SCALABLE METHOD TO PRODUCE SODIUM MANGANESE NICKEL IRON OXIDE CATHODE ACTIVE MATERIAL

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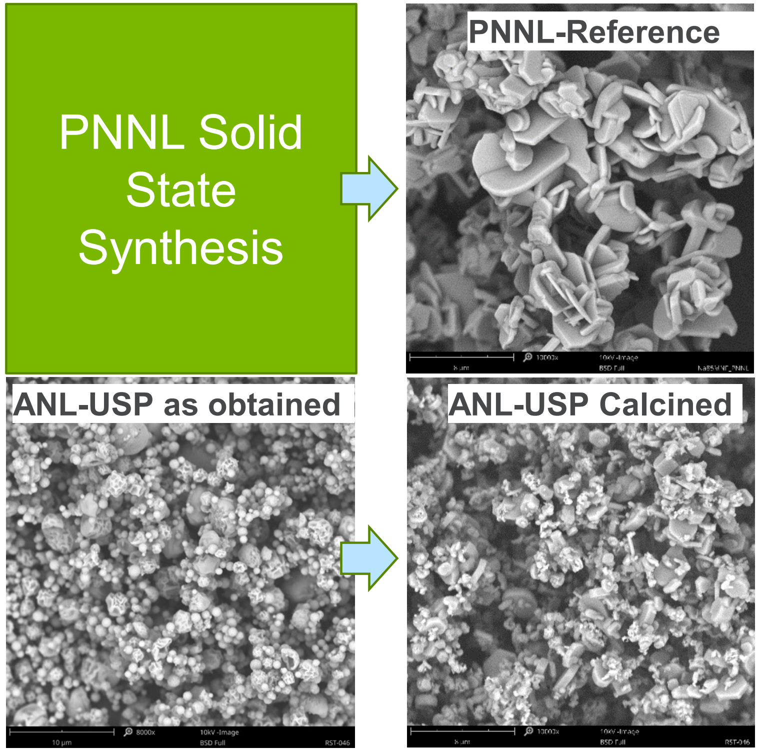
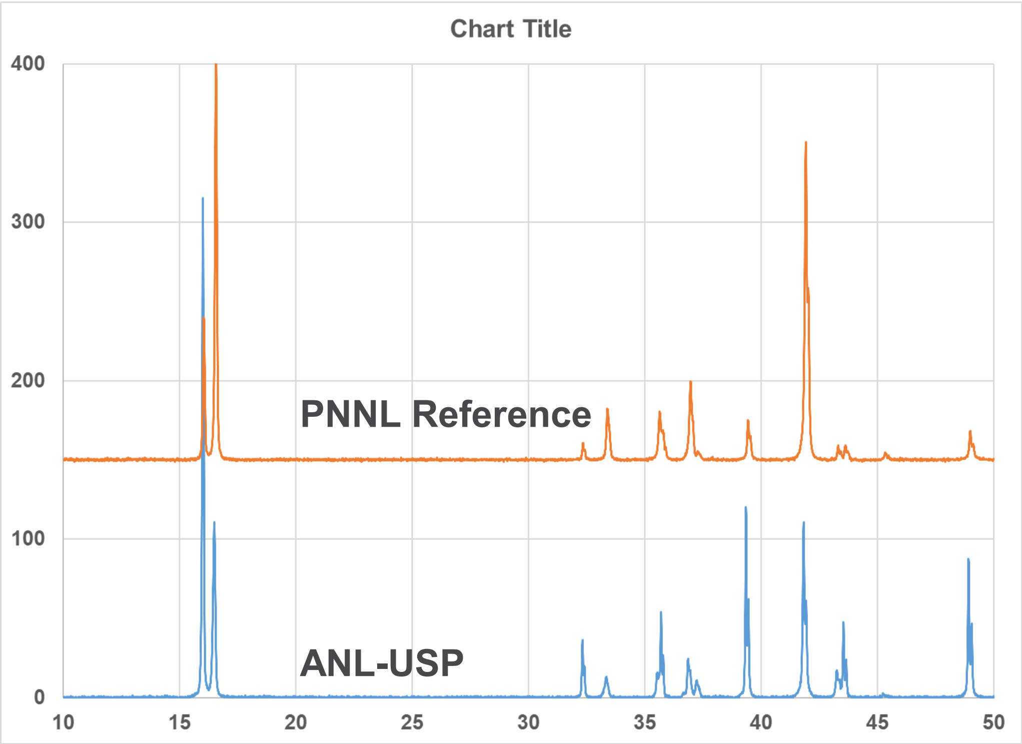
FY23 Objective, Challenges and Technical Accomplishments

- A promising sodium cathode materials with composition of $Na_{0.85}Mn_{0.50}Ni_{0.40}Fe_{0.10}O_2$ was developed at PNNL
- The material was initially made in gram scale using solid-state synthesis (milling and step-wise calcining at high temperature)
- The original lab-scale process is energy intense and hard to scale up due to lack of control over the powder particles size and morphology that is essential to high performance.
- Argonne has been tasked with developing a reproducible and scalable manufacturing process and provide PNNL with quantity of the material sufficient for prototyping and large-scale validation.
- Argonne explores emerging manufacturing technologies in our capability to address the challenges.
- Ultrasonic Spray Pyrolysis (RSP), spray dry and aqueous co-precipitation techniques were explored to assess feasibility of the technologies to mass produce the material in an economic feasible and environmental-friendly way.

FY23 Technical Accomplishments – Ultrasonic Spray Pyrolysis

- Ultrasonic (Reactive) Spray Pyrolysis was used to generate precursor (green) powders for the NaNiMnFe.
- A combined aqueous nitrate solution of Na, Ni, Me, Fe were used as a feedstock.
- USP was performed using 900 °C tube furnace temperature with residence time around 0.3 second.
- The PNNL calcination protocol was performed on the USP powder to achieve phase identical with the original sample.





