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Sandia National Laboratories

Alkaline Zn-based Batteries for Grid Storage

PRESENTED BY

Timothy N. Lambert, Sandia National Laboratories

Argonne National Laboratories Virtual Presentation

June 17, 2021

U.S. DEPARTMENT OF ENERGY NNSA

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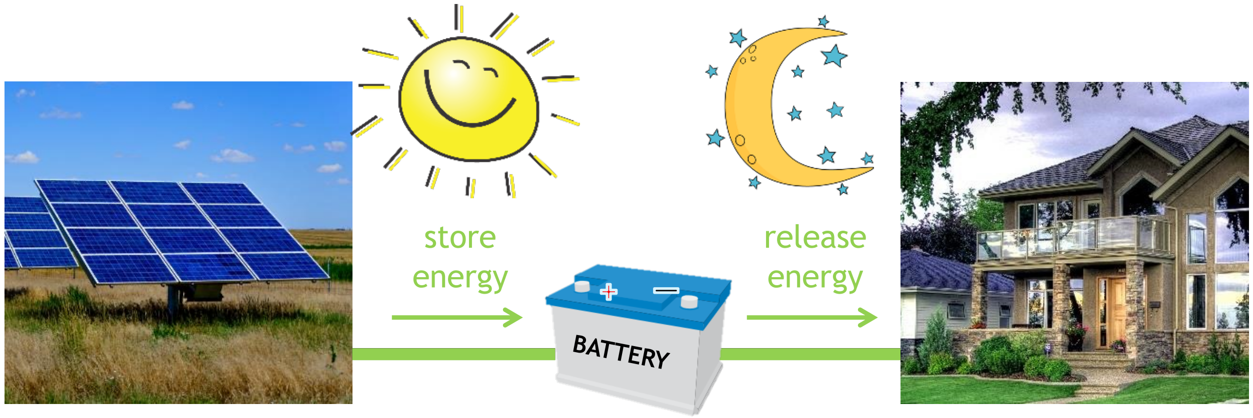
Grid Energy Storage



- Grid-level energy storage systems needed to enable intermittent renewables
- Li-ion, Na-ion, Pb-acid battery systems have been implemented but pose safety and environmental risks
- Successful grid storage must be safe, reliable, low-cost and energy dense
- Large “Industrial Scale Production” is needed

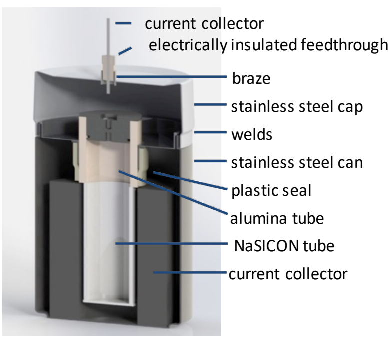
Center for Sustainable Systems, University of Michigan. 2016. "U.S. Energy Storage Factsheet." Pub. No. CSS15-17.
Energy Sage. n.d. “Ground Mount Solar Panels: Top 3 Things You Need to Know”

M. B. Lim, T. N. Lambert, B. R. Chalamala. “Rechargeable Alkaline Zinc-Manganese Oxide Batteries for Grid Storage: Mechanisms, Challenges and Developments” Mater. Sci. Eng. R Rep. 2021, 143, 100593. https://doi.org/10.1016/j.mser.2020.100593

DOE-OE/Sandia Efforts for Large Format Cells

Molten Na

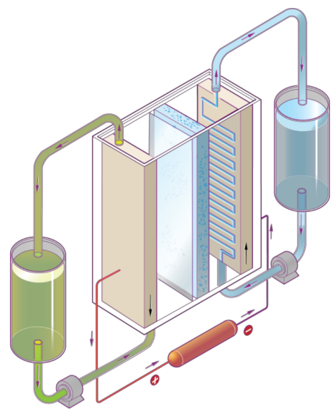
High Conductivity Separators for Low Temperature Molten Sodium Batteries



Robust ceramic separators exhibit low Na^+ conductivity at lower, more cost effective temperatures (120-180 °C).

Flow Batteries

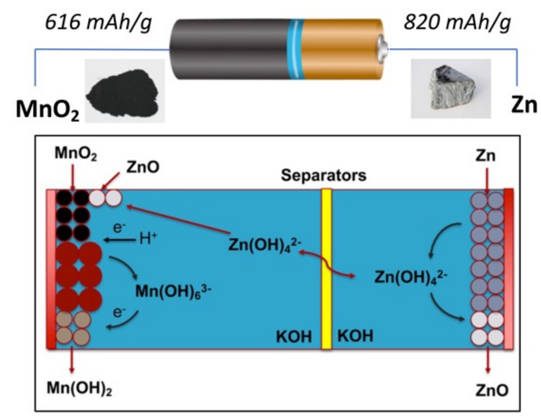
Crossover in Redox Flow Batteries



Cross over of the electroactive species through the separator leads to severe capacity decay in flow battery systems.

Aqueous Zn Batteries

Zn Crossover



Zincate diffusion and subsequent poisoning of MnO_2 impairs reversibility and lifetimes

M. Lim and T. N. Lambert "Rechargeable Zinc Batteries for Grid Storage" DOE Energy Storage Handbook 2021, https://www.sandia.gov/ess-ssl/eshb/

M. B. Lim, T. N. Lambert, B. R. Chalamala. "Rechargeable Alkaline Zinc-Manganese Oxide Batteries for Grid Storage: Mechanisms, Challenges and Developments" Mater. Sci. Eng. R Rep. 2021, 143, 100593. https://doi.org/10.1016/j.mser.2020.100593

All have challenges currently being addressed by research

Alkaline Zn Battery Efforts at SNL

Alkaline Zn-based Batteries (Zn/MnO_2, Zn/Cu_2S, Zn/CuO, Zn/Ni)

- Increased Zn DOD and Zn Cycle Life
- Development of Separators for Selective Crossover [Na^+,K^+/HO^- vs $Zn(OH)_4^{2-}$, $Bi(OH)_3^-$, $Cu(OH)_4^{2-}$]
- Development of new Cathode Chemistries [Cu_2S] & [CuO]
- Roadmap for Zn/MnO_2 to $\leq$ \$50/kWh [at scale, cell level]

OE Team

Sandia National Laboratories — Dr. Timothy Lambert

CUNY The City University of New York Energy Institute — Prof. Sanjoy Banerjee and Dr. Damon Turney

NM State University — Prof. Igor Vasiliev

Northeastern University — Prof. Joshua Gallaway

Lawrence Livermore National Laboratory — Dr. Cheng Zu

Urban Electric Power — Prof. Sanjoy Banerjee, Dr. Gautam Yadav, Mr. Gabe Cowles

Acknowledgements

- Babu Chalamala, Manager, Energy Storage Technology & Systems, Sandia
- Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability (OE)
- Energy & Climate Investment Area, Laboratory Directed Research & Development (LDRD), Sandia
- **SNL Co-authors and ALL Collaborators**

Zn Batteries (Re: Cost, Safety & Reliability)

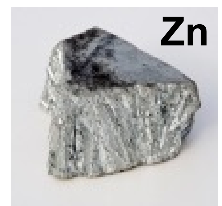
Alkaline zinc batteries are one of the core DOE/OE technologies for grid storage and feature energy-dense, safe, abundant, low-cost materials

Alkaline Batteries Today

Wikipedia, user Aney, 2005

Wikipedia, user NicoJenner, 2015

- Well-established supply chain for consumer products
- >10B units produced, $7.5B global market (2019)
- Traditional 1° alkaline batteries ~ < $20/kWh
- Aqueous, long shelf life, EPA certified for disposal
- High achievable energy density
  - Zn/MnO_2 ~ 400 Wh/L
  - Zn/Ni ~ 300 Wh/L
  - Zn/Air ~ 1400 Wh/L



- 13M tons (2019)
- ~ $1.25/lb (2019)

γ-MnO_2

- 19M tons Mn ores (2019)

USGS Mineral Commodity summaries, 2020

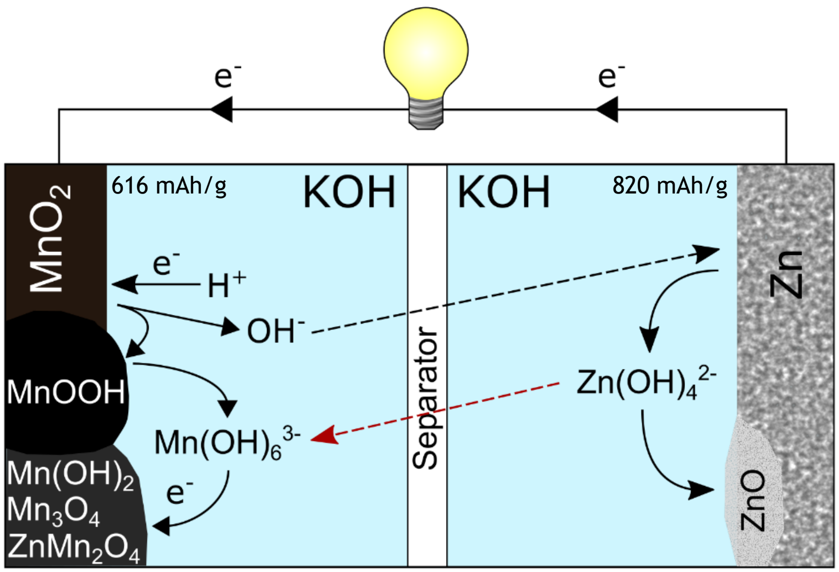
KOH

- Potash ~ 61M tons (2019)
- ~$400/ton (2020)
- Aqueous, non-flammable

Reversibility and Cycle life are the Challenges/Opportunities

Technical Challenges Facing Zn/MnO_2

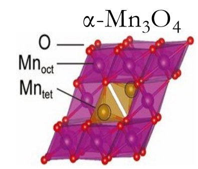
Problem: ***Cycling Zn/MnO_2 (both electrodes) at high capacities for thousands of cycles - not realized***



Alkaline Zn-MnO_2 battery

Cathode:

- Irreversibility of Cathode
- Susceptibility to Zinc poisoning



PNAS 115 (23), E5261 (2018)

$ZnMn_2O_4$

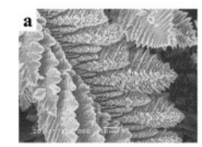
Mater. Chem. Phys. 130, 39 (2011)

Separator:

- Zincate crossover

Anode:

- Shape Change
- Dendrite Growth
- Irreversible ZnO Passivation



J. Electrochem. Soc., 163 (9), A1836 (2016)

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).

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

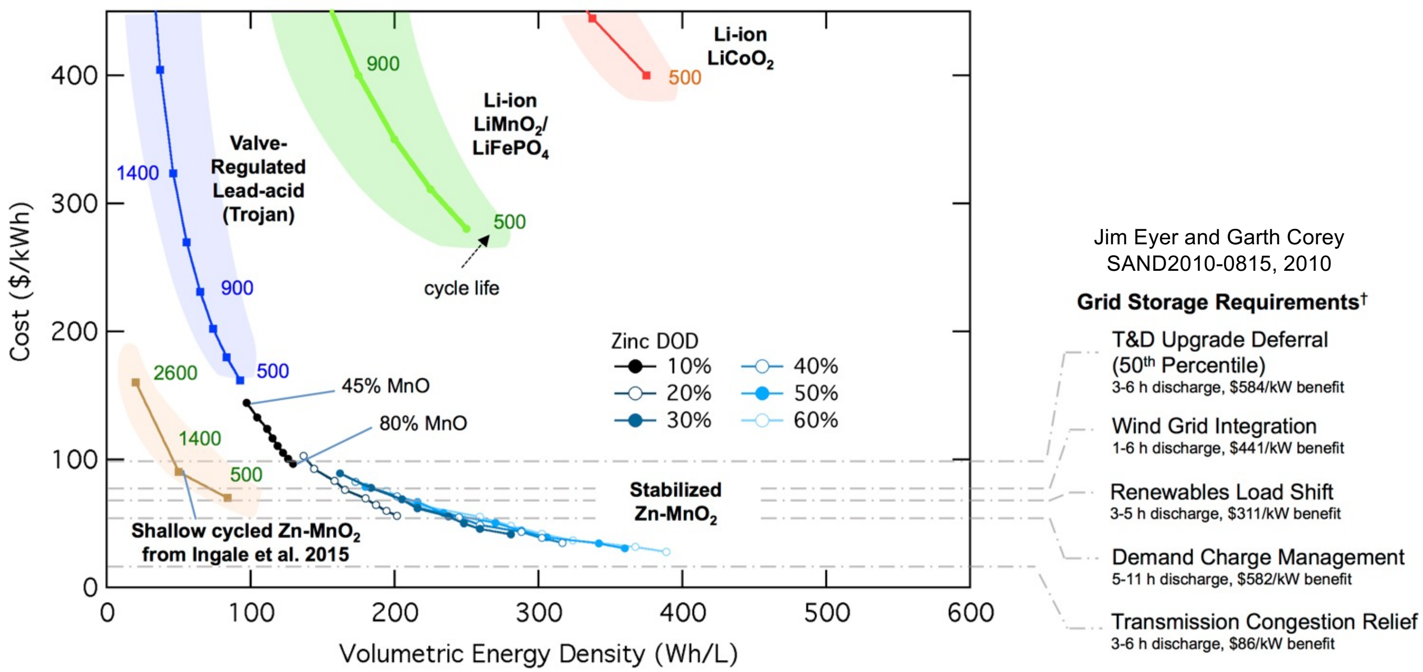
G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, *Nat. Commun.*, 8, 14424 (2017).

R&D: > 2V High Voltage system offers promise of increased energy density

G. G. Yadav, D. Turney, J. Huang, X. Wei and S. Banerjee, *ACS Energy Lett.*, *4,* 9, 2144 (2019).

Alkaline Zn/MnO_2 Batteries

(Image adapted from CCNY)



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

Zn Batteries

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

BATTERY DEVELOPMENT ROADMAP

Basis of comparison: 300 cycles / 4h charge / 4h discharge (Peak shaving application)

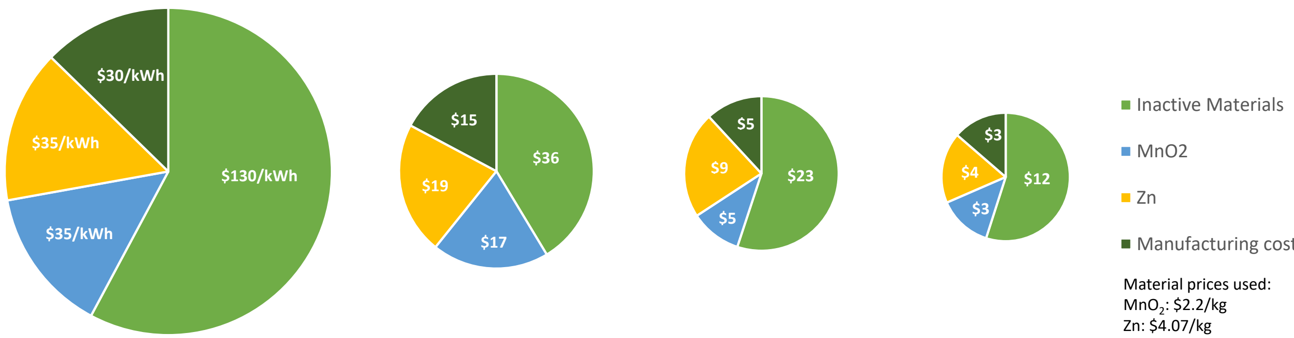
URBAN ELECTRIC POWER

Sanjoy Banerjee
Gautam Yadav
Gabe Cowles

GEN 1 — GEN 2

2020 BATTERY 1: $230/KWH | **2021** BATTERY 2: $87/KWH | **2023** BATTERY 3: $42/KWH | **2025** BATTERY 4: $22/KWH

Battery 1
Nameplate capacity
123 Ah
12V, 97 Wh/L



Material prices used:
MnO_2: $2.2/kg
Zn: $4.07/kg

2020 – Battery 1
- Proton insertion battery
- 20% MnO_2 (1e) / 10% Zn (2e)
- $230/kWh Manufactured Cost

