Process R&D for Electrochemical Energy Storage Materials Manufacturing

Presentation ID: 705

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Project Overview

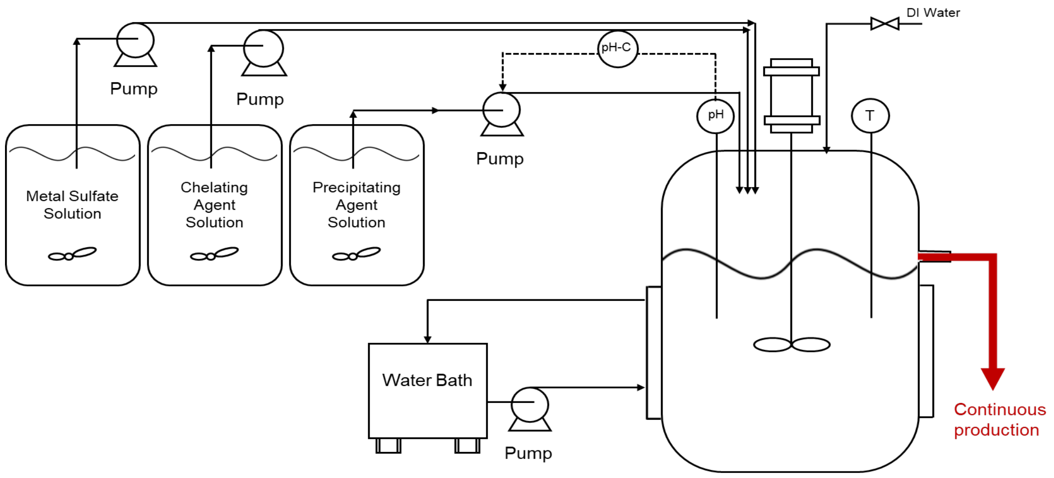
- **Project Goal:**
  - Establish the U.S.-based large-scale synthesis strategies of cathode active materials (CAMs) for sodium-ion battery (SIB) manufacturing for stationary storage application that does not rely on foreign technology or material
- **Current Practice:**
  - Solid state synthesis as state-of-art route (ball mill)
- **Why ANL MERF:**
  - Ability to develop new technologies
  - Scalability of new processes and materials
  - Provide sufficient amounts of desirable CAMs to PNNL for prototyping and large-scale validation
- **Innovation:**
  - FY24: ultrasonic spray pyrolysis, spray drying, solid-state synthesis
  - FY25: 2 new aqueous coprecipitation techniques
- **Impact:**
  - Established new scalable synthesis strategies for new pre-CAMs and CAMs with promising properties
- **Alignment:**
  - Supply CAMs (multiple ≥100-g batches) to PNNL for grid-level stationary SIB electrochemical evaluation in pouch cell format

Background

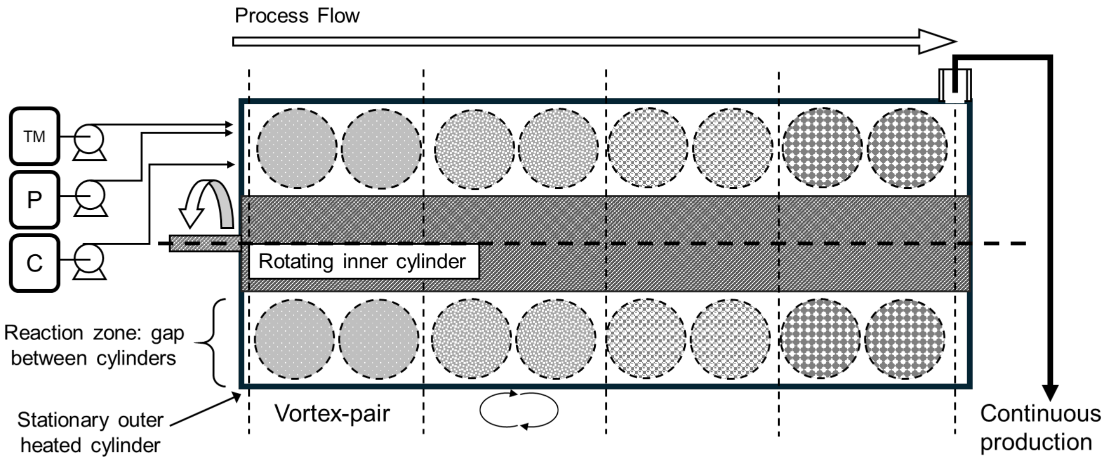
- SIBs are promising
  - Reduction of critical materials usage
  - Low cost
  - Good safety features
- A promising SIB CAM with a composition of $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (NaMNF) was developed at PNNL for stationary storage applications
- The material was initially made at gram scale via solid-state synthesis (prolonged milling and step-wise high-temperature calcination)
  - Limited scalability
  - Energy-intensive
  - Poor control on particle size and morphology

Established two scalable coprecipitation synthesis routes for precursor of CAM (pCAM) at kg level

Conventional ammonia- and NaOH-based coprecipitation via continuous stirred tank reactor (CSTR)

