

# Progress in Aqueous Zn-based Batteries

*PRESENTED BY*

Timothy N. Lambert

DOE-OE Peer Review, Albuquerque, New Mexico,  
October 11 – October 13, 2022.

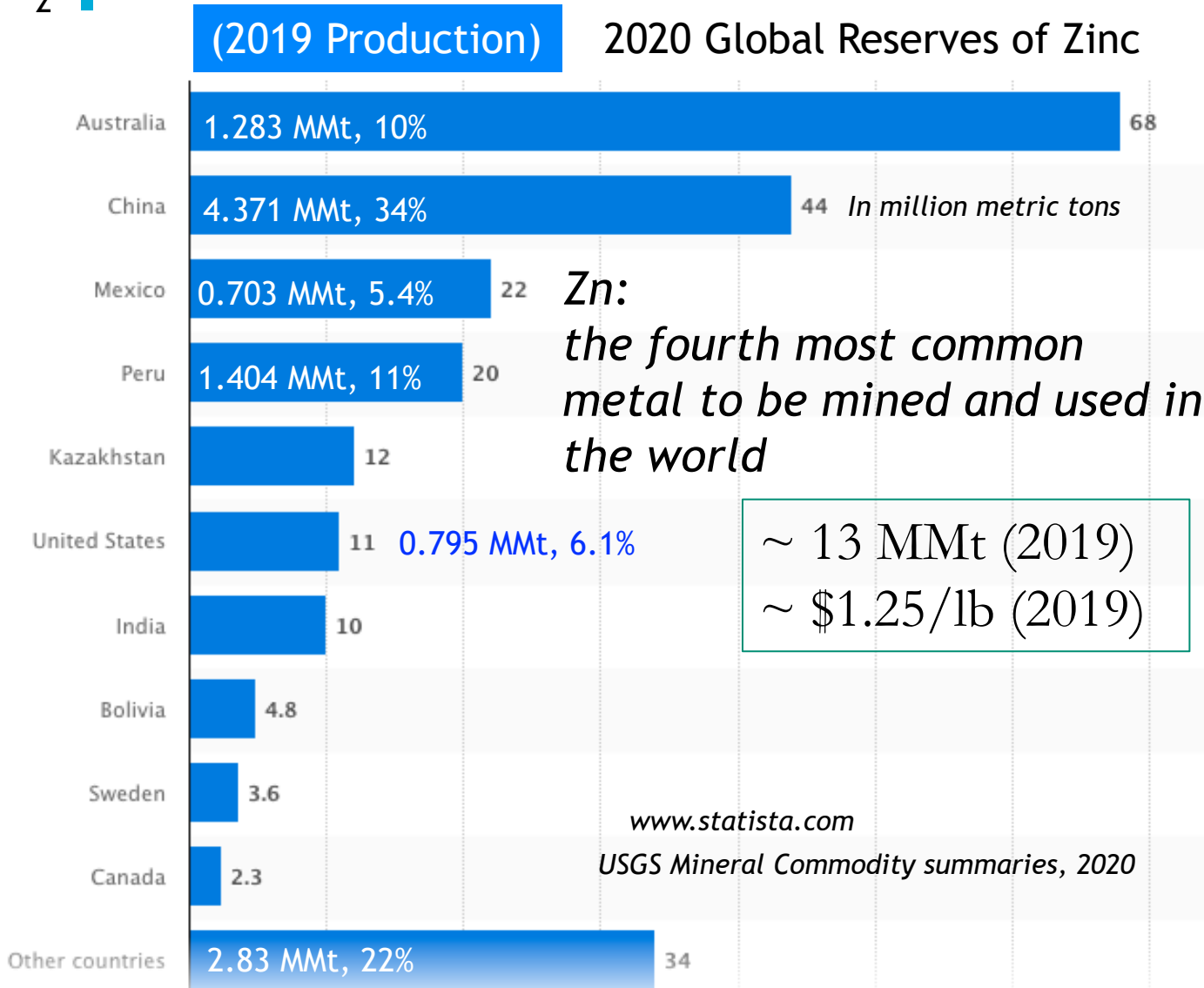
Presentation ID # 702



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SAND2022-13718 PE

# A case for Zn-based batteries



<https://www.usgs.gov/centers/nmic/zinc-statistics-and-information>

## Zn



1° Alkaline Zn/MnO<sub>2</sub> as an exemplar



Wikipedia, user Aney, 2005

- Existing supply chain
- > 10B units Zn/MnO<sub>2</sub> 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<sub>2</sub> ~ 400 Wh/L
  - Zn/Air ~ 1400 Wh/L
  - Zn/Ni ~ 300 Wh/L
  - Zn/CuO\* ~ 400 Wh/L

Low Cost, readily available ~ Energy Equity

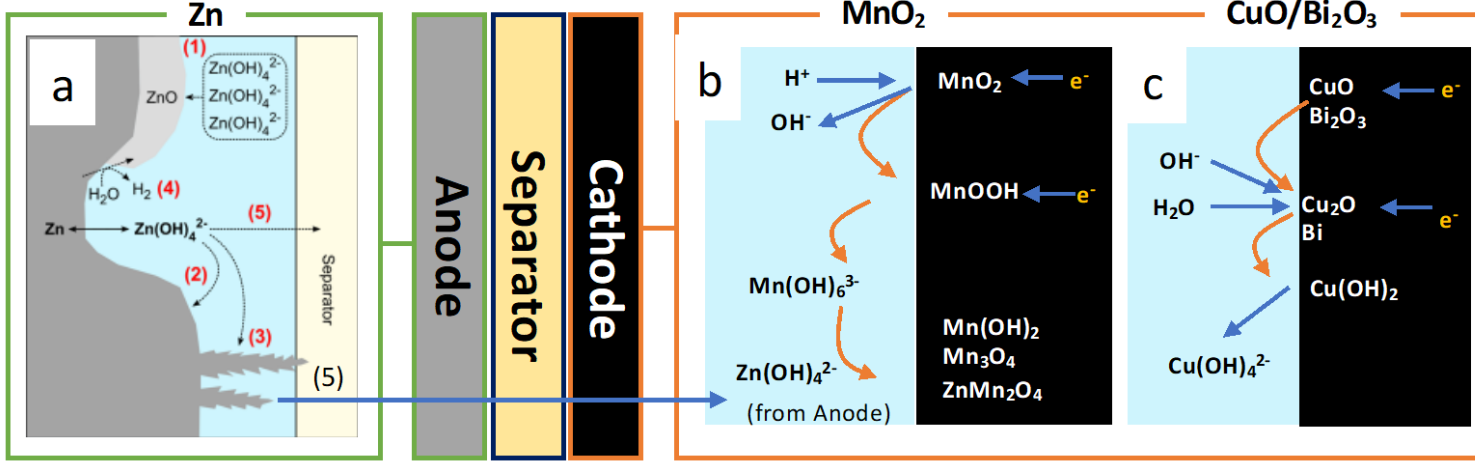
High Energy Density ~ Long Duration Energy Storage

# 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*

Schematic for Alkaline Zn Battery



## Cathode - conversion electrode

- (1)  $\text{MnO}_2$  crystal structure breakdown,  $\text{Mn(OH)}_6^{3-}$  irreversible phases, susceptible to Zn poisoning
- (2)  $\text{CuO} - \text{Cu}_2\text{O}$  reversibility, soluble  $\text{Cu(OH)}_4^{2-}$
- (3) High Capacity at lower Voltage

Adapted from Vinod et al. manuscript in preparation for *Accounts of Materials Research*

## Zn Anode - conversion electrode

- (1) passivation, (2) shape change (3) dendrite formation, (4)  $\text{H}_2$  evolution (5)  $\text{Zn(OH)}_4^{2-}$  crossover

## Separators

Crossover of soluble "ate" complexes (Zn, Cu, Bi...)

## Electrolyte

Low voltage and spillable

# PROJECT TEAM – Sandia National Laboratories and Collaborators



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

## Collaborative Efforts on Batteries



Low Cost Batteries



(Na battery Project/Assisted with Mechanical Testing)

## 2022 OE Peer Review Team Presentations

Sanjoy Banerjee (UEP/CCNY)  
*Progress in the Development and Deployment of Zinc Manganese Dioxide Batteries*

Amy Marschilok (SBU)  
*Mechanistic Studies of Zinc Anode Batteries*

Joshua Gallaway (NU):  
*Li and Na ion intercalation in layered MnO<sub>2</sub> cathodes enabled by using bismuth as a cation pillar*

*Ten Poster Presentations:*

A. Frischknecht (SNL), I. Vasiliev (NMSU), C. Zhu (LLNL), S. Banerjee (CUNY-EI/UEP), T. Lambert (SNL)

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Low Cost  
Batteries



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## 2022 OE Peer Review Team Results

10 (+2) Publications

15 Invited Presentations

7 Contributed Presentations

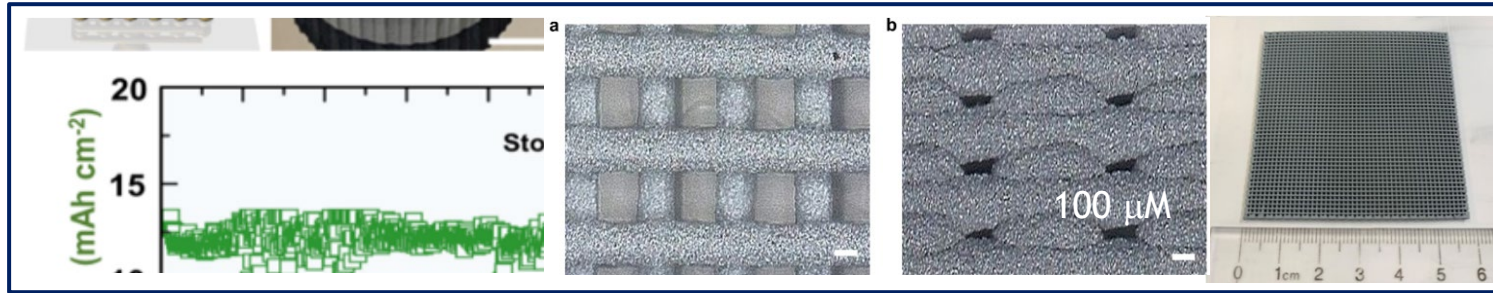
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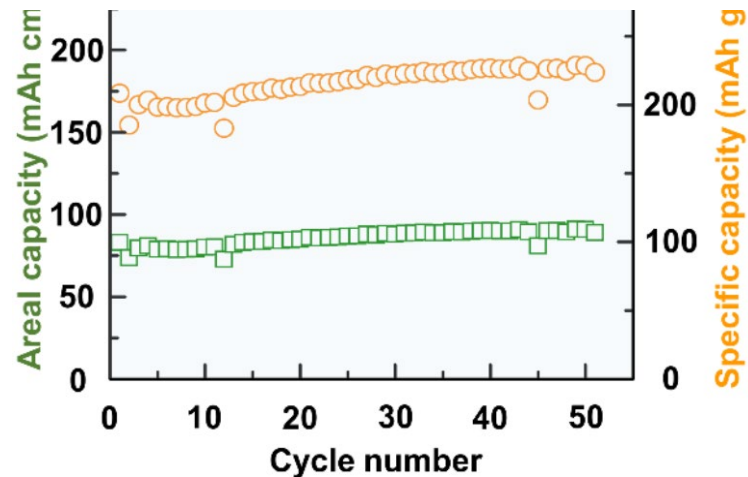
# Zn Anode Highlights



