Advanced Characterization and Data-Driven Insights into Sodium-Ion Battery Cathodes

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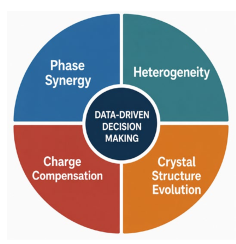
Project Profile

Topic: Sodium Batteries
Vertical: Materials and System Innovation
Strategic Pathway: Stabilize
Project start and finish: FY2025-FY2026

Problem, Objectives & Relevance

- Sodium-ion batteries are a promising low-cost, scalable, and sustainable alternative to lithium batteries for LDES
- Practical deployment is limited by fundamental materials challenges that require advanced characterization.

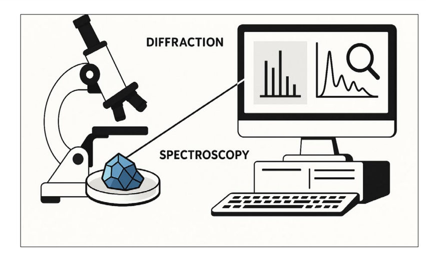
Objectives



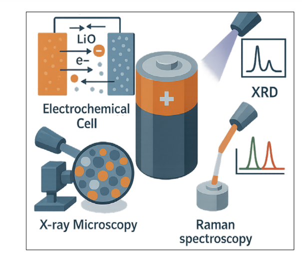
- **Investigate phase synergy** to enable high-voltage, high capacity and durability
- **Elucidate crystal structure** evolution
- **Map phase, charge and compositional heterogeneity**
- **Decipher cation/anion redox** for charge compensation
- **Integrate AI-ML analytics** to accelerate innovations

Relevance: The SLAC–Stanford Battery Center advances SIBs using advanced characterization techniques, including synchrotron methods, to enable the design of low-cost electrode materials. In collaboration with PNNL, this work supports the DOE Office of Electricity's mission to improve grid storage performance, reliability, and cost reduction.

Approach & Milestones



Materials/Electrode Characterization

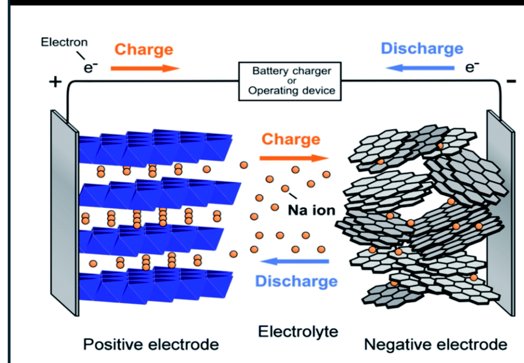


Cell-Level Characterization

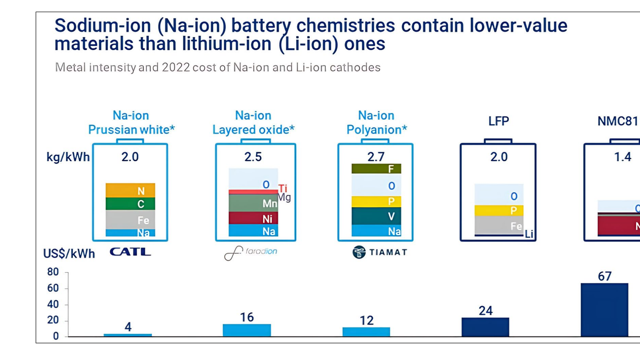
- Electrochemical testing (galvanostatic cycling, GITT, EIS) of O3, P2, and biphasic O3-P2 $Na_xMn_{0.5}Ni_{0.4}Fe_{0.1}O_2$
- Crystal structure evolution via ex-situ lab-scale XRD, and synchrotron operando XRD in pouch cell
- Electrode heterogeneity mapping using micro-Raman, micro-XRF, and transmission X-ray microscopy (TXM)
- Charge compensation analysis through synchrotron-based XAS, RIXS, XRS, and Mössbauer spectroscopy.

