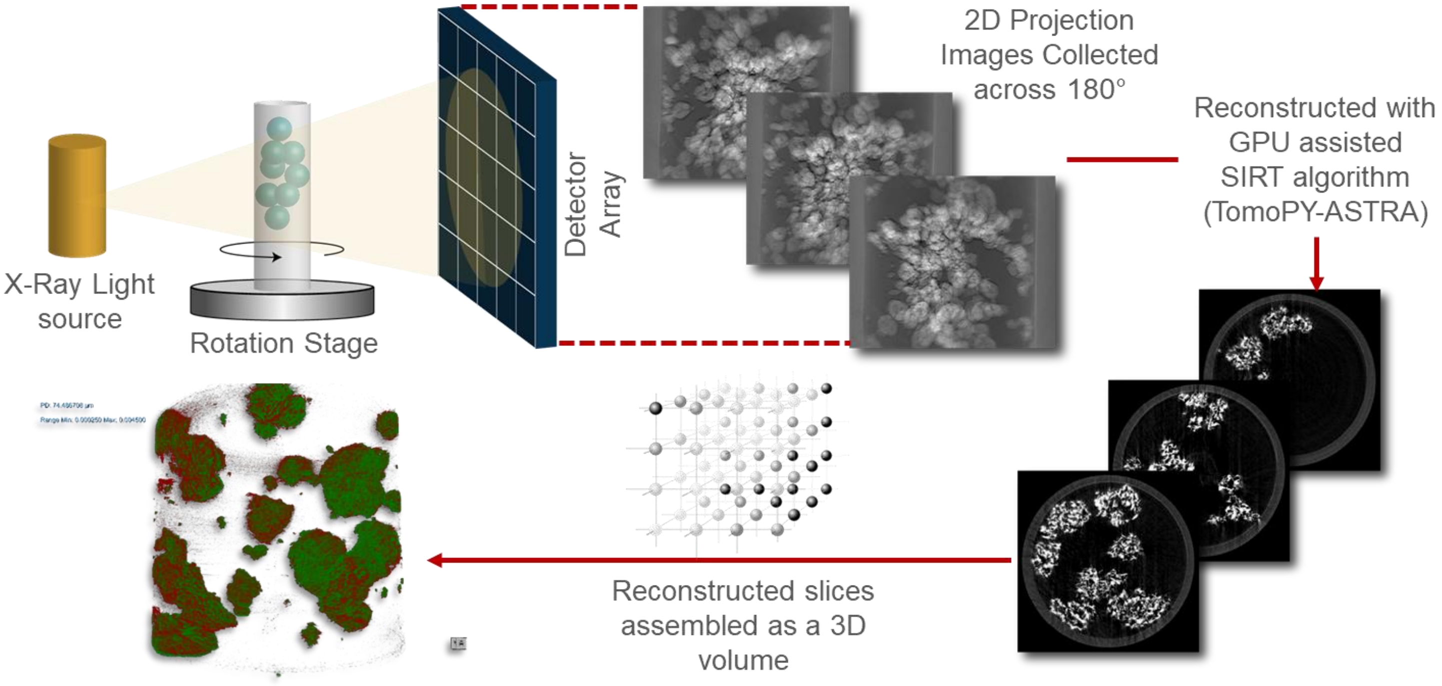


Sample	First Charge Capacity, C/10 (mAh/g)	First Discharge Capacity, C/10 (mAh/g)	First Cycle Efficiency (%)	Capacity Retention (%)
TODA NMC111	171.9±0.1	154.7±0.2	90.0±0.1	97.5
UPC-NMC622-850°C	179.0±0.9	156.8±0.4	87.6±0.1	82.0
UPC-NMC622-900°C	184.5±1	163.9±0.5	88.8±0.6	67.8
UPC-NMC622-950°C	184.8±0.5	159.6±0.2	86.4±0.1	70.2

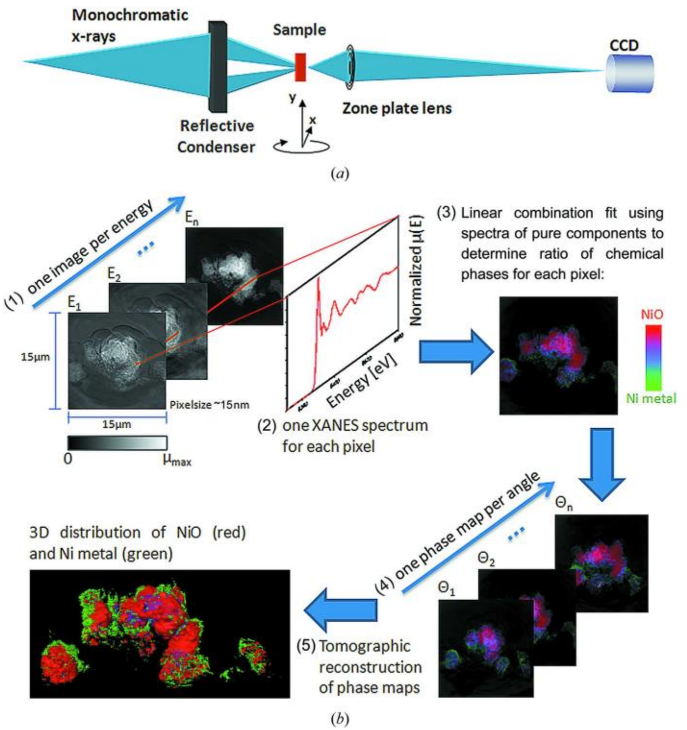
NONDESTRUCTIVE 3D IMAGING THROUGH TOMOGRAPHIC TRANSMISSION X-RAY MICROSCOPY (TXM)



