PROCESS R&D FOR ELECTROCHEMICAL ENERGY STORAGE MATERIALS MANUFACTURING

Sodium-Ion Battery Cathode Active Material Upscaling Syntheses

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PROJECT PROFILE

Topic: Sodium Batteries | Vertical: Materials and Systems Innovation

Strategic Pathway: Grow

Project start and finish: FY24 - FY26

PROBLEM

Background & Significance

- Lithium-ion batteries are expensive for grid energy storage, therefore developing sodium-ion batteries (SIBs) with good affordability is essential [1]
- Layered cathode active materials (LCAMs) with high-energy feature is promising for SIB-based grid energy storage [2]
- State-of-art syntheses of SIB LCAMs rely on solid-state synthesis: unfavorable LCAM morphology, unscalable (time- and energy-consuming) [2]

Objectives

We are exploring and upscaling novel LCAM preparation strategies

- Tunable LCAM chemical (P2/O3 phased $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (NaMNF541)) and physical properties
- Cost-effective manufacturing

APPROACHES

- **Establish a conventional chemical based coprecipitation synthesis strategy with continuous stirred tank reactor (CSTR) with various sodiation calcination protocols**
- **Explore secondary particle engineering of LCAMs via continuous aerosol flow spray pyrolysis (CAFSP) reactor**
- Ensure scalability: kg-level continuous process manner
- Enable affordability: time- and energy-saving syntheses
- Enable tunability: LCAM particle size and dopants

