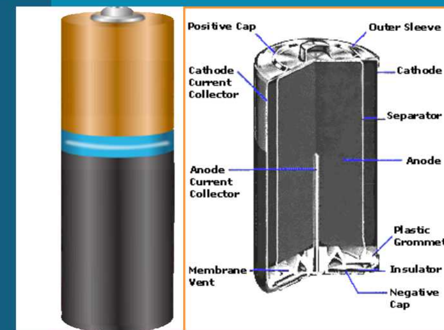
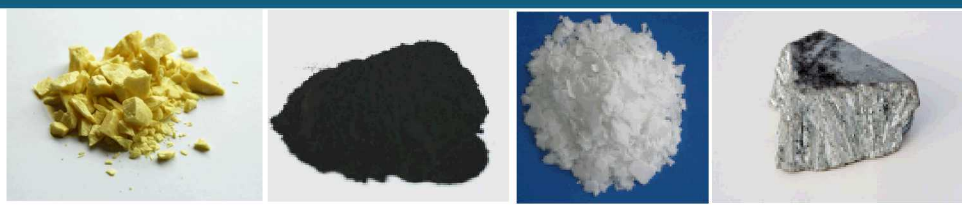
SAND2019-6559C

# Advances in Alkaline Storage Batteries and their Potential Impact for Society



S　$MnO_2$　KOH　Zn

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# Grid Storage needs Large Format Cells

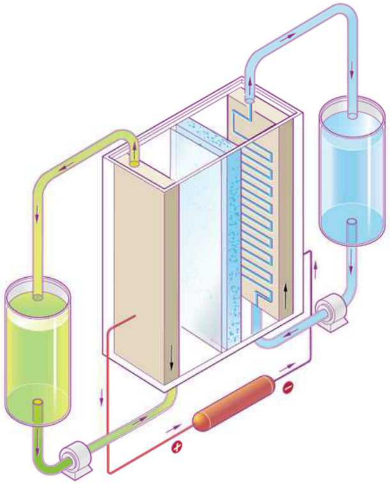
Engineering costs are significant for small format cells. Large format cells are needed to reduce overall system costs.

Large format cells also allow for tighter integration of power electronics, sensors, SOH monitoring at the cell level.

**High Conductivity Separators for Low Temperature Molten Sodium Batteries**

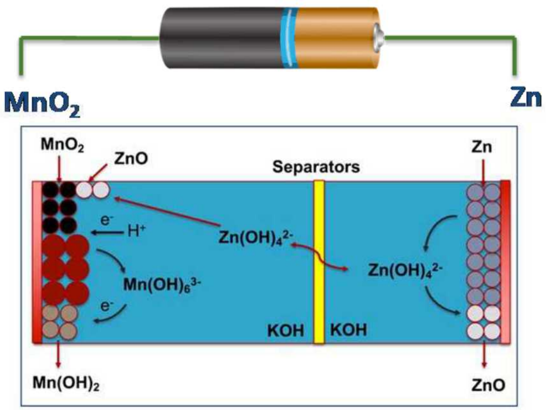

Robust ceramic separators exhibit low $Na^{+}$ conductivity at lower, more cost effective temperatures (120-180 °C).

**Crossover in Redox Flow Batteries**



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

**Zincate poisoning of $MnO_2$ in $Zn/MnO_2$ Batteries**




Zincate diffusion and subsequent poisoning of $MnO_2$ impairs reversibility and significantly decreases lifetimes.

# History of Rechargeable Zn-$MnO_2$ Batteries

- Early commercial products based on cylindrical formats (Union Carbide, Rayovac, BTI, ...)
  - Focused on consumer markets, rapid development of Li-ion batteries made small cell business not competitive
- Resurgence in the field for stationary storage


J. Daniel-Ivad and K. Kordesch, "Rechargeable Alkaline Manganese Technology: Past-Present-Future," ECS Annual Meeting, May 12-17, 2002

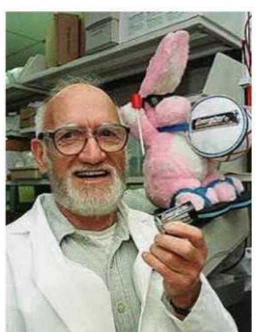
**1866** — Primary, Low Power — $1^{st}$ Zn- $MnO_2$ battery

**1950** — Primary — Alkaline Zn-$MnO_2$ battery

**1970** — Limited Capacity, Poor Energy Density — 5% Rechargeable Capacity

**1980** — Potentiodynamic, Poor Cycle Life — 60-80% Rechargeable Capacity

**2010-2016** — Stabilized full-cycling MnO2 — **2010-2014**: CUNY Energy Institute shallow-cycle $MnO_2$; **2014-2016** Stabilized full-cycling $MnO_2$



Halina Wroblowa

S. Banerjee, Symposium on Grid Energy Storage, MRS Spring Meeting, 2015; G. Yadav, CUNY Energy Institute, 2018

# Rechargeable Alkaline Zn-$MnO_2$ Batteries

*2 e⁻* / *820 mAh/g*


Energy density of primary cell: up to 400 Wh/L or 150 Wh/kg

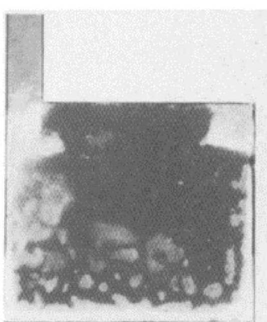
*2 e⁻* / *616 mAh/g*

## Anode

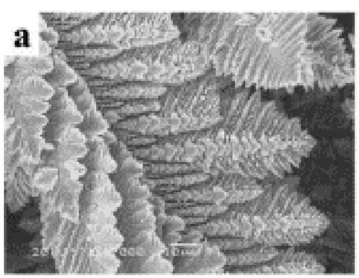
- Passivat
- Shape cl
- Dendrit

## Issues

- ucture breakdown
- ase(s) formed
- ning

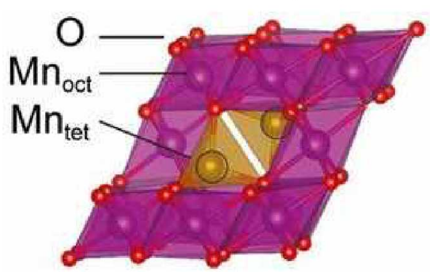


J. Electrochem. Soc., 138 (2), 645 (1991)



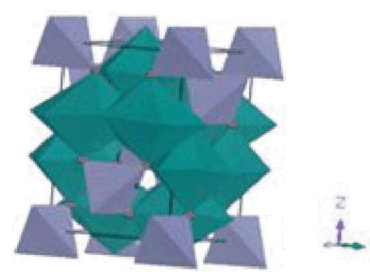

J. Electrochem. Soc., 163 (9), A1836 (2016)

α-$Mn_3O_4$




*PNAS* 115 (23), E5261 (2018)

