Engineering Rechargeability in MnO_2 Cathodes for low-cost and safe batteries

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Zinc & Lead Session, ID #505

Northeastern University
College of Engineering

Outline

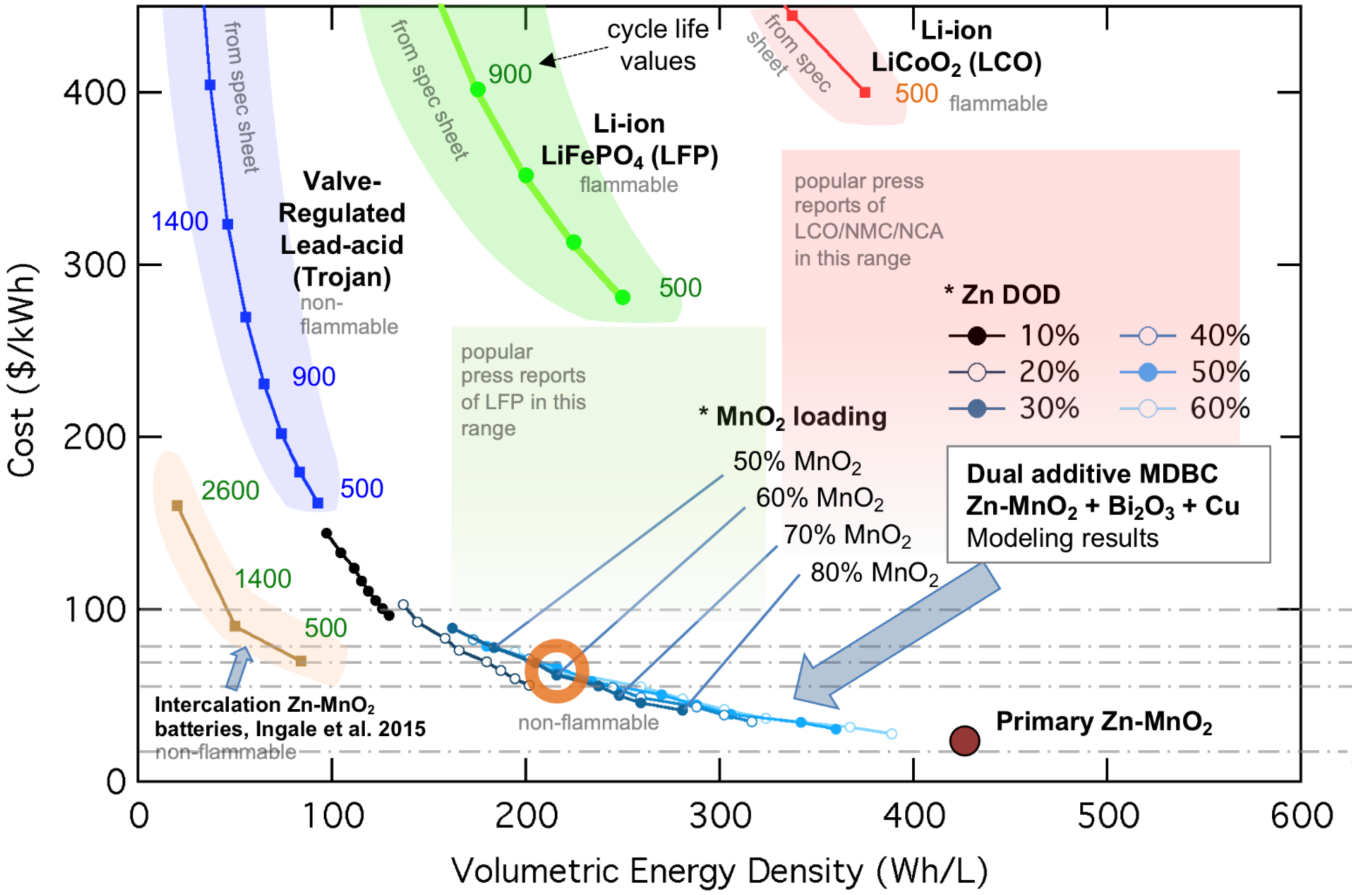
1. Project Background and Motivation
   - List of technical Tasks

2. **Task 2**: Doped MnO_2 for low-cost Li-ion and Na-ion "beyond Li-ion" batteries

3. **Task 3**: Mechanistic studies of doped MnO_2 for low-cost Zn-MnO_2 systems

4. **Task 4**: Mechanistic collaboration with SNL: Zn-CuO

GOAL: Low-cost and safe Zn-MnO_2 grid batteries



Engineering a deep-cycled MnO_2 electrode

- Zinc depth of discharge (DOD)
- MnO_2 cathode mass loading

Jim Eyer and Garth Corey, SAND2010-0815 (2010)

Grid Storage Projected Cost Benefits:

- T&D Upgrade Deferral (50th Percentile)
  3-6 h discharge, $584/kW benefit
- Wind Grid Integration
  1-6 h discharge, $441/kW benefit
- Renewables Load Shift
  3-5 h discharge, $311/kW benefit
- Demand Charge Management
  5-11 h discharge, $582/kW benefit
- Transmission Congestion Relief
  3-6 h discharge, $86/kW benefit

Our group's work is on improvement of the MnO_2 cathode.

Turney; Yadav; **Gallaway**; et al, "Aqueous Mn-Zn and Ni-Zn Batteries for Sustainable Energy Storage." *in Energy-Sustainable Advanced Materials,* **2021**.

