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Exceptional service in the national interest

Cheap,
Abundant
& Safe
Materials

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Alkaline Batteries for Grid Storage Applications

September 26th 2018, Santa Fe, New Mexico

Timothy N. Lambert

Sandia National Laboratories

Supported by: Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability

Grid Energy Storage

Sandia National Laboratories

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

Intermittent sources requires storage

Alkaline Zn/MnO_2 Batteries

- **Cost**
  - Traditional primary batteries - $18-25 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

URBANELECTRIC POWER
http://www.urbanelectricpower.com

Other OE Funded Projects:
- **Roll to Roll Manufacturing @ UEP**
- **Field Tests @ NM and NY**

Reversibility and Cycle life are the Challenges

Poster: Profs. Banerjee and De Angelis, Advanced Battery Manufacturing Initiative

Alkaline Zn/MnO_2 Batteries

Two classes of rechargeable Zn/MnO_2 batteries:

One Electron

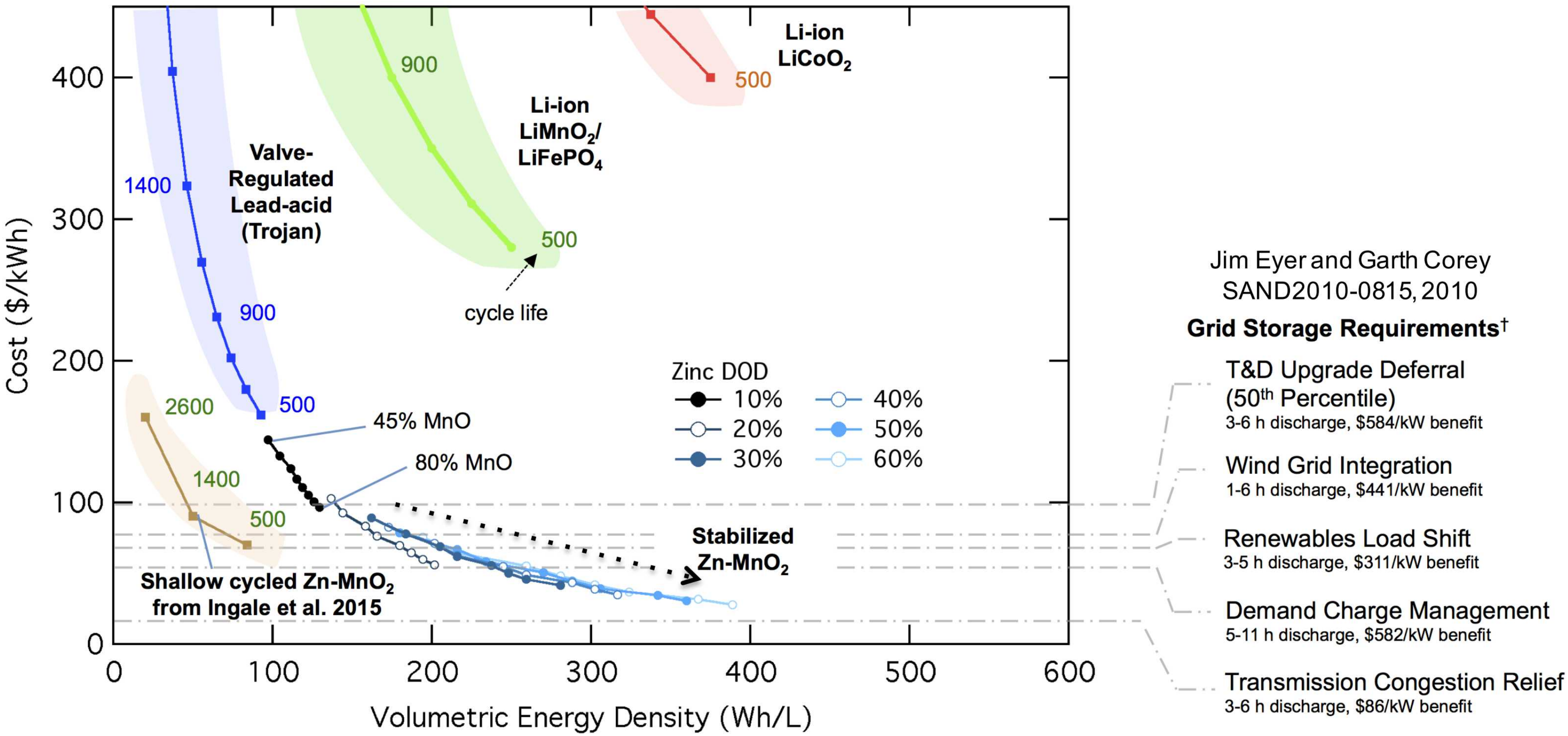
- 308 mAh/g-MnO_2
- Historically limited cycle-ability
- > 3000 rechargeable cycles shown under limited depth of discharge conditions
- Technology has been commercialized by Urban Electric Power
- ~ $150 per kWh (2019)

Two Electron

- 616 mAh/g-MnO_2
- Historically limited cycle-ability
- Recently stabilized with Cu, Bi, CNT additives to demonstrate > 3000 cycles vs. $Ni(OH)_2$
- 900 cycles vs. Zn reported with use of $Ca(OH)_2$ interlayer
- Projected ~ $50 per kWh

Zn-MnO_2 Batteries for Grid Storage

Opportunity exists to Increase Capacity and Decrease Costs

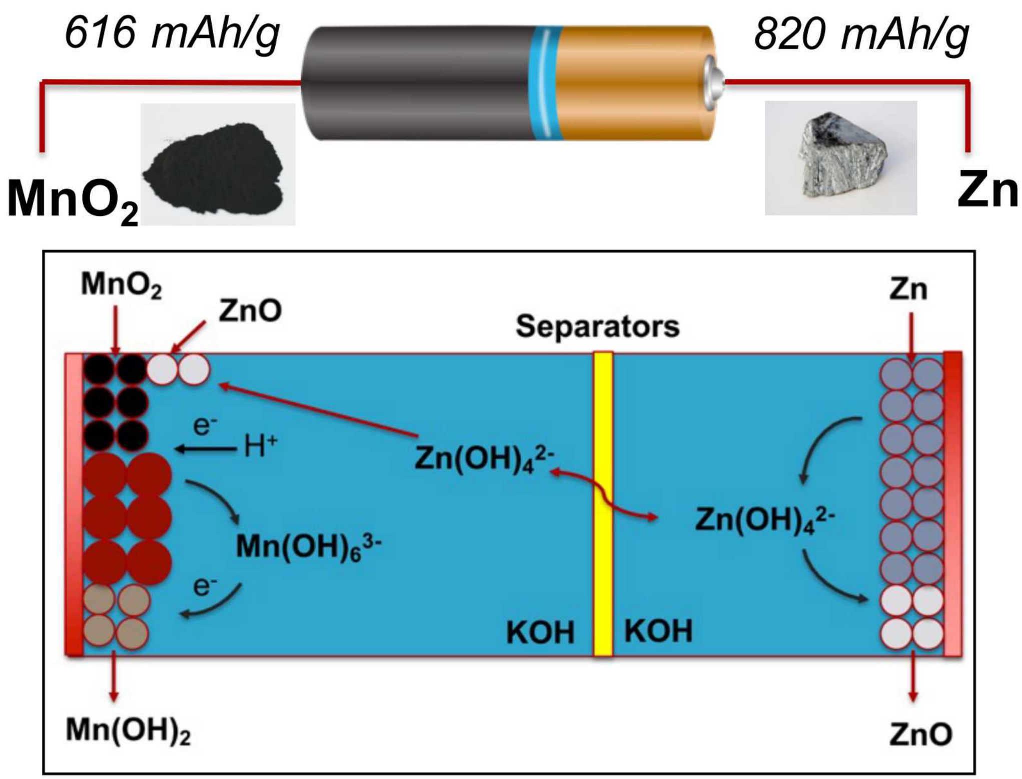


OE Goal: Achieve Low Cost/High Energy Density Storage for the Grid

1. Continue to Support Limited Depth-of-Discharge (DOD) Efforts
2. Develop Higher Capacity Batteries that are even more Cost Effective

N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

Alkaline Zn/MnO_2 Batteries



<u>*Issues to be addressed*</u>

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

N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

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

G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nat. Commun., 8, 14424 (2017).

