Operando Studies to Enumerate the Electrochemical Phase Transformations of MnO_2

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Outline

1. Northeastern University
2. MnO_2 as an inexpensive, safe, non-toxic cathode material
3. The Role of Bi Doping: Disordered Birnessite
4. Synthesis of Doped Birnessites δ-$(A_x,B_y)MnO_2$

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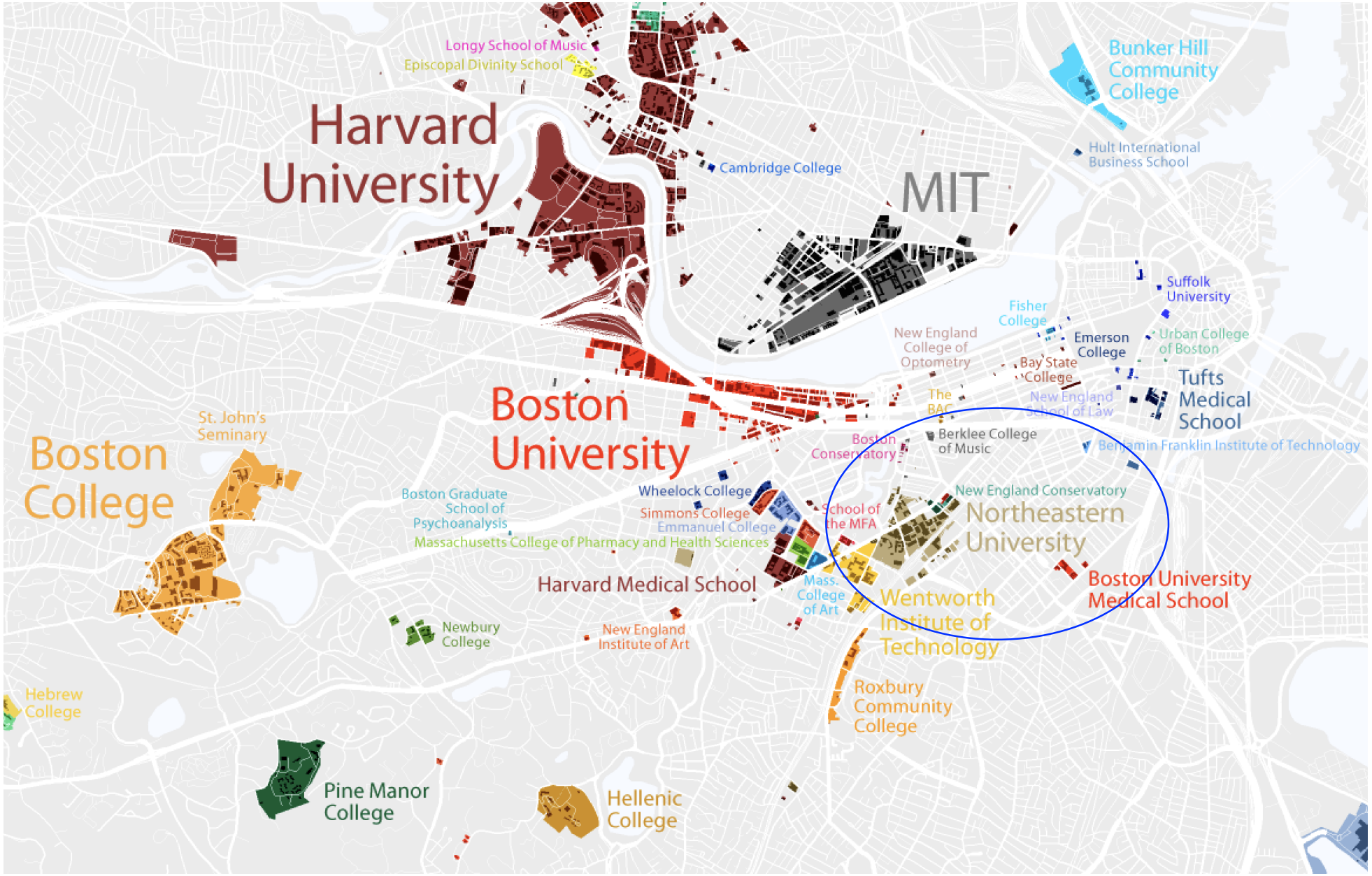


MnO_2 as an inexpensive, safe, non-toxic cathode material

Alkaline Zn-MnO_2

Zn-MnO_2

MnO_2 (+)

+ Cheap
+ Abundant
+ Safe
+ ~$1/lb

Electrolyte(KOH)

* Cheap
* Abundant
* Aqueous-based
* Much safer than organic electrolytes

Zn (-)

- Cheap
- Abundant
- Safe
- ~$0.9/lb

- Zn and MnO_2 are high-capacity materials
  - Zn: **817 mAh/g** (2-electron)
  - MnO_2: **617 mAh/g** (2-electron)
- Aqueous: lower potential than Li-ion (organic)
  - 1.5 V nominal