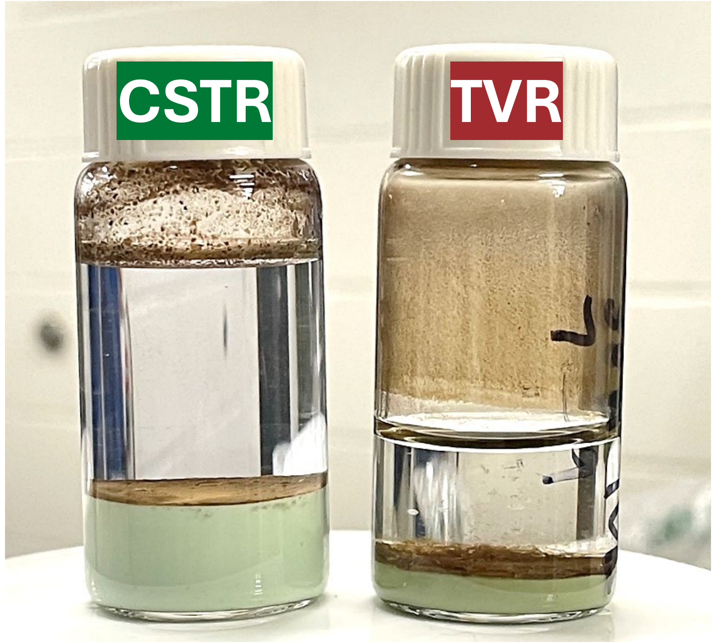


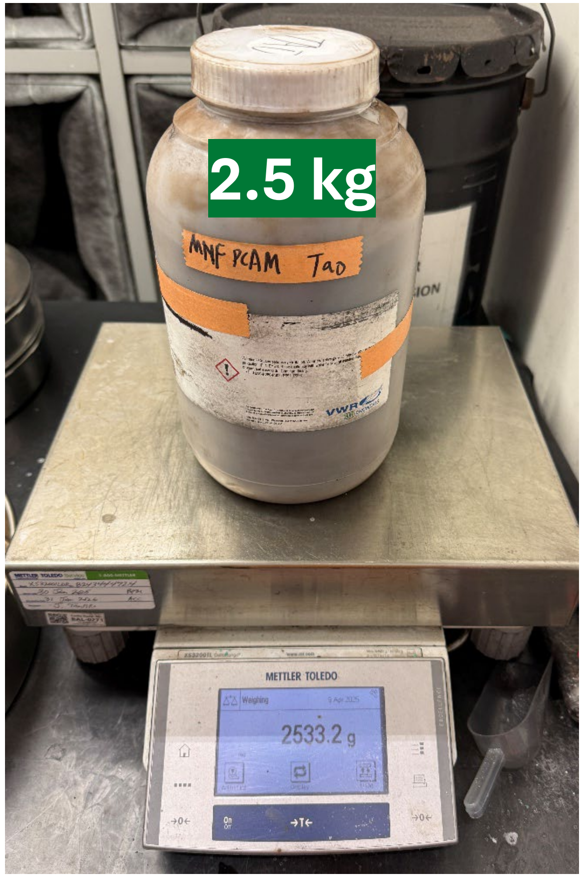
New ammonia-free coprecipitation via Taylor Vortex reactor (TVR)



Goal

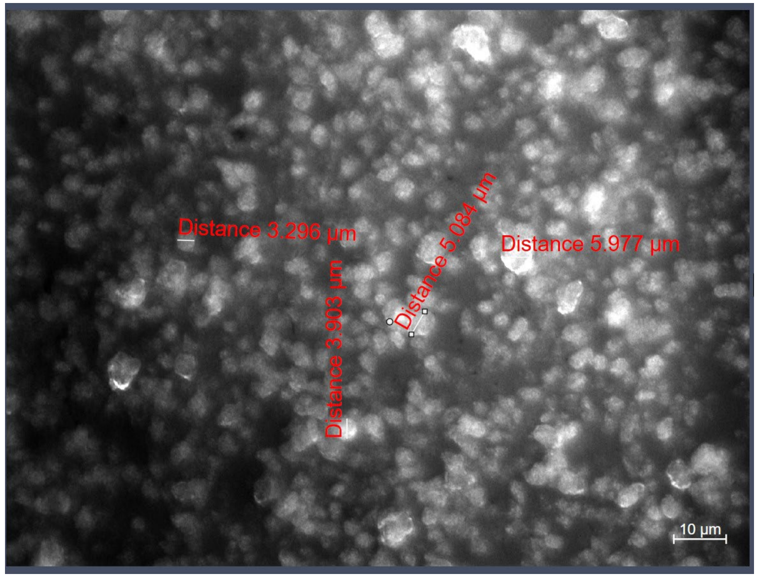
- Matched Mn/Ni/Fe stoichiometry: 5/4/1
- Particle size and morphology control
- Scalability



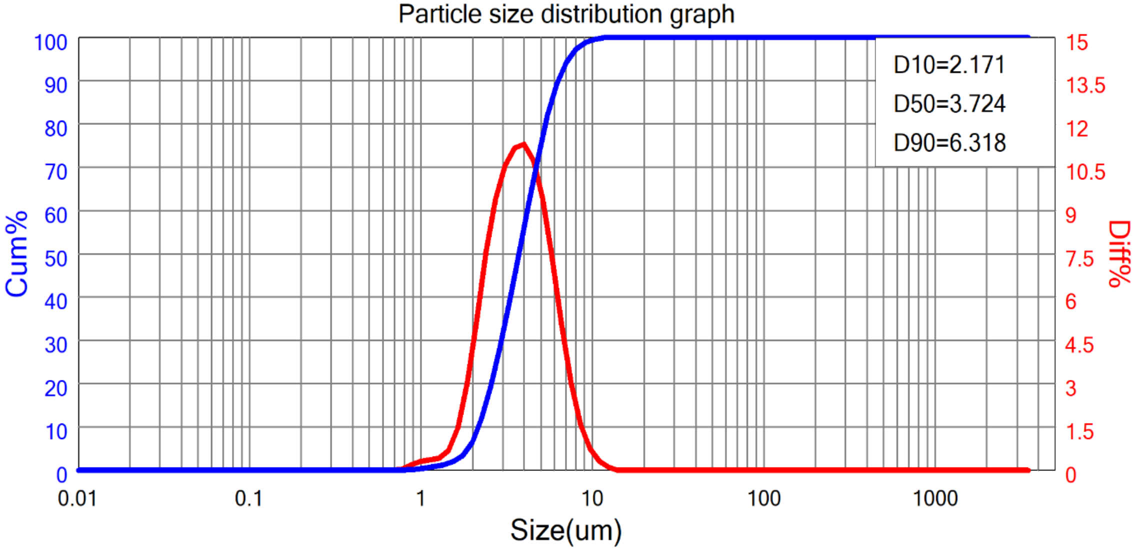


CSTR: Successful formation of secondary particles with size of ~4 micron, wanted stoichiometry and even elemental distribution