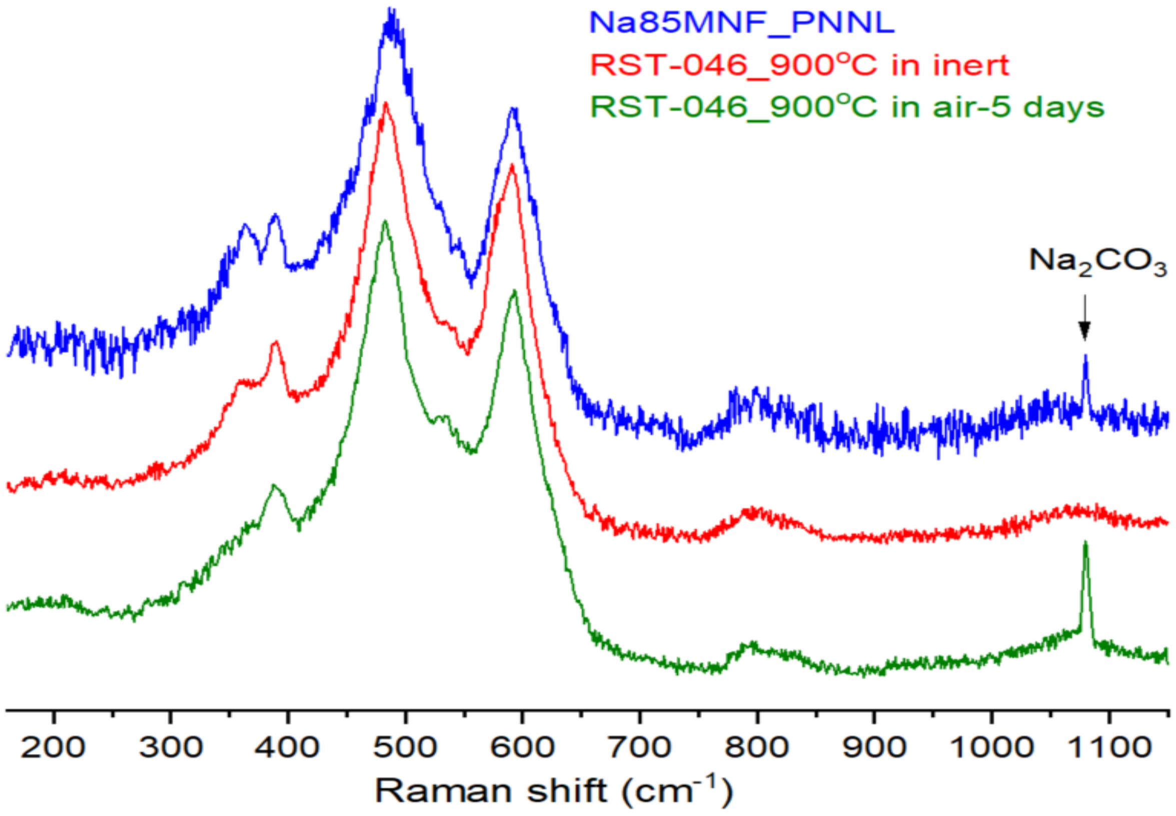
ICP analysis

	Mol ratio			
	Fe	Mn	Na	Ni
ANL-SP	0.055	0.279	0.437	0.226
Na85MNF_PNNL	0.053	0.272	0.450	0.222

- XRD shows similar phase obtained with major crystal texture differences.
- Grain size of ANL-USP sample derived from droplet size distribution of ultrasonic aerosol generation.
- The spherical particle shape in the green powder was not preserved by calcination whereas each aerosol generated particle appears to have transformed into single crystals of the target phase.

FY23 Technical Accomplishments – How to handle the material?

Raman of ANL-USP Na85MNF: inert environ vs. air exposure for 3-days



After air-exposure for 3 days

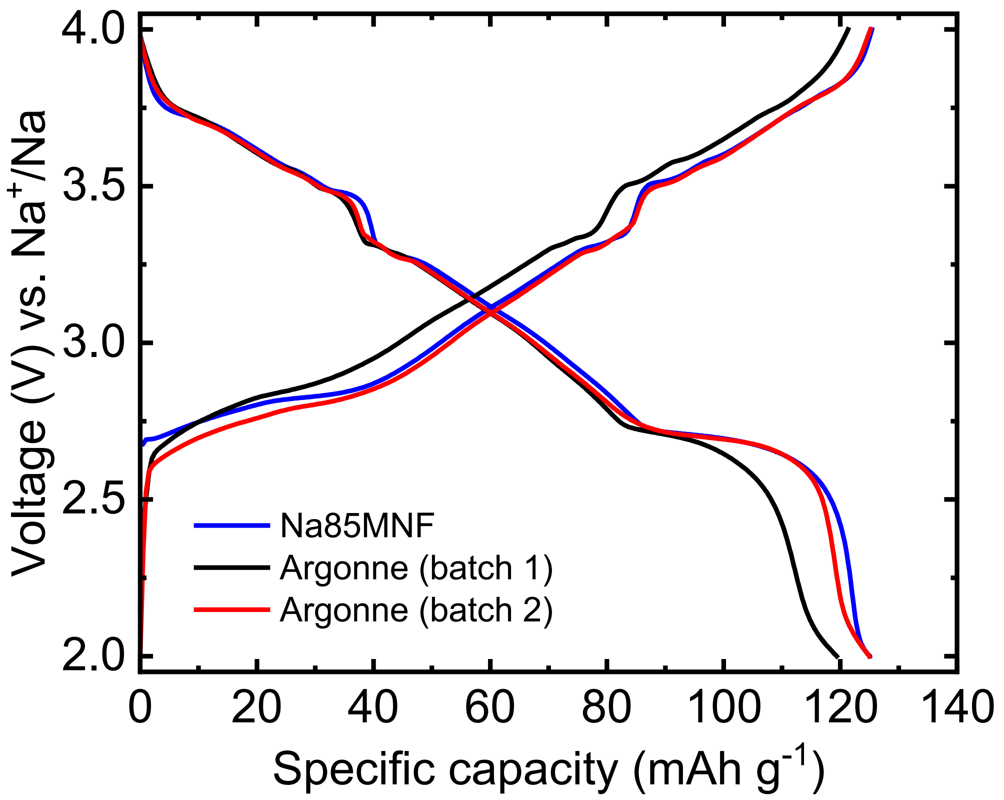
- Na_2CO_3 increases
- Band at 363 cm-1 decreases