Manganese oxides

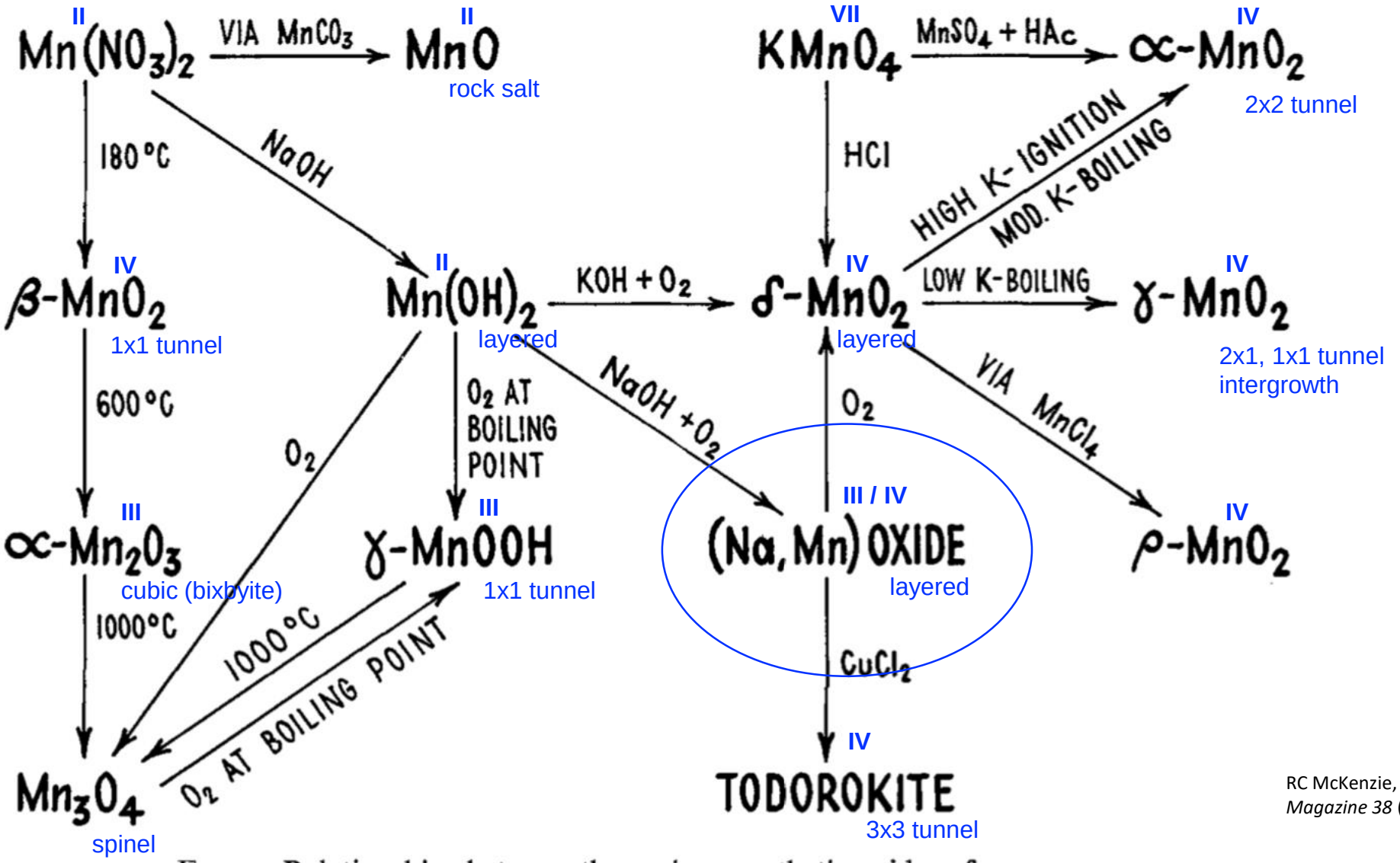
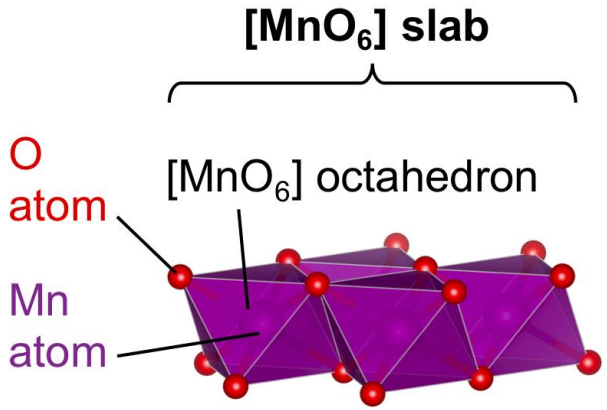
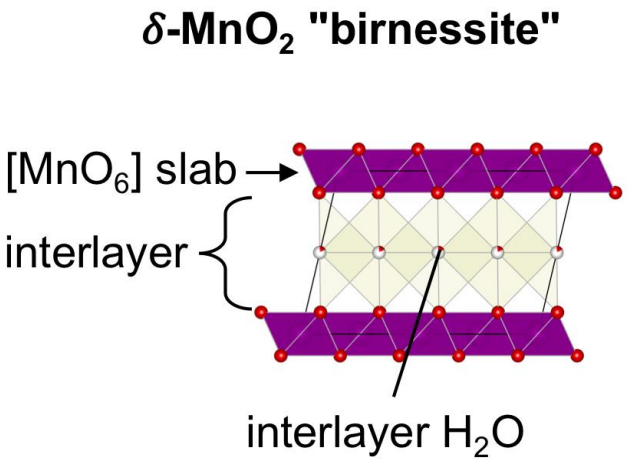