Additives enable MnO_2 rechargeability

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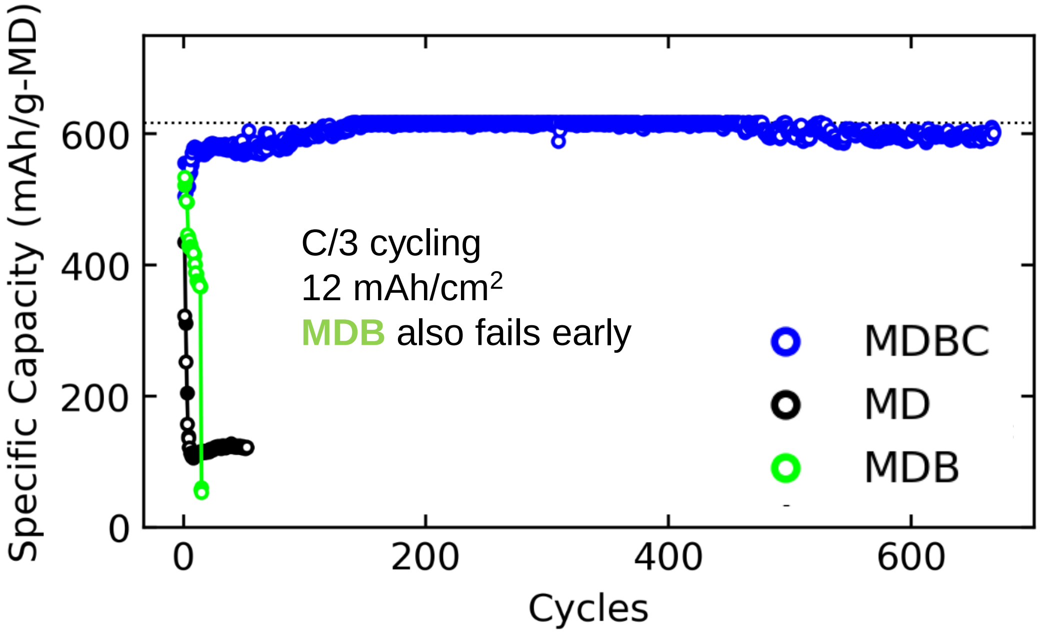
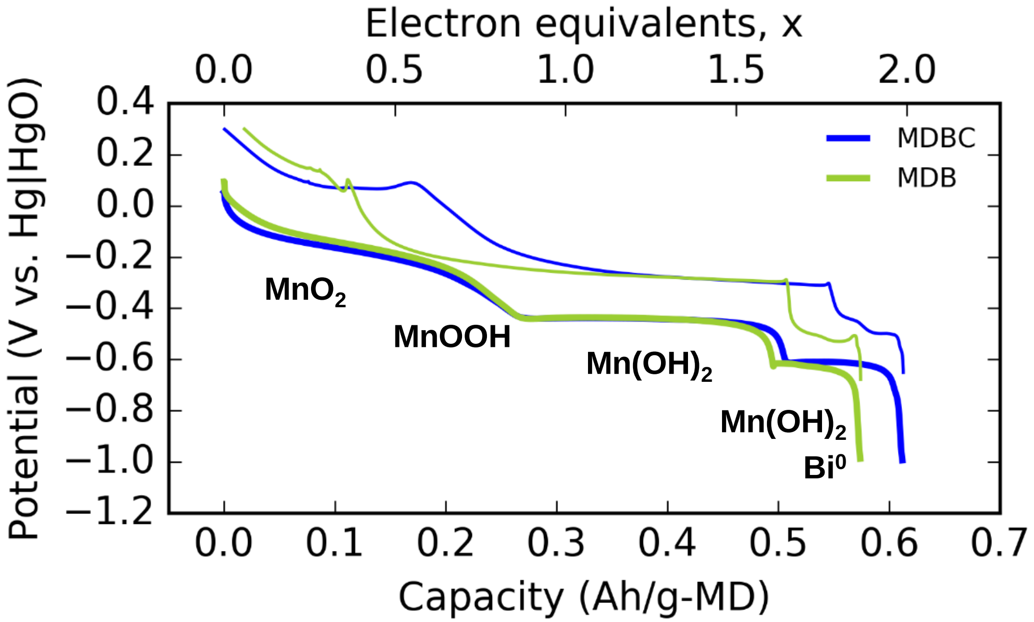
MDB: MnO_2 + Bi_2O_3 — Ford Motor Company, 1980s

MDBC: MnO_2 + Bi_2O_3 + Cu — City College of New York (CCNY), 2017





2010-2015, City College of New York, ARPA-E
"Low-Cost Grid-Scale Electrical Storage Using a Flow-Assisted Rechargeable Zinc-Manganese Dioxide Battery"

Yadav et al. *Nature Comm.*, 8 (2017) 14424.
~617 mAh/g (100% DOD)

Additives enable rechargeability

- Bi_2O_3 allows MnO_2 to recharge
- Addition of Cu allows this to reach high cycle life at high mass loading.

However: Challenges remain for implementation

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1. The mechanism of both Bi and Cu additives are unknown

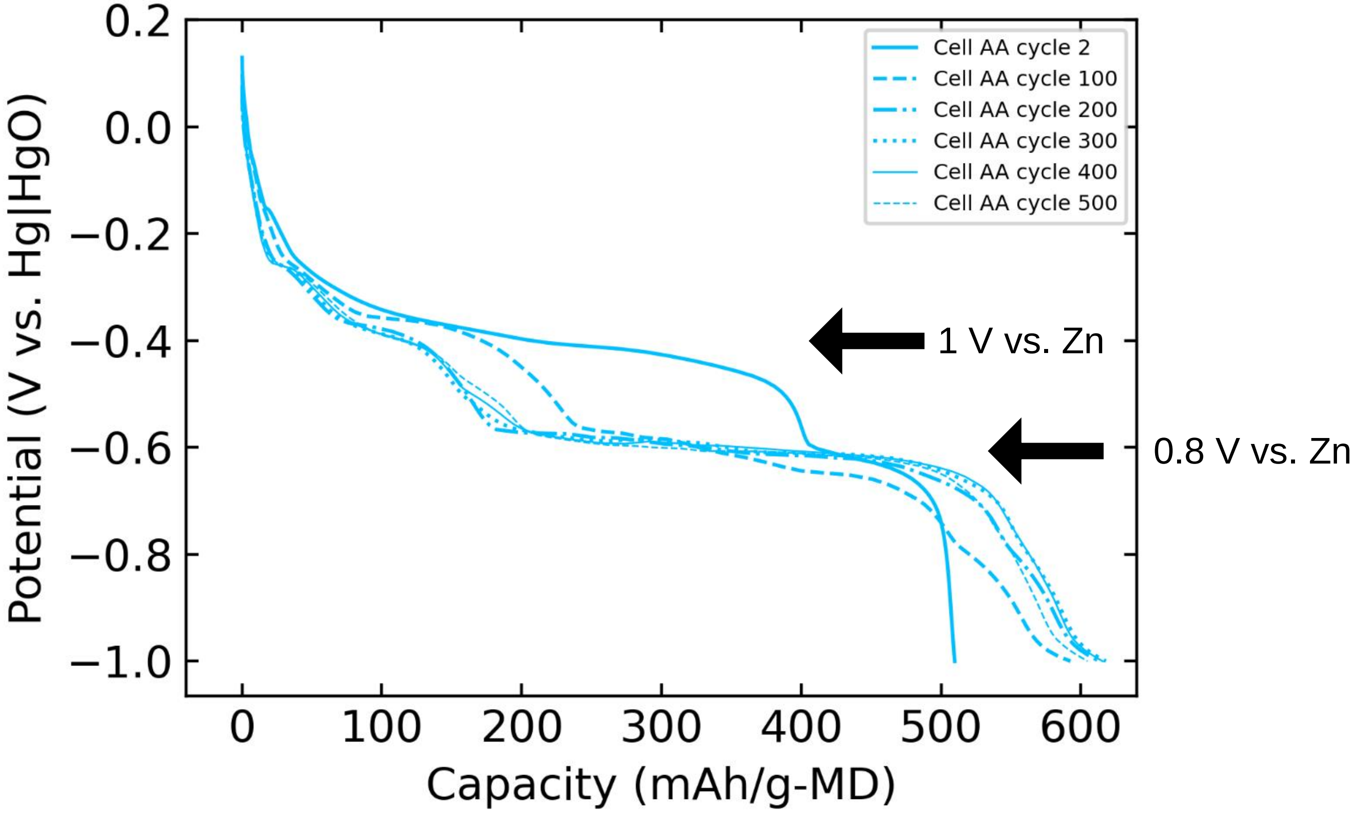
- Bi is sometimes hypothesized to stabilize the MnO_2 structure by acting as a "molecular pillar"

2. A single cathode active material is desired

3. The Bi and Cu-doped MnO_2 electrode undergoes voltage loss

- Higher cathode voltage is desired for high energy density.