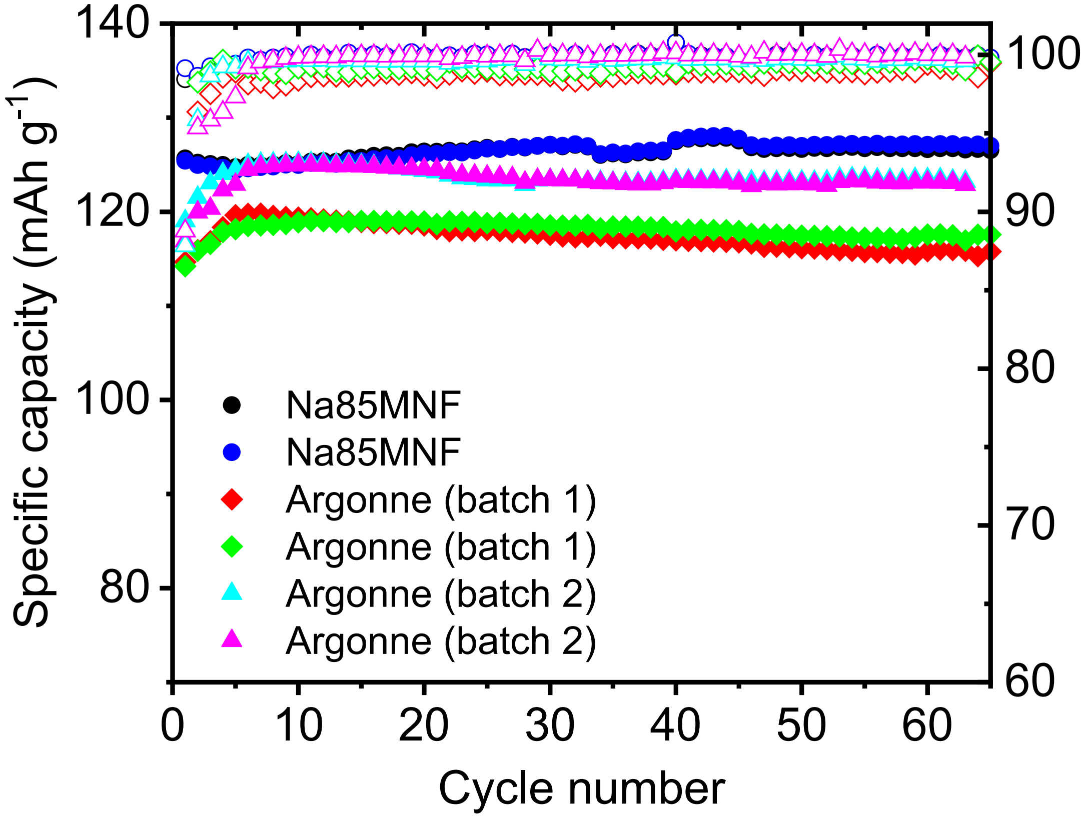
- Conclusion: The material is sensitive to ambient environment and needs to be handled properly to preserve desired composition, phase, property and functionality.

FY23 Technical Accomplishments – Performance of USP materials

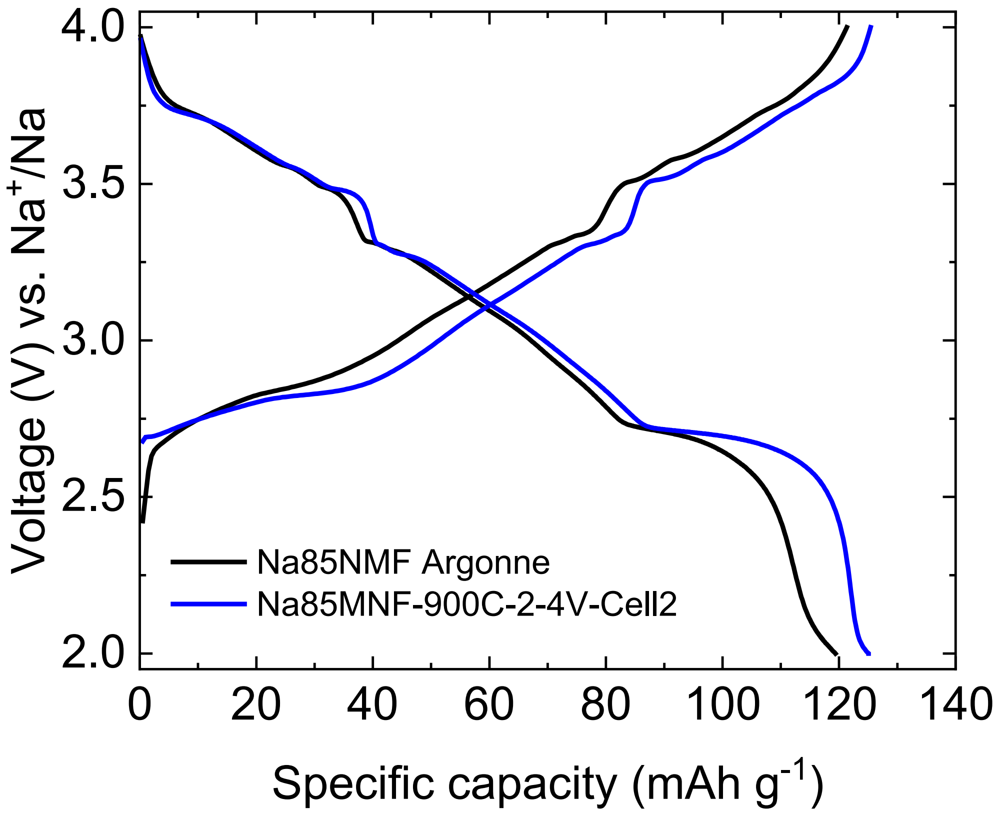
A 10 g sample of Argonne USP produced material was sent to PNNL for electrochemical performance evaluation.