OE - Alkaline Battery Research

Dr. Timothy Lambert

Alkaline Batteries for Grid Storage

Dr. Jonathon Duay
David Arnot
Dr. Matthew Lim
Kristin Maus

Prof. Sanjoy Banerjee

Stable Zinc Anodes for High-Energy-Density Rechargeable Aqueous Batteries & Manufacturable Low-Cost MnO_2 Birnessite cathode

Prof. Robert Messinger
Dr. Gautum Yadav
Michael D'Ambrose
Jinchao Huang
Dr. Damon Turney
Michael Nyce
Snehal Kohlekar
Brendan Hawkins

Prof. Igor Vasiliev

Theoretical Studies of the Electrochemical Behavior of γ-MnO_2 Cathode Material in Rechargeable Zn/MnO_2 Batteries

Birendra A. Magar (LDRD funded)

Prof. Joshua Gallaway

Understanding Phase Change Processes of Energy Storage Materials

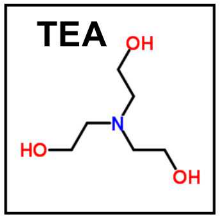
Began Sept 1, 2018

Matthew Kim

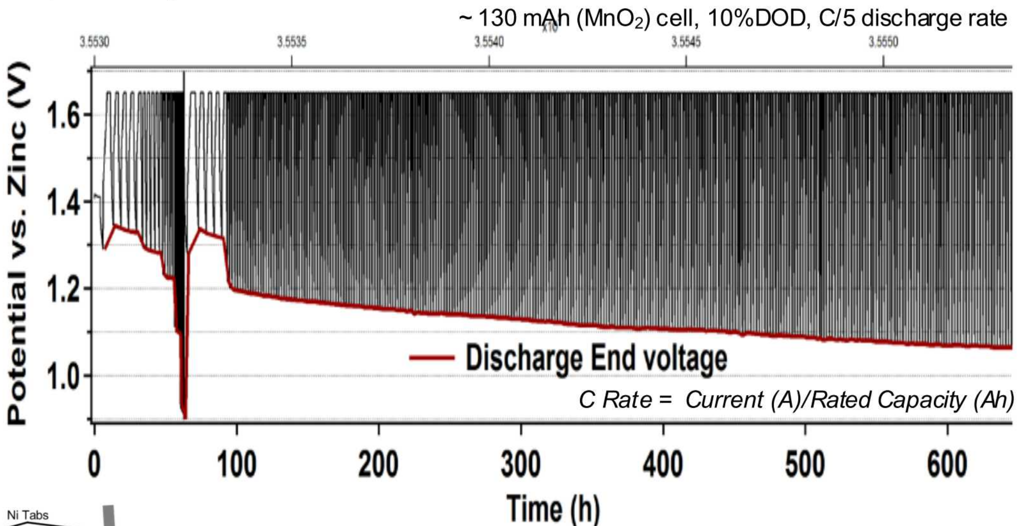
Also leveraging SNL-LDRD and CINT Proposal

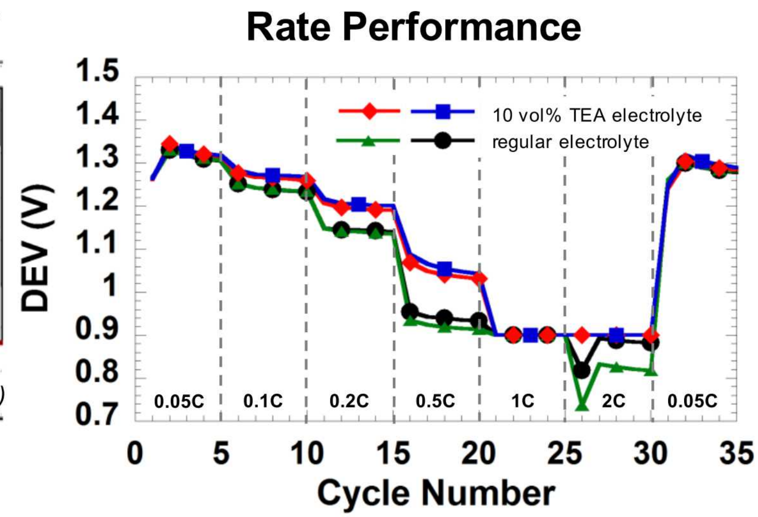
TEA additive in limited DOD Zn/MnO_2

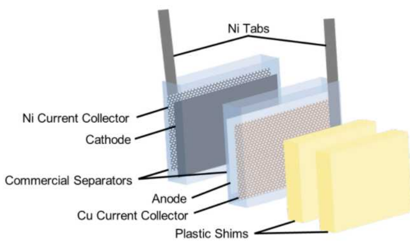
- Triethanolamine reported to complex w/ Mn^{3+} and Mn^{2+} in alkaline
- Previously examined for full $1e^-$ and $2e^-$ discharges
- Thought to impact only second e-