MDBC: MnO_2 + Bi_2O_3 + Cu



Our goal is to solve #1
in order to engineer a solution to #2 and #3

Proposed mechanism of MnO_2 cycling with Bi

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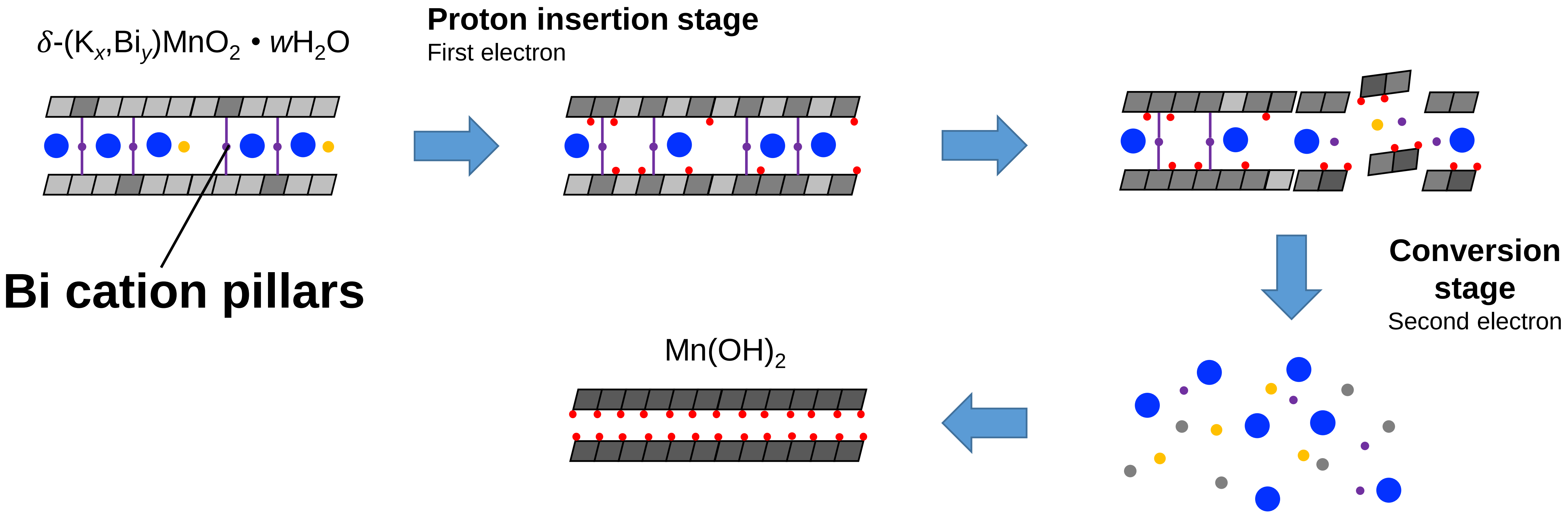
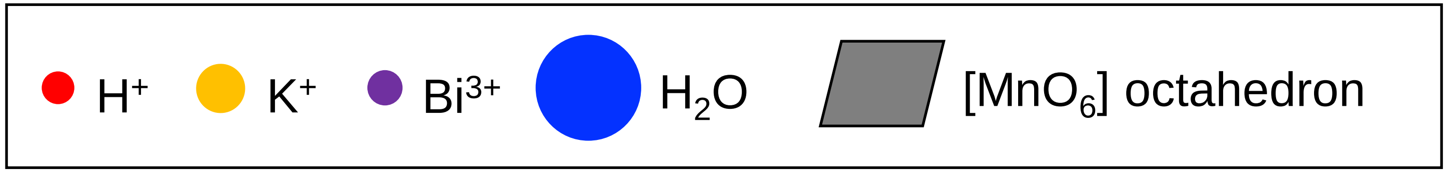


$$\boldsymbol{\delta\text{-MnO}_2} + 2H_2O + 2e^- \rightleftharpoons \mathbf{Mn(OH)_2} + 2OH^-$$



Our 2021 and 2022 Tasks

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Task 2: Reversible Intercalation in MnO_2 in non-aqueous systems

The effect of Bi pillaring on MnO_2 cathode used for non-aqueous intercalation batteries

- **Li-ion**
- **Na-ion "beyond Li-ion"**

The all-Mn layered oxide cathode can lower the cost of these batteries and make them appropriate for grid applications.

Nature of the Bi pillaring effect will be clarified through this study

Task 3: The effect of Bi in aqueous MnO_2 systems

Deep science on aqueous mechanism. Does Bi:

- Leave the MnO_2 structure as a hydrated $[Bi(H_2O)_n]^{3+}$ species
- Remain as a coordinated $[BiO_x]$ cluster

Identifying this intermediate will elucidate underlying mechanism in the MnO_2 system

Task 4: Structural effect of Bi doping in alkaline CuO batteries

Collaboration with Timothy Lambert's group at SNL on Bi doping in Zn-CuO batteries

Our 2021 and 2022 Tasks

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Task 2: Reversible Intercalation in MnO_2 in non-aqueous systems

- 2.1: Structural and Morphological Effect of Bi Doping
- 2.2: Ion Exchange Methods
- 2.3: Li-ion Battery Cycling
- 2.4: Li-ion Battery Electrochemical Characterization

Complete in 2021

- 2.5: Li-ion Battery Operando X-ray Diffraction
- 2.6: Solid Electrolyte Li-ion Battery
- 2.7: Beyond Li-ion Cycling

Task 3: The effect of Bi in aqueous MnO_2 systems

- 3.1: Crystal structure changes during MnO_2 cycling in a wide range of d-spacings
- 3.2: MnO_2 operando spectroscopy — **Complete in 2021**
- 3.3: MnO_2 structure modeling

Task 4: Structural effect of Bi doping in alkaline CuO batteries

- 4.1: Operando EDXRD — **Complete in 2021**
- 4.2: Operando X-ray spectroscopy

2021 Accomplishments

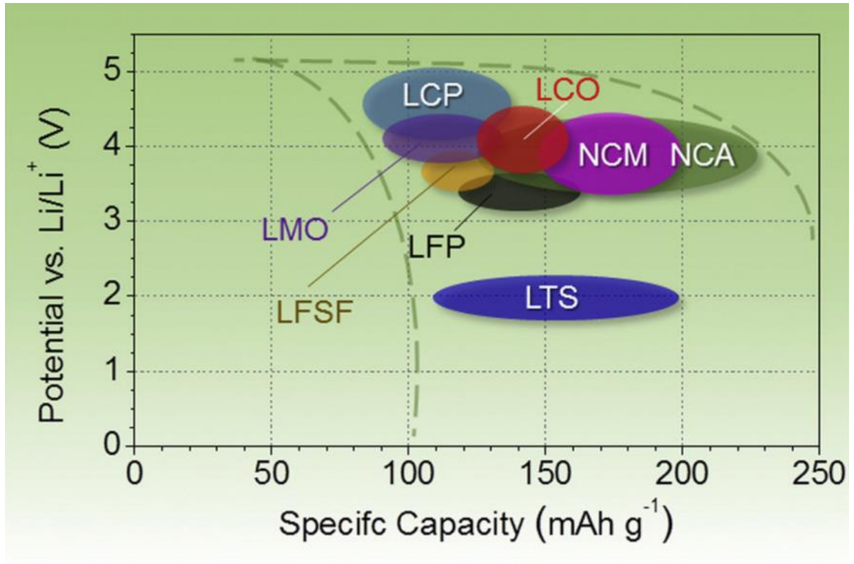
Remaining Tasks are for 2022

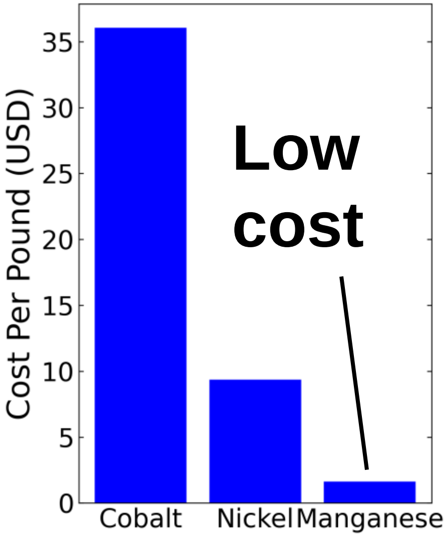
Poster:
Kim MA and Gallaway JW, "Enabling stable Li-ion cycling of a Mn layered oxide via Bi-doping."