Advanced manufacturing of 3D Zn - custom form and long cycle life Zn

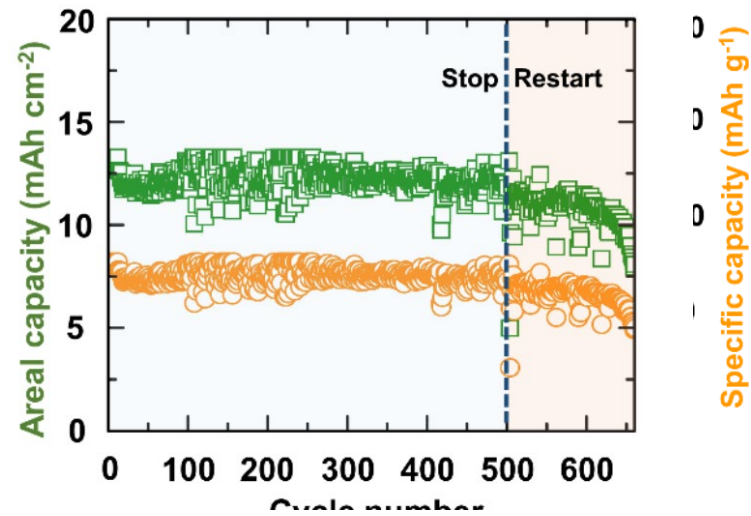


3D-Zn || Ni utilizing PGE

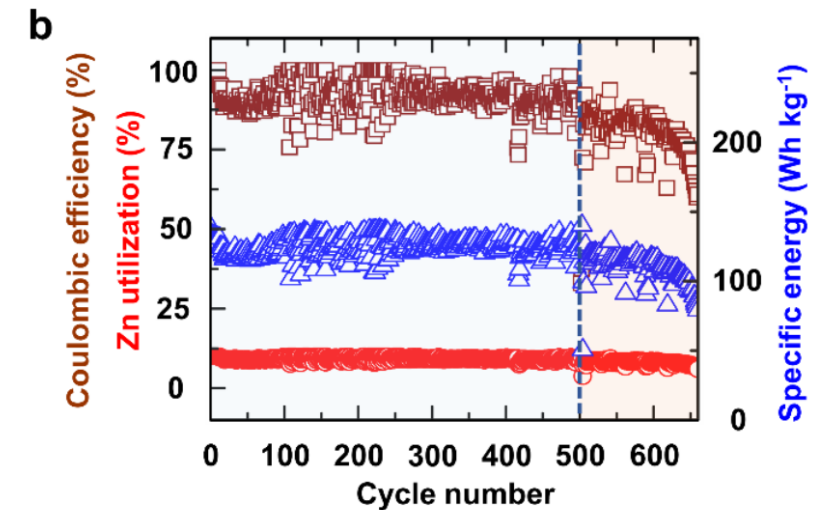


f

Areal Capacity & Mass Loading



Cumulative Capacity



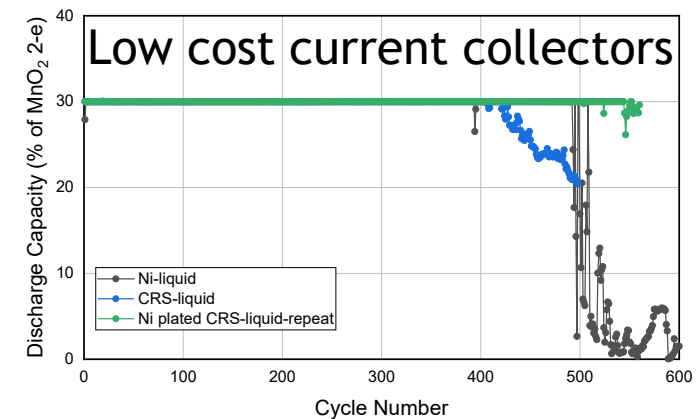
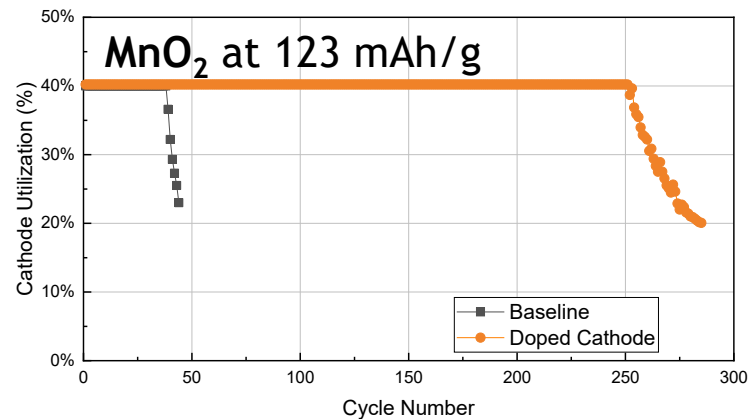
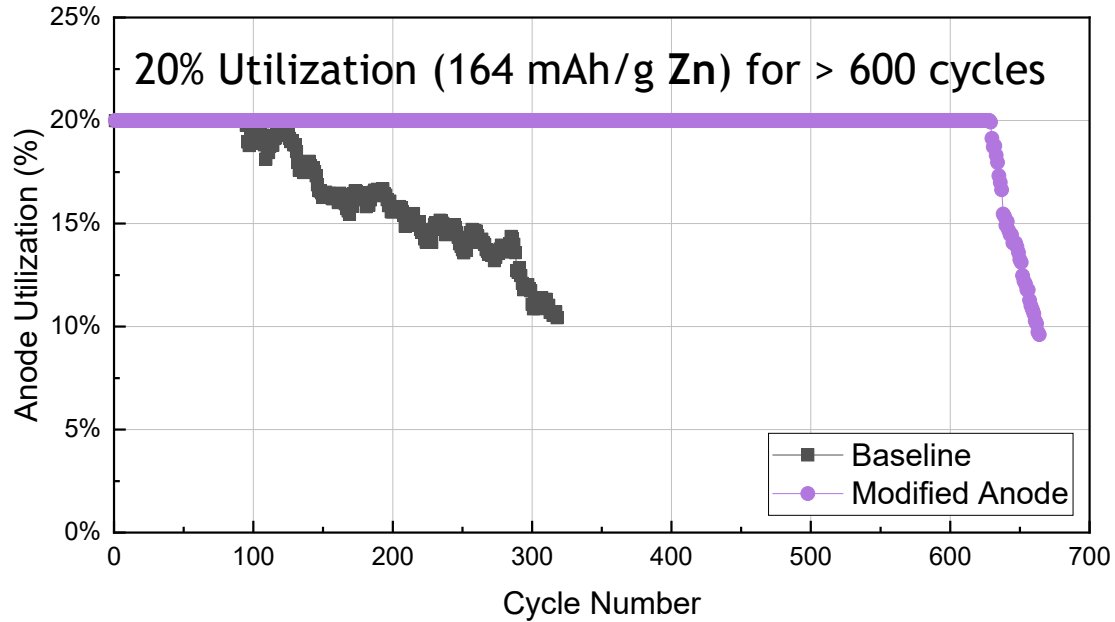
*Publication:* C. Zhu et al. *Small Structures* 2022, submitted.

*Poster:* C. Zhu et al.

# Zn Anode and MnO<sub>2</sub> Highlights



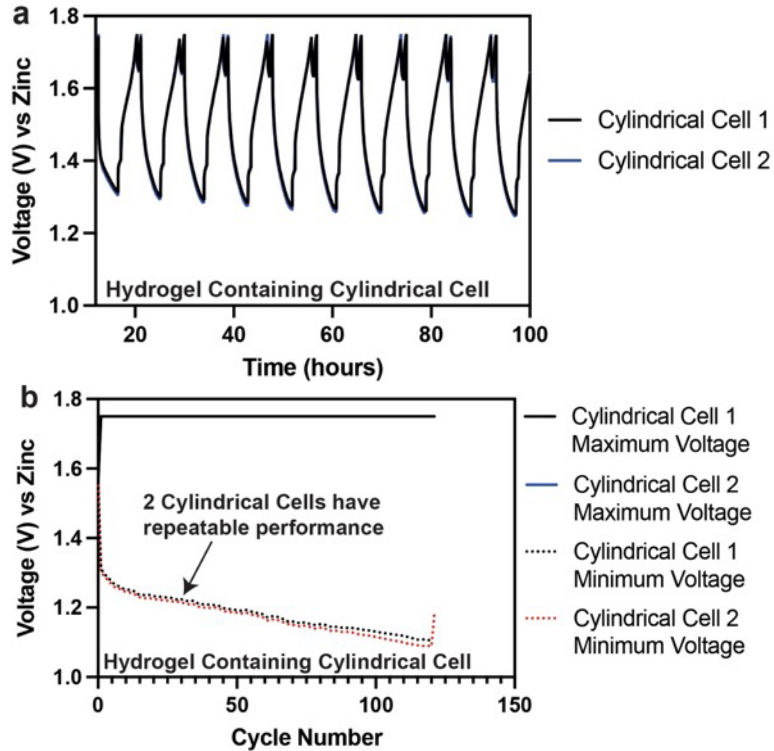
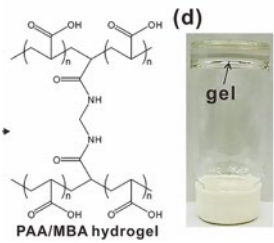
Manufacturing Low cost electrode formulations for high cycle life and energy



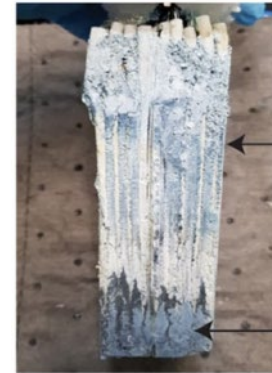
Poster: J. Huang et al.

Publications: M. D'Ambrose et al. *in preparation*. G. Yadav et al. 2022 *in preparation*.

# Development of Non-spillable PGE Zn/MnO<sub>2</sub> Highlights



Liquid KOH



Stray Zn converted to ZnO

Stray Zn

PGE



No Stray Zn

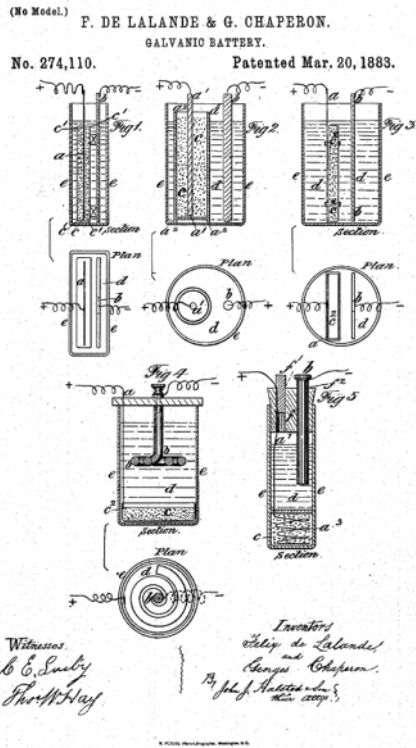
1. A non-spillable Zn-MnO<sub>2</sub> battery that meets DOT requirements for safe transportability
2. An in-situ polymerization method enhances contact with the electrode and reduces corrosion.
3. The hydrogel reduces zincate migration, formation of stray Zn particles and manganese dissolution to increase the utilization of the electrode materials.
4. The hydrogel also enhance the safety by reducing dendrite formation that often leads to short circuits.

**Publication:** J. Cho et al 2022 *Polymers* 14 (3), 417.

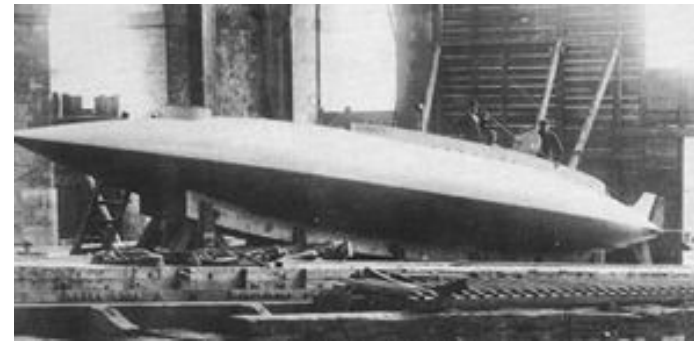
**Posters:** J. Cho et al. and J. Huang et al.



