Cheap, Abundant & Safe Materials =

Advanced Zinc-Manganese Oxide Alkaline Batteries

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Timothy N. Lambert
Sandia National Laboratories
Grid Energy Storage

Need:
Safe, reliable, **low-cost** electrochemical storage

**Alkaline Zn/MnO₂ Batteries**

- **Cost**
  - Traditional primary batteries - $18 per kWh
  - Low-cost materials and manufacturing
  - Established supply chain

- **Safety**
  - Aqueous chemistry
  - Non-flammable
  - EPA certified for landfill disposal

- **Reliability**
  - Long shelf-life
  - Limited thermal management required

*Reversibility and Cycle life are the Challenges*
Toward Low Cost/High Volumetric Energy Storage

1. Support Limited Depth-of-Discharge Efforts
2. Develop Higher Capacity Batteries
Alkaline Zn/MnO$_2$ Batteries

**Issues to be addressed**

**Cathode:**
- Irreversibility of Cathode
- Susceptibility to Zinc poisoning

**Separator:**
- Zincate crossover

**Anode:**
- Shape Change
- Dendrite Growth
- Irreversible ZnO Passivation

*Limiting Depth of Discharge has been shown to be a viable approach*


*Full 2e$^-$ can be stabilized but is still susceptible to zinc poisoning*

The Team

Dr. Timothy Lambert
Dr. Jonathon Duay
Maria Kelly
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Dr. Eric Allcorn

(CINT)
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Prof. Robert Messinger
Dr. Gautum Yadav
Michael D’Ambrose
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Dr. Damon Turney
Michael Nyce
Snehal Kohlekar
Jinchao Huang

Also leveraging SNL-LDRD and CINT Proposal
Summary for Project

FY 17 Accomplishments

1. Comprehensive study of electrolyte additive on limited DOD Zn/MnO₂ batteries: Extend battery lifetime by ~ 300%
2. Developed new assay to determine zincate diffusion constants for separators
3. Examined use of zincate impermeable ceramic separator for limited DOD Zn/MnO₂ Batteries
4. Analysis of zinc cycle life: Increased DOD on zinc anode: > 500 cycles@15% DOD
5. Examined effect of charging protocols on Zn/MnO₂ cycle life
6. Development of a model describing the behavior of γ-MnO₂ in shallow-cycled Zn/MnO₂ batteries
7. Development of improved zincate blocking separators

Manuscripts

2. J. Duay, M. Kelly and T. N. Lambert “Effect of triethanolamine on rechargeable Zn/MnO₂ alkaline batteries under reduced depth of discharge conditions” manuscript submitted.

Presentations


Other

1. “Understanding the electrochemical processes in alkaline Zn-MnO₂ batteries” CINT User Proposal accepted.
Anode

Shape Change

Dendrite Growth

Improved Anode DOD @ CUNY-EI

Irreversible ZnO Passivation


Theoretical Study of H Trapping by $\gamma$-MnO$_2$

**Research Objectives**

- Develop a model describing the behavior of $\gamma$-MnO$_2$ in shallow-cycled Zn/MnO$_2$ batteries.
- Examine structural changes occurring in $\gamma$-MnO$_2$ during the initial discharge reaction.
- Investigate the mechanism of formation of the $\alpha$-MnOOH phase.
- Study the influence of DOD and the cycle life of rechargeable Zn/MnO$_2$ batteries.

**Computational Methods**

- Quantum ESPRESSO* plane wave electronic structure code
- Density functional theory + ultra-soft pseudopotentials
- Revised generalized gradient approximation (PBEsol)

* http://www.quantum-espresso.org

Discharge reaction in the $\gamma$-MnO$_2$ cathode:

$$\text{MnO}_2 + x\text{H}_2\text{O} + xe^- \rightarrow \text{MnO}_{2-x}(\text{OH})_x + x\text{OH}^-$$

I. Vasiliev et al. “Ab initio studies of proton insertion in shallow-cycled gamma-MnO$_2$” manuscript in preparation.
Theoretical Study of H Trapping by $\gamma$-MnO$_2$

Calculated Lowest Energy Structures of MnO$_{2-x}$(OH)$_x$ for 0 ≤ x ≤ 1

- Protonation produces significant structural distortions in $\gamma$-MnO$_2$.
- Energy of H-insertion is lower for 2x1 R-MnO$_2$ tunnels than for 1x1 $\beta$-MnO$_2$ tunnels.
- Protonation is carried out in three stages: (1) 1 H atom is inserted in each 2x1 tunnel, (2) 2 H atoms are inserted in each 2x1 tunnel, (3) 1 H atom is inserted in each 1x1 tunnel.