Raw Material Consumption
MnO_2: 15 MT/MWh
Zn: 10 MT/MWh

2021 – Battery 2
- Proton insertion battery
- 40% MnO_2 (1e) / 20% Zn (2e)
- $87/kWh Manufactured Cost

Raw Material Consumption
MnO_2: 7.5 MT/MWh
Zn: 5 MT/MWh

2023 – Battery 3
- Conversion battery
- 75% MnO_2 (2e) / 50% Zn (2e)
- $42/kWh Manufactured Cost

Raw Material Consumption
MnO_2: 2.2 MT/MWh
Zn: 2.4 MT/MWh

2025 – Battery 4
- Dual-electrolyte battery
- 100% MnO_2 (1e) / 50% Zn (2e)
- $22/kWh Manufactured Cost

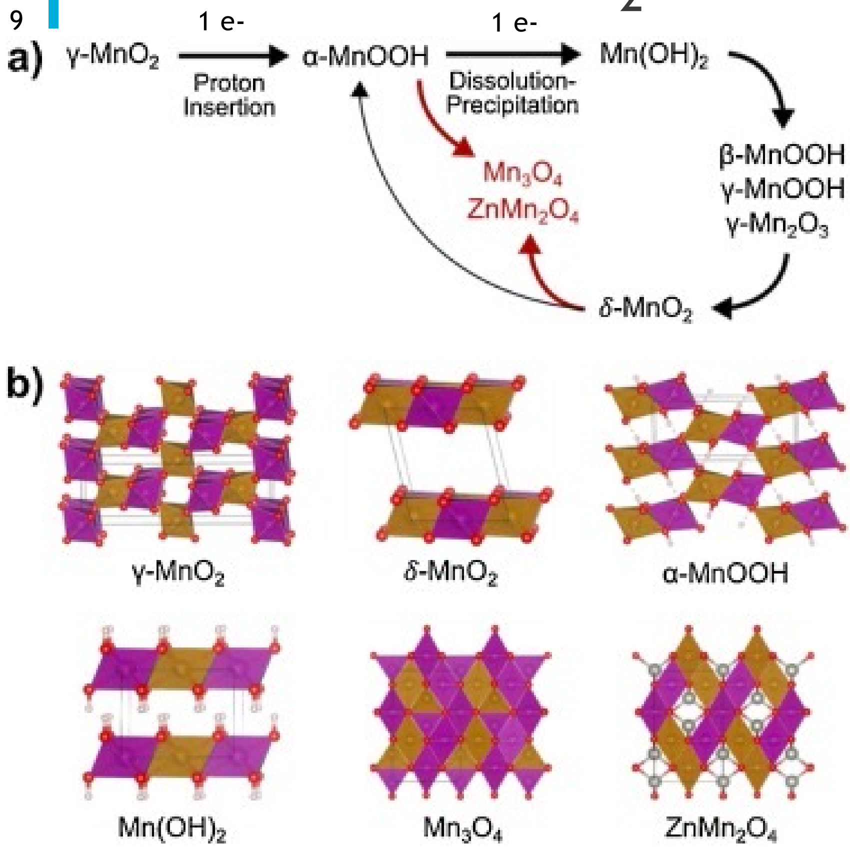
Raw Material Consumption
MnO_2: 1.4 MT/MWh
Zn: 1 MT/MWh

7

S. Banerjee (UEP) "From Concept through Product to Market: Rechargeable Zinc Manganese Dioxide Batteries" 2020 DOE Office of Electricity Energy Storage Program Annual Peer Review

E. D. Spoerke et al. "Driving Zn-MnO_2 Grid-Scale Batteries: A Roadmap to Cost Effective Energy Storage" *manuscript submitted*.

Alkaline Zn/MnO_2 Batteries



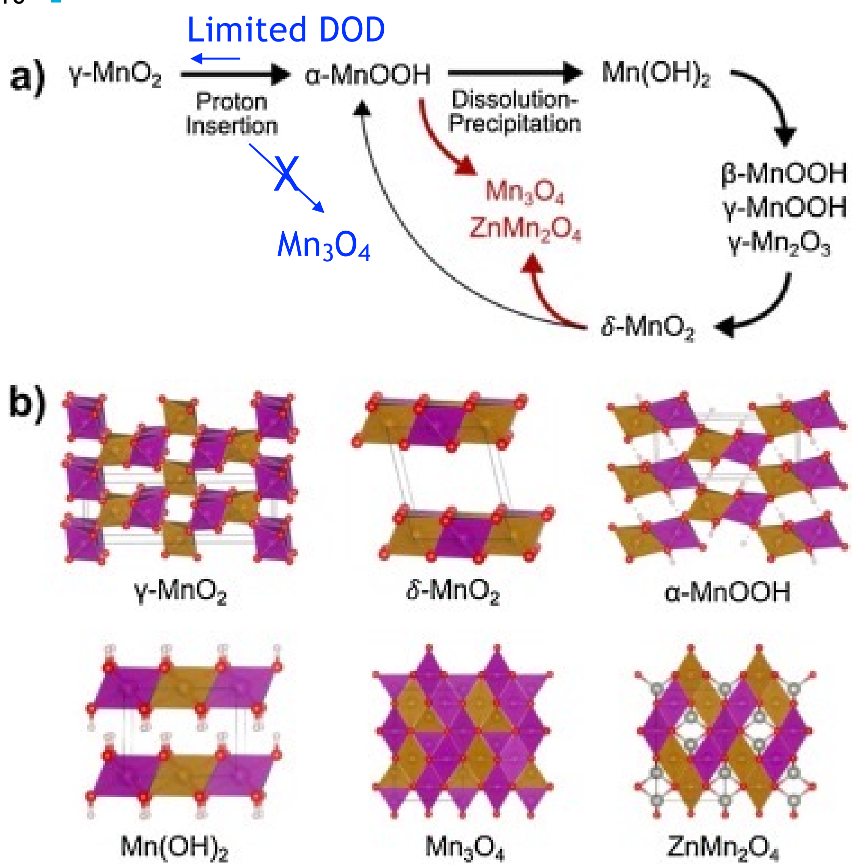
One Electron - proton insertion

- 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
- Utilizes low DOD Zn anode

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).
I. Vasiliev, B. A. Magar, J. Duay, T. N. Lambert and B. Chalamalu, J. Electrochem. Soc. 2018 165 (14), A3517-A3524. DOI: 10.1149/2.1161814jes.

Alkaline Zn/MnO_2 Batteries



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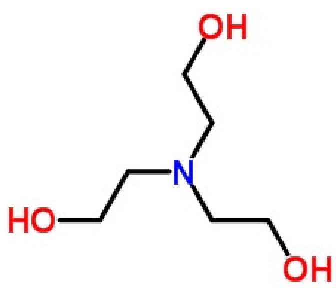
Improving Zn-MnO_2 Battery Performance

Chemical additives often used to improve battery performance

- Cathode Additives: Bi_2O_3, MgO, Sr-, Ba-, and Ti-based compounds
- Anode Additives: In, Bi, Pb, $Ca(OH)_2$

Triethanolamine (TEA)

- Known to form complexes with Mn^{2+} and Mn^{3+}
- Previous work claimed triethanolamine binds solubilized Mn^{2+} and Mn^{3+}, which could mitigate the formation of irreversible species

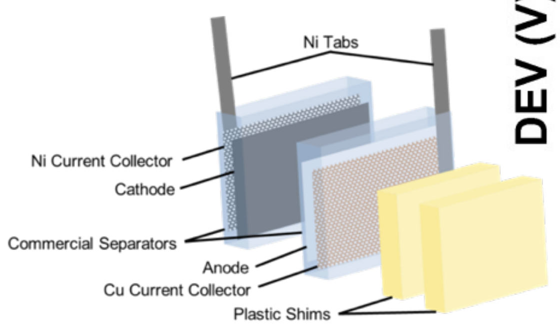


→ Comprehensive analysis of TEA effect in limited DOD cells

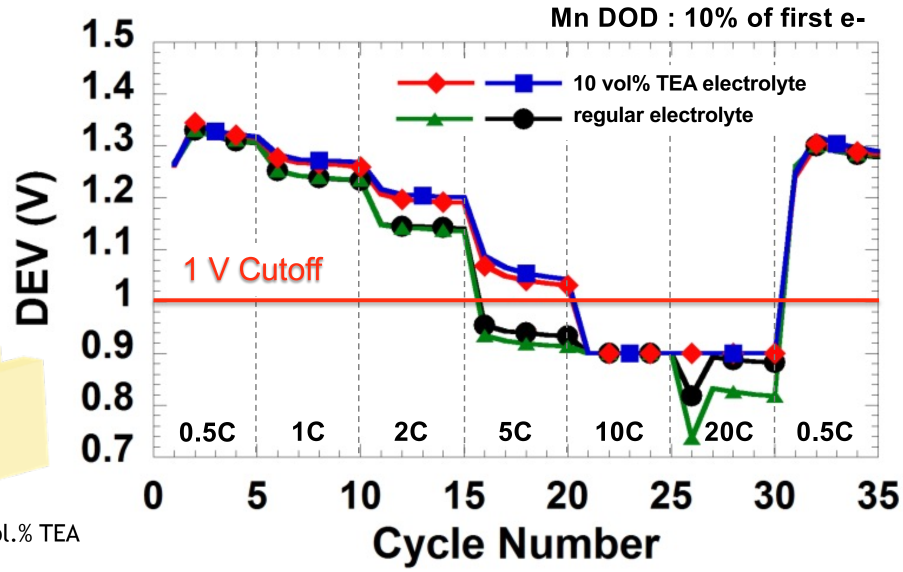
A. Kozawa and R. A. Powers, *J. Electrochem. Soc.*, **113** 870 (1966).
A. Kozawa and J. F. Yeager, *J. Electrochem. Soc.*, **112**, 959 (1965).
M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

Rate Performance

- COTS materials
- Cathode-limited
- < 1.5% DOD on Zn



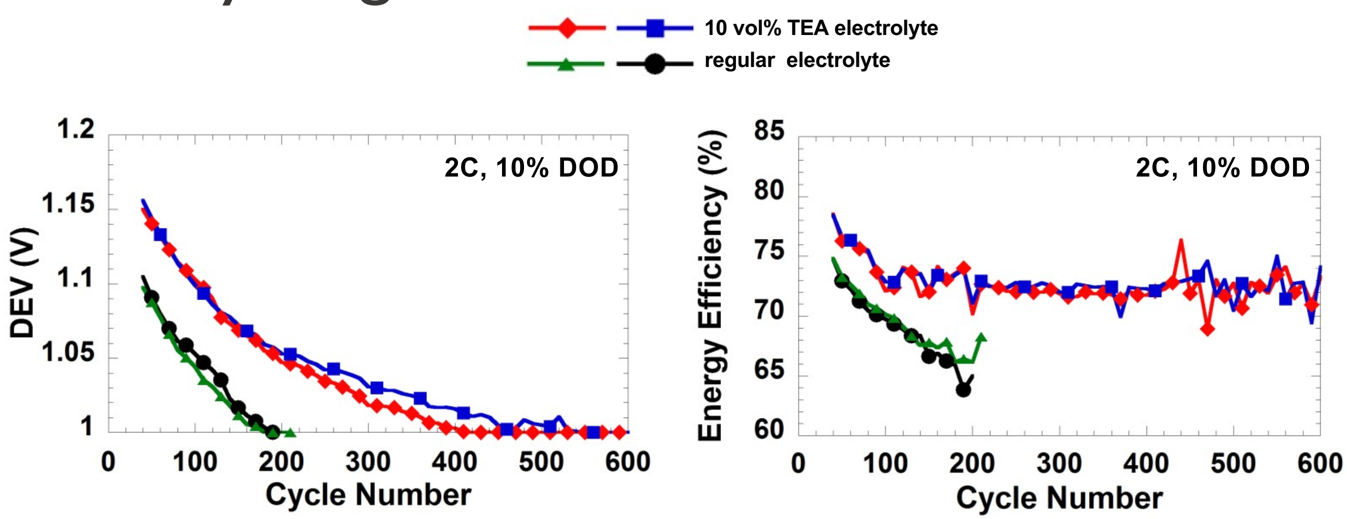
Electrolyte: 32 wt.% KOH with/without 10 vol.% TEA



- 5 cycles each of C/2, 1C, 2C, 5C, 10C, 20C (based on cycled capacity)
- Cells prepared with TEA exhibit 29, 58, and 121 mV higher DEV at 1C, 2C, 5C
- All cells drop below 1V at 10C and 20C rates – high resistivity of MnO_2
- Cells with TEA exhibit enhanced performance at higher rates

M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

Extended Cycling



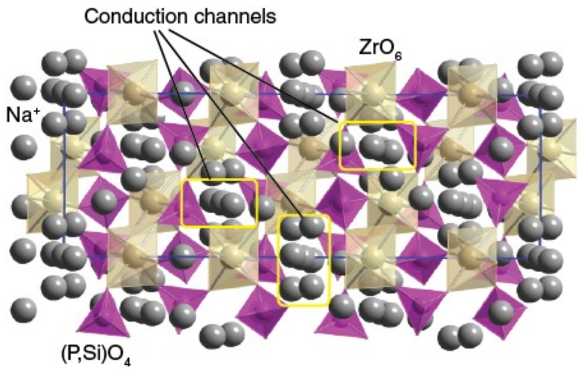
- Cycled at 2C, 10% DOD until failure (80% of cycled capacity remaining)
- Baseline Cells: 183-198 cycles, TEA Cells: 483-653 cycles
- TEA extends cycle lifetime by 297%
- Zn: harder to reduce, lower surface area, more soluble, and less transport through separator……….

