Li and Na ion intercalation in layered MnO_2 cathodes enabled by using bismuth as a cation pillar

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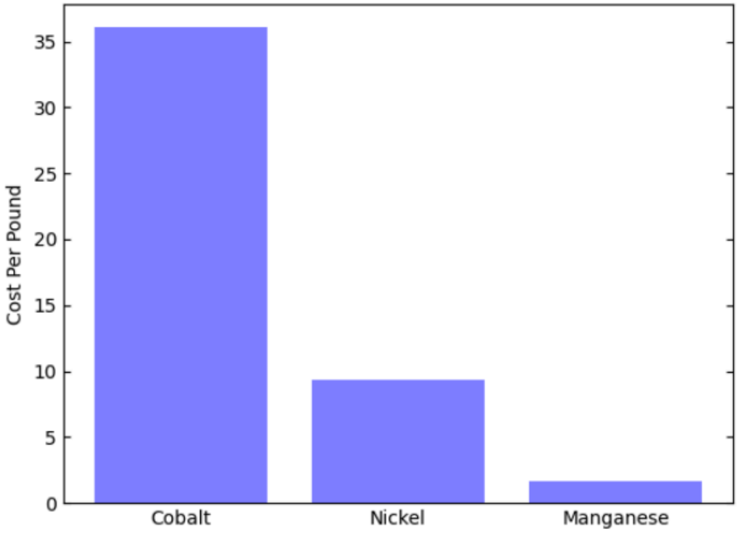
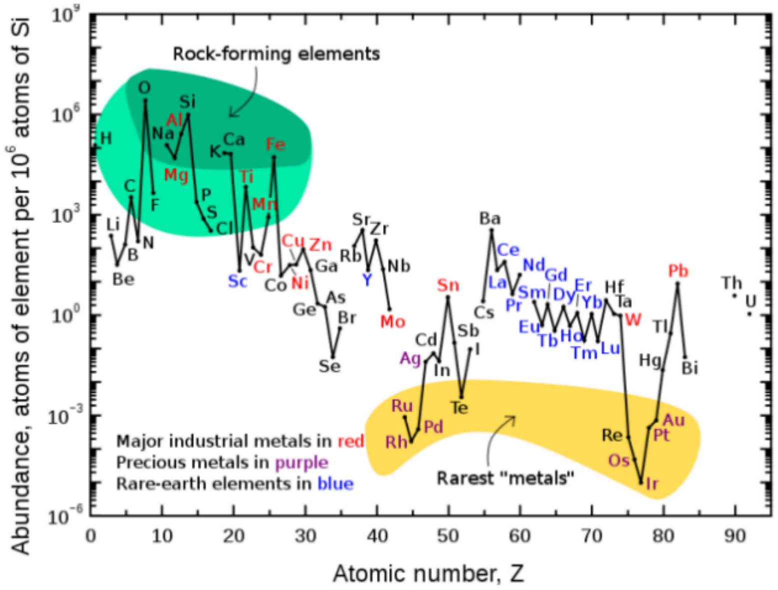
Northeastern University
College of Engineering

Project Overview

Northeastern College of Engineering

- Establishing new battery technologies based on **Earth-abundant materials** is critical for incorporating batteries into the grid. This includes potential anode materials Zn and Na, and cathodes based on oxides of Mn and Cu.
- The overall goal of the project is to better understand material properties in battery materials, particularly phase changes during cycling as observed by operando materials characterization. We develop MnO_2 for use in batteries and collaborate with SNL on operando synchrotron characterization.
- Recent work has led us to explore **MnO_2 as a cathode** in non-aqueous intercalation batteries. This would improve cost and make Li-ion or Na-ion batteries appropriate for the grid if Co and Ni were eliminated.



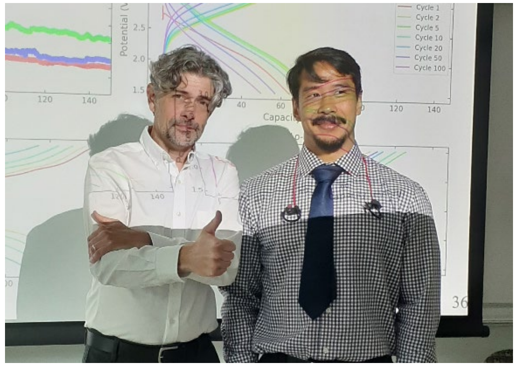


Project Team

Gallaway Lab
Analysis of Complex Electrochemical Systems (ACES)

- **Northeastern University**
  - Matthew A. Kim (PhD student)
  - Bebi Patil (postdoc)
  - Andrea Bruck (postdoc)

Matt Kim's dissertation defense



- **Sandia National Lab collaborators**
  - Ciara Wright
  - Noah Schorr
  - Timothy Lambert
  - Zachary Piontkowski

Project Achievements

Research Highlights

- Samples of layered MnO_2 doped with small amounts of Bi. The amount of Bi was controlled with precision. The effect of Bi doping on the MnO_2 structure and material properties was characterized.
- Li-ion and Na-ion batteries made with Bi-doped MnO_2 had greater capacity and stability than undoped material.