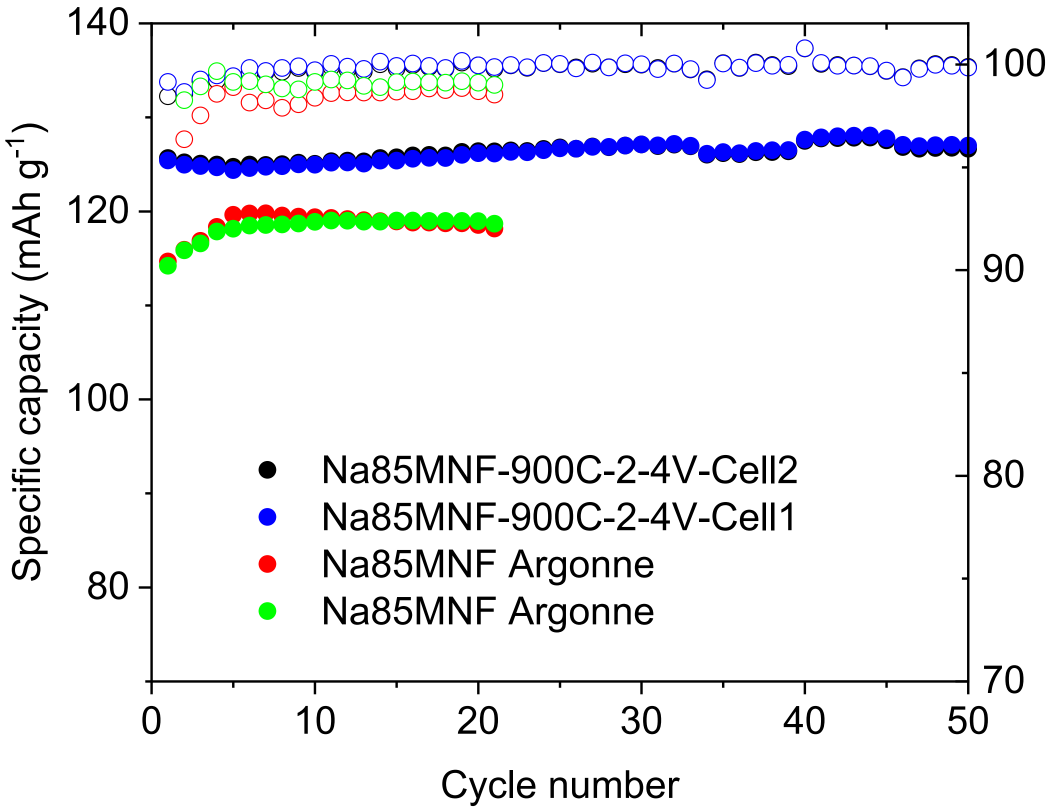
Electrode composition: CAM: C65: PVDF = 80:10:10
Voltage window: 2.0 – 4.0 V vs. Na^+/Na
Rate = 0.5C = 60 mAh/g





FY23 Technical Accomplishments - Performance of USP materials

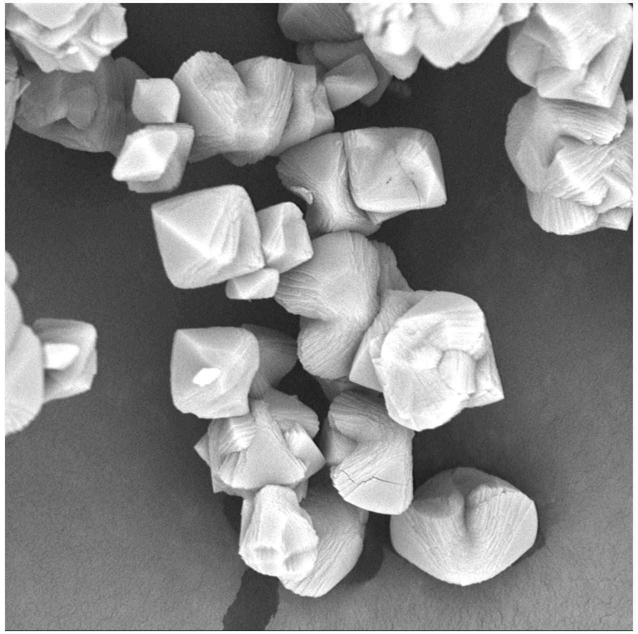




- Although the RSP cathode loading is slightly lower, the specific capacity is smaller (by ~5-7 mAh/g) than lab scale sample. The CE of the USP sample also is (~98.8% to 99.1%).
- We hypothesize that because USP particle is small and not as dense. Slightly higher P2/O3 ratio leads to slightly lower specific capacity.