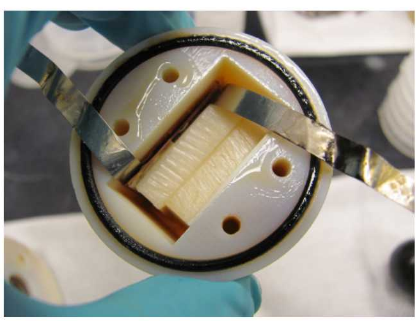


10 vol% TEA
< 1.5% Zn DOD
~ 200 mAh cells

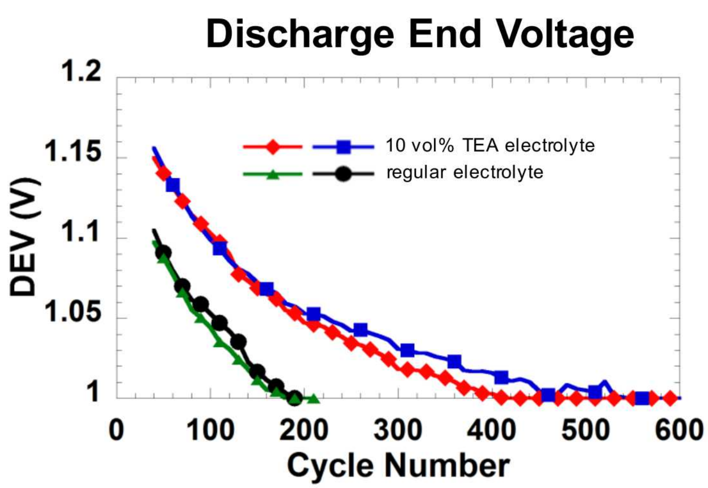


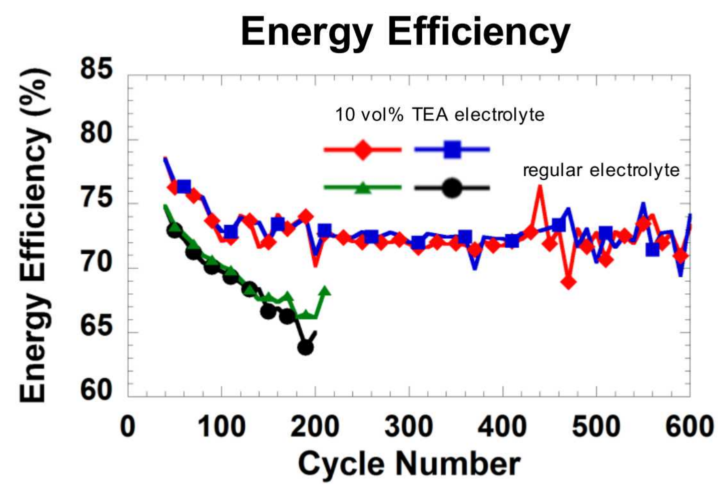






~ 300% increase in cycle life





Poster: Matthew Lim, Rechargeable Alkaline Zinc-Manganese Oxide Batteries for Grid Storage

M. Kelly at al. *J. Electrochem. Soc.* **2017**, *164 (14),* A3684-A3691. DOI:10.1149/2.0641714jes.

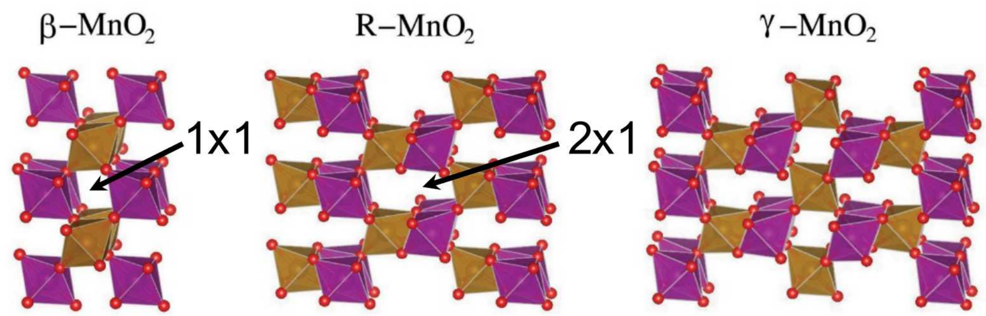
Theoretical Study of H^+ Insertion into β-, R-, & γ-MnO_2

First-electron discharge reaction in MnO_2:

$$MnO_2 + xH_2O + xe^- \rightarrow MnO_{2-x}(OH)_x + xOH^-$$

In a simplified form, it can be written as:

$$MnO_2 + xH^+ + xe^- \rightarrow MnO_{2-x}(OH)_x$$



Summary

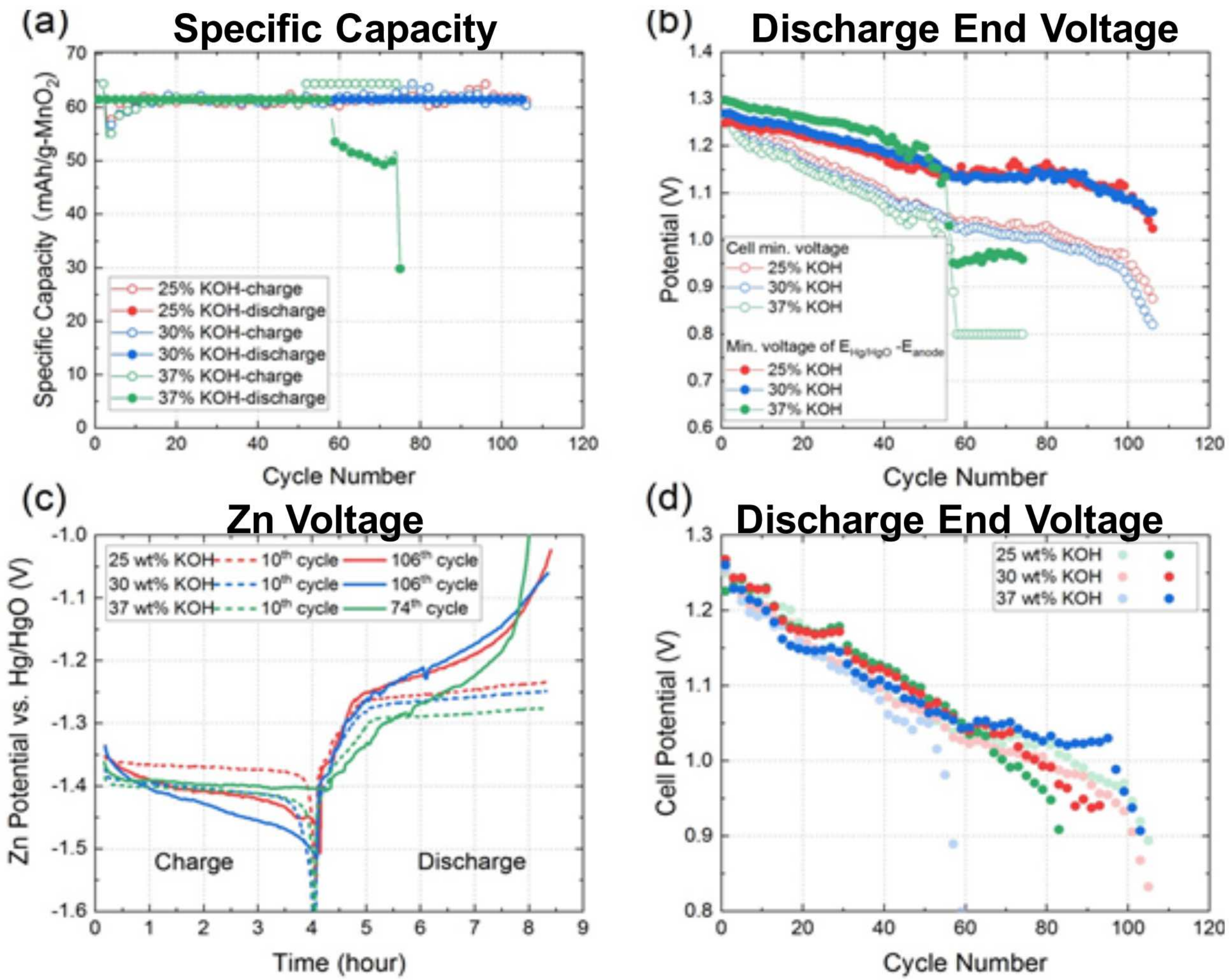
- At low DOD, the reduction of MnO_2 in alkaline Zn/MnO_2 batteries is governed by H^+ insertion into the crystalline structure of MnO_2.
- Studied effect of (2 x1) vs. (1 x 1) channel protonation on structural distortions, cell volumes, structural breakdown in MnO_2 polymorphs.
- Cell volumes of protonated MnO_2 polymorphs increase with increasing DOD due to the increase of the effective radii of Mn ions.
- Initially, inserted protons occupy 2x1 tunnels of γ-MnO_2 producing groutite (α-MnOOH).
- Protonation of 1x1 tunnels leads to structural breakdown of γ-MnO_2.
- Our study explains the presence of groutite and the absence of manganite (γ-MnOOH) among the reaction products of partially reduced γ-MnO_2.