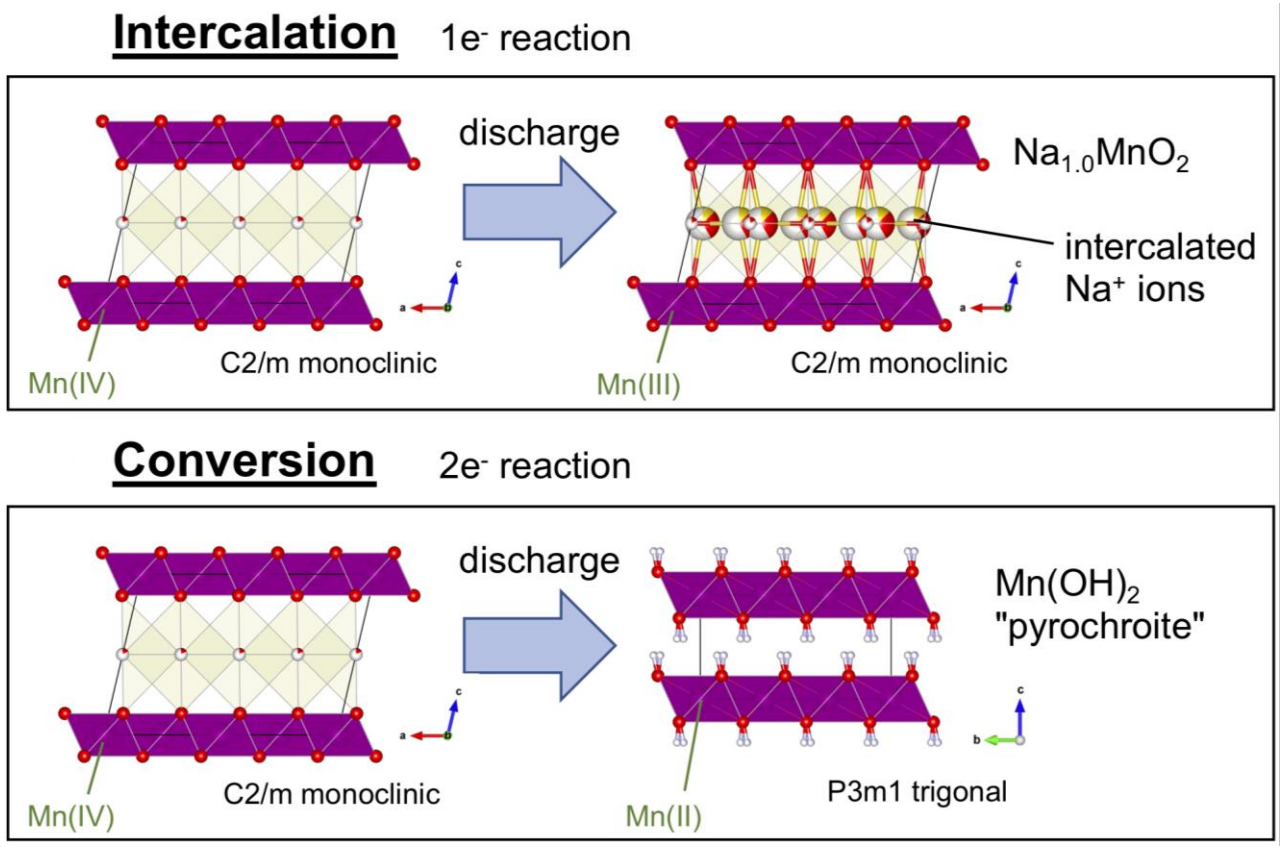
FIG. 2. Relationships between the various synthetic oxides of manganese.

RC McKenzie, *Mineralogical Magazine 38* (1971) 493-502.

Layered δ–MnO_2 "birnessite"







Bi as a dopant, used to modify the reactions
(Bi is electrochemically active)

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Bismuth Enables the Formation of Disordered Birnessite in Rechargeable Alkaline Batteries

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Dr. Andrea Bruck

The Role of Bi Doping: Disordered Birnessite

Operando Experiments: Alkaline MnO_2 Cycling

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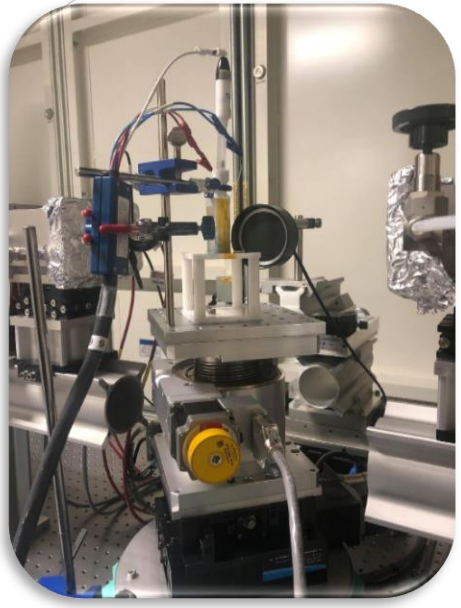
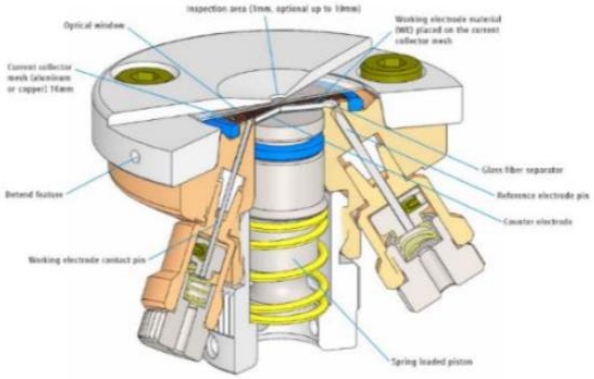


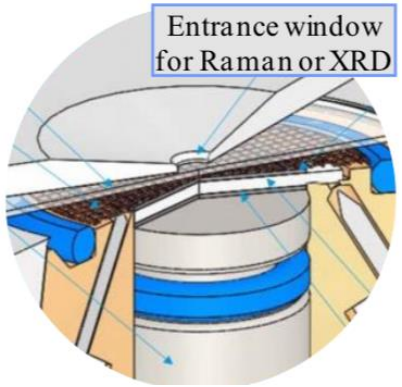
Goal: rationally engineer the Bi + MnO_2 system

