Zn-based Batteries

Timothy. N. Lambert, Matthew B. Lim, D. J. Arnot, Igor V. Kolesnichenko, Noah B. Schorr, Rachel L. Habing, Logan S. Ricketts, Elijah I. Ruiz

PRESEN TED BY

Timothy N. Lambert

DOE-OE Peer Review, Virtual Presentation, Albuquerque, New Mexico, September 29 – October 31, 2020

SAND2020-10172
Session OVERVIEW – Zn-based Batteries

OE supports RESEARCH & DEVELOPMENT needs of battery chemistries that could impact Grid Storage: Reliable and resilient electricity system

03:35 - 03:55 PM
Session Summary / Zinc-Based Batteries
Timothy Lambert, SNL

03:55 - 04:10 PM
From Concept Through Product to Market: Rechargeable Zinc Manganese Dioxide Batteries
Sanjoy Banerjee, CCNY

04:10 - 04:25 PM
Engineering an Aqueous Energy Dense Manganese Dioxide | Zinc Battery to Challenge Lithium - Ion’s Dominance
Yadav Gautam, UEP

04:25 - 04:40 PM
Operando Studies to Enumerate the Electrochemical Phase Transformations of MnO₂
Joshua Gallaway, Northeastern University

04:40 - 04:55 PM
Advanced Aqueous Zn Batteries
Xiaolin Li, PNNL

04:55 - 05:10 PM
Mechanistic Probes of Zinc Anode Aqueous Electrolyte Batteries
Esther Takeuchi, Stony Brook University
Alkaline zinc batteries are one of the core DOE/OE technologies for grid storage and feature energy-dense, safe, abundant, low-cost materials.

Alkaline-Zn/MnO₂ Batteries Today

- Well-established supply chain for consumer products
- >10B units produced, $7.5B global market (2019)
- Traditional primary alkaline batteries ~ < $20/kWh
- Aqueous, long shelf life, EPA certified for disposal
- High achievable energy density
  - Zn/MnO₂ ~ 400 Wh/L
  - Zn/Ni ~ 300 Wh/L
  - Zn/Air ~ 1400 Wh/L

Reversibility and Cycle life are the Challenges/Opportunities
**PROJECT TEAM – Sandia National Laboratories and Collaborators**

**Alkaline Batteries for Grid Storage**
Stephen Budy, Igor Kolesnichenko, Matthew Lim, Noah Schorr, David Arnot, Rachel Habing, Logan Ricketts, Elijah Ruiz, Nelson Bell

Timothy Lambert

**Stable Zinc Anodes for High-Energy-Density Rechargeable Aqueous Batteries**
Damon Turney, Michael D’Ambrose, Jungsang Cho, Brendan Hawkins, Jinchao Huang, Snehal Kolhekar, Michael Nyce, Xia Wei, Prof. Rob Messinger

Prof. Sanjoy Banerjee

**Theoretical Studies of the Electrochemical Behavior of Solid-State Cathode Materials in Rechargeable Alkaline Zn/MnO$_2$ and Zn/Cu$_2$S Batteries**
Birendra A. Magar, Nirajan Paudel

Prof. Igor Vasiliev

**Understanding Phase Change Processes of Energy Storage Materials**
Andrea Bruck, Matthew Kim

Prof. Joshua Gallaway

**Advanced Materials for Next Generation Batteries**
Amy Marschilok, Ken Takeuchi

Prof. Esther Takeuchi
PROJECT TEAM – Sandia National Laboratories and Collaborators

Membrane Modeling

Amalie Frischknecht

Advanced Manufacturing Research (FY19/20 Funding)
Advanced Manufacturing Research - Second electron Research Extension (FY21 Funding)
Gabe Cowles, Gautam Yadav, Jinchao Huang, Aditya Upreti, Meir Weiner, Valerio DeAngelis, Sanjoy Banerjee

In FY21 also ..........

Collaborative research to advance solid state ion conductors for emerging batteries
Ryan Hill, Andrew Meyer, w/Erik Spoerke (SNL)

In FY21 also ..........