I. Vasiliev et al. “Ab initio studies of proton insertion in shallow-cycled gamma-MnO$_2$” manuscript in preparation.
Theoretical Study of H Trapping by $\gamma$-MnO$_2$

- Binding energy per H atom decreases significantly with increasing DOD.
- Volume of protonated $\gamma$-MnO$_2$ phase increases nonlinearity with increasing DOD.
- Initially, inserted protons occupy 2x1 tunnels of $\gamma$-MnO$_2$ producing $\alpha$-MnOOH.
- Protonation of 1x1 tunnels leads to structural breakdown of MnO$_2$-$x$(OH)$_x$.
- Battery life cycle can be extended by limiting protonation to 1 H atom per 2x1 tunnel.

I. Vasiliev et al. “Ab initio studies of proton insertion in shallow-cycled gamma-MnO$_2$” manuscript in preparation.
TEA additive in limited DOD Zn/MnO$_2$

- Triethanolamine reported to complex with Mn$^{3+}$ and Mn$^{2+}$ in alkaline
- Previously examined for full 1e- and 2e- discharges
- Thought to impact only second e-

\[ \text{C Rate} = \frac{\text{Current (A)}}{\text{Rated Capacity (Ah)}} \]

\[ \sim 130 \text{ mAh (MnO}_2\text{)} \text{ cell, 10\%DOD, C/5 discharge rate} \]

J. Duay et al. “Effect of triethanolamine on rechargeable Zn/MnO$_2$ alkaline batteries under reduced depth of discharge conditions” manuscript submitted.
Need for Selective Separators

- Research by Ford in the 1980s showed that the MnO$_2$ cathode could be stabilized at low loadings in the absence of Zinc
- New stabilized 2e- cathodes are 100% reversible in the absence of Zinc

**Imperative need for zinate blocking separators**
**Separators – Ceramic Separator**

**Battery Assembly Schematic**

**NaSICON**

2.54 cm

**NaSuper Ionic CONductor**

\[ \text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}, \ 0 < x < 3 \]

NaSICON purchased from Ceramatec

**SEM/EDS analysis after cycling**

<table>
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<tr>
<th>Element</th>
<th>Atomic %</th>
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<tr>
<td>Au K</td>
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<tr>
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<td>Zn K</td>
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**Zinc-Based Particles**

**Ceramic Separators in NaOH electrolyte are viable at low rates**

**Graph**

- **Celgard + Cellophane Separator**
- **0.5 mm NaSICON Separator**
- **1.0 mm NaSICON Separator**

- **Discharge End Voltage**
- **Cycle Number**

J. Duay et al. manuscript in preparation.
Method utilizes Anodic Stripping Voltammetry

**Oxidation/Cleaning of Electrode**

- **ZnO**
  - \( \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \)

- **PbO**
  - \( \text{PbO(s)} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{Pb(OH)}_3^- \)

- **CdO**
  - \( \text{CdO(s)} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{Cd(OH)}_3^- \)

- **Bi\(_2\)O\(_3\)**
  - \( \text{Bi}_2\text{O}_3\text{(s)} + 3\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Bi(OH)}_4^- \)

**Plating/Accumulation of Metal**

**Oxidation/Stripping of Metal**

Semi-quantitative limits of detection (LOD): ppb levels

Selective - different metals are resolved by their stripping/oxidation potential

**Method utilizes hydroxide complexation/solubility**

- Sensitive
- Selective

First ever ASV method for zinc in alkaline

Special thanks to Eric Allecorn for help in designing and printing

http://www.porexfiltration.com/learning-center/technology/precipitation-microfiltration/

Separators

- Compares favorably vs. ICP and Complexometric methods
- Faster experiment times, very reproducible, low limit of detection
- First demonstration of ASV measurement of Zinc in alkaline
- Will allow for rapid screening of newly developed membranes

Summary for Project

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**Presentations**


**Other**

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Advanced Zn-MnO$_2$ Alkaline Batteries

**FY 18 Path Forward**
1. Establish method for *in situ* Raman spectroscopic interrogation of Zn/MnO$_2$ cells
2. Develop optimized Zn anode with increased depth-of-discharge and cycle lifetime
3. Advanced separator development
4. Examine 2e- discharge of MnO$_2$ using zincate blocking membrane
5. Finish *ab initio* (DFT) model of hydrogen trapping by gamma-MnO$_2$ in shallow-cycled MnO$_2$ electrodes

**Acknowledgements**
Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability is thanked for his financial support of this project.