Poster: Birendra Magar, Ab Initio Studies of Electrolytic MnO_2 in Shallow-Cycled Rechargeable Zn/MnO_2 Batteries

I. Vasiliev, *et al. manuscript under review.*

Optimizing Electrolyte Conditions for High TRL Zn-MnO_2 Alkaline Batteries

Sandia National Laboratories

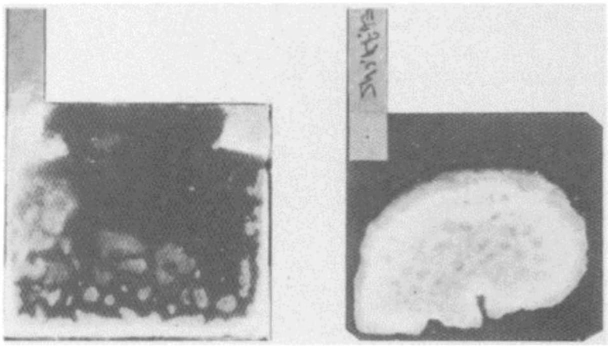


Cycling performance with various [KOH]: (a) capacity, (b) voltage at end of discharge, (c) Zn voltage curves; (d) voltage at end of discharge for the repeat subset of cells.

Poster: Damon Turney, Stable Zinc Anodes for High-Energy-Density Rechargeable Aqueous Batteries

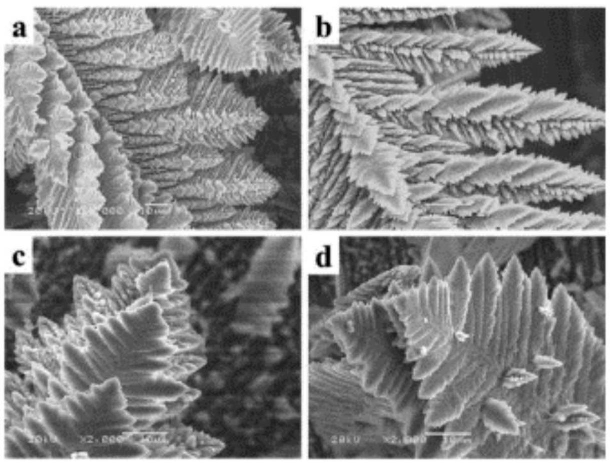
Zn Anode – Increasing DOD

Shape Change



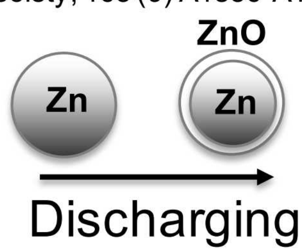
Journal of The Electrochemical Society, 138 (2) 645-664 (1991)

Dendrite Growth



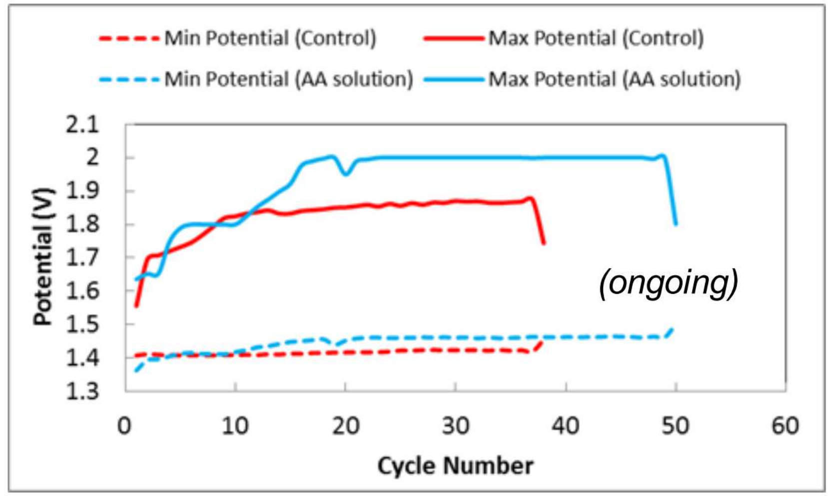
Journal of The Electrochemical Society, 163 (9) A1836-A1840 (2016)

Irreversible ZnO Passivation



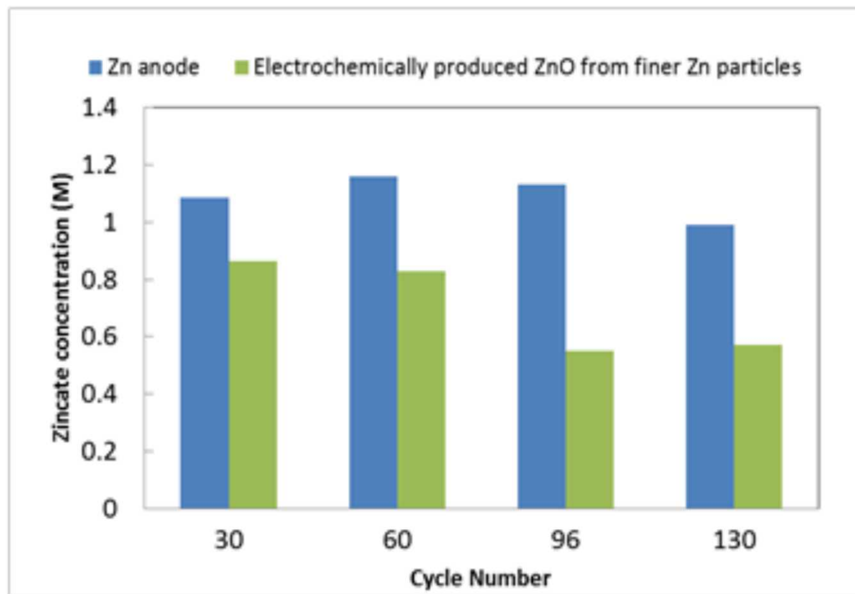
Improved Anode DOD @ CUNY-EI

Ammonium acetate additive increase cell voltage



15% DOD
2V Charge
1.2V Discharge

Smaller Zn results in less dendrites/shape change



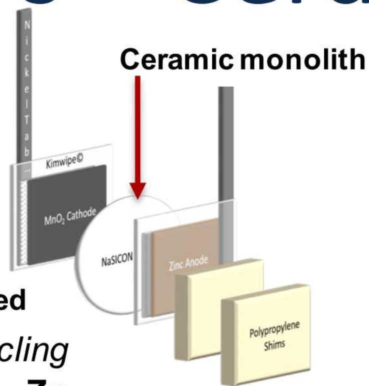
Poster: Damon Turney, Stable Zinc Anodes for High-Energy-Density Rechargeable Aqueous Batteries