https://thoracickey.com/basic-principles-in-computed-tomography-ct/



TXM WITH ELEMENTAL SPECIFICITY



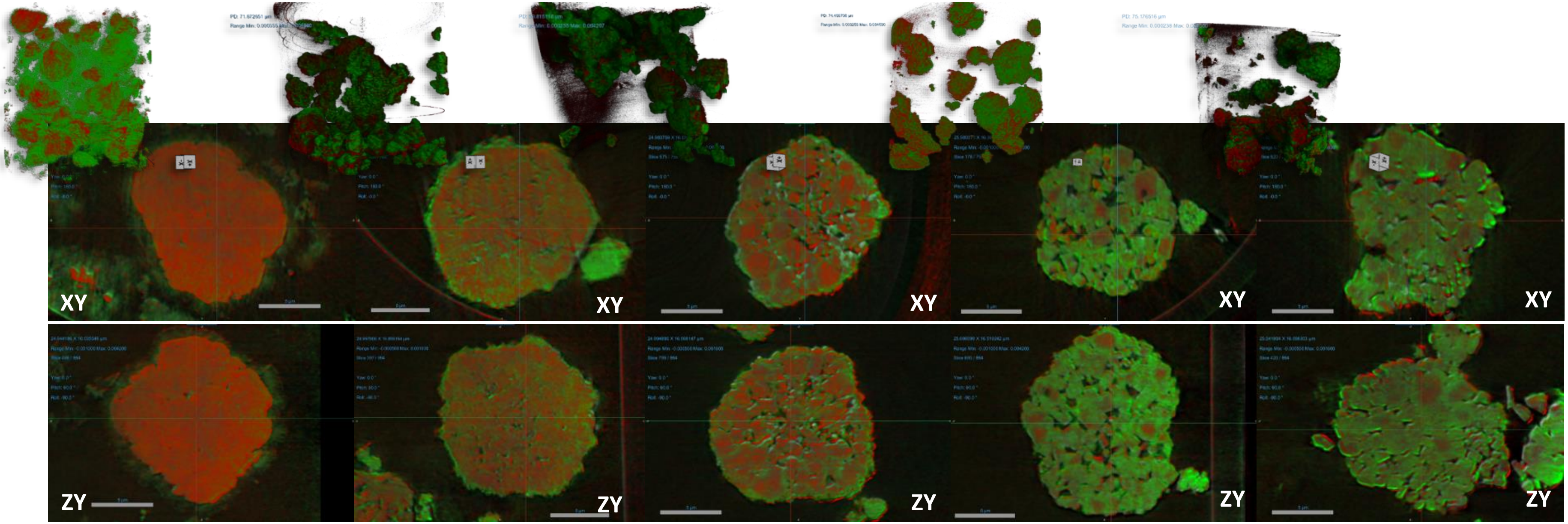
Meirer, F.; Cabana, J.; et.al. *J. Synchrotron Radiat.* **2011**, *18* (5), 773–781. https://doi.org/10.1107/S0909049511019364

- Chemical resolution is achieved through selection of a single wavelength
- Absorption "edge": Core electron promotion to a higher energy level → sharp increase in X-ray absorbance
- Absorption increases with atomic number, due to the increased interaction with the larger electron cloud
- Relative chemical ratios: difference between above edge and below edge

ELEMENTAL SPECIFIC TOMOGRAPHIC TRANSMISSION X-RAY MICROSCOPY (TXM)