M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

NaSICON Ceramic Separator

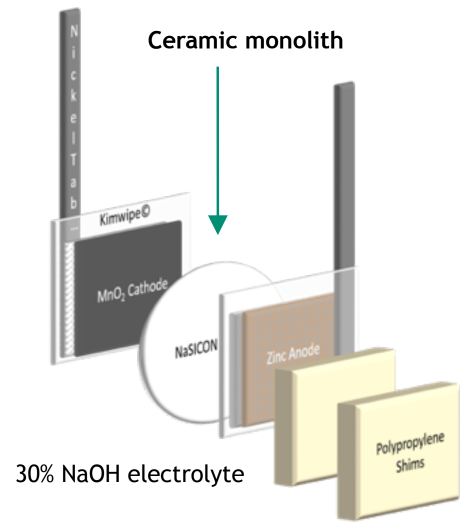
NaSuper **I**onic **CON**ductor

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

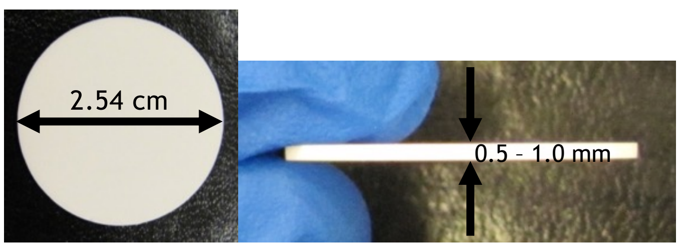


http://www.chemtube3d.com/solidstate/SSNASICON.htm

Battery Assembly Schematic



NaSICON purchased from Ceramatec

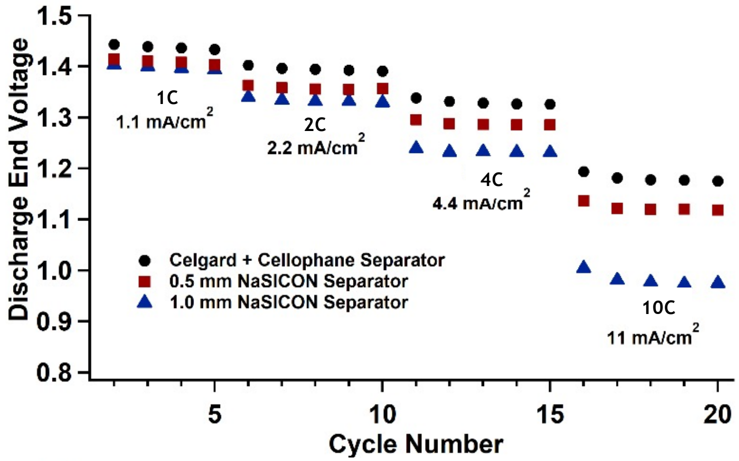


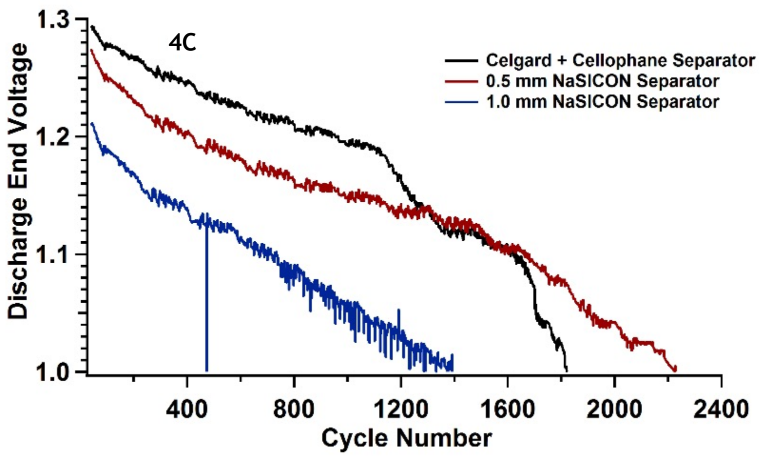
100% Selective Membrane

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

J. Duay, *et al. J. Power Sources* **2018**, *395*, 430-438. DOI:10.1016/j.jpowsour.2018.05.072.

Effect on 5% DOD Cells



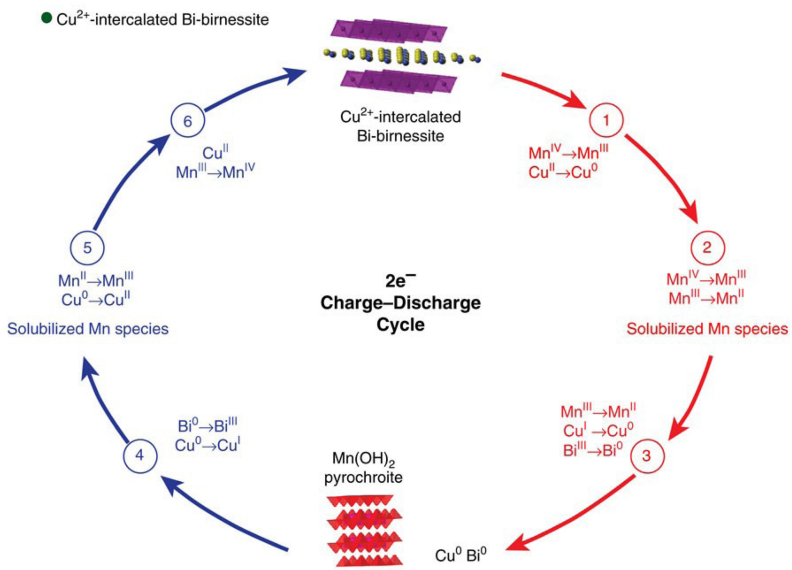


At relevant discharge rates for grid storage, the thinner **0.5 mm NaSICON doesn't decrease DEV significantly** despite having >2.5x lower conductivity than conventional separators

As NaSICON is thinned and becomes less resistive, its advantages become more apparent, increasing cell lifetime by 22%

J. Duay, *et al. J. Power Sources* **2018**, *395*, 430-438.

Alkaline Zn/MnO_2 Batteries



Two Electron - Conversion Cathode

- 616 mAh/g-MnO_2
- Historically limited cycle-ability
- Cycles 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 (at scale)

Full $2e^-$ equivalent can be realized, 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).

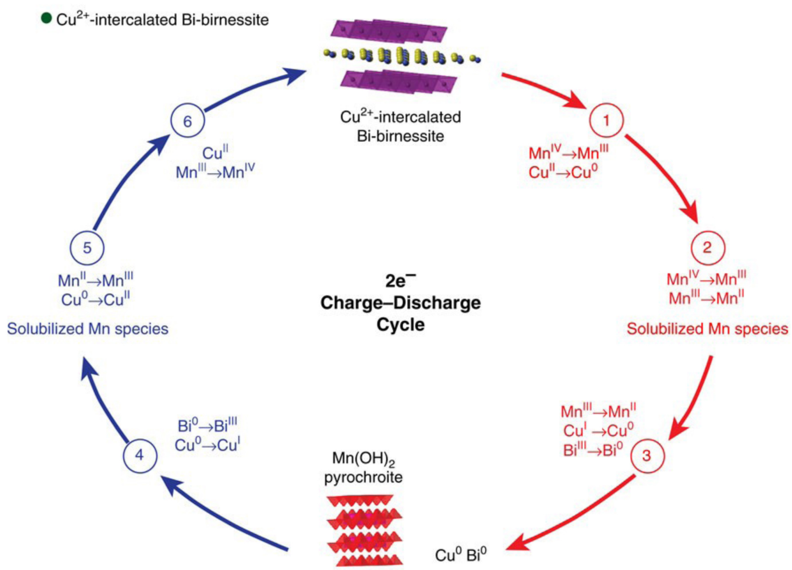
→ ~$50/kWh Targeted

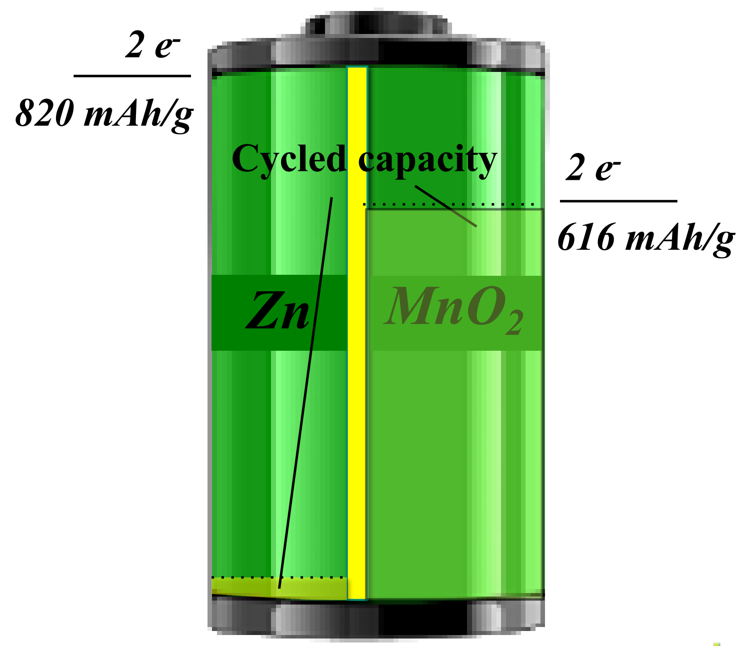
URBAN ELECTRIC POWER

Founded 2012

Alkaline Zn/MnO_2 Batteries

Two Electron - 2e- DOD





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URBAN ELECTRIC POWER

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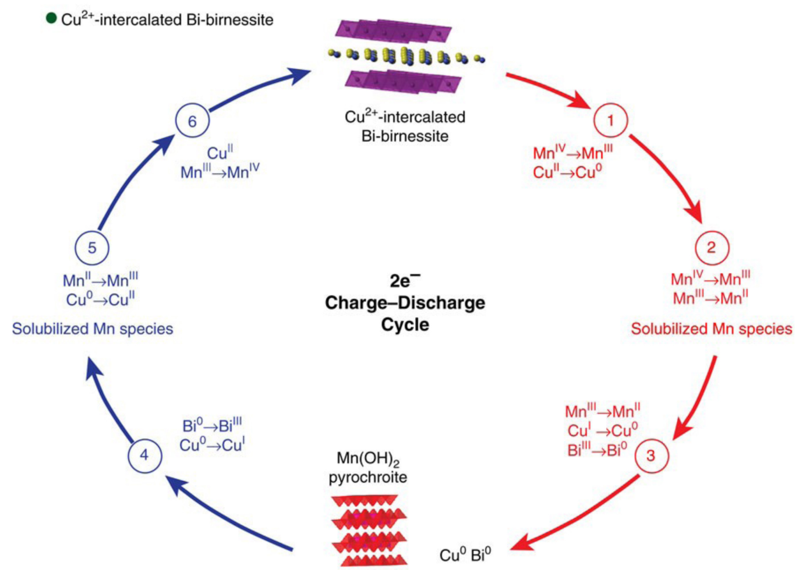
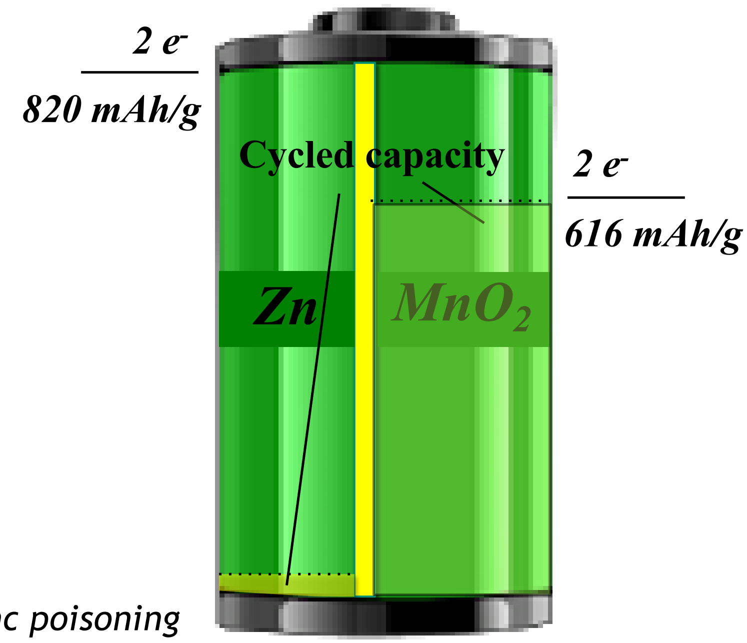
Alkaline Zn/MnO_2 Batteries



Two Electron - 2e- DOD



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

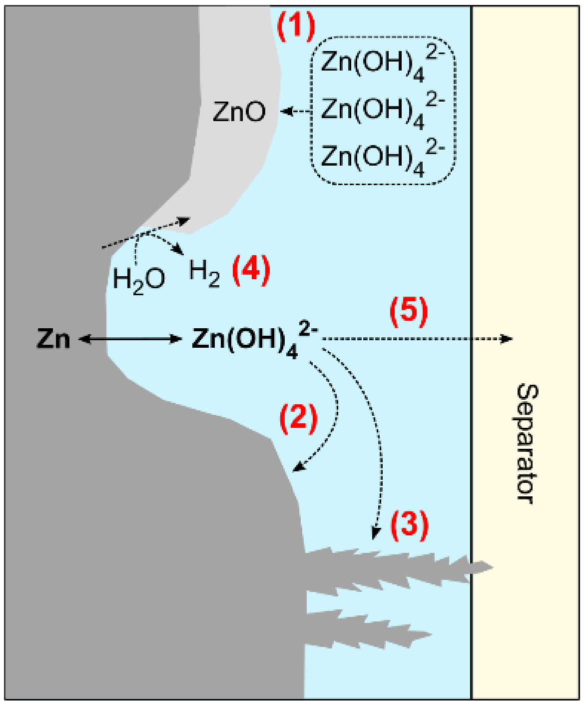
Challenges: High DOD Zn, Selective Separator

Also: Solid State? Other Cathodes ?

Alkaline Zn Anode

INCREASE UNDERSTANDING and the DEPTH OF DISCHARGE (CAPACITY) OF Zn ELECTRODE

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



Performance-Limiting Issues

1) Passivation
2) Shape change
3) Dendrite formation
4) H_2 evolution
5) Zincate crossover

Caused by solubility of ZnO in KOH [as $Zn(OH)_4^{2-}$] and subsequent precipitation of ZnO and Zn

Restricting migration of zincate is key

Dissolved zincate helps! *(Zn/Ni Batteries)*

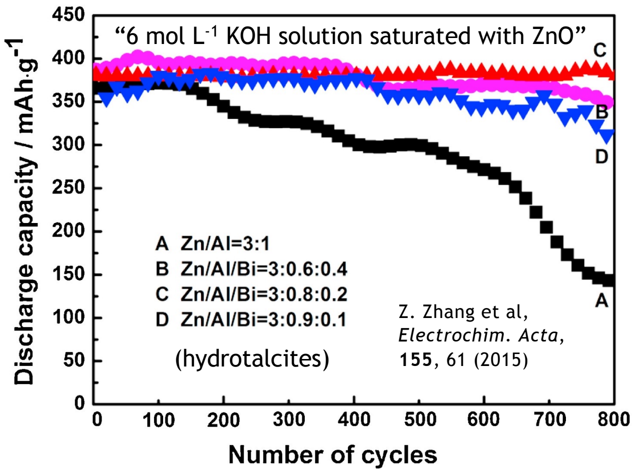
M. B. Lim, T. N. Lambert and E. I. Ruiz "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at Increased Depth-of-Discharge" J. Electrochem. Soc. 2020, 167, 060508. DOI:10.1149/1945-7111/ab7e90

ZnO-Saturated Electrolyte

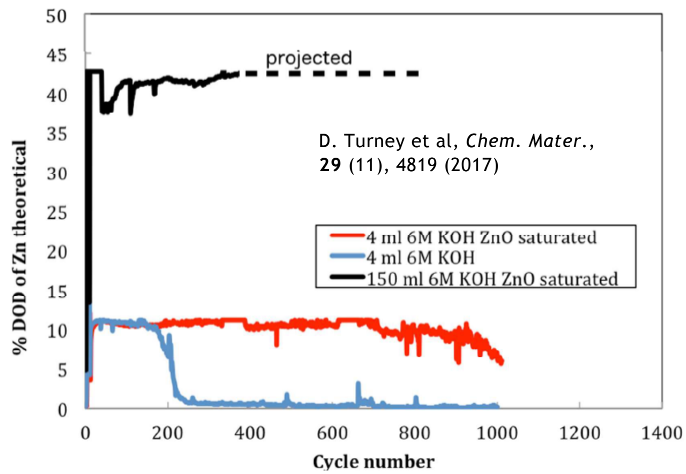
- Pre-saturating electrolyte with ZnO can minimize dissolution and long-range migration of zinc from anode
- Can also reduce the rate of H_2 evolution
- Saturated-ZnO electrolytes have been previously reported for Zn-Ni cells but most do not mention the amount of electrolyte relative to anode
  - Leads to artificially inflated metrics if cell is flooded
- No systematic study to date on effect of ZnO saturation alone at different levels of Zn DOD

J. Fu et al., *Adv. Mater.* **29**, 1604685 (2017).
A. Mainar et al., *Energy Science & Engineering* **6**, 174 (2018).

Bi-doped Zn-Al layered double hydroxides (Zn-Al-Bi LDH



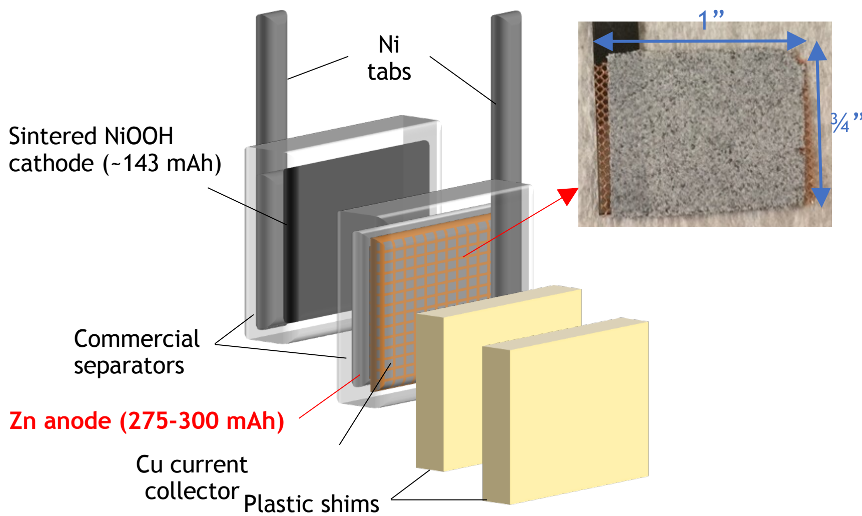
Z. Zhang et al, *Electrochim. Acta*, **155**, 61 (2015)

