

Progress in Aqueous Zn-based Batteries

PRESENTED BY

Timothy N. Lambert

DOE-OE Peer Review, Santa Fe, New Mexico, October 24 – October 26, 2022.

Presentation ID # 701



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security

Administration under contract DE-NA0003525. SAND2023-113670

Low Cost Aqueous Batteries based on Zinc

<u>Program Objective</u>: Develop the understanding, materials, methods, components & technologies to enable low cost Zn-based batteries for grid and long duration energy storage

- Zinc-based batteries offer an energy dense, safe and readily manufacturable technology
- OE Funded Project collaboratively investigates new materials and chemistries while supporting technology maturation and US manufacturing
- Zn/(1e-)MnO₂, Zn/(2e-)Bi,Cu-MnO₂, Zn/(2e-)Bi-CuO, Zn/Ni...... Zn/air, Zn-ion, Zn/S



Photos provided by UEP

h







Low Cost, readily available ~ Energy Equity

Zn



1° Alkaline Zn/MnO₂ as an exemplar



Wikipedia, user Aney, 2005

- Existing supply chain
- > 10B units Zn/MnO_2 produced (2019)
- \$7.5B global market (2019)
- Affordable ~ 20/kWh
- Aqueous w/long shelf life
- EPA certified for disposal (safe)
- High achievable energy density
 - $Zn/MnO_2 \sim 400 Wh/L$
 - $Zn/Air \sim 1400 Wh/L$
 - Zn/Ni ~ 300 Wh/L
- $Zn/CuO \sim 400 Wh/L$

High Energy Density ~ Long Duration Energy Storage

Low Cost Aqueous Batteries based on Zinc

How does one obtain reliable high capacity conversion chemistry in aqueous Zn batteries? Obtaining High DOD at both electrodes for thousands of cycles remains a challenge



Adapted from "A Critical Comparison of Mildly Acidic versus Alkaline Zinc Batteries" Acc. Mater. Res. 2023 4, 4, 299-306.

Zn Anode - conversion electrode

(1) passivation, (2) shape change (3) dendrite formation, (4) H_2 evolution (5) $Zn(OH)_4^{2-1}$

crossover

4

How to control zincate and interfacial interactions for maximum capacity? High DOD w/out complicated 3D architectures?

















Separators Crossover of soluble "ate" complexes

How does one control ion selectivity, migration?

Electrolyte

High voltage and non-spillable

How to engineer electrolyte to enable safe, long cycle life, higher voltage?

(2) CuO Cu₂O reversibility, soluble Cu(OH)₄²⁻

What is the mechanism, intermediates, more efficient use of additives?

Low Cost Aqueous Batteries based on Zinc

⁵ How does one obtain reliable high capacity conversion chemistry in aqueous Zn batteries ? Obtaining High DOD at both electrodes for thousands of cycles remains a challenge

National

Laboratories

Zn Anode

J. Electrochem. Soc. 2020, DOI:10.1149/1945-7111/ab7e90. Small Structures 2022, DOI:10.1002/sstr.202200323. ACS Appl. Energy Mater. 2023, DOI:10.1021/acsaem.3c00572. Separators and Polymer Gel Electrolytes

Adv. Energ. Mater. DOI:10.1002/aenm.202101594. (*high Zn DOD*) ACS Applied Energy Mater. 2022, DOI:10.1021/acsaem.2c01605. ACS Appl. Polym. Mater. 2022, 10.1021/acsapm.1c01798. ACS Appl. Mater & Interface 2020, DOI:10.1021/acsami.0c14143. J. Power Sources 2018, DOI: 10.1016/j.jpowsour.2018.05.072. Mater. Horiz. 2022 DOI:10.1039/D2MH00280A. (*high voltage*) Polymer 2022, DOI: 10.3390/polym140304417.