FY23 Technical Accomplishments – Co-precipitation technique

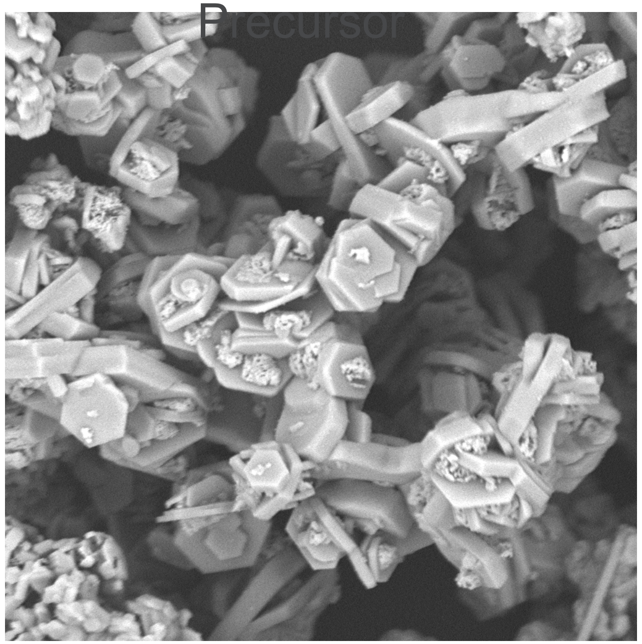
$Mn_{50}Ni_{40}Fe_{10}$ Precursor



ICP	Mn	Ni	Fe
	0.506	0.398	0.096

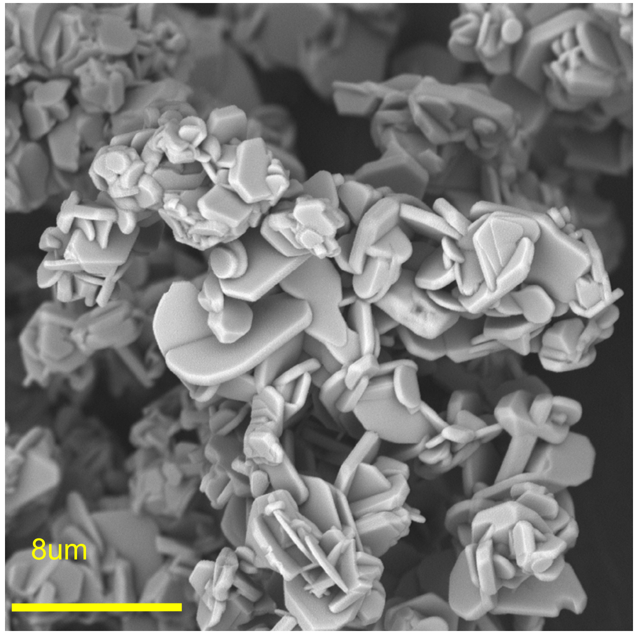
Tube Furnace in O_2

$Na_{085}Mn_{50}Ni_{40}Fe_{10}$ Precursor



ICP	Na	Mn	Ni	Fe
	0.464	0.267	0.214	0.052

PNNL Baseline



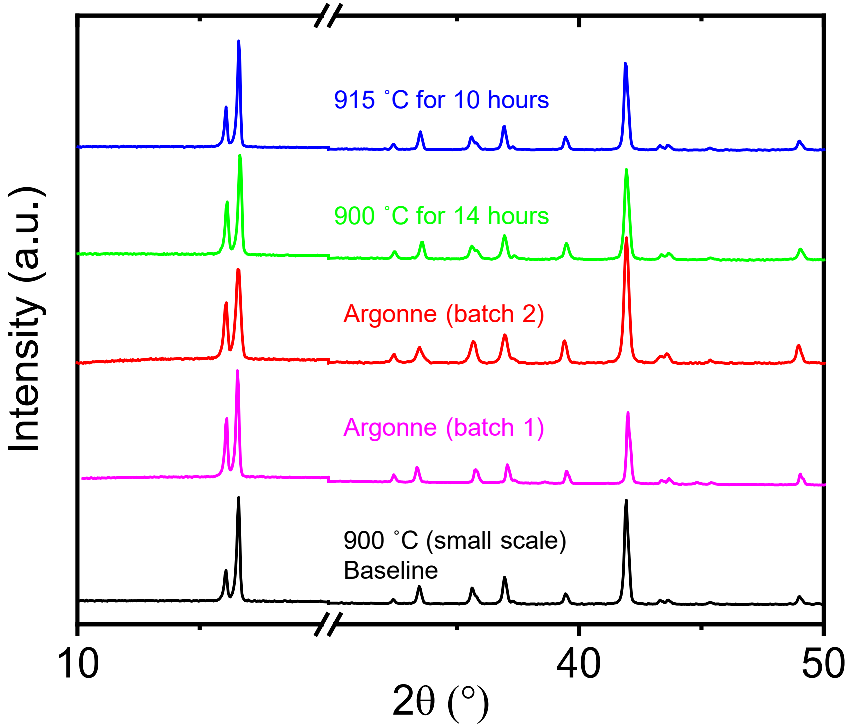
ICP	Na	Mn	Ni	Fe
	0.450	0.272	0.222	0.053

- The $Mn_{50}Ni_{40}Fe_{10}$ precursor powder was obtained through batch co-precipitation reaction of stoichiometric transition-metal salts and chelating/precipitating agent.
- The precursors were mixed with Na_2CO_3 and sodiated through the PNNL calcination protocol to obtain the same composition and similar morphology as the PNNL cathode reference material.

FY23 Technical Accomplishments – Sodiation/calcining study

The electrochemical performance of the material apparently depends on ratio of P2/O3 phases although the relationship is not clear.

MERF ran several experiments varying temperature and time to investigate impact of calcining conditions on the phase composition of the material.



Batch 1 and 2 sample has slightly higher P2/O3 ratio than lab reference sample.

Batch 1 is made from MERF USP sample following PNNL calcining protocol.

Batch 2 is made from MERF co-precipitated precursor following PNNL calcining protocol.