Month/Year	Tasks	Status
Feb 2025	Identify the role of phase synergy at different voltage	completed
Dec 2025	Identify anion/cation redox	completed
Mar 2026	Track structural evolution across multiple phases	completed
Aug 2026	Map heterogeneity and correlate using AI/ML	On-going

Background: SIBs and MNF541 Cathodes

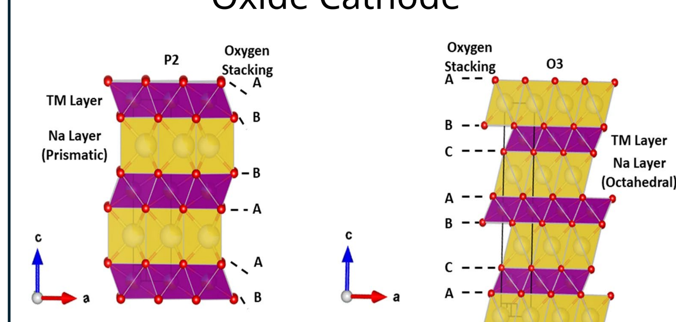


(RSC Adv., 2022,12, 23284)

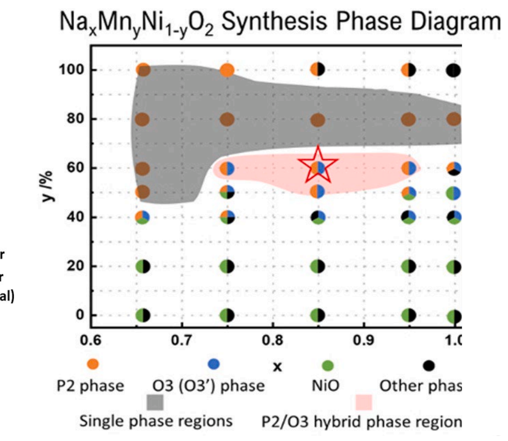


(The Na-ion market outlook) (Wood Mackenzie 02-21-2023)

Layered Transition Metal Oxide Cathode



$Na_xMn_yNi_{1-y}O_2$ Synthesis Phase Diagram

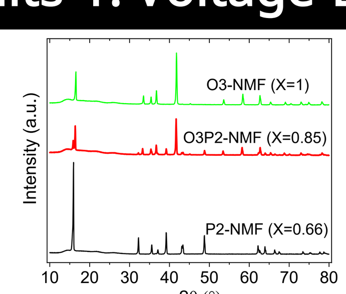


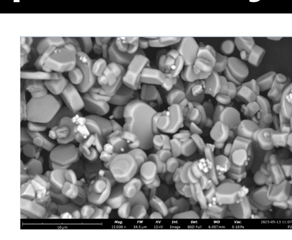
(Nano Energy, 2021, 89, 106371)

- $Na_xMn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (Na_x-MNF541) offers high performance and cost competitiveness
- Phase tuning via Na content:
  x = 1.0 → O3, x = 0.85 → O3-P2 and x = 0.66 → P2
- Selected to study phase synergy, redox processes, phase evolution, and heterogeneity across wide voltage range.