ASV Analysis of Zn, Cu or Bi in Alkaline conditions Electroanalysis 2020, DOI: 10.1002/elan.202060412. Electroanalysis 2017, DOI:10.1002/elan.201700337. Electroanalysis 2017, DOI:10.1002/elan.201700526. Air Cathodes

ACS Catalysis 2023, DOI:10.1021/acscatal.3c01348. Select Reviews

Acc. Mater. Res. 2023 DOI:10.1021/accountsmr.2c00221. J. Electrochem. Soc. 2020, DOI:10.1149/1945-7111/ab9406. Frontiers in Chemistry 2022. DOI:10.3389/fchem.2021.809535. MRS Energy Sustain. 2021, DOI:10.1557/s43581-021-00018-4. Mater. Sci. Eng. R Rep. 2021, DOI:10.1016/j.mser.2020.100593. DOE Energy Storage Handbook 2021, https://www.sandia.gov/ess-ssl/eshb/



h

POWER

FY 23 PROJECT TEAM – Sandia National Laboratories&Collaborators 🛅

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



2023 OE Peer Review Team Presentations

Timothy Lambert (SNL): Progress in Aqueous Zn-based batteries

Gautam Yadav (UEP): Zinc-Manganese Dioxide Batteries for Long Duration Energy Storage Systems

Sanjoy Banerjee (UEP) Progress with Manufacturing and Deploying Zn-MnO₂ Batteries

Eight Poster Presentations (5 Pls):

S. Banerjee (CUNY-EI/UEP), A. Frischknecht (SNL), J. Gallaway (NU), T. Lambert (SNL), B. Wygant (SNL) FY 23 Accomplishments:

5 publications (+5 in Preparation), 8 Invited Presentations, 7 Contributed Presentations

FY 23: Zn Anode Highlights

Objective: Evaluate additives/KOH electrolyte to enable high capacity Zn anodes to be realized with low-cost roll to roll pasted electrodes



- Manufacturability: Pasted electrodes compatible with industrial manufacturing: 9.1-14 mAh/cm²
- Type of Zn: ZnO > Zn (@15 or 30% Zn DOD)
- Cycle Life: 10%, 20% KOH >>37% KOH
- Additives: CTAB, [Ca(OH)₂:Bi₂O₃], Laponite
- Bi appears to 'open pores' in the microstructure of the electrode
- In situ XRD = zincate 'capture' upon cycling w/ $Ca(OH)_2$ less shape change
- Performance comes at the slight cost of volume and weight best cumulative Ah/mL and (7x) Ah/g for pasted electrodes

Publication: M. J. D'Ambrose et al. "Performance Advances of Industrial-Design Rechargeable Zinc Alkaline Anodes via Low-Cost Additives" ACS Appl. Energy Mater. 2023, 6, 11, 6091-6103.

Poster: P. Yang et al. "Understanding the Role of Calcium Zincate $(Ca[Zn(OH)_3]_2 \cdot 2H_2O)$ in Improving Cycle Life and Performance in Rechargeable Alkaline Zinc Batteries" *Manuscript in Preparation: P. Yang et al.*

 $Zn + 4 OH^{-} = Zn(OH)_{4}^{2-} + 2e^{-}$ $Zn(OH)_{4}^{2-} = ZnO + 2OH^{-} + H_{2}O$

FY 23: Modeling Highlights

8

Objective: Develop computational models to understand ion transport mechanisms



- 1) Zinc batteries use high concentration KOH. Showed that MD can capture behavior up to 12M
- 2) Zincate $[Zn(OH)_4]^{2-}$ forms in zinc batteries. New model agrees with experiment
- New model enables simulations of 3) zincate/KOH in PGE and

separators

Polymer Gel





blue = C red = 0yellow = K^+

J Electrochem Soc 1997, 144, 1278

Pessine, E. J., Agostinho, S. M. L. & Chagas, H. C. Canadian J. of Chemistry 1986, 64, 523-527.