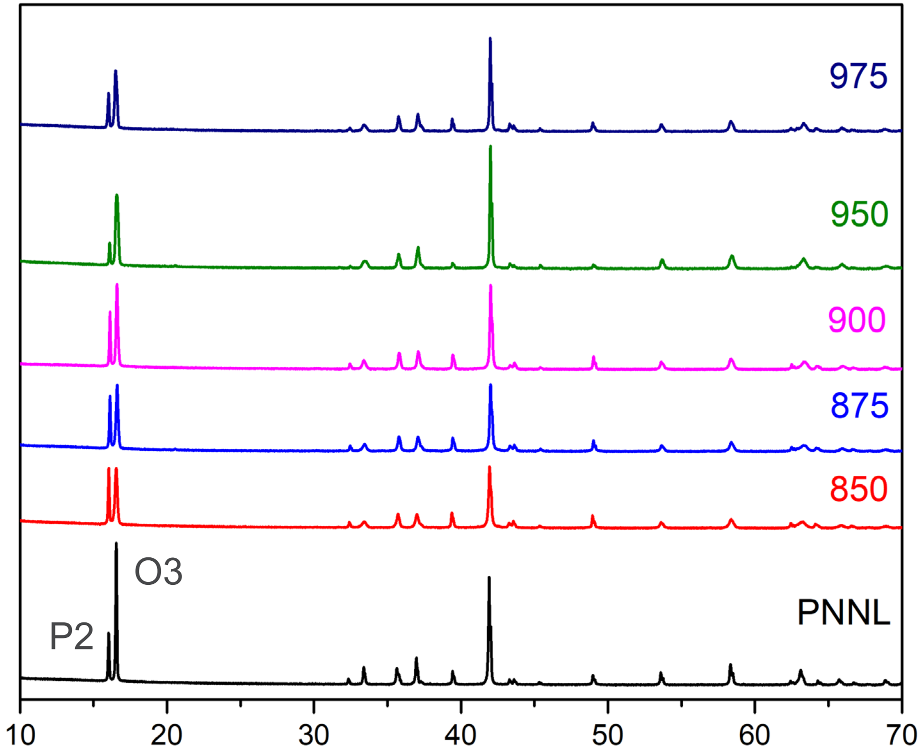
Conclusion: Higher temperature and shorter time provide material with phases ratio closest to PNNL baseline.

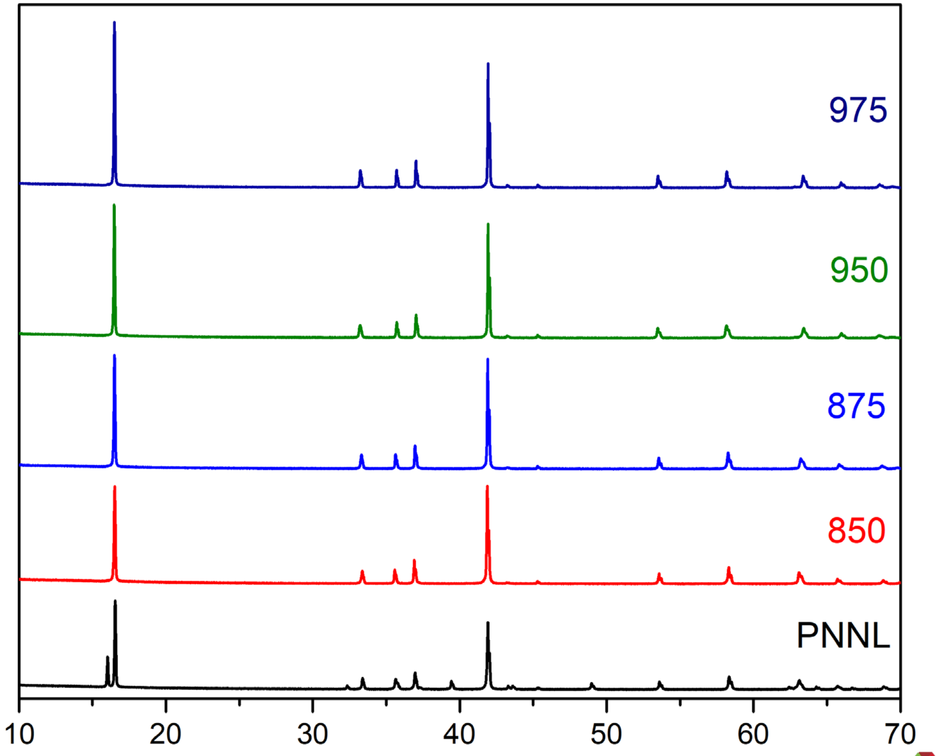
FY23 Technical Accomplishments – Is mixing important?

Ball-milling the precursor and sodium carbonate only forms the O3 phase after calcining (left chart)

Acoustically mixing the precursor and sodium carbonate forms 2 phases (P2 & O3) after calcining (left chart). The ratio of the 2 phases changes with calcination temperature.
Caveat: Exposure to ambient temperature/environment also changes the ratio!

No apparent difference observed between 10h vs 14h at the same temperature.





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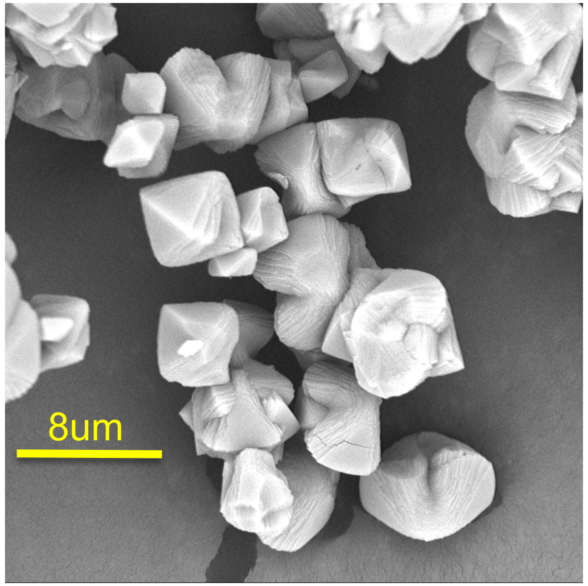
FY23 Technical Accomplishments - Co-precipitation scale up