Results-1: Voltage-Dependent Synergy

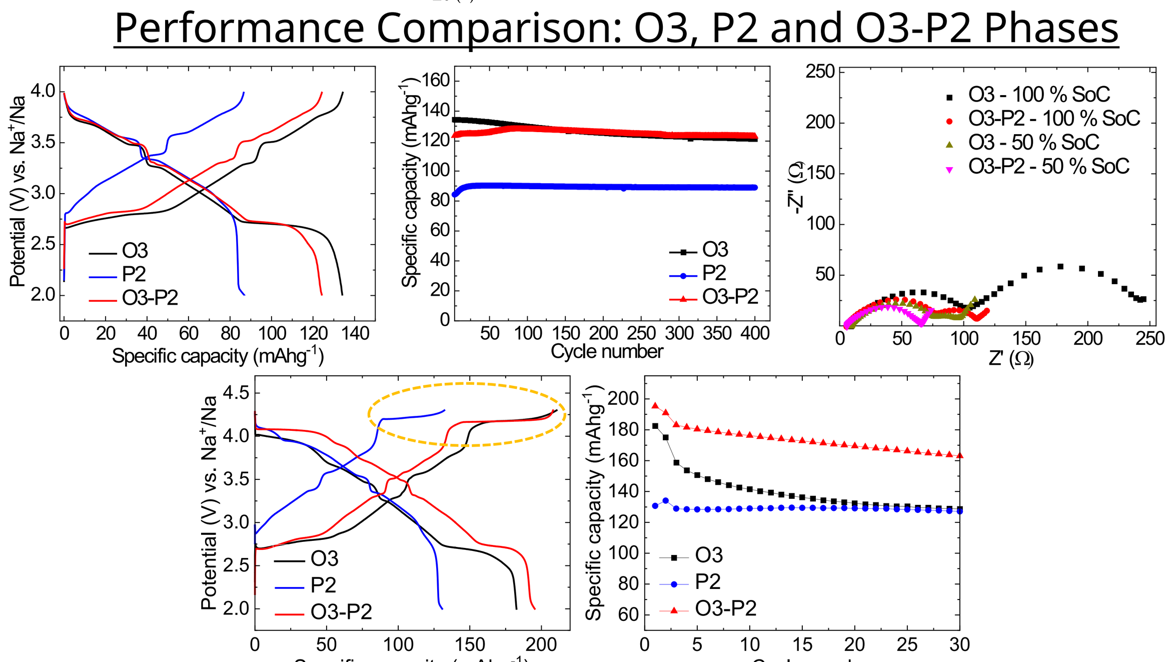
X = 0.85 shows biphasic O3-P2





Particle size: 2- 5 um

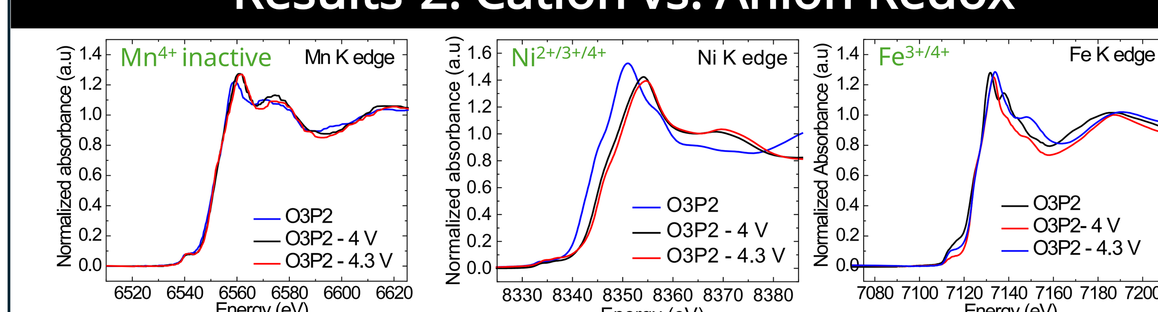
Performance Comparison: O3, P2 and O3-P2 Phases

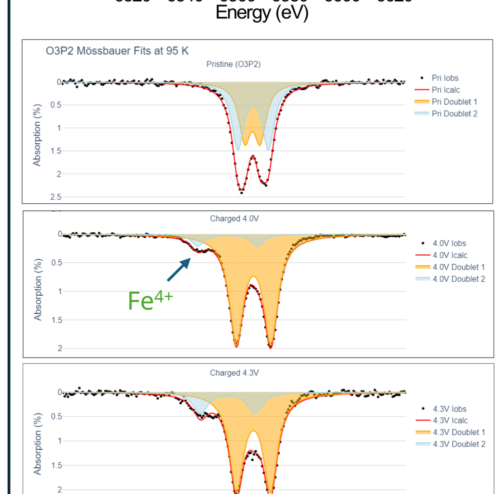


X in $Na_xMNF541$	Phase	Specific discharge capacity (2-4 V)	Average discharge voltage	Capacity retention	Specific discharge capacity (2-4.3 V)
X=0.66	P2	87 $mAhg^{-1}$	3.3 V	99 %	130
X=0.85	O3-P2	124 $mAhg^{-1}$	3.1 V	97.5 %	195
X=1	O3	134 $mAhg^{-1}$	2.9 V	89 %	182