Publications

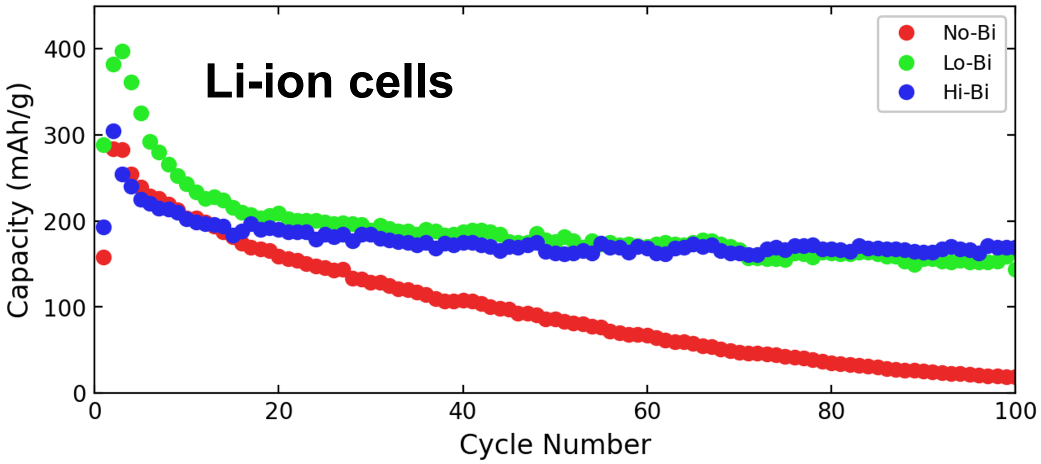
- PhD dissertation: Matthew A. Kim, "Low-cost MnO_2 intercalation cathodes enabled by using bismuth as a pillaring agent," Northeastern University, 2022.
- M.A. Kim, E.K. Zimmerer, Z. Piontkowski, N.B. Schorr, J.S. Okasinski, A.C. Chuang, T.N. Lambert, and J.W. Gallaway, "Li and Na ion intercalation in layered MnO_2 cathodes enabled by using bismuth as a cation pillar" (in preparation)

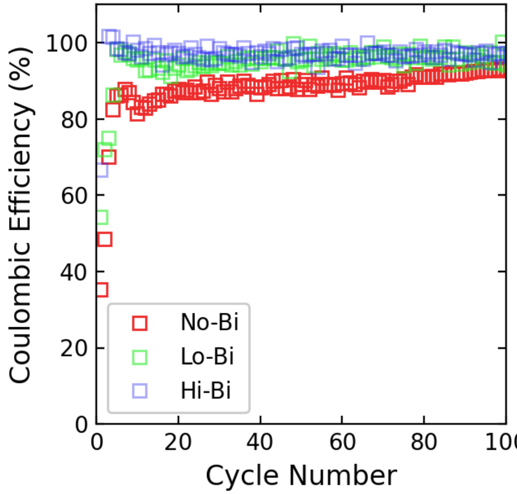
Collaborations

- Research on structure-property relationships in Bi-doped MnO_2 undertaken with Sandia National Lab colleagues: Zachary Piontkowski, Mark Rodriguez, Tim Lambert group.
- Collaborative synchrotron characterization of battery systems with Tim Lambert group. Experiments in 2022: Zn-CuO system EXAFS (NSLS-II), EDXRD (APS).

Bi doping of MnO_2 improves cycling

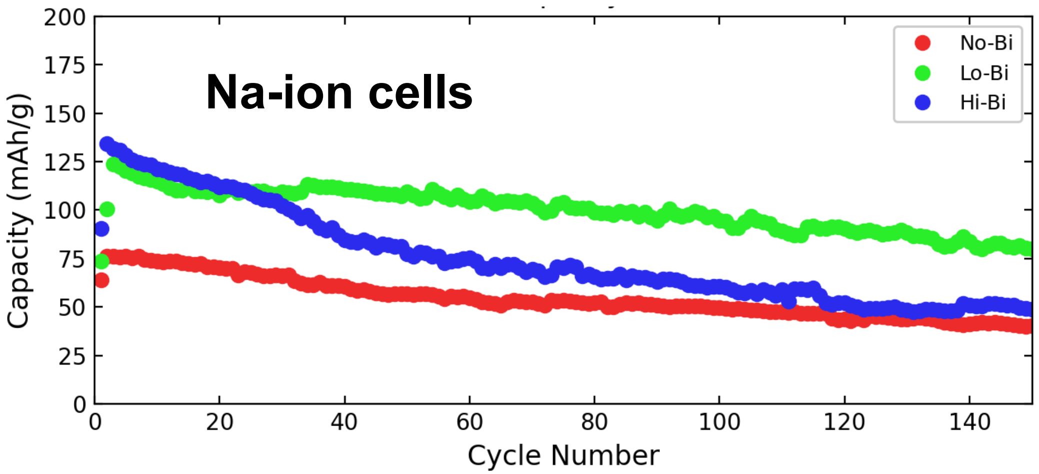
For non-aqueous alkali-ion batteries Bi-doping of MnO_2 improves cycling: **Enables MnO_2 as a cathode**.