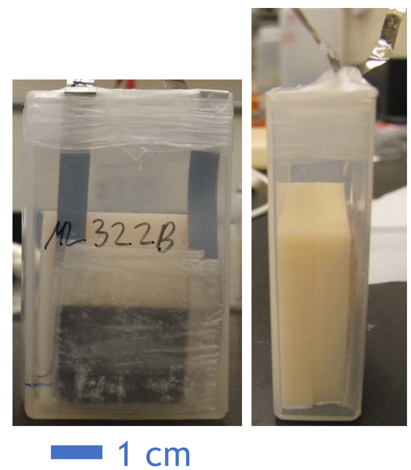


D. Turney et al, *Chem. Mater.*, **29** (11), 4819 (2017)

Battery Assembly and Testing

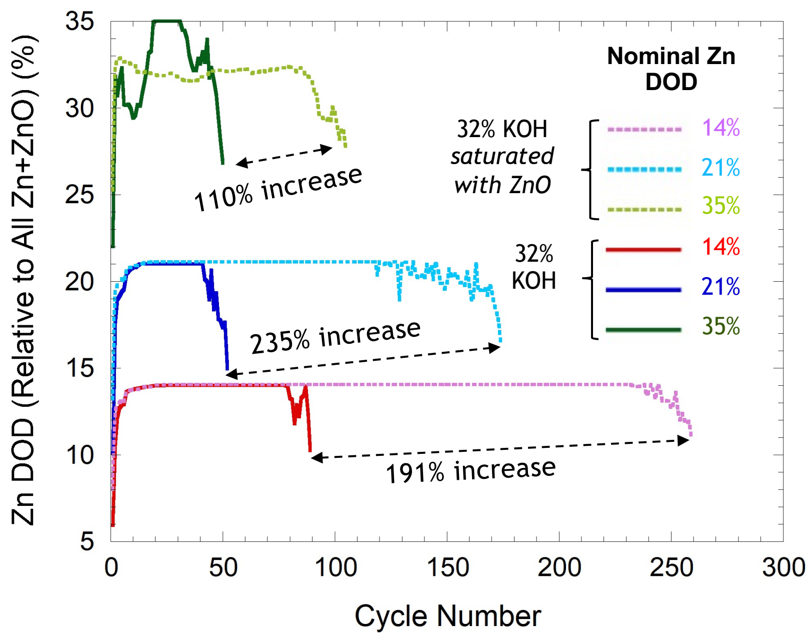
Due to the sensitivity of MnO_2 to $Zn(OH)_4^{2-}$, use NiOOH as the cathode material instead to examine the effect of ZnO saturation at different Zn DOD.

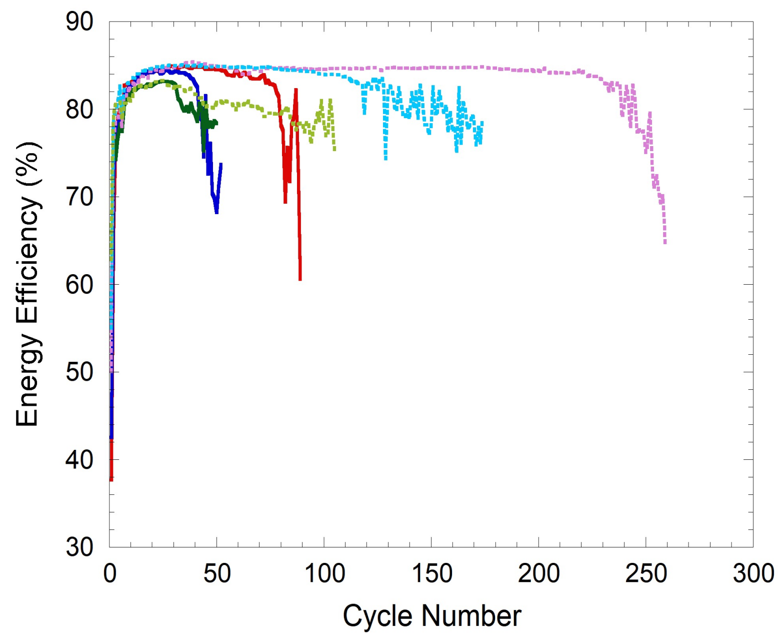




- 3 mL 32% KOH electrolyte with/without saturated ZnO
  - Zn(II) saturation concentration ≈ 0.74 mol/L → **119 mAh** in dissolved ZnO
- Cycled between 1 and 1.93 V vs. Zn at C/10 relative to full anode capacity = **75 mA/g$_{anode}$**
- Zn DOD limits of 14%, 21%, 35% **relative to all Zn+ZnO in system**

Improved Cycle Life at High DOD with Zincate (Zn/Ni) – 32% KOH

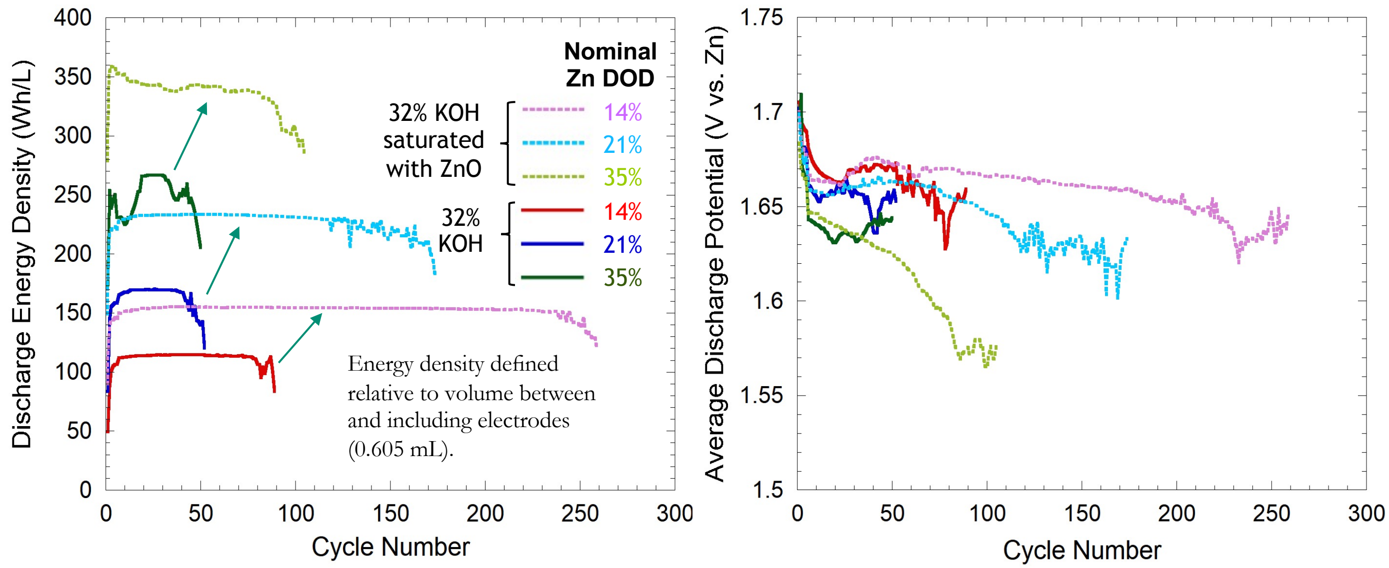




Cells with ZnO-saturated electrolyte last significantly longer with similar energy efficiency to cells with regular electrolyte cycled at same DOD, *even when including dissolved ZnO in capacity*

M. B. Lim, T. N. Lambert and E. I. Ruiz "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at Increased Depth-of-Discharge" J. Electrochem. Soc. 2020, 167, 060508. DOI:10.1149/1945-7111/ab7e90

Cell Energy



- Energy density is a misleading metric due to possible contribution of pre-dissolved ZnO from the electrolyte reservoir and higher cycled capacity of cells with saturated electrolyte
- Average discharge potential is more informative (= discharge energy / discharge capacity)
  - No energy losses due to voltage between cells cycled in saturated vs. regular electrolyte at same DOD

M. B. Lim, T. N. Lambert and E. I. Ruiz "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at Increased Depth-of-Discharge" J. Electrochem. Soc. 2020, 167, 060508.
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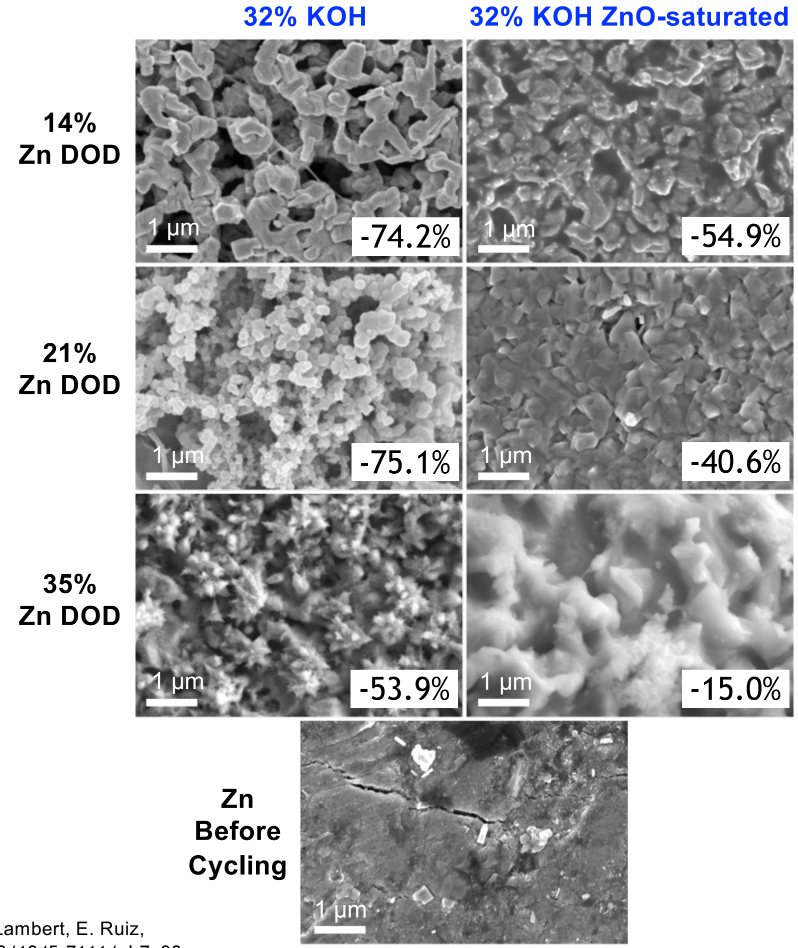
Post-Mortem Anode Characterization

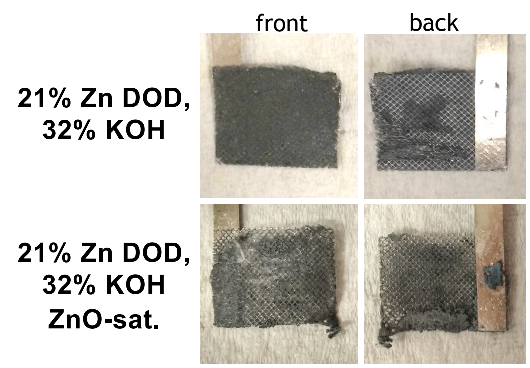


M. Lim, T. Lambert, E. Ruiz,
DOI:10.1149/1945-7111/ab7e90

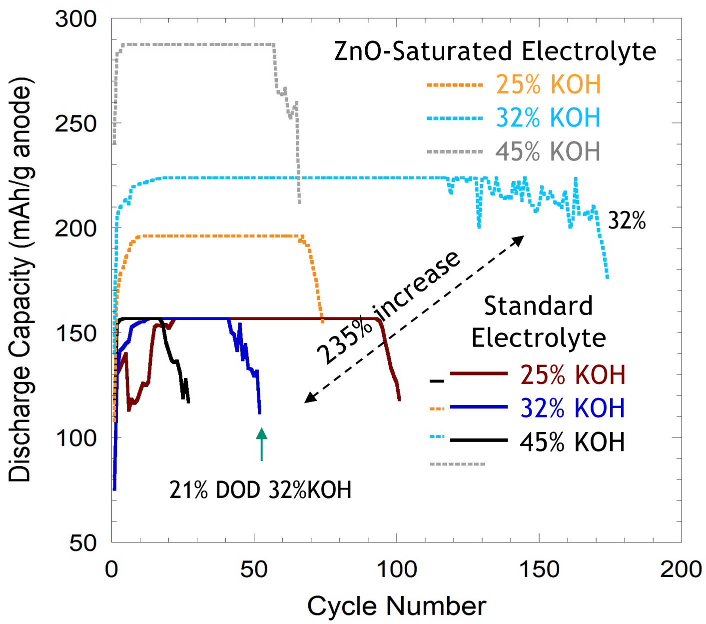
Cells disassembled in charged state following failure (80% of nominal cycled capacity).

