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PROCESS R&D FOR ELECTROCHEMICAL ENERGY STORAGE MATERIALS MANUFACTURING

PRESENTATION ID: 701

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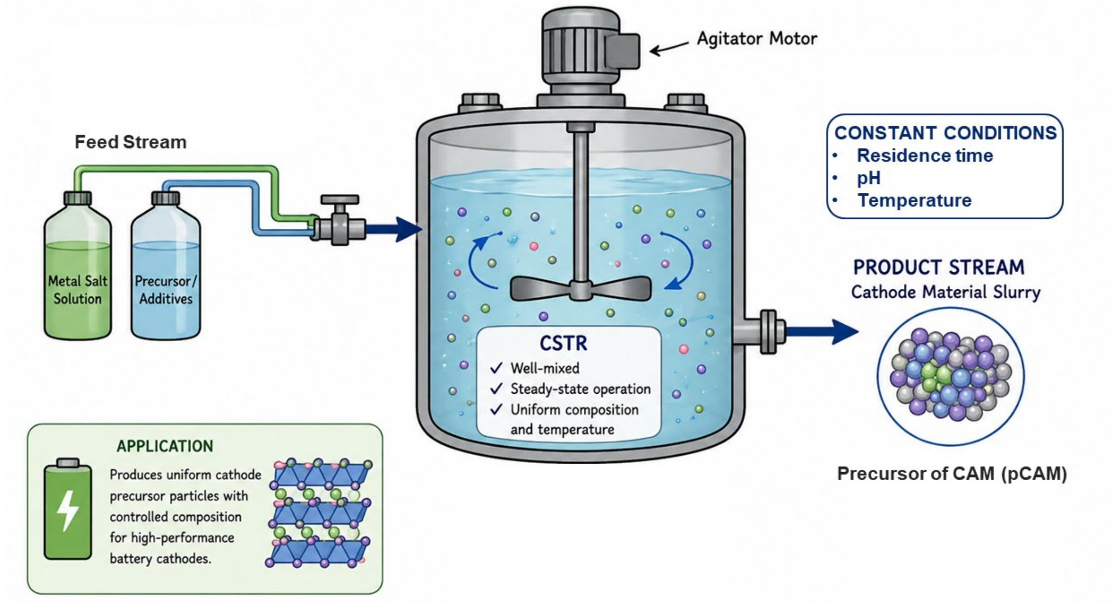
PROJECT OVERVIEW

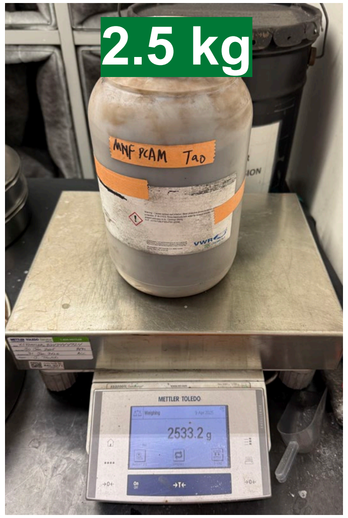
- ANL MERF Goal:
  - —Developing reproducible and scalable manufacturing strategies
  - —Upscaling syntheses of desired sodium-ion battery (SIB) cathode active materials (CAMs): P2/O3 hybrid phased $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (NaMNF)
- Current Practice and Challenges: solid state synthesis as state-of-art route (ball mill and long high-temp. calcination)
  - —Limited scalability
  - —Energy-intensive
  - —Poor control on particle size and morphology
- Why ANL MERF:
  - —Ability to develop new technologies
  - —Scalability of new processes and materials
- Innovation and Duration:
  - —FY24: ultrasonic spray pyrolysis, spray drying, solid-state synthesis
  - —FY25: 2 new aqueous coprecipitation techniques
  - —FY26: various time- and energy–saving sodiation calcination protocols together with secondary particle engineering of NaMNF CAMs via continuous aerosol flow spray pyrolysis (CAFSP)
- Impact: Established new scalable synthesis strategies of new precursor-CAMs (pCAMs) and CAMs with promising properties for the U.S.-based battery manufacturing
- Vertical/Investment Area: Materials and Systems Innovation
- Alignment/Supports: facilitate the SIB manufacturing in the U.S. and SIB-based grid energy storage

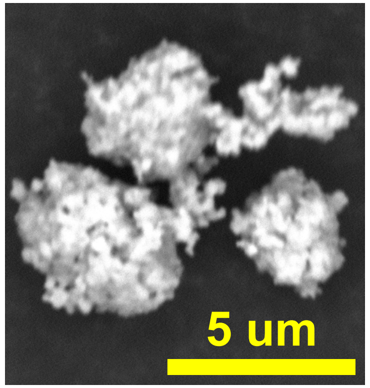
APPROACH 1: COPRECIPITATION WITH VARIOUS SODIATION CALCINATION STRATEGIES

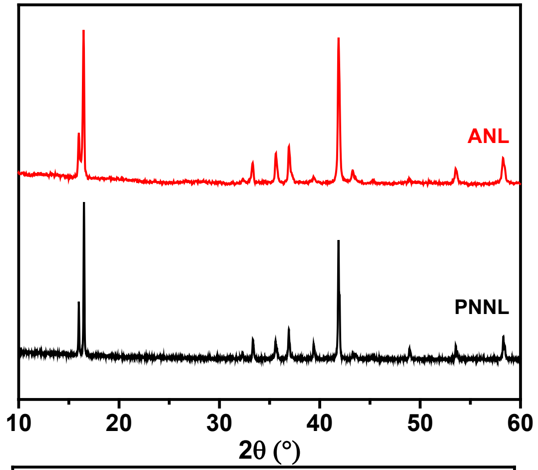
- Matched P2/O3 phase ratio
- Matched stoichiometry
- Preferred particle size distribution and morphology
- Scalability

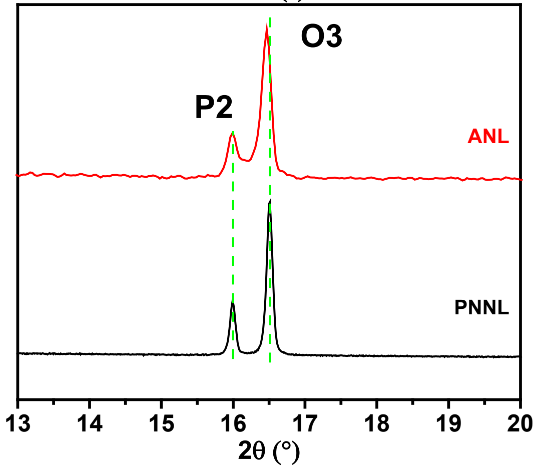
Conventional ammonia- and NaOH-based coprecipitation via continuous stirred tank reactor (CSTR)