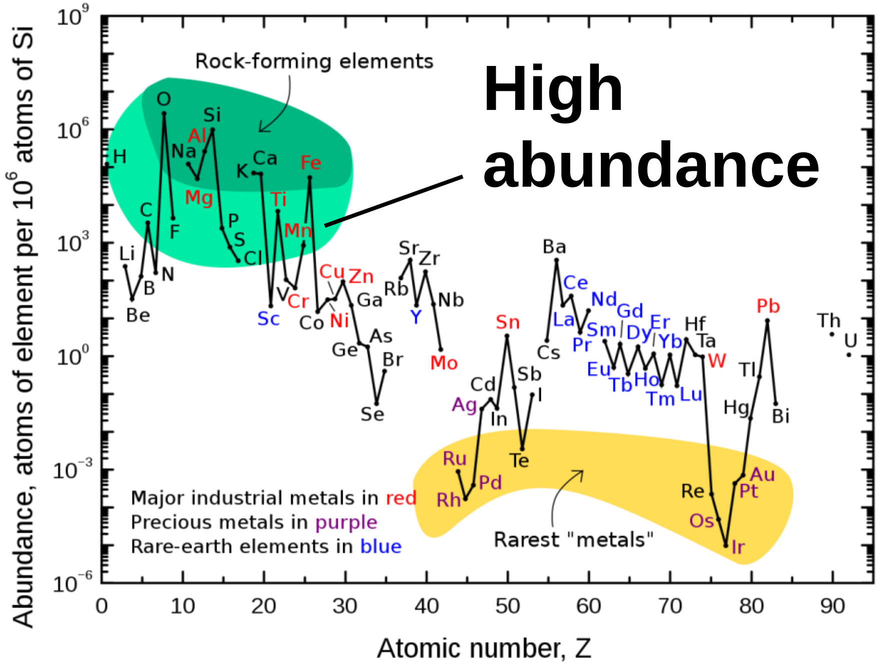
Matthew Kim

Task 2: Reversible intercalation in MnO_2 in non-aqueous systems

Layered MnO_2 Li-ion battery cathode







Spinel manganese oxide (LMO) has low capacity and poor stability.

Layered manganese oxide has high theoretical capacity comparable to cobalt oxide.

- Cost of Co is high. Replacement with Mn would dramatically lower cost.
- Co is regionally locked. Mn is extremely widely available.
- Mn is less environmentally hazardous and less toxic

Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G., Li-ion battery materials: present and future. Materials Today 2015, 18 (5), 252-264.
Market Insider markets.businessinsider.com (accessed March 18, 2021)
Anderson, Don L.; "Chemical Composition of the Mantle", Theory of the Earth, pp. 147-175

Doped δ-MnO_2 target material

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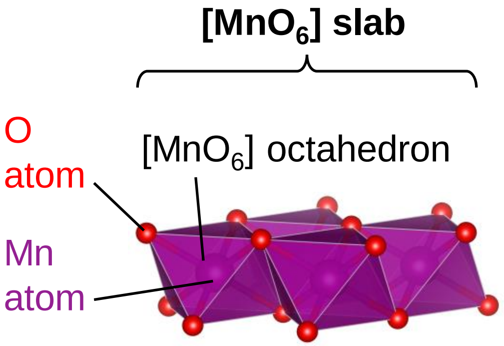
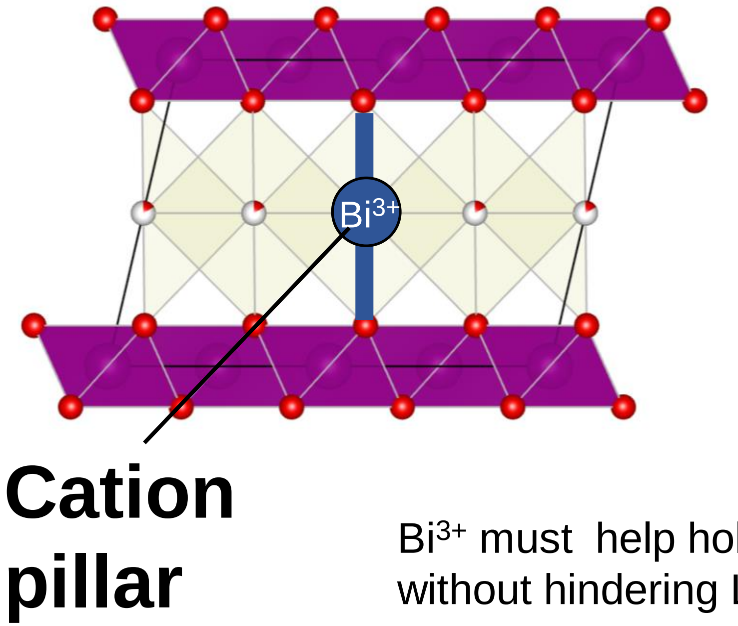


δ-MnO_2 is a layered oxide where Mn is the primary transition metal. It is analogous to CoO_2, the most common Li-ion battery cathode.

δ-MnO_2



We seek a "permanent pillaring" effect, whereby Bi^{3+} stabilizes the material to allow repeated Li^+ cycling.

Bi^{3+} must help hold the layers together, without hindering Li^+ transport.

δ-MnO_2 can be synthesized several ways

Resulting Material: Crystallinity	Resulting Material: Interlayer Cations (A)	Method	
Disordered	K^+	Wet synthesis from Mn salts	Wet methods
		Sol-gel synthesis	
Crystalline	Mg^{2+}	Autoclaved $Mg(MnO_4)_2$	
Crystalline	K^+	Fine powder $KMnO_4$ heated	High temperature
Crystalline	K^+ and Bi^{3+}	Fine powder $KMnO_4$ + $Bi(NO_3)_3$ heated	
Disordered	K^+ and Cu^{1+} K^+ and Mg^{2+} K^+ and Bi^{3+*}	Cation salt inserted in birnessite	Cation exchange
Crystalline	K^+ and Bi^{3+*}	Cation salt inserted in birnessite	

We tried many methods to produce δ-MnO_2 with cations inserted into the interlayer.

The indicated high temperature method produced crystalline material and enabled the amount of Bi^{3+} to be tuned.