Biphasic O3-P2 MNF541 shows overall best performance

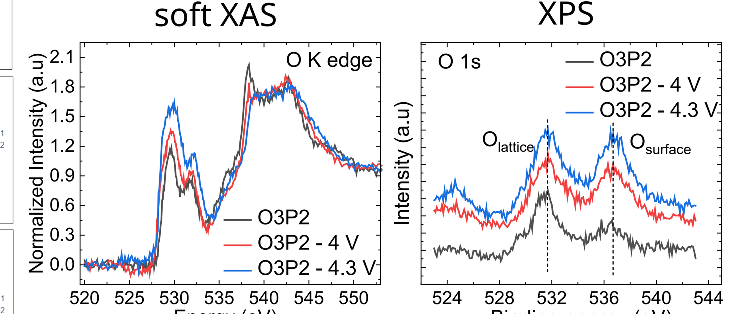
Results-2: Cation vs. Anion Redox



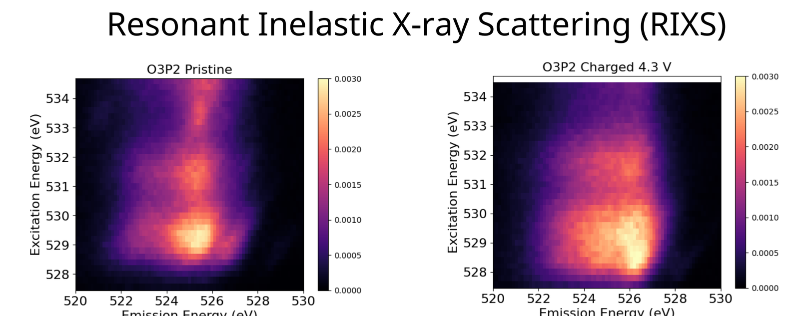


Probing Oxygen Redox

soft XAS XPS



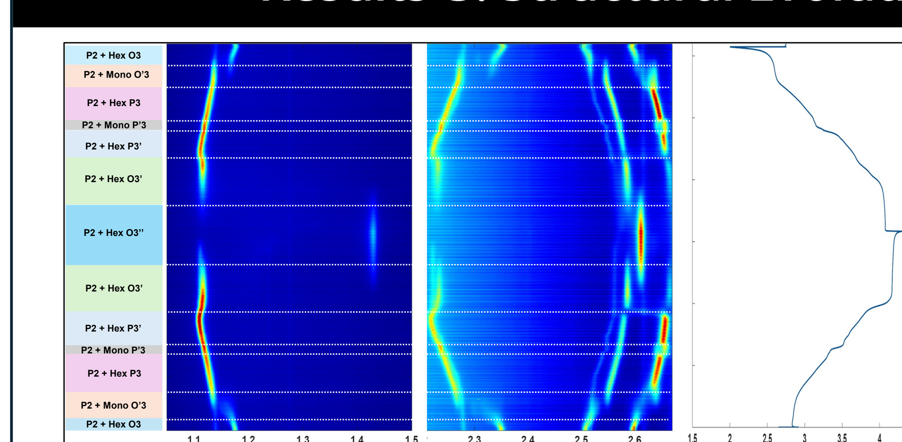
Resonant Inelastic X-ray Scattering (RIXS)



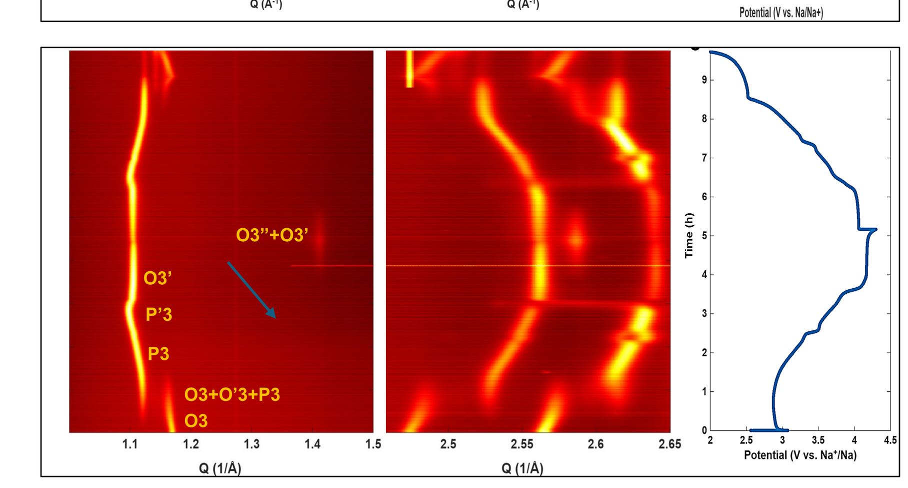
Ni^{2+} mainly contributes to the capacity, with Fe^{3+} also participating