Slurry optical microscope



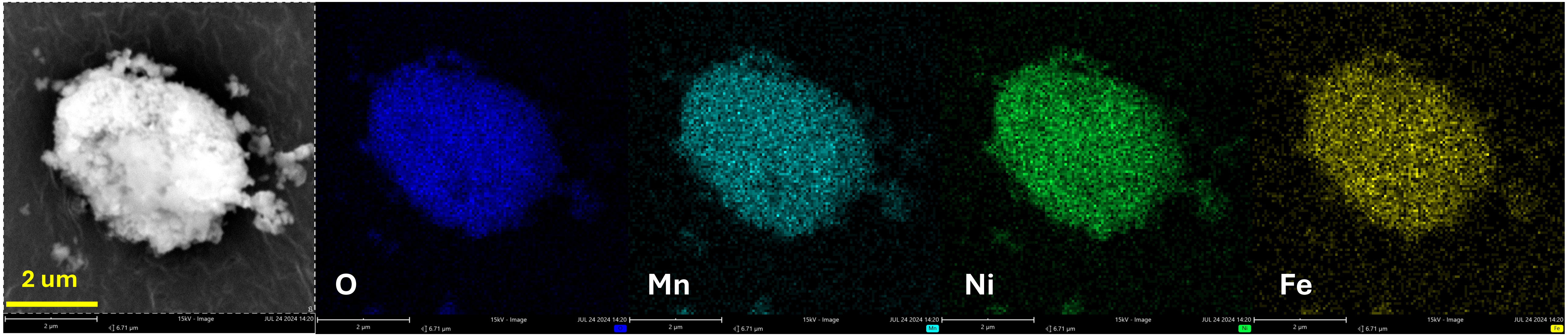
Particle size analysis



ICP

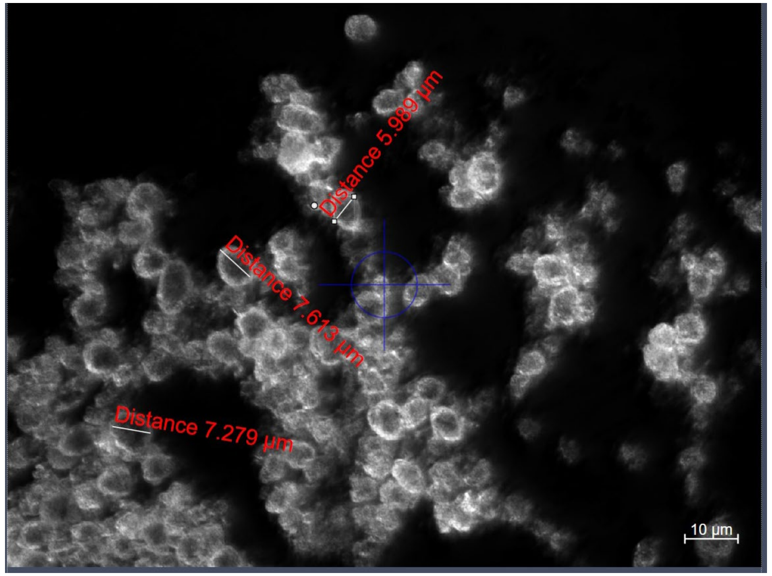
Element	mol %
Mn	50.9
Ni	39.5
Fe	9.6

Tap density: 1.1 g/cc

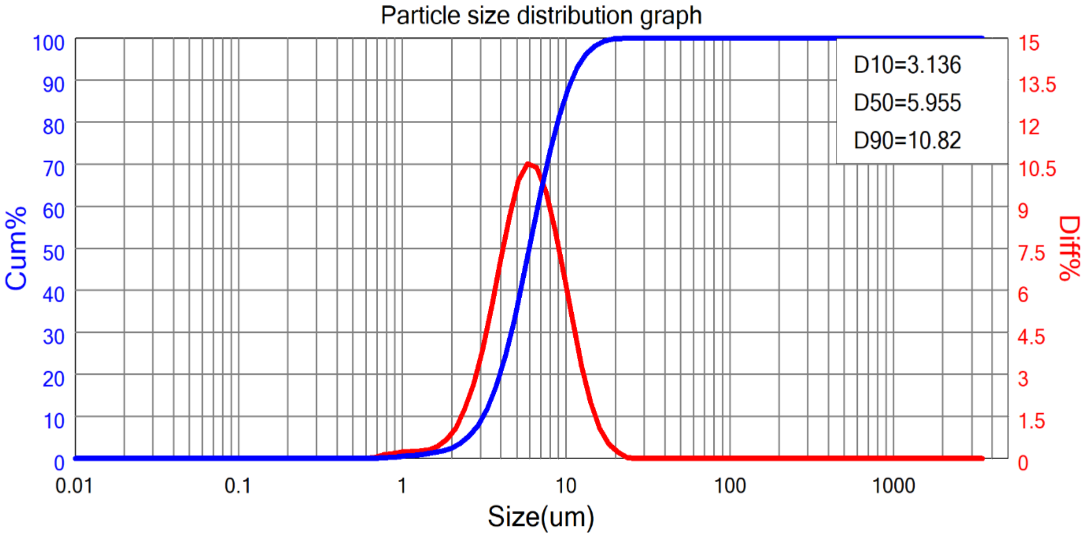


TVR: Successful formation of secondary particles with size of ~6 micron, wanted stoichiometry and even elemental distribution