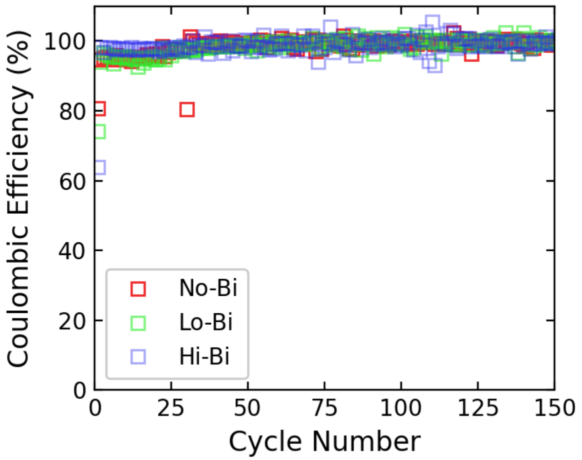




δ-(K_x,Bi_y)-$MnO_2 \bullet nH_2O$

	x	y	n
No-Bi	0.308	0	0.17
Lo-Bi	0.332	0.013	0.27
Hi-Bi	0.384	0.043	0.30





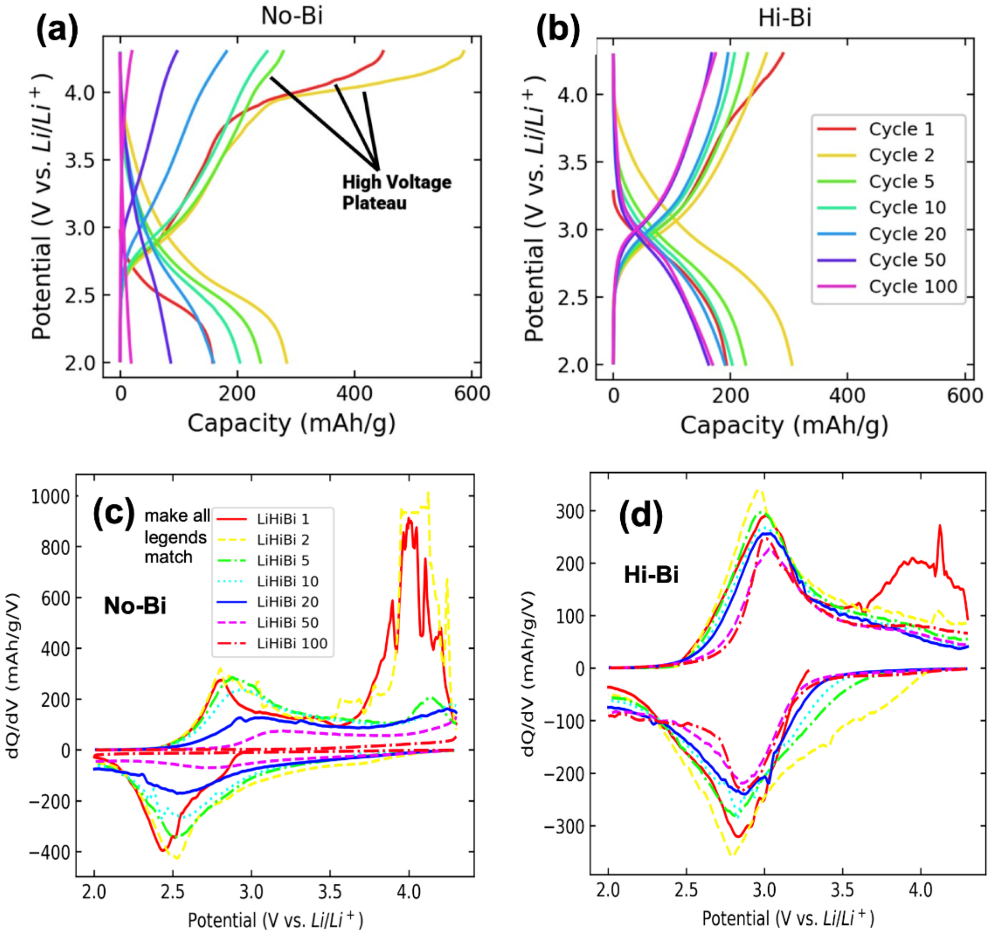
- Lo-Bi doping level was better for **Na-ion batteries**.
- Hi-Bi was better for **Li-ion batteries**.