**Team Members**

<table>
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<tr>
<th>SNL</th>
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<th>NMSU</th>
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Zn-MnO$_2$ Batteries for Grid Storage

Opportunity exists to Increase Capacity and Decrease Costs

Toward Low Cost/High Volumetric Energy Storage

1. Support Limited Depth-of-Discharge Efforts
2. Develop Higher Capacity Batteries

The end

Thank you
Battery Fabrication

- COTS materials
- 10 vol% TEA added to electrolyte
- 3D printed cells with pressure relief valve
- Cathode-limited cells (< 1.5% DOD on Zn)
- ~ 200 mAh capacity

Cycling Protocol

DOD controlled by time and C-rate

1. Constant current charge
2. Constant voltage charge
3. Rest step
4. Constant current discharge
5. Rest step

\[ M \times T \times C = \text{Discharge Current} \]

M: Mass of Active Material (g)
T: Theoretical Capacity of Material (mAh/g)
C: C-rate (h\(^{-1}\))
Low DOD discharge is viable technology

\[ \text{Zn} \quad \text{MnO}_2 \]

\[
\begin{align*}
2 \text{e}^- &= 820 \text{ mAh/g} \\
2 \text{e}^- &= 616 \text{ mAh/g} \\
1 \text{e}^- &= 308 \text{ mAh/g}
\end{align*}
\]

- Limited DOD provides for highly reversible system
- 2013 Urban Electric Power startup in NYC
- $100 – 150 /kWh

http://www.urbanelectricpower.com

Opportunity exists to drastically increase capacity
Limited DOD Cycling

Reversibility can be maintained when only a fraction of the first e\textsuperscript{-} step is cycled.

\[ \gamma-\text{Mn}^{IV}O_2 \]

Ramsdellite-like (2x1 channels)
Pyrolusite intergrowths (1x1 channels)

\[ \alpha-\text{Mn}^{III}OOH \]

Volume expansion
\[ \text{Mn}^{3+} (0.645 \text{ Å}) > \text{Mn}^{4+} (0.530 \text{ Å}) \]

\[ \text{Formation of undesirable phases from soluble Mn}^{3+} \]

\[ \text{Mn}_3\text{O}_4 \]
\[ \text{ZnMn}_2\text{O}_4 \]
\[ \text{Mn}_2\text{O}_3 \]
\[ \text{Mn(OH)}_2 \]

Cathode issues
- Only 5-10% of total capacity
- Crystal Structure Breakdown
- Inactive Phase(s) formed
- Zinc poisoning

Anode issues
- < 10% of total capacity
- Shape Changes
- Passivation
- Dendrite Formation

- Limited DOD provides for highly reversible system
- 2013 Urban Electric Power startup in NYC
- ~ $100/kWh

- Wh
ALKALINE BATTERY TECHNOLOGY

- Crystal structure breakdown
- Formation of Inactive phases
- Zinc poisoning
- Diffusion of zincate ions
- Shape change
- Passivation
- Dendrite formation

617mAh/g

MnO₂(+)  Zn(-)

820mAh/g

5-10% of total capacity

2-8% of total capacity
Failure Mechanisms of Cathode

1. Instability of Mn(III) resulting in formation of irreversible $\text{Mn}_3\text{O}_4$

2. Zn poisoning forming irreversible $\text{ZnMn}_2\text{O}_4$ (even before 1st full 1 e-)
Stabilized Zn-MnO Battery Development (ARPA-E)

Chemistry relies on formation of a \textit{layered} birnessite MnO$_2$ structure and \textit{stabilizing} this structure for thousands of cycles.

\textbf{Prismatic} battery design for pasted Zn and stabilized MnO

\textbf{Two additives} stabilize this structure: Bi + “A”
Separators

- Compares favorably vs. ICP and Complexometric methods
- Faster experiment times, very reproducible, low limit of detection
- First demonstration of ASV measurement of Zinc in alkaline
- Will allow for rapid screening of newly developed membranes
Anodic Stripping Voltammetry (ASV)

-Historically done on Hg drop electrodes
-Usually done in buffered solutions

Sensitive
-limits of detection (LOD): ppb levels
Selective
-different metals are resolved by their stripping/oxidation potential

ASV with *in situ* Plated Bi Films

-Bi film electrodes increasingly replacing Hg

### Bi film electrodes

- less toxic than Hg
- low sensitivity to dissolved oxygen
- better reproducibility
- no need for electrode conditioning

*Typically done in buffered pH ~4 solutions due to insoluble metal oxides at higher pH levels*

During stripping, the element of interest is stripped from the Bi film.
Alkaline Aqueous Chemistry (pH>14)