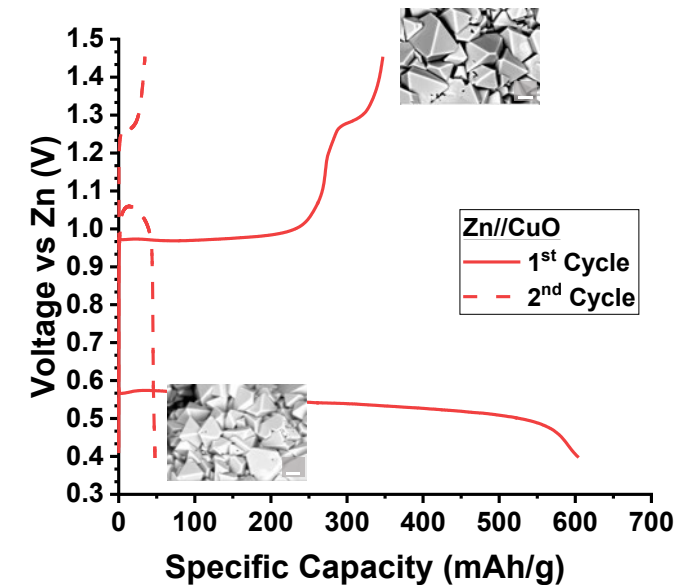
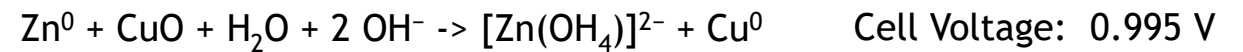
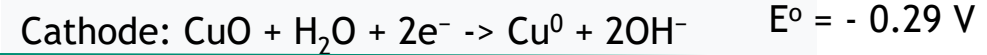
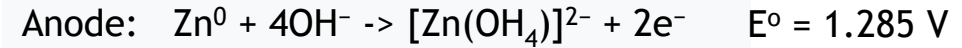
# Development of CuO Cathode (674 mAh/g)



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



*Gymnote in 1889*



Cu<sub>2</sub>O Octahedra: on Charge and Discharge  
(scale bar = 2 μm)

**Almost 140 years of no reported  
rechargeable CuO cathode**

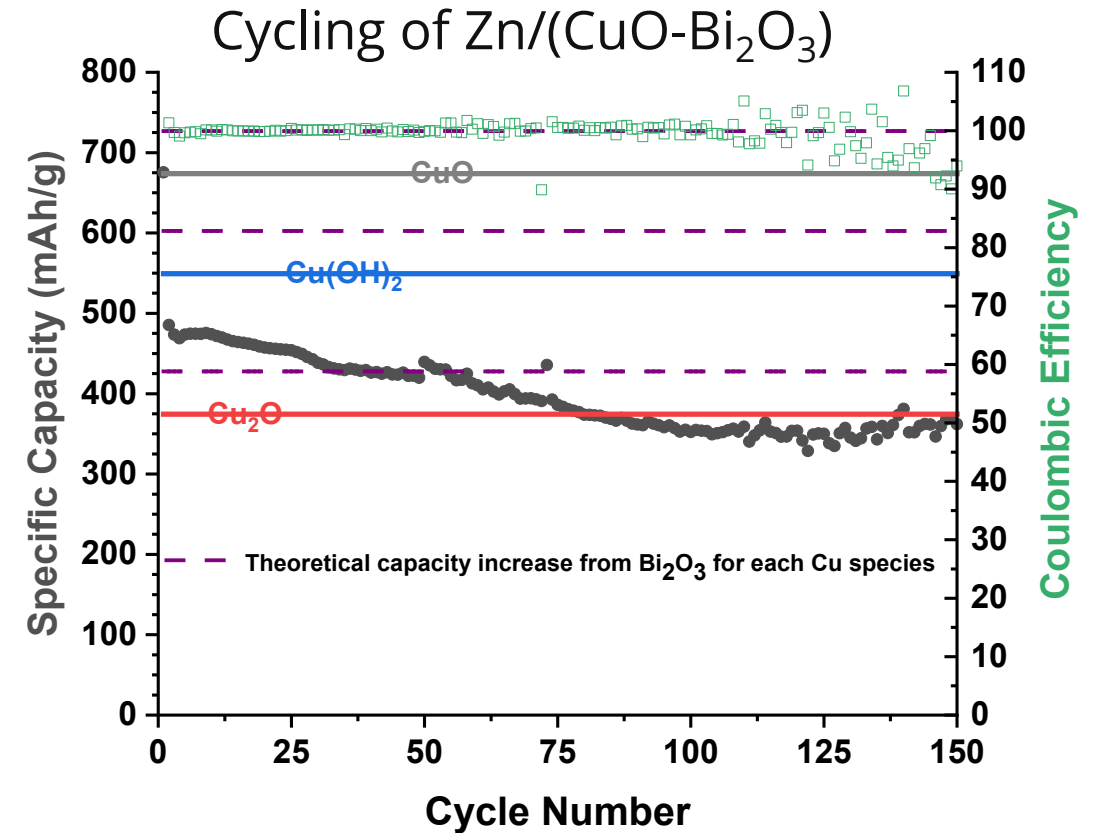
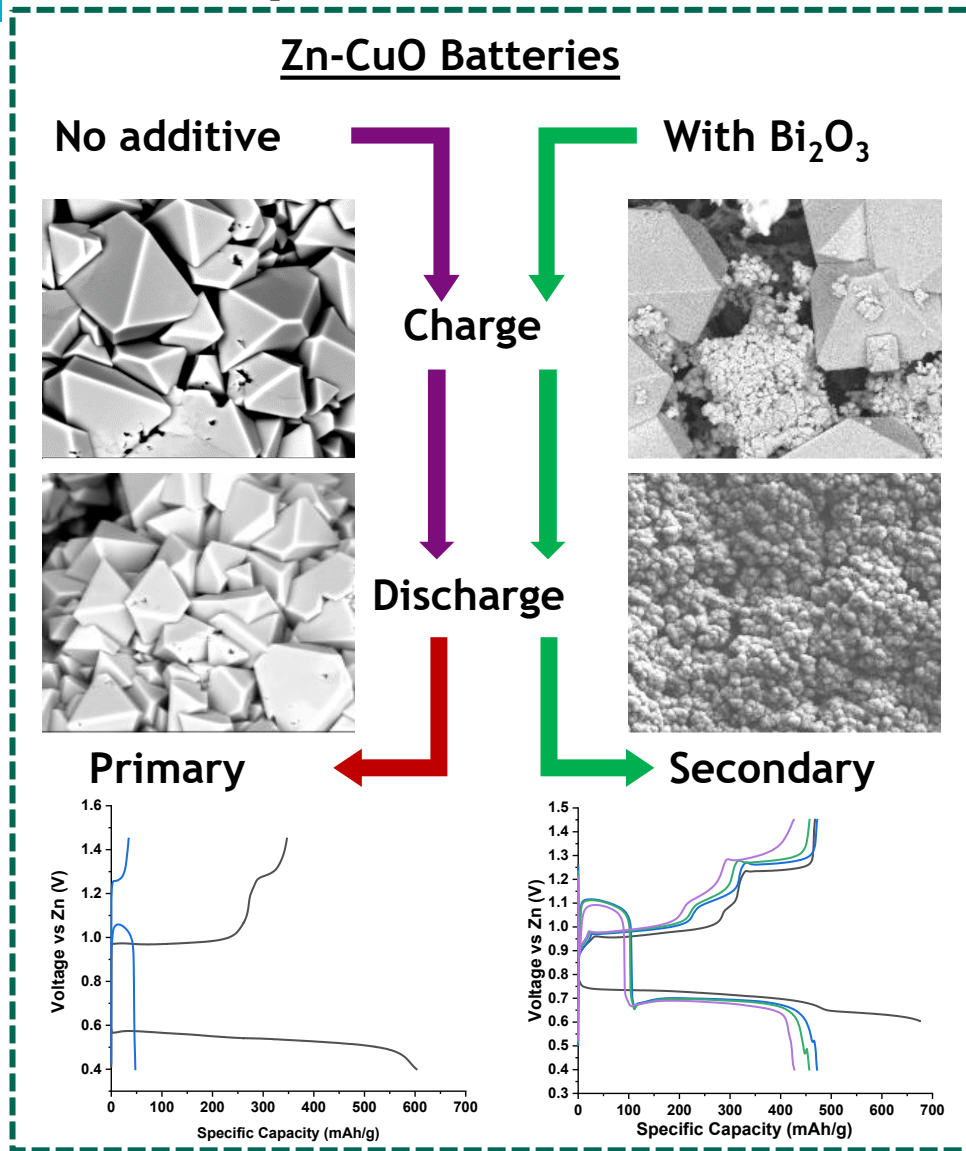
**1883**

**2021**

*Publication:*

N. Schorr et al. *ACS Appl. Energy Mater.* 2021, 4, 7, 7073-7082.

# Development of CuO Cathode (674 mAh/g)



- Cu<sub>2</sub>O detrimental feature to cycling in Cu cycling
- Bi promotes reduction of Cu<sup>II</sup> and Cu<sup>I</sup>
- Bi decreases cell resistance
- Bi decreases Cu(OH)<sub>2</sub> solubility, less Cu(OH)<sub>4</sub><sup>2-</sup>
- No new mixed (Cu/Bi) phase observed
- Capacity settles in at ~ 1e-

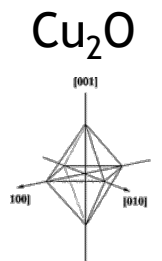
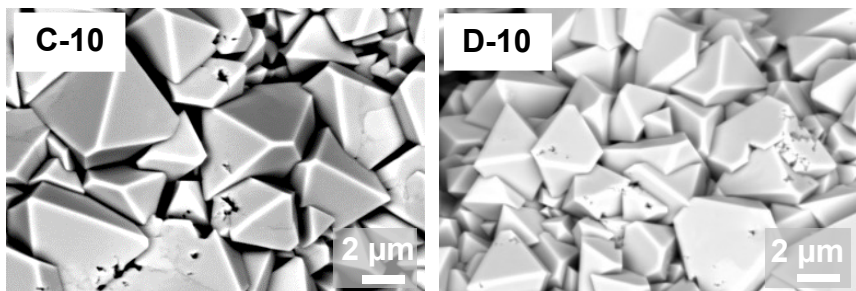
## Publications

N. Schorr et al. *ACS Appl. Energy Mater.* 2021, 4, 7, 7073-7082.

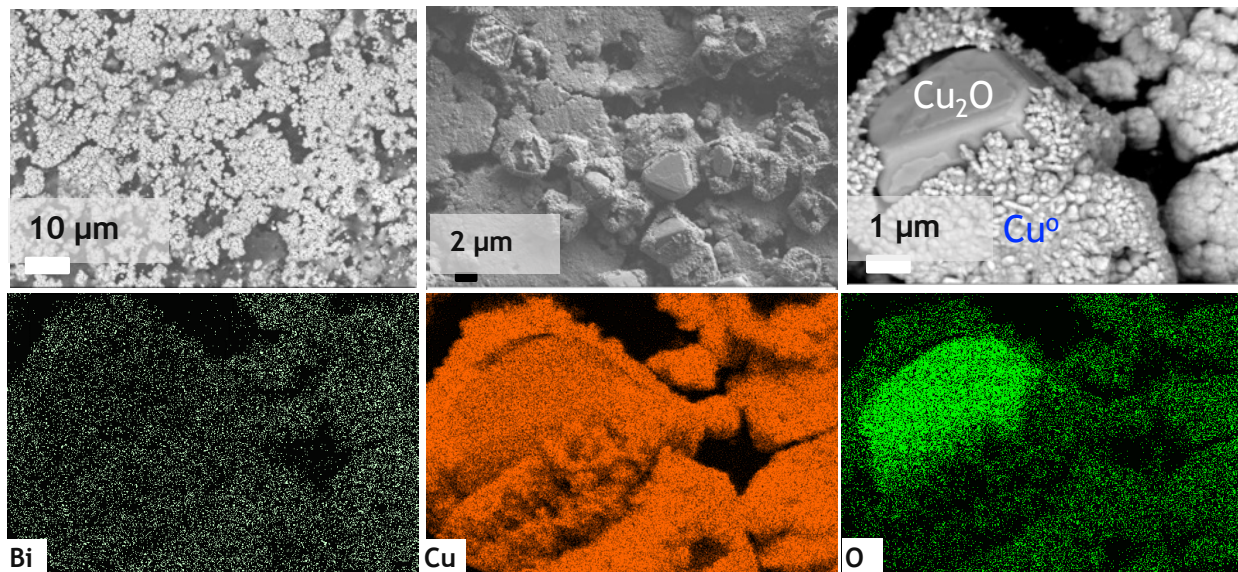
# Development of CuO Cathode (674 mAh/g)