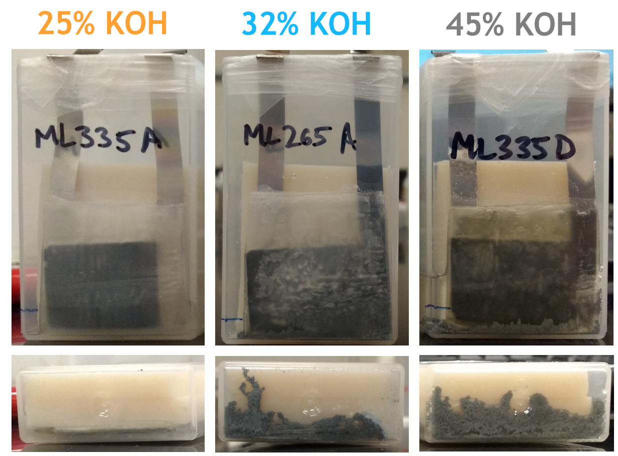
Inset = % mass loss of anode after cycling

- Anodes cycled in ZnO-saturated electrolyte yield more compact Zn deposits indicative of more homogeneous current density
- They also lose less mass despite showing significant Zn deposition on the bottom of the electrode and through the separator
- Re-pairing experiments confirm that failure was due to anode



Effect of KOH Concentration at 21% Zn DOD





Initial wt.% KOH	mol/L Zn(II) at Saturation	mAh in Dissolved ZnO
25	0.45	72.4
32	0.74	119
45	1.50	241

J. Electrochem. Soc. 1967, **114**, 1045.

J. Chem. Soc, Faraday Trans. 2, 1974, **70**, 1978.

M. Lim, T. Lambert, E. Ruiz,
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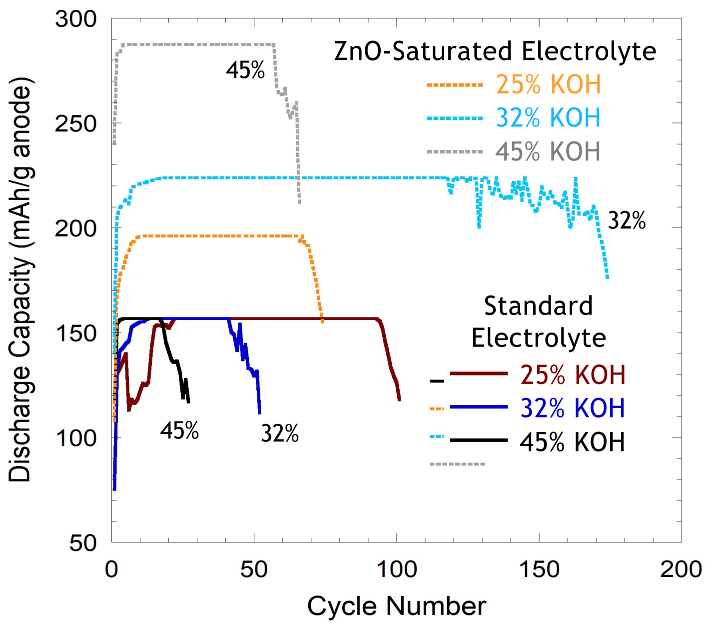
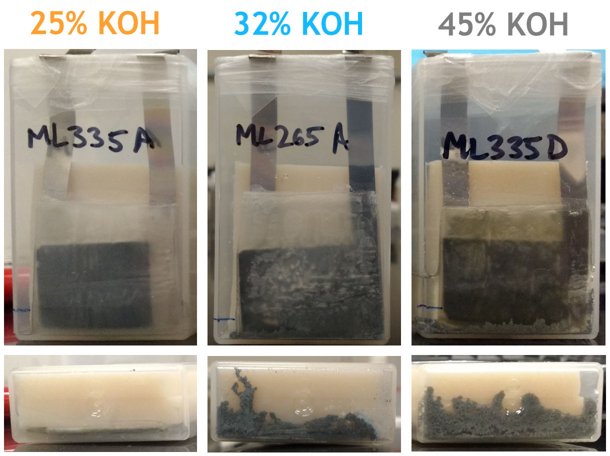


- Cells with 45% KOH fail more quickly with more zinc growth outside the electrode than cells with less concentrated electrolyte



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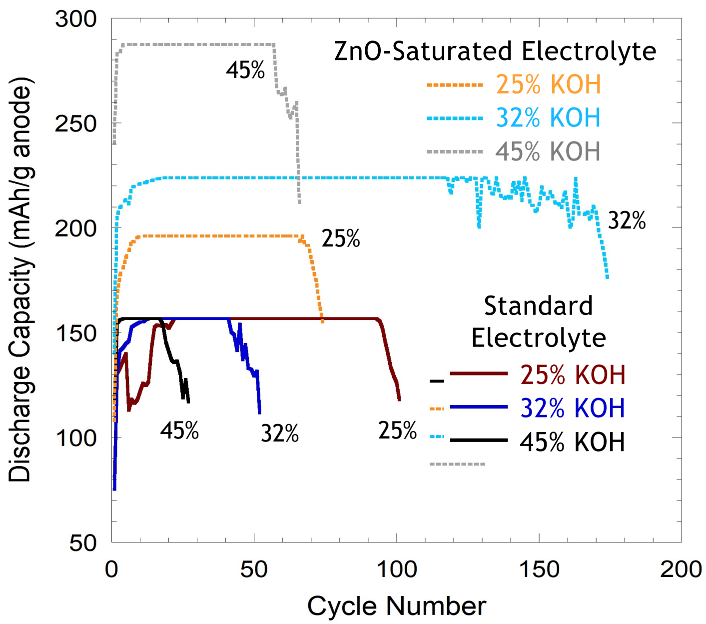
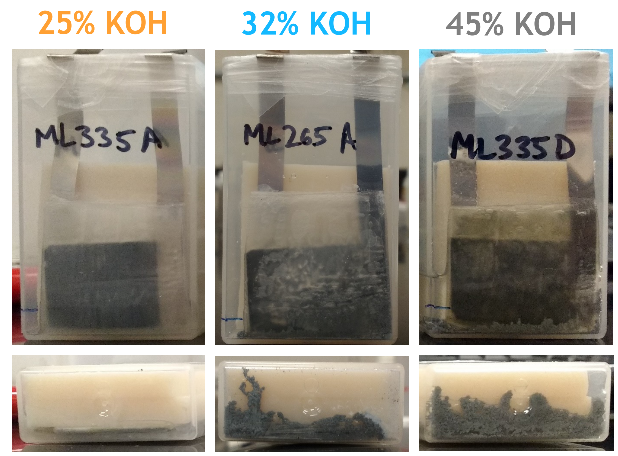


- Cells with 45% KOH fail more quickly with more zinc growth outside the electrode than cells with less concentrated electrolyte
- ZnO saturation *reduces* cycle life in 25% KOH
  - May be due to lower saturation concentration of ZnO → increased passivation



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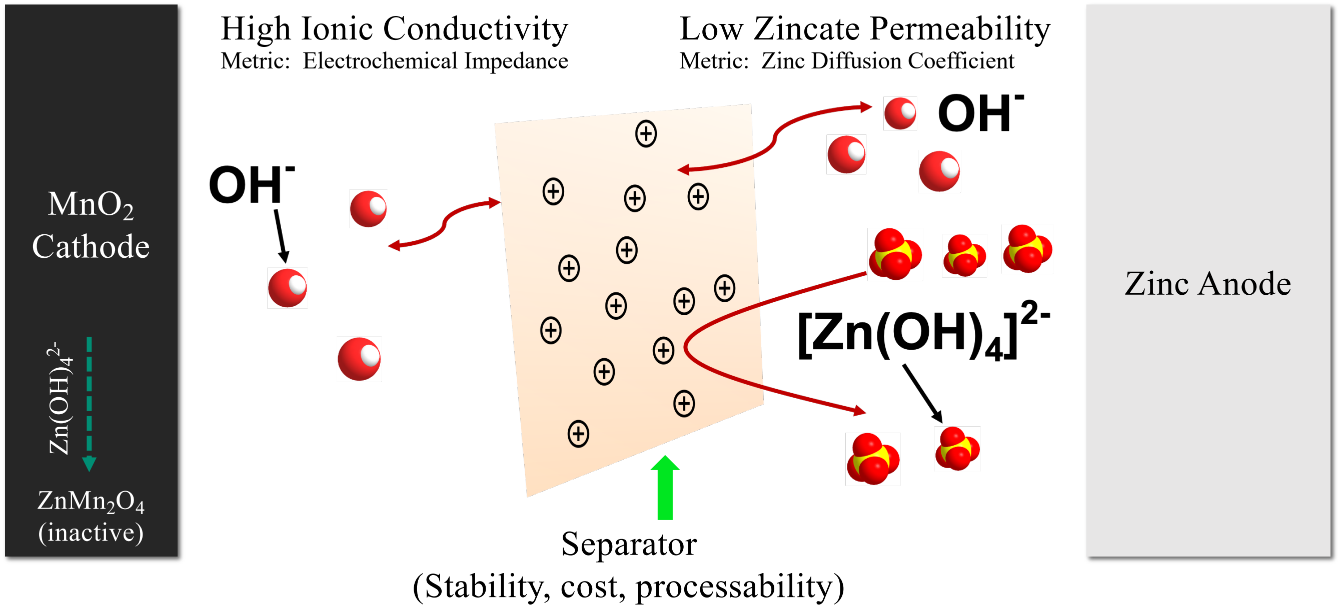
Selective Separator Approach to Improving Zn Batteries ?



Can we successfully compartmentalize the Zn anode ?

1. *Zincate electrolyte beneficial for Zinc anodes?* — *Zn/Ni* ✓
2. ***Can selective separator be used to create in situ zincate ?*** — *Zn/Separator/Ni*
3. ***Anode and Cathode cycle life extension ?*** — *Zn/Cu,Bi-MnO_2 or Zn/CuO*

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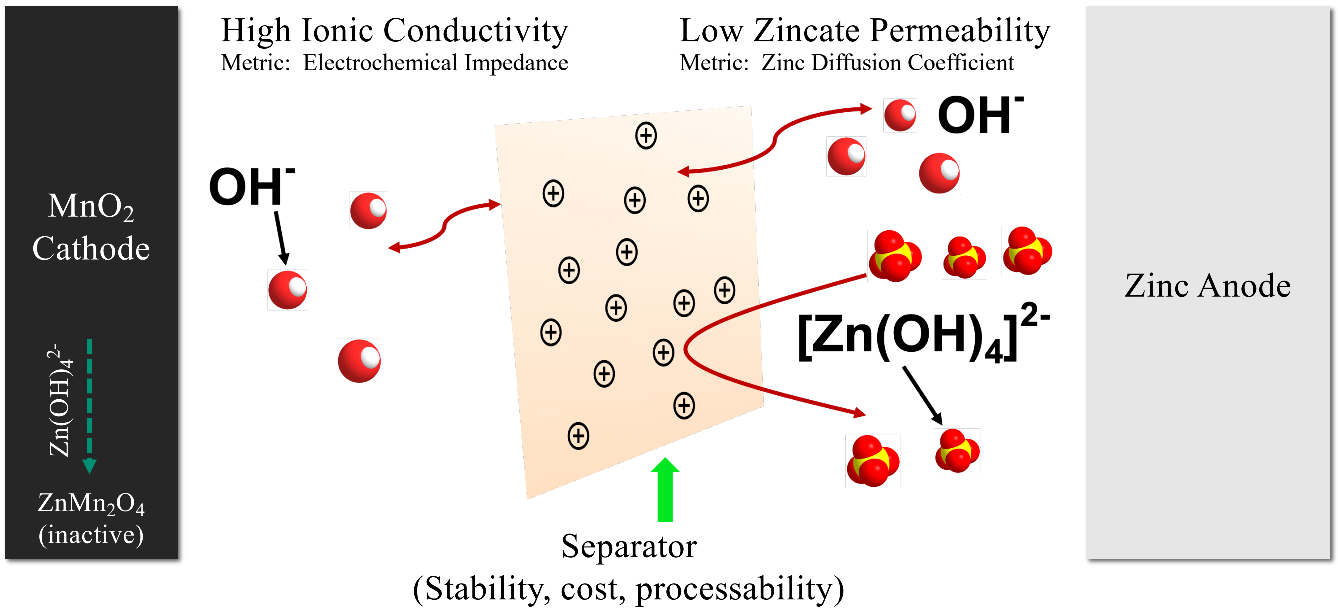

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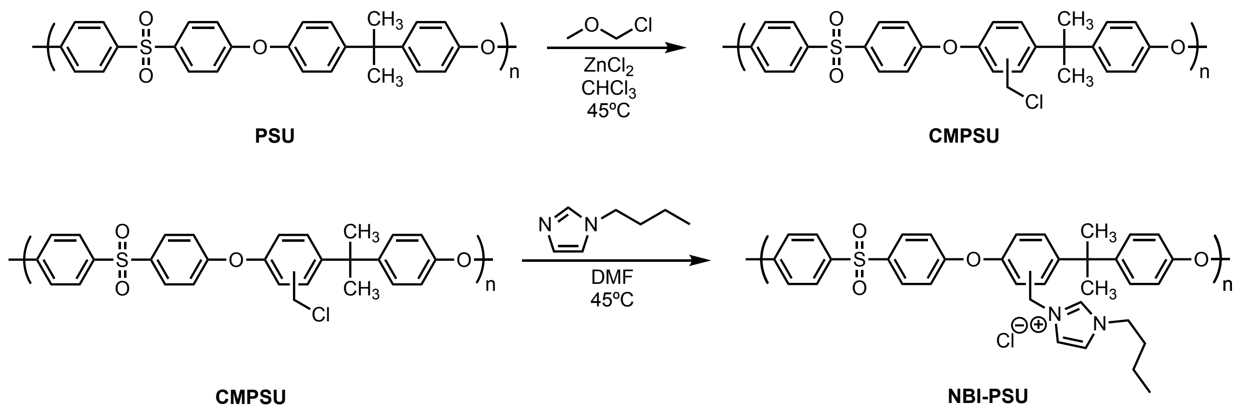
Synthesis of Polymeric Selective Separators



Synthesized NBI-PSU contained a degree of functionalization of 1 N-butylimidazolium per repeat unit of polymer.

NBI-PSU was then blended with commercial (unmodified) PSU in various ratios to mimic a lower overall degree of functionalization:

PSU Only = 0-NBI PSU
1 NBI-PSU/3 PSU = 25-NBI PSU
1 NBI-PSU/1 PSU = 50-NBI PSU
NBI-PSU Only = 100-NBI PSU

I. V. Kolesnichenko et al. ACS Appl. Mater & Interface 2020, http://dx.doi.org/10.1021/acsami.0c14143.

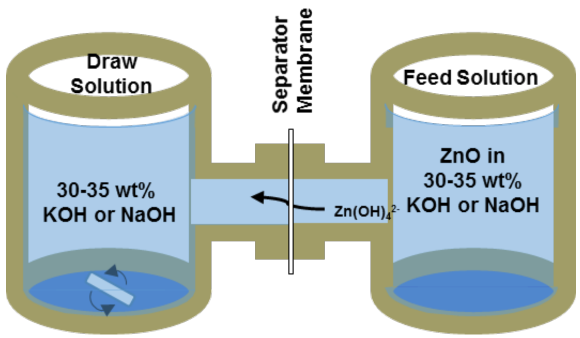
Zincate Diffusion Coefficient Necessary ?

-It depends on the lifetime of the battery as well as its geometry

-Diffusion coefficient of Zincate:

$$D = \frac{V_b L}{At} \ln\left(\frac{C_A}{C_A - C_B}\right)$$

E.g. ~ 50 mAh cell



V_b: 3 mL on "draw side"

L: 25 microns

A: 5 cm^2 membrane area

t: time elapsed

C_A: 2 M zincate in the "feed" solution

C_B: Assume $\leq$ 0.1 M zincate in the "draw" solution is acceptable

D = 7.7 x 10^{-5} cm^2 / [lifetime of battery needed (min)]

1 month = 2 x 10^{-9} cm^2/min

1 year = 1.5 x 10^{-10} cm^2/min

@ 5 years = 3 x 10^{-10} cm^2/min

Zincate Diffusion Coefficient Necessary ?

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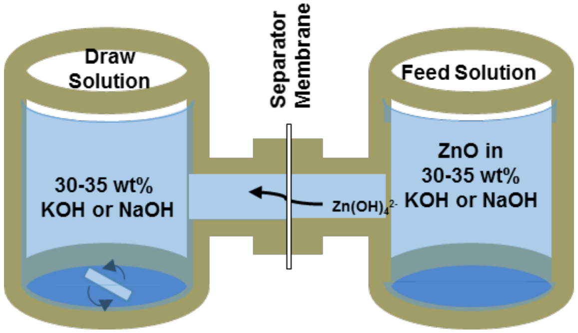
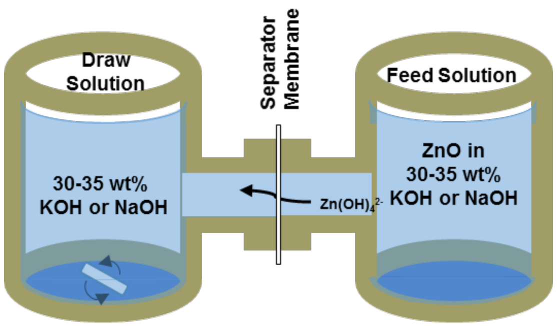


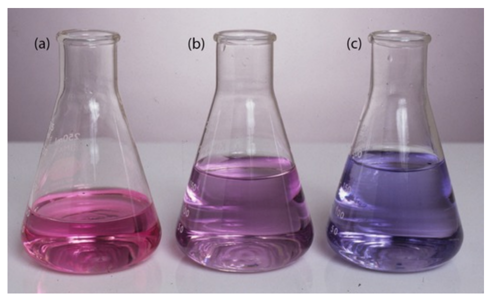
How Measure ?

Ex situ analysis – Separator Crossover Determination ?