Three-dimensional printing of architected Zinc electrodes for rechargeable Zn-MnO₂ batteries
Cheng Zhu
Marcus Worsley

In FY21 also ..........
OE supports RESEARCH & DEVELOPMENT, MANUFACTURING and DEMONSTRATION of Potentially Wide Impact, Low Cost Energy Storage Technologies

Collaborative Efforts on Zn-batteries

2020 OE Peer Review Team Presentations

S. Banerjee (CUNY-EI/UEP)
From Concept Through Product to Market: Rechargeable Zinc Manganese Dioxide Batteries

G. Yadav (UEP)
Engineering an Aqueous Energy Dense Manganese Dioxide|Zinc Battery to Challenge Lithium-Ion’s Dominance

J. Gallaway (NEU)
Operando Studies to Enumerate the Electrochemical Phase Transformations of MnO₂

E. Takeuchi (SBU)
Mechanistic Probes of Zinc Anode Aqueous Electrolyte Batteries

I. Vasiliev (NMSU), D. Turney (CUNY-EI), A. Frischknecht (SNL)
Poster Presentations
**Technical Challenges Facing Zn/MnO₂**

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

**Separator:**
- Zincate crossover

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

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**Problem:** Cycling Zn/MnO₂ (both electrodes) at high capacities for thousands of cycles - not realized

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


*R&D: Full 2e⁻ equivalent can be realized, susceptible to zinc poisoning*


*R&D: > 2V High Voltage system offers promise of increased Energy Density*

RESULTS: (SNL) Zn Battery Posters - DOE OE Energy Storage Virtual Peer Review 2020

SNL led Posters:
- D. Arnot et al. “Anodic Stripping Voltammetry Detection of Bismuth, Copper and Zinc and its Role in Evaluating Battery Separators”
- I. V. Kolesnichenko et al. “Polysulfone-Based Zincate-Blocking Separators for Secondary Zn-MnO₂ Batteries”
- M. Lim et al. “Flexible Ion-Selective Separators for Alkaline Zinc Batteries”
- A. Frischknecht et al. “Atomistic Simulations of Sulfone-based Polymer Electrolytes for Alkaline Batteries”

CCNY led Posters:
- D. Turney et al. “In operando synchrotron observations of aqueous Zn-MnO₂ materials evolution”
- S. Kolhekar et al. “Effect of KOH concentration on Mn(III) dissolution in Rechargeable γ-MnO₂ cathodes”
- M. D’Ambrose “Failure Mechanisms of Zinc Anodes in Rechargeable Alkaline Cells”
- B. Hawkins et al. “Reversible Electrochemical Control of ZnO Electronic Properties and Defect Structure in Zn Alkaline Batteries”
- D. Dutta et al. “Molecular-Level Investigation of Concentrated Acetate Electrolytes for High-Voltage Aqueous Zinc Batteries using NMR Spectroscopy”
- J. Huang et al. “Electrochemical Evaluation of the Application of Hydrogel Electrolytes to Rechargeable Zn|MnO₂ Alkaline Batteries”

NEU led Posters:
- A. Bruck et al. “Bismuth Enables the Formation of Disordered Birnessite in Rechargeable Alkaline Batteries”
- M. A. Kim et al. “Synthesis of birnessite with inserted cations and its application in rechargeable batteries”

NMSU led Posters:
- B. A. Magar et al. “Ab Initio Studies of the Cycling Mechanism of MnO₂ Cathodes Modified with Bi, Cu, and Mg in Rechargeable Zn/MnO₂ Batteries”
- N. Paudel et al. “Influence of Surfaces and Structural Defects on the Electrochemical Properties of MnO₂ in Rechargeable Zn/MnO₂ Batteries”

StonyBrook led Posters:
- E. Takeuchi et al. “Vanadium Oxide Cathodes for Beyond Li-Ion Energy Storage”
- E. Takeuchi et al. “Manganese Oxide Cathodes for Aqueous Zinc Anode Batteries”

UEP led Posters:
- M. Weiner et al. “Investigating electrochemical reactions of MnO₂ and Mn ions in Acidic Electrolyte”
- A. Upreti et al. “Functional hydrogels with enhanced physiochemical properties for highly energy dense rechargeable Zn-MnO₂ batteries”
PROJECT OBJECTIVES