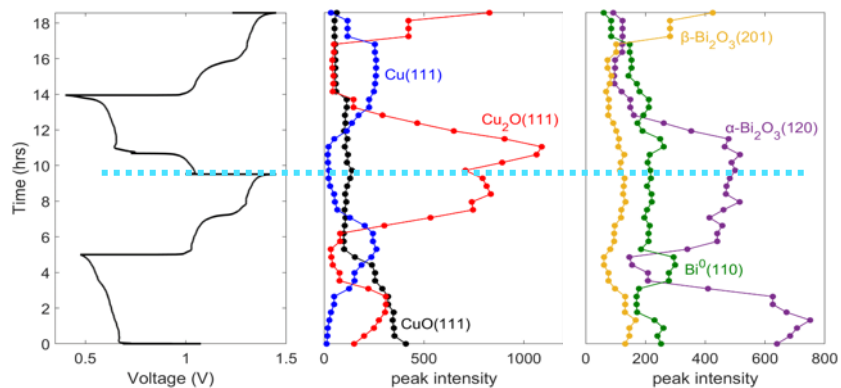
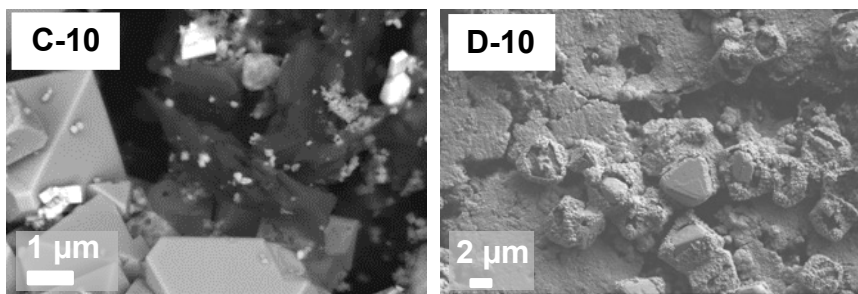
CuO cathode (no additive)



CuO/ $\text{Bi}_2\text{O}_3$  10x Discharge

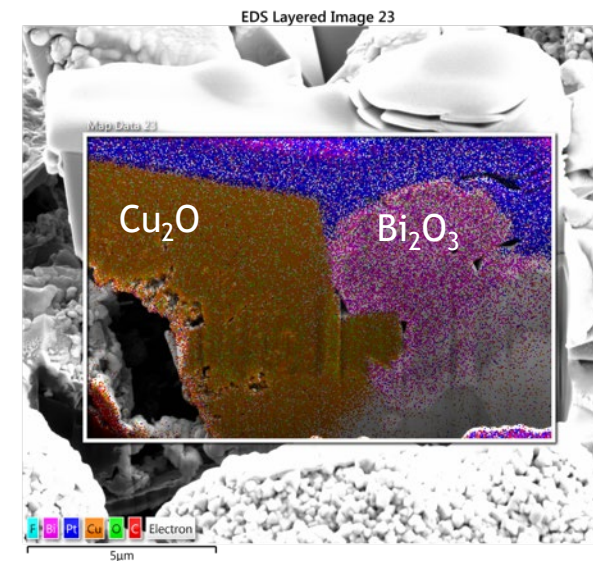
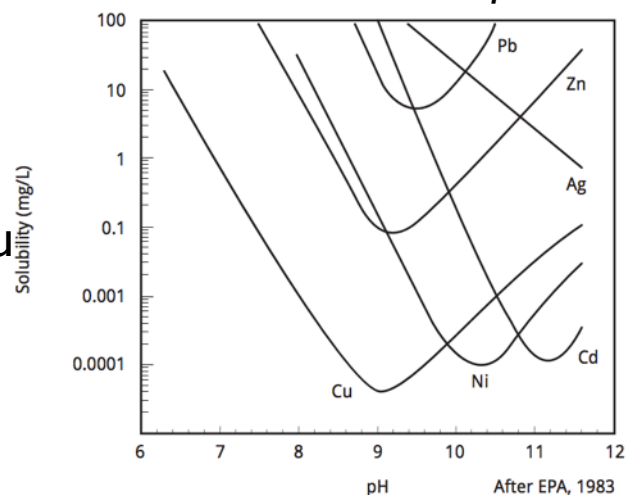


CuO/ $\text{Bi}_2\text{O}_3$  cathode



EDXRD  
No CuO  
No Bi/Cu  
mixed  
phases

Soluble "ate" complexes



[Publications](#)

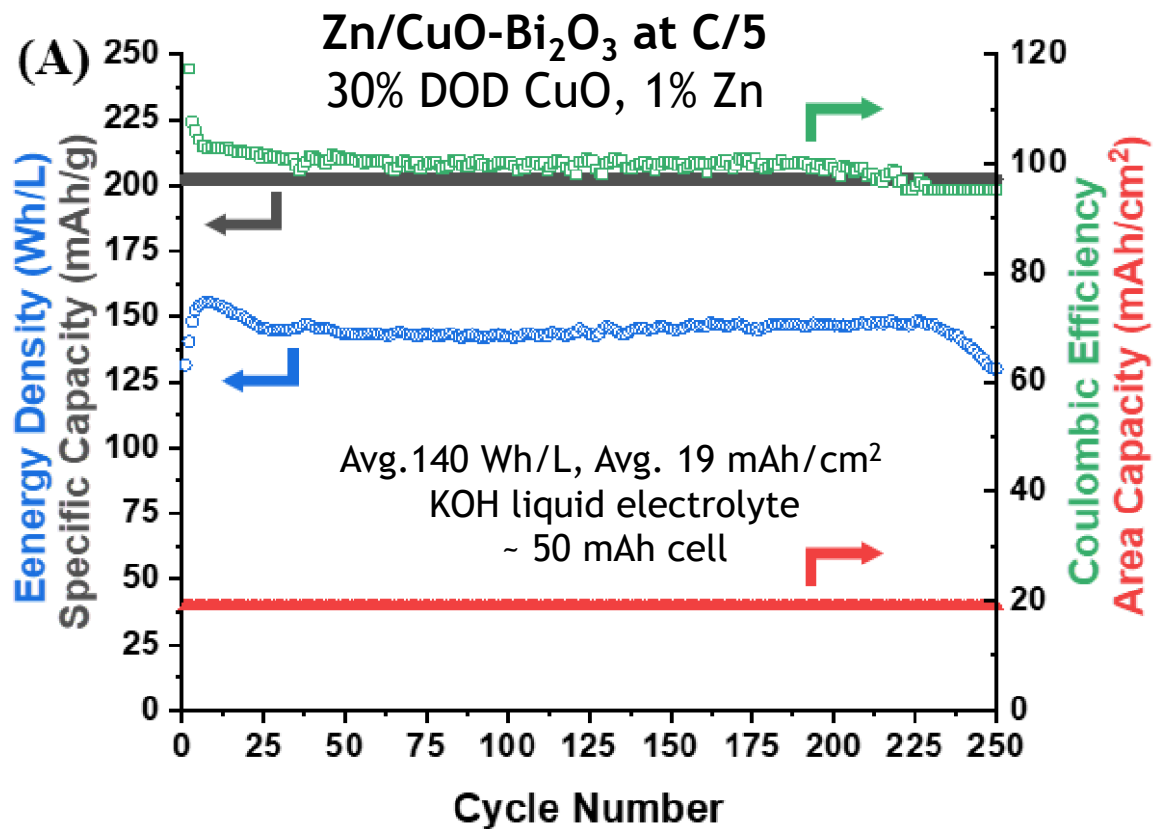
N. Schorr et al. *ACS Appl. Energy Mater.* 2021, 4, 7, 7073-7082.

# Zn/CuO - Highlights



## Bi-additive enables 1<sup>st</sup> Rechargeable Alkaline Zn/CuO Battery

Limited DOD Strategy 1



~140-250 Wh/L demonstrated in R&D Batteries  
using aqueous KOH electrolyte

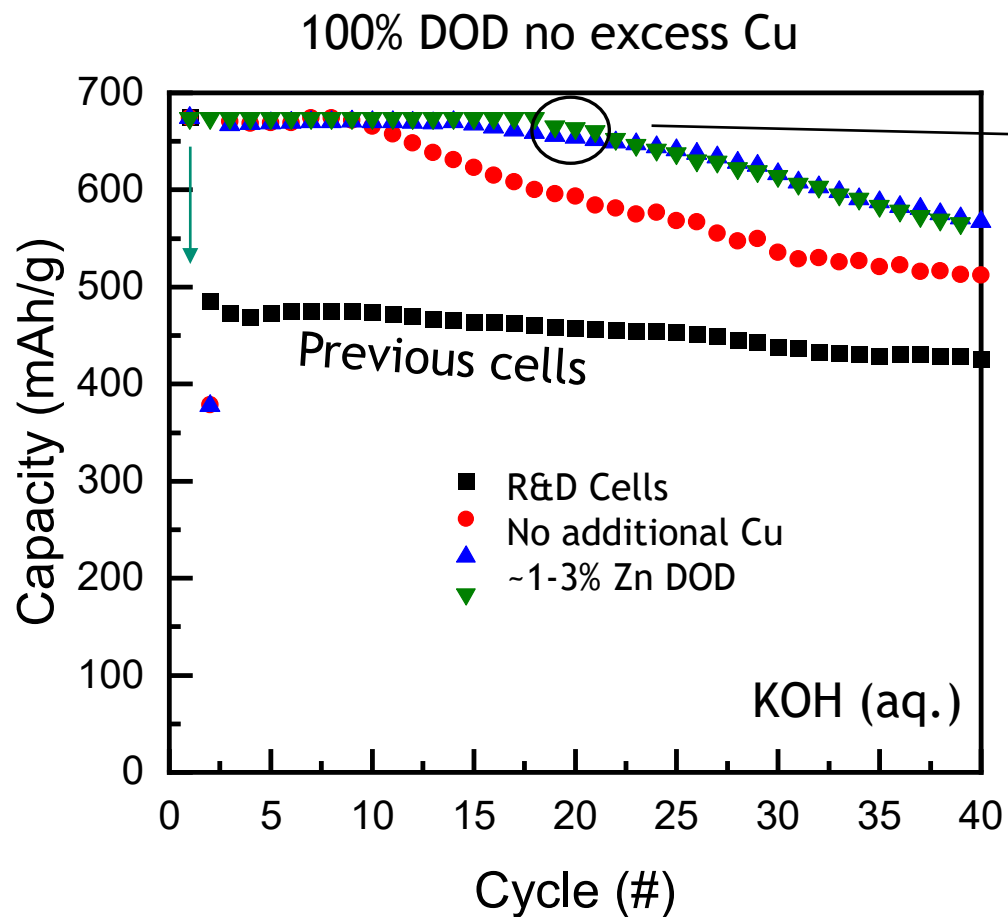
*Wh/L calculated using volume of electrode pack  
including current collectors*

250 cycles: 30% DOD<sub>CuO</sub> (200 mAh g<sup>-1</sup> cathode)  
Average areal capacity 19 mAh cm<sup>-2</sup>  
Coulombic Efficiency above 99%