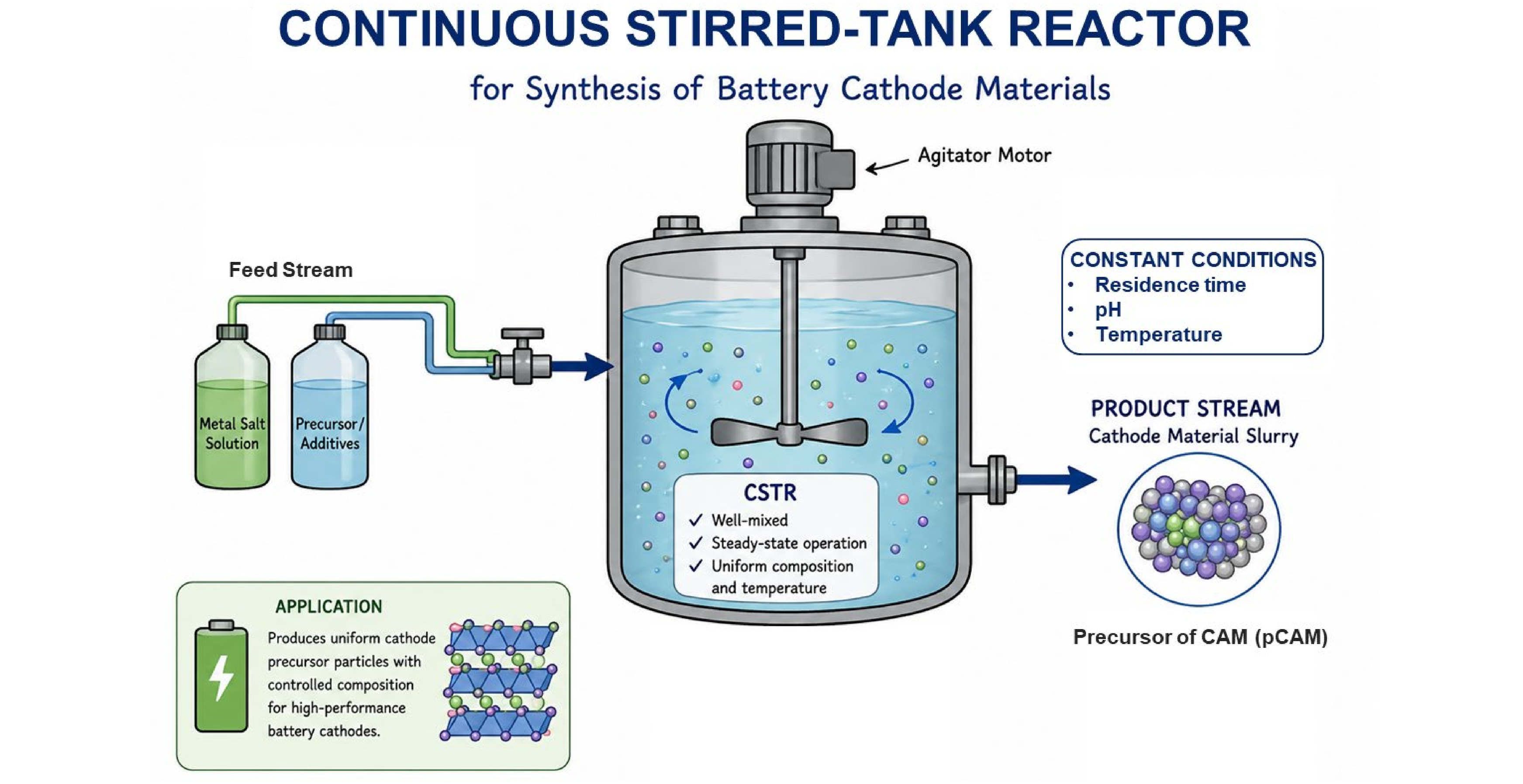

Figure 1. Schematic demonstration of CSTR coprecipitation.