Slurry optical microscope



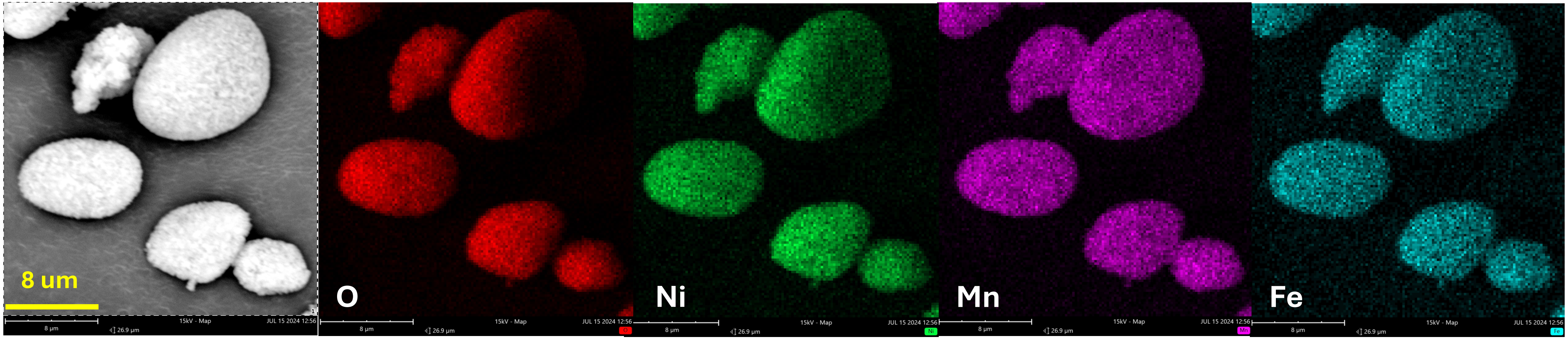
Particle size analysis



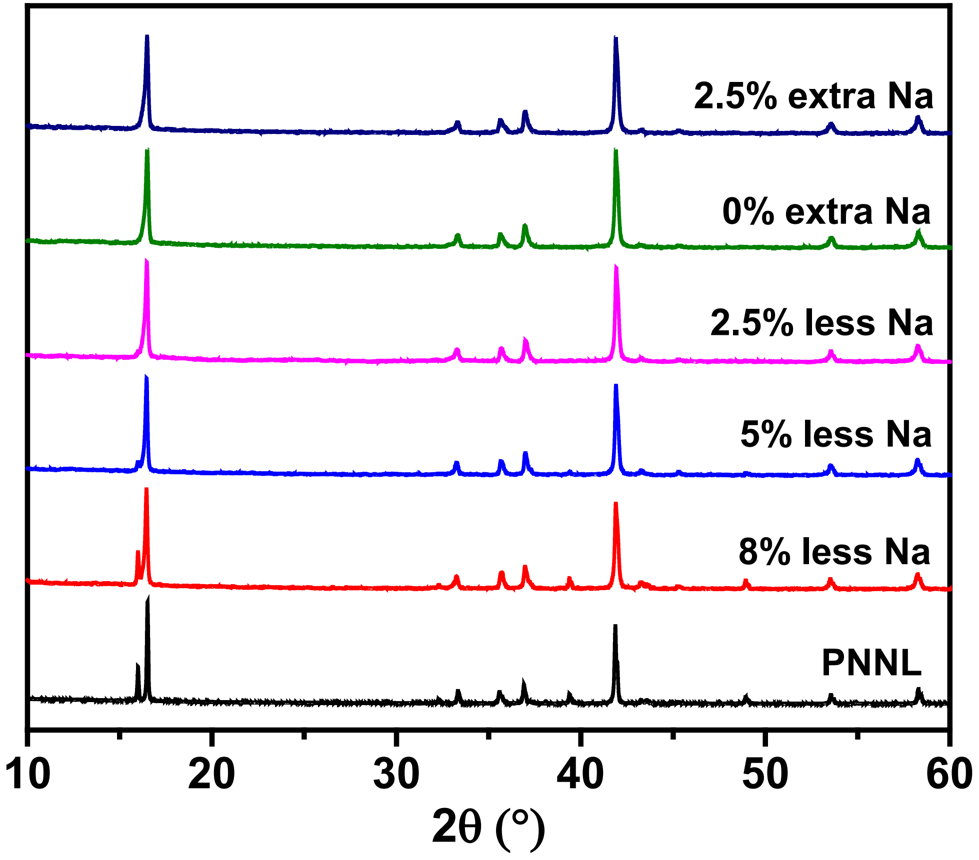
ICP

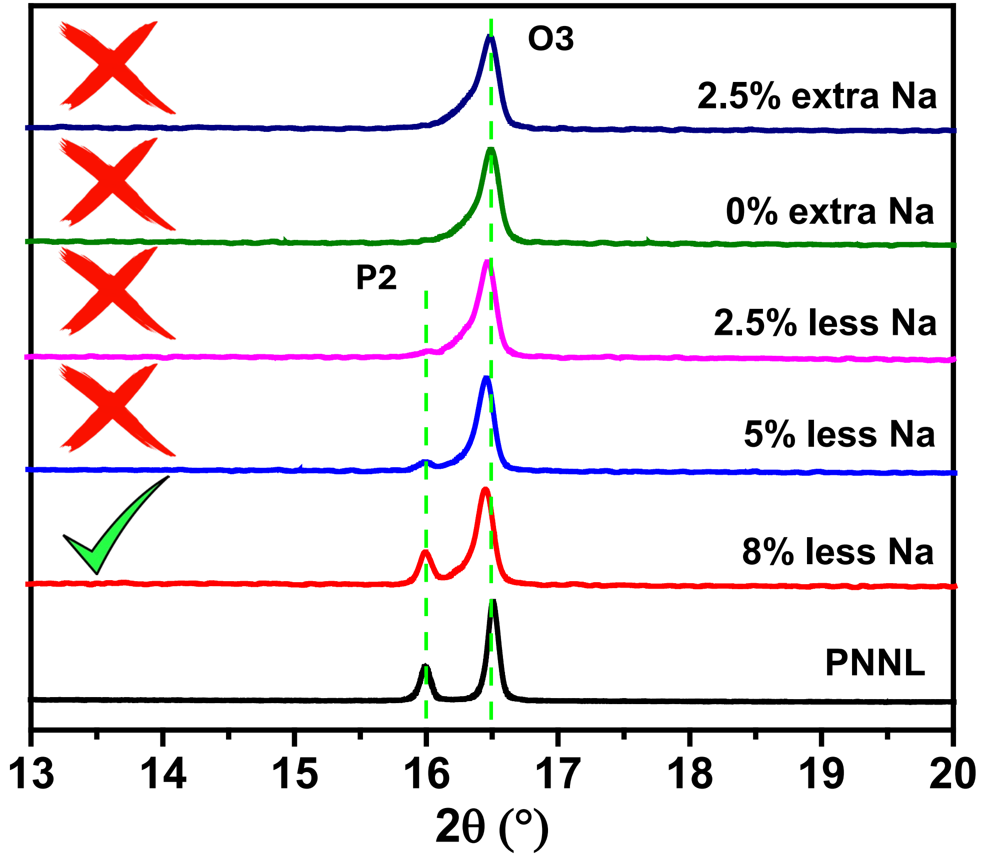
Element	mol %
Mn	48.4
Ni	42.1
Fe	9.6

Tap density: 1.14 g/cc



Successful NaMNF CAM P2/O3 phase ratio control





ANL

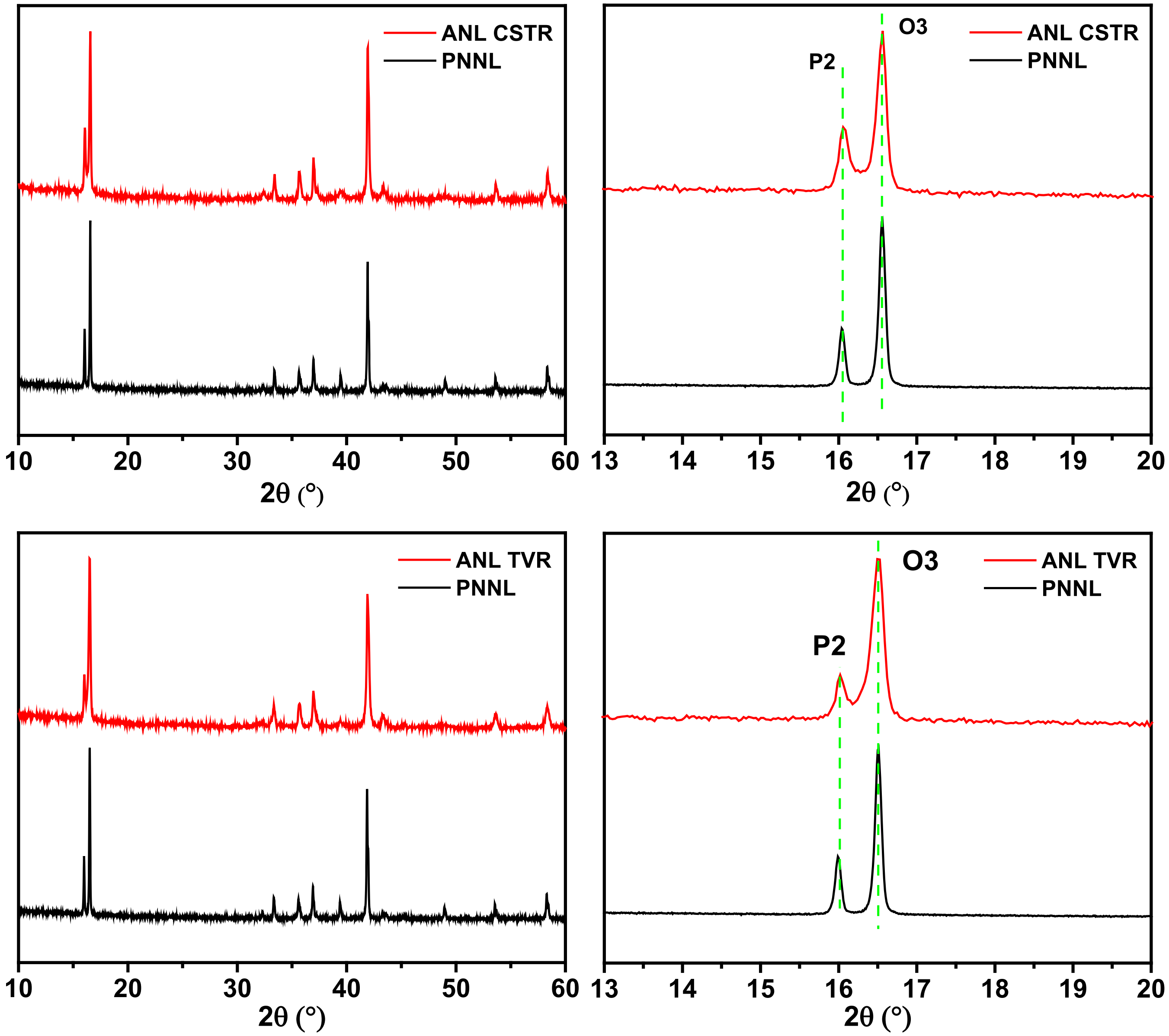
- Coprecipitation
- Na_2CO_3
- 500 °C - 5h, 900 °C - 10h
- 5 °C/min