Unknown: mechanism of action for Bi

Approach: begin with a synthesized K-birn physically mixed with Bi_2O_3

Method: *operando* X-ray diffraction, X-ray spectroscopy, and Raman spectroscopy





Synthesized K-birnessite

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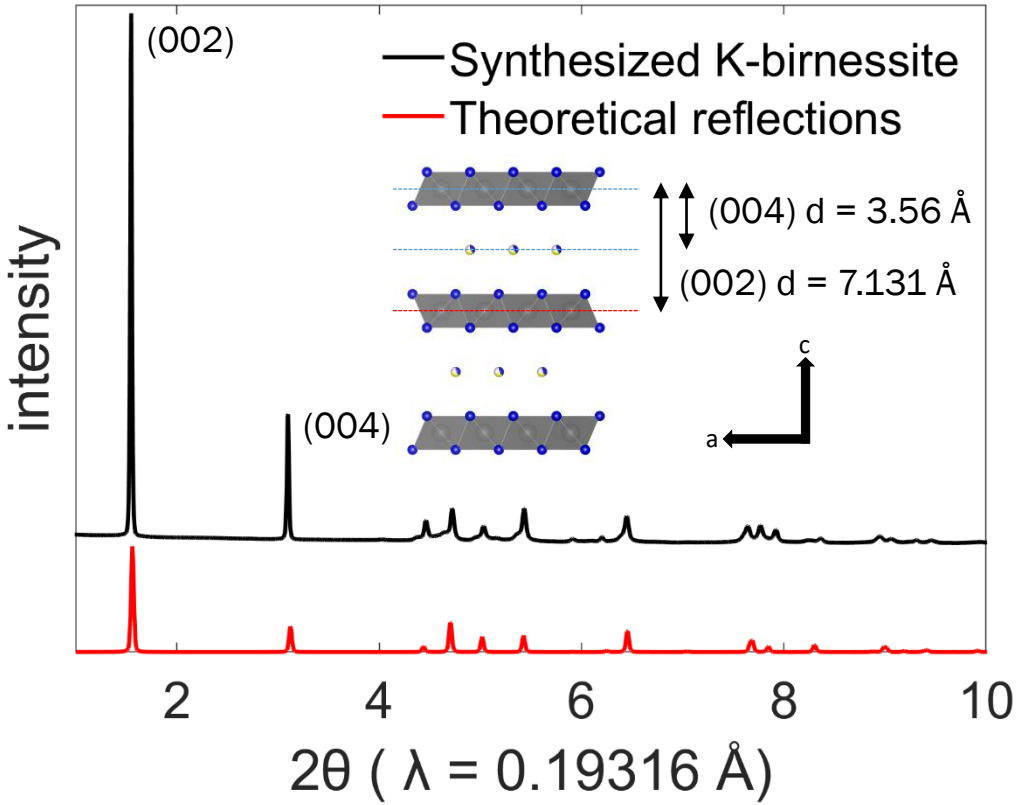
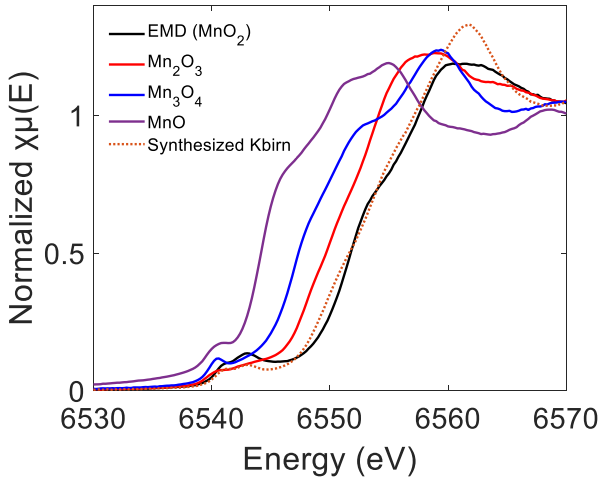
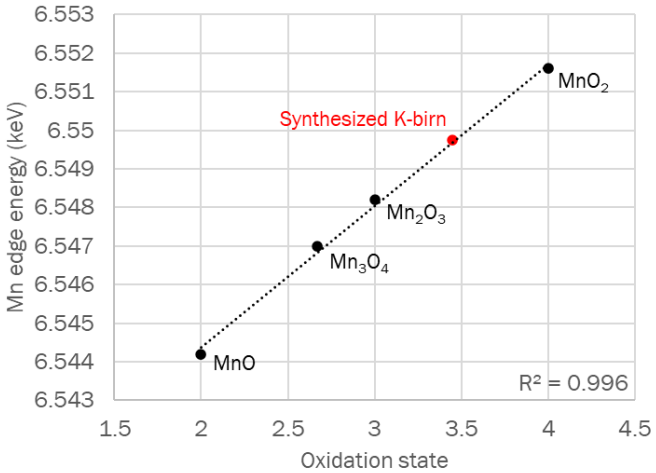
XRD