Inductively Coupled Plasma – Mass Spectrometer

- -time intensive
- -lots of glassware
- -requires acidic solutions (2% HNO_3)
- -requires total dissolved solids < 0.2%
- -huge dilution > 300X
- -expensive bulky equipment
- - < ppb limit of detection (ideal situations)



Eriochrome Black T

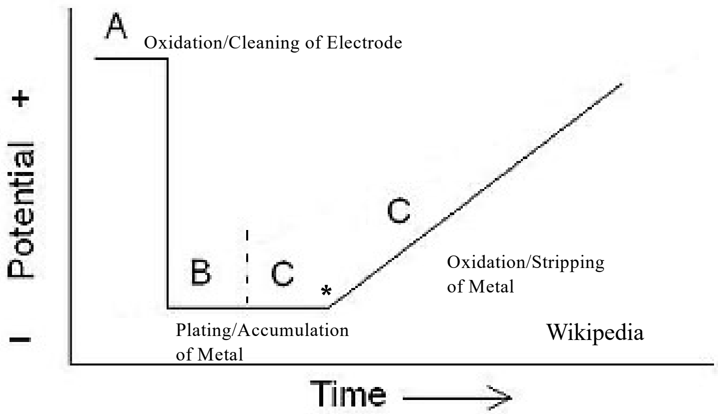
Colorimetric Titration with EDTA

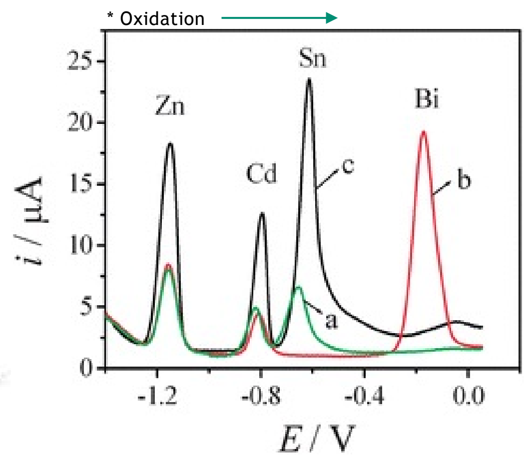
- -Difficult Endpoint Determination
- -Requires pH ≤ 11
- -Use of ammonium buffer
- -Dilution > 20X
- -ppm limits of detection

UV/Vis Spectrometer

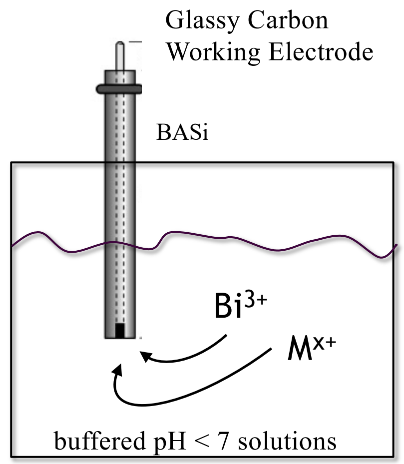
Anodic Stripping Voltammetry (ASV)

-historically done on Hg drop electrodes
-done in buffered (acidic) solutions
-Bi film electrodes increasingly replacing Hg





Analyst, **2012**, 137, pp. 614-617



-Bi is plated onto an passive electrode with the element of interest
-During stripping, the element of interest is stripped from the Bi film

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

Ex situ analysis - Alkaline Aqueous Chemistry (pH > 14)

Insoluble metal oxides become soluble by hydroxide complexation

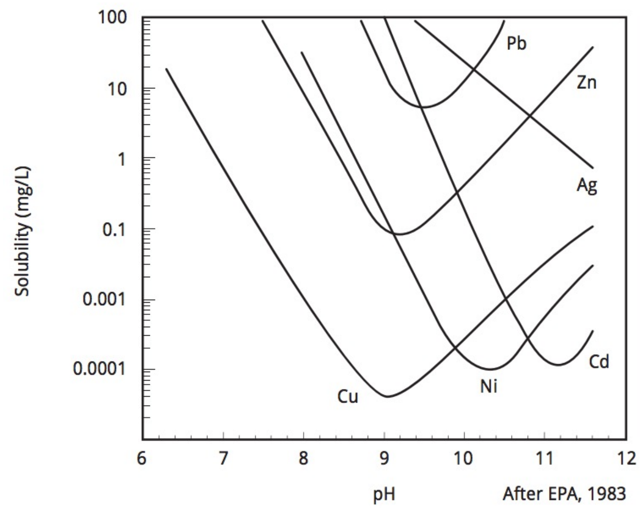
$ZnO(s) + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$

$PbO(s) + H_2O + OH^- \rightarrow Pb(OH)_3^-$

$CdO(s) + H_2O + OH^- \rightarrow Cd(OH)_3^-$

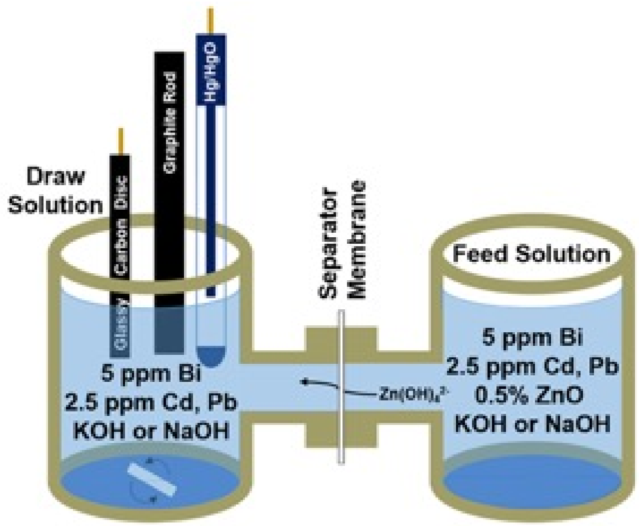
$Bi_2O_3(s) + 3H_2O + 2OH^- \rightarrow 2Bi(OH)_4^-$

This should allow for the opportunity to use ASV to measure Zn ion species in highly alkaline environments for the first time



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

Ex situ analysis - ASV



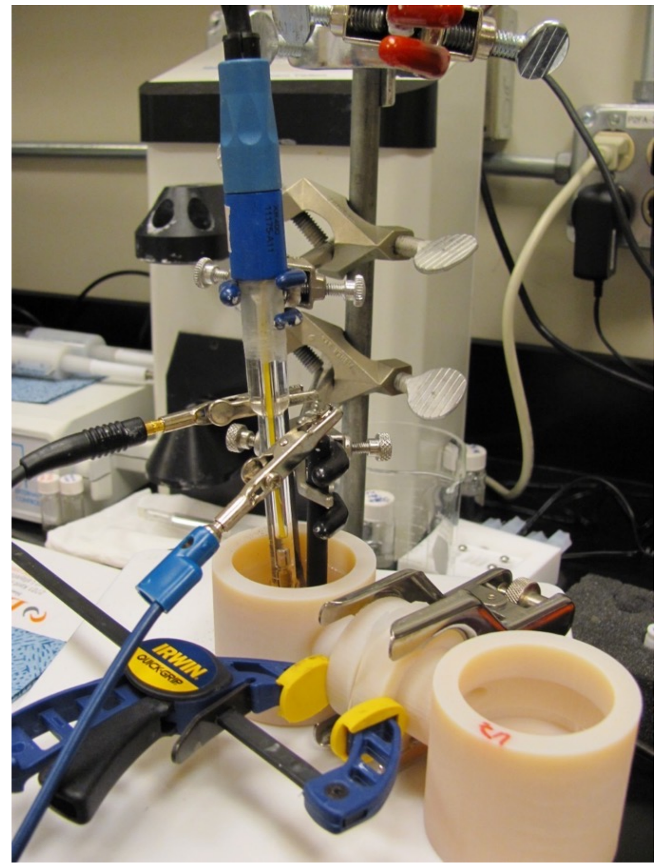
ASV to measure Zn, Cu or Bi

***Ex Situ* Assays:**

ASV Analysis of Zn, Cu or Bi in Alkaline conditions

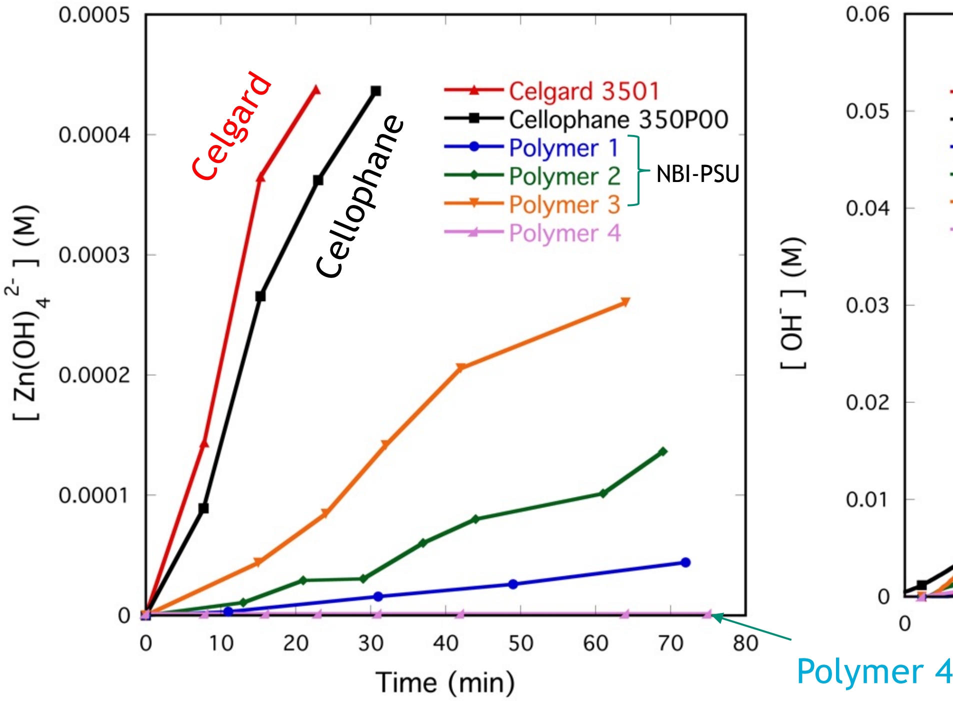
J. Duay, et al. *Electroanalysis* DOI: 10.1002/elan.201700337 (Zn w/Bi, Cd, Pb)
J. Duay et al. *Electroanalysis* DOI: 10.1002/elan.201700526 (Cu w/Pb)
D. Arnot et al. *Electroanalysis* DOI: 10.1002/elan.202060412 (Bi w/Pb)

ASV in real time for Diffusion Coefficients

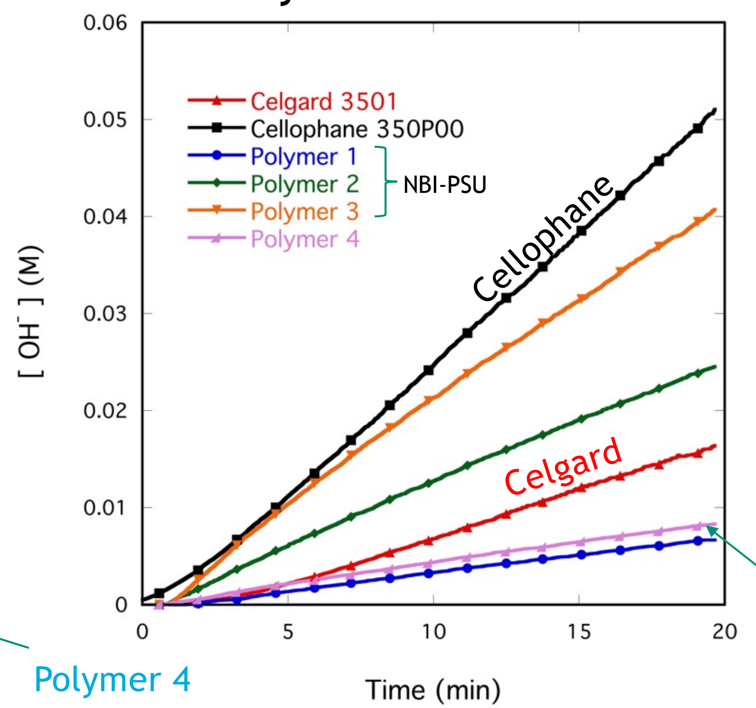


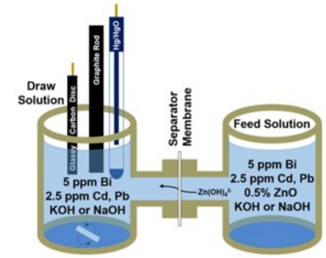
Hydroxide Selective Separators

Zincate Diffusion



Hydroxide Diffusion





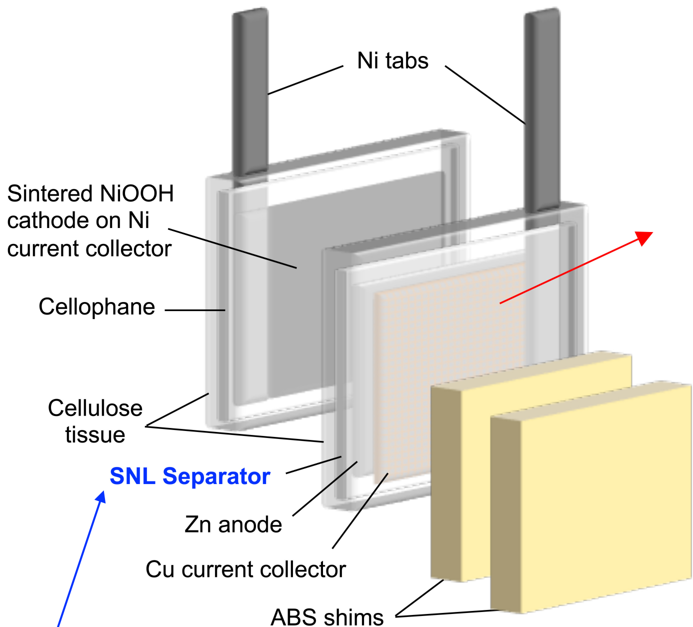
Ex Situ **Assay: ASV Analysis of Zn, Cu and Bi in Alkaline conditions**

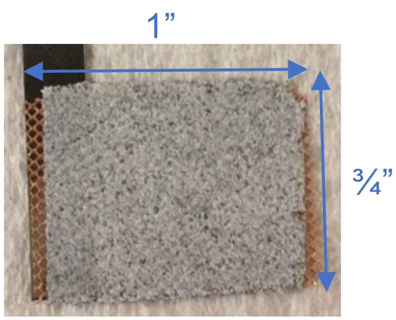
J. Duay, et al. *Electroanalysis*
DOI: 10.1002/elan.201700337
DOI: 10.1002/elan.201700526.
D. Arnot et al. *Electroanalysis*
DOI: 10.1002/elan.202060412

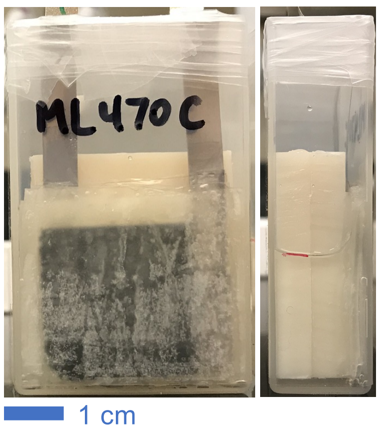
$$D = \frac{V_b L}{At} ln\left(\frac{C_A}{C_A - C_B}\right)$$

Polymer 4: $D_{HO^-}/D_{Zn(OH)_4^{2-}}$ ~ 10,000
ASV LOD for zincate ~ 0.026 mM

In situ - Utilization of flexible separator to enable increased Zn DOD ?