$ZnMn_2O_4$



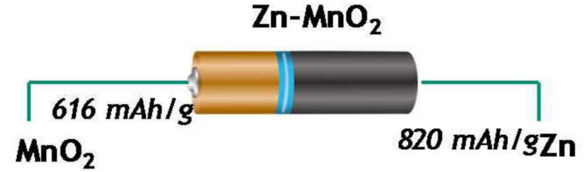
Mater. Chem. Phys. 130, 39 (2011)

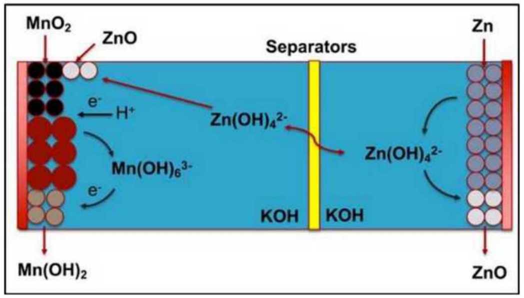
# Limited DOD


- 1000+ cycles shown under limited depth-of-discharge (DOD) conditions
  - ≤ 20% of 1st $MnO_2$ electron, ≤ 2.5% of total Zn
- Technology has been commercialized by Urban Electric Power
  - ~20 Wh/L, $150-250/kWh

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

# Full Utilization of 2e$^-$




## On the MnO$_2$ Cathode

- Regeneration of cathode structure on solution/dissolution/precipitation cycle
- Formation of Inactive phases
- Reducing susceptibility to Zinc poisoning

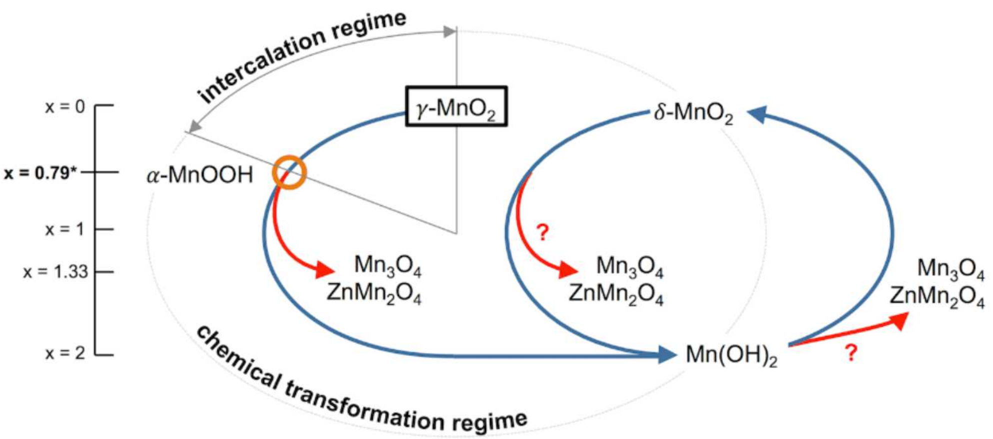
## Separator

- Reduce Zincate crossover

## On the Zn Anode

- Control shape change
- Passivation
- Reduce dendrite formation

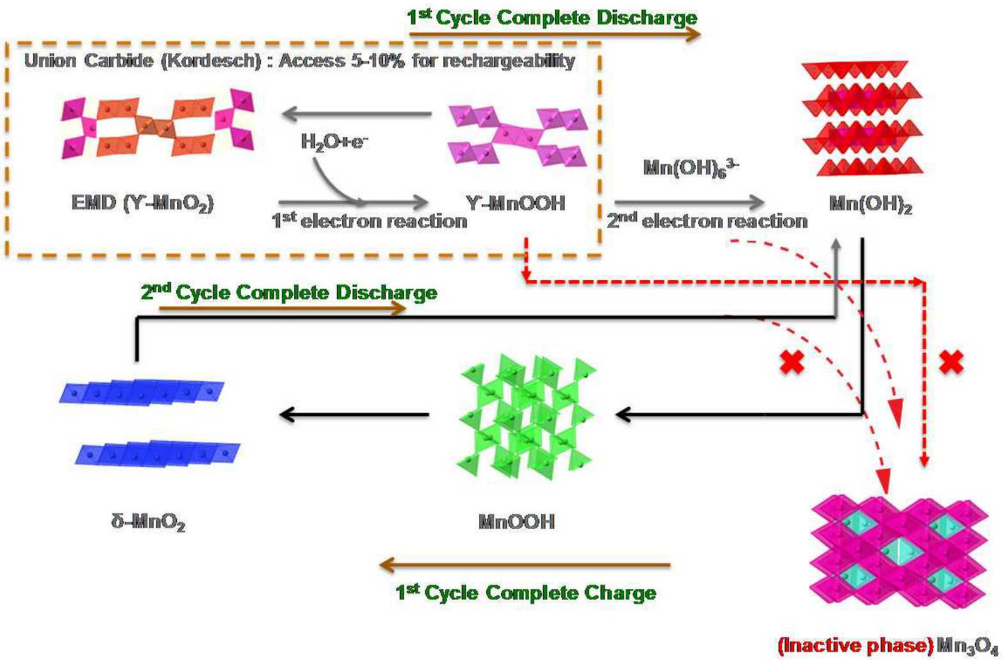
Need improvements in materials utilization, process optimization and engineering of large format cells