SNL FY Objective 1 - INCREASE UNDERSTANDING and the DEPTH OF DISCHARGE (CAPACITY) OF Zn ELECTRODE

PROBLEM: Zn Capacity has not been realized for thousands of cycles at high DOD

Performance-Limiting Issues

1) Passivation
2) Shape change
3) Dendrite formation
4) H₂ evolution
5) Zincate crossover

Caused by solubility of ZnO in KOH (as Zn(OH)₄²⁻) and subsequent precipitation of ZnO and Zn

Restricting migration of zincate is key

RESULTS - FOUR POSTERS:
M. Lim et al., M. D’Ambrose et al. B. Hawkins et al., J. Huang et al.
PROJECT OBJECTIVES

SNL FY Objective 2 – DEMONSTRATE ZINCATE BLOCKING SEPARATOR

PROBLEM: High Capacity Bi/Cu-MnO₂ only cycles well in absence of Zn – Need to prevent Zincate [Zn(OH)₄²⁻] Crossover to MnO₂ Cathode

Properties of an Effective Separator:

• Stability in alkaline electrolyte (pH >14)
• High ionic conductivity
• High hydroxide permeability
• Low zincate permeability
• Ease of Fabrication/Processing

RESULTS - POSTERS:
1. D. Arnot et al. “Anodic Stripping Voltammetry Detection of Bismuth, Copper and Zinc and its Role in Evaluating Battery Separators”
2. I. V. Kolesnichenko et al. “Polysulfone-Based Zincate-Blocking Separators for Secondary Zn-MnO₂ Batteries”
**PROJECT RESULTS**

*Ex Situ – Hydroxide Selective Separator Successfully Developed*

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**RESULTS**

3 POSTERS: I. Kolesnichenko et al., M. Lim et al., D. Arnot et al.

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**ASV Analysis of Zn, Cu and Bi in Alkaline conditions**

J. Duay, et al.

*Electroanalysis*

DOI: 10.1002/elae.201700337

DOI: 10.1002/elae.201700526.

D. Arnot et al.

*Electroanalysis*

Bi ASV

Manuscript Submitted FY20

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**Polymer 4**

$D_{\text{HO}^-}/D_{\text{Zn(OH)}^4^-} \approx 10,000$

ASV LOD for zincate $\approx 0.026$ mM
PROJECT RESULTS (for Objective 2)

In Situ - Hydroxide Selective Separator leads to 4-fold increase in Cycle Life

- Synthesized new PSU polymer
- Cast into Flexible Membrane
- More selective than COTS separators
- C/10 (2e- of MnO₂) cycling data under ‘low electrolyte’ conditions provides a 4-fold increase in cycle life

RESULTS (in collaboration with CCNY and UEP)

** Manuscript:** I. V. Kolesnichenko et al. “Zincate-Blocking Functionalized Polysulfone Separators for Secondary Zn/MnO₂ Batteries” *manuscript under review.*

** POSTER:** I. Kolesnichenko *et al.* “Polysulfone-Based Zincate-Blocking Separators for Secondary Zn-MnO₂ Batteries”
PROJECT RESULTS (for Objective 1)

Utilization of flexible separator (Polymer 4) to enable increased Zn DOD

Scalable Zn/ZnO powder-based anode (very similar to UEP electrode)

Polymer Separator – minimal volume change or complexity to cell

RESULTS

POSTER: M. Lim et al. “Flexible Ion-Selective Separators for Alkaline Zinc Batteries”
PROJECT RESULTS (for Objective 1)

Flexible separator (Polymer 4) enables increased Zn DOD and cycle life

Selective Separator prevents zincate crossover and impedes Zn growth enabling longer cell life

- Selective Separator enables > 150 cycles
- Achieves Average DOD of 32%
- 198% Increase in cycle life is obtained
- Achieves average Energy Density of 180 Wh L⁻¹

Increased cycle life of energy-dense Zn electrodes without adding significant volume, complexity (or cost?) to the system