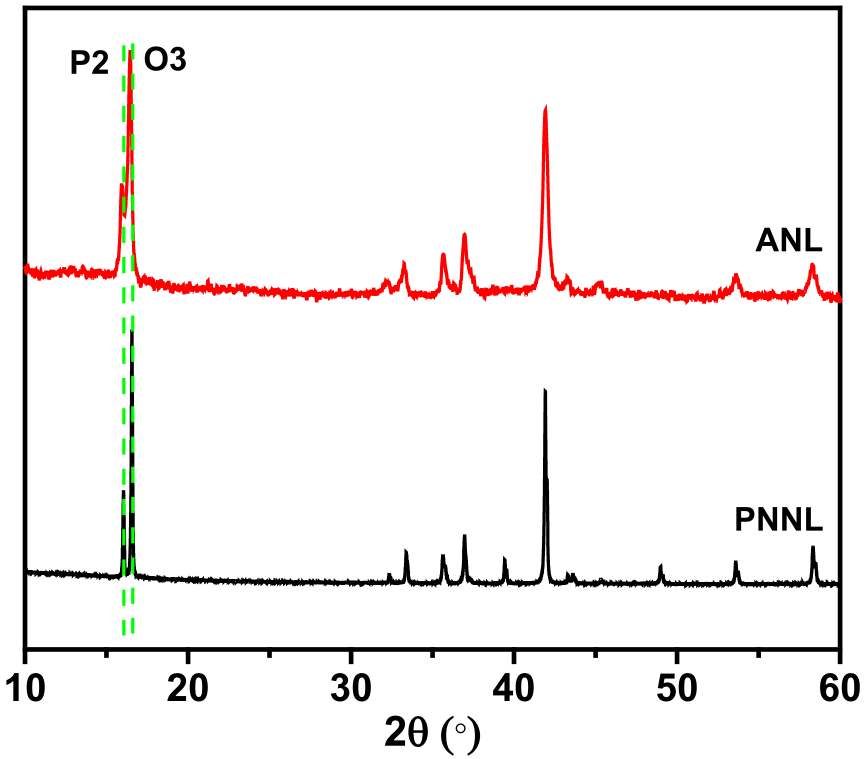


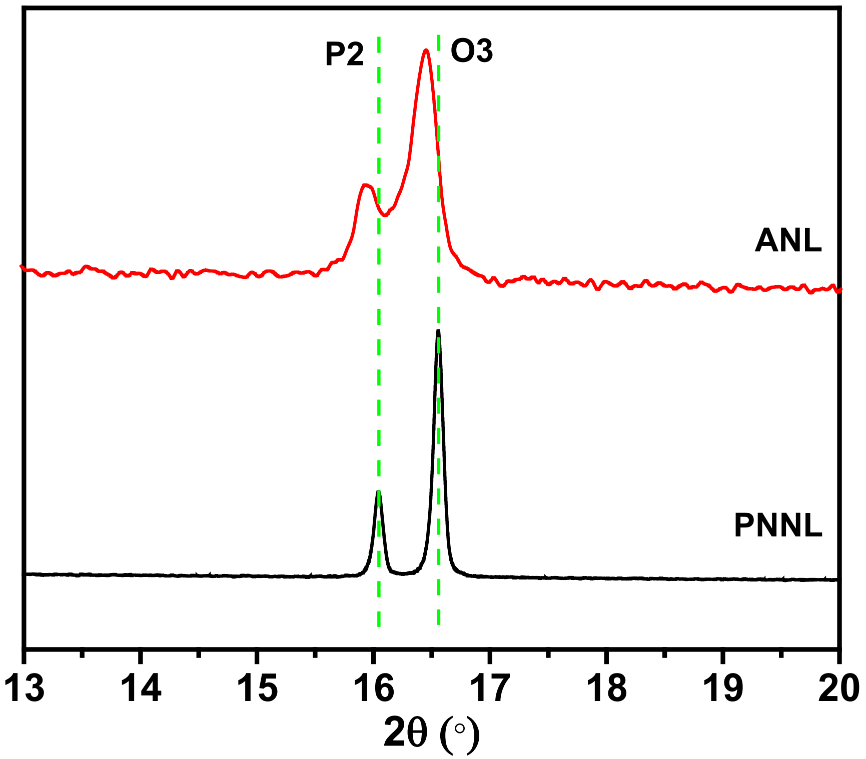


ANL	PNNL
• Coprecipitation	• Solid-state synthesis
• Na_2CO_3	• Na_2CO_3
• 500 °C - 5h, 900 °C - 10h	• 500 °C - 5h, 900 °C - 14h
• 5 °C/min	• 5 °C/min

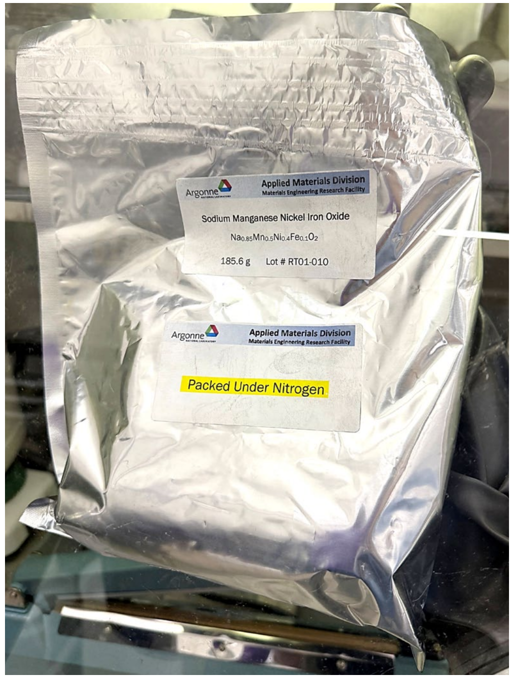
	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL CSTR	44.7	27.5	22.5	5.3

ANL has successfully realized novel energy saving upscaling synthesis of NaMNF (185.6 g) via oxide pCAM at lowered calcination temp. (800 °C), leading to matched P2/O3 phase ratio with less Na ($Na_{0.81}$MNF)





Tap density: ~1.3 g/cc



	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL (0.86 Na)	43.9	28.2	22.5	5.4

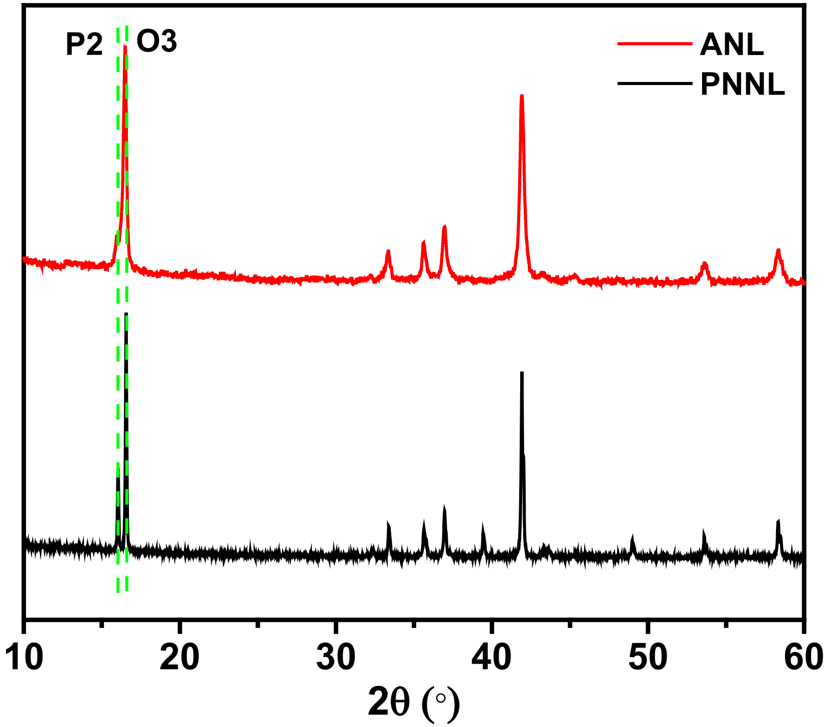
ANL

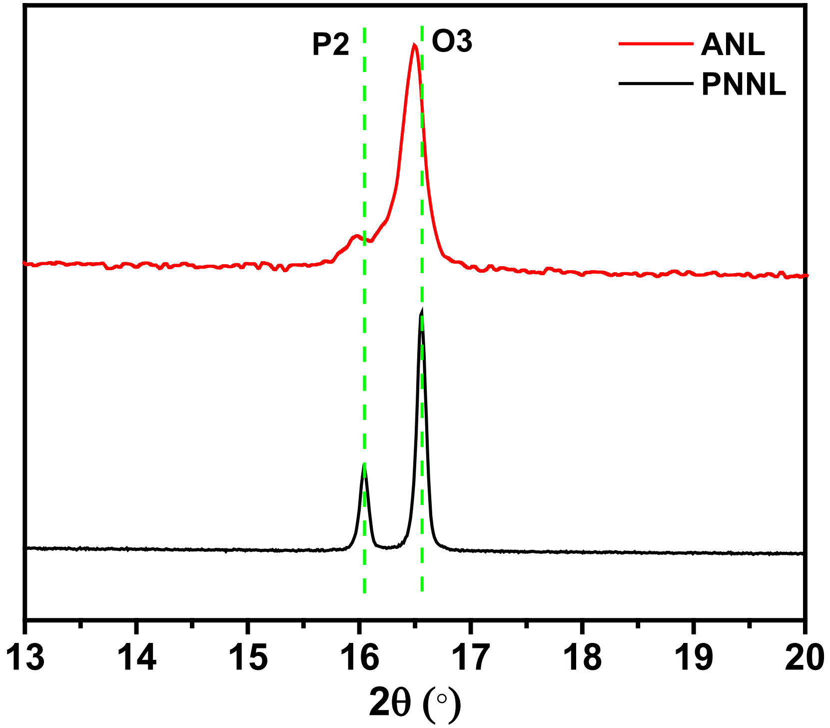
- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C, 2 h, 5 °C/min
- pCAM (O) – CAM: 800 °C, 10 h, 5 °C/min