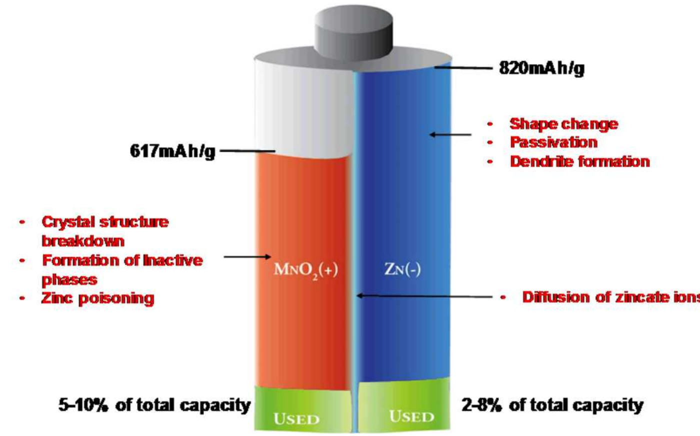



Failure Mechanisms of Cathode

Instability of Mn(III) resulting in formation of irreversible $Mn_3O_4$ and Zn poisoning forming irreversible $ZnMn_2O_4$

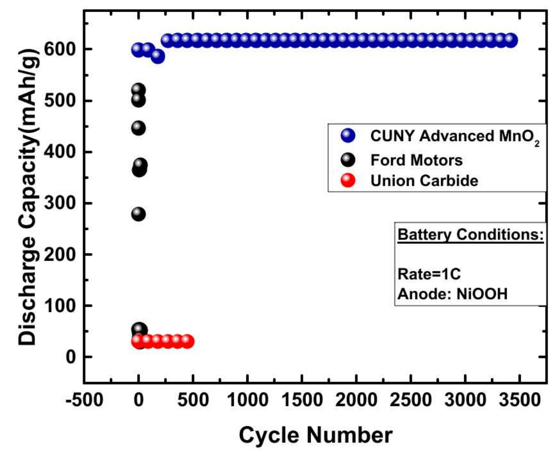
# Making $MnO_2$ Fully Rechargeable




- Chemistry relies on formation of a layered birnessite $MnO_2$ structure and stabilizing this structure for thousands of cycles
- $MnO_2$ goes through a complete regeneration process during each cycle

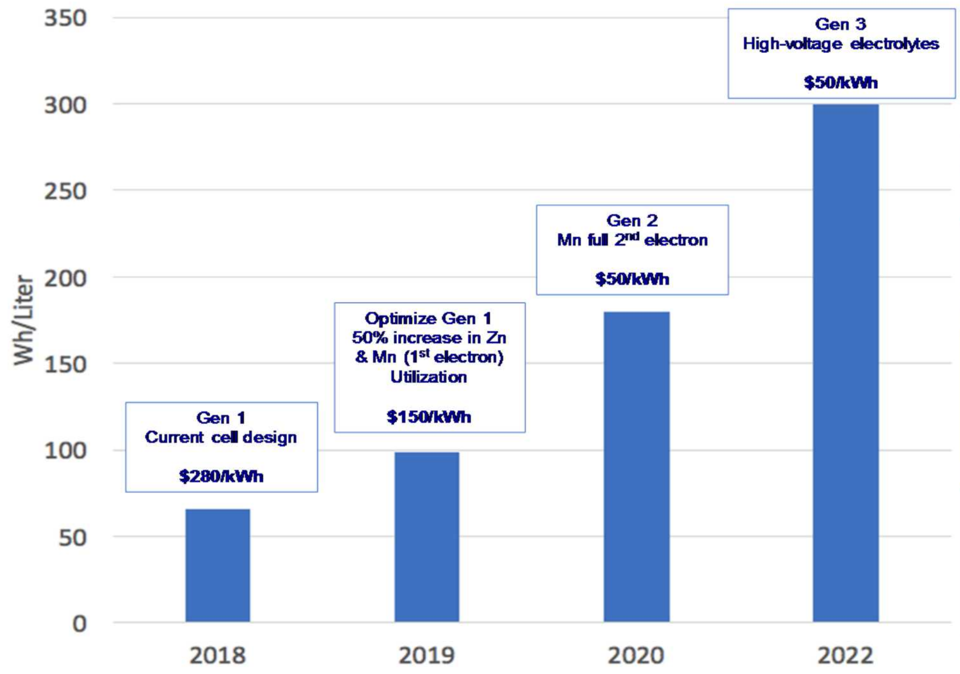
G.G. Yadav, J.W. Gallaway, D.E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nature Communications, vol. 8, 14424 (2017). doi:10.1038/ncomms14424




$MnO_2$ cycling data against reference anode

# Potential for Zn-$MnO_2$ Cells at \$50/kWh

- Recent breakthroughs in making $MnO_2$ fully rechargeable. Based on the formation of a layered birnessite $MnO_2$ structure and stabilizing this structure for thousands of cycles.
- Improvement in energy density and cost by improvement in zinc utilization
- Cathode degradation mitigation by improvements controlling Zn migration across separator
- Potential for \$50/Wh cells with high cycle-rechargeability of Zn-$MnO_2$




Source: CUNY Energy Institute

URBAN ELECTRIC POWER

Source: S. Banerjee, CUNY Energy Institute
DOE OE Energy Storage Program Peer Review 2018

# Zn Anode – Increasing Cycle Life at High DOD

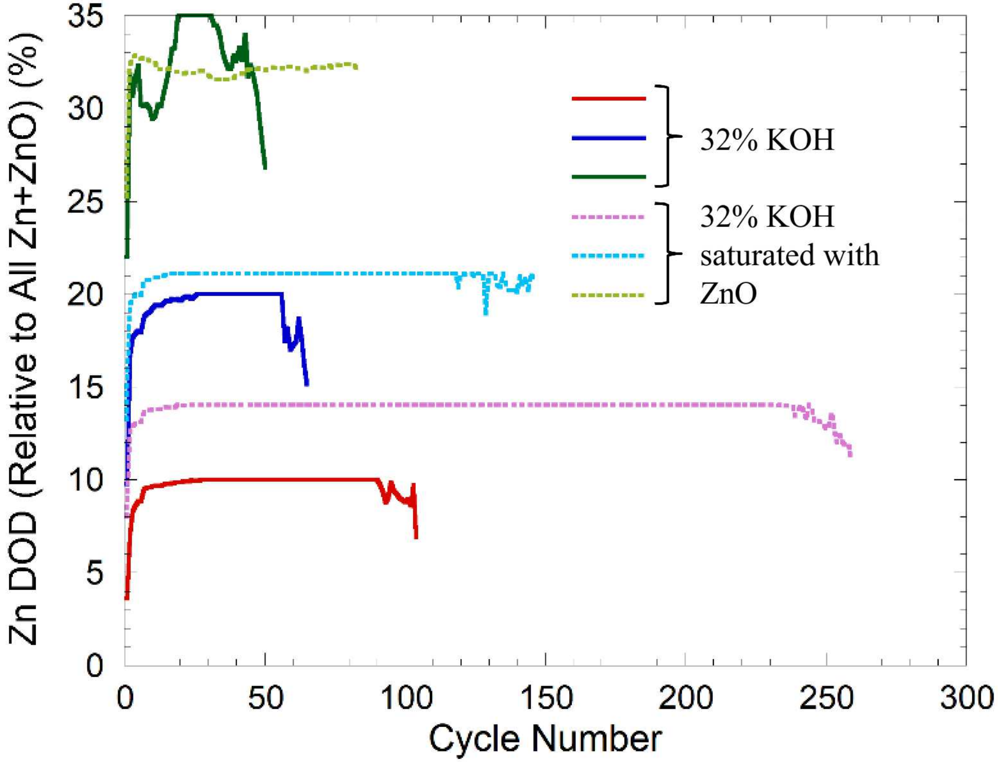
***Pre-saturating electrolyte with ZnO can minimize dissolution and migration of zinc from the anode***