Fe^{3+} contribution increases to ~20%, with no detectable anion redox

Results-3: Structural Evolution



O3-P2 /Na cell



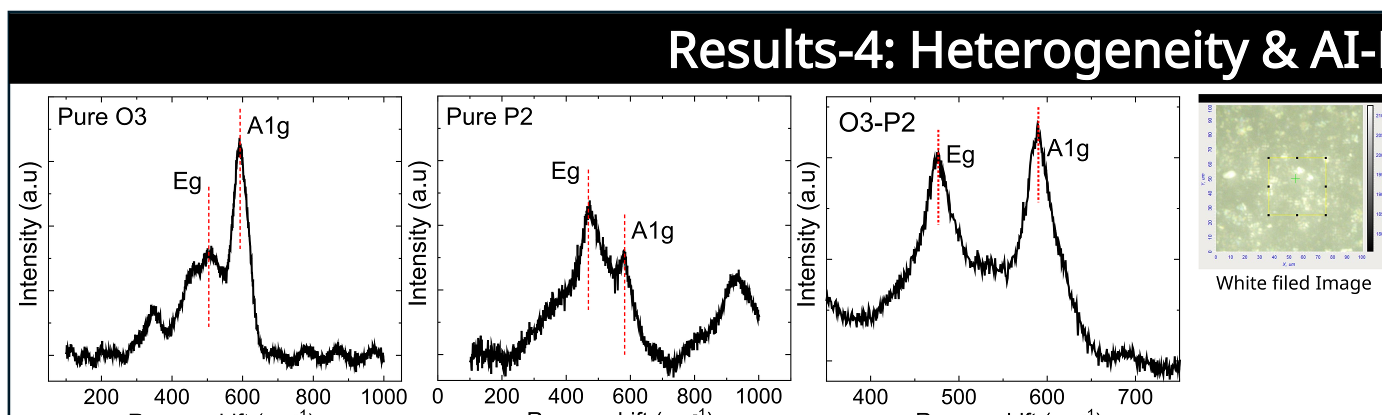
O3/Na cell

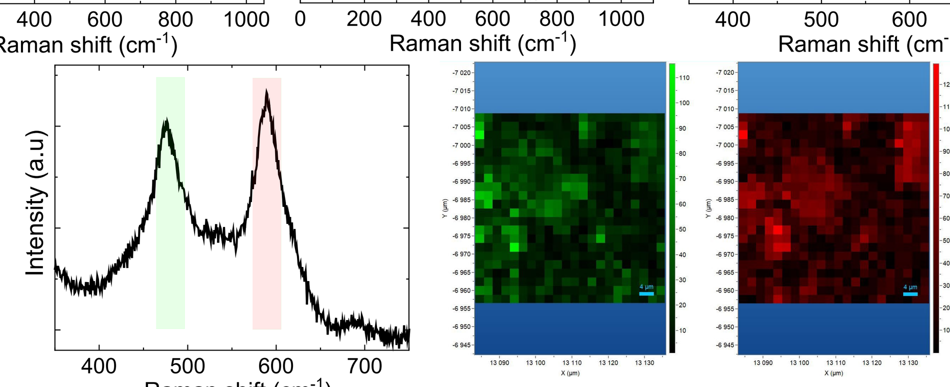
Both O3-P2 and O3 show multiple phase transition (O3-P3-O3′-O3″)

Phase transition is more reversible in O3-P2 compared to O3

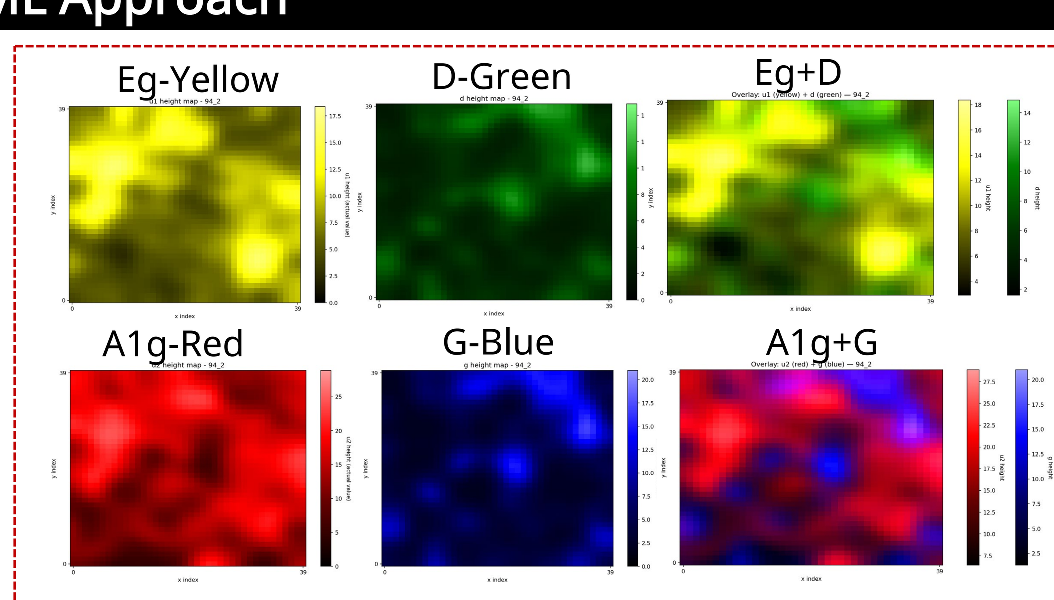
Minor P2 phase in O3-P2 acts as a structural scaffold