PNNL

- Ball mill oxides and Na_2CO_3
- 500 °C – 5 h, 900 °C – 14 h, 5 °C/min

ANL has successfully realized novel energy saving upscaling synthesis of NaMNF (213.6 g) via oxide pCAM at lowered calcination temp. (800 °C), leading to mismatched P2/O3 phase ratio with matched Na stoichiometry ($Na_{0.85}$MNF)





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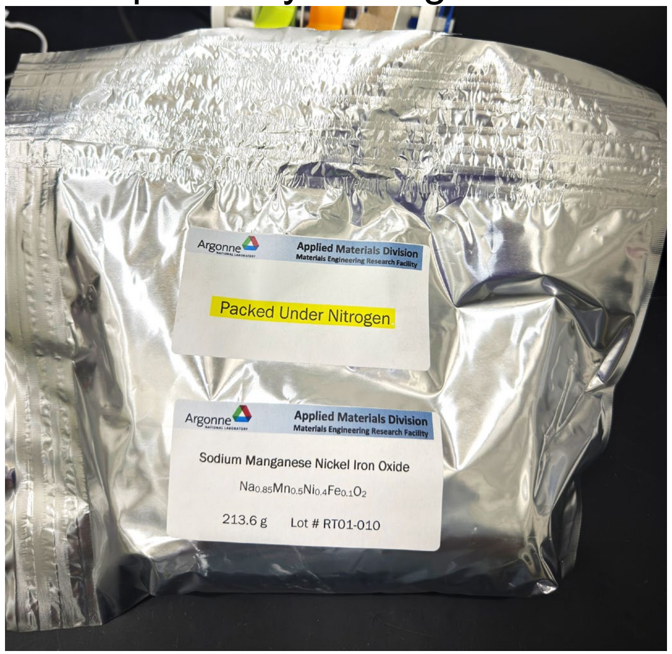


	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL (0.89 Na)	45.6	27.3	21.8	5.3

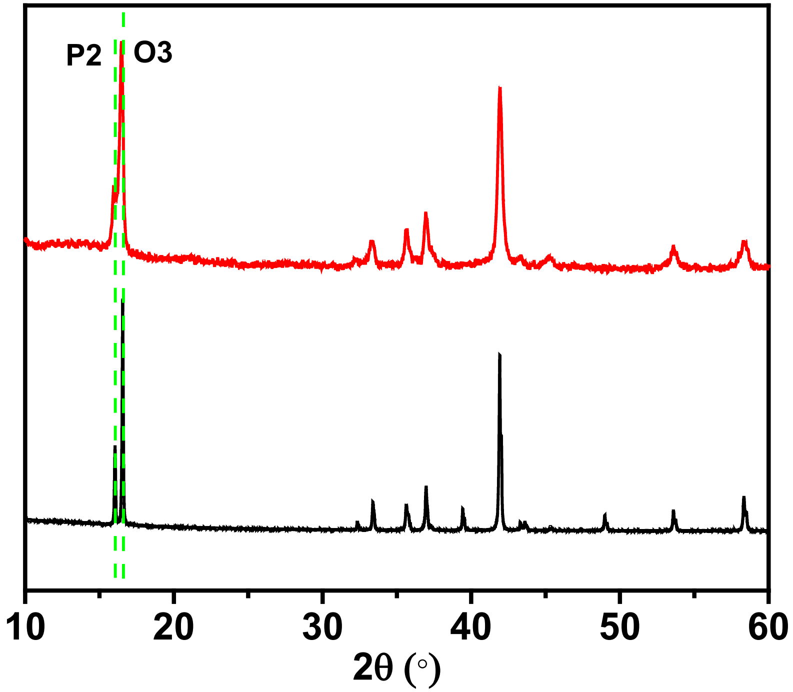
ANL

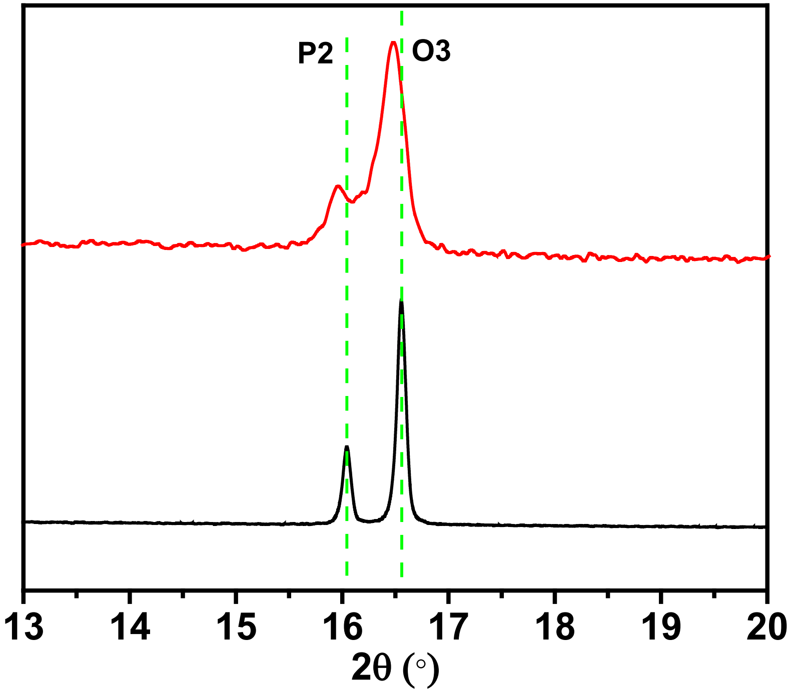
- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C – 2 h, 5 °C/min
- pCAM (O) – CAM: 800 °C – 10 h, 5 °C/min

PNNL

- Ball mill oxides and Na_2CO_3
- 500 °C - 5 h, 900 °C – 14 h, 5 °C/min

ANL has successfully realized more energy saving upscaling synthesis of $Na_{0.85}$MNF (64.6 g) via oxide pCAM at reduced calcination temp. and duration (800 C for 6 h), alleviating the mismatching between P2/O3 phase ratio and Na stoichiometry





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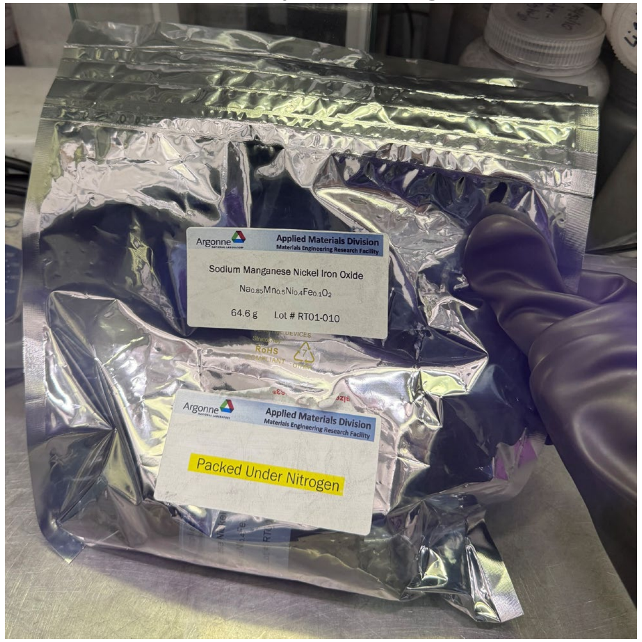
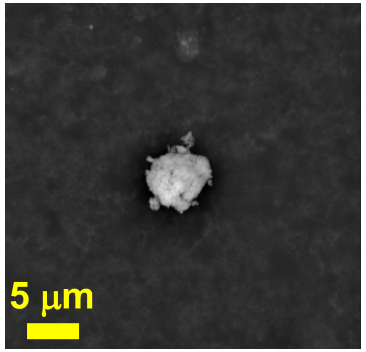