Separators – Ceramic Separator

Battery Assembly Schematic

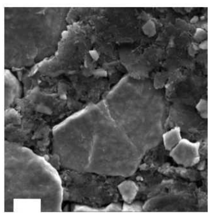
100% Selective Membrane

- **Na+ ions (~10^{-3} S/cm)**
- **No through separator Zn transport detected**

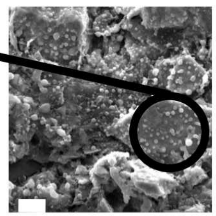


Cathode Post cycling

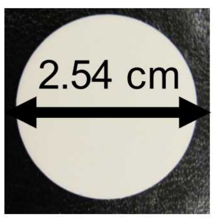
No Zn w/ NaSICON



Zn w/ Celgard+Cellophane

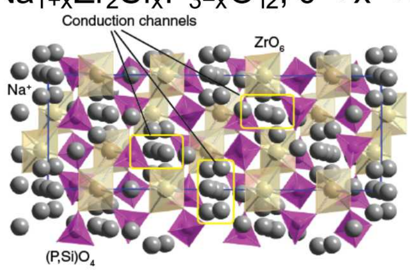


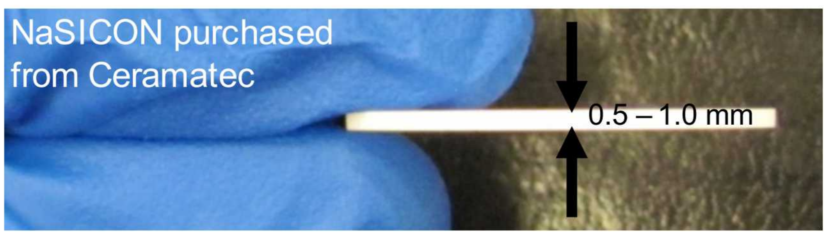
NaSICON



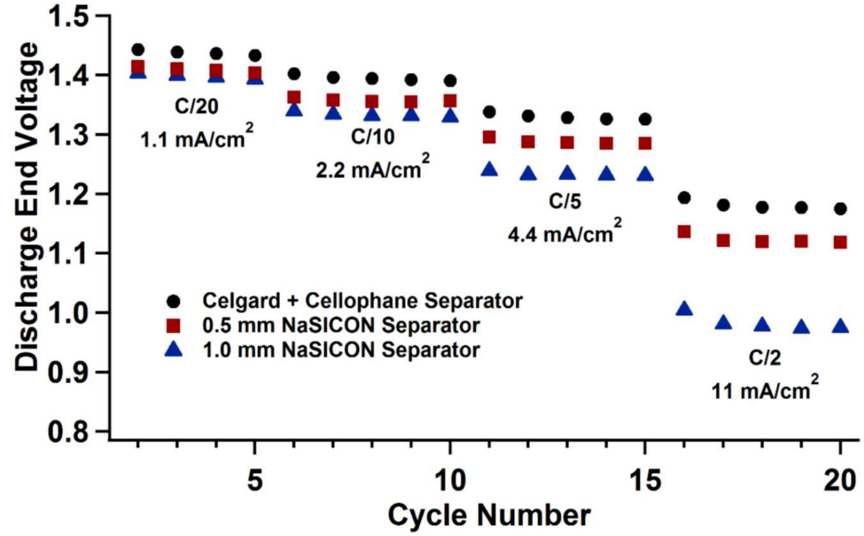
NaSuper **I**onic **CON**ductor

$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, 0 < x < 3

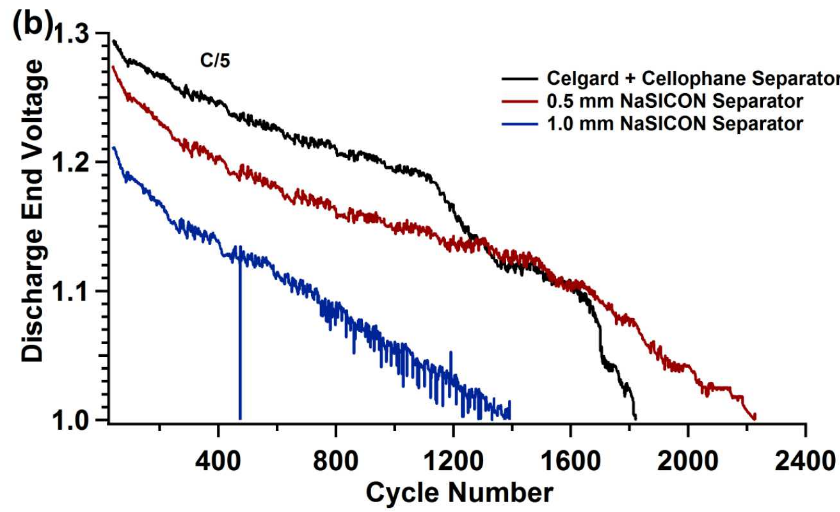




Ceramic Separators in NaOH electrolyte are viable at low rates



0.5 mm NaSICON increases cell lifetime

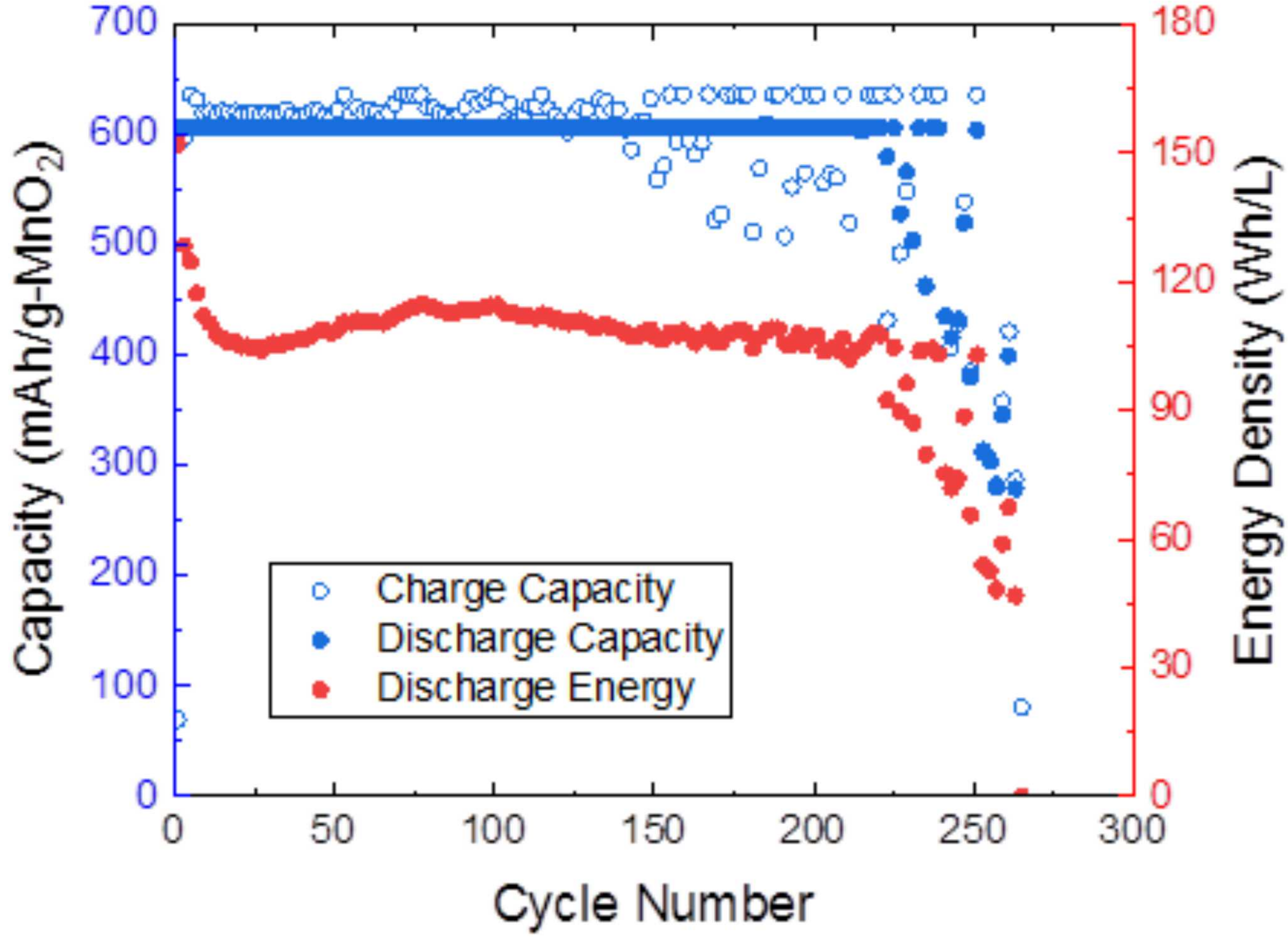


Poster: Jonathon Duay, Evaluation of a Ceramic Separator for use in Rechargeable Alkaline Zn/MnO_2 Batteries

Separators – Polymer Separator

Reversibility of 2 e^- Birnessite cathode in Zn/MnO_2 can be maintained when a zincate blocking separator is utilized.

PVA polymer based separator



J. Huang *et al.* Electrochem. Commun. **2017**, *81*, 136–140. DOI:10.1016/j.elecom.2017.06.020.

Summary for Project

FY 18 Accomplishments

1. Finalized a comprehensive study of TEA electrolyte additive on limited DOD Zn/MnO_2 batteries: Extended lifetime by ~300%
2. Demonstrated a 22% increase in lifetimes using a NaSICON ceramic separator for limited DOD Zn/MnO_2 Batteries – Zincate blocking ceramic membrane
3. Finalized model development describing the behavior of γ-MnO_2 in shallow-cycled Zn/MnO_2 batteries
4. Developed volume-averaged electrode simulation capabilities based on COMSOL and custom-built finite difference
5. Demonstrated 100% utilization of Zn in electrodes for ~ 50 cycles
6. Demonstrated Reversibility for $2e^-$ Birnessite cathode with PVA-based separator

FY 18 Manuscripts

1. M. Kelly, J. Duay, T. N. Lambert and R. Aidun "Effect of Triethanolamine on Rechargeable Zn/MnO_2 Alkaline Batteries Under Limited Depth of Discharge Conditions" *J. Electrochem. Soc.* **2017**, *164 (14)* A3684-A3691. DOI:10.1149/2.0641714jes.
2. J. Duay, M. Kelly and T. N. Lambert "Evaluation of a Ceramic Separator for Use in Rechargeable Alkaline Zn/MnO_2 Batteries" *J. Power Sources* **2018**, *395*, 430–438. DOI:10.1016/j.jpowsour.2018.05.072.
3. J. Huang, G. G. Yadav, J. W. Gallaway, X. Wei, M. Nyce, S. Banerjee "A calcium hydroxide interlayer as a selective separator for rechargeable alkaline Zn/MnO_2 batteries" *Electrochem. Commun.* **2017**, 81, 136–140. DOI:10.1016/j.elecom.2017.06.020.
4. I. Vasiliev, B. A. Magar, T. N. Lambert, J. Duay and B. Chalamala "*Ab initio* studies of proton insertion in shallow-cycled gamma-MnO_2" *manuscript submitted.*

Summary for Project

Presentations/Abstracts

1. T. N. Lambert, J. Duay, R. Aidun and J. E Ortiz-Santiago "Development of Anodic Stripping Voltammetry in Alkaline Electrolyte with Applications toward Screening Metal Ion Diffusion Selectivity in Battery Separators" **17th International Conference on Electroanalysis (ESEAC 2018) Rhodes, Greece, June 3-7th, 2018.**