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

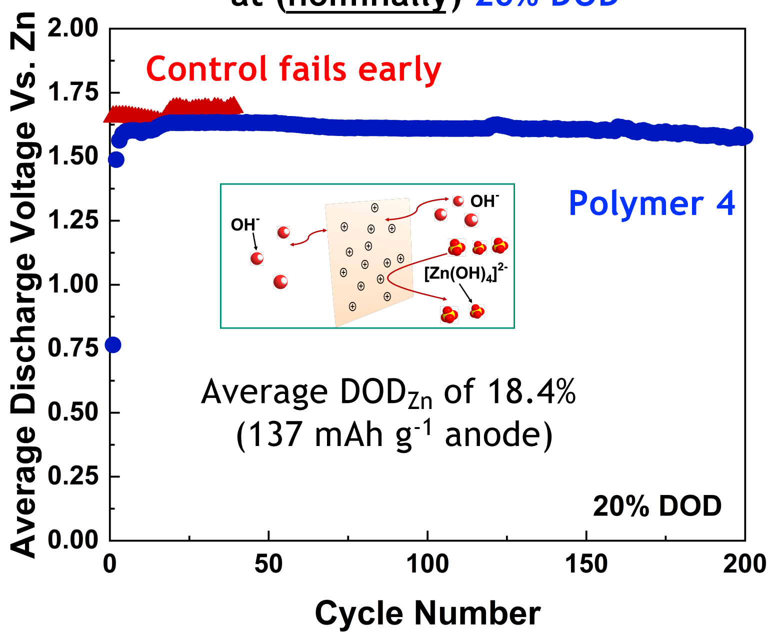
Polymer Separator – minimal volume change or complexity to cell

< 1% volume change to cell

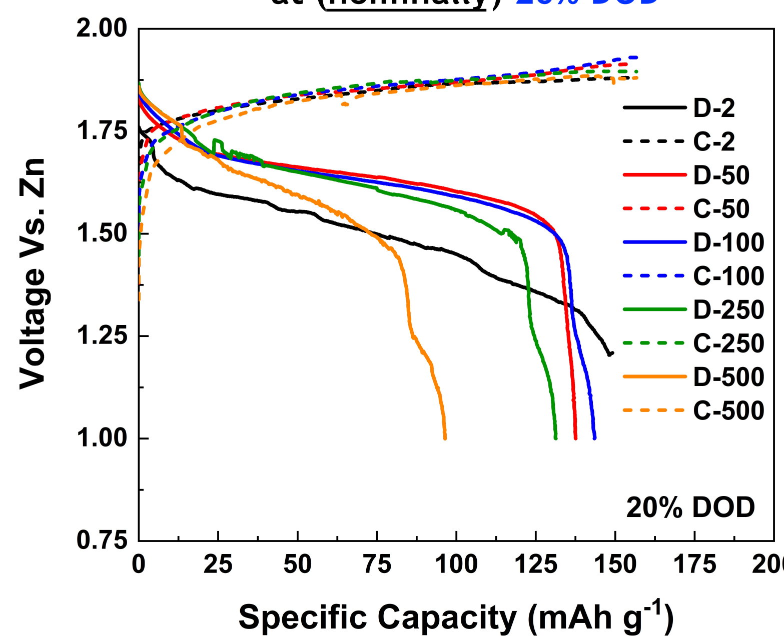
D. Arnot et al. manuscript submitted

Zn/Ni: Flexible separator enables increased Zn DOD and cycle life

Average Potential During Discharge at (nominally) 20% DOD



Discharge-Charge Profiles at (nominally) 20% DOD



550 cycles: Average DOD_{Zn} of 16.3% (~122 mAh g^{-1} anode)

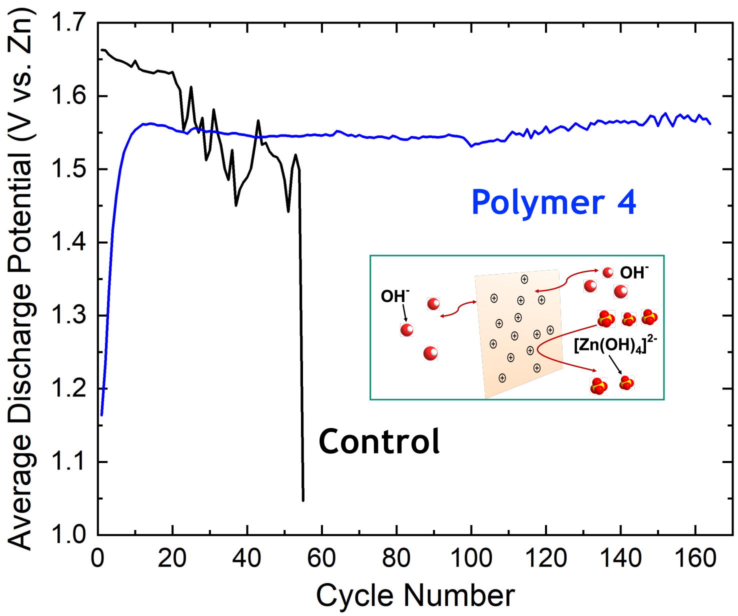
83.1% Zn and 9.8% ZnO

[Zincate sat'd solution was only 259 cycles at a 14% DOD_{Zn}]

D. Arnot et al. manuscript submitted

Zn/Ni: Flexible separator enables increased Zn DOD and cycle life

Average Potential During Discharge at (nominally) 50% DOD



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

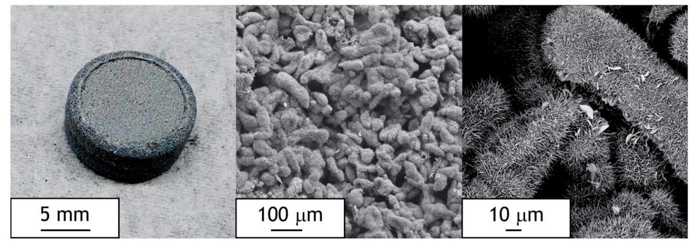
- Selective Separator enables > 150 cycles
- Achieves Average DOD of 32%
- 198% Increase in cycle life is obtained
- Achieves average Energy Density of 180 Wh L^{-1}
- Less than 1% change in Cell Volume

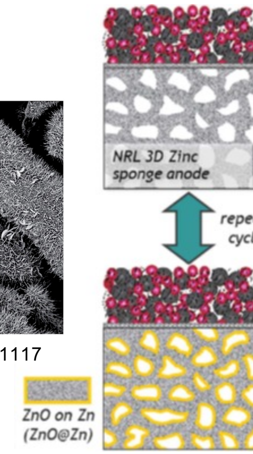
Increased cycle life of energy-dense Zn electrodes without adding significant volume, complexity (or cost?) to the system

D. Arnot et al. manuscript submitted

COMPARISON TO OTHER HIGH DOD Zn ANODES

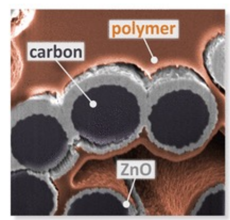
- Parker et al., Science 2017, 356 (6336), 415.
  - 3D Zn sponge
  - 111 cycles above 20% DOD (including 85 cycles at 40% DOD limit)
  - Anode capacity ~ 100 mAh/cm^2





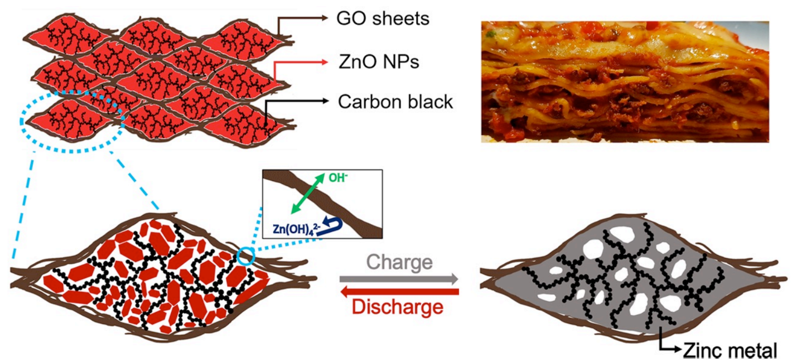
Energy Environ. Sci. 2014, 7, 1117
Science 2017, 356, 415

- Stock et al., ACS Applied Energy Materials 2018, 1 (10), 5579-5588.
  - C mesh/ZnO/anion-exchange ionomer core-shell structure
  - 67 cycles with 40.5% average DOD
  - Anode capacity ~ 5.7 mAh/cm^2



ACS Appl. Energy Mater. 2018, 1, 5579

- Yan et al., ACS Applied Energy Materials 2018, 1 (11), 6345-6351.
  - ZnO nanoparticles in "lasagna-like" GO matrix
  - 150 cycles with 82.2% average DOD
  - Anode capacity ~0.66 mAh/cm^2

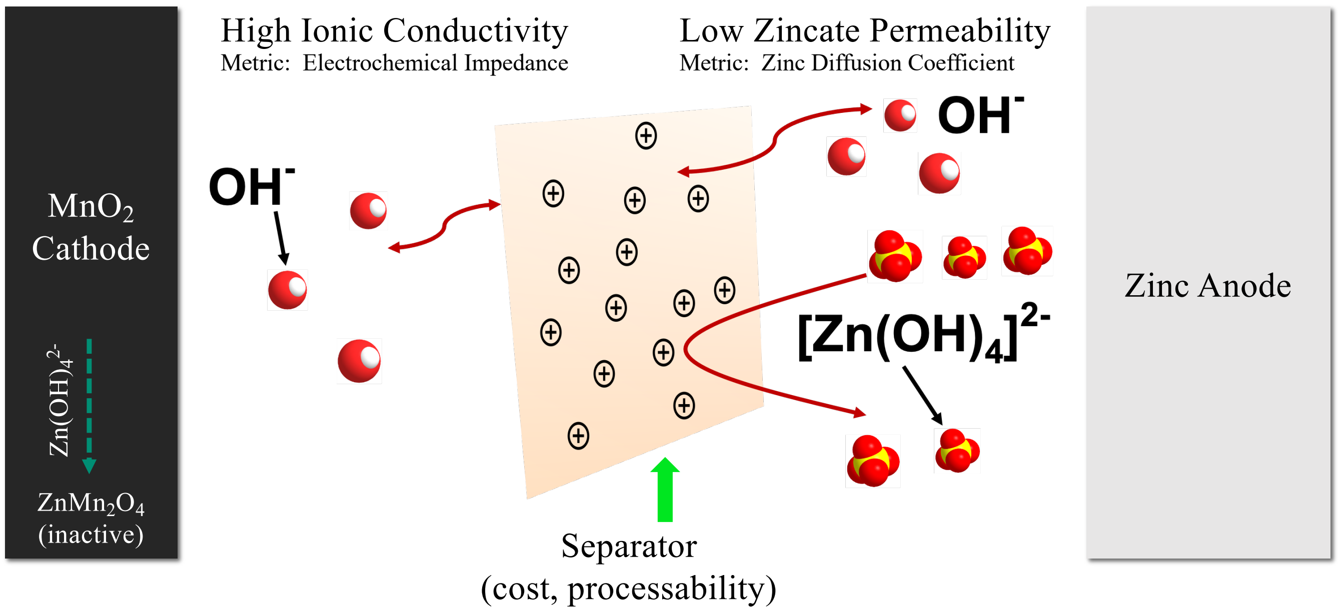


ACS Appl. Energy Mater. 2018, 1, 6345

- **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/cm^2**

D. Arnot et al. manuscript submitted

Selective Separator Approach to Improving Zn/MnO_2 ?



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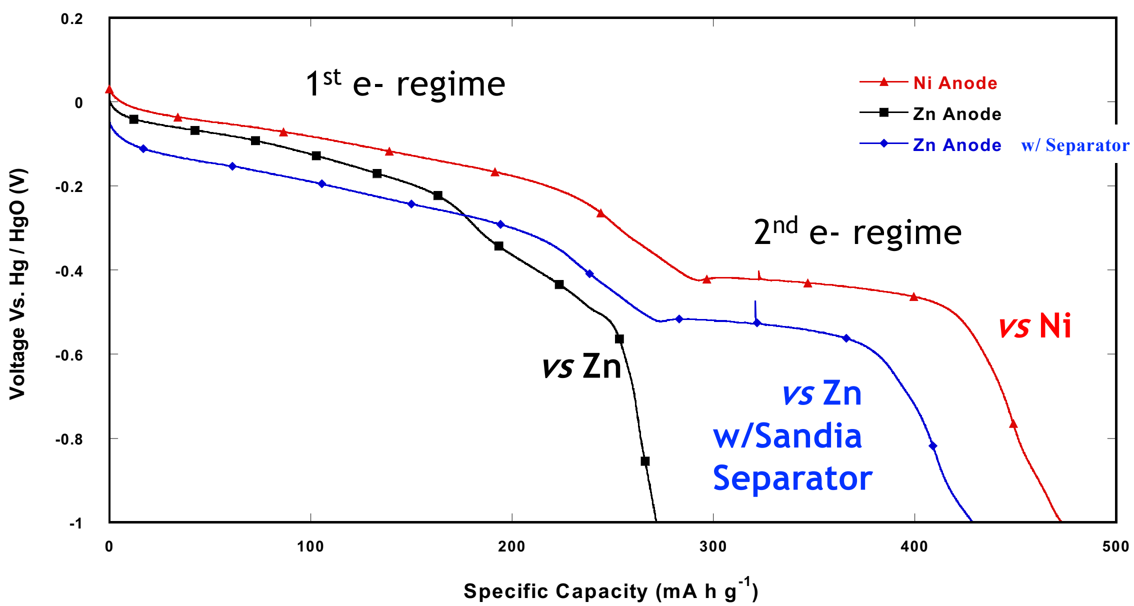
PROJECT RESULTS

In Situ – Separator effective at blocking zincate crossover in Zn/MnO_2 Battery

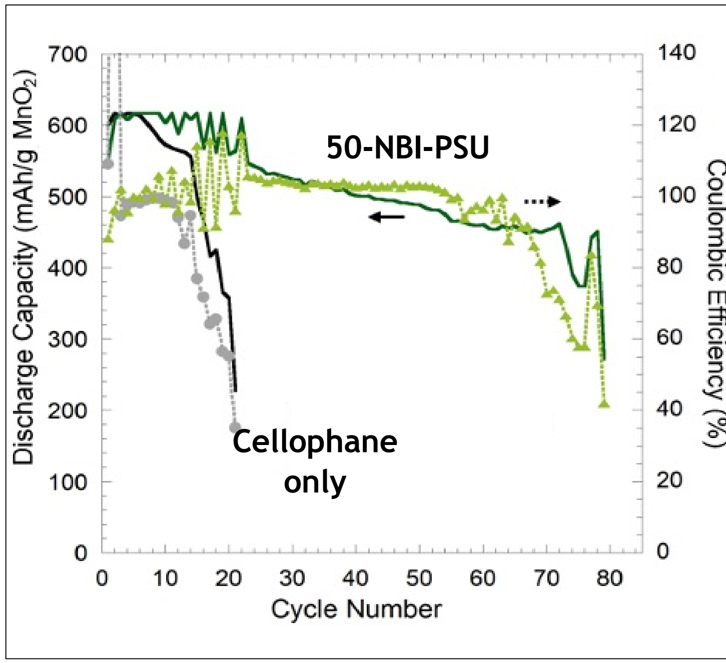
Discharge of Zn / MnO_2 Primary Cells confirms $Zn(OH)_4^{2-}$ blocking

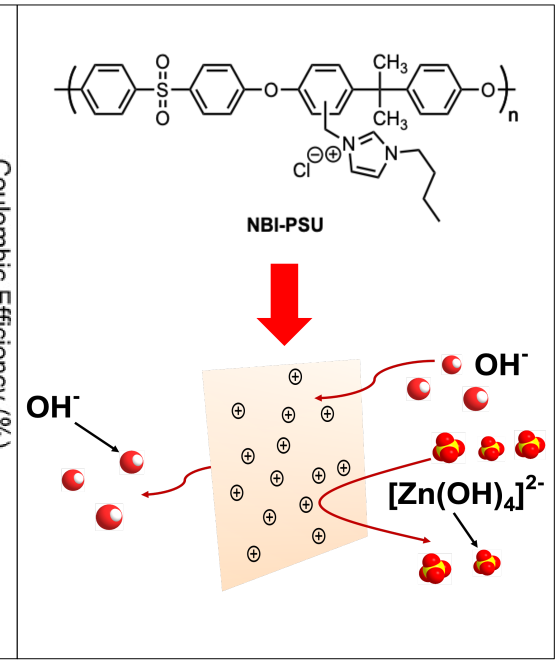


Polymeric Selective Separators-Battery Testing with 2e- Bi,Cu-MnO_2

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

- Cast into Flexible Membrane
- 50-NBI PSU was *inserted* between a Bi/Cu-stabilized MnO_2 cathode (from collaborators at CUNY) and an excess Zn anode with 25% KOH – limited electrolyte
- Cycled at C/10 to 100% of the 2e- MnO_2 capacity (≈10% Zn DOD) and voltage limits of -1 to 0.35 V vs. Hg/HgO





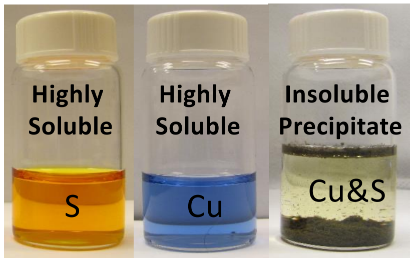
I. V. Kolesnichenko et al. ACS Appl. Mater & Interface 2020, http://dx.doi.org/10.1021/acsami.0c14143.