	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
ANL	44.7	28.4	21.6	5.3



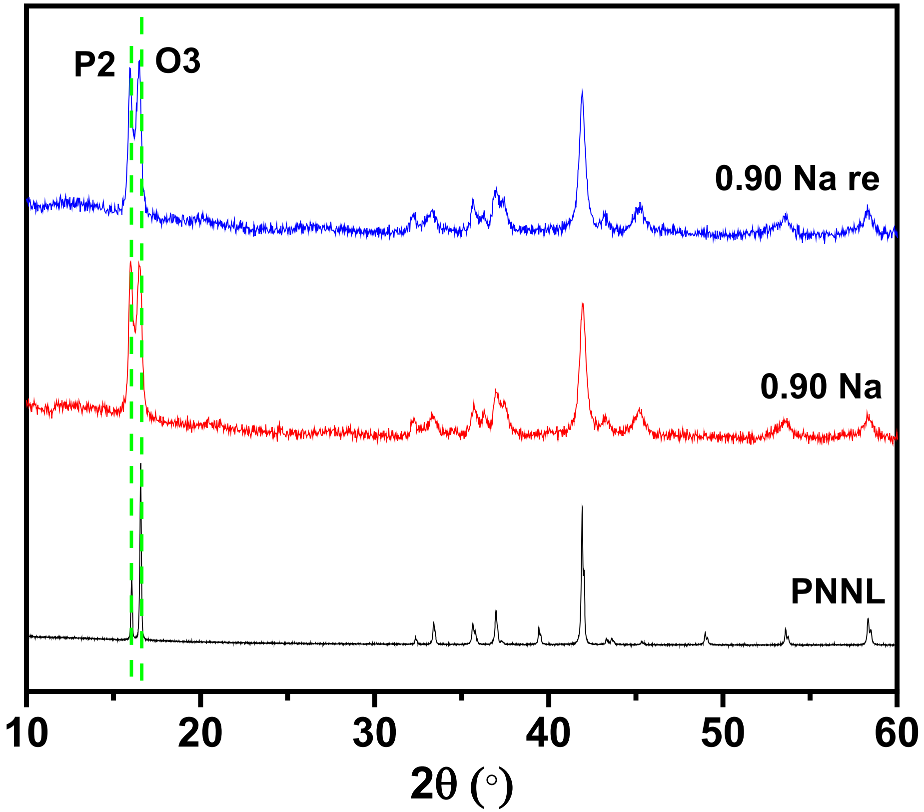
ANL

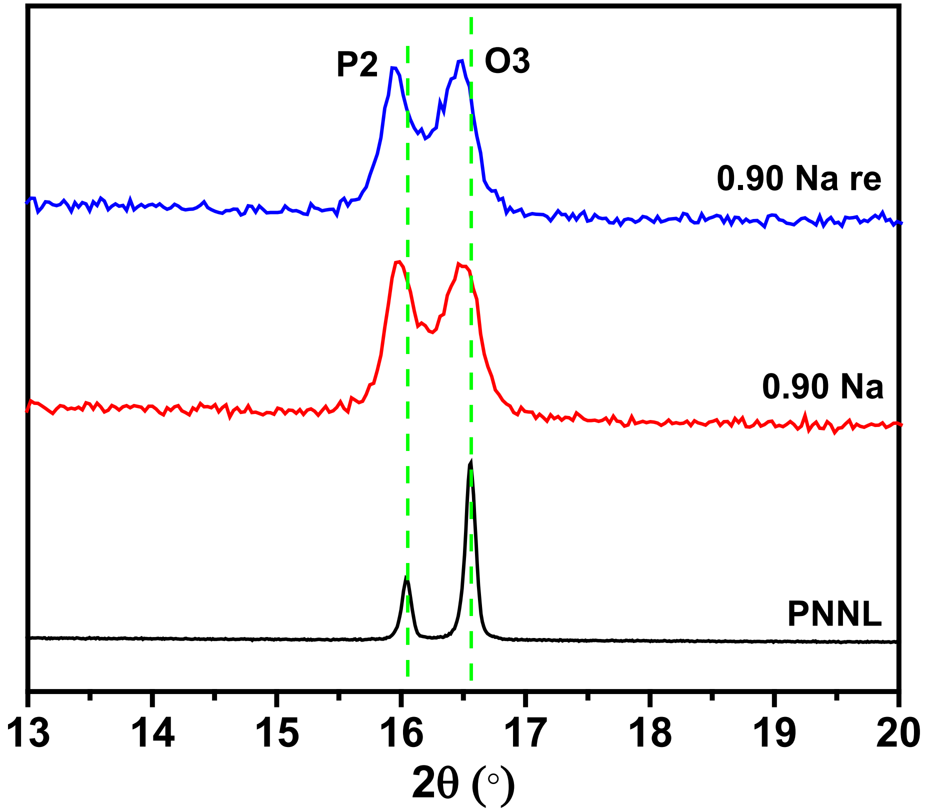
- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C – 2 h, 5 °C/min
- pCAM (O) – CAM: 800 °C – 6 h, 5 °C/min

PNNL

- Ball mill oxides and Na_2CO_3
- 500 °C – 5 h, 900 °C – 14 h, 5 °C/min

2 h scale-up calcination was not successful due to largely mismatched P2/O3 phase ratio





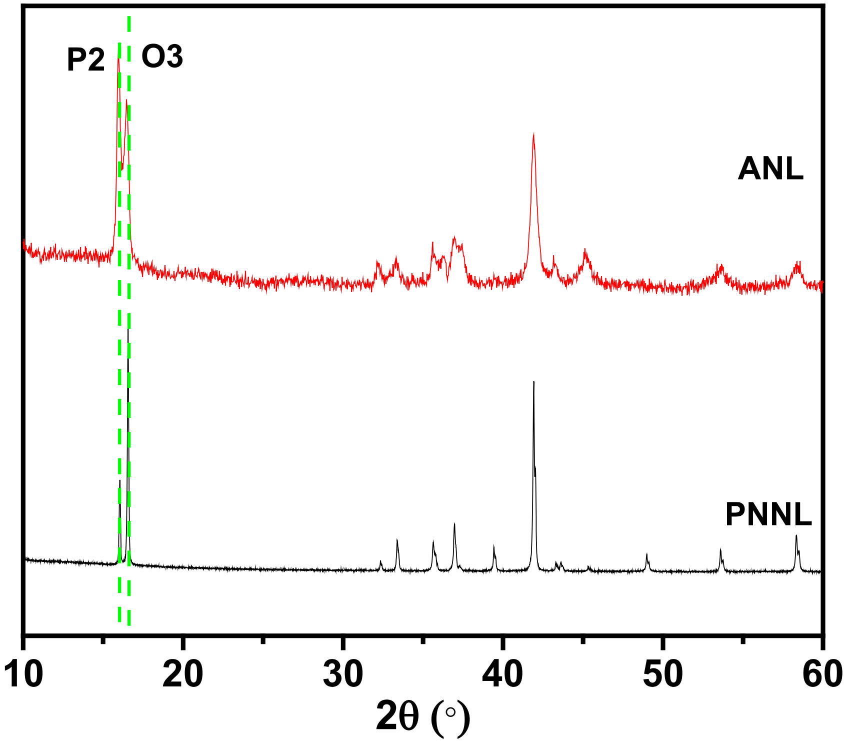
	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
0.90 Na	44.8	27.4	22.4	5.4
0.90 Na re	44.4	28	22.2	5.3