PNNL

- Solid-state synthesis
- Na_2CO_3
- 500 °C - 5h, 900 °C - 14h
- 5 °C/min

Successfully scale-up syntheses of NaMNF with favorable properties

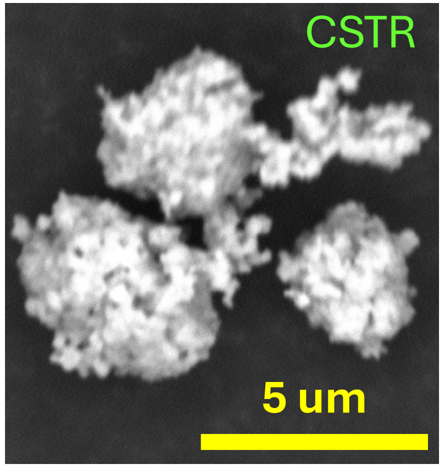
Matched phase ratio

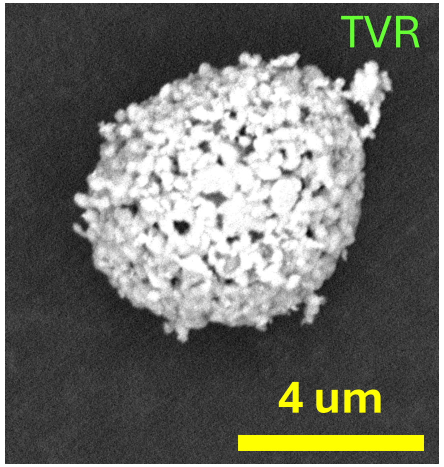


Comparable stoichiometry

	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL CSTR	44.7	27.5	22.5	5.3
ANL TVR	45.2	27.0	22.5	5.3

Well-maintained structural integrity





ANL

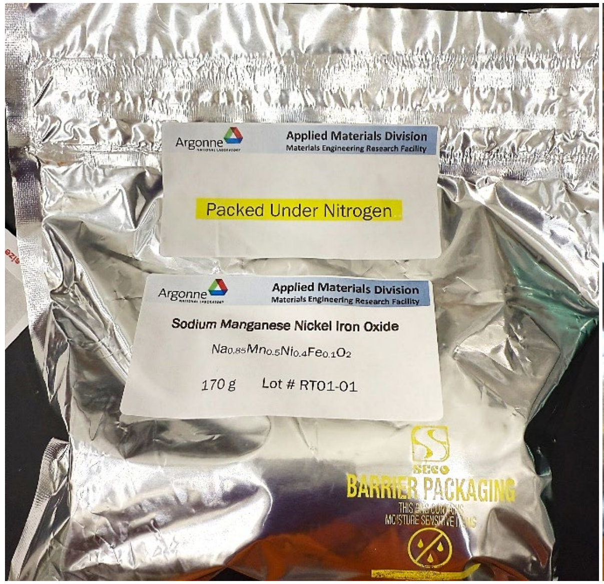
- Coprecipitation
  - CSTR
  - TVR
- Na_2CO_3
- 500 °C - 5h, 900 °C - 10h
- 5 °C/min

PNNL

- Solid-state synthesis
- Na_2CO_3
- 500 °C - 5h, 900 °C - 14h
- 5 °C/min

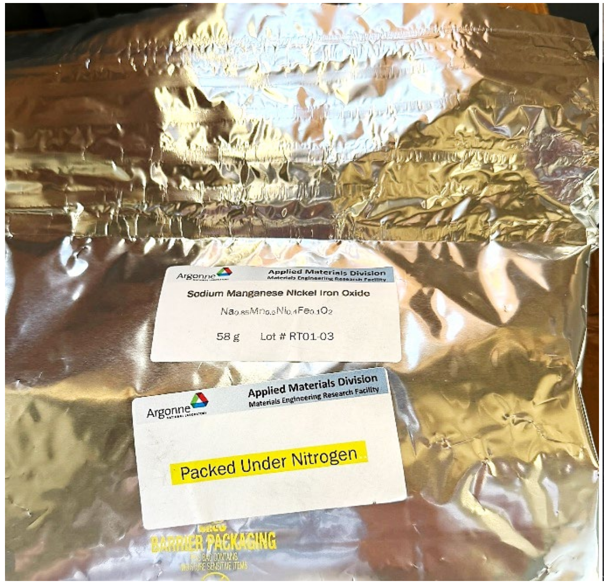
Successfully deliveries of several batches (reproducibility) of NaMNF from CSTR- and TVR-based coprecipitated hydroxide pCAM

