Advanced Characterization of Sodium-Ion Battery Cathodes: Synergy, Heterogeneity, and Reaction Mechanism

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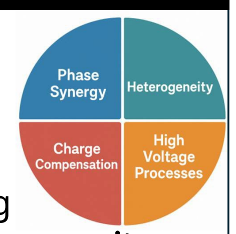
Overview

Objectives

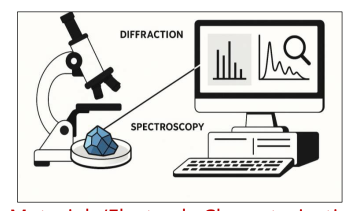


- **Elucidate performance–cost tradeoffs** through advanced characterization
- **Investigate phase interactions** to enable high-voltage, capacity and long-term cycling
- **Map electrode level phase and charge heterogeneity** using advanced spatial characterization techniques
- **Uncover charge compensation** mechanisms via synchronized diagnostics
- **Identify high-voltage degradation and rate-limiting** processes to guide mitigation

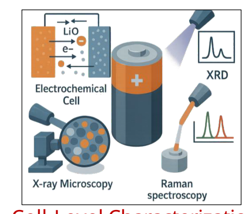
Relevance

The SLAC-Stanford Battery Center is advancing sodium-ion batteries (SIBs) as a scalable, cost-effective alternative to lithium-ion battery technologies for grid energy storage. Through advanced characterization techniques, including synchrotron methods, and in-depth studies of material behavior, battery reactions, and heterogeneity across length scales, the team provides critical insights into the design of low-cost materials, and electrode structures. In collaboration with PNNL, this research directly supports the DOE Office of Electricity's mission to improve grid storage solutions by increasing energy density, extending cycle life, and reducing costs.

Approach & Milestones



Materials/Electrode Characterization

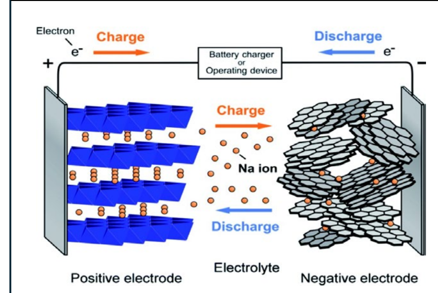


Cell-Level Characterization

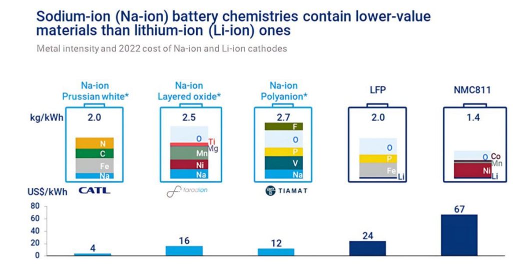
- Electrochemical testing (galvanostatic cycling, GITT, EIS) of O3, P2, and biphasic O3-P2 $Na_xMn_{0.5}Ni_{0.4}Fe_{0.1}O_2$
- Phase/compositional purity confirmation via lab-scale XRD, microscopy, Raman spectroscopy, and XAS
- Electrode heterogeneity mapping using micro-Raman, micro-XRF, and transmission X-ray microscopy (TXM)
- Charge compensation analysis through synchrotron-based XAS, XRD, XRF, and Mössbauer spectroscopy.

Month/Year	Tasks	Status
Feb 2024	Identify and visualize the phase purity and synergy	completed
Dec 2024	Develop methods to map phase/charge heterogeneity	completed
Mar 2025	Identify charge compensation processes	completed
Aug 2025	Probe high voltage processes and cell degradation	On-going