ANL

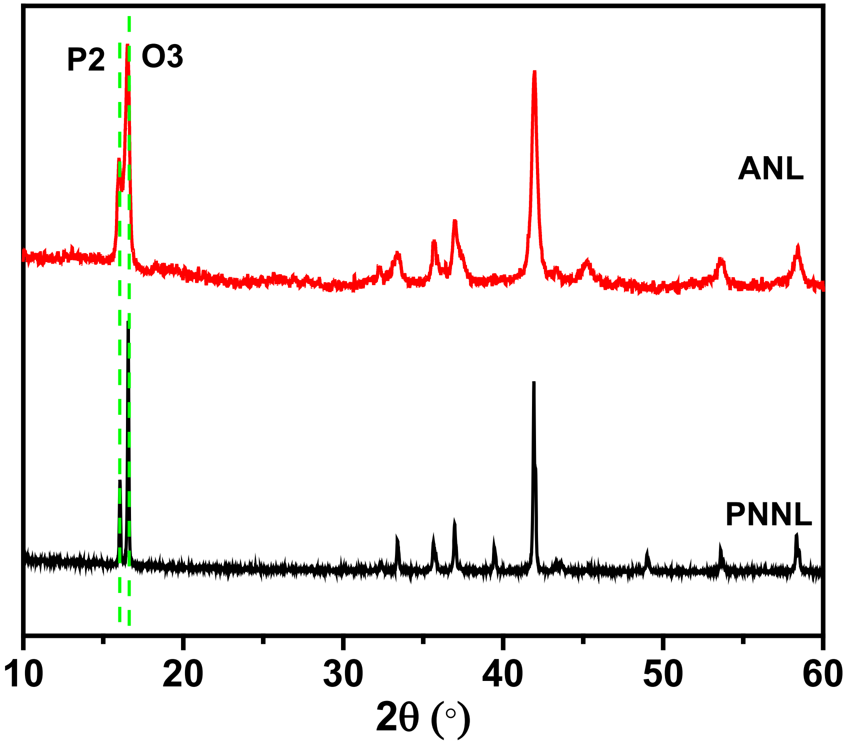
- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C – 2 h, 5 °C/min
- pCAM (O) – CAM: 800 °C – 2 h, 5 °C/min

Harmonization of P2/O3 phase ratio and Na stoichiometry: add more time (4 h) for successful upscaling synthesis of $Na_{0.85}$MNF (104.5 g)

3 h



4 h



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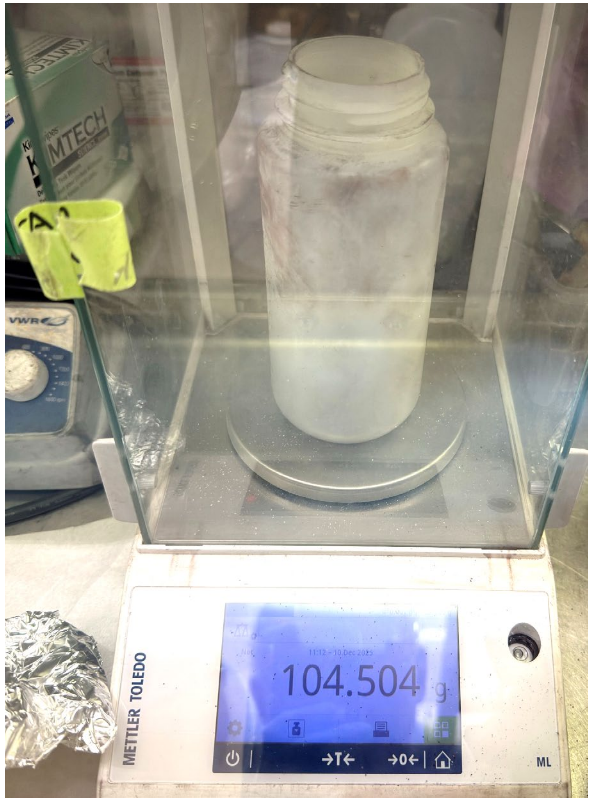
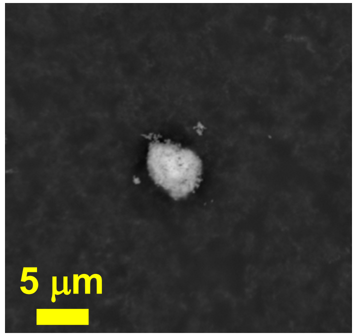


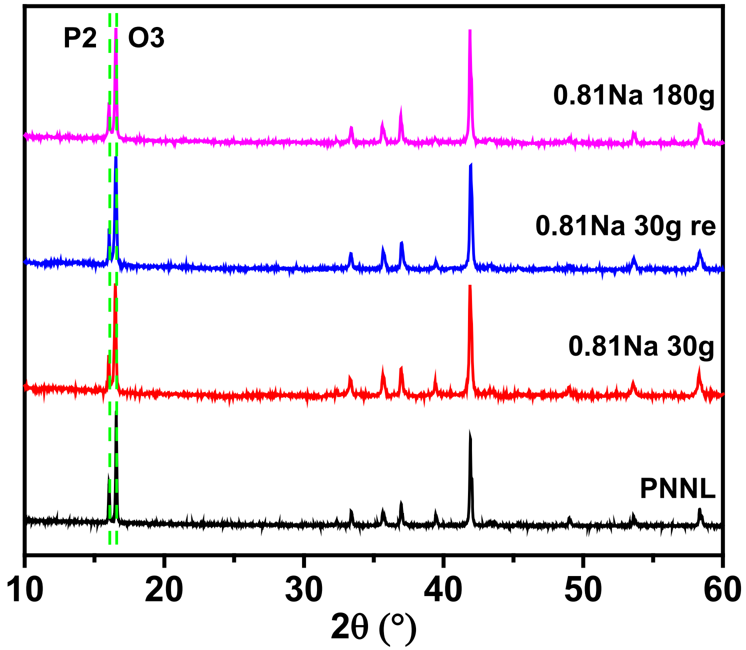
ANL

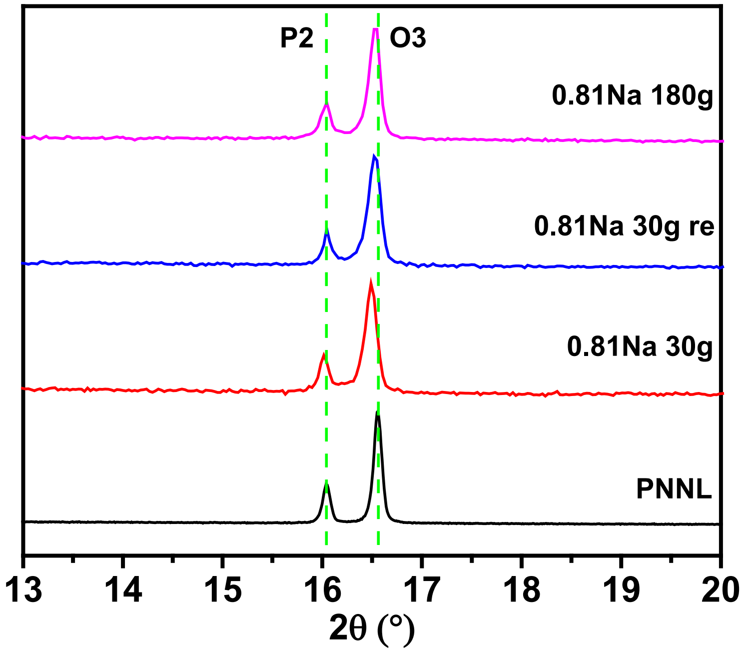
	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.2	22.2	5.3
4 h	45.1	27.6	22.0	5.3
3 h	45.5	27.0	22.2	5.3