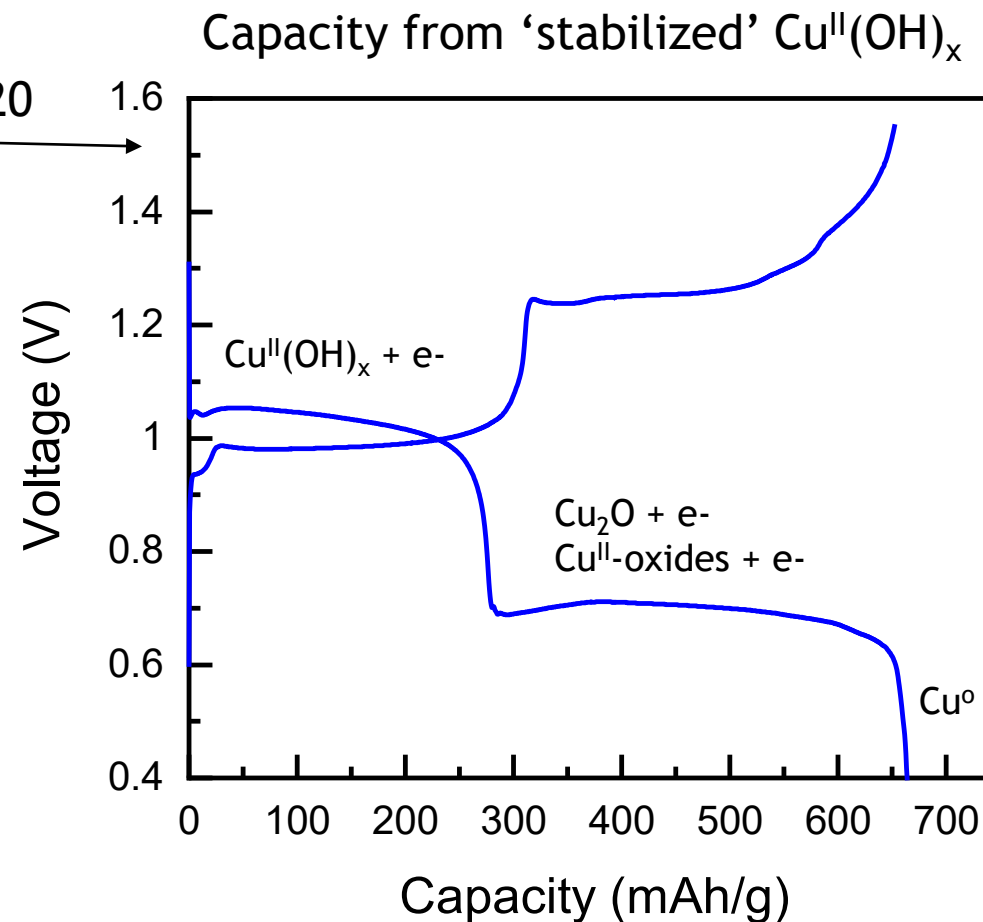
### Publications

N. Schorr et al. *ACS Appl. Energy Mater.* 2021, 4, 7, 7073-7082.

## FY 22 Efforts include optimizing CuO specific capacity

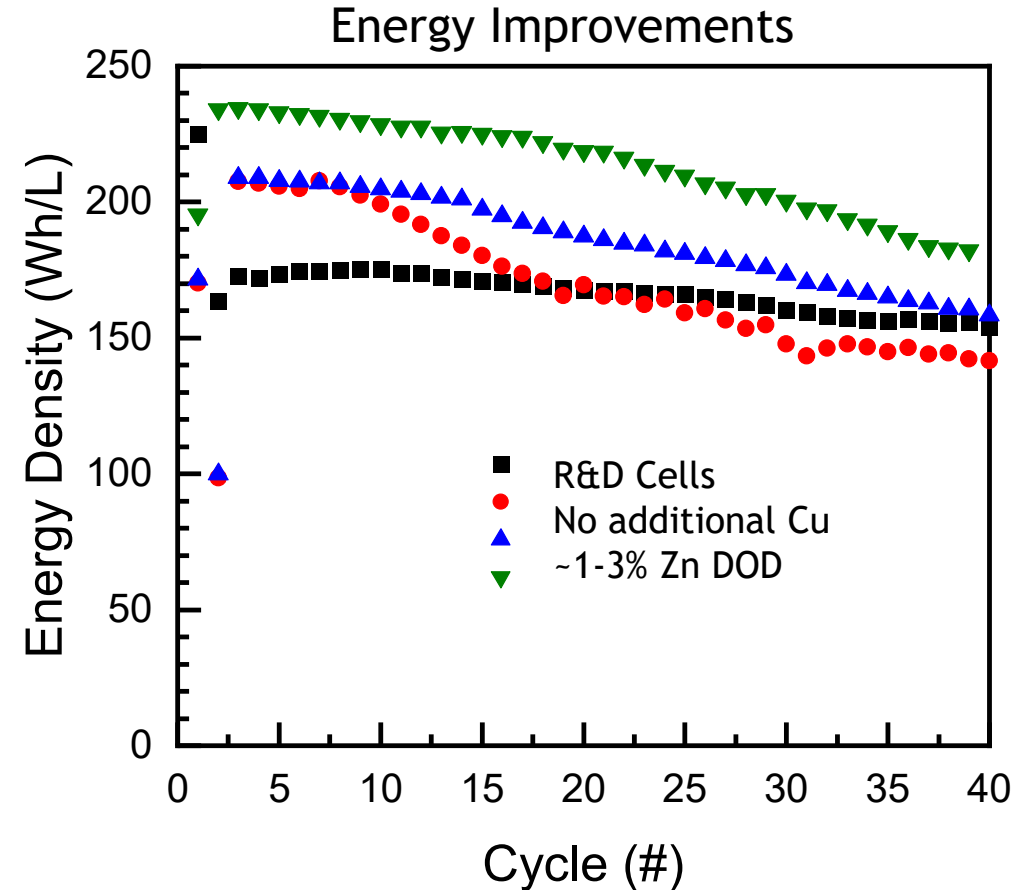
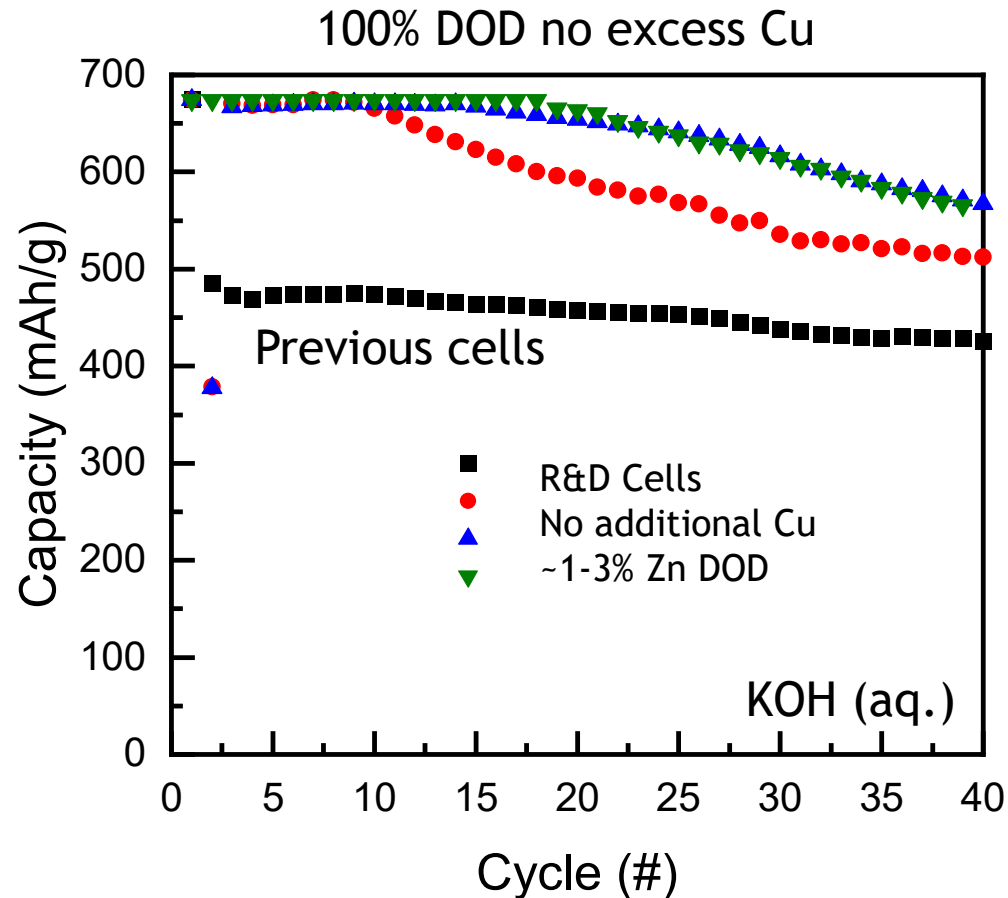


Cycle 20



★ 1<sup>st</sup> gen CuO ~ 500 mAh/g @ Cycle 2  
 ~ 375 mAh/g @ Cycle 75

## FY 22 Efforts include Energy Improvements

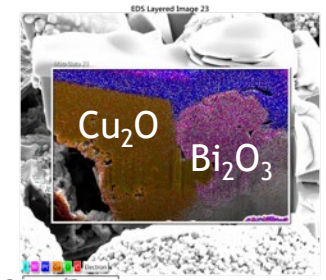


- R&D Cells with No additional Cu, 1-3% Zn DOD
- Capacity and Energy Increases associated with high voltage plateau retention
- OTT-TCF: Goal is Zn/CuO with  $\geq 200$  Wh/L for 100 cycles in 10 and 100 Ah, w/COTS Power converters

# Nanoscale Carbon Coated Cu/Bi

Nanoscale approach could provide for more intimate contact?

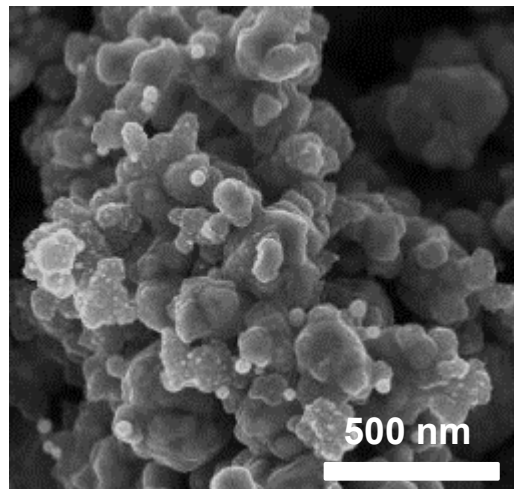
Carbon coated CuO could provide for increased conductivity, provide for cuprate/bismuthate trapping and affect resistive phases/morphologies ?