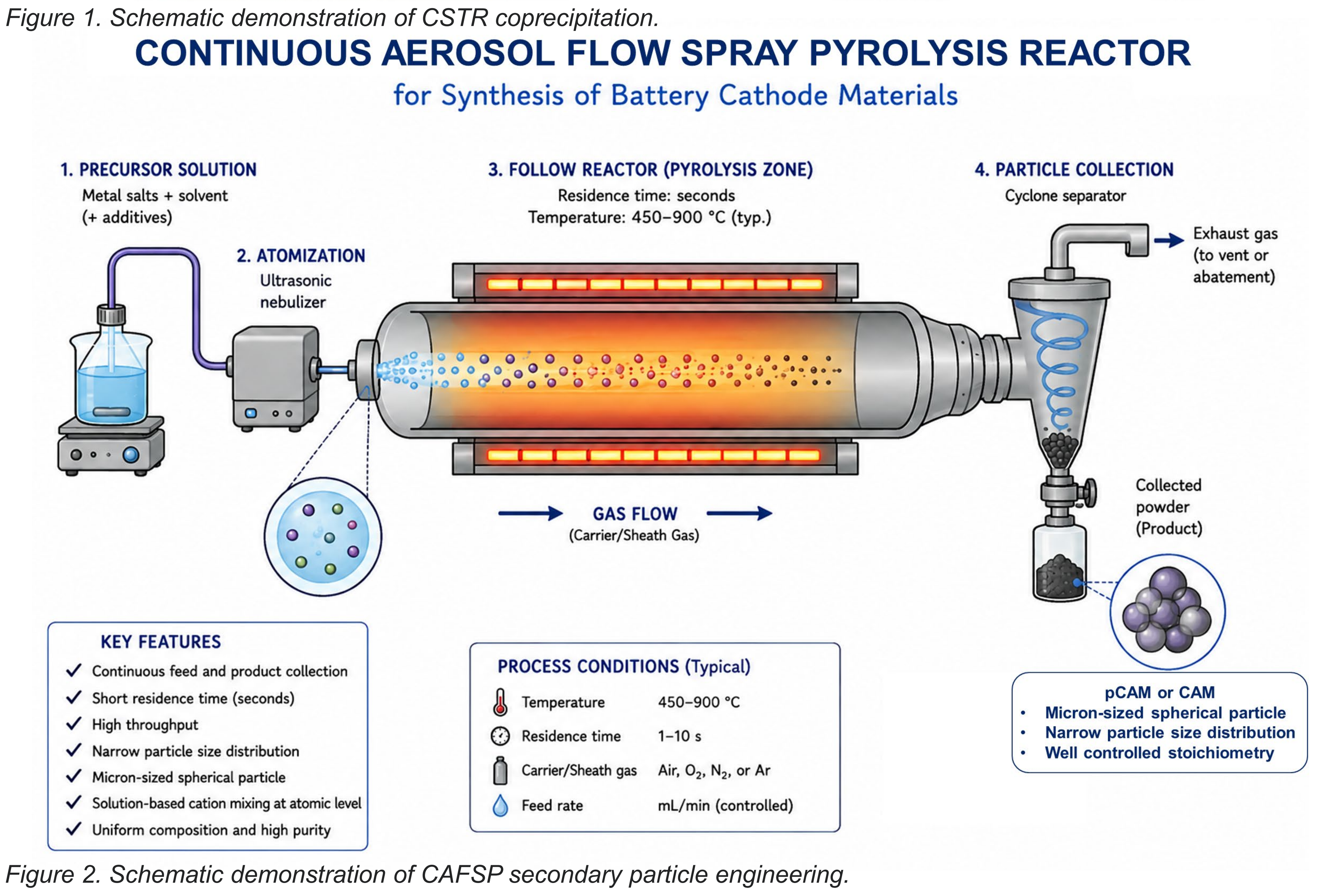

Figure 2. Schematic demonstration of CAFSP secondary particle engineering.

RESULTS

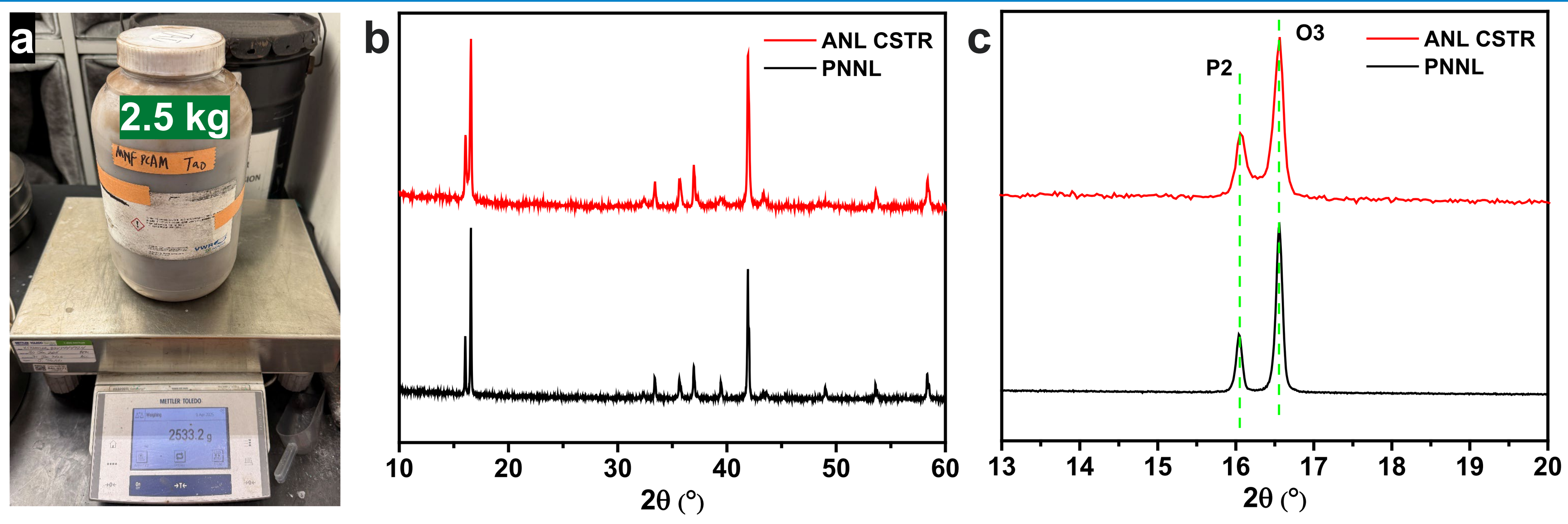

Figure 3. a) kg-level CSTR coprecipitation. b & c) Full-scale and zoomed-in XRD patterns for demonstration of good sodiation calcination control on P2/O3 phase ratio.

Table 1. Core information of various sodiation calcination protocols of CSTR-based pCAM.