RESULTS

POSTER: M. Lim et al. “Flexible Ion-Selective Separators for Alkaline Zinc Batteries”
PROJECT RESULTS (for Objective 1)
Flexible separator (Polymer 4) enables increased Zn DOD

Average Potential During Discharge at (nominally) 50% DOD

Selecting Separator prevents zincate crossover and impedes Zn growth enabling longer cell life

- Selective Separator enables > 150 cycles
- Achieves Average DOD of 32%
- 198% Increase in cycle life is obtained
- Achieves average Energy Density of 180 Wh L⁻¹

Increased cycle life of energy-dense Zn electrodes without adding significant volume, complexity (or cost?) to the system

RESULTS
Manuscript: D. Arnot and Matthew Lim et al. manuscript in preparation
Poster: M. Lim et al. “Flexible Ion-Selective Separators for Alkaline Zinc Batteries”
COMPARISON TO OTHER HIGH DOD Zn ANODES

• Parker et al., Science 2017, 356 (6336), 415.
  • 3D Zn sponge
  • 111 cycles above 20% DOD (including 85 cycles at 40% DOD limit)
  • Anode capacity ~ 100 mAh/cm²

  • C mesh/ZnO/anion-exchange ionomer core-shell structure
  • 67 cycles with 40.5% average DOD
  • Anode capacity ~ 5.7 mAh/cm²

  • ZnO nanoparticles in “lasagna-like” GO matrix
  • 150 cycles with 82.2% average DOD
  • Anode capacity ~0.66 mAh/cm²

• Our work
  • Scalable Zn/ZnO powder-based anode w/flexible separator (i.e. similar to UEP Zn-electrode)
  • 164 cycles above 25% DOD with 32.4% average DOD
  • Anode capacity ~ 60 mAh/cm²
**PROJECT OBJECTIVES**

SNL FY Objective 3 – USE MODELING TO UNDERSTAND CATHODE MECHANISMS AND ION TRANSPORT

**PROBLEM:** Cathode cycling mechanism are not well understood

![Diagram showing cathode cycling mechanism](image)

**PROBLEM:** Selective ion transport mechanisms are not well understood

![Diagram showing selective ion transport](image)

**RESULTS**


**POSTER:** B. Ale Magar et al. “Ab Initio Studies of the Cycling Mechanism of MnO₂ Cathodes Modified with Bi, Cu, and Mg in Rechargeable Zn/MnO₂ Batteries”

**POSTER:** N. Paudel et al. “Influence of Surfaces and Structural Defects on the Electrochemical Properties of MnO₂ in Rechargeable Zn/MnO₂ Batteries”

**POSTER:** A. Frischknecht et al. “Atomistic Simulations of Sulfone-based Polymer Electrolytes for Alkaline Batteries”

**PROPOSAL:** ***NEW CINT User Proposal (2020AU0134):** T. N. Lambert, A. Frischknecht et al. Nanoscale Morphology and Ion Transport in Membrane Separators for Rechargeable Alkaline Batteries ***
SNL FY Objective 4 - DEVELOPMENT OF NEW LOW COST HIGH CAPACITY BATTERY CHEMISTRIES

Sulfur is known to have a high theoretical specific capacity: 1650 mA h g⁻¹

➢ ~1500 mAh g⁻¹ (S)
➢ ~300 mAh g⁻¹ (Cu₂S)
➢ ~ 23 mAh cm⁻²
➢ >135 Wh L⁻¹
➢ ~ 250 cycles

Electrode transitions from Sulfur electrochemistry to Copper Electrochemistry

Copper electrochemistry is not sufficiently stable to cycle well

Leads to failure

RESULTS
PROJECT RESULTS (FY 20)

SNL FY Objective 4 - DEVELOPMENT OF NEW LOW COST HIGH CAPACITY BATTERY CHEMISTRIES

Edison-LaLande Battery (Primary Cell)

Edison-LaLande Battery. PAT. Mar. 20, 1883. OTHER PATENTS APPLIED FOR

Anode: $\text{Zn}^0 + 4\text{OH}^- \rightarrow [\text{Zn(OH}_4]^2^- + 2\text{e}^-$