2. J. Duay, T. N. Lambert, M. Kelly and R. Aidun "Advanced Zinc-Manganese Oxide Batteries" **2018 Nano Structures for Electrical Energy Storage (NEES) Spring Meeting (A DOE Energy Frontier Research Center),** CINT Core Facility, Albuquerque, New Mexico, May 23-24, 2018.
3. T. N. Lambert, J. Duay and J. E. Ortiz-Santiago "Development of Anodic Stripping Voltammetry in Alkaline Electrolyte and Application for Screening Zincate Diffusion Selectivity in Battery Separators" **233rd ECS Meeting**, Seattle, WA, May 13-17, 2018.
4. M. Kelly, J. Duay, T. N. Lambert and R. Aidun "Evaluation of Triethanolamine as an Additive to Improve Alkaline Zn/MnO2 Battery Rechargeability Under Limited Depth of Discharge Conditions" **2018 MRS Spring Meeting**, Phoenix, AZ, April 2-6th, 2018.
5. J. Duay, T. N. Lambert, M. Kelly "Evaluation of a Ceramic Separator for Use in Rechargeable Alkaline Zn/MnO2 Batteries" **2018 MRS Spring Meeting**, Phoenix, AZ, April 2-6th, 2018.
6. B. A. Magar, I. Vasiliev, T. N. Lambert, J. Duay and B. Chalamala "First-Principles Study of Hydrogen Trapping in Electrolytic Manganese Dioxide" **Annual Meeting of the APS Four Corners Section**, Fort Collins, CO, October 20-21, 2017.
7. J. Duay, T. N. Lambert and R. Aidun "Screening of Alkaline Zinc Battery Separators using Anodic Stripping Voltammetry" **2017 Electrical Energy Storage Applications and Technologies Meeting**, San Diego, CA, October 11-13th, 2017.
8. M. Kelly, J. Duay, T. N. Lambert and R. Aidun "Improving Alkaline Zn/MnO_2 Battery Cycle-ability Under Limited Depth of Discharge Conditions with a Triethanolamine Additive" **29th Annual Rio Grande Symposium on Advanced Materials**, Albuquerque, New Mexico, October 9th, 2017. (Maria Kelly Awarded Outstanding Student Talk).
9. Failure Analysis of the Rechargeable Porous Zinc Electrode in Alkaline Electrolyte. M D'Ambrose, GG Yadav, D Turney, JW Gallaway, M Nyce, RJ Messinger, **ECS Meeting Abstracts, 55-55**
10. Immobilizing Zincate Ions for Long-Cycle High-Energy-Density Aqueous Batteries. J Huang, GG Yadav, D Turney, JW Gallaway, M Nyce, S Kolhekar, **ECS Meeting Abstracts, 2572-2572**
11. In-Operando Surface Chemistry of Nickel and Copper Current Collectors During Zinc Electro-Deposition and DissolutionD Turney, JW Gallaway, GG Yadav, M D'Ambrose, S Banerjee, J Huang, **ECS Meeting Abstracts, 140-140**
12. Electrochemically Produced Zinc Oxide Electrode in Rechargeable Alkaline Batteries. S Kolhekar, D Turney, GG Yadav, M Nyce, S Banerjee, **ECS Meeting Abstracts, 53-53**
13. Cycle Life Study and Failure Analysis of the Rechargeable Porous Zinc Electrode in Alkaline Electrolyte. M D'Ambrose, RJ Messinger, S Banerjee, GG Yadav, D Turney, **Electrochemical Society (ECS) 232nd Meeting**
14. Understanding the Effect of Zinc and Achieving Long Cycle Life in Cu-Intercalated Bi-Birnessite/Zinc Batteries. GG Yadav, X Wei, J Huang, JW Gallaway, D Turney, M Nyce, S Banerjee, **Electrochemical Society (ECS) 232nd Meeting**
15. On the Fly EIS Tracking of Rechargeable Alkaline Zn-MnO2 Batteries for Large-Scale UseJW Gallaway, S Bliznakov, GG Yadav, D Turney, N Ingale, M Nyce, **Electrochemical Society (ECS) 232nd Meeting**

Other

1. "Understanding the electrochemical processes in alkaline Zn-MnO_2 batteries" CINT User Proposal.