Pixel color representative of relative Ni and Co concentration

Differential absorption between above and below K-edge for Ni and Co



Precursor → 750°C → 800°C → 850°C → 900°C

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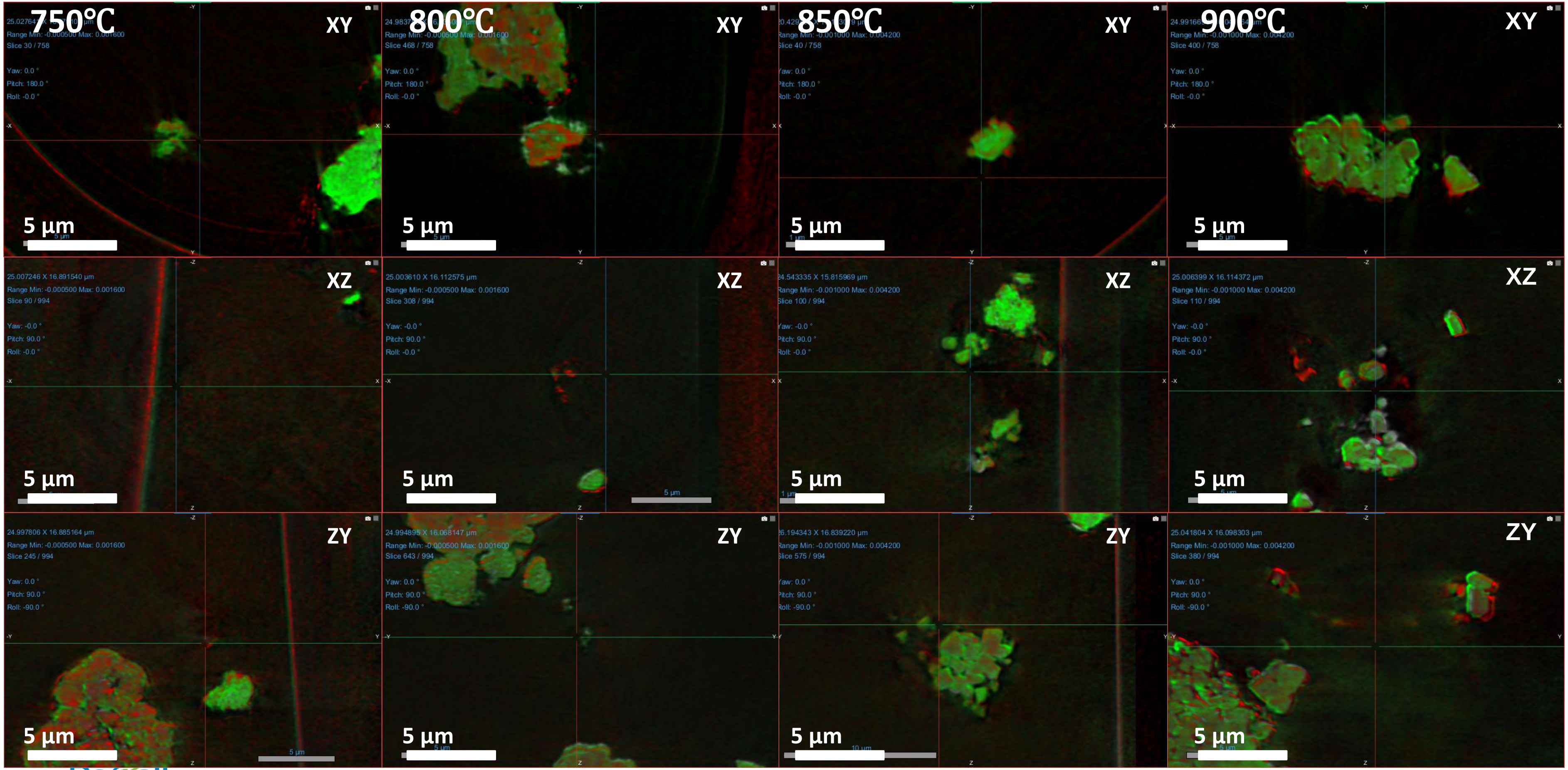
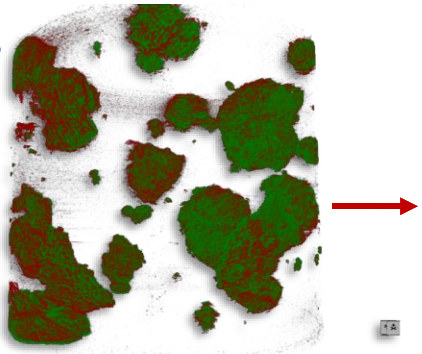
ENTIRE 3D VOLUMES FROM ELEMENTAL TXM