Doped δ-$(K_x,Bi_y)MnO_2 \cdot wH_2O$

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Chemical formula of $(K_xBi_y)MnO_2 \cdot wH_2O$

x	y	w	Chemical formula	Molar mass (excluding H_2O)
0.377	0.156	0.56	$K_{0.377}Bi_{0.156}MnO_2$	134.18 g/mol
0.404	0.084	0.53	$K_{0.404}Bi_{0.084}MnO_2$	120.31 g/mol
0.384	0.043	0.52	$K_{0.384}Bi_{0.043}MnO_2$	110.87 g/mol
0.365	0.018	0.52	$K_{0.365}Bi_{0.018}MnO_2$	104.97 g/mol
0.332	0.013	0.40	$K_{0.332}Bi_{0.013}MnO_2$	102.63 g/mol
0.315	0.01	0.53	$K_{0.315}Bi_{0.010}MnO_2$	101.29 g/mol
0.315	0.006	0.46	$K_{0.315}Bi_{0.006}MnO_2$	100.58 g/mol
0.306	0.002		$K_{0.306}Bi_{0.002}MnO_2$	99.36 g/mol
0.308	0.0	0.26	$K_{0.308}MnO_2$	98.97 g/mol

We have produced a series of materials that vary in amount of Bi^{3+}, which is given by "**y**" in the chemical formula.

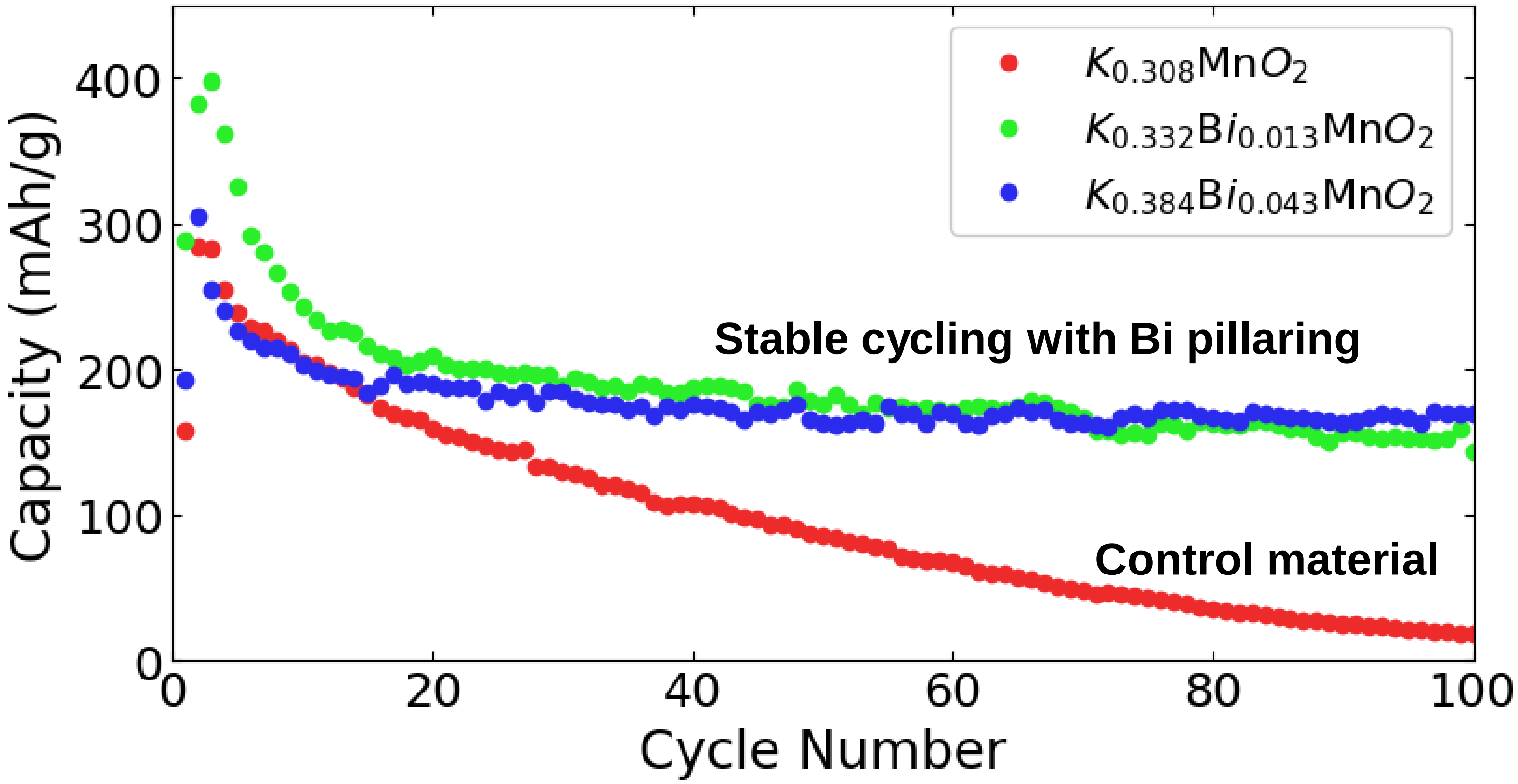
All materials are highly crystalline and therefore straightforward to characterize.

Higher y generally correlates to higher x and w.

Values for x and y from inductively coupled plasma (ICP).
Values for w from thermogravimetric analysis (TGA).

Li-ion battery cycling with Bi-pillared MnO_2

Li-ion half-cell results
in CR2032 format, C/10 rate



- Cycling results show that Bi^{3+} successfully stabilizes the material.
- It is possible that Bi^{3+} stabilizes the material by preventing conversion to $LiMn_2O_4$ spinel.

This is the most favorable stabilization of layered MnO_2 reported, to our knowledge.

Material characterization of (K_x,Bi_y)-MnO_2

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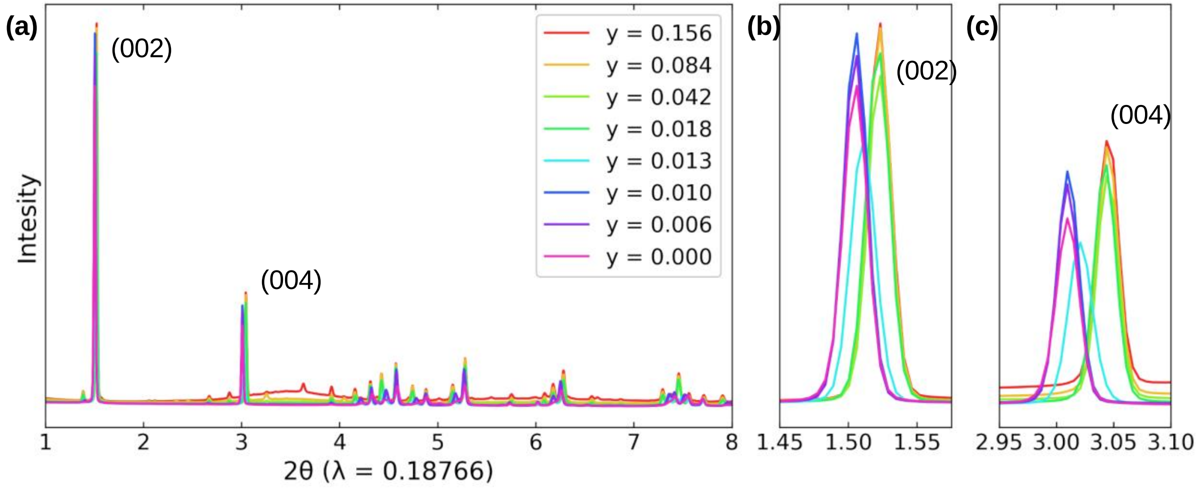
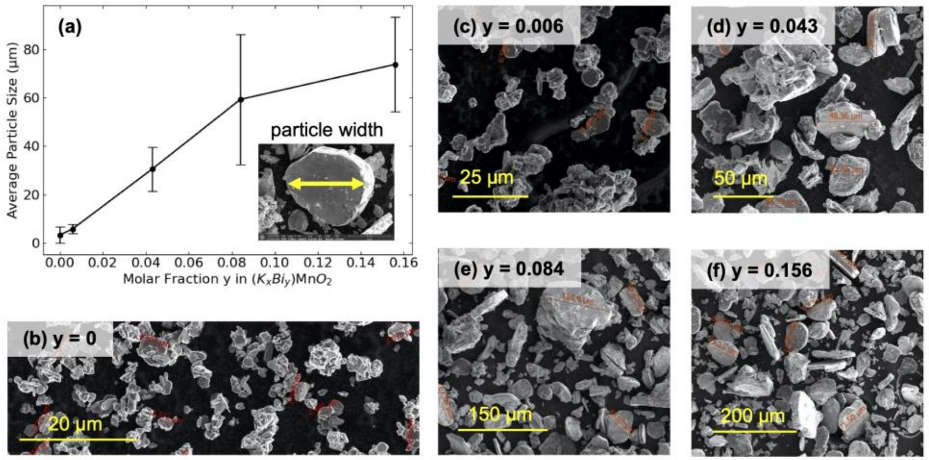
XRD results of $(K_xBi_y)MnO_2$ at various values of y.