Background: SIBs and MNF541 Cathodes

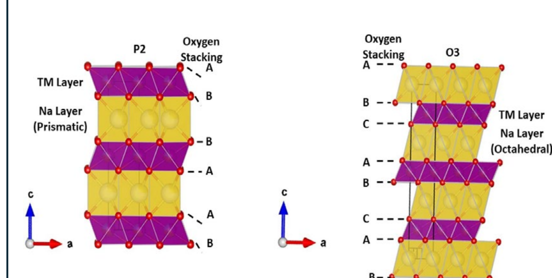


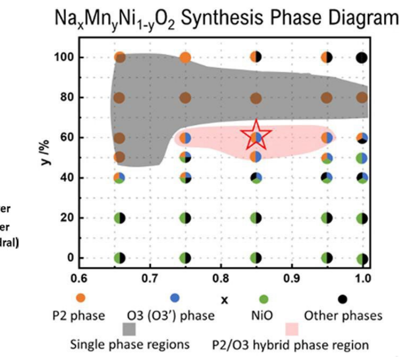
(RSC Adv., 2022,12, 23284)



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

Layered Transition Metal Oxide Cathode



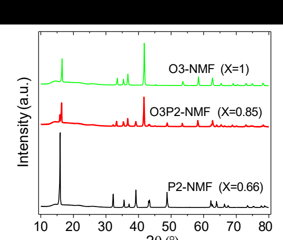


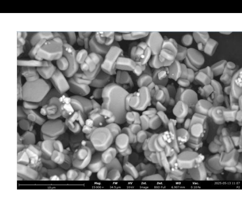
(Nano Energy, 2021, 89, 106371)

- $Na_xMn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (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
- Chosen for further study to assess phase synergy, charge compensation, and electrode level heterogeneity

Technical Progress: Phase Synergy

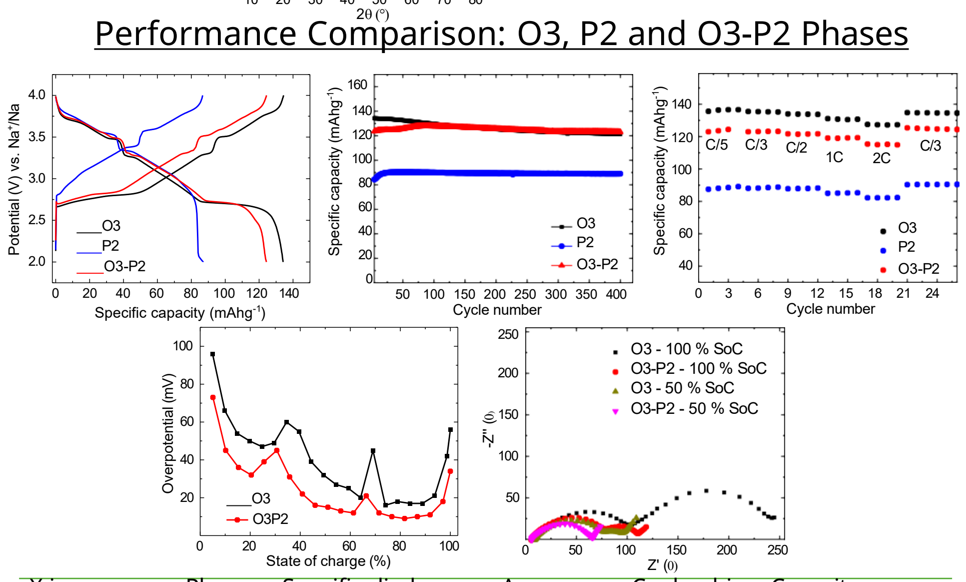
X = 0.85 shows biphasic O3-P2





Particle size: 2- 5 um

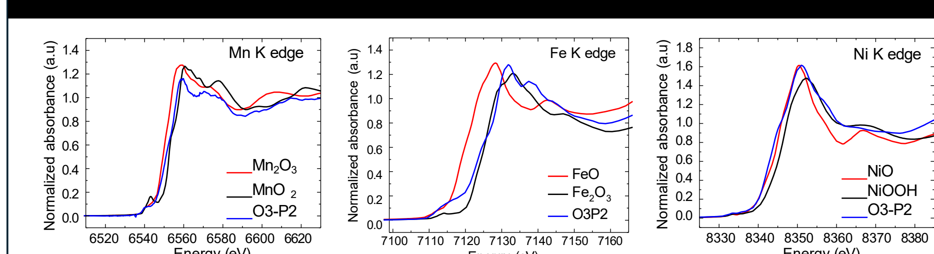
Performance Comparison: O3, P2 and O3-P2 Phases