Advanced Zn-MnO_2 Alkaline Batteries

FY 19 Path Forward

1. Perform *in operando* Raman characterization of Zn anode in Zn/MnO_2
2. Continue to Increase DOD and Understanding of Zn Anodes in Zn/MnO_2
3. Develop Lower cost Birnessite Cathodes – towards $50/kWh target
4. Development of New Separators that Exclude Zincate
5. Effect of Membranes on Cycling MnO_2 and Zn/MnO_2 Batteries
6. Construct a theoretical phase diagram outlining the possible redox reaction pathways in the δ-MnO_2 electrode.
7. *In operando* diffraction studies on MnO_2 and new cathode materials

Acknowledgements

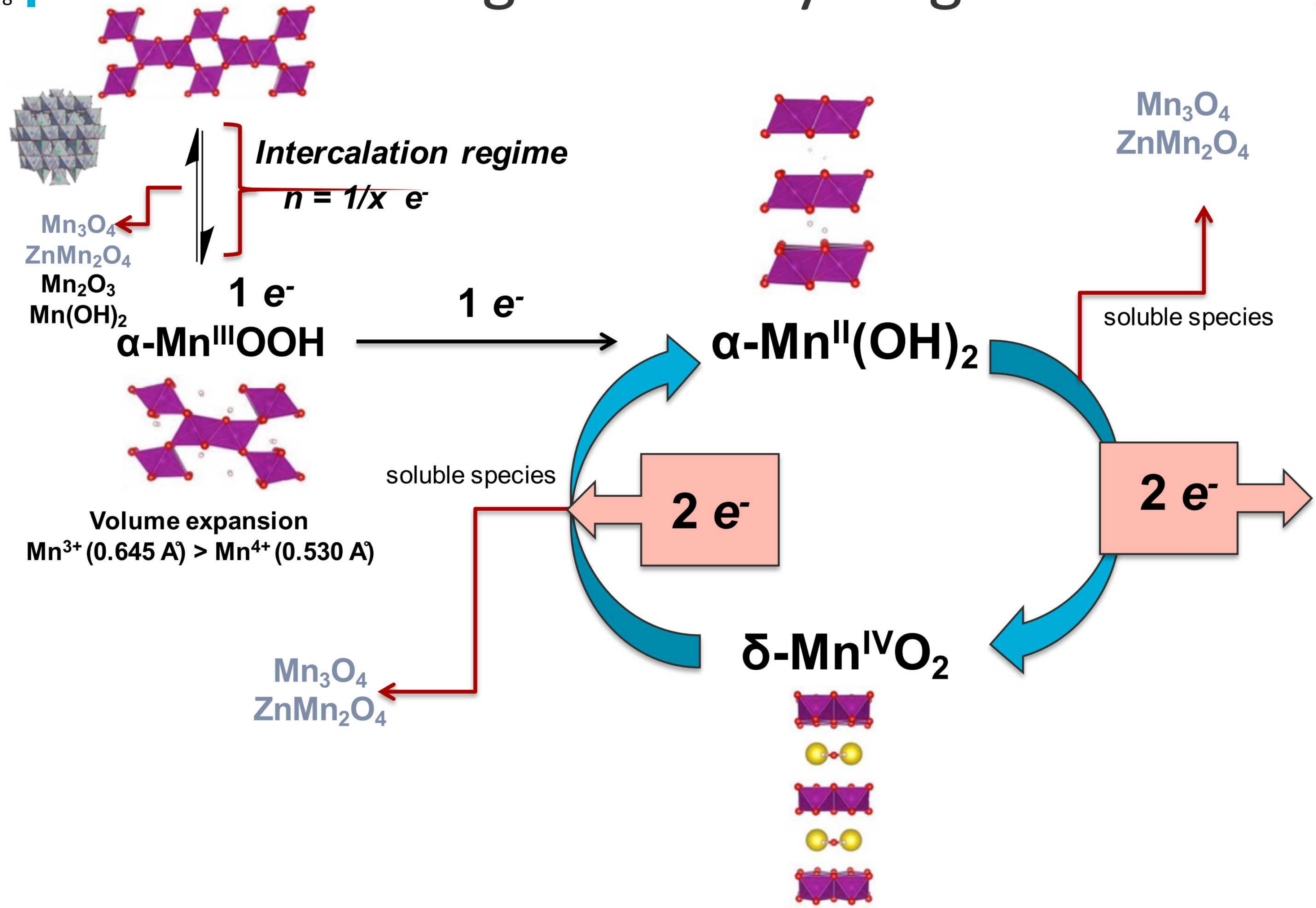
- Dr.Babu Chalamala, Sandia National Laboratories
- Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability
- Team Members

SNL	*CUNY-EI*		*NMSU*
Dr. Jonathon Duay	Prof. Sanjoy Banerjee		Prof. Igor Vasiliev
Dr. Matthew Lim	Dr. Damon Turney		Birendra Magar
Maria Kelly	Dr. Gautum Yadav		
Ruby Aidun	Michael D'Ambrose	Snehal Kohlekar	
Julian Vigil	Michael Nyce	Jinchao Huang	
Ivan Pineda-Dominguez	Brendan Hawkins		

Thank you

Extra Slides

Cathode Changes with Cycling



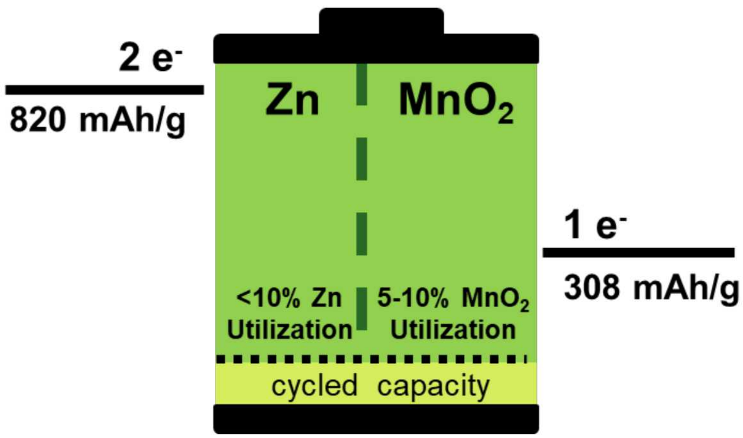
B. J. Hertzberg *et al.*, *Chem. Mater.*, **28**, 4536 (2016).
N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, *J. Power Sources*, **276**, 7 (2015).
G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, *Nat. Commun.*, **8**, 14424 (2017).
G. G. Yadav, X. Wei, J. Huang, J. W. Gallaway, D. E. Turney, M. Nyce, J. Secor, and S. Banerjee, *J. Mat. Chem.* A**, 5**, 15845 (2017).