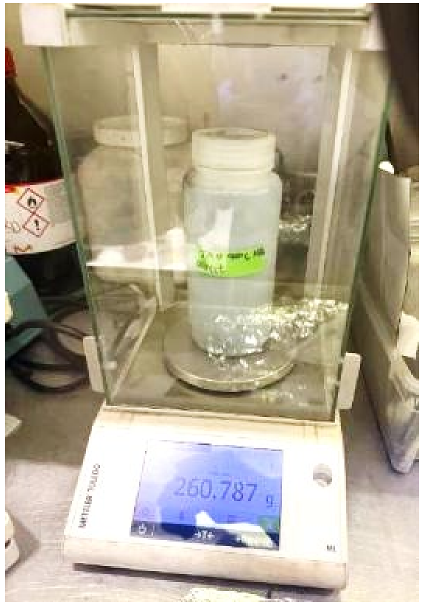
- CSTR coprecipitation
- pCAM (OH) – pCAM (O): 450 °C – 2 h, 5 °C/min
- pCAM (O) – CAM: 800 °C – 3 or 4 h, 5 °C/min

Conventional SIB CAM sodiation mainly relies on stepwise calcination, but ANL has successfully realized more energy saving upscaling synthesis (260.8 g) via direct sodiation of CSTR hydroxide pCAM

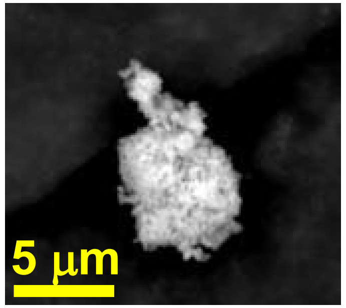




Tap density: ~1.2 g/cc



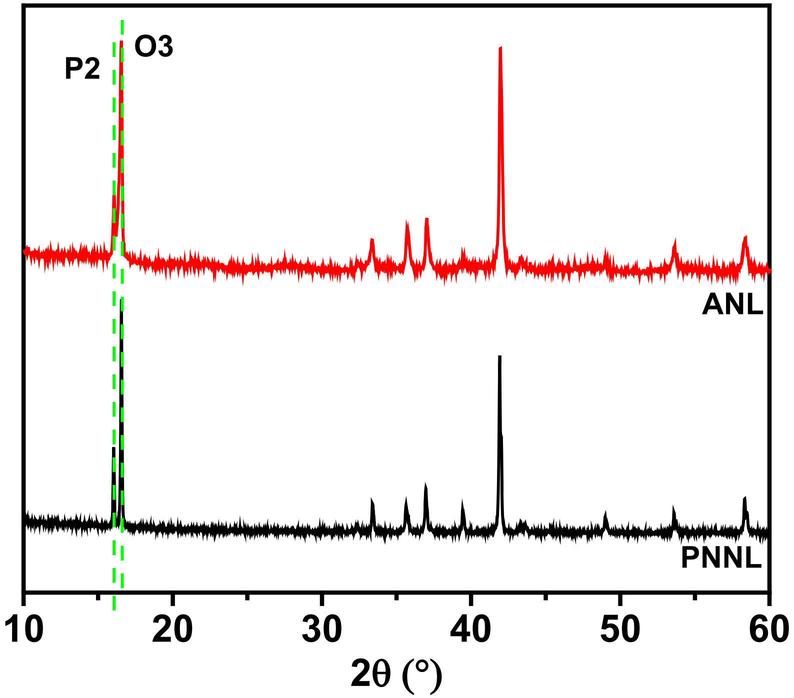
	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.5	22.2	5.3
0.81Na 180g	45.0	27.6	22.1	5.3
0.81Na 30g re	45.4	27.2	22.1	5.3
0.81Na 30g	45.2	27.3	22.1	5.4

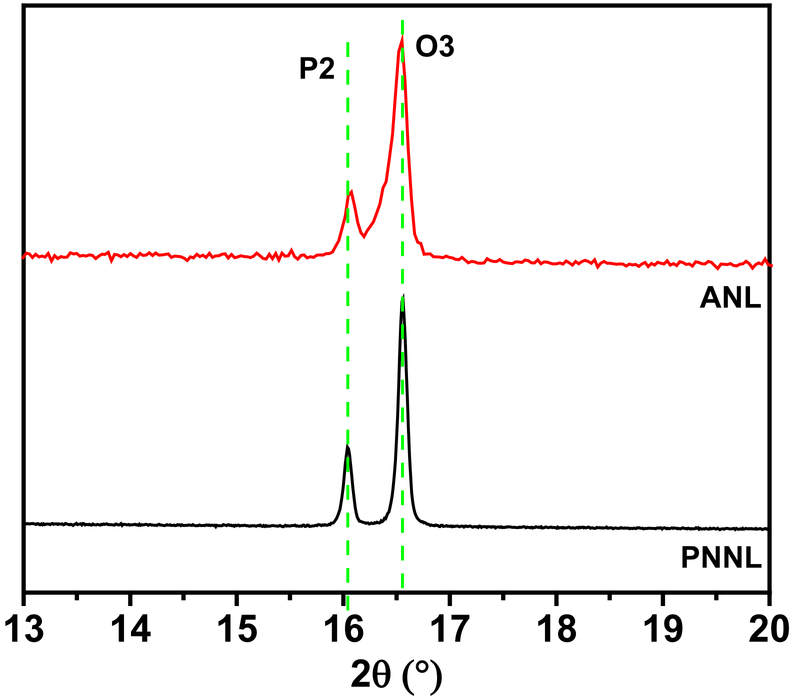


ANL
- CSTR with ammonia and NaOH
- pCAM (OH) – CAM: 900 °C – 14 h, 5 °C/min

PNNL
- Ball mill oxides and Na_2CO_3
- 500 °C – 5 h, 900 °C – 14 h, 5 °C/min

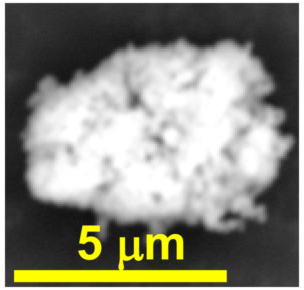
ANL has successfully realized energy saving upscaling synthesis of NaMNF (151.7 g) via reducing direct sodiation calcination duration (10 h)





Tap density: ~1.2 g/cc

	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.5	22.2	5.3
ANL	45.1	27.4	22.2	5.3