Insoluble metal oxides become soluble by hydroxide complexation

\[
\begin{align*}
\text{ZnO}(s) + \text{H}_2\text{O} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_4^{2-} \\
\text{PbO}(s) + \text{H}_2\text{O} + \text{OH}^- & \rightarrow \text{Pb(OH)}_3^{-} \\
\text{CdO}(s) + \text{H}_2\text{O} + \text{OH}^- & \rightarrow \text{Cd(OH)}_3^{-} \\
\text{Bi}_2\text{O}_3(s) + 3\text{H}_2\text{O} + 2\text{OH}^- & \rightarrow 2\text{Bi(OH)}_4^{-}
\end{align*}
\]

This allows for the opportunity to use ASV to measure metal ion species in highly alkaline environments for the first time.
Zinc stripping peak is only well-defined and Gaussian in the presence of Bi, Cd, and Pb….why?
Zinc ASV Curves for Various Films

Zinc stripping peak is only well-defined and Gaussian in the presence of Bi, Cd, and Pb....why?
Need for all three Cd, Pb, and Bi?

All three have been used as **additives in battery grade Zn** where ‘plating’ and ‘stripping’ of Zn is necessary.

Cadmium (Cd)
- increases hydrogen overpotential
- known to alloy with Zn

Lead (Pb)
- increases hydrogen overpotential
- known as alternative ASV film to Bi

Bismuth (Bi)
- increases hydrogen overpotential
Need for Selective Separators

Zinc Anode  \( \text{Zn(OH)}_4^{2-} \)  \( > 6 \text{M KOH} \)  MnO\(_2\) Cathode

MnO\(_2\) Cathode After Cycling

Fig. 5. Effect of the introduction of zinc on capacity retention of modified MnO\(_2\) electrodes: 1) chemically modified electrode; 2) physically modified electrode; 3) physically modified electrode in 9M KOH + 0.1M Zn(OH)\(_4\)^{2-}.

- Research by Ford in the 1980s showed that the MnO\(_2\) cathode could be stabilized at low loadings \textit{in the absence of Zinc}
- New stabilized 2e- cathodes are 100% reversible \textit{in the absence of Zinc}

\textit{Imperative need for zinctate blocking separators}
Separators – Analysis Method?

ICP Metal ion analysis

- Inductively Coupled Plasma – Mass Spectrometer
- Perkin-Elmer
- Time intensive
- Lots of glassware
- Requires acidic solutions (2% HNO₃)
- Requires total dissolved solids <0.2%
- Huge dilution >300X
- Expensive bulky equipment

Complexometric Titrations

- UV/Vis Spectrometer
- Difficult Endpoint Determination
- Requires pH ≤ 11
- Use of ammonium buffer
- Dilution >20X
- Ppm limits of detection
CUNY Battery Research Timeline

- **Flow-Assisted Ni-Zn Battery:**
  - UEP Power Battery, 30 kWh String, 100 kWh Installation (NYSERDA, DOE NETL)

- **Ni-Zn Vehicle Battery:**
  - (NYSERDA)

- **Shallow-Cycled Zn-MnO\textsubscript{2} Battery:**
  - UEP Production Product. <$100/kWh cost, >4000 cycles, Cathode based on 60 mAh/g-MnO\textsubscript{2} (ARPA-E)

- **Stabilized Zn-MnO Battery:**
  - Bismuth-stabilized birnessite concept realized with novel chemistry discovery. (ARPA-E)
  - Focuses on Energy density (Wh/L). Targets <$50/kWh cost, >500 cycles, 180 Wh/L.
  - Cathode based on 600 mAh/g-MnO\textsubscript{2} (NYSERDA)

- **Flow-Assisted Zn Anode**

- **Pasted Zn Anode**

- **NiOOH Cathode**

- **Shallow-Cycled MnO\textsubscript{2} Cathode**

- **Stabilized MnO\textsubscript{2} Cathode** (Birnessite, Full-Cycle)
DEVELOPMENT OF Zn-MnO₂ BATTERY

**1866**
1st MnO₂-Zn battery

**1950**
Alkaline MnO₂-Zn battery

**1970**
5% Rechargeable Capacity

**1980**
60-80% Rechargeable Capacity

**2010-2016**
- 2010-2014: ARPA-E Support of CUNY shallow-cycle MnO₂
- 2014-2016: ARPA-E support of CUNY stabilized full-cycling MnO₂

**Primary**
- Low Power

**Limited Capacity**
- Poor Energy Density

**Potentiodynamic**
- Poor Cycle Life

**Radiology**
- Limited Capacity

**Halina Wroblowa**