Alkaline Zn/MnO_2 Batteries

Two classes of rechargeable Zn/MnO_2 batteries:

One Electron

- 308 mAh/g-MnO_2
- Historically limited cycle-ability
- > 3000 rechargeable cycles shown under limited depth of discharge conditions
- \$100 - \$150 per kWh
- Technology has been commercialized by Urban Electric Power

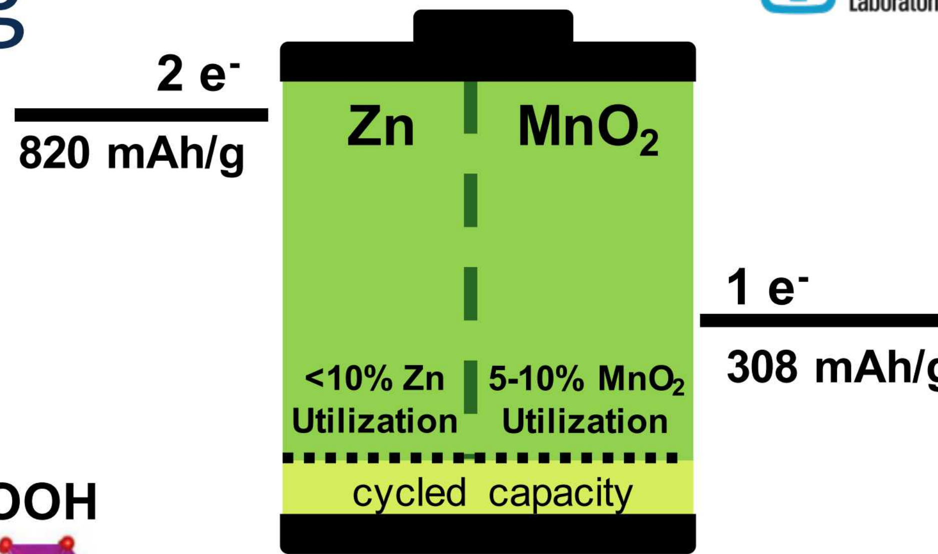


Cathode issues
- Only 5-10% of total capacity
- Crystal Structure Breakdown
- Inactive Phase(s) formed
- Zinc poisoning

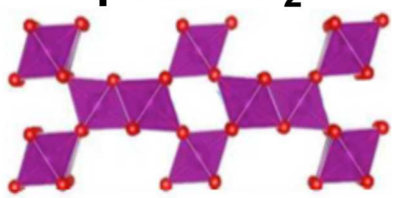
Anode issues
- < 10% of total capacity
- Shape Changes
- Passivation
- Dendrite Formation

Limited DOD Cycling

Reversibility can be maintained when only *a fraction of the first e^- step is cycled.*



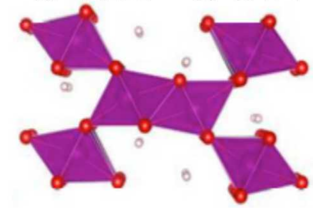
γ-$Mn^{IV}O_2$



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

Intercalation Regime
$n = {}^{1}/_{x}\ e^-$
$\rightleftharpoons$

α-$Mn^{III}OOH$



Volume expansion
Mn^{3+} (0.645 Å) > Mn^{4+} (0.530 Å)

Formation of undesirable phases from soluble Mn^{3}+

Mn_3O_4
$ZnMn_2O_4$
Mn_2O_3
$Mn(OH)_2$

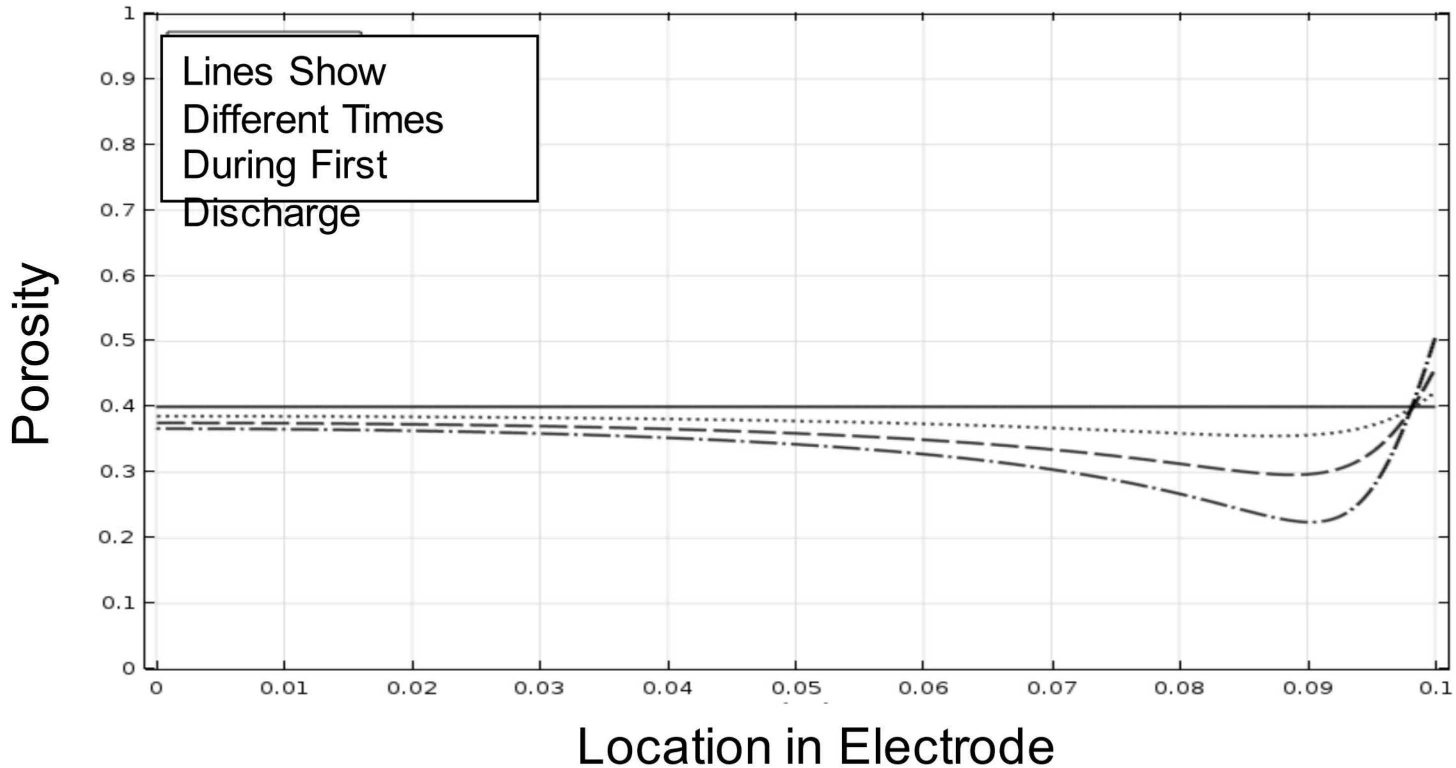
Cathode issues
- Only 5-10% of total capacity
- Crystal Structure Breakdown
- Inactive Phase(s) formed
- Zinc poisoning

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
- ~ $150/kWh (2019)

Zn Anode – Increasing DOD

Developing Volume-Average Porous Electrode Computer Simulations



Goals:
1) Predict location and conditions of zero porosity (pore clogging)
2) Predict locations of excessive pH variations
3) Optimize electrode thickness and effects of porosity additives