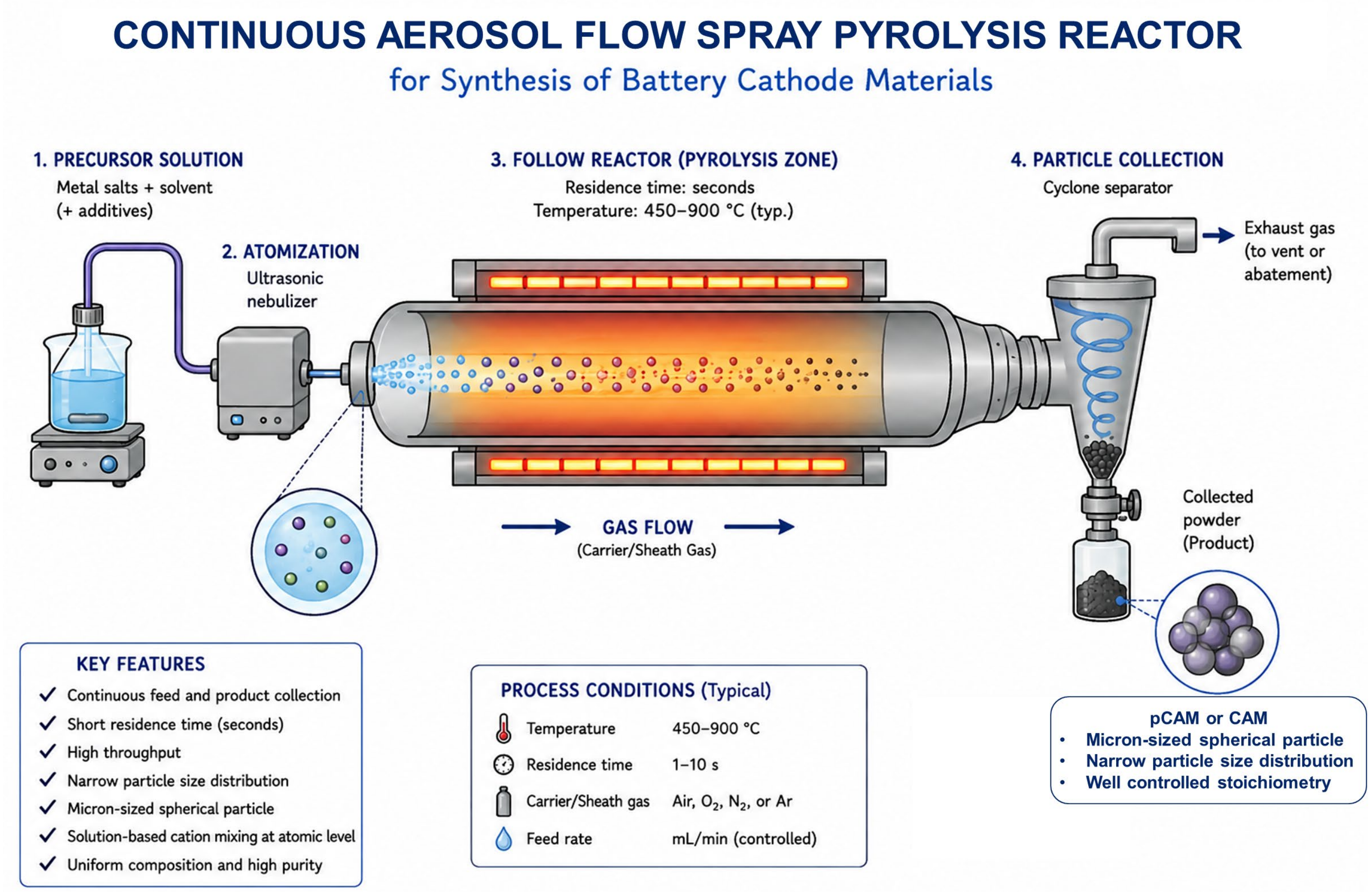
ANL

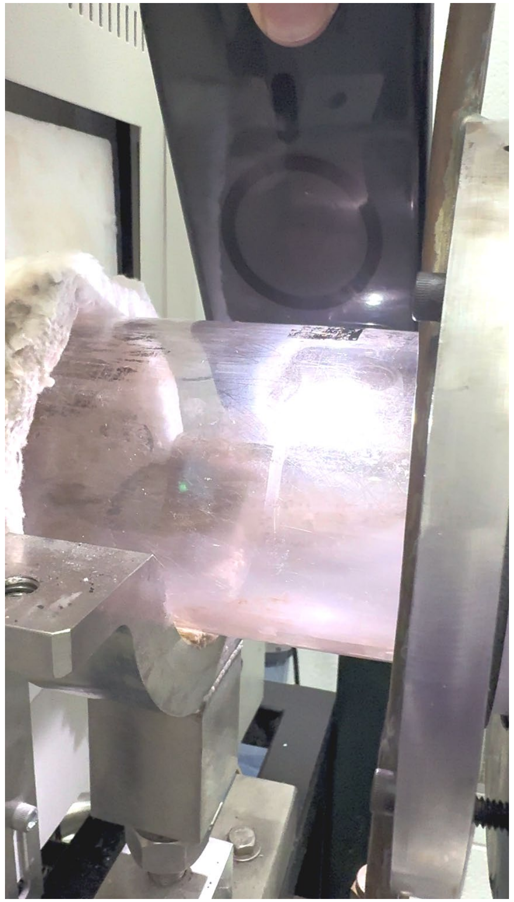
- CSTR with ammonia and NaOH
- pCAM (OH) – CAM: 900 °C – 10 h, 5 °C/min

PNNL

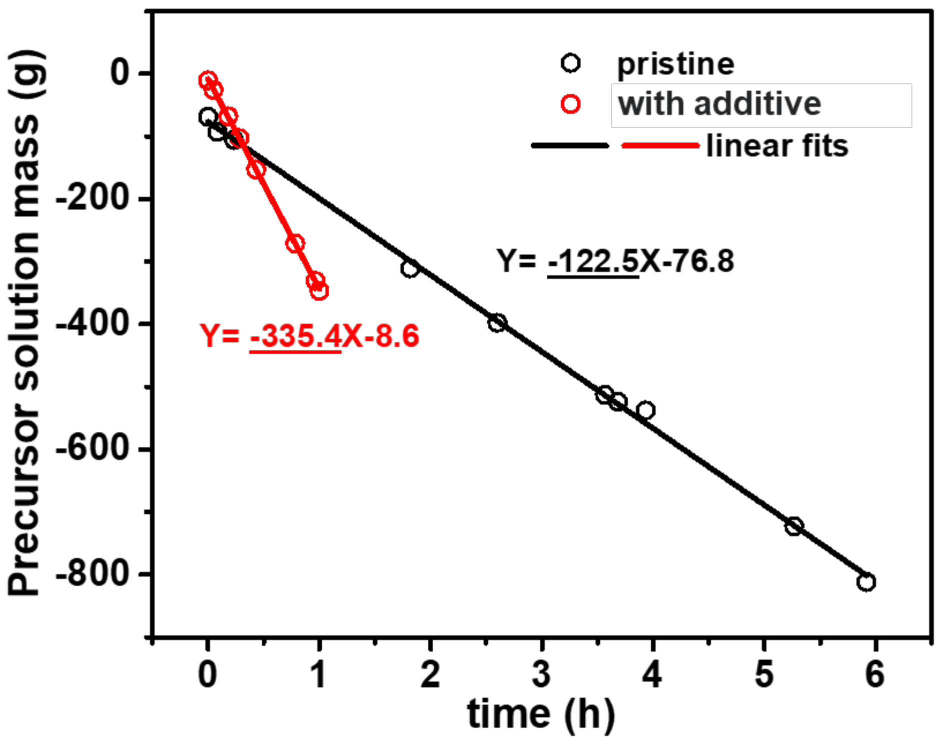
- Ball mill oxides and Na_2CO_3
- 500 °C – 5 h, 900 °C – 14 h, 5 °C/min

APPROACH 2: SECONDARY PARTICLE ENGINEERING OF NaMNF VIA CONTINUOUS AEROSOL FLOW SPRAY PYROLYSIS (CAFSP)