KOH/Zincate/H₂ in PGE underway

Result: Zincate 1st ever, new computational models could impact whole family of alkaline Zn-batteries *Poster:* A. Frischknecht "Enabling simulations of Alkaline electrolytes in Zinc Batteries" In Preparation: A. Frischknecht et al. "Force Fields for High Concentration Aqueous KOH and Zincate"

FY 23: Polymer Gel Electrolyte Results

Objective: Develop/understand polymer gel electrolytes for optimized Zn/high-capacity conversion cathode batteries

High Capacity Bi, Cu-MnO₂ cathodes requires excess Bi and Copper for long cycle life Soluble bismuthate [$Bi(OH)_3^{-}$] and cuprate [$Cu(OH)_4^{2-}$] can lead to capacity loss and shorting (Cu)



2e- Cu,Bi-MnO₂: G. Yadav et al 2017 Nature Commun. 8, 14424.

Development of Bobbin-type Cells including w/PGE Low cost manufacturing. UEP: Gabe Cowles and Dr. Gautam Yadav Combining modeling of "ate" species with experimental data should enable improved cells

Poster: J. Cho et al. "Ionic Diffusion in Hydrogel Electrolytes for Two-electron Zn-MnO₂ Batteries" *Manuscript In Preparation*: J. Cho et al. "The incorporation of hydrogels into Zn | MnO₂ rechargeable batteries allowing for the transportability and ion diffusion for the 2nd electron reaction of MnO₂"

9

Development of CuO Cathode (674 mAh/g) – Zn/CuO Batteries





Mixing Bi₂O₃ into the cathode formulation promotes cycle-ability

10

Zn/CuO batteries are the focus of a DOE OTT-TCF Office of Technology Transitions - Technology Commercialization Fund Award

Optimizing Cathode Performance

11



 $V_{avg} = 0.89V$

400

300

500

FY 23 results

- > 200 Ah of CuO electrodes (w/UEP)
- Demonstrated ~8V, 2.88Ah Zn/CuO Battery module
- **Demonstarted power converter compatibility**
- Target: 200 Wh/L, 100 cycles

8.2V, 2.88 Ah Zn/CuO Battery Module



V. DeAngelis, J. Mueller, O. Dutta (SNL)



Commercial Partner for: Manufacturing larger Ah, polymer gel electrolyte, higher capacity Zn

URBAN

POWER

ELECTRIC

FY 23: Bi, Additives, Electrolytes Highlight



12

Impact of Bi content

Limited Zn DOD

- 1. Reducing Bi quantity improves energy density while retaining capacity benefits
- 2. Both soluble and solid Bi play a role in mediating Zn-CuO battery cycling
- 3. Other additives, the use of coatings, and electrolyte modifications can also impact/improve battery performance
- 4. Understanding capacity decay and improving battery lifetimes are important next steps

Energy Density Capacity Effects



Impact of Additive/Electrolyte Choice

Poster: B. Wygant et al. "Improving Alkaline Zinc-Copper Oxide Batteries through Chemical Modifications"

FY 23: Optimizing Cathode Formulations - Highlights

Original CuO/Bi₂O₃ 10x Discharge

13



ħ

'Improved' CuO/Bi₂O₃ 10x Discharge

Poster: B. Wygant et al. "Improving Alkaline Zinc-Copper Oxide Batteries through Chemical Modifications"

FY23: Water-in-Salt-Electrolytes for Zn Batteries - Highlights



14



- Voltage Window is improved but not due to H₂O activity (reaction kinetics and SEI layers)
- Zn dendrites are reduced in WiSE
- Lower HER in WiSE than KOH
- Ion mass transfer is too slow for 'commercially relevant' cells in WiSE
- Dilution improves mass transfer but at cost of voltage window

Poster: D. Turney et al. "Practicality and electrochemistry of acetate water-in-salt electrolyte (WiSE) for zinc battery cycling" *Poster*: D. Dutta et al. "Comparing Hydrogen Evolution Rates in Potassium Acetate and Potassium Hydroxide based Electrolytes for Zinc Aqueous Batteries" *Manuscript in prep*: D. Turney et al.