All cathodes at loading 1.5 - 2.5 mg/cm^2

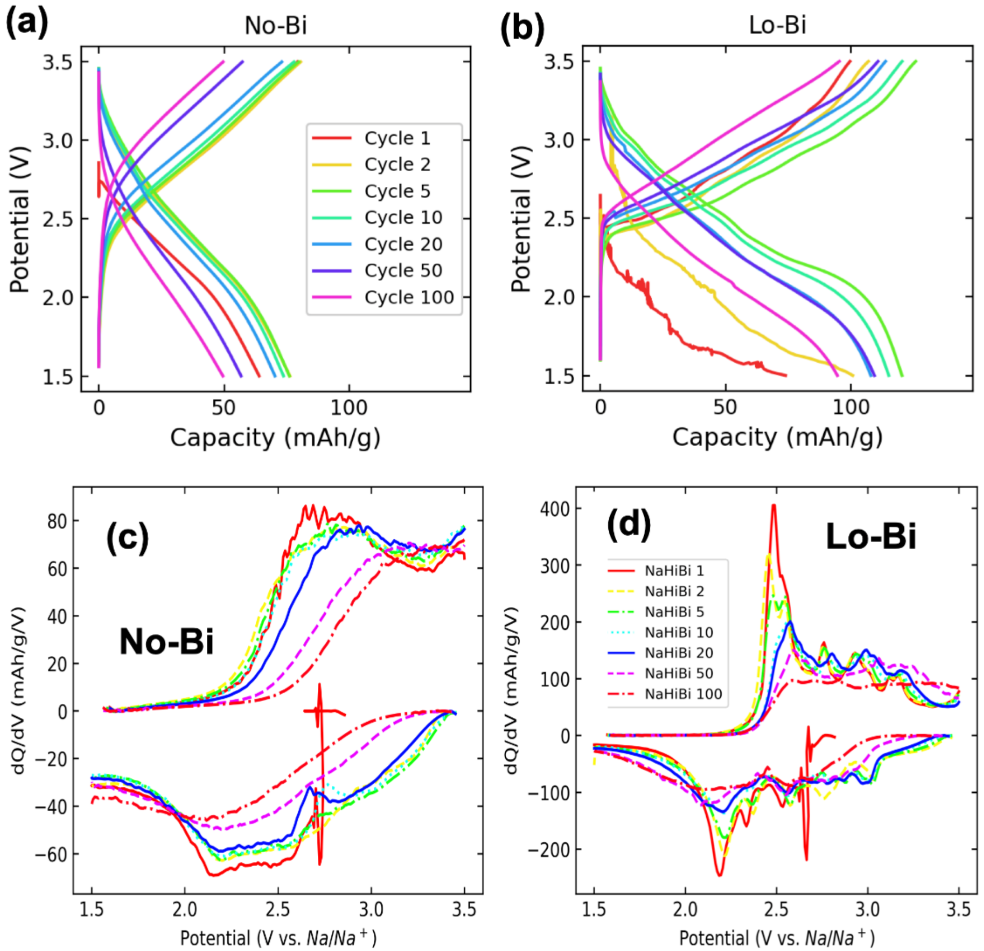
Bi doping of MnO_2 improves cycling: Details

For non-aqueous alkali-ion batteries Bi-doping of MnO_2 improves cycling: **Enables MnO_2 as a cathode**.