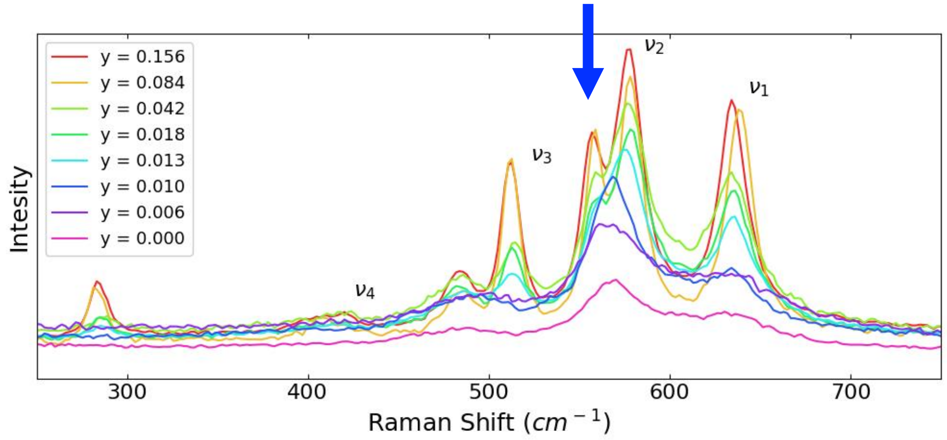
Data collected at NSLS-II, beamline 28-ID (XPD)



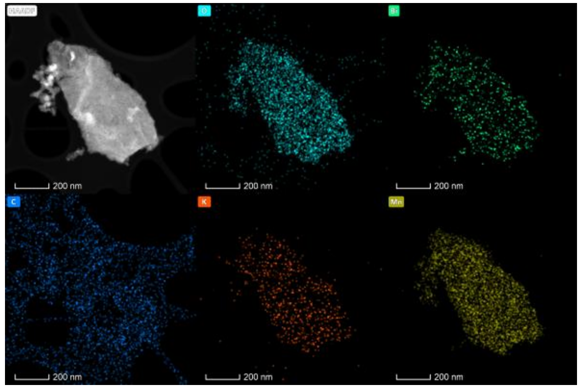
Morphology of $(K_xBi_y)MnO_2$ at various values of y



Raman results of $(K_xBi_y)MnO_2$ at various values of y



EDS of $(K_xBi_y)MnO_2$ at various values of y



Poster:
Goulart J, Guida D, and Gallaway JW, "Operando characterization of rechargeable alkaline batteries for grid scale storage."