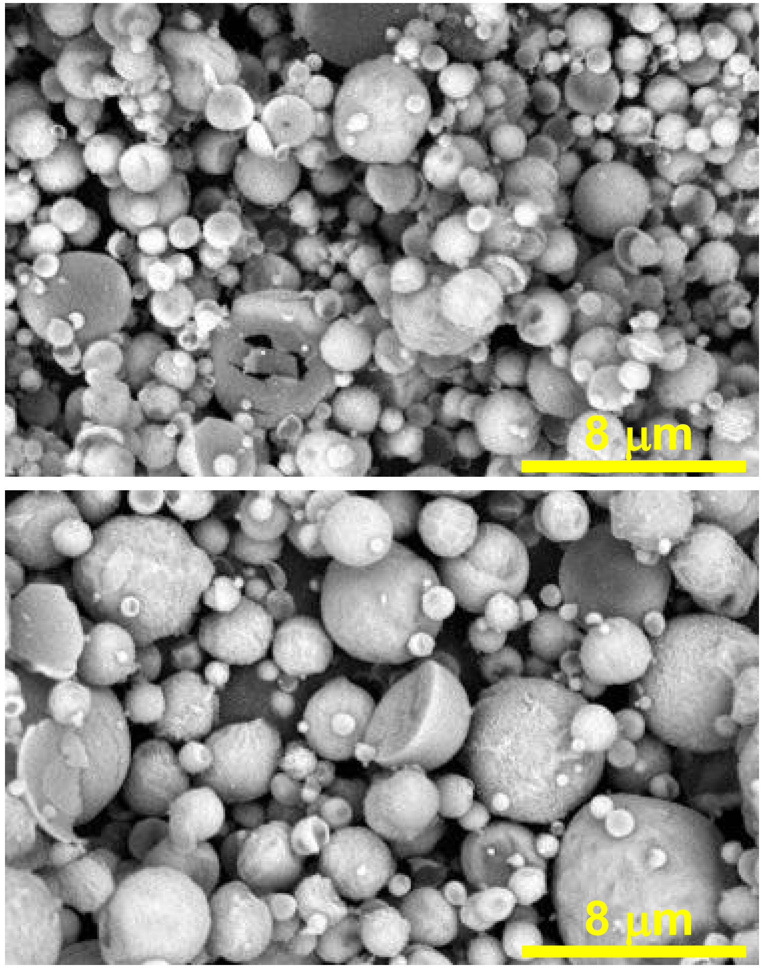




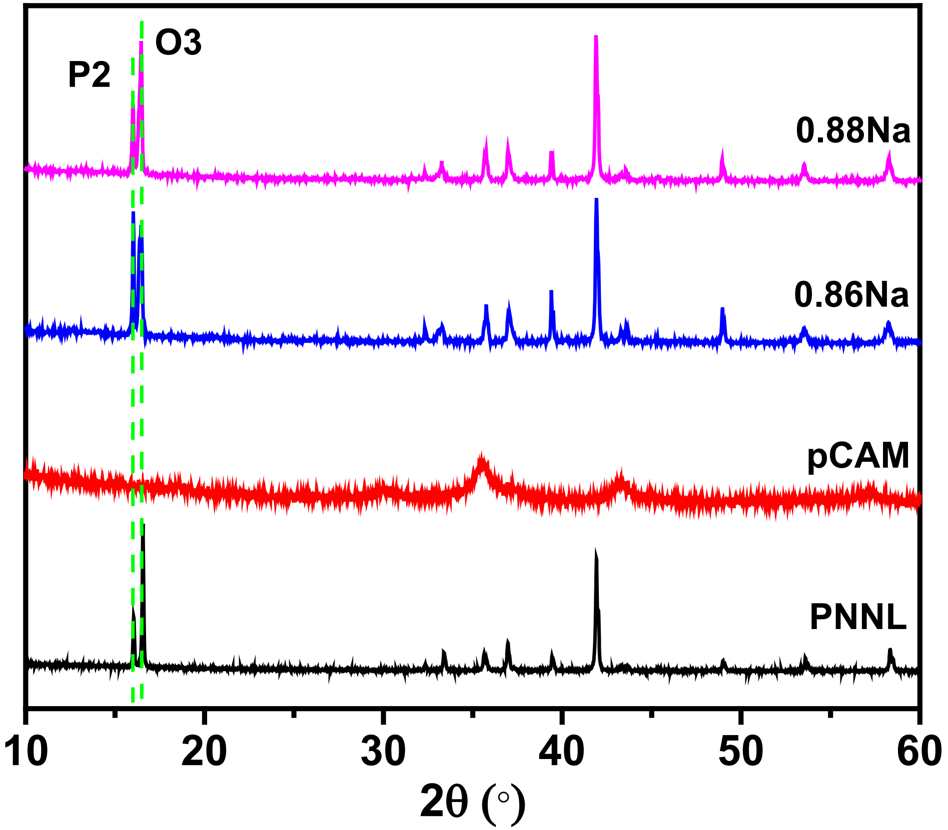
ANL successfully conducted precursor solution engineering to enable high-throughput CAFSP processing capability, probing preferential formation of spherical-like secondary particles with tunable particle size

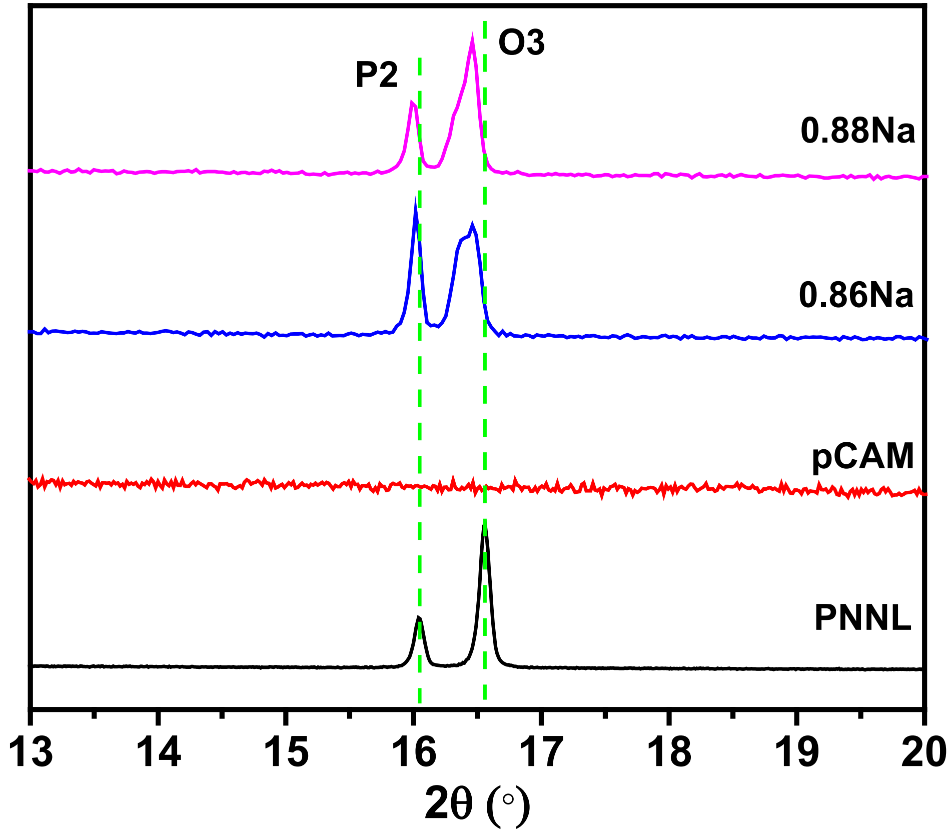


- ~Tripled processing rate
- Still trying to make it even higher



CAFSP-based oxide pCAM can be easily sodiated and tuned for phase ratio and stoichiometry





Oxide pCAM direct sodiation (established in FY25)

- 900 °C – 10 h, 5 °C/min

	Na (mol %)	Mn (mol %)	Ni (mol %)	Fe (mol %)
PNNL baseline	45.0	27.5	22.2	5.3
0.88Na	43.4	29.4	21.8	5.5
0.86Na	42.9	29.8	21.8	5.5

CONCLUSION & IMPACT

- Successfully established a conventional chemical based CSTR coprecipitation synthesis strategy with **various sodiation calcination protocols in time- and energy-saving manner**
  - Oxide pCAM to NaMNF CAMs at various reduced temp. and/or duration
  - Hydroxide pCAM directly to NaMNF CAMs (no hours' low temp. hold)
  - Preliminary time-and-expense (TAE) cost analysis: ~18% cost saving from state-of-art solid-state ($15.64/kg NaMNF) at material and methodology levels
- **Achieved good preliminary results on CAFSP-based secondary particle engineering**
  - Developed additives to enable high-throughput processing capability
  - Probed preferential formation of spherical-like secondary particles
  - Probed tunability on particle size

FUTURE DIRECTION/NEXT STEPS

- Explore further possibility on time- and energy-saving CAM syntheses
- Probe sodiation calcination protocol impact on SIB performance at consumer electronic device CAM loading level (>2.0 mAh/cm^2) to down-select prepared NaMNF CAMs for further PNNL pouch cell analyses
- Conduct synchrotron operando X-ray tests to reveal sodiation mechanism for calcination optimization
- Optimize CAFSP process for denser and larger CAMs via secondary particle engineering

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  - Marcos Lucero
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