$Mn_{50}Ni_{40}Fe_{10}$ Precursor



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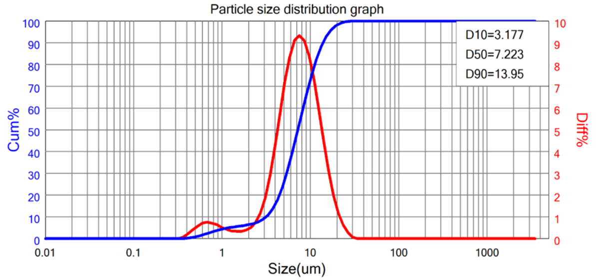
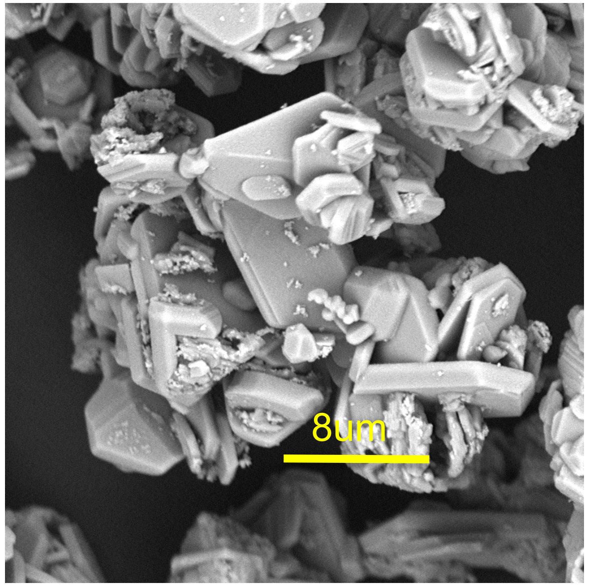


$Na_{87}Mn_{50}Ni_{40}Fe_{10}O_2$



ICP	Na	Mn	Ni	Fe
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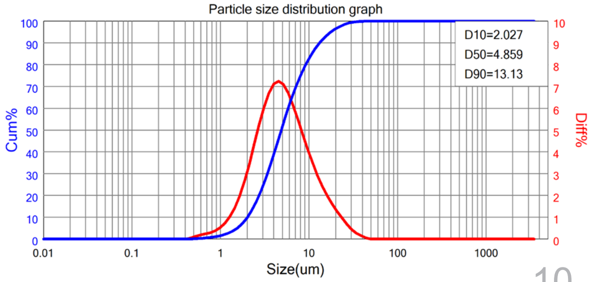