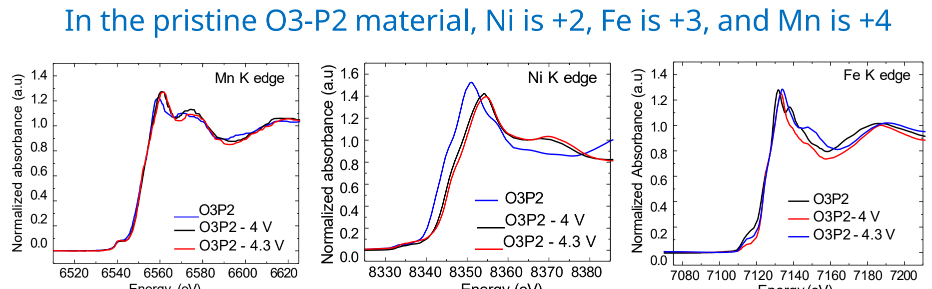
X in Na_xMNF541	Phase	Specific discharge capacity after formation	Average discharge voltage	Coulombic efficiency	Capacity retention after 400 cycles
X=0.66	P2	87 $mAhg^{-1}$	3.3 V	99.9 %	99 %
X=0.85	O3-P2	124 $mAhg^{-1}$	3.1 V	99.9 %	97.5 %
X=1	O3	134 $mAhg^{-1}$	2.9 V	99.7 %	89 %