FY 23: Zn/air – New Electrocatalysts (SNL LDRD/CINT/OE funding)



Objective: Demonstrate Bi-directional Oxygen electrocatalysis with Nickel sulfo-selenides and determine optimum formulation

Synthesis of NiS_xSe_y

 Hydrothermal reaction to produce series of Ni₃S_{2-x}Se_x (NiSSe) powders



- Characterization shows that the materials show a transition from Ni_3S_2 to Ni_3Se_2 , but that the S/Se in the material is evenly distributed within discreet particles

- Zn/air demonstration with NiS_xSe_y
- Testing in a flow Zn-air battery shows improved BOE performance for NiSSe compared to commercial Pt/C



- 1. Hydrothermal synthesis is a simple, tunable method for producing mixed metal chalcogenides
- 2. Electrocatalytic performance of NiSSe materials is promising, and suggests that Se-rich materials may be suitable BOEs for Zn-air batteries
- 3. Exploration of more earth-abundant metals (e.g., Fe, Mn) will help further improve costs for developing and building Zn-air batteries

New FY 24 OE Effort in Zn-air started

Publication: B. R. Wygant et al. "The Effects of Compositional Tuning on the Bifunctional Oxygen Electrocatalytic Behavior of Nickel Sulfoselenides" ACS Catalysis 2023 13, 13, 9245-9253.

Poster: B. Wygant et al. "Transition Metal Multi-chalcogenides as Bifunctional Oxygen Electrodes for Zinc-air Batteries"

16 **PROJECT TEAM - RESULTS**

RESULTS: Zn Project Battery Posters - DOE OE Energy Storage Virtual Peer Review 2023

OE Peer Review 2023 Posters:

- 1. A. Frischknecht "Enabling Simulations of Alkaline Electrolytes in Zinc Batteries"
- 2. D. Dutya et al. "Comparing Hydrogen Evolution Rates in Potassium Acetate and Potassium Hydroxide based Electrolytes for Zinc Aqueous Batteries"
- 3. J. Cho et al. "Ionic Diffusion in Hydrogel Electrolytes for Two-electron Zn-MnO₂ Batteries"
- 4. D. Turney et al. "Practicality and electrochemistry of acetate water-in-salt electrolyte (WiSE) for zinc battery cycling"
- P. Yang et al. "Understanding the Role of Calcium Zincate (Ca[Zn(OH)₃]₂·2H₂O) in Improving Cycle Life and Performance in Rechargeable Alkaline Zinc Batteries"
- 6. B. Wygant et al. "Improving Alkaline Zinc-Copper Oxide Batteries through Chemical Modifications"
- 7. B. Wygant et al. "Transition Metal Multi-chalcogenides as Bifunctional Oxygen Electrodes for Zinc-air Batteries"
- 8. Erik K. Zimmerer "Spectroscopic Characterization of Rechargeable Alkaline Batteries for the Grid"

17 **PROJECT - RESULTS**

RESULTS: Zn Project Battery Publications - DOE OE Energy Storage Virtual Peer Review 2023

Publications:

- C. Zhu, N. B. Schorr, Z. Qi, B. R. Wygant, D. E. Turney, G. G. Yadav, M. A. Worsley, E. B. Duoss, S. Banerjee, E. D. Spoerke, A. van Buuren, T. N. Lambert "Direct Ink Writing Of 3D Zn Structures as High Capacity Anodes For Rechargeable Alkaline Batteries" Small Structures 2022, 4, 4, 2200323.
- 2. Invited Review: M. Vind, N. B. Schorr, B. Sambandam, S. Kim, S. Lee, T. N. Lambert, J. Kim "A Critical Comparison of Mildly Acidic versus Alkaline Zinc Batteries" Acc. Mater. Res. 2023 4, 4, 299-306.
- 3. M. J. D'Ambrose, D. E. Turney, M. N. Nyce, T. N. Lambert, S. Banerjee, G. G. Yadav "Performance Advances of Industrial-Design Rechargeable Zinc Alkaline Anodes via Low-Cost Additives" ACS Appl. Energy Mater. 2023, 6, 11, 6091-6103.
- M. A. Kim, E. K. Zimmerer, Z. T. Piontkowski, M. A. Rodriguez, N. B. Schorr, B. R. Wygant, J. S. Okasinski, A. C. Chuang, T. N. Lambert, J. W. Gallaway "Li-ion and Na-ion intercalation in layered MnO₂ cathodes enabled by using bismuth as a cation pillar" J. Mater. Chem. 2023 11, 11272-11287.
- 5. B. R. Wygant, B. A. Washington, C. N. Wright, G. A. Goenaga-Jiménez, T. A. Zawodzinski, T. N. Lambert "The Effects of Compositional Tuning on the Bifunctional Oxygen Electrocatalytic Behavior of Nickel Sulfoselenides" ACS Catalysis 2023 13, 13, 9245-9253. 10.1021/acscatal.3c01348.

RESULTS: Zn Project Battery Presentations - DOE OE Energy Storage Virtual Peer Review 2023

Invited Presentations:

- 1. A. L. Frischknecht, "Using Molecular Dynamics Simulations to Relate Morphology to Water and Ion Dynamics in Hydrated Polymers," 243rd Electrochemical Society (ECS) Meeting, Boston, MA, May 29, 2023.
- 2. A. L. Frischknecht, "Insights into Hydrated Ion-Conducting Polymers from Molecular Dynamics Simulations," Complex Fluids Design Consortium Annual Meeting, University of California, Santa Barbara, January 27, 2023.
- 3. A. L. Frischknecht, "Insights into Hydrated Ion-Conducting Polymers from MD Simulations," Departmental Seminar, Chemical Engineering Department, University of New Mexico, Albuquerque, NM, October 26, 2022.
- 4. A. L. Frischknecht, "Insights into Hydrated Ion-Conducting Polymers from MD Simulations," Departmental Seminar, Chemical and Biological Engineering Department, Princeton University, Princeton, NJ, October 5, 2022.
- 5. T. N. Lambert, B. R. Wygant, C. Wright, J. Gallaway, A. Stavola, E. Zimmerer, V. DeAngelis, J. Mueller, O. Dutta, I. Vasiliev, K. Acharya, N. Paudel, B. A. Magar, G. G. Yadav, G. Cowles, S. Banerjee "Energy Dense Rechargeable Cubased Cathodes for Alkaline Zn/Cu Batteries" ACS Fall 2022, San Francisco, CA, August 13-17, 2023.
- 6. T. N. Lambert, B. R. Wygant, C. Wright, J. Gallaway, A. Stavola, E. Zimmerer, V. DeAngelis, J. Mueller, O. Dutta, I. Vasiliev, K. Acharya, N. Paudel, B. A. Magar "Progress Towards the Development and Understanding of Energy Dense Rechargeable Batteries Utilizing Zn and Cu" 243rd ECS Meeting, Boston, MA, May 28-June 2, 2023.
- 7. S. Banerjee "Development of Commercial-Scale High Energy Density Aqueous Zinc Manganese Dioxide Alkaline Batteries for Long Duration Storage" 243rd ECS Meeting, Boston, MA, May 28-June 2, 2023.
- 8. S. Banerjee "Development of Rechargeable Zinc Manganese Dioxide Batteries From Concept through Product to Market"

19 **PROJECT - RESULTS**

RESULTS: Zn Project Battery Presentations - DOE OE Energy Storage Virtual Peer Review 2023

Contributed Presentations:

- 1. T. N. Lambert, B. R. Wygant, C. Wright, J. Gallaway, A. Stavola, E. Zimmerer, V. DeAngelis, J. Mueller, O. Dutta, I. Vasiliev, K. Acharya, N. Paudel, B. A. Magar, G. G. Yadav, G. Cowles, S. Banerjee "The Development of Energy Dense Rechargeable Zn/CuO Batteries" 3rd International Zinc-air and other Zinc batteries workshop (IZABW), Ulm, Germany, September 18-19, 2023.
- T. N. Lambert, B. R. Wygant, C. Wright, J. Gallaway, A. Stavola, E. Zimmerer, V. DeAngelis, J. Mueller, O. Dutta, I. Vasiliev, K. Acharya, N. Paudel, B. A. Magar "Progress Towards the Development and Understanding of Energy Dense Rechargeable Batteries Utilizing Zn and Cu" TechConnect World Innovation Conference and Exposition" Washington, DC, June 19-21, 2023.
- 3. B.R. Wygant, C. N. Wright, B. A. Washington, G. A. Goenaga-Jiménez, T. A. Zawodzinski, T. N. Lambert "Compositional Tuning of Nickel Sulfoselenides for Use as Bifunctional Oxygen Electrocatalysts in Aqueous Electrochemical Energy Storage" 243rd Electrochemical Society (ECS) Meeting, Boston, MA, May 28 - June 2, 2023.
- 4. P. Yang, D. E. Turney, T. N. Lambert, S. O'Brien and S. Banerjee "Studying the Addition of Metallic Zinc (Zn) to Rechargeable Alkaline Calcium Zincate (CaZn2(OH)6·2H2O) Anodes" AIChE 4th Battery and Energy Storage Conference, The City College of New York, New York City, United States, October 26-28, 2022.
- 5. J. Cho P. Yang, D. E. Turney, G. G. Yadav, M. Nyce, T. N. Lambert and S. Banerjee "Understanding of ion diffusion for non-spillable Zn | MnO2 rechargeable batteries allowing for 2nd electron MnO₂ cycling in hydrogel electrolytes" AIChE 4th Battery and Energy Storage Conference, The City College of New York, New York City, United States, October 26-28, 2022.
- 6. D. Dutta, D. E. Turney, R. Messinger, T. N. Lambert and S. Banerjee "Koutecky-Levich Study of the Hydrogen Evolution Reaction on a Zinc Rotating Disk Electrode in Traditional Alkaline and Acetate-Based Water-in-Salt (WiSE) Electrolytes" AIChE 4th Battery and Energy Storage Conference, The City College of New York, New York City, United States, October 26-28, 2022.
- 7. J.W. Gallaway, M.A. Kim, E.K. Zimmerer, T.N. Lambert, and N.B. Schorr "Li-Ion and Na-Ion Intercalation in Layered MnO2 Cathodes Enabled by Using Bismuth as a Cation Pillar" Symposium A03: Large Scale Energy Storage 14, The Electrochemical Society 243rd Meeting, Boston MA, May 2023.

PROJECT CONTACTS 20



Timothy N. Lambert tnlambe@sandia.gov

Tim Lambert



Ray Byrne rhbyrne@sandia.gov

Ray Byrne

FY 21 Sandia Team





Bryan Wygant





Nelson Bell



Erik Spoerke

ACKNOWLEDGEMENTS







Imre Gyuk

THIS WORK WAS SUPPORTED THROUGH THE ENERGY STORAGE PROGRAM, MANAGED BY DR. IMRE GYUK, WITHIN THE U.S. DEPARTMENT OF **ENERGY'S OFFICE OF** ELECTRICITY

£

OUR MANY COLLABORATORS!







URBAN electric POWER









This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Acknowledgements

(h)

"Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC (NTESS), a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration (DOE/NNSA) under contract DE-NA0003525. This written work is authored by an employee of NTESS. The employee, not NTESS, owns the right, title and interest in and to the written work and is responsible for its contents. Any subjective views or opinions that might be expressed in the written work do not necessarily represent the views of the U.S. Government. The publisher acknowledges that the U.S. Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this written work or allow others to do so, for U.S. Government purposes. The DOE will provide public access to results of federally sponsored research in accordance with the DOE Public Access Plan."