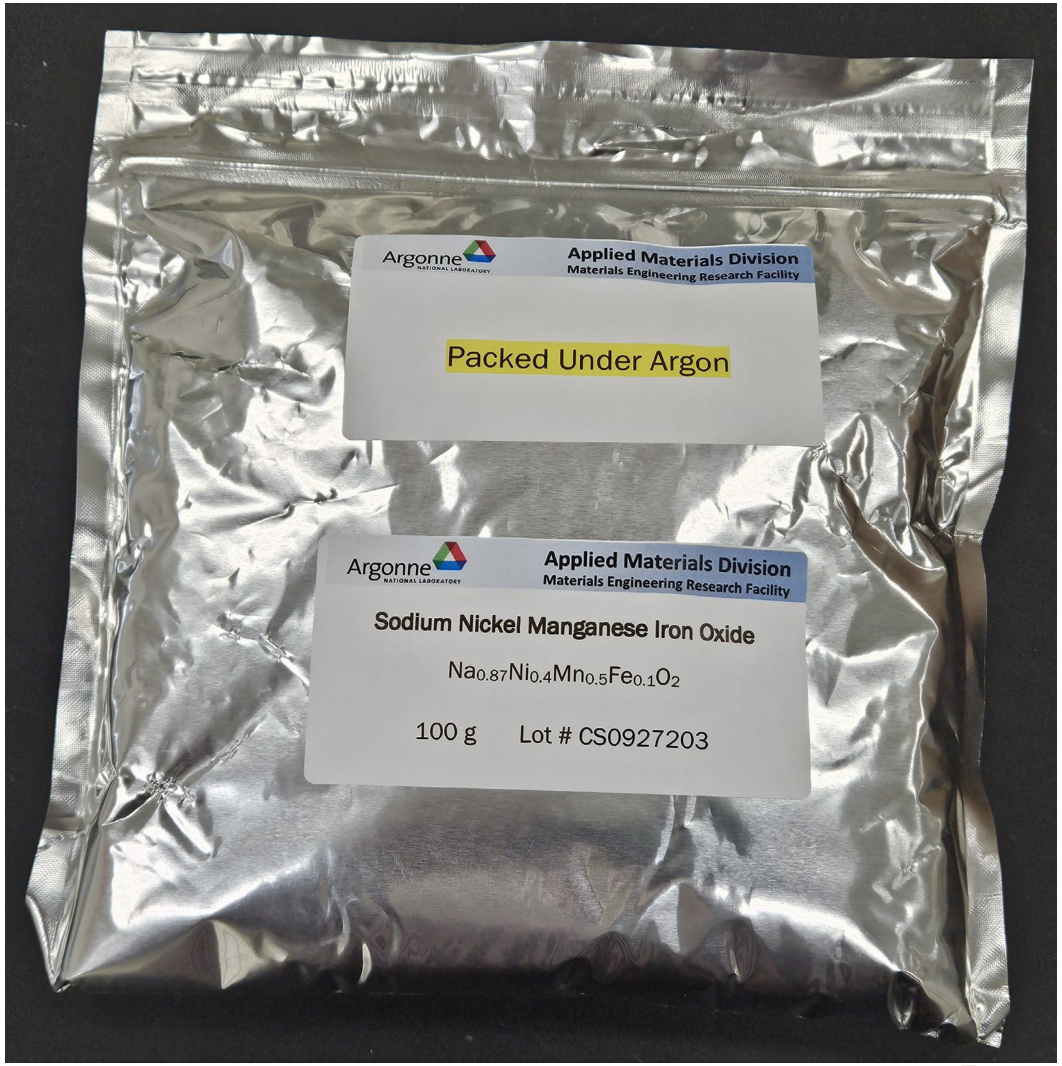

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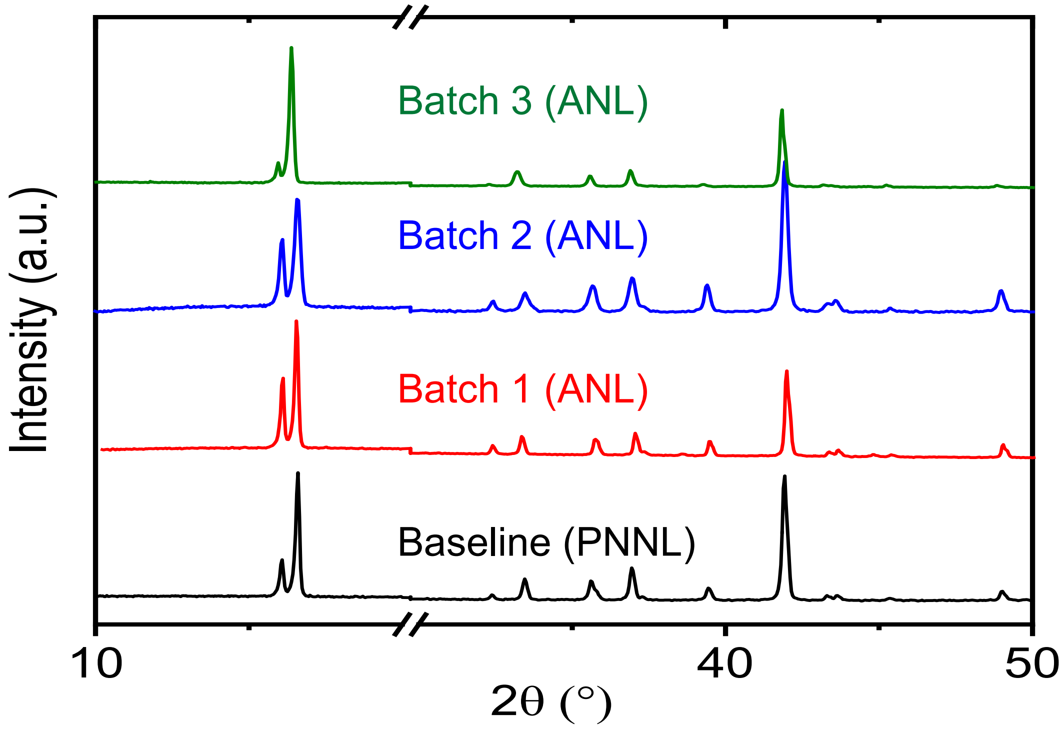
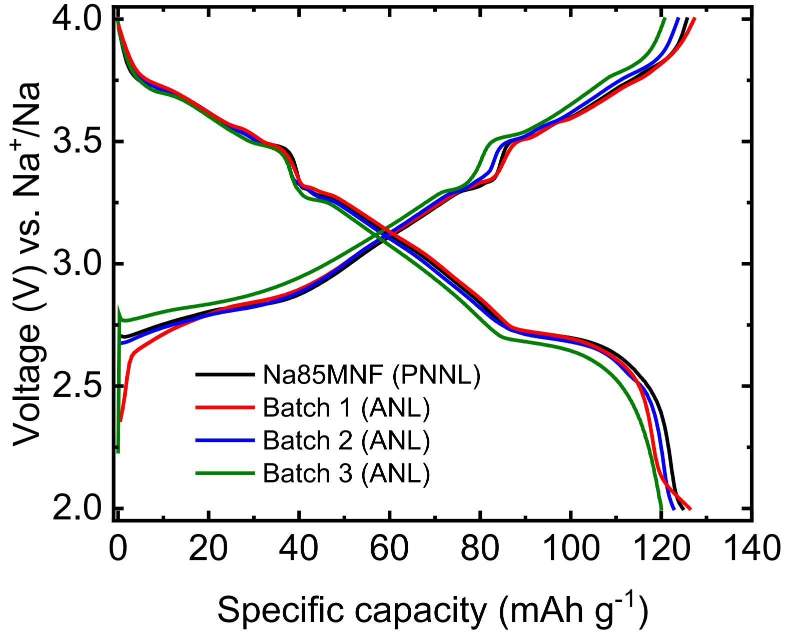
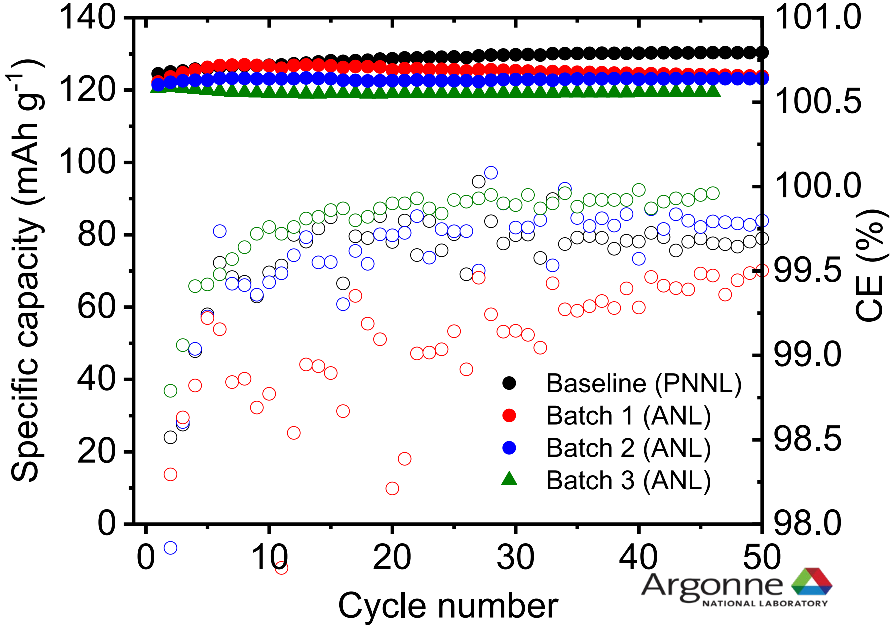
FY23 Technical Accomplishments - Summary

- Argonne MERF developed scalable aqueous co-precipitation process for producing MNF precursor and NaMNF active cathode materials with composition selected by PNNL.
- The developed method can be extended to other cathode active materials formulations.







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  - Carrie Siu

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  - Xiaolin Li (Xiaolin.Li@pnnl.gov) and team

We are open to ideas and collaborations. Please visit the relevant pages for more info and contacts.

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