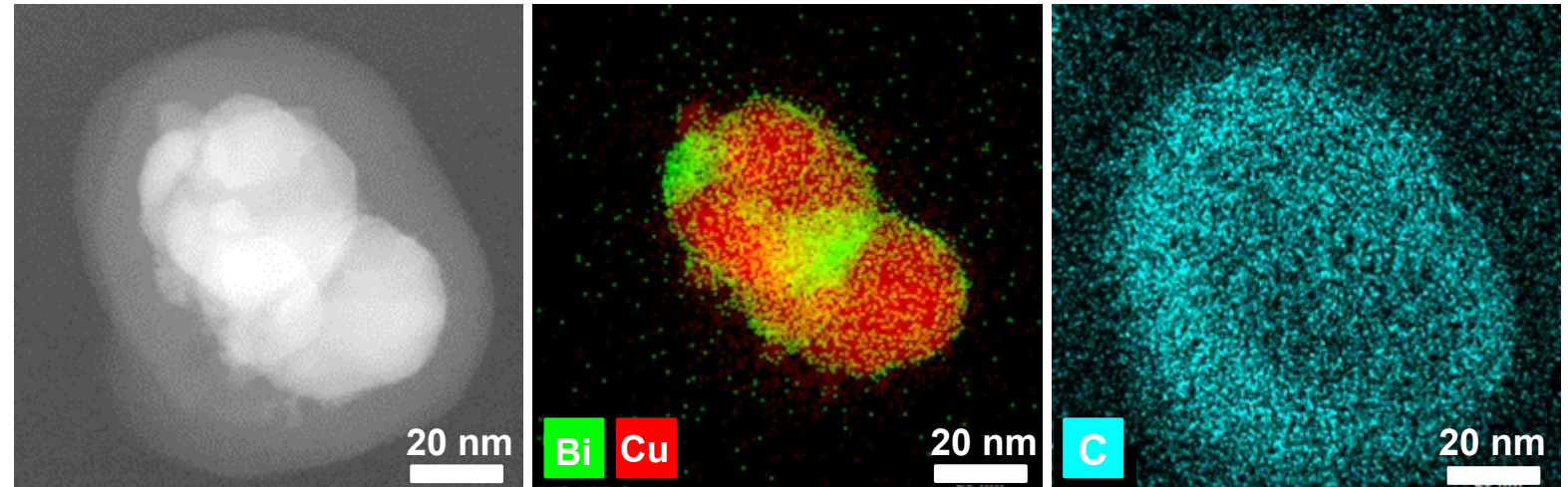
CuO/Bi<sub>2</sub>O<sub>3</sub>@PDA

600 °C, 5% H<sub>2</sub>/Ar

Cu/Bi@C



Cu/Bi@C



- Raman: amorphous C
- TGA/DTA and EA: = ~ 8 wt.% Carbon Coating (~ 20 nm)
- TEM: Nanoscale Cu/Bi@C
- Metallic Cu and Bi are produced - not the oxides

*Poster:* N. Schorr et al.

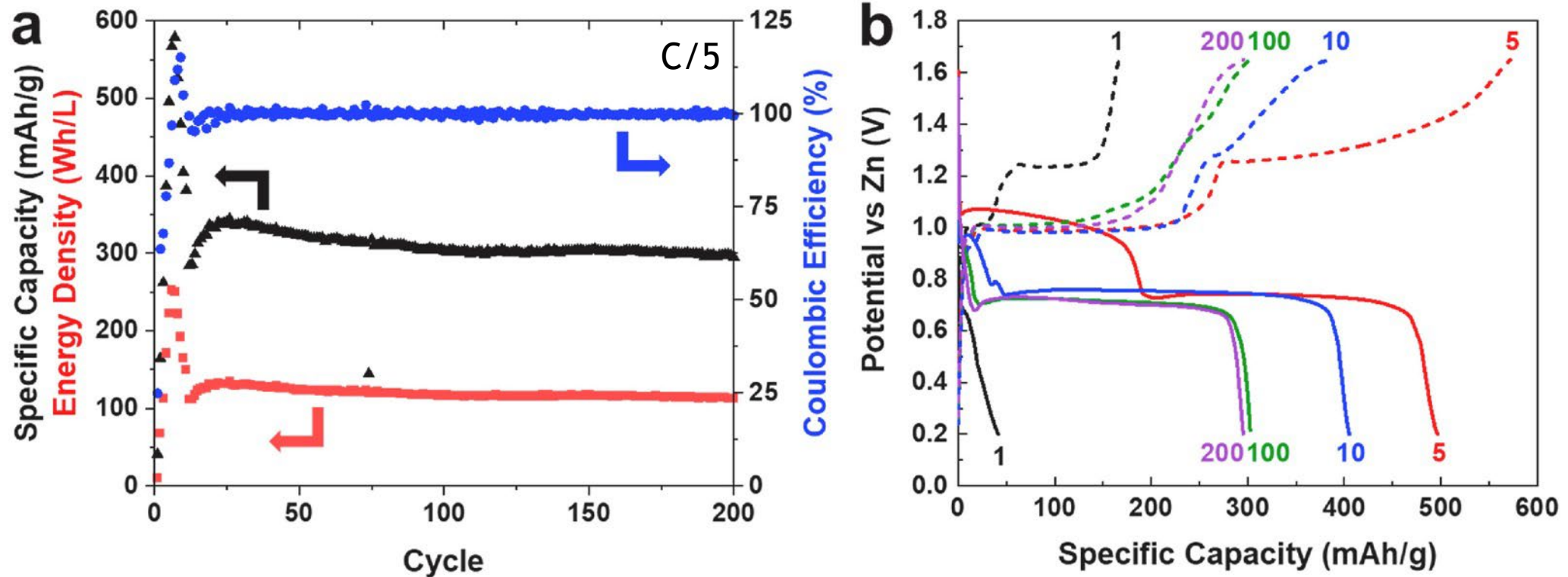
*Publication:* D. Arnot et al. *J. Power Sources* 2022, 529, 231168.

# Copper Coated Cu/Bi



After an initial break-in period -

Cu/Bi@C provide for stable cycling with good capacity



*Loss of high voltage plateau consistent with loss of initial capacity (soluble cuprate)*

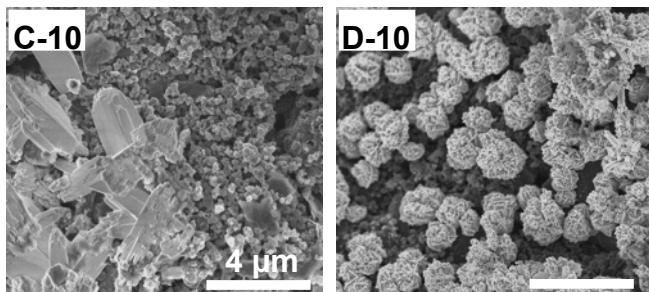
*Publication:* D. Arnot et al. *J. Power Sources* 2022, 529, 231168.

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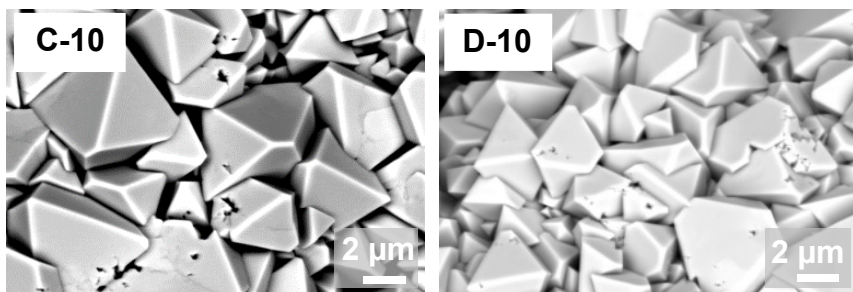


# Copper Coated Cu/Bi

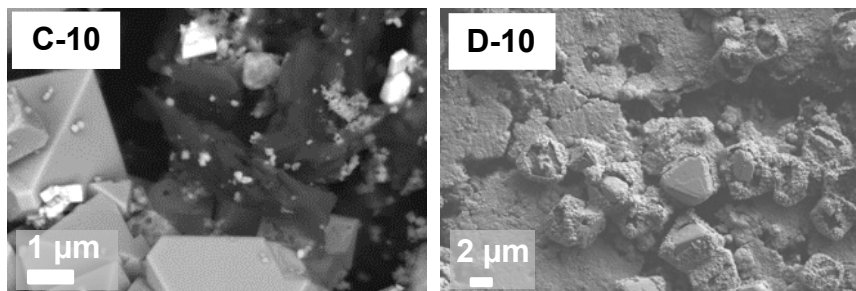
Cu/Bi@C cathode



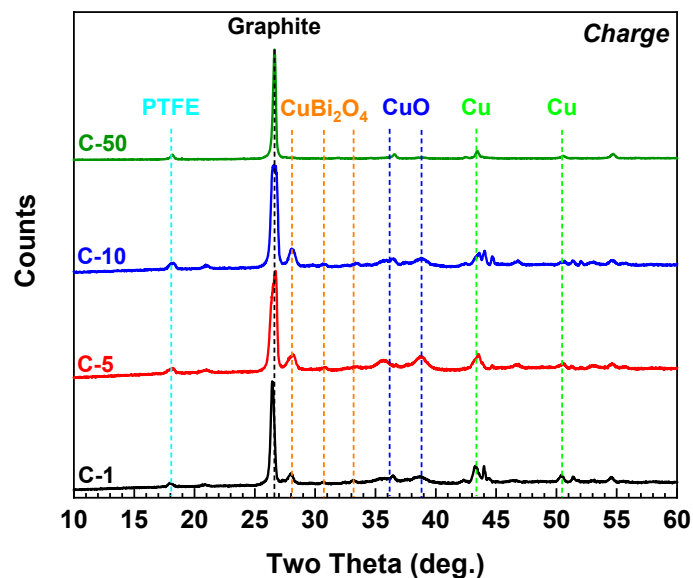
CuO cathode (no additive)



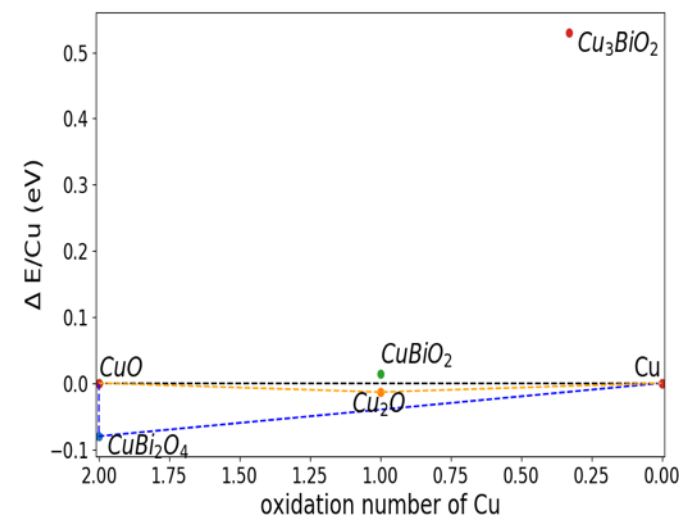
CuO/Bi<sub>2</sub>O<sub>3</sub> cathode



New CuBi<sub>2</sub>O<sub>4</sub> phase



Formation Energies of Cu species



Bi and carbon coating:

- Prevents the formation of detrimental Cu<sub>2</sub>O structures
- Promotes CuBi<sub>2</sub>O<sub>4</sub> and CuO phases upon charge
- DFT calculations support CuBi<sub>2</sub>O<sub>4</sub> as favored species for Cu(II)
- C provides for Cu@C cycling (no Bi) – not shown

*Promising new example of developing reversible Cu cathodes*

[Publication](#)

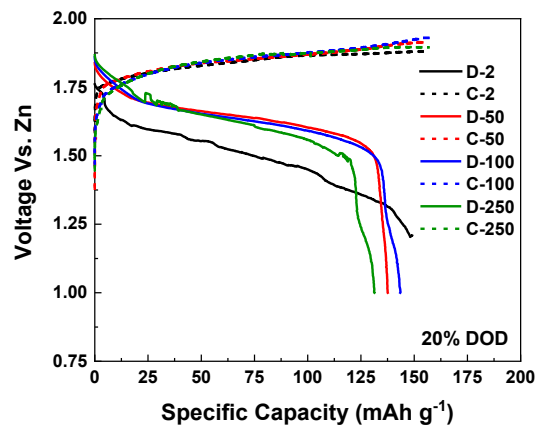
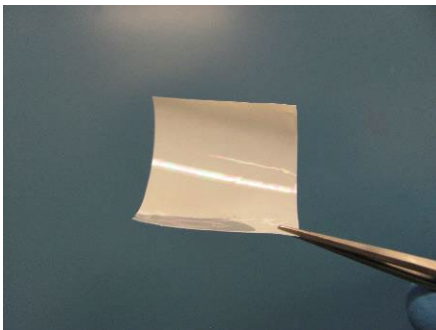
[Poster](#)