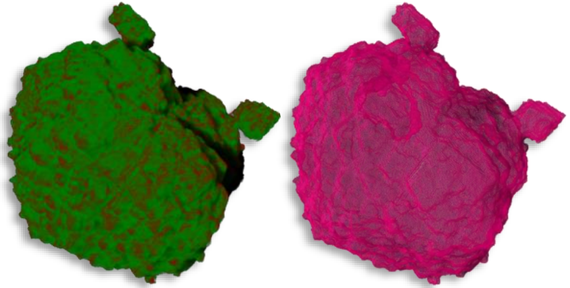


QUANTIFICATION OF NI-RICH DIFFUSION IN 3D

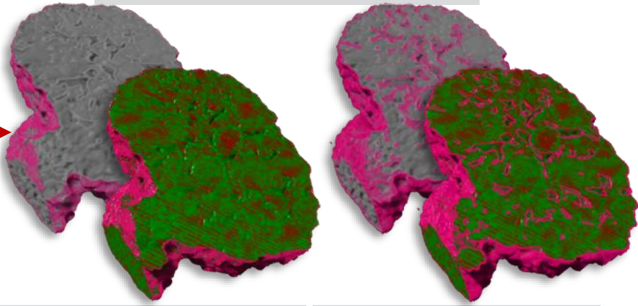


3D Reconstruction

Particle Segmentation



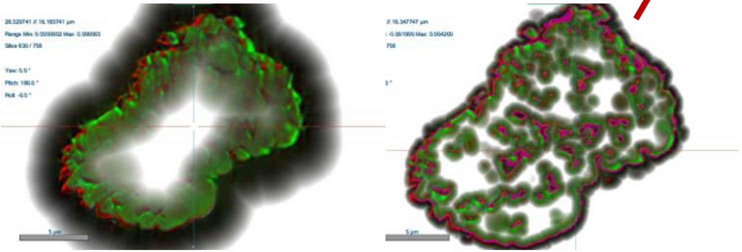
Surface Calculations



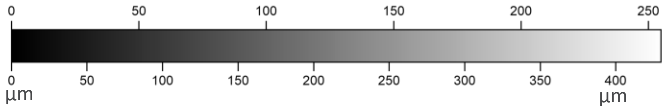
Secondary Particle Surfaces

Primary Particle Surfaces

Euclidean Distance Mapping



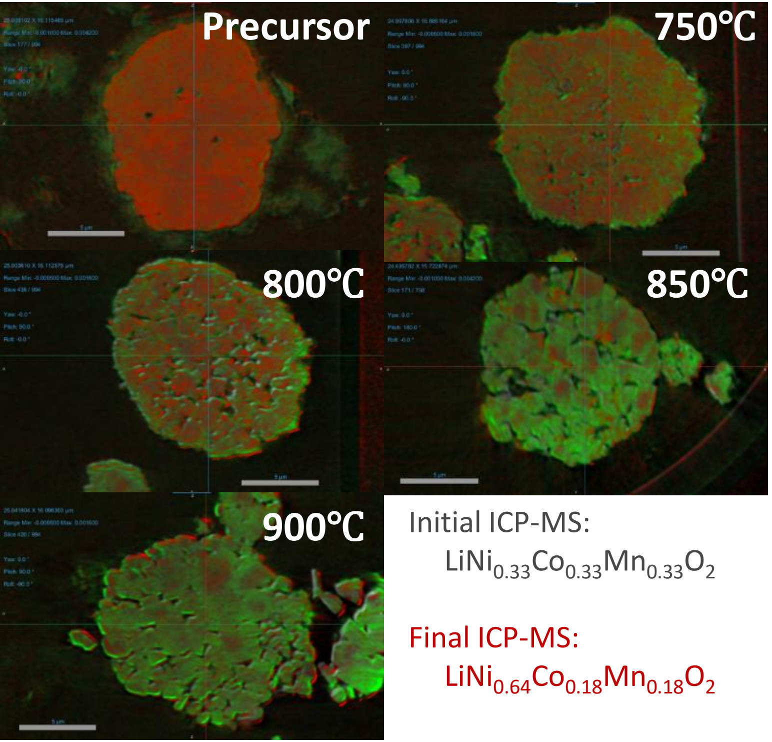
Pixel Color in Transform



Normalized Distance Away From Reference Based on Pixel Resolution (ex. 29 nm/pixel)

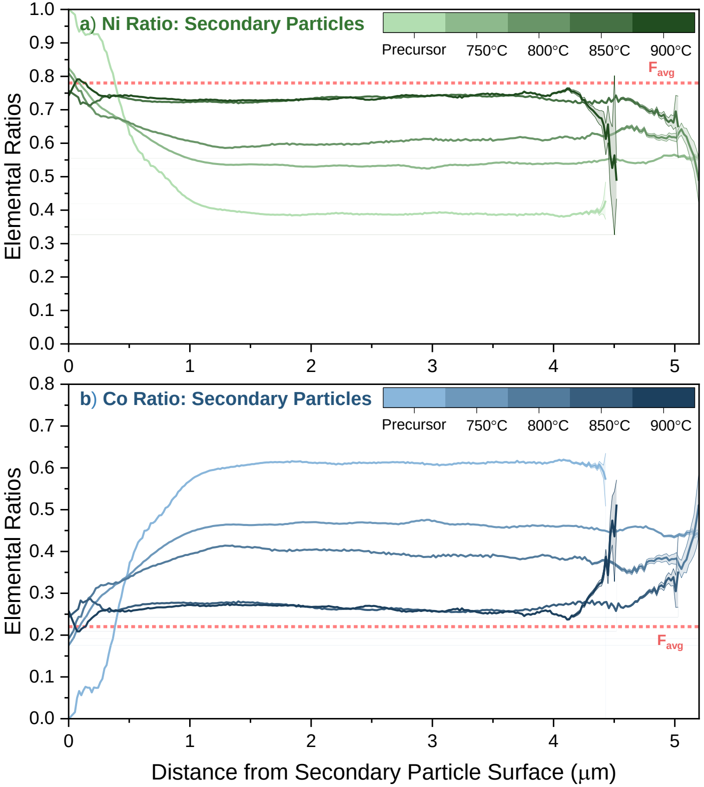
ELEMENTAL RATIOS FROM THE SURFACES OF THE SECONDARY PARTICLES

Mean ratios extracted from the plots of elemental density with 99%CI



Initial ICP-MS:
$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$

Final ICP-MS:
$LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$



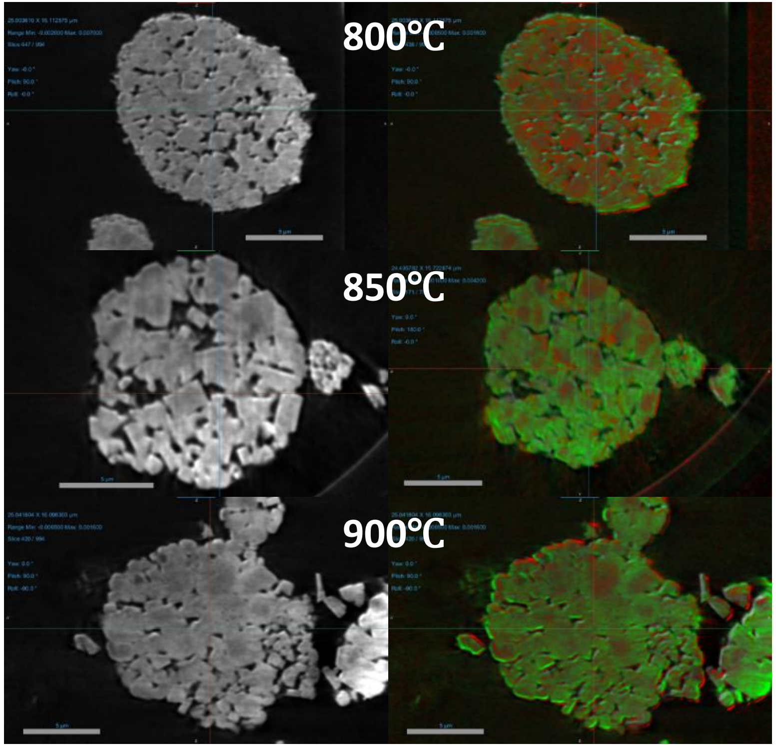
$$\text{Elemental Ratios} = \frac{Elem._{int}}{Ni_{int} + Co_{int}}$$