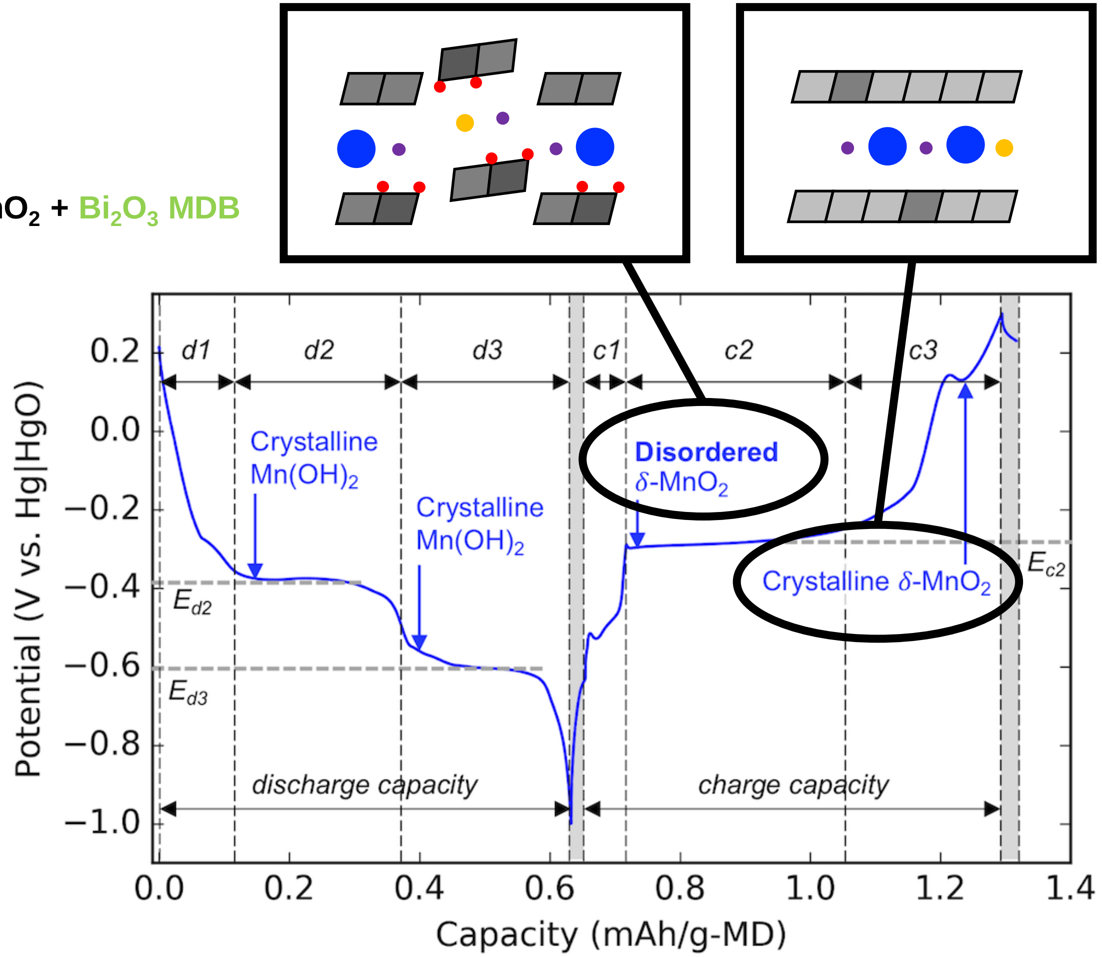
James Goulart
with
Dom Guida

Dr. Andrea
Bruck

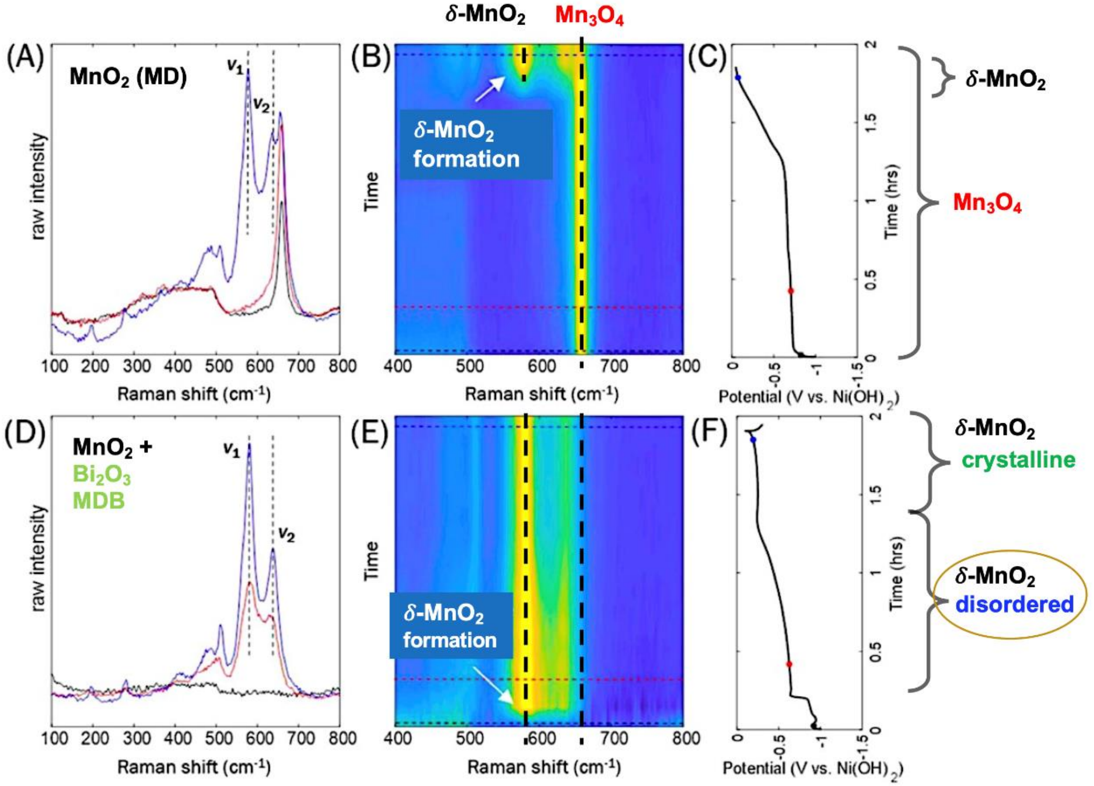
Task 3: The effect of Bi in aqueous MnO_2 systems

2020 Publication

MnO_2 + Bi_2O_3 MDB

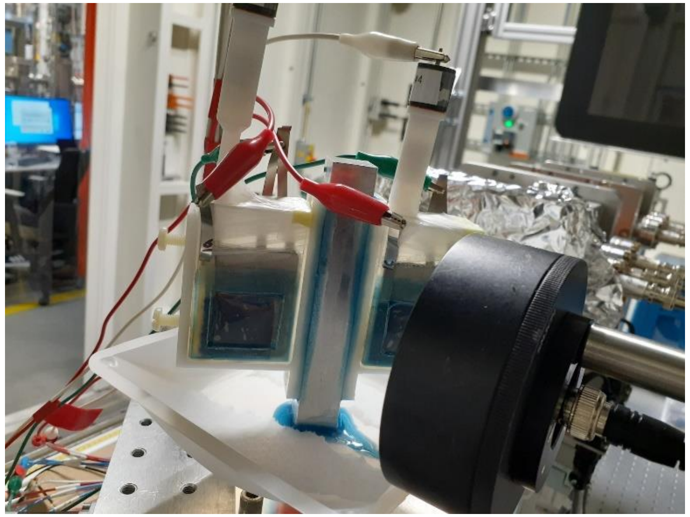


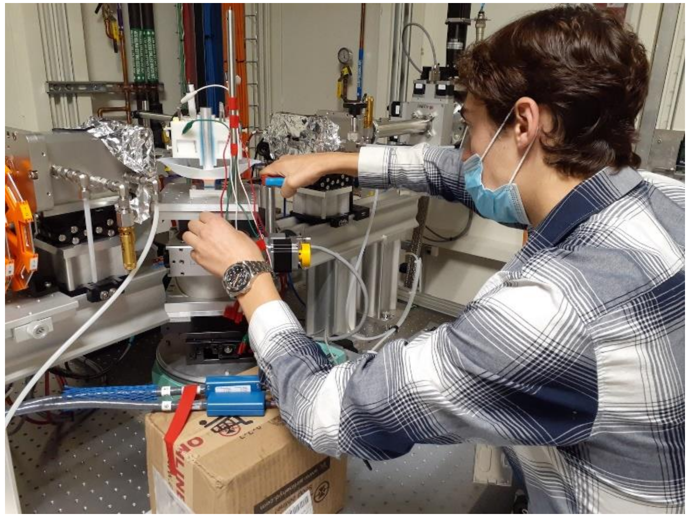
Operando Raman Spectroscopy



Bruck; **Kim**; Ma; Ehrlich; Okasinski; **Gallaway**, "Bismuth Enables the Formation of Disordered Birnessite in Rechargeable Alkaline Batteries." *Journal of The Electrochemical Society* **2020,** *167* (11), 110514.

2021-2022 Tasks





Task 3.2 data collected at NSLS-II

- Operando Quick Extended X-ray absorption fine structure (QEXAFS)
- Atomic positions around Bi atoms
- <u>Conducting data analysis currently</u>
- Also operando Raman underway