D. Arnot et al. *J. Power Sources* 2022, 529, 231168. K. Acharya et al. Theoretical studies of...

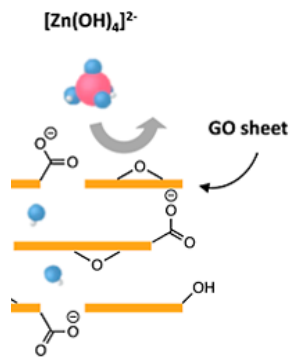
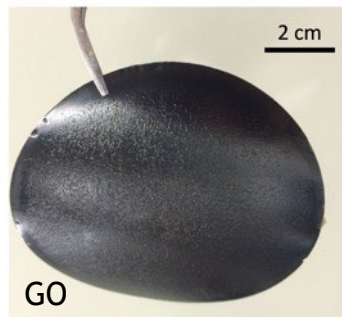
# Development of Separators to control diffusion of “ate” complexes



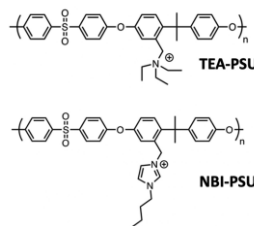
## NC-Celgard



## GO/PVA



## PSU-Membranes

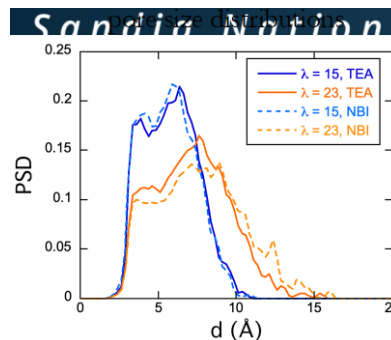
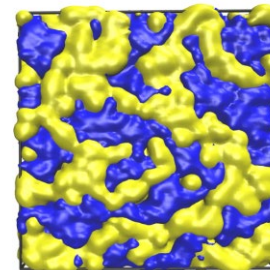
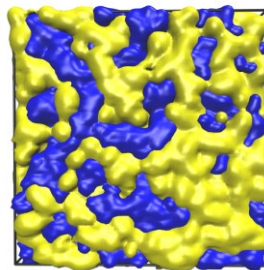


zincate “size” ~ 5-5.5 Å  
zincate will diffuse less in NBI

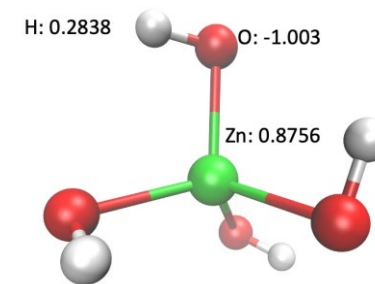
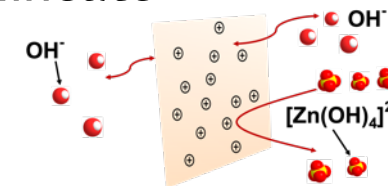
$$\lambda = \# \text{ water/cation}$$

$$\lambda = 15$$

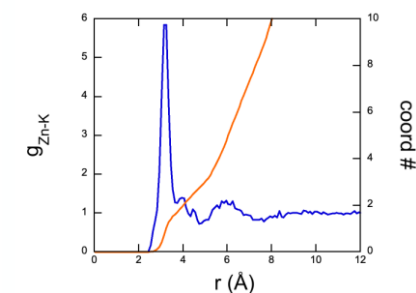
$$\lambda = 23$$



## Zincate



$\text{K}^+$  coordinates more strongly with zincate than with  $\text{OH}^-$



**Publications:** D. Arnot et al. *Adv. Energ. Mater* 2022, J. Huang et al 2022 *ACS Appl. Energy Mater.* 2022.

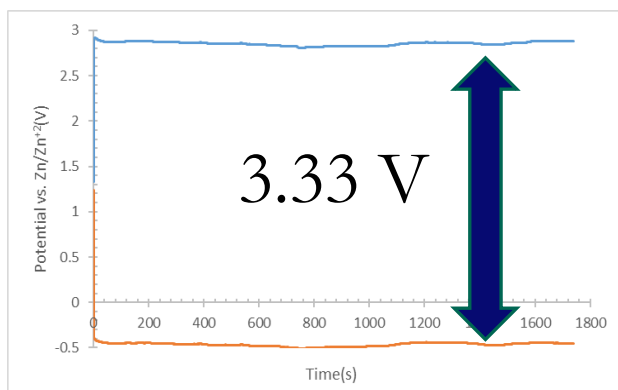
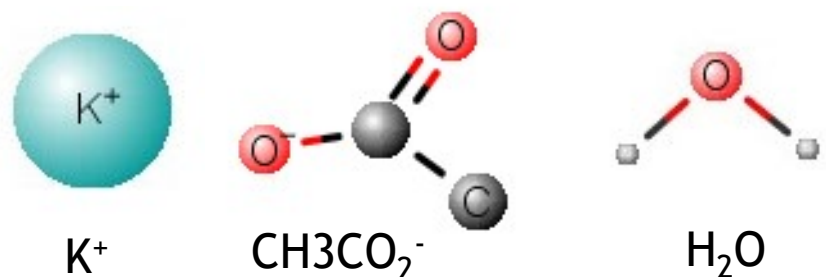
A. Frischnecht et al., *ACS Appl. Polym. Mater.*, 2022.

**Posters:** A. Frischnecht et al., J. Huang et al. and B. Wygant et al.

# Addressing the Low Voltage of Aqueous Zn Batteries

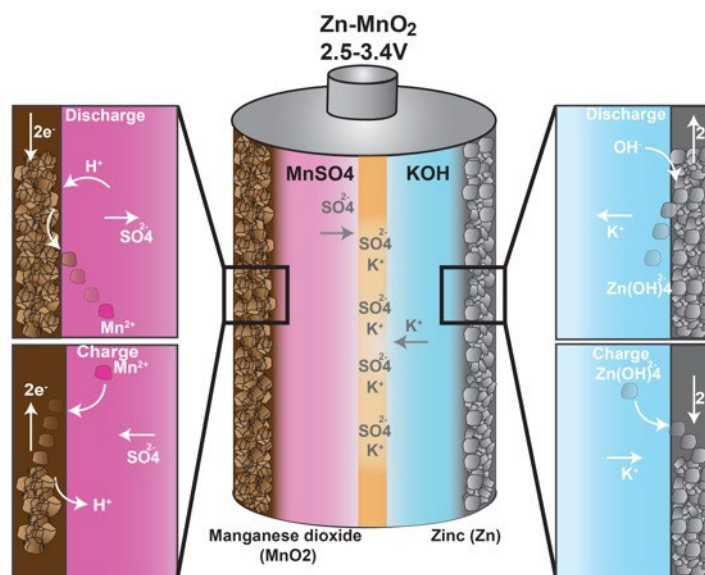


## Water-In-Salt Electrolytes (WiSE)



- 3.33V Window
- ~ 16x lower HER than KOH(aq)

## Dual electrolyte Approach to High Voltage



Dual electrolyte/Buffer gel provides for high voltage membrane-less batteries

*Poster:* D. Dutta et al.

*Publications:* G. G. Yadav et al. *Materials Horizons* 2022.

# PROJECT CONTACTS



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Babu Chalamala

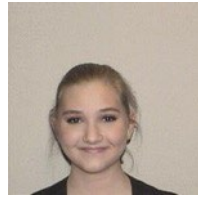
## FY 21 Sandia Team



Noah Schorr



Bryan Wygant



Rachel Habing



Ciara Wright



David Arnot



Logan Ricketts



Erik Spoerke



Howard Passell



Nelson Bell

# 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!



# Thank you



Extra Slides

**RESULTS: (SNL) Zn Project Battery Posters - DOE OE Energy Storage Virtual Peer Review 2022****SNL led Posters:**

1. A. Frischknecht et al. “Models for Simulations of Alkaline Electrolytes in Zinc Batteries”
2. N. Schorr et al. “Rechargeable Alkaline Zn-Cu Batteries Enabled by Carbon Coated Cu/Bi Particles”
3. B. Wygant et al. “Metal Ion Sensing and Quantification by Anodic Stripping Voltammetry (ASV) for Study of Alkaline Battery Separators”

**CUNY-EI led Posters:**

4. D. Dutta et al. “Acetate-based water-in-salt electrolytes (WiSE) for improved zinc battery cycling”
5. J. Cho et al. “Hydrogel Electrolytes Ensuring the Transportability and the 2nd Electron Reaction of Zn-MnO<sub>2</sub> Alkaline Batteries”
6. P. Yang et al. “Investigating Anodes Based on Calcium Zincate (Ca[Zn(OH)<sub>3</sub>]<sub>2</sub>-2H<sub>2</sub>O) for Improved Cycle Life in Rechargeable Alkaline Zinc Batteries”

**NMSU led Posters:**

7. K. Acharya et al. “Theoretical Studies of the Discharge Mechanism of CuO Cathodes Modified with Bi<sub>2</sub>O<sub>3</sub> in Rechargeable Zn/CuO Batteries”

**LLNL led Posters:**

8. C. Zhu et al. “Additive Manufacturing of High-Capacity 3D Zn Anodes for Rechargeable Alkaline Batteries”

**UEP led Posters:**

9. G. G. Yadav et al. “The Performance of Low Cost and Highly Energy Dense Hybrid Zinc|Manganese Dioxide-Copper Scaled-Cells”
10. J. Huang et al. “Zinc-Manganese Dioxide Battery Development and Commercialization at Urban Electric Power”



## FY22 Publications (12 total = 10 published, 2 in peer review)

1. D.J. Arnot, M.B. Lim, N.S. Bell, N.B. Schorr, R.C. Hill, A. Meyer, Y.T. Cheng, T.N. Lambert “High Depth-of-Discharge Zinc Rechargeability Enabled by a Self-Assembled Polymeric Coating” *Adv. Energ. Mater.*, 2021, DOI:10.1002/aenm.202101594.
2. D.J. Arnot, N.B. Schorr, I.V. Kolesnichenko, T.N. Lambert “Rechargeable Alkaline Zn-Cu Batteries Enabled by Carbon Coated Cu/Bi Particles” *Journal of Power Sources*, 529, 2022, 231168, DOI: 10.1016/j.jpowsour.2022.231168
3. J. Cho, G.G. Yadav, M. Weiner, J. Huang, A. Upreti, X. Wei, R. Yakobov, B. Hawkins, M. Nyce, T.N. Lambert, D.J. Arnot, N.S. Bell, N.B. Schorr, D. Turney, G. Cowles, S. Banerjee “Hydroxyl Conducting Hydrogels Enable Low-Maintenance Commercially Sized Rechargeable Zn-MnO<sub>2</sub> Batteries for Use in Solar Microgrids” *Polymers*, 2022, 14 (3), 417, DOI: 10.3390/polym140304417. (*Invited Manuscript*)
4. A.L. Frischknecht, P.J. in 't Veld, I.V. Kolesnichenko, D.J. Arnot, T.N. Lambert “Morphology and Dynamics in Hydroxide-Conducting Polysulfones” *ACS Appl. Polym. Mater.*, 2022 4, 4, 2470-2480, DOI: 10.1021/acsapm.1c01798.
5. B.E. Hawkins, D.E. Turney, R.J. Messinger, A.M. Kiss, G.G. Yadav, S. Banerjee, T.N. Lambert “Electroactive ZnO: Mechanisms, Conductivity, and Advances in Zn Alkaline Battery Cycling” *Adv. Energy Mater.* 2022, 12, 2103294, DOI: 10.1002/aenm.202103294.
6. J. Huang, G.G. Yadav, D.E. Turney, J. Cho, M. Nyce, B.R. Wygant, T.N. Lambert, S. Banerjee “Ion-Selective Graphene Oxide/Polyvinyl Alcohol Composite Membranes for Rechargeable Alkaline Zinc Manganese Dioxide Batteries” *ACS Applied Energy Materials*, 2022, DOI: 10.1021/acsaem.2c01605.
7. E.D. Spoerke, H. Passell, G. Cowles, T.N. Lambert, G.G. Yadav, J. Huang, S. Banerjee, B.R. Chalamala “Driving Zn-MnO<sub>2</sub> Grid-Scale Batteries: A Roadmap to Cost-Effective Energy Storage” *MRS Energy & Sustainability*, 9, pp. 13-18 (2022), DOI: 10.1557/s43581-021-00018-4.