177 g on 10/30/24

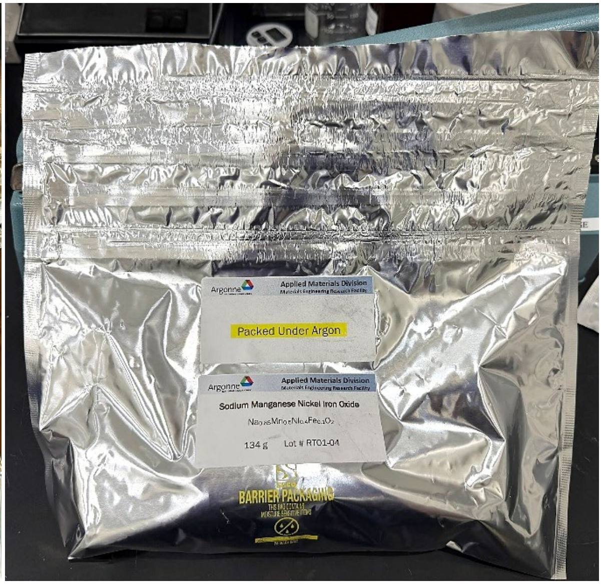


144 g on 11/7/24

58 g on 11/7/24



134 g on 11/21/24

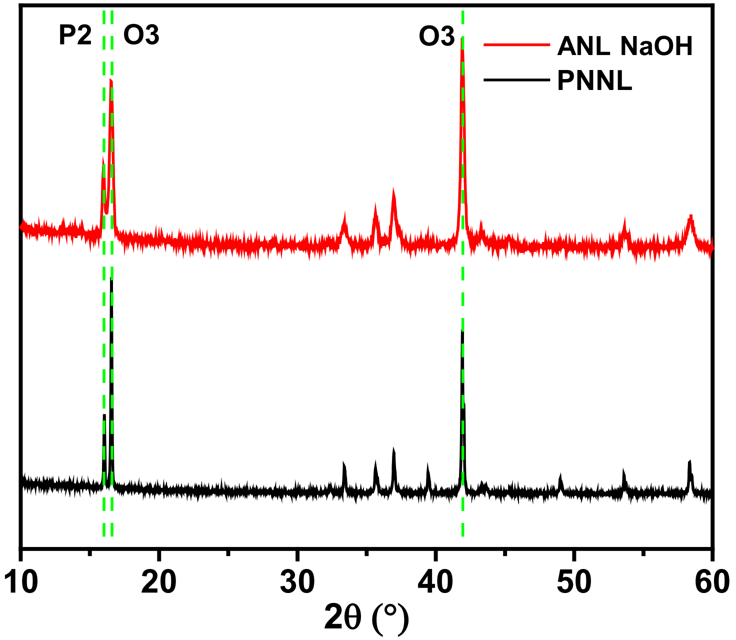


Total in 2024: 513 g

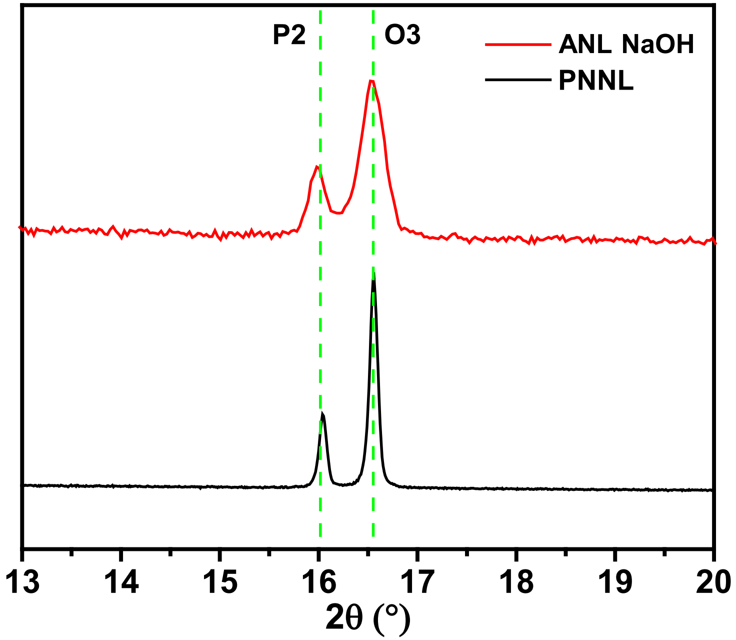
Glovebox-based tube furnace with mass spectrometer at ANL MERF: material handling, processing and operando analysis in inert atmosphere

- NaMNF is extremally sensitive to ambient atmosphere (moisture and carbon dioxide)
- Designed for up to 1 kg
- Precise control and monitor of calcination temperature (thermal probe embedded into sample), especially for large scale

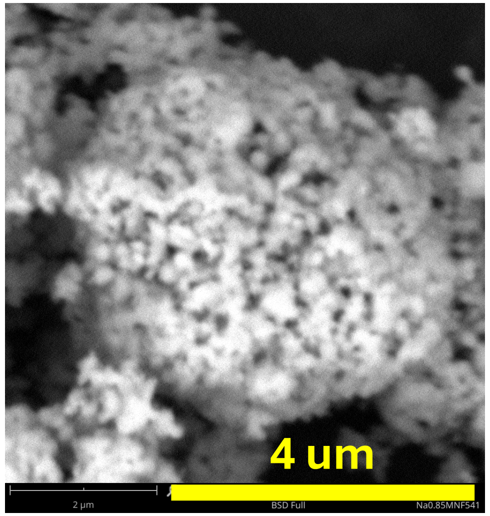
NaOH (fine powder, ambient-sensitive) sodiation: successful energy saving (temp. and duration) in the glovebox-based tube furnace for NaMNF with favorable properties