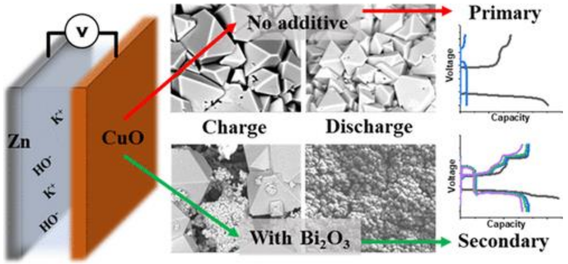
Dr. Timothy Lambert

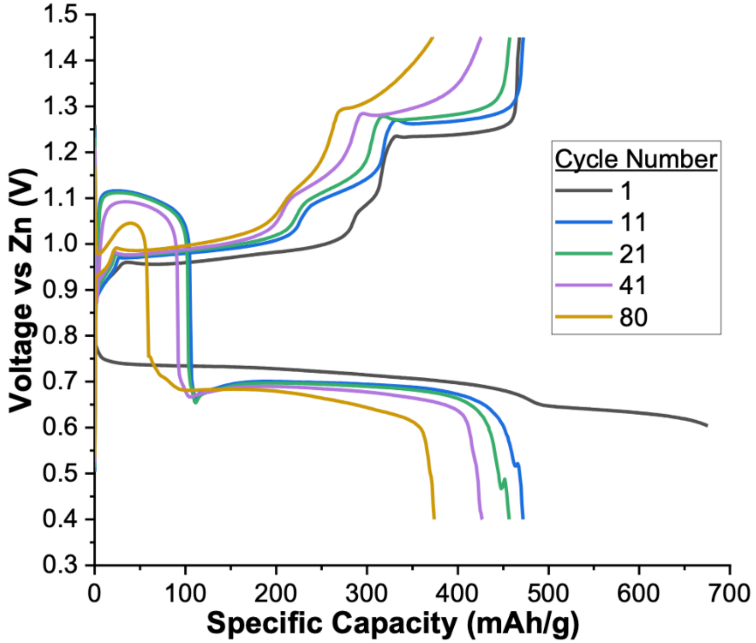
David Arnott

Dr. Noah Schorr

Task 4: Structural effect of Bi doping in alkaline CuO batteries

Rechargeable
$Zn|(CuO-Bi_2O_3)$ batteries
2-electron cathode

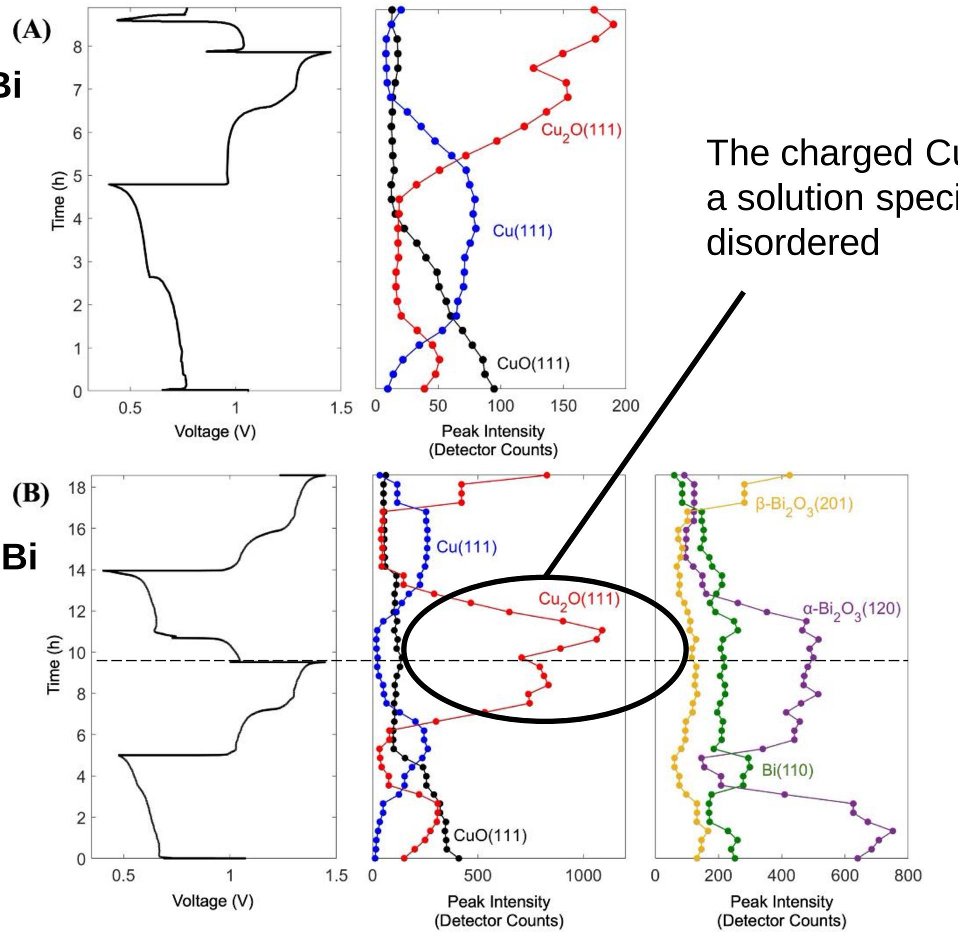




Operando energy dispersive X-ray diffraction (EDXRD)

No Bi

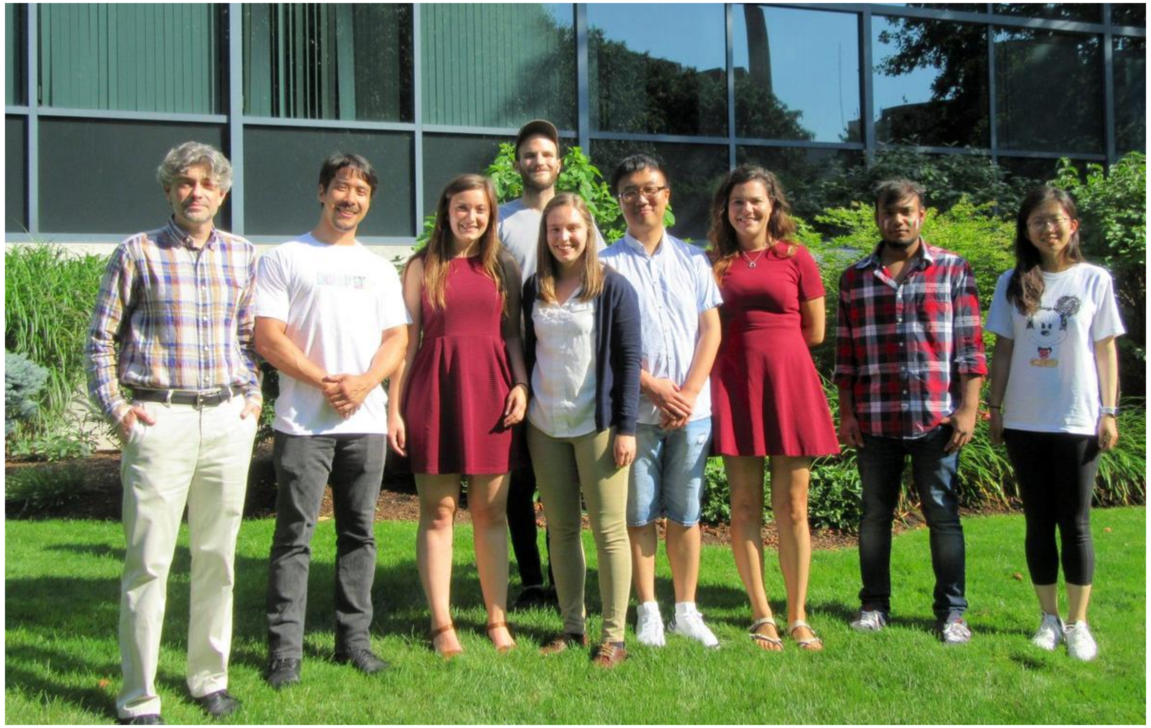
With Bi



The charged Cu(II) is a solution species or disordered

Schorr; Arnot; **Bruck**; Duay; Kelly; Habing; Ricketts; Vigil; **Gallaway**; Lambert, "Rechargeable Alkaline Zinc/Copper Oxide Batteries." *ACS Applied Energy Materials* **2021,** *4*, 7073-7082.

Acknowledgements



Gallaway Lab, Northeastern University

Postdoctoral
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- Dominick Guida

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- Tristan Owen
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