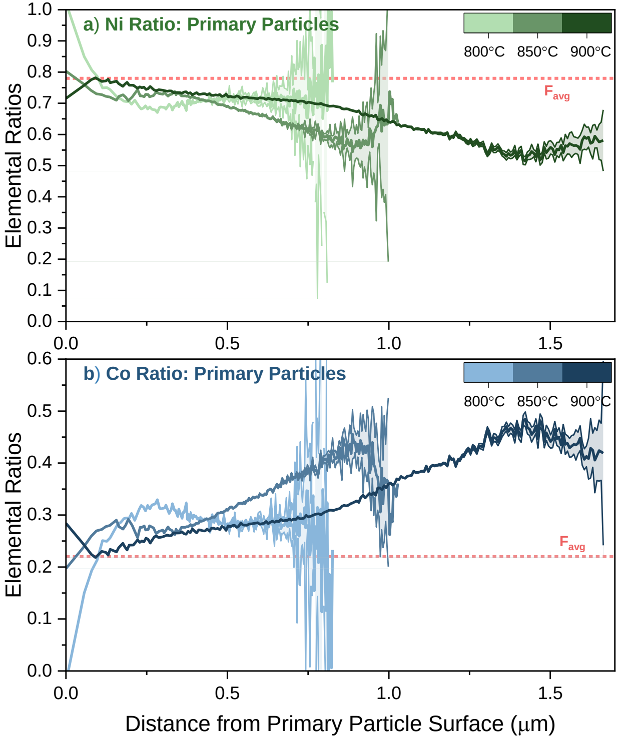
Ni:Co (F_{avg})= 0.78:0.22

Elemental content evens to the NMC622 composition at the secondary particle level at 850°C and 900°C

ELEMENTAL RATIOS FROM THE SURFACES OF THE PRIMARY PARTICLES

Mean ratios extracted from the plots of elemental density with 99%CI





Initial ICP-MS:

$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$

Ni:Co (I_{avg})= 0.5:0.5

Final ICP-MS:

$LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$

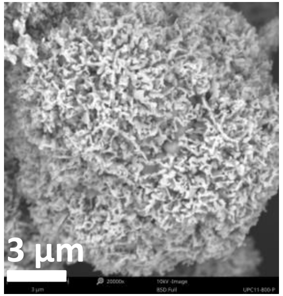
Ni:Co (F_{avg})= 0.78:0.22

Ni-gradient remains in the primary particles with a higher Ni composition at the grain boundaries

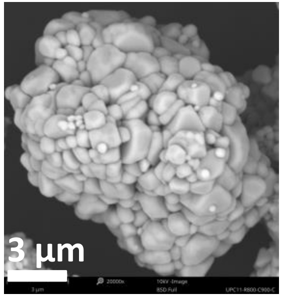
IF YOU CAN SEE IT, YOU CAN IMPROVE IT

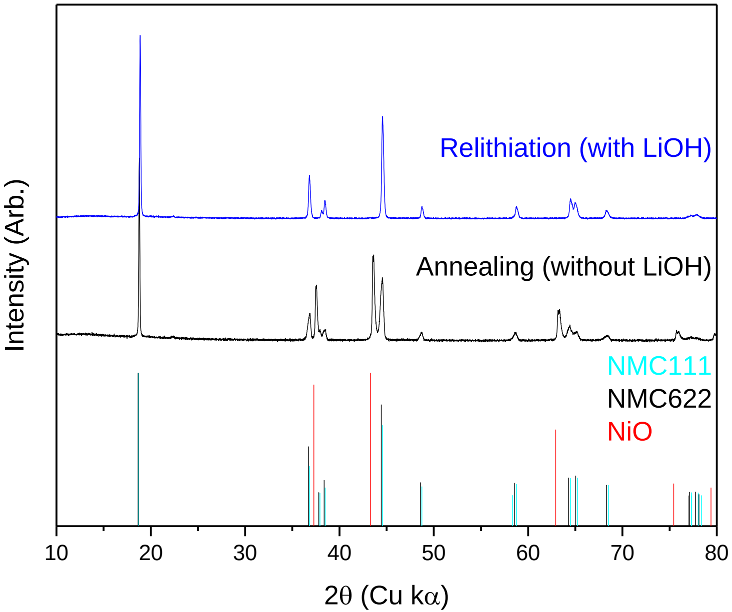
Improving performance with annealing and relithiation optimization

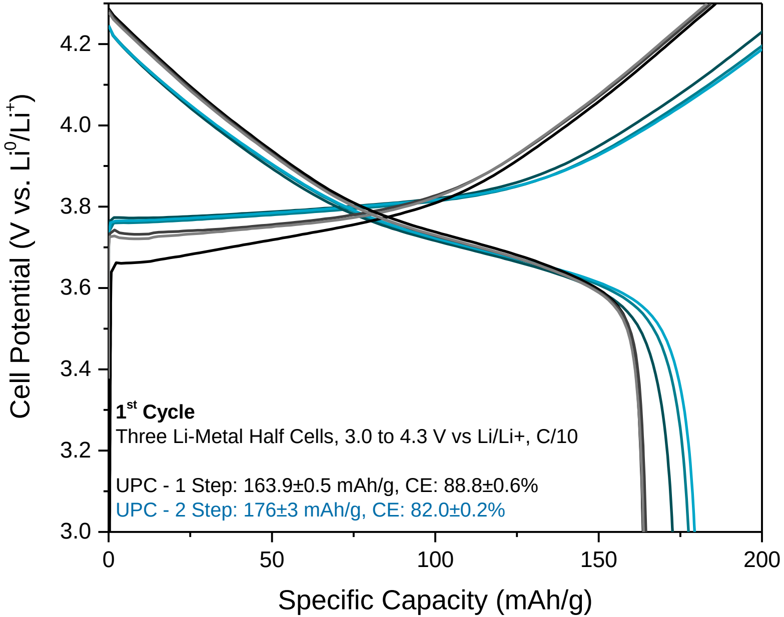
1. Annealing (without LiOH)