Results-4: Heterogeneity & AI-ML Approach

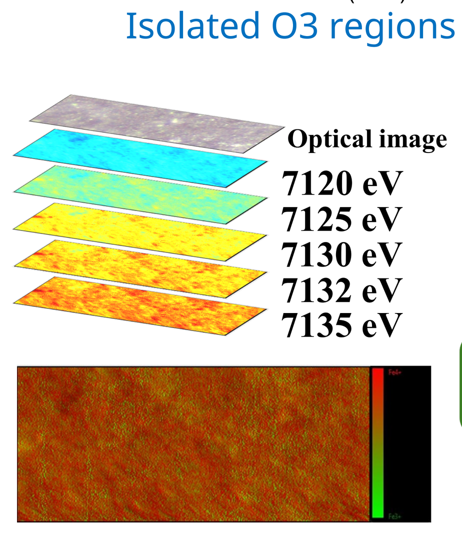




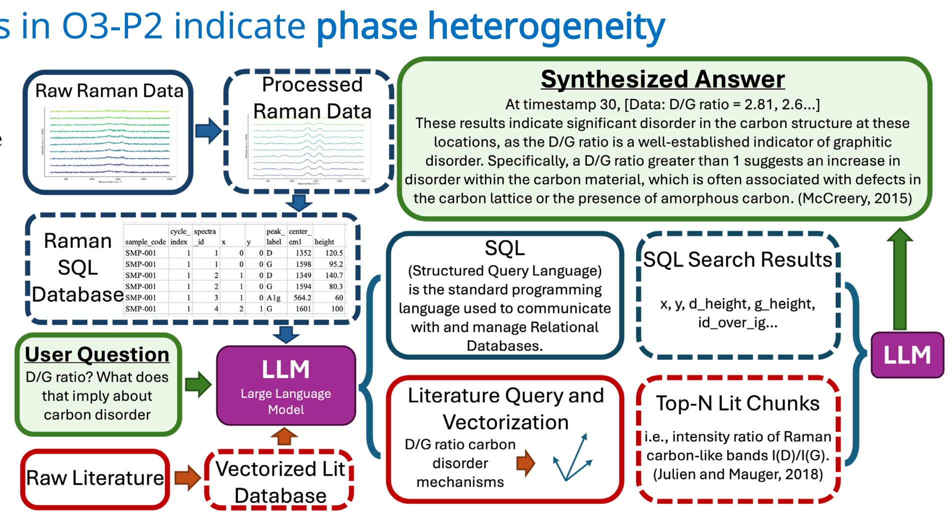
Isolated O3 regions in O3-P2 indicate phase heterogeneity



Mapping the distribution of active materials and carbon



$Fe^{3+/4+}$ shows charge heterogeneity



AI-ML pipeline for Data analysis

Key Outcomes

(i) A validated cathode design strategy leveraging phase engineering and compositional tuning.

(ii) Transferable advanced characterization workflows that combine operando XRD, XAS, and Raman with spatial mapping.

(iii) An AI-assisted materials screening pipeline that accelerates the down-selection of promising materials.

Conclusions & Impact

- Biphasic O3-P2 $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ outperforms O3 and P2, demonstrating phase synergy design for improved performance
- Phase synergy depends on voltage, and improves both specific capacity and capacity retention at high voltages (> 4 V vs. Na^+/Na)
- XAS, RIXS, and Mössbauer analyses reveal Ni^{2+}-dominated redox, with Fe^{3+} activation mainly above 4 V and negligible anion redox
- XRD suggests reversible phase transitions in O3-P2, and micro-Raman and micro-XANES reveal phase and charge heterogeneity
- High-throughput line-scan Raman integrated with AI/ML enables rapid, parallelized analysis and predictive materials design

Future Directions

- **Expand Material Library:** Investigate next-generation low-cost cathode materials beyond the baseline MNF541
- **Establish Structure–Property-Performance** Relationships: Find how composition, microstructure, and synthesis conditions influence structure, properties, & electrochemistry
- **Leverage AI/ML Approaches:** Explore AI and ML to analyze data, uncover correlations, and optimize synthesis and processing

**Any proposed future work is subject to change based on funding levels*

Acknowledgements

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