Li-ion cells

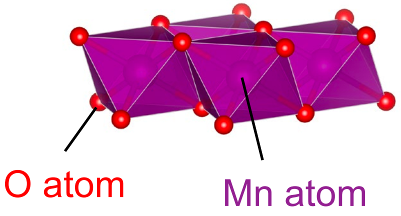


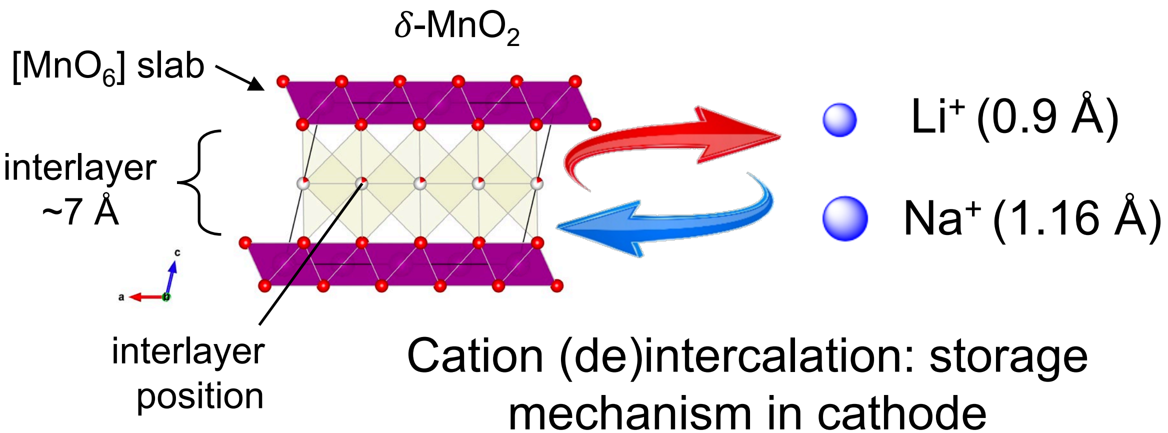
Na-ion cells



The effect of Bi doping on MnO_2

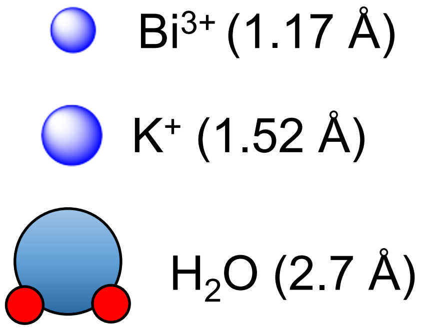
Small amounts of Bi doping change layered MnO_2 significantly



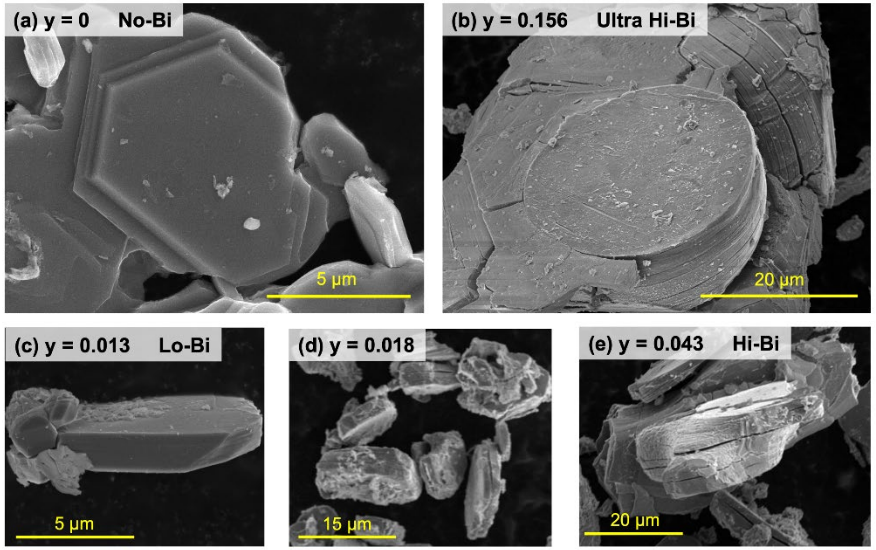


Cation (de)intercalation: storage mechanism in cathode

Other species in the interlayer



- Bi^{3+}, K^+, and H_2O all play a structural role.
- "Crystal water" is part of the material.



- Higher amounts of Bi^{3+} increase particle size
- Morphology changes
- Layered structure is maintained