**Zn/Ni(OH)$_2$**

Anode capacity = 746 mAh/g

C/10 relative to full anode capacity ≈ 75 mA/g$_{anode}$

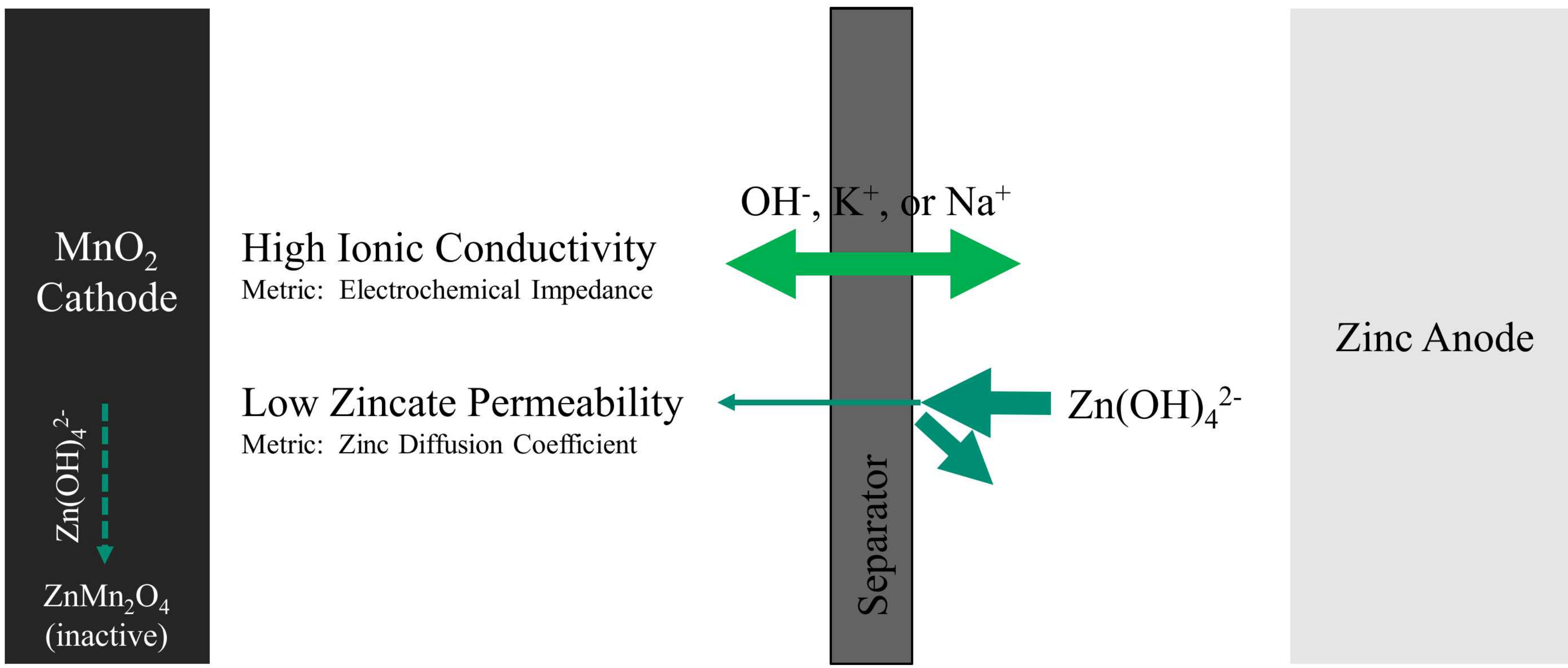
Excess Ni(OH)$_2$




M. Lim *et al.* unpublished results

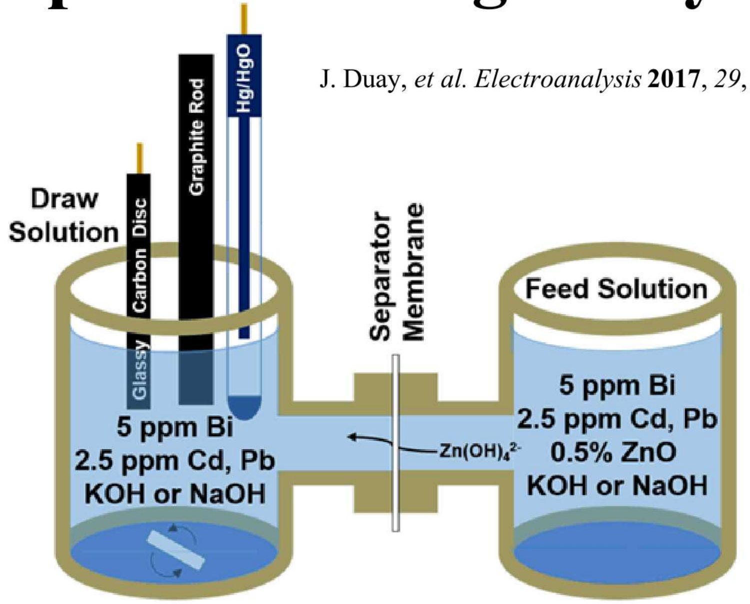
- Important to account for ZnO in electrolyte for specific capacity calculation
- Cells tested at ~14% Zn DOD in saturated electrolyte show 149% longer cycle life than 10% Zn DOD cells in regular electrolyte
- Cells tested at ~21% Zn DOD in saturated electrolyte show 125+% longer cycle life than 20% Zn DOD cells in regular electrolyte