Synthesis Route	Precursor	Sodiation Protocol (ramp at 5 C°/min)	NaMNF541 ICP Stoichiometry (Na:Mn:Ni:Fe, mol.%)	Delivery Amount (g)	Date
Baseline PNNL solid-state synthesis	Metal oxides	500C°-5h, 900C°-14h	45.0:27.2:22.2:5.3	X	X
CSTR coprecipitation	Oxide pCAM (from hydroxide pCAM)	800C°-10h	43.9:28.2:22.5:5.4 (matched phase ratio)	186	8/27/25
			45.6:27.3:21.8:5.3 (mismatched phase ratio)	214	10/1/25
		800C°-6h	44.7:28.4:21.6:5.3	75	11/4/25
		800C°-4h	45.1:27.6:22.0:5.3	105	12/16/25
	Hydroxide pCAM	900C°-14h	45.0:27.6:22.1:5.3	261	3/19/26
		900C°-10h	45.1:27.4:22.2:5.3	152	5/8/26

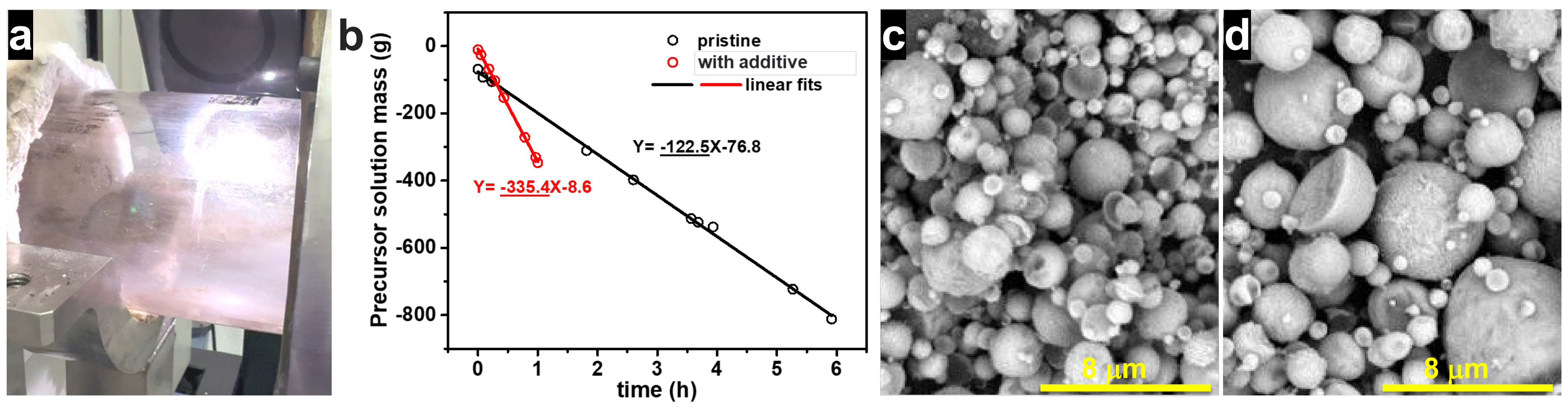

Figure 4. a) Digital photo for demonstration of continuous aerosol follow in the CAFSP reactor. b) Demonstration of the success in developing additives for CAFSP high-throughput capability. c & d) SEM images for demonstration of preferential formation of spherical-like secondary particles with tunable particle size.

CONCLUSIONS & 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 NaMNF541 LCAMs at various reduced temp. and/or duration
  - Hydroxide pCAM directly to NaMNF541 LCAMs (no hours' low temp. hold)
- **Achieved good preliminary results on CAFSP-based LCAM secondary particle engineering**
  - Developed additives to enable high-throughput processing
  - Probed preferential formation of spherical secondary particles
  - Probed tunability on particle size

FUTURE DIRECTIONS

- Explore further possibility on time- and energy-saving LCAM 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 NaMNF541 LCAMs 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 LCAMs via secondary particle engineering

References

1. Hirsh, H.; et al. Sodium-Ion Batteries Paving the Way for Grid Energy Storage. *Adv. Energy Mater.* **2020**, *10* (32), 2001274.
2. Xi, B.; et al. A General Strategy for Batch Development of High-Performance and Cost-Effective Sodium Layered Cathodes. *Nano Energy* **2021**, 89, 106371.

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