Confirmed hexagonal $P6_3/mmc$ symmetry

XANES

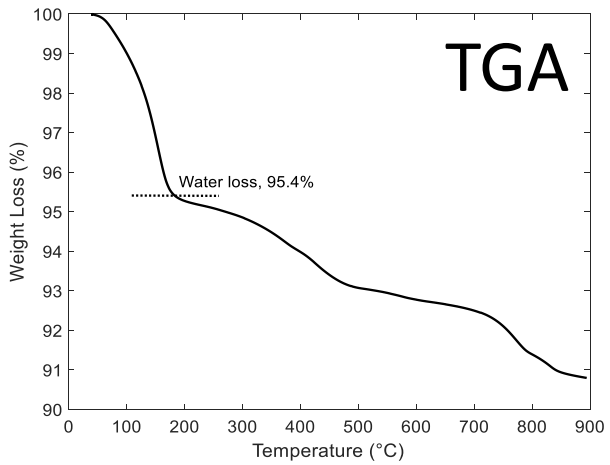




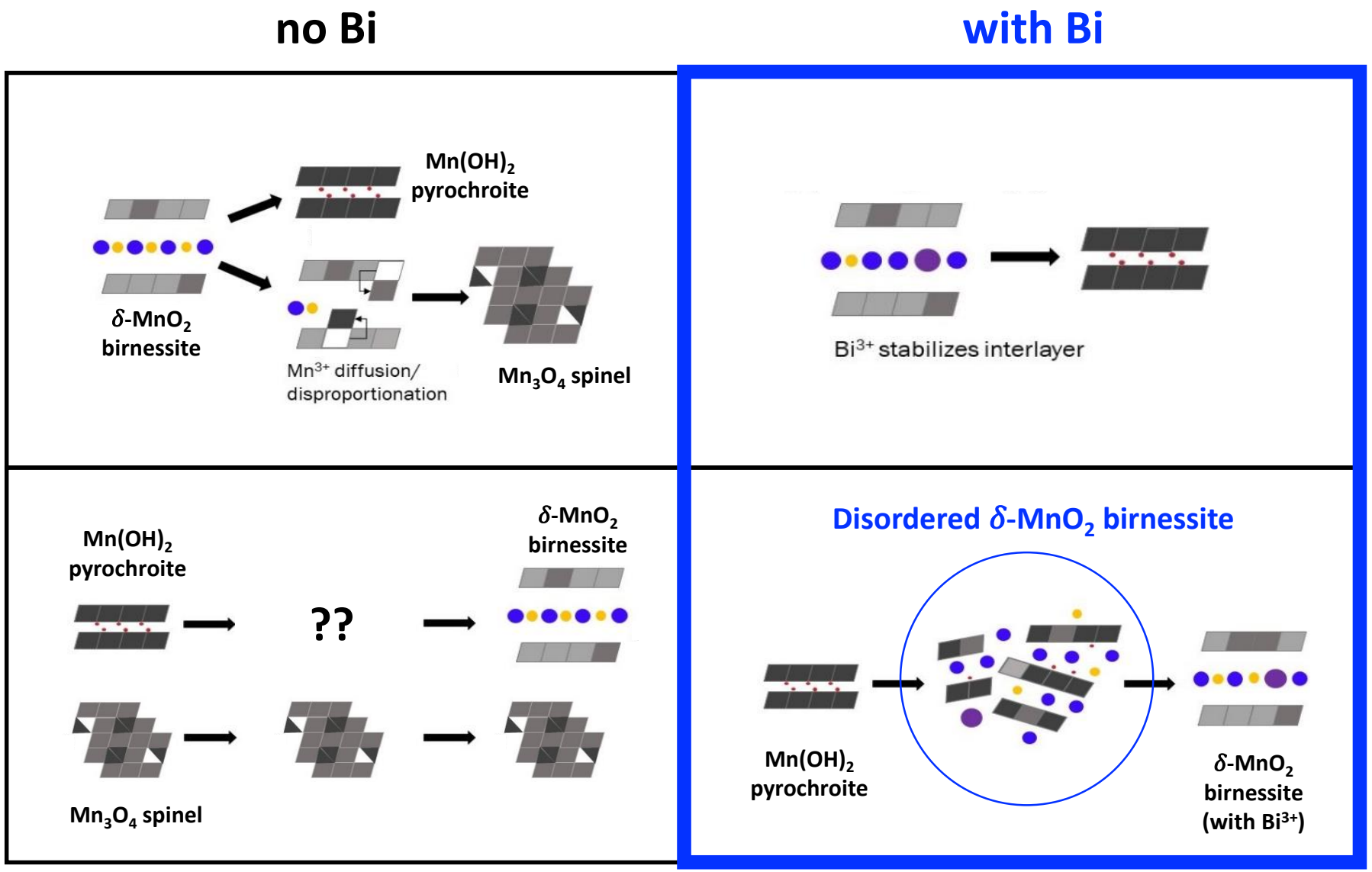
$K_{0.22}MnO_2 \bullet 0.26\ H_2O$

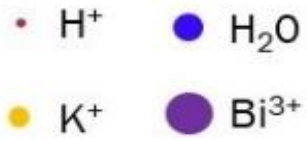
476 mAh/g

1.78 e^- equivalents



Mechanistic Findings of this Investigation

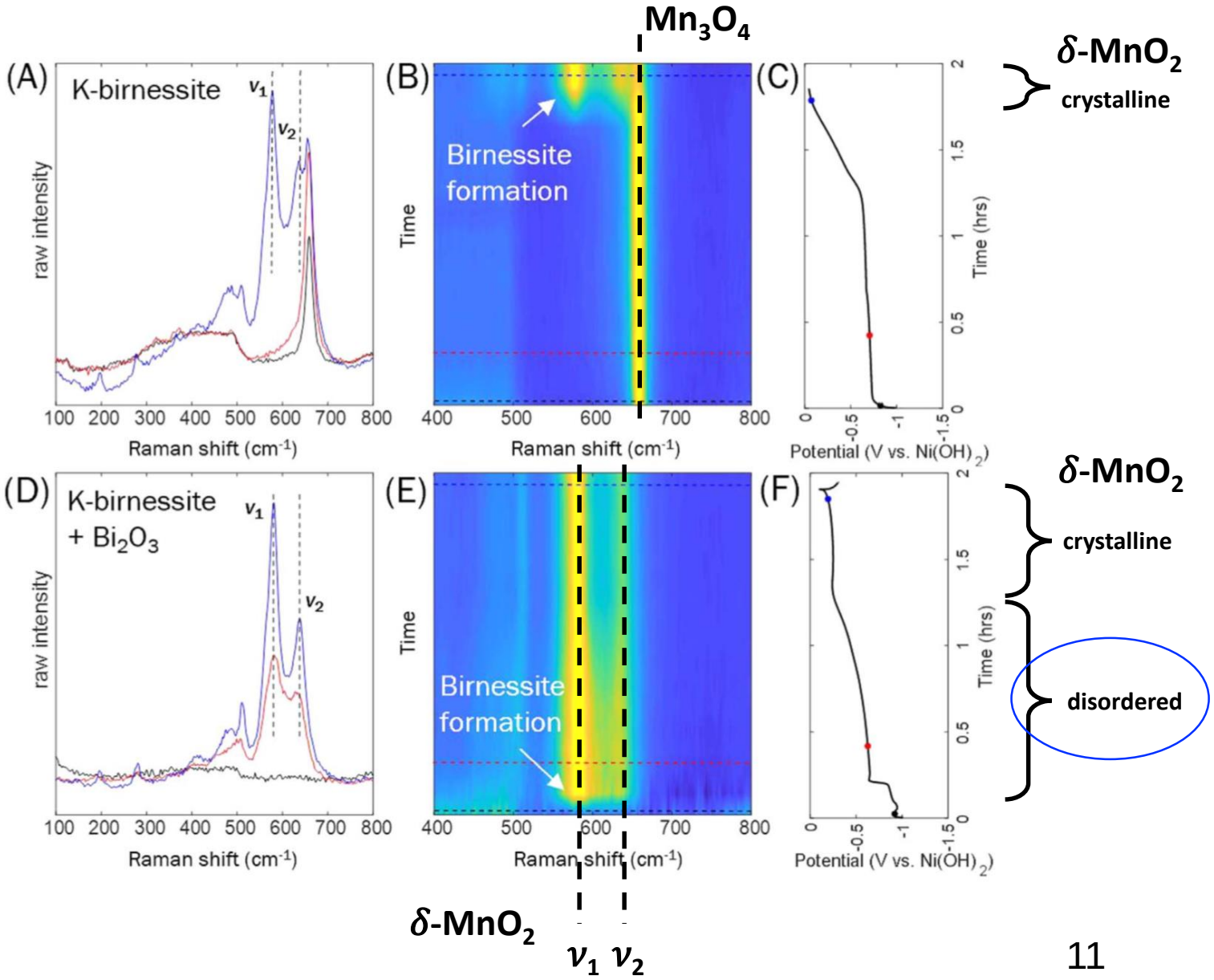




Operando Raman Spectroscopy

- In K-birnessite electrode, a peak at 659 cm^{-1} indicates the Mn_3O_4 phase present at the beginning of discharge and throughout charge