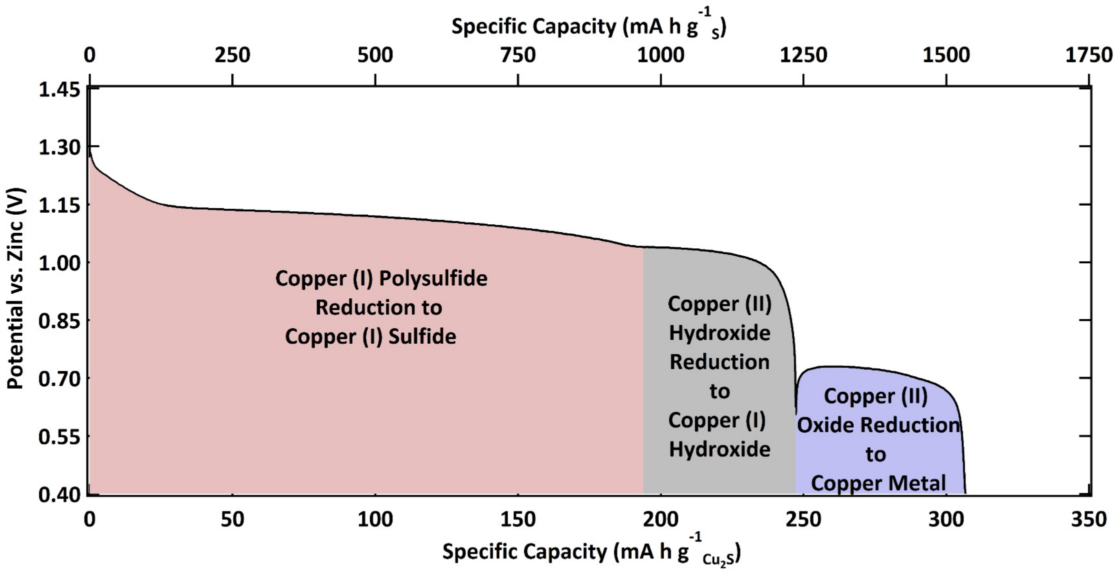
DEVELOPMENT OF NEW LOW COST HIGH CAPACITY BATTERY CHEMISTRIES

Sulfur is known to have a high theoretical specific capacity:
1650 mA h g^{-1}

Zn/Cu_2S

- ~1500 mAh g^{-1} (S)
- ~300 mAh g^{-1} (Cu_2S)
- ~ 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

J. Duay et al. *J. Electrochem. Soc.* **2019** *166 (4)*, A687-A694. DOI:10.1149/2.0261904jes.

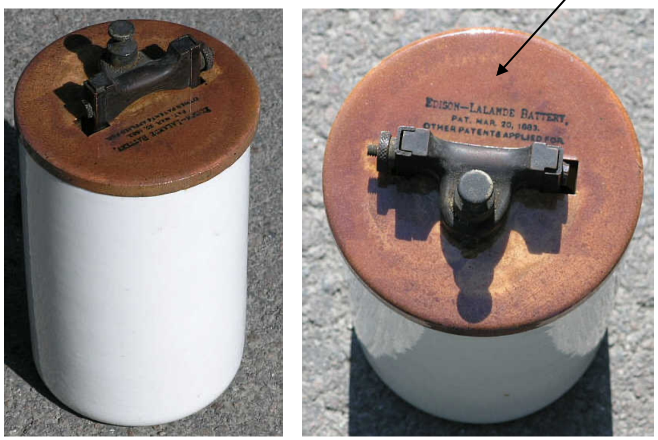
DEVELOPMENT OF NEW LOW COST HIGH CAPACITY BATTERY CHEMISTRIES

Anode: $Zn^0 + 4OH^- \rightarrow [Zn(OH_4)]^{2-} + 2e^-$ $E^o = 1.285$ V

Cathode: $CuO + H_2O + 2e^- \rightarrow Cu^0 + 2OH^-$ $E^o = -0.29$ V

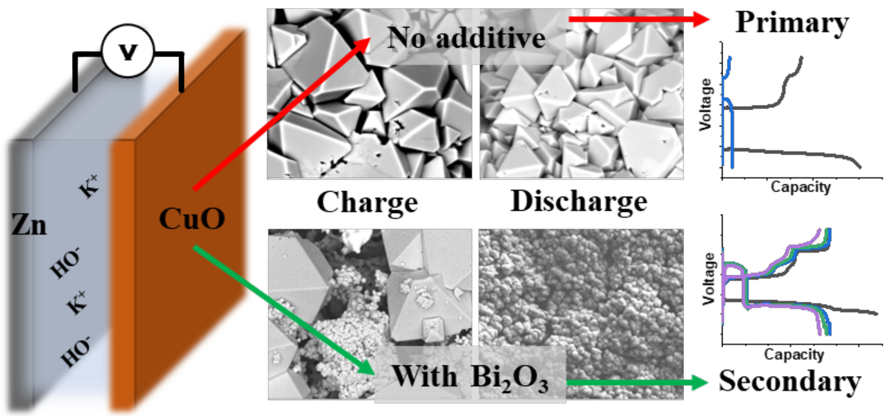
$Zn^0 + CuO + H_2O + 2\ OH^- \rightarrow [Zn(OH_4)]^{2-} + Cu^0$ Cell Voltage: 0.995 V

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



Edison-Lalande Battery (Primary Cell)

Addition of Bi_2O_3-additive leads to reversible Zn/CuO



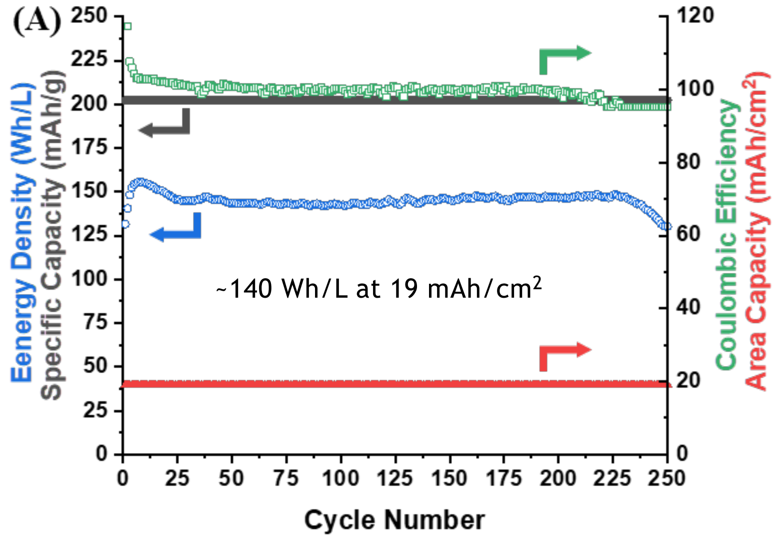
Bi decreases cell resistance and promotes Cu reduction

N. Schorr *et al. ACS Appl. Energy Mater. manuscript in press.*

Development of Cu-based Cathodes

1st Rechargeable Alkaline Zn/CuO Battery

Zn/$CuO-Bi_2O_3$ at C/5
30% DOD CuO, 1% Zn



Zn-ion/α-MnO_2 batteries, ~100-250 mAh/g, ~ 1-3 mAh/cm^2
Limited DOD Alkaline Zn/MnO_2: 10% MnO_2 DOD, ~40 Wh/L for 500 cycles

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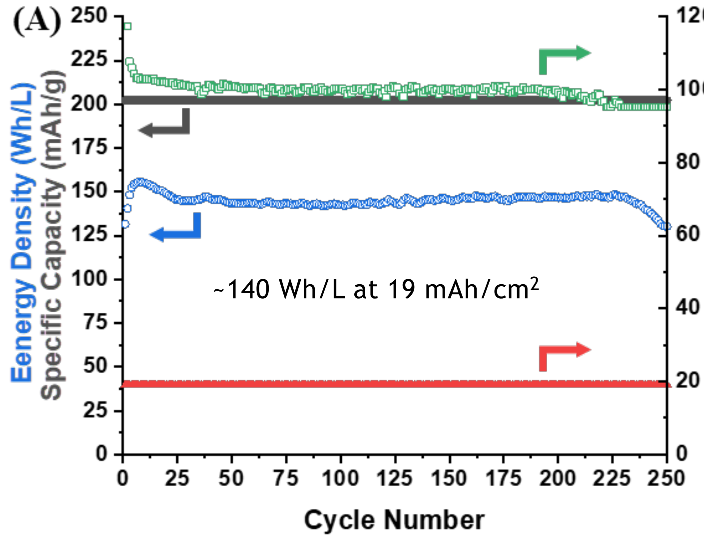
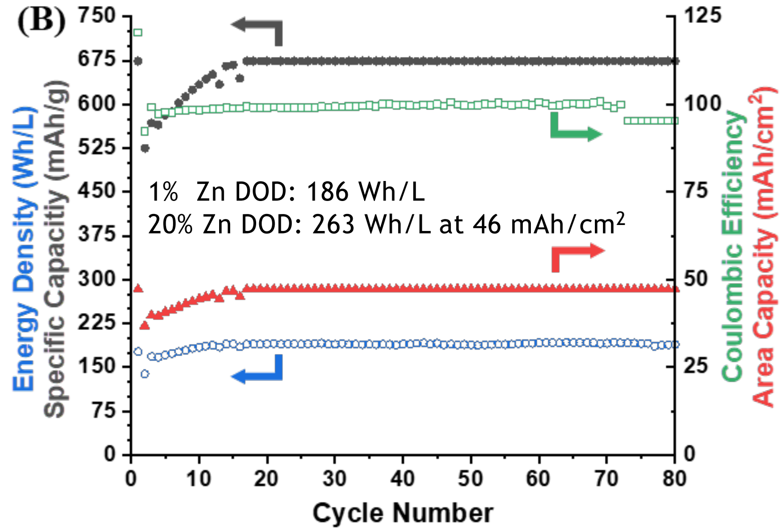


Zn/CuO-Bi_2O_3-Cu at C/5
100% DOD CuO



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FUTURE WORK TO INCLUDE TECHNOLOGY DEVELOPMENT → *Target: 10Ah, 100Ah @200 Wh/L for 100 cycles*

N. Schorr *et al. ACS Appl. Energy Mater. manuscript in press.*

Summary

1. **Grid Storage requires large scale production of low cost, safe and reliable batteries batteries**
   - Zn-based batteries could be Li-ion Energy at < Pb-acid cost
   - Roadmap to get to << $100/kWh when produced at scale
   - Move from 1 e- MnO_2 insertion cathode to 2 e- Bi/Cu-MnO_2 conversion cathodes

2. **Low DOD Zn (~ 20%) needs to become High DOD Zn ($\geq$ 50%)**
   - Zincate is good (Zn), zincate is bad (MnO_2) - % KOH matters

3. **Separator Development is needed for alkaline Zn-based cells**
   - Zn/Ni – benefit to the Zn electrode > zincate
   - Preventing zincate crossover – minimizes cathode poisoning, shorting (MnO_2 and CuO)

4. **ASV allows for easy real time analysis of diffusion coefficients**
   - Zn, Cu and Bi

5. **Bi-stabilized CuO allows for the first Zn/CuO re-chargeable battery**
   - Energy density of ~ 140 to 260 Wh L^{-1} demonstrated (R&D stage)
   - Among the highest energy density reported for Zn/Conversion cathode battery
   - Tech maturation and Future Roadmap ongoing

Project Contacts


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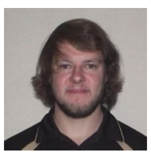
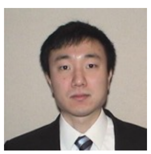
ACKNOWLEDGEMENTS

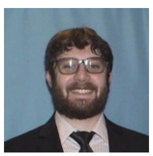

Imre Gyuk

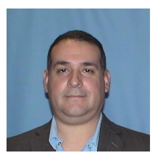
THIS WORK WAS SUPPORTED THROUGH THE ENERGY STORAGE PROGRAM, MANAGED BY DR. IMRE GYUK, WITHIN THE U.S.DEPARTMENT OF ENERGY'S OFFICE OF ELECTRICITY

FY 20 Sandia Team


Igor Kolesnichenko

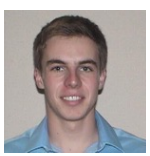

Matthew Lim

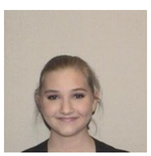

Noah Schorr

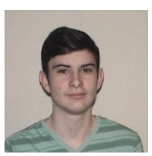

Stephen Budy

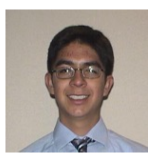

Bryan Wygant

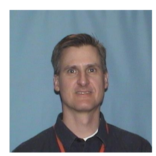
And COLLABORATORS!

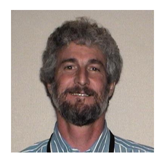

David Arnot


Rachel Habing


Logan Ricketts


Elijah Ruiz


Nelson Bell


Howard Passell

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Project Team – Sandia National Laboratories and Collaborators

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Alkaline Batteries for Grid Storage

CUNY The City University of New York Energy Institute

Prof. Sanjoy Banerjee

Damon Turney, Michael D'Ambrose, Junsang Cho, Brendan Hawkins, Snehal Kolhekar, Michael Nyce, Xia Wei, Prof. Rob Messinger

Stable Zinc Anodes for High-Energy-Density Rechargeable Aqueous Batteries

Prof. Igor Vasiliev

Birendra A. Magar, Nirajan Paudel

Theoretical Studies of the Electrochemical Behavior of Solid-State Cathode Materials

Prof. Joshua Gallaway

Andrea Bruck, Matthew Kim

Understanding Phase Change Processes of Energy Storage Materials

Stony Brook University

Prof. Esther Takeuchi

Amy Marschilok, Ken Takeuchi

Advanced Materials for Next Generation Batteries

URBAN ELECTRIC POWER

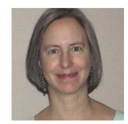
Gabe Cowles

Gautam Yadav

Gabe Cowles, Gautam Yadav, Jinchao Huang, Aditya Upreti, Meir Weiner, Valerio DeAngelis, Sanjoy Banerjee

Advanced Manufacturing Research

Sandia National Laboratories



Amalie Frischknecht

Membrane Modeling

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

Lawrence Livermore National Laboratory

Cheng Zhu

Marcus Worsley

Tony Van Buuren

3D electrodes for rechargeable Zn-MnO_2 batteries

Prof. Yang-Tse (YT) Cheng

Ryan Hill, Andrew Meyer

Collaborative research to advance solid state ion conductors for emerging batteries *[w/Erik Spoerke (SNL)]*

Thank you