Biphasic O3-P2 MNF541 shows overall best performance

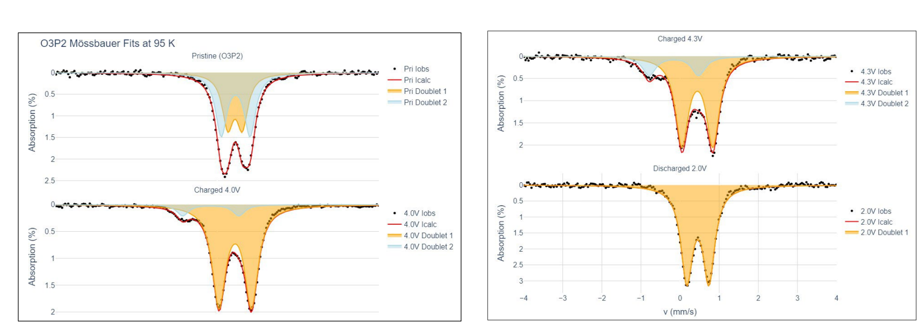
Technical Progress: Charge Compensation



In the pristine O3-P2 material, Ni is +2, Fe is +3, and Mn is +4

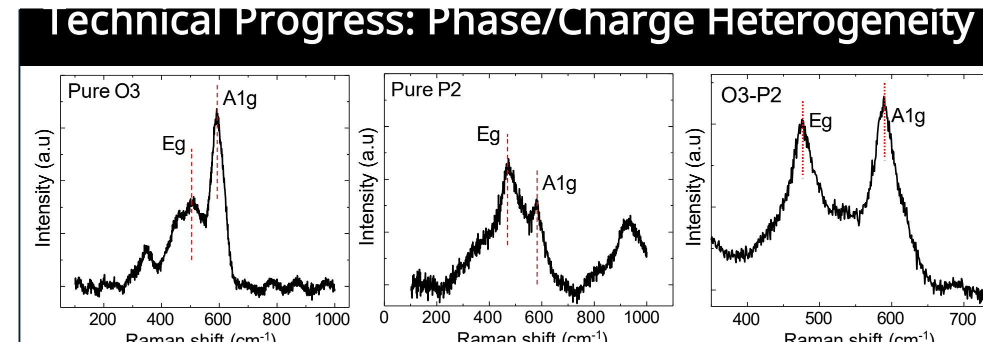


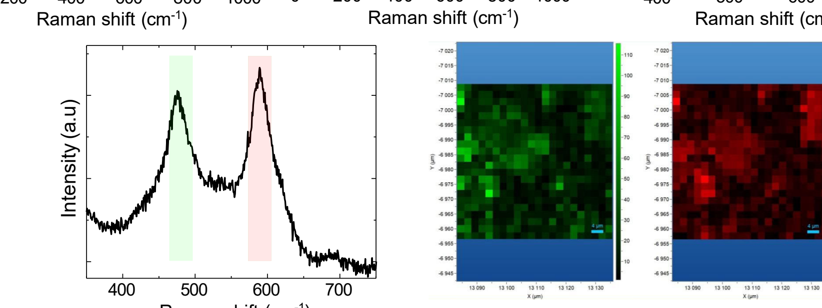
Ni^{2+} mainly contributes to the capacity, with Fe^{3+} also participating



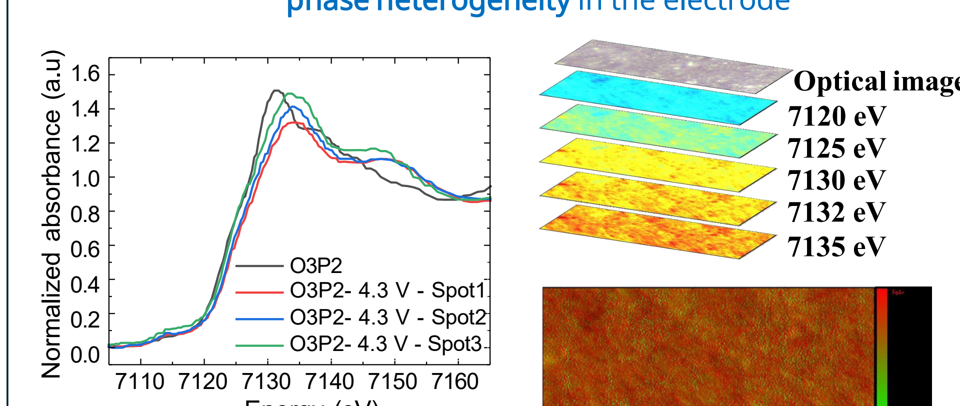
Fe^{3+} contribution increases to 20 % at 4.3 V; the reaction is reversible

Technical Progress: Phase/Charge Heterogeneity





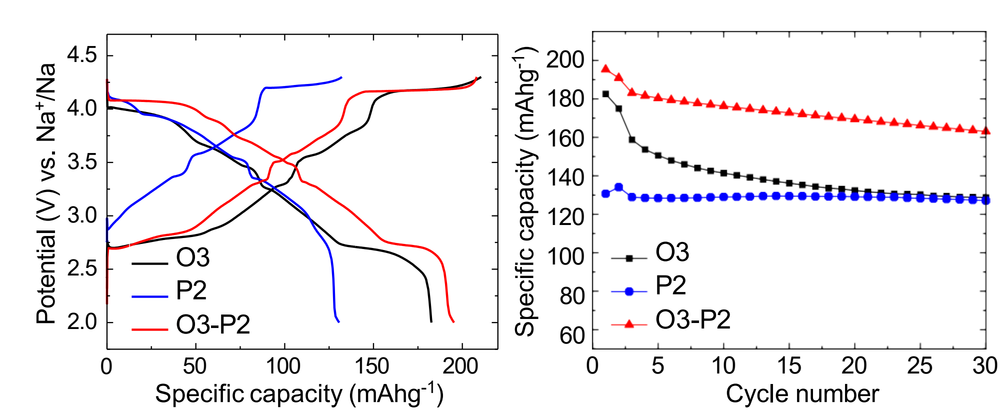
Isolated O3 regions observed in O3-P2 highlight **phase heterogeneity** in the electrode