- Birnessite forms on second plateau with Bi_2O_3 present
- This **birnessite we consider the disordered phase** because it was not detectable via diffraction and is consistent with a H_2O rich interlayer.

Chen D., Ding D., Li X., Waller G. H., Xiong X., El-Sayed M. A. and Liu M. 2015 *Chem. Mater.* **27** 6608



Redox Activity from Operando XANES

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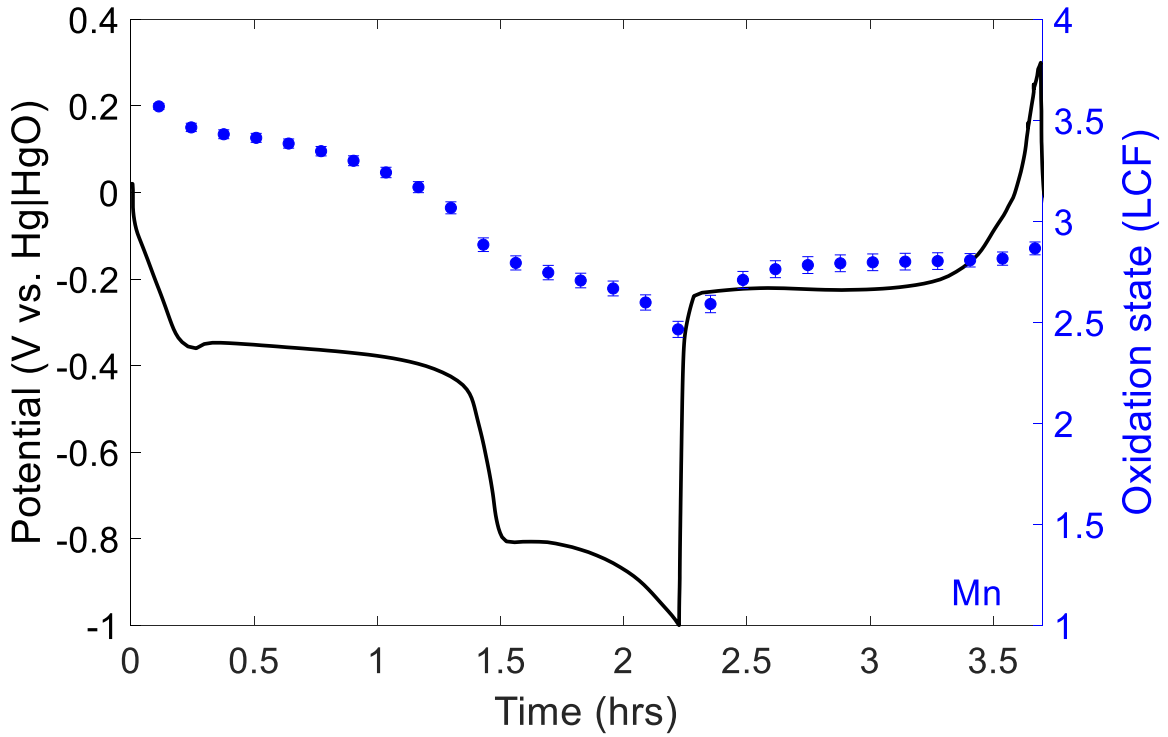
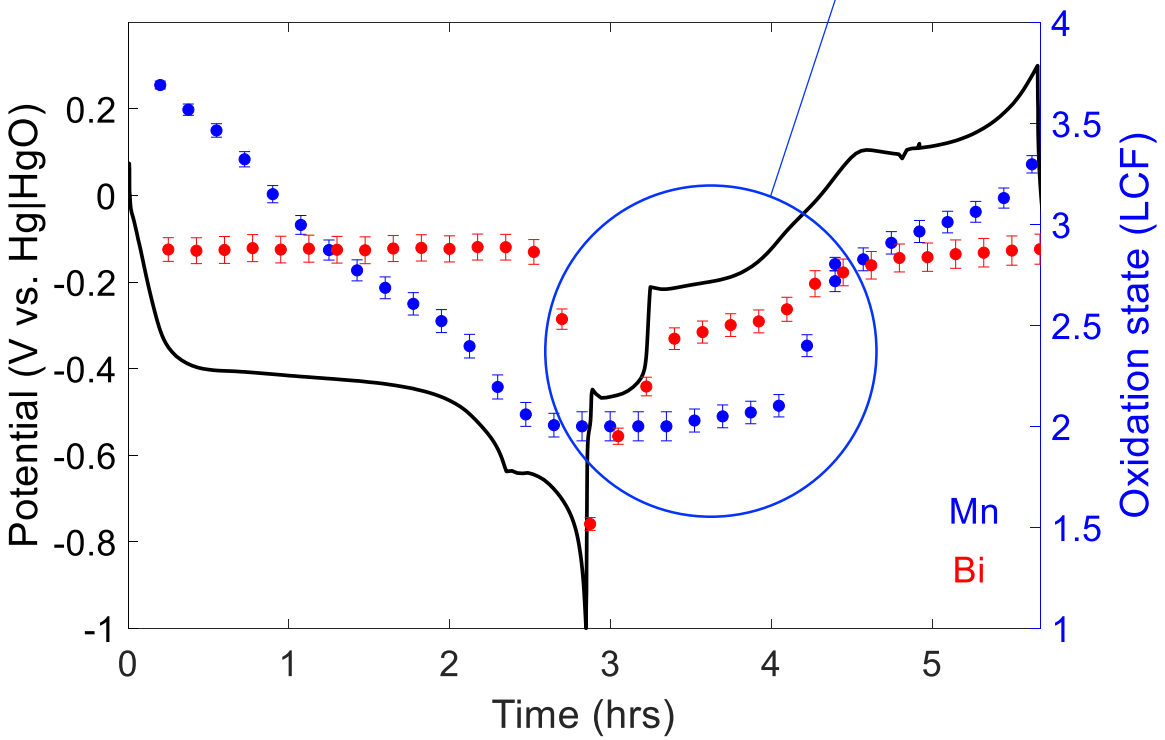
K-birnessite