2. Relithiation (with LiOH)







✓ Adding an annealing step to promote before relithiation improves the initial capacity to 176±3 mAh/g

❑ Samples will be imaged with TXM to confirm any improvements in the homogeneity of Ni content

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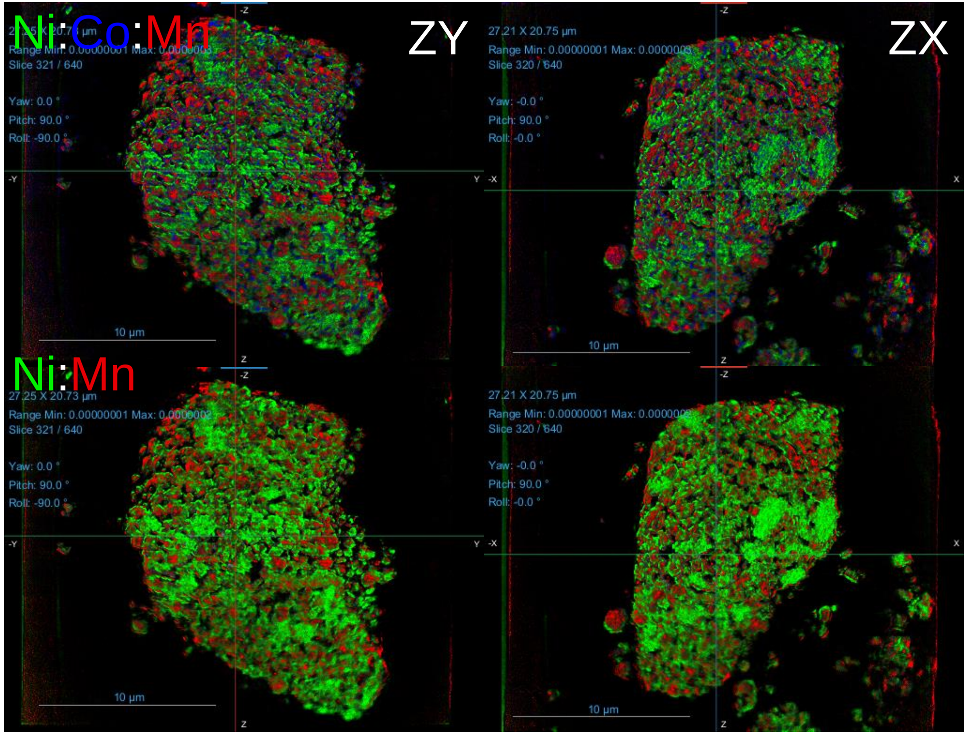
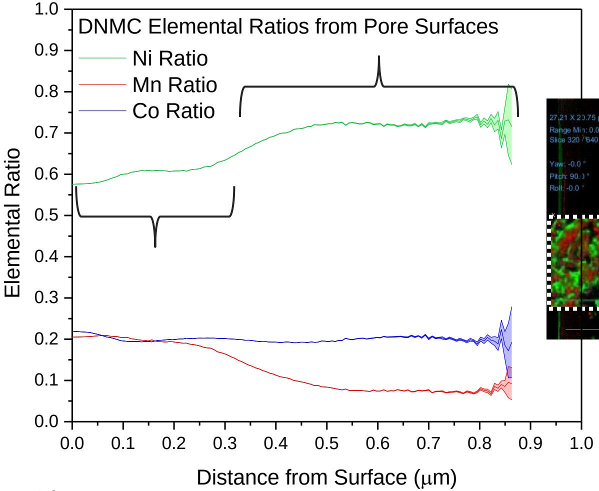
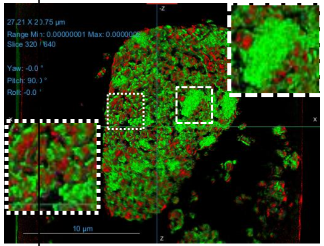
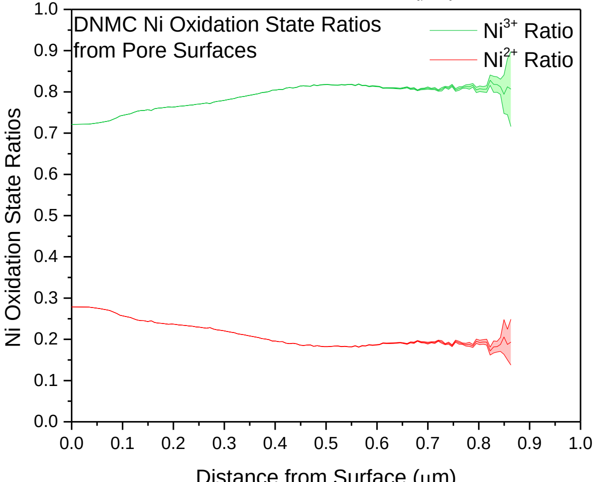
EVALUATING OTHER UPCYCLING PROCESSES









- Smaller particles have a more even elemental distribution
- Larger particles have higher Co:Ni mixing compared to Mn:Ni