## PROJECT RESULTS



### FY22 Publications (12 total = 10 published, 2 in peer review)

8. B.R. Wygant, T.N. Lambert “Thin Film Electrodes for Anodic Stripping Voltammetry: A Mini-Review” *Frontiers in Chemistry*, Vol. 9, 2022, 2296-2646 (*Invited Manuscript for Special Issue: Recent Advances of Metal-Film Electrodes for Trace Electrochemical Analysis*).
9. Chunmei Ban, Amy C. Marschilok, “The 2022 Applied Physics by Pioneering Women: A Roadmap - 11. Opportunities and Challenges in Development of Multivalent Batteries,” *Journal of Physics D Applied Physics*, 2022, in press.
10. “Beyond Li-Ion Batteries for Grid-Scale Energy Storage,” G.P. Wheeler, L. Wang, A.C. Marschilok, in *Elements in Grid Energy Storage*, Ed. B. Chalamala, V. Sprenkle, I. Gyuk, R. Masiello, R. Byrne, V. Gupta. Cambridge Elements, 2022.
11. Z. Cheng, N. Schorr, B. Wygant, A. Van Buuren, G.G. Yadav, T.N. Lambert, D.E. Turney, E. Spoerke “Direct Ink Writing of 3D Zn Structures as High-Capacity Anodes for Rechargeable Alkaline Batteries” *Submitted to Small Structures*.
12. Jason Kuang, Shan Yan, Lisa M. Housel, Steven N. Ehrlich, Lu Ma, Kenneth J. Takeuchi, Esther S. Takeuchi, Amy C. Marschilok, Lei Wang, “Manganese Molybdate Cathodes with Dual-redox Centers for Aqueous Zinc-ion Batteries: Impact of Electrolyte on Electrochemistry,” *ACS Sustainable Chemistry and Engineering*, revision under review.





## FY 22 Presentations (22 total = 15 invited and 7 contributed )

1. *Invited talk:* A.L. Frischknecht “Insights into Hydrated Ion-Conducting Polymers from MD Simulations” ACS POLY workshop on Polymers for Fuel Cells, Energy Storage, and Conversion, Napa, CA, May 15-18, 2022.
2. *Invited Talk:* A.L. Frischknecht “Morphology and Ion Transport in Hydrated Ion-Containing Polymers” American Physical Society March Meeting, Chicago, IL, March 14-18, 2022.
3. *Invited Talk:* T.N. Lambert, N.B. Schorr, B. Wygant, R. Habing, C. Wright, A.M. Bruck, M. Kim, J. Goulart, J.W. Gallaway “The Discovery and Development of Rechargeable Zn/CuO Batteries” 241st Electrochemical Society (ECS) Meeting, Vancouver, BC, Canada, May 29 - June 2, 2022.
4. *Invited Talk:* T.N. Lambert “Developing New chemistries for Alkaline Zn-based Batteries” NAATBatt International Workshop on Zinc Battery Technology IV, December 16, 2021.
5. *Invited Talk:* G.G. Yadav, M. Weiner, A. Upreti, J. Huang, X. Wei, T.N. Lambert, N.B. Schorr, N.S. Bell, S. Banerjee “The Advent of Aqueous >2.85V Zn-MnO<sub>2</sub> Batteries: Uncovering Novel Mechanisms in This New High Voltage Chemistry” 241st Electrochemical Society (ECS) Meeting, Vancouver, BC, Canada, May 29 - June 2, 2022.
6. *Invited Talk:* G. G. Yadav “The Advent of Aqueous >2.85V Zn-MnO<sub>2</sub> batteries: Uncovering Novel Mechanisms in this New High Voltage Chemistry” NY-BEST Annual Fall Energy Storage Technology and Innovation Conference. 2021
7. *Invited Talk:* G. G. Yadav, J. Huang, M. Weiner, S. Yang, K. Vitale, S. Rahman, K. Keane and S. Banerjee. "Improvements in Performance and Cost Reduction of Large-Scale Rechargeable Zinc|Manganese Dioxide Batteries and a Future Roadmap Driven through Real World Applications". Electrochemical Society 241, 2022.



## FY 22 Presentations (22 total = 15 invited and 7 contributed )

8. *Invited Talk:* G. G. Yadav, M. Weiner, A. Upreti, J. Huang, X. Wei, T. N. Lambert, N. B. Schorr, N. Bell and S. Banerjee. "The Advent of Aqueous >2.85V Zn-MnO<sub>2</sub> batteries: Uncovering Novel Mechanisms in this New High Voltage Chemistry". Electrochemical Society 241, 2022.
9. *Invited Talk:* S. Banerjee. "Zinc-Based Energy Storage System Deployments and Developments for Transition to a Clean Energy Future". Electrochemical Society 241, 2022.
10. *Invited Talk:* A.C. Marschilok et al. "Aqueous Zinc Ion Systems for Large Scale Electrochemical Energy Storage: Progress and Opportunities," 241st Electrochemical Society Meeting, May 31, 2022, Vancouver, Canada.
11. *Invited Talk:* A.C. Marschilok et al. "Electrochemistry Based and Coupled Characterization of Energy Storage Materials and Systems," International Battery Association Meeting, October 2-7, 2022, Bled, Slovenia, invited.
12. *Invited Talk:* E.S. Takeuchi et al. "Rechargeable Zinc Based Batteries for Large Scale Storage," Tech Connect World Innovation Conference, June 12-14 2022, National Harbor Maryland, Energy Storage Session.
13. *Invited Talk:* K.J. Takeuchi "Investigation of Zinc/Manganese Oxide Batteries for Large Scale Energy Storage," Stony Brook University, Tech Connect World Innovation Conference, June 12-14 2022, National Harbor Maryland, Batteries Beyond Lithium Session, invited.
14. *Invited Talk:* A.C. Marschilok et al. "Tuning Materials Properties of Sodium Vanadium Oxide (NaV<sub>3</sub>O<sub>8</sub>, NVO) for Aqueous Zn Batteries," Stony Brook University, Tech Connect World Innovation Conference, June 12-14 2022, National Harbor Maryland, Batteries Beyond Lithium Session.
15. *Invited Talk:* A.C. Marschilok et al. "Energy Storage to Energy Systems Approaches for a Sustainable Energy Future" Presidential Sustainability Symposium, Sept. 21, 2022, Hofstra University, New York, invited.

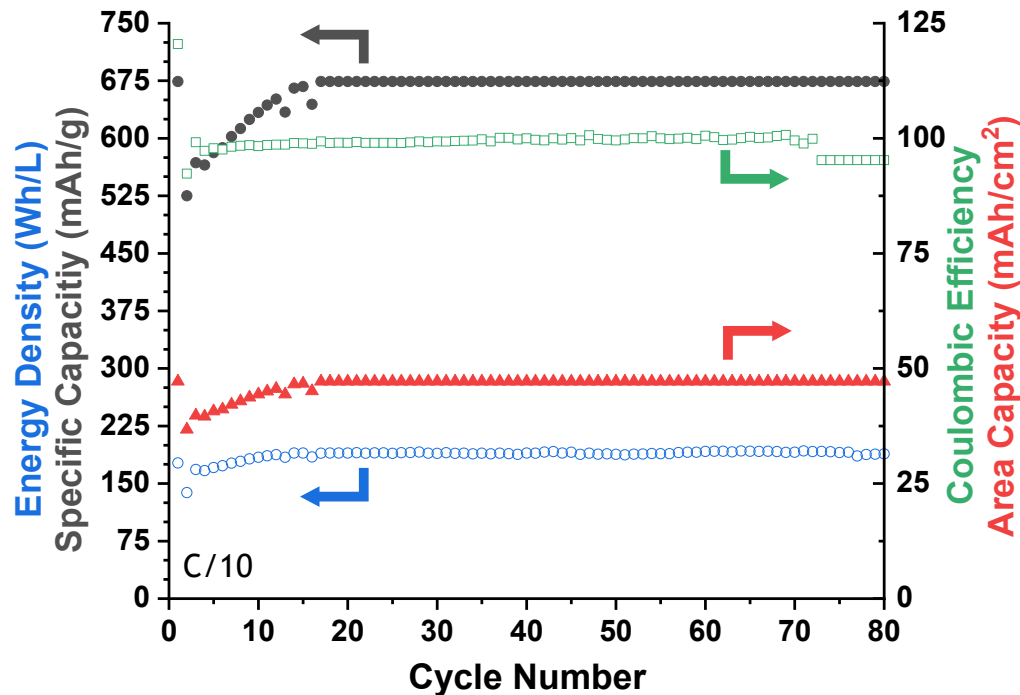


## FY 22 Presentations (22 total = 15 invited and 7 contributed )

16. K. Acharya, N. Paudel, B. Ale Magar, T.N. Lambert, I. Vasiliev “Ab Initio Study of the Discharge Mechanism of CuO Cathodes Modified with Bi<sub>2</sub>O<sub>3</sub> in Zn/CuO Batteries” American Physical Society March Meeting, Chicago, IL, March 14-18, 2022.
17. B. Ale Magar, N. Paudel, T.N. Lambert, I. Vasiliev “Ab initio Studies of the Electrochemical Properties of Zn and ZnO in Rechargeable Zn/MnO<sub>2</sub> Batteries” American Physical Society March Meeting, Chicago, IL, March 14-18, 2022.
18. J. Cho, G. Yadav, J. Huang, M. Nyce, M. Weiner, T.N. Lambert, S. Banerjee “The Low-Maintenance Application of Hydrogel Electrolytes to Zn|MnO<sub>2</sub> Rechargeable Batteries” 2021 AIChE Annual Meeting, Boston, MA, November 7-11, 2021.
19. B. Hawkins, D.E. Turney, G. Yadav, A.M. Kiss, T.N. Lambert, S. Banerjee, R. Messinger “Electrochemically Active ZnO Discharge Product Formed in Rechargeable Zn-Alkaline Batteries: Performance Effects and Mechanistic Insights” 2021 AIChE Annual Meeting, Boston, MA, November 7-11, 2021.
20. N. Paudel, B. Ale Magar, K. Acharya, T.N. Lambert, I. Vasiliev “First-Principles Study of the Surface Properties of ZnO Anode Material in Rechargeable Zn/MnO<sub>2</sub> Batteries” American Physical Society March Meeting, Chicago, IL, March 14-18, 2022.
21. N.B. Schorr, D.J. Arnot, A.M. Bruck, J. Gallaway, T.N. Lambert “Copper Oxide Cathodes for Rechargeable Alkaline Zinc Batteries” 2021 MRS Fall Meeting and Exhibit, November 30 - December 7, 2021.
22. B. R. Wygant, T. N. Lambert “Zinc Batteries” Contributions to 2-day series tutorial to Government Accountability Office (GAO).

## Bi-additive enables 1<sup>st</sup> Rechargeable Alkaline Zn/CuO Battery

Limited DOD Strategy 2 - use Cu<sup>0</sup> as an additive



80 cycles: 100% DOD<sub>CuO</sub> (674 mAh g<sup>-1</sup> cathode)

Average areal capacity 46 mAh cm<sup>-2</sup>

Average energy density 186 Wh L<sup>-1</sup> (1% Zn)

Average energy density 263 Wh L<sup>-1</sup> (10% Zn)

- ~ 100% CuO DOD can be achieved
- CuO is ‘tolerant’ of zincate but Zn/CuO is prone to shorting (soluble Zn and Cu)
- Shorting can be mitigated with separators or polymer gel electrolyte ?
- Technical Challenges with Zn still apply
- Tens to hundreds to thousands (?) of cycles depending on DOD, rate etc.

*Could cover from microsecond to day-long outages.*