Structural effect of small amounts of Bi^{3+}

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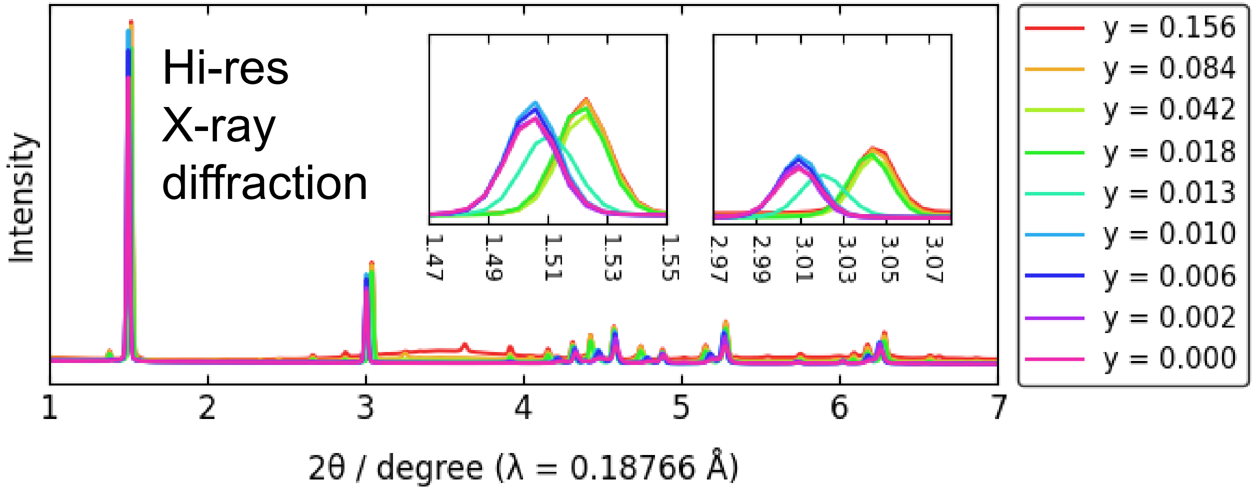
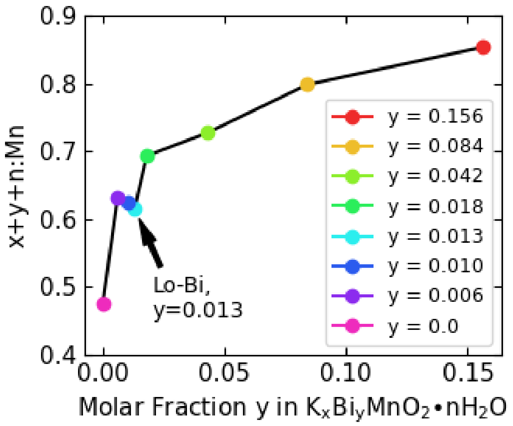
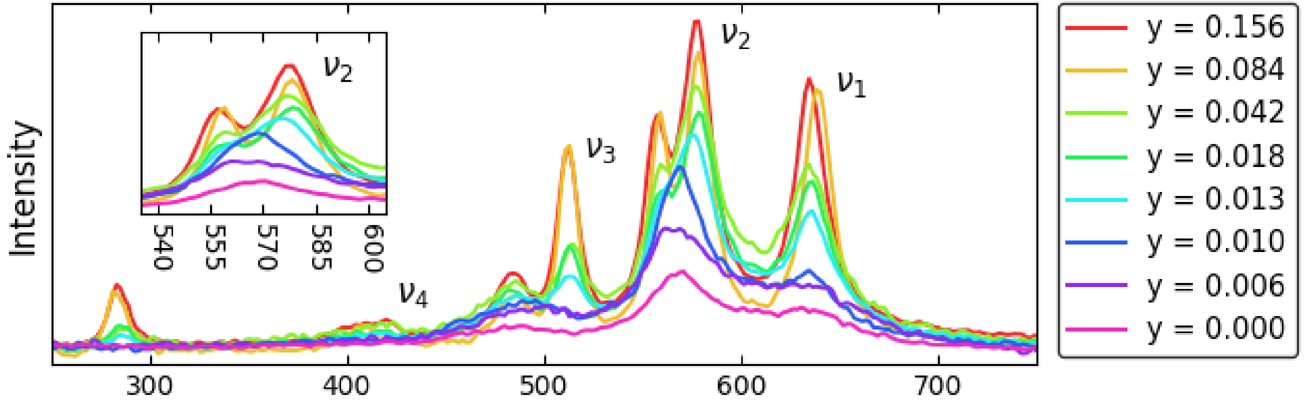


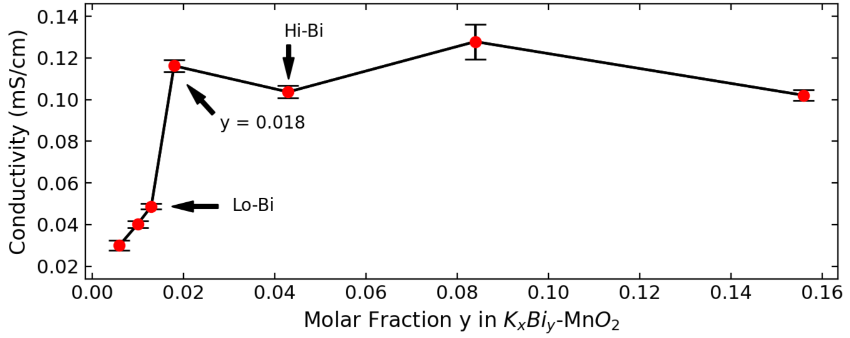
- Increasing Bi allows almost all interlayer positions to be filled