K-birnessite + Bi_2O_3

Both **Mn** and **Bi** electrochemistry observed here



Mechanistic Conclusions

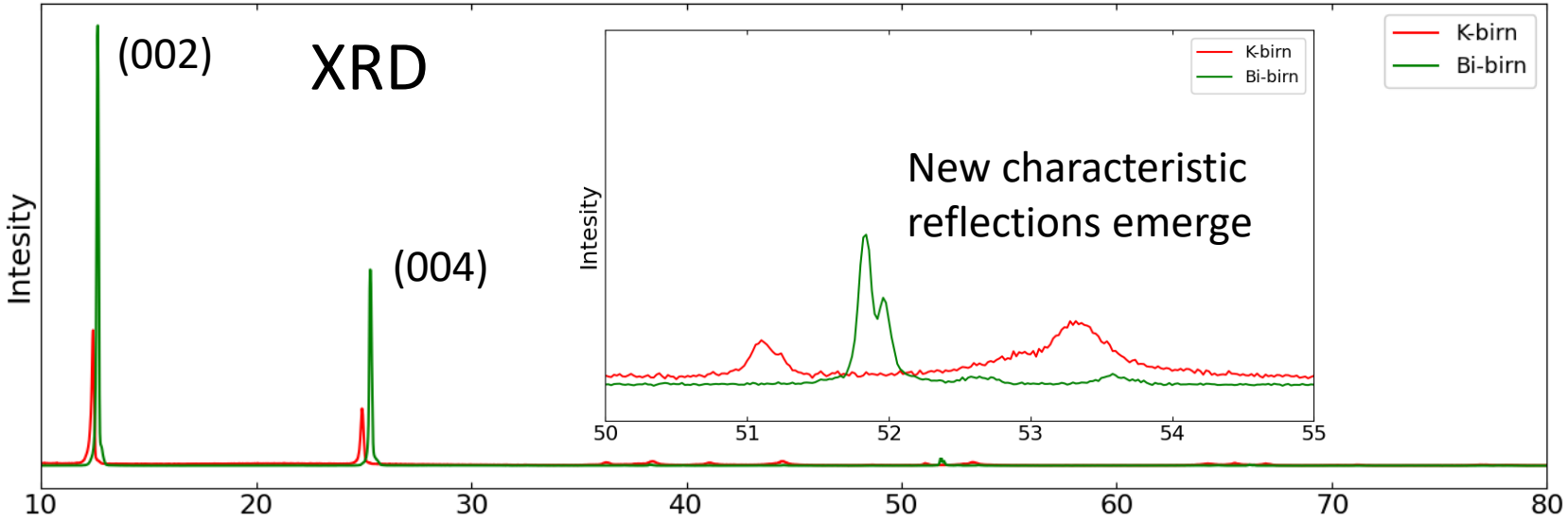
1. We detected a disordered δ-MnO_2 during charge
   - This is enabled by Bi^{3+}
   - Bi^{3+} is often hypothesized to "pillar" layered structures during discharge
   - We hypothesize: Bi^{3+} templates or otherwise guides formation of the layered birnessite structure during charge.

2. Operando EXAFS shows unknown Bi species
   - We are working to identify the dynamic Bi species in alkaline systems
   - May be general in both the MnO_2 (CCNY) and CuO (SNL) systems