# Features of a Good Zn-$MnO_2$ Battery Separator

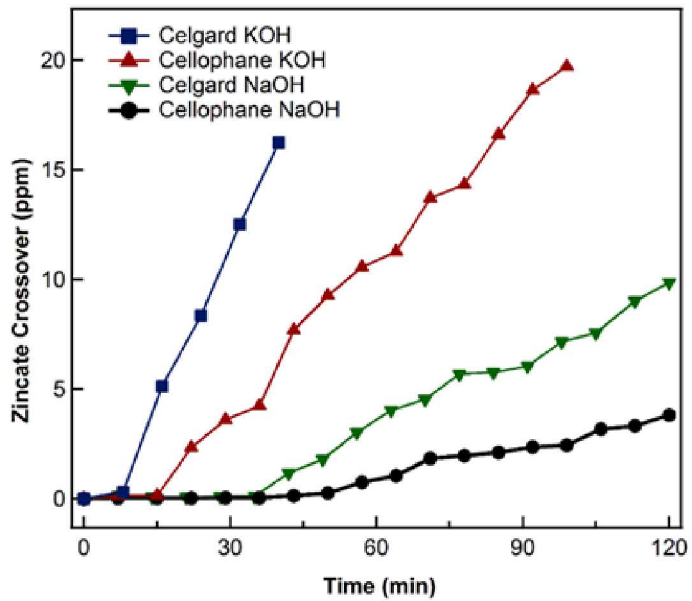



***A selective membrane/separator is needed that allows charge-carrying ions through but blocks or limits Zn (zincate)***

# Rapid Screening Assay for Separators



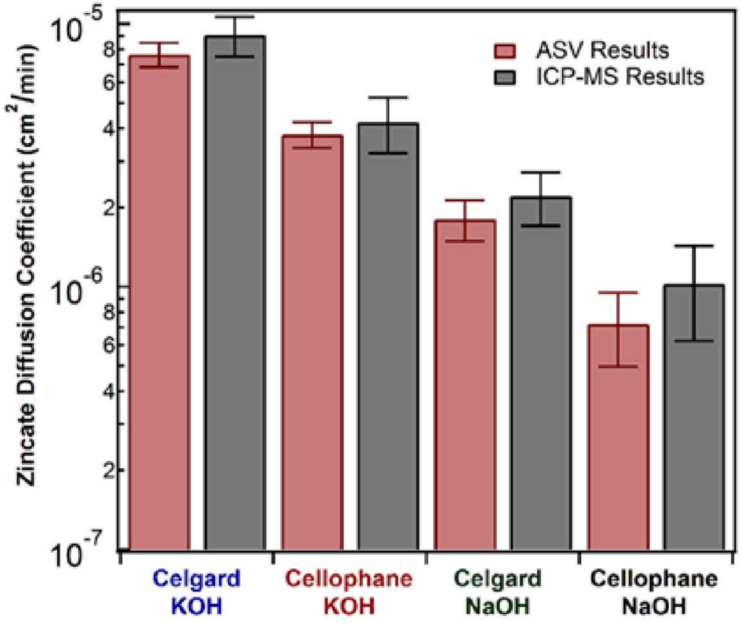

J. Duay, *et al. Electroanalysis* **2017**, *29*, 2261–2267




***ASV results are similar to ICP-MS with much shorter experimental times and no need for dilution or pH modification***

| Method | Dilution Factor | Experimental LOD | Timeframe of Experiment |
|---|---|---|---|
| **ASV (this work)** | **0** | **1.6 ± 0.6 ppm** | **Hours** |
| ICP-MS | >300x | 0.009 ppm<br>7.5 ± 2.4 ppm* | Days |
| Complexometric Titration | >20x | 1 ppm<br>96 ± 24 ppm* | Weeks |

