Engineering Rechargeability in MnO$_2$ Cathodes for low-cost and safe batteries

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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

Our group's work is on improvement of the MnO$_2$ cathode.
Additives enable rechargeability

**MDB**: MnO\(_2\) + Bi\(_2\)O\(_3\)  
Ford Motor Company, 1980s

**MDBC**: MnO\(_2\) + Bi\(_2\)O\(_3\) + Cu  
City College of New York (CCNY), 2017

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

~617 mAh/g (100% DOD)

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Additives enable rechargeability

- Bi\(_2\)O\(_3\) allows MnO\(_2\) to recharge
- Addition of Cu allows this to reach high cycle life at high mass loading.
However: Challenges remain for implementation

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.

Our goal is to solve #1 in order to engineer a solution to #2 and #3
Proposed mechanism of MnO$_2$ cycling with Bi

\[ \delta-(K_xBi_y)\text{MnO}_2 \cdot w\text{H}_2\text{O} \]

**Bi cation pillars**

**Proton insertion stage**

First electron

**Conversion stage**

Second electron

**Equation:**

\[ \delta\text{-MnO}_2 + 2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{Mn(OH)}_2 + 2\text{OH}^- \]
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 $[\text{Bi(H}_2\text{O)}_n]^{3+}$ species
- Remain as a coordinated $[\text{BiO}_x]$ 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

### Task 2: Reversible Intercalation in $\text{MnO}_2$ 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
- **2.5**: Li-ion Battery Operando X-ray Diffraction
- **2.6**: Solid Electrolyte Li-ion Battery
- **2.7**: Beyond Li-ion Cycling

**Complete in 2021**

### Task 3: The effect of Bi in aqueous $\text{MnO}_2$ systems

- **3.1**: Crystal structure changes during $\text{MnO}_2$ cycling in a wide range of d-spacings
- **3.2**: $\text{MnO}_2$ operando spectroscopy
- **3.3**: $\text{MnO}_2$ structure modeling

**Complete in 2021**

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

- **4.1**: Operando EDXRD
- **4.2**: Operando X-ray spectroscopy

**Complete in 2021**

### Remaining Tasks are for 2022

**Accomplishments**
Task 2: Reversible intercalation in $\text{MnO}_2$ in non-aqueous systems
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

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 $\delta$-MnO$_2$ target material**

$\delta$-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.

**$\delta$-MnO$_2$ can be synthesized several ways**

<table>
<thead>
<tr>
<th>Crystallinity</th>
<th>Interlayer Cations (A)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disordered</td>
<td>K$^+$</td>
<td>Wet synthesis from Mn salts</td>
</tr>
<tr>
<td>Crystalline</td>
<td>Mg$^{2+}$</td>
<td>Autoclaved Mg(MnO$_2$)$_2$</td>
</tr>
<tr>
<td>Crystalline</td>
<td>K$^+$</td>
<td>Fine powder KMnO$_4$ heated</td>
</tr>
<tr>
<td>Crystalline</td>
<td>K$^+$ and Bi$^{3+}$</td>
<td>Fine powder KMnO$_4$ + Bi(NO$_3$)$_3$ heated</td>
</tr>
<tr>
<td>Disordered</td>
<td>K$^+$ and Cu$^{1+}$</td>
<td>Cation salt inserted in birnessite</td>
</tr>
<tr>
<td>Crystalline</td>
<td>K$^+$ and Mg$^{2+}$</td>
<td></td>
</tr>
<tr>
<td>Crystalline</td>
<td>K$^+$ and Bi$^{3+*}$</td>
<td></td>
</tr>
</tbody>
</table>

We tried many methods to produce $\delta$-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.