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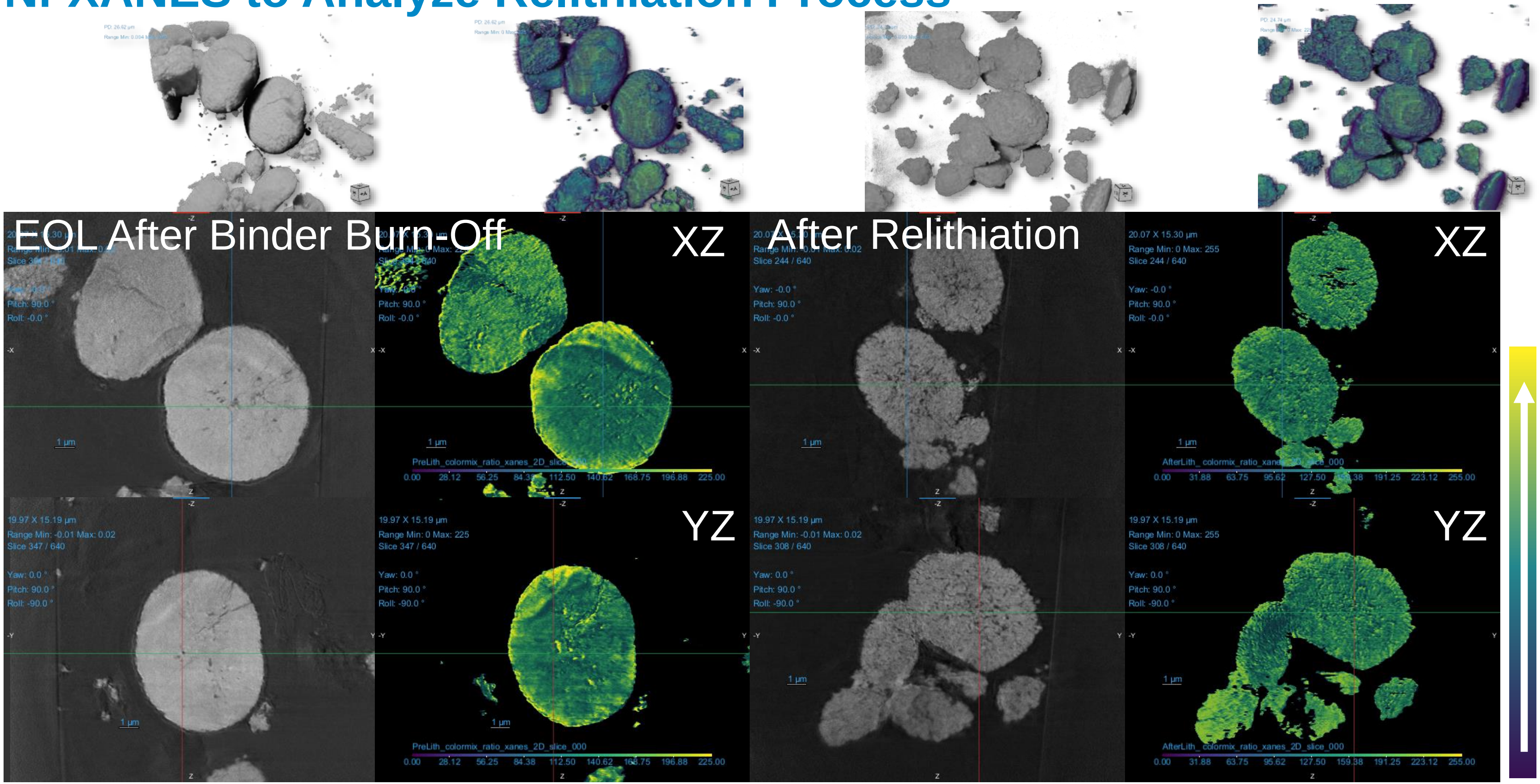
FUTURE DIRECTIONS

Ni-XANES to Analyze Relithiation Process



Ni^{3+} Ratio Increases

SUMMARY

- A fast (~1.5 hr) and effective method to convert low-capacity cathode material into higher capacity by introducing higher Ni compositions.

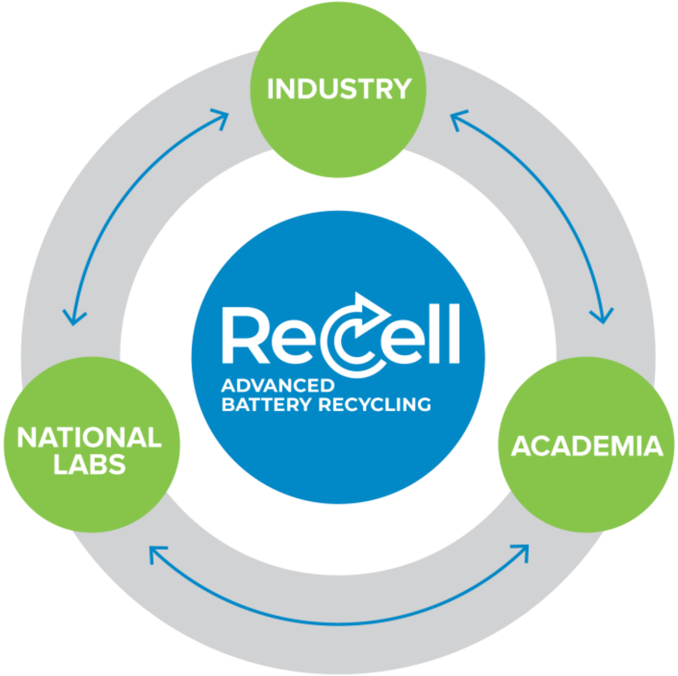
✓ This conversion improved the initial capacity (C/10, 3.0 to 4.3 V vs. Li/Li^{+}) from 154.7±0.2 mAh/g to 176±3 mAh/g

Tackling battery recycling from separations to advanced characterization to gain fundamental knowledge of what is required to provide recycled cathodes for reuse