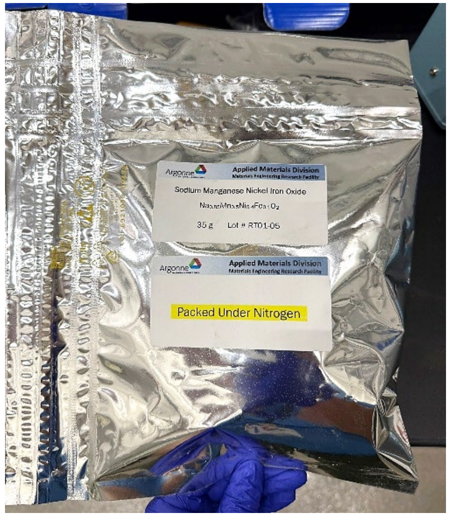
Matched phase ratio



Well-maintained structural integrity



35 g on 3/10/25



Comparable stoichiometry

	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL	47.7	25.8	21.4	5.1

ANL

- Coprecipitation
- NaOH
- 500 °C - 5h, 850 °C - 10h
- 5 °C/min

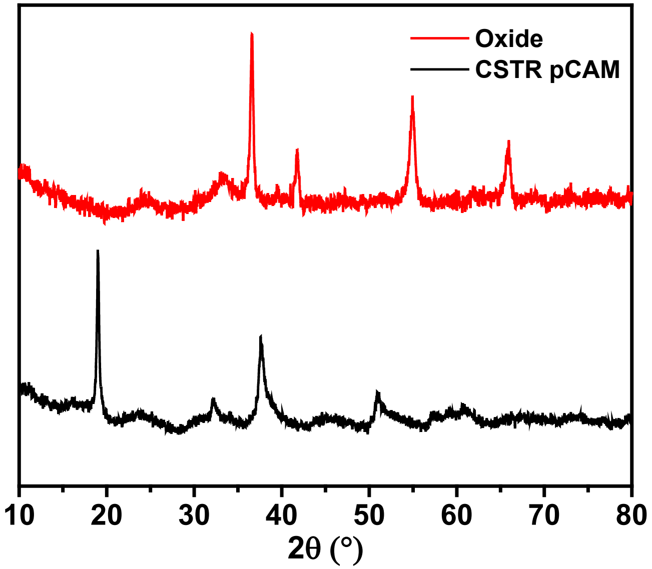
PNNL

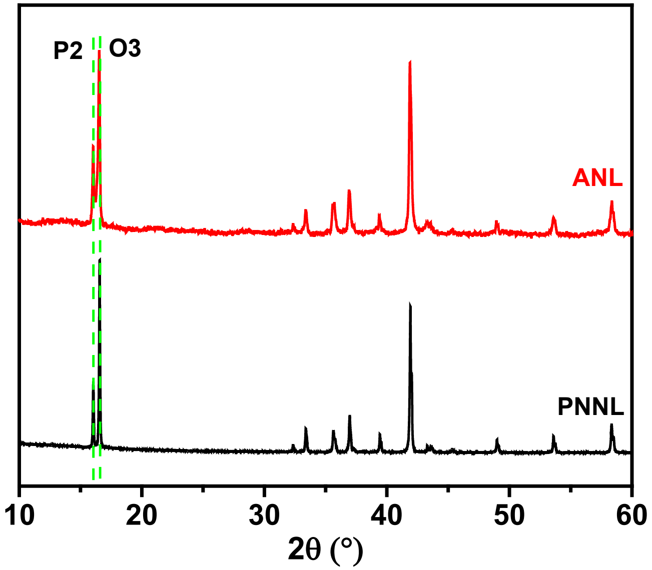
- Solid-state synthesis
- Na_2CO_3
- 500 °C - 5h, 900 °C - 14h
- 5 °C/min

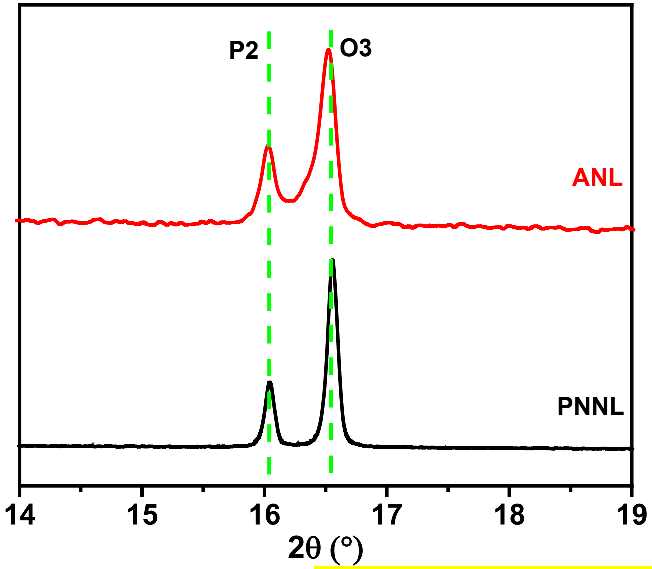
Oxide pCAM: a new successful NaMNF upscaling synthesis route