Cathode: $\text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cu}^0 + 2\text{OH}^-$

$E^o = 1.285 \text{ V}$

$E^o = -0.29 \text{ V}$

$\text{Zn}^0 + \text{CuO} + \text{H}_2\text{O} + 2\text{ OH}^- \rightarrow [\text{Zn(OH}_4]^2^- + \text{Cu}^0$

Cell Voltage: 0.995 V

PLAN: FUTURE WORK TO INCLUDE DEVELOPMENT WITH UEP

FY 20: 1st rechargeable Alkaline Zn/CuO Battery

➢ Up to 674 mAh g$^{-1}$ (CuO)

➢ ~ 40 mAh cm$^{-2}$

➢ ~ 260 Wh L$^{-1}$

RESULTS

PATENT APPLICATION: T. N. Lambert and J. Duay

PUBLICATION: N. Schorr et al. manuscript submitted (In Collaboration with NEU).
**PROJECT RESULTS - Summary**

**FY 20 Accomplishments**

1. **Demonstrated Increased Cycle life of Energy Dense Zn:**
   - > 150 cycles at Average DOD$_{Zn}$ 32% @ 180 Wh L$^{-1}$ (198% lifetime increase over control)
   - > 350 cycles at Average DOD$_{Zn}$ = 17% @ 132 Wh L$^{-1}$ (897% lifetime increase over control)
   - *Use of selective separator = No significant volume or complexity added to the system*

2. **Demonstrated Increased Cycle life of Energy Dense Zn/(Cu/Bi-MnO$_2$) cells:**
   - Synthesis of new cationic polysulfone-based separator and membranes
   - (Partial) Zincate screening demonstrated
   - Four-fold increase in cycle life under low electrolyte conditions

3. **Developed the first Zn/CuO re-chargeable battery**
   - Energy density of ~ 260 Wh L$^{-1}$
   - Among the highest Energy Density reported for Zn/Conversion cathode battery
   - (not shown in detail, see Poster, D. Arnot et al.)

4. **Developed Anodic Stripping Voltammetry for Bi in Highly Alkaline Electrolyte**
   - Limit of DOD ~ 8.5 ppb
   - Can now more efficiently screen separators for Zn, Cu and Bi crossover
PROJECT RESULTS

FY 20 Manuscripts (15 total = 8 published, 6 in peer review, 1 in preparation)


6. N. B. Schorr et al “Rechargeable Alkaline Zinc/Copper Oxide Batteries” manuscript submitted.

7. B. E. Hawkins et al. “Reversible Electrochemical Control of Conductivity, Color, and Native Defect Structure of ZnO” manuscript submitted.


14. A. C. Marschilok et al. "Energy dispersive X-ray diffraction (EDXRD) for operando materials characterization within batteries" Physical Chemistry Chemical Physics, 2020. DOI:10.1039/D0CP00778A. https://pubs.rsc.org/en/content/articlehtml/2020/cp/d0cp00778a?casa_token=LWjji-kV7QAAAAAA:y9TvijTJ94WlAYIl33yQFCkatRhOavhhE1C0kIeOYxy5Vbf7r7dGwNMgt3U0sjCDFJGEVYu93vC
FY 20 Presentations (37 Presentations)


**PROJECT RESULTS**

**FY 20 Presentations continued...**


**PROJECT RESULTS**

**FY 20 Presentations continued...**


21. **Invited Talk:** G. G. Yadav, Engineering an Aqueous Energy Dense Manganese Dioxide|Zinc Battery to Challenge Lithium-Ion’s Dominance, Invited Talk at the American Institute of Chemical Engineers (AIChE) Battery and Energy Storage Workshop, 21 October 2019, New York, NY.


FY 20 Presentations continued...


27. E. Takeuchi, “From Medical Applications to the Environment: the Important Role of Electrochemical Energy Storage,” Cary lecture, Georgia Institute of Technology, March 4-5, 2020, Atlanta, GA.


http://meetings.aps.org/Meeting/4CS19/Session/E02.6
FY 20 Presentations continued...


Proposals:

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&

OUR MANY COLLABORATORS!

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