**Cation pillar**

Bi$^{3+}$ must help hold the layers together, without hindering Li$^+$ transport.
Doped $\delta$-(K$_x$Bi$_y$)MnO$_2$ $\cdot$ wH$_2$O

Chemical formula of (K$_x$Bi$_y$)MnO$_2$ $\cdot$ wH$_2$O

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>w</th>
<th>Chemical formula</th>
<th>Molar mass (excluding H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.377</td>
<td>0.156</td>
<td>0.56</td>
<td>K$<em>{0.377}$Bi$</em>{0.156}$MnO$_2$</td>
<td>134.18 g/mol</td>
</tr>
<tr>
<td>0.404</td>
<td>0.084</td>
<td>0.53</td>
<td>K$<em>{0.404}$Bi$</em>{0.084}$MnO$_2$</td>
<td>120.31 g/mol</td>
</tr>
<tr>
<td>0.384</td>
<td>0.043</td>
<td>0.52</td>
<td>K$<em>{0.384}$Bi$</em>{0.043}$MnO$_2$</td>
<td>110.87 g/mol</td>
</tr>
<tr>
<td>0.365</td>
<td>0.018</td>
<td>0.52</td>
<td>K$<em>{0.365}$Bi$</em>{0.018}$MnO$_2$</td>
<td>104.97 g/mol</td>
</tr>
<tr>
<td>0.332</td>
<td>0.013</td>
<td>0.40</td>
<td>K$<em>{0.332}$Bi$</em>{0.013}$MnO$_2$</td>
<td>102.63 g/mol</td>
</tr>
<tr>
<td>0.315</td>
<td>0.01</td>
<td>0.53</td>
<td>K$<em>{0.315}$Bi$</em>{0.010}$MnO$_2$</td>
<td>101.29 g/mol</td>
</tr>
<tr>
<td>0.315</td>
<td>0.006</td>
<td>0.46</td>
<td>K$<em>{0.315}$Bi$</em>{0.006}$MnO$_2$</td>
<td>100.58 g/mol</td>
</tr>
<tr>
<td>0.306</td>
<td>0.002</td>
<td>0.26</td>
<td>K$<em>{0.306}$Bi$</em>{0.002}$MnO$_2$</td>
<td>99.36 g/mol</td>
</tr>
<tr>
<td>0.308</td>
<td>0.0</td>
<td>0.26</td>
<td>K$_{0.308}$MnO$_2$</td>
<td>98.97 g/mol</td>
</tr>
</tbody>
</table>

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

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.
Li-ion battery cycling with Bi-pillared MnO$_2$

Cycling results show that Bi$^{3+}$ successfully stabilizes the material.

It is possible that Bi$^{3+}$ stabilizes the material by preventing conversion to LiMn$_2$O$_4$ spinel.

This is the most favorable stabilization of layered MnO$_2$ reported, to our knowledge.
**Material characterization of \((K_xBi_y)\text{-MnO}_2\)**

**XRD results of \((K_xBi_y)\text{-MnO}_2\) at various values of \(y\).**

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

![XRD graphs showing intensity vs. 2θ for \((K_xBi_y)\text{-MnO}_2\) at various \(y\) values](image)

**Raman results of \((K_xBi_y)\text{-MnO}_2\) at various values of \(y\)**

![Raman spectra showing intensity vs. Raman shift for \((K_xBi_y)\text{-MnO}_2\) at various \(y\) values](image)

**Morphology of \((K_xBi_y)\text{-MnO}_2\) at various values of \(y\)**

![Morphology images showing particle width and morphological changes for \((K_xBi_y)\text{-MnO}_2\) at various \(y\) values](image)

**EDS of \((K_xBi_y)\text{-MnO}_2\) at various values of \(y\)**

![EDS images showing elemental distribution for \((K_xBi_y)\text{-MnO}_2\) at various \(y\) values](image)
Poster: Goulart J, Guida D, and Gallaway JW, "Operando characterization of rechargeable alkaline batteries for grid scale storage."

Task 3: The effect of Bi in aqueous MnO$_2$ systems
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.
Task 3.2 data collected at NSLS-II

- Operando Quick Extended X-ray absorption fine structure (QEXAFS)
- Atomic positions around Bi atoms
- Conducting data analysis currently
- Also operando Raman underway
Task 4: Structural effect of Bi doping in alkaline CuO batteries
Rechargeable Zn|(CuO–Bi₂O₃) batteries
2-electron cathode

Operando energy dispersive X-ray diffraction (EDXRD)

No Bi

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

With Bi

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