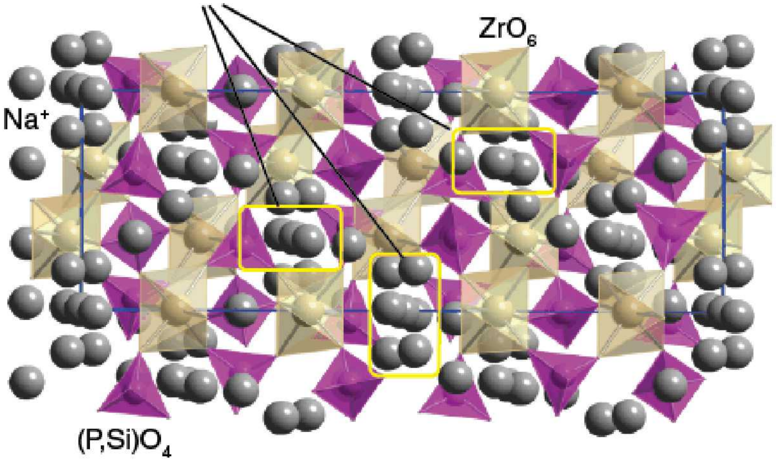
* LODs obtained in our lab



# NaSICON Ceramic Separator

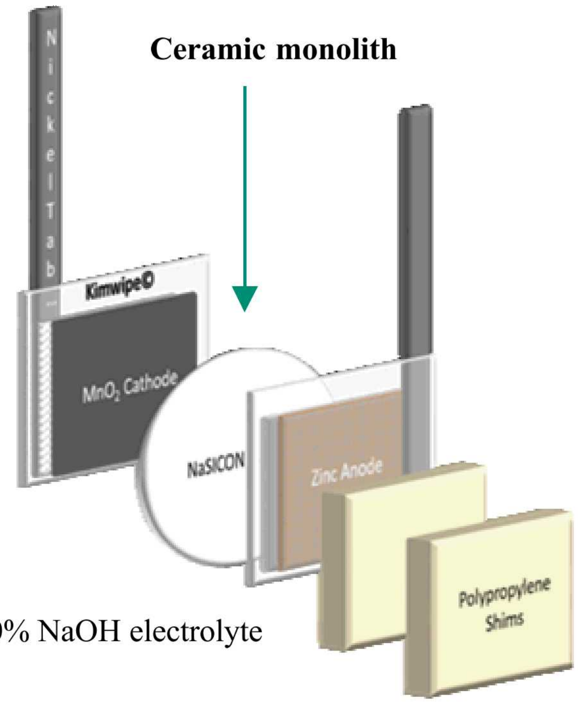
**Na**Super **I**onic **CON**ductor

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

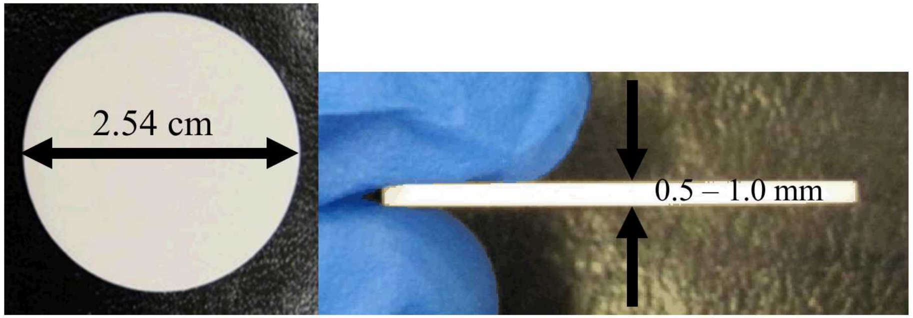



http://www.chemtube3d.com/solidstate/SSNASICON.htm

**Battery Assembly Schematic**




**NaSICON purchased from Ceramatec**

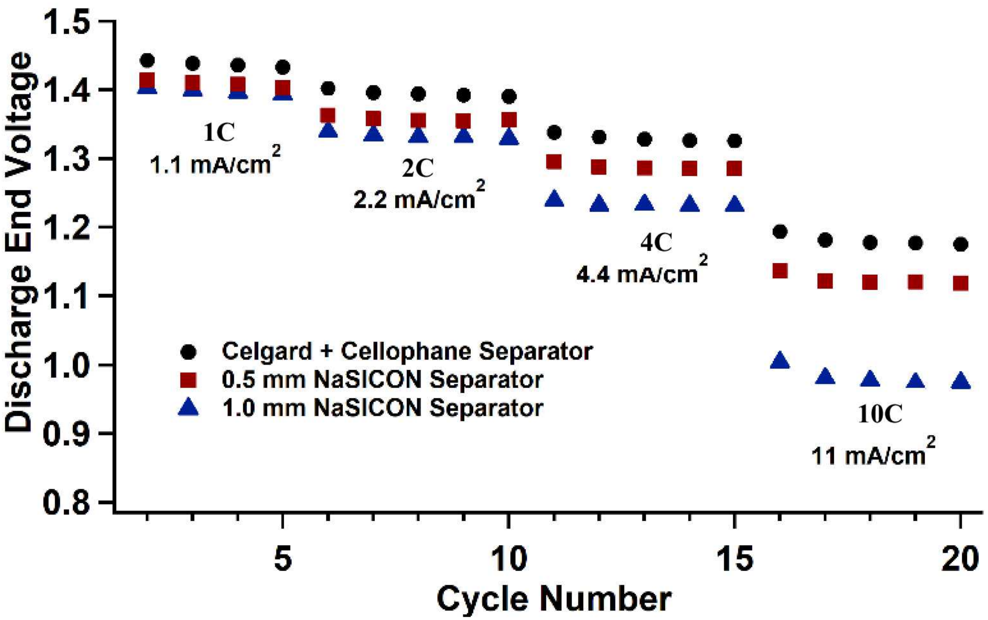



**100% Selective Membrane**

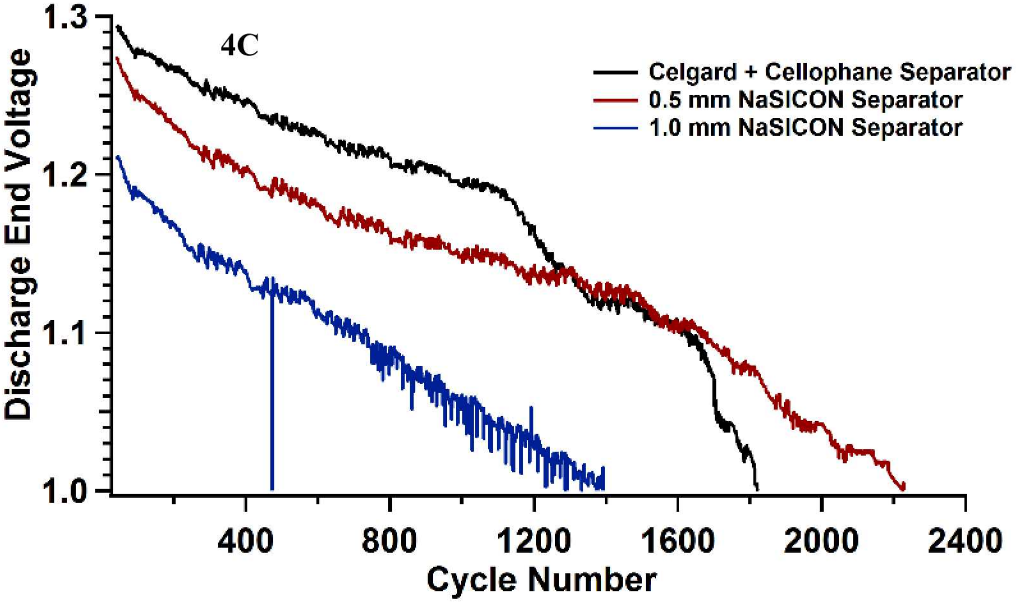
- **Conducts $Na^+$ ions (~$10^{-3}$ S/cm)**
- **No detectable through-separator Zn transport**