Raman spectroscopy



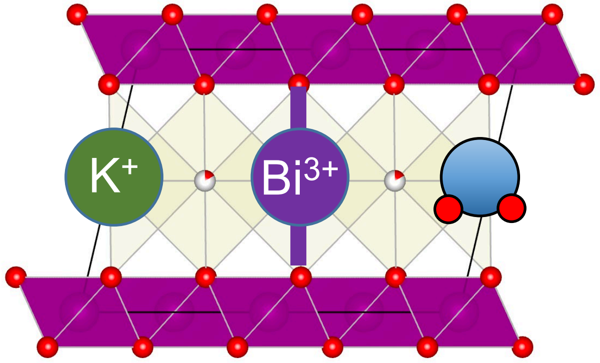
- Increasing Bi increases conductivity

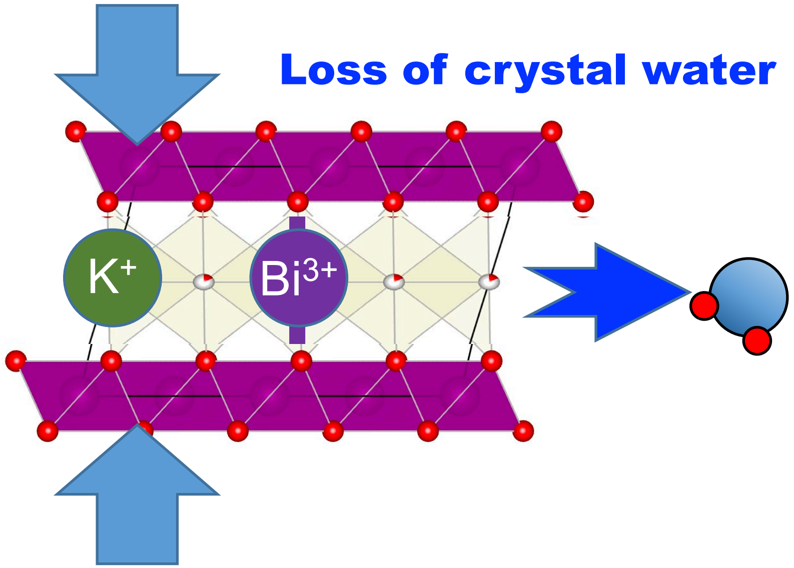


- Bi doping increases long-range crystallinity

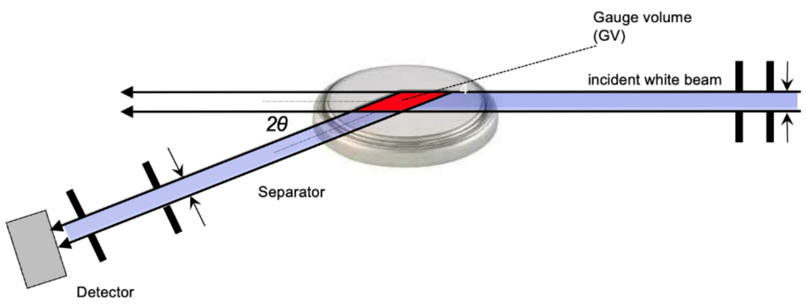
Why does Bi doping stabilize cathodes?

- The Bi^{3+} serves as a **cation pillar** for the layered structure.
- The Bi^{3+} cations increase crystallinity by arranging in the interlayer, **assuming a superstructure**.
- When wetted with carbonate electrolyte, high dopings of Bi (Hi-Bi, >4%) cause **loss of the crystal water**. This collapses the interlayer.
    - This is beneficial in the case of Li-ion cells due to the small size of Li^{+}.
    - For Na-ion cells, low Bi doping (Lo-Bi, <2%) maintains the crystal water and interlayer size. This is beneficial due to the larger size of Na^{+}.