$Fe^{3+/4+}$ shows **charge heterogeneity** across the electrode

Future Research: High Voltage Processes & AI guided Materials Screening

High voltage processes



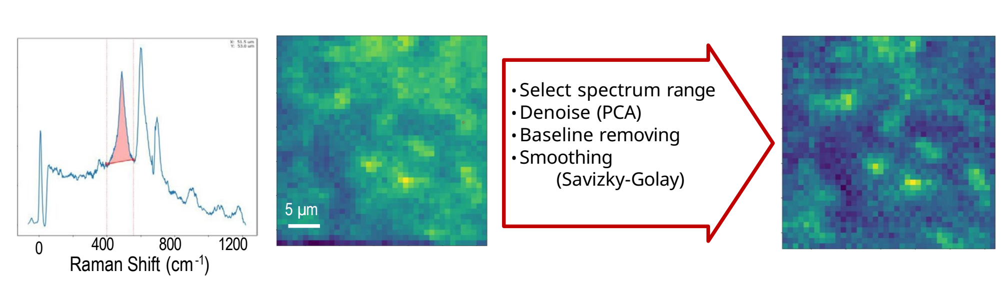
X in Na_xMNF541	Phase	Specific discharge capacity after formation	Specific capacity after 30 cycles
X=0.66	P2	132 $mAhg^{-1}$	126 $mAhg^{-1}$
X=0.85	O3-P2	195 $mAhg^{-1}$	160 $mAhg^{-1}$
X=1	O3	182 $mAhg^{-1}$	130 $mAhg^{-1}$

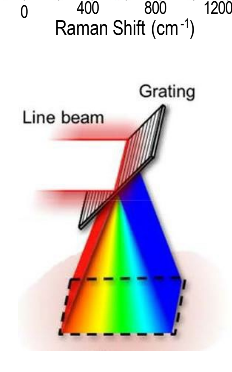
- O3-P2 NMF delivers ~200 mAh g^{-1} at 4.3 V but suffers capacity fade

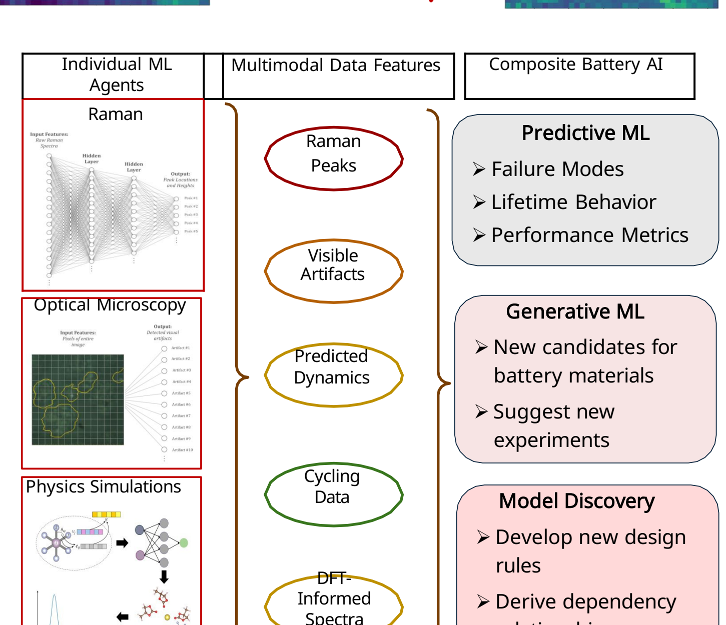
Future work

- investigate the origin of high-voltage capacity, including $Fe^{4+/3+}$ redox, and potential anion (oxide) participation
- Identify phase transitions and degradation pathways at high voltage to guide mitigation strategies

High-throughput materials screening (HTMS)







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

Summary

- Biphasic O3-P2 $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (MNF541) cathode outperforms monophasic O3 and P2, demonstrating phase synergy as a pathway to enhanced performance.
- XAS and Mössbauer analyses identify Ni^{2+} as the dominant redox center, with Fe^{3+} mainly active above 4 V.
- Micro-Raman mapping of electrode reveals isolated O3 regions, confirming phase heterogeneity in biphasic O3-P2.
- Micro-XRF analysis uncovers charge heterogeneity across the electrode.
- O3-P2-MNF541 delivers ~200 mAh/g at 4.3 V but shows significant capacity fade; ongoing studies focus on charge compensation and degradation mechanisms.
- High-throughput screening is enabled by line-scan Raman integrated with simulation and AI/ML, allowing rapid, parallelized analysis and predictive insight into material properties.

Acknowledgements

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