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



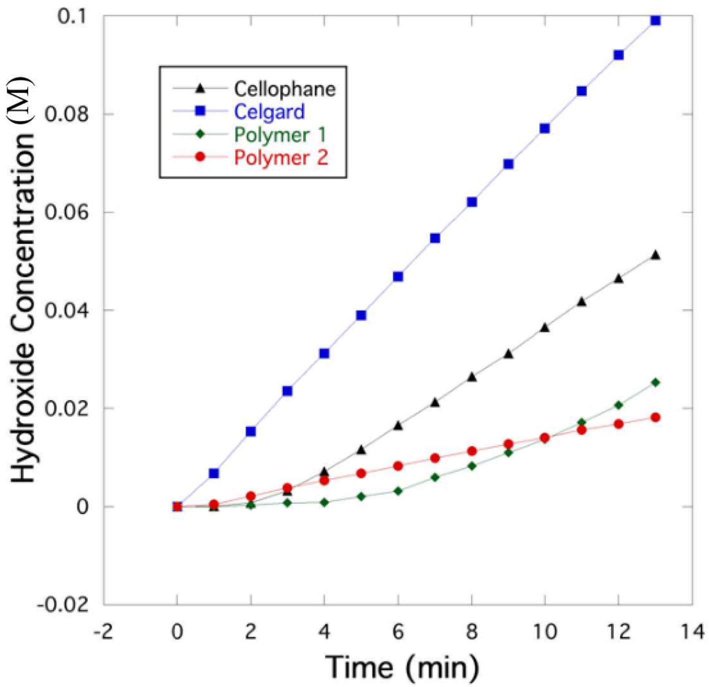

As NaSICON is thinned and becomes less resistive, its advantages become more apparent, increasing cell lifetime by 22%

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

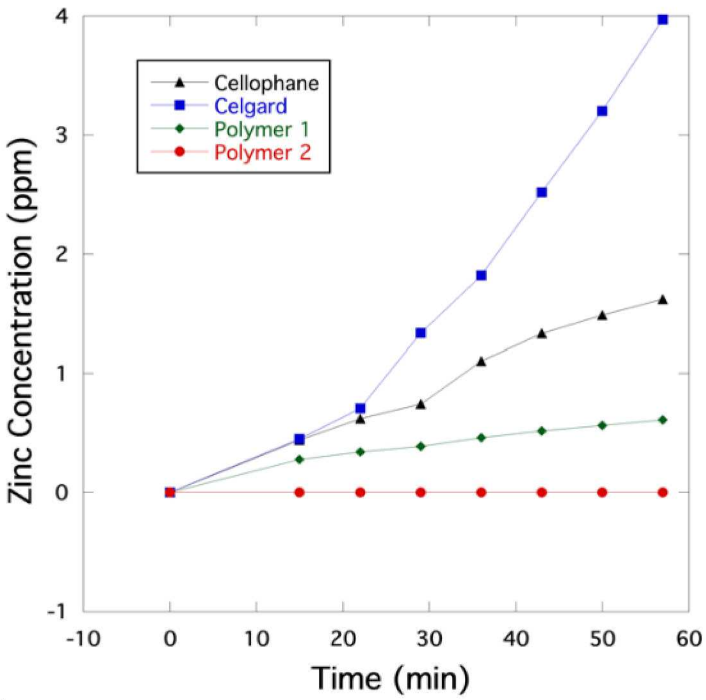
# Flexible Polymeric Separators

*Development of flexible polymers that allow for selective ion transport (lower cost, higher volumetric energy density and more flexible battery assembly)*

## Hydroxide Diffusion




## Zincate Diffusion




T.N. Lambert *et al.* unpublished results

| Separator | $D_{OH^-}$ ($cm^2$/min) | $D_{[Zn(OH)_4]^{2-}}$ ($cm^2$/min) | Selectivity Ratio |
|---|---|---|---|
| Cellophane | $1.74 \cdot 10^{-5}$ | $1.41 \cdot 10^{-6}$ | 12.3 |
| Celgard | $6.72 \cdot 10^{-6}$ | $1.58 \cdot 10^{-6}$ | 4.25 |
| Polymer 1 | $5.38 \cdot 10^{-6}$ | $5.56 \cdot 10^{-8}$ | 96.8 |
| **Polymer 2** | $\mathbf{3.03 \cdot 10^{-6}}$ | $\mathbf{3.66 \cdot 10^{-11}}$ | $\mathbf{8.28 \cdot 10^{4}}$ |

Polymer 2 is effectively 100% selective for hydroxide

# Alkaline Sulfide/Polysulfide Cathodes

Sulfur is known to have a high theoretical specific capacity:

**1650 mA h g$^{-1}$**

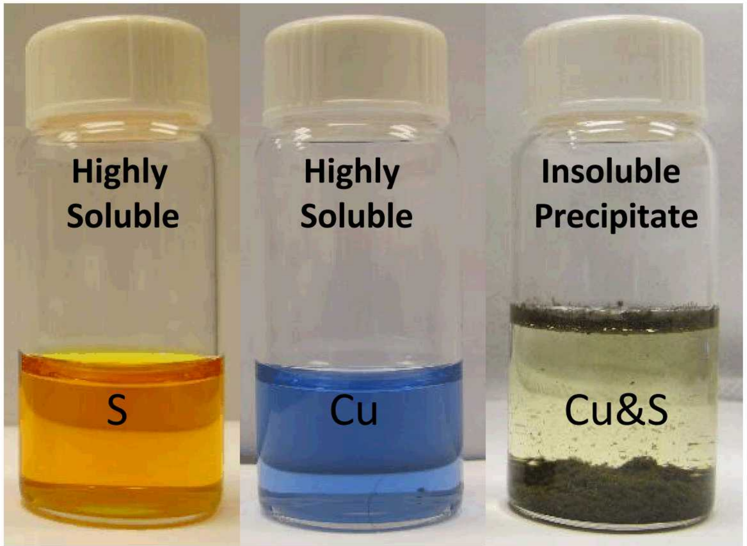
**Soluble** Sulfide Chemistry in Alkaline

$S_5^{2-} + 5H_2O + 8e^- \rightarrow 5HS^- + 5OH^-$ 0.003 V vs. SHE (1)

$S_4^{2-} + 4H_2O + 6e^- \rightarrow 4HS^- + 4OH^-$ 0.033 V vs. SHE (2)

$S_3^{2-} + 3H_2O + 4e^- \rightarrow 3HS^- + 3OH^-$ 0.097 V vs. SHE (3)

$S_2^{2-} + 2H_2O + 2e^- \rightarrow 2HS^- + 2OH^-$ 0.298 V vs. SHE (4)