Operando Mechanistic Studies

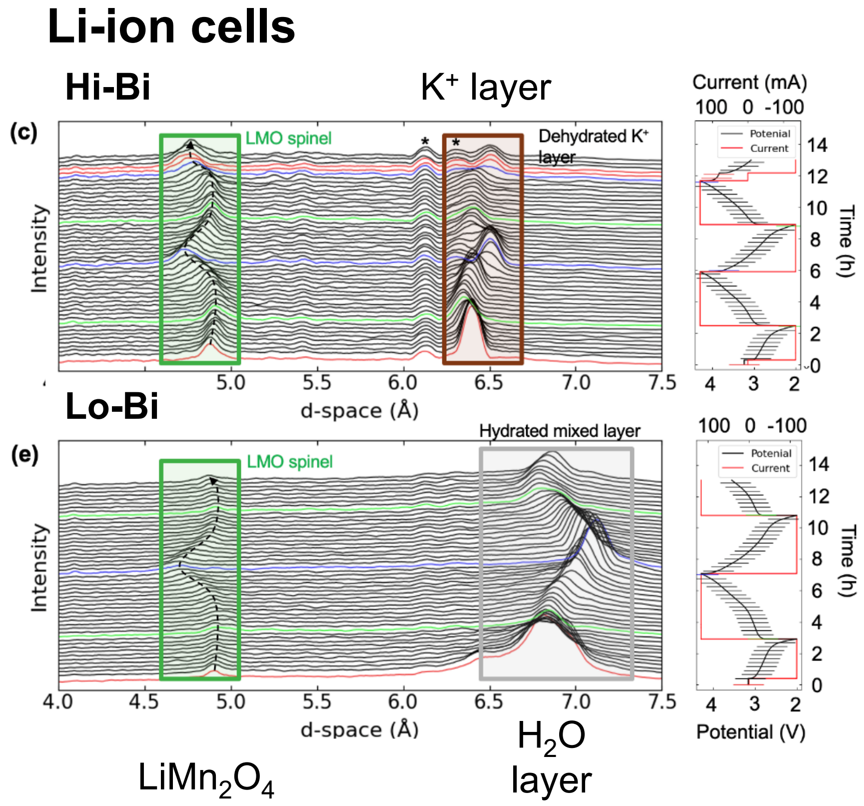


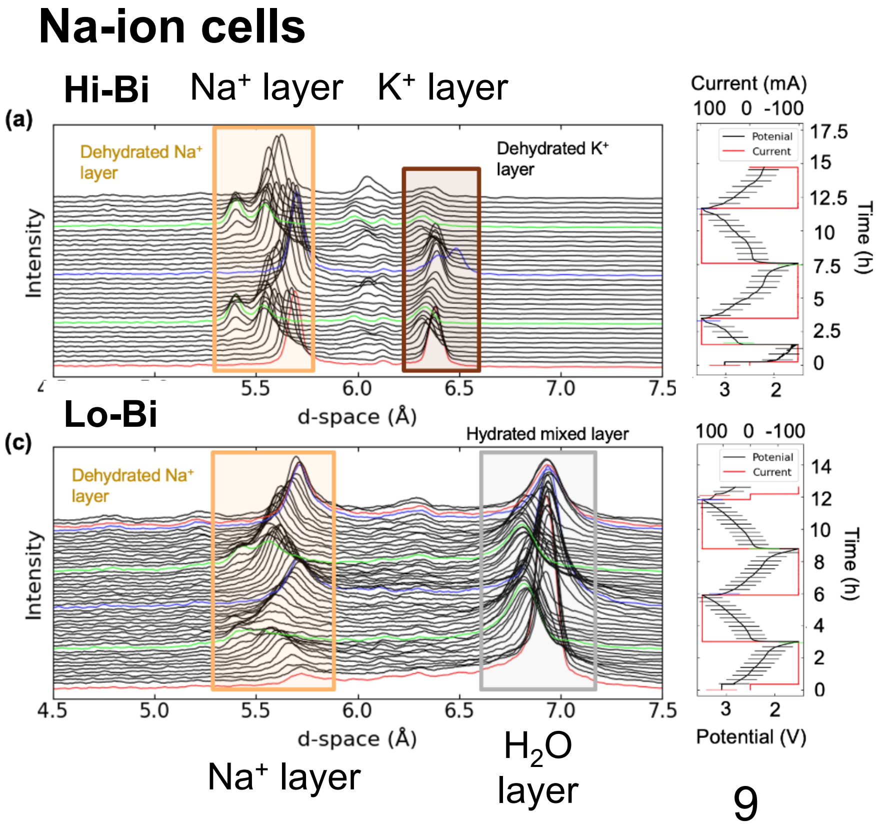
❑ **Small-angle EDXRD (synchrotron technique)**

- Data acquired from within hermetically sealed coin cells.
- (Ex situ analysis was not possible due to hygroscopic nature.)
- Small angle provides information on largest d-spacings, i.e. interlayers.

Hi-Bi results in dehydrated interlayers

- A dehydrated interlayer is smaller (~5.5 Å for Na^+ and ~6.4 Å for K^+)
- Better Li^+ cycling would be expected in a smaller interlayer. Na^+ would be the opposite.
- Some spinel (active) was also formed in the Li-ion case.





Summary

❑ Project achievements

- Bi-doped MnO_2 was produced in a well-controlled manner and characterized.
- Bi doping was shown to stabilize both Li-ion and Na-ion cycling, but at different concentration levels. Operando mechanistic characterization revealed this was due to the effect on crystal water.
- Collaborative operando experiments were performed with the Tim Lambert group at SNL, using both APS (Argonne) and NSLS-II (Brookhaven).
- Structural knowledge about Bi-doped MnO_2 is also useful in rechargeable Zn-MnO_2 systems, where Bi imparts rechargeability to the MnO_2 cathode. This effect is not mechanistically understood, and is relevant to OE program research.

❑ Future work

- Intercalation of the Zn^{2+} ion.
- Increase working voltage of low-cost Na-ion battery materials.
- Evaluation of the Bi-doped MnO_2 crystalline superstructure.
- Operando work on the Zn-CuO system with SNL.

Acknowledgements

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