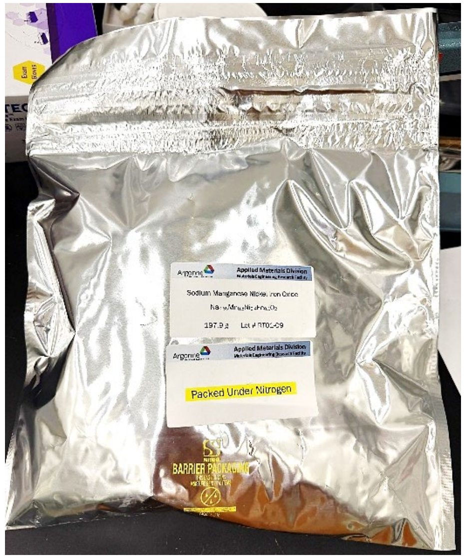
Matched phase ratio

198 g on 5/14/25

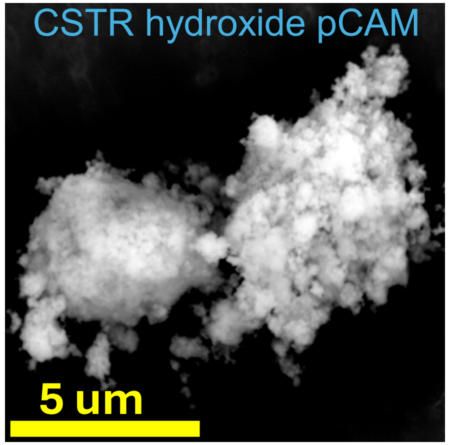


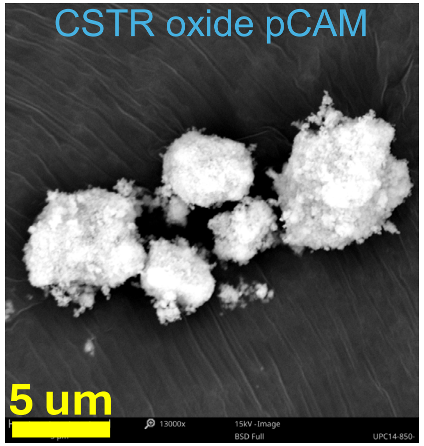


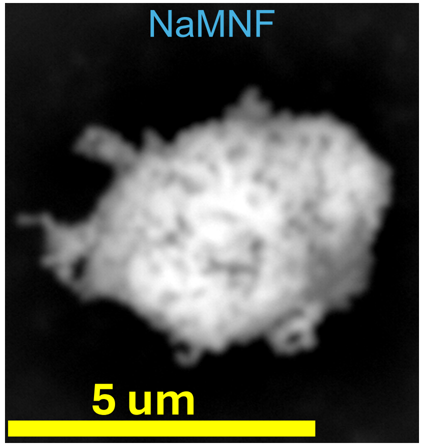




Well-maintained structural integrity







Comparable stoichiometry

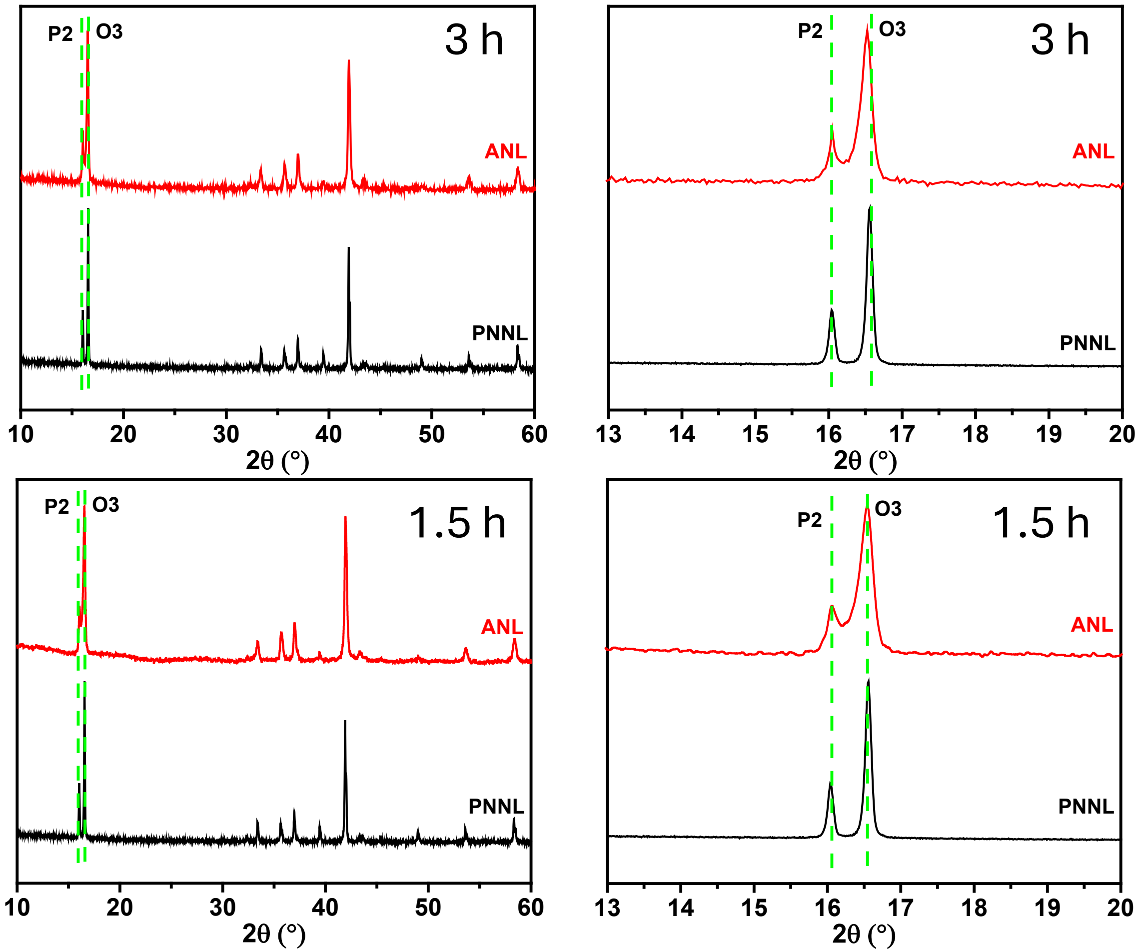
	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL	44.8	27.5	22.3	5.4

ANL
- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C, 2h, 5 °C/min
- Na_2CO_3
- pCAM (O) – CAM: 900 °C, 6h, 5 °C/min

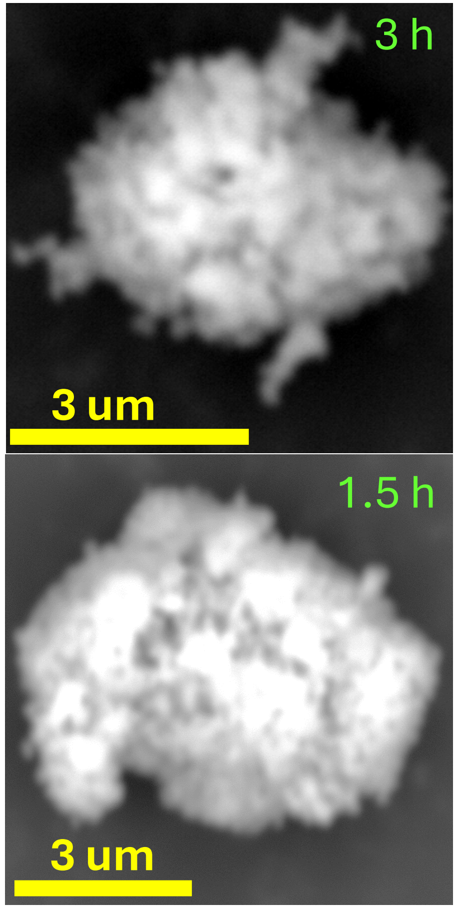
PNNL
- Solid-state synthesis
- Na_2CO_3
- 500 °C - 5h, 900 °C - 14h, 5 °C/min

Oxide pCAM enables much shortened NaMNF upscaling synthesis time (even 1.5 h)

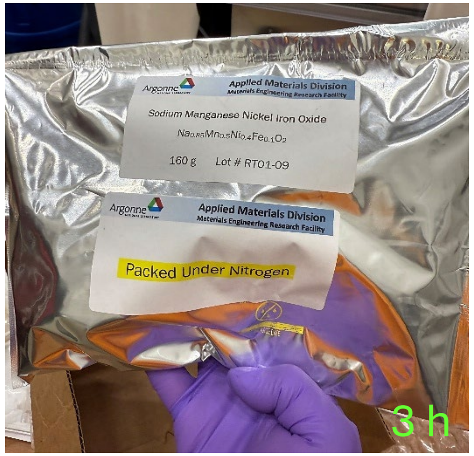
Matched phase ratio



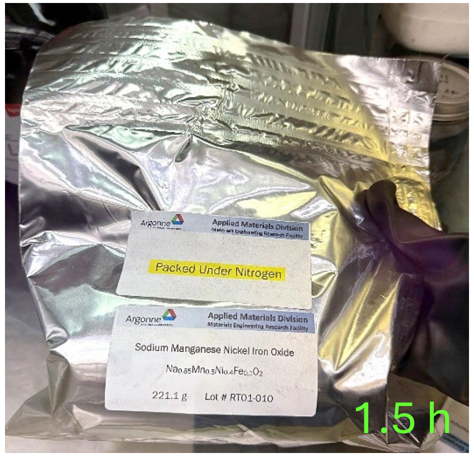
Well-maintained structural integrity



160 g on 6/16/25



221 g on 7/11/25



Comparable stoichiometry

	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL 3 h	45.1	27.7	21.8	5.3
ANL 1.5 h	45.1	27.4	22.1	5.4

ANL

- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C, 2h, 5 °C/min
- Na_2CO_3
- pCAM (O) – CAM: 900 °C, 3 or 1.5 h, 5 °C/min

Summary

- Successful syntheses of NaMNF via several techniques at large scale
  - 3 routes in FY24: ultrasonic spray pyrolysis, spray drying, solid-state synthesis
  - 2 aqueous coprecipitation techniques with various sodiation strategies (FY24&25)
    - CSTR
    - TVR
    - pCAM: hydroxide and oxide
    - Sodiation agent: Na_2CO_3 and NaOH
    - Calcination protocol: temp. and duration
    - desirable P2/O3 phase ratio
    - matched stoichiometry
    - well-maintained structural integrity
    - scalability
- Various batches of NaMNF samples have been delivered (>1.1 kg in total for FY25) to PNNL for electrochemical evaluation in pouch cell format
- These preparation strategies can be potentially transferable to other SIB CAMs (formulations)
  - Phase ratio adjustment for PNNL's performance optimization
- Exploring more possible synthesis strategies

Acknowledgements

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  - Krzysztof Pupek (May 9, 2025)
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  - Marcos Lucero
  - Fred Omenya