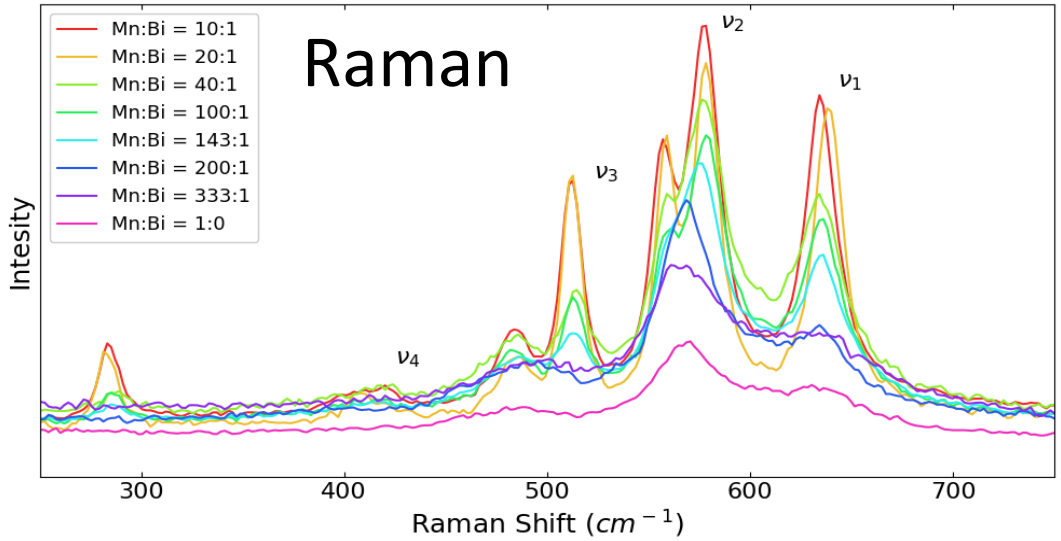
Synthesis of Doped Birnessites δ-$(A_x,B_y)MnO_2$

Matthew Kim

Crystalline δ-$(K_x,Bi_y)MnO_2$ "Bi-birn"



A shift to smaller 2θ indicates a contraction of the interlayer spacing to 7.0 Å with Bi.



Varying Mn:Bi from 10:1 to 333:1

Evolution of vibrational bands allows a way to characterize the material structure

Synthetic Conclusions

1. We have made doped birnessite δ-(A_x,B_y)MnO_2 with high tunability
   - Multiple dopants were introduced
   - Crystallinity was also controlled
   - Crystalline Bi-birnessite was obtained for the first time to our knowledge

2. Highly crystalline material simplifies structural characterization
   - **Ongoing work:** What are structure-function relationships in:
     - alkaline systems (H^+ charge carrier)
     - non-aqueous systems (Li-ion, beyond Li-ion)

Thank you

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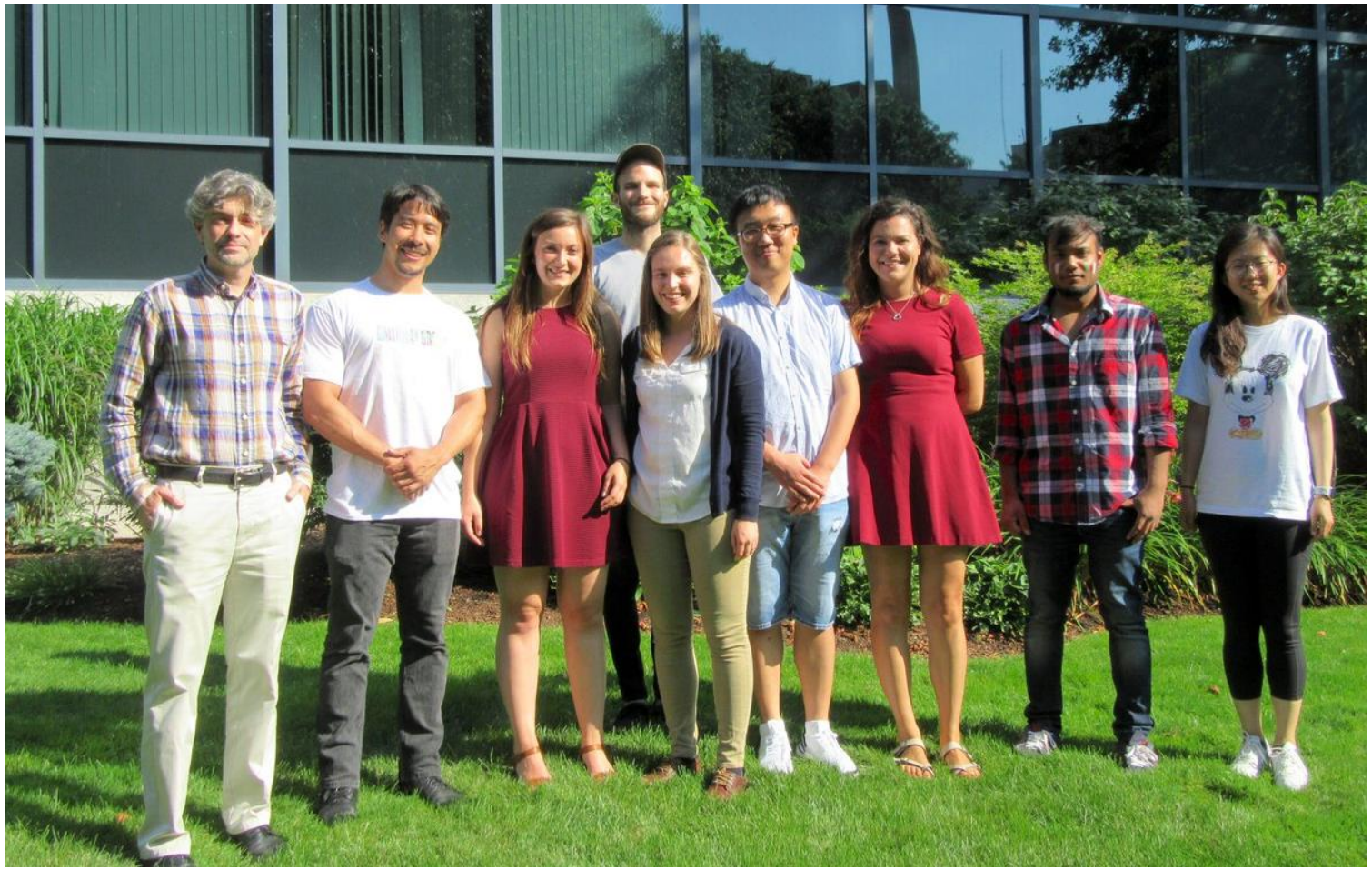

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