WRAP UP

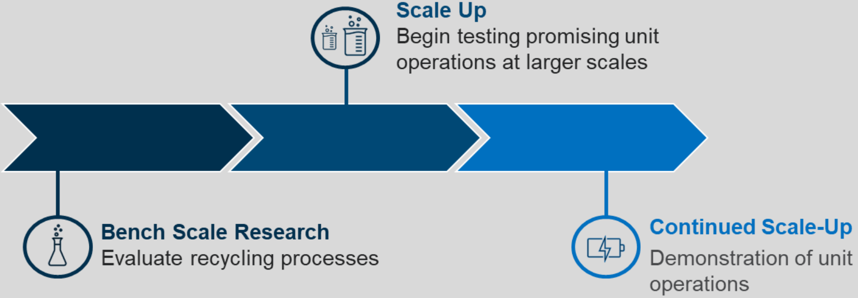
RECELL CENTER COLLABORATION

Working Together to Solve Recycling Challenges



Bringing together battery recycling expertise from national laboratories, universities, and industry to bridge the gaps that are keeping us from realizing the most successfully advanced battery recycling infrastructure

Typical Process Workflow



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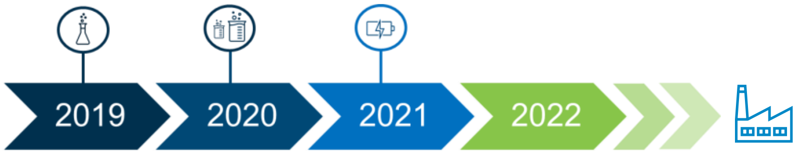
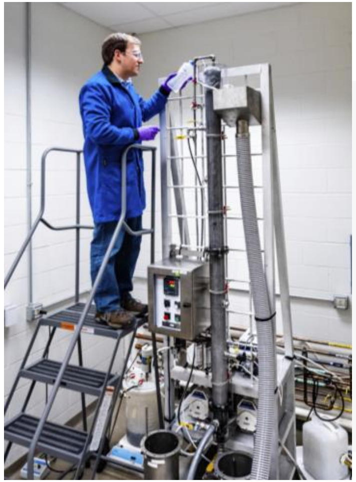
BEYOND THE BENCH: DIRECT RECYCLING AT SCALE

Expansion of ReCell Center into Large Highbay Space

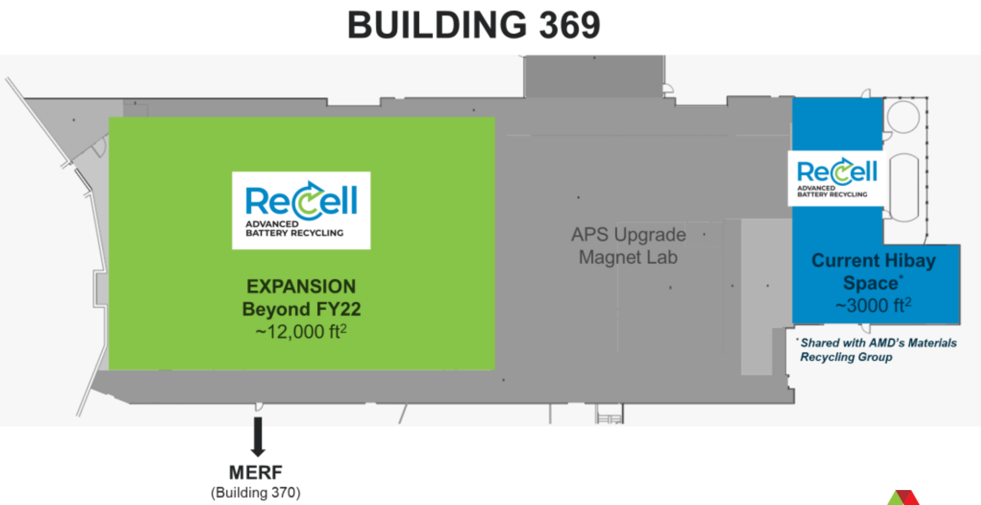
- Provide space for pilot scale equipment capable of handling 10 kg/day (~2.5 tons/year)
- Transfer new recycling technologies to industry



Battery Shredding



Froth Flotation



BATTERY RECYCLING PILOT PLANT

Beyond the Bench: Direct Recycling at Scale

- Renovation of 12,000 ft^2 of highbay space (expected completion Spring 2024)
- Provide space for pilot scale equipment capable of handling 10 kg/day (~2.5 tons/year)
- Transfer new recycling technologies to industry

Pilot-Scale Electrodialysis

Remove ions from solution

Pilot-Scale Aspirator

Remove light materials (foam, thin plastics)

Pilot-Scale Rare Earth Roll

Separate magnetic materials

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RECELL INDUSTRY COLLABORATION MEETING

Hosted at Argonne

- Provided an opportunity for ReCell and industry stakeholders to exchange challenges and ideas
- Meeting included stakeholders from every corner of the vehicle battery value chain
- Another meeting will be hosted in **August 27-28**

November 2019 *(134 people, 76 organizations)*
April 2023 *(146 people, 81 organizations)*

RECELL PARTNERSHIPS, SPONSORS, AND COLLABORATORS

LABORATORY COLLABORATIONS

Argonne National Laboratory

NREL National Renewable Energy Laboratory

Oak Ridge National Laboratory

INL Idaho National Laboratory

UNIVERSITY COLLABORATIONS

Michigan Technological University

WPI

UC San Diego

Tennessee State University

INDUSTRY COLLABORATIONS

24M

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EastPenn

Farasis

FCA Fiat Chrysler Automobiles

NAATBatt International

General Motors

OnTo

Renewance

Retriev Technologies

RSR Corporation

SNT Spiers New Technologies

USABC United States Advanced Battery Consortium LLC

+Volta Energy Technologies

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