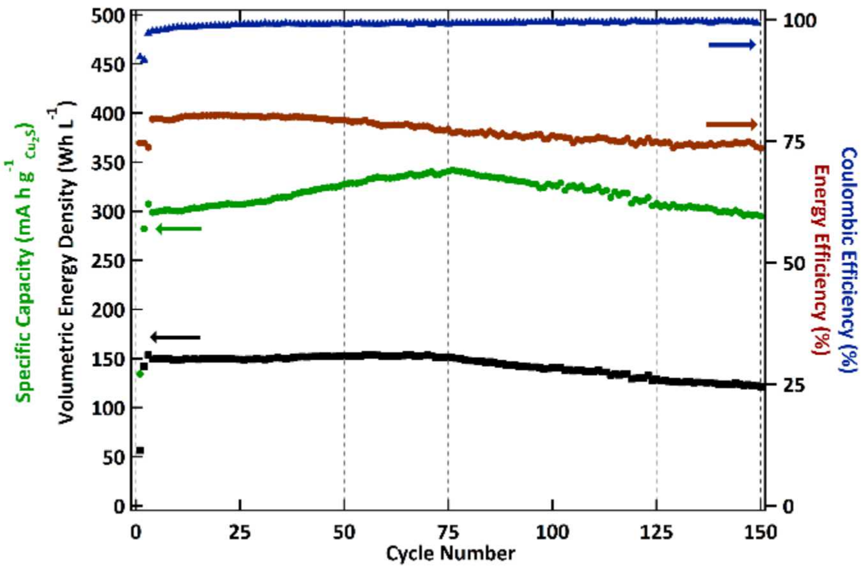


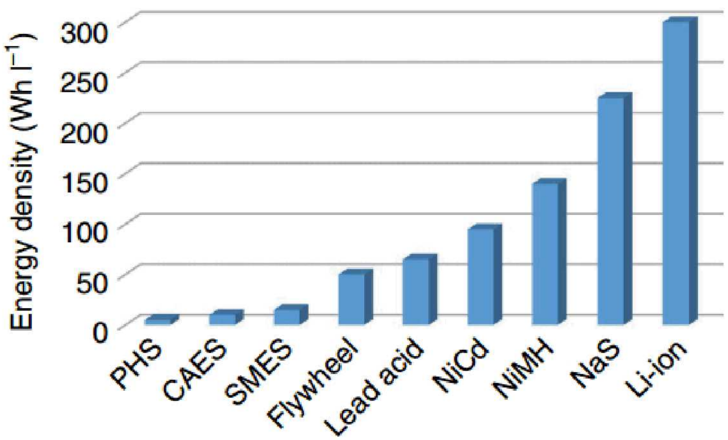

Empirically Derived Theoretical Performance Metrics for **Solid-State $Cu_2S$/Zn Battery**

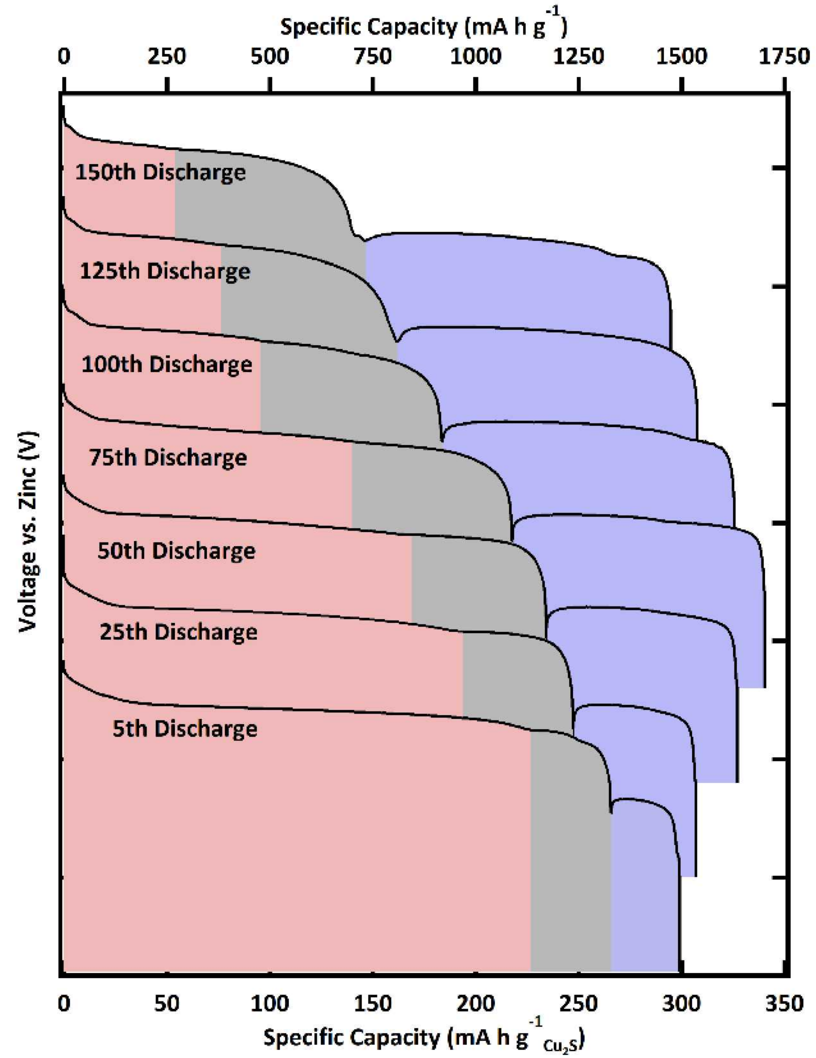
| Chemical Reduction Equation | Polysulphide Species | # of e$^-$ per S atom | Potential vs. Zinc (V) | Specific Capacity (mA h g$^{-1}$ $_S$) | Specific Capacity (mA h g$^{-1}$ $_{Cu2S}$) |
|---|---|---|---|---|---|
| (1) | $\mathbf{S_5^{2-}}$ | 1.60 | 1.202 | 1340 | 268 |
| (2) | $\mathbf{S_4^{2-}}$ | 1.50 | 1.232 | 1256 | 251 |
| (3) | $\mathbf{S_3^{2-}}$ | 1.33 | 1.296 | 1117 | 223 |
| (4) | $\mathbf{S_2^{2-}}$ | 1.00 | 1.497 | 838 | 168 |

J. Duay, T.N. Lambert *et al.* ***J. Electrochem. Soc.*** **2019** volume 166, issue 4, A687-A694

# $Cu_2S$ Cathodes




**Energy Density is Comparable to NiMH and NaS, but safer and cheaper**

**What is the mechanism of conversion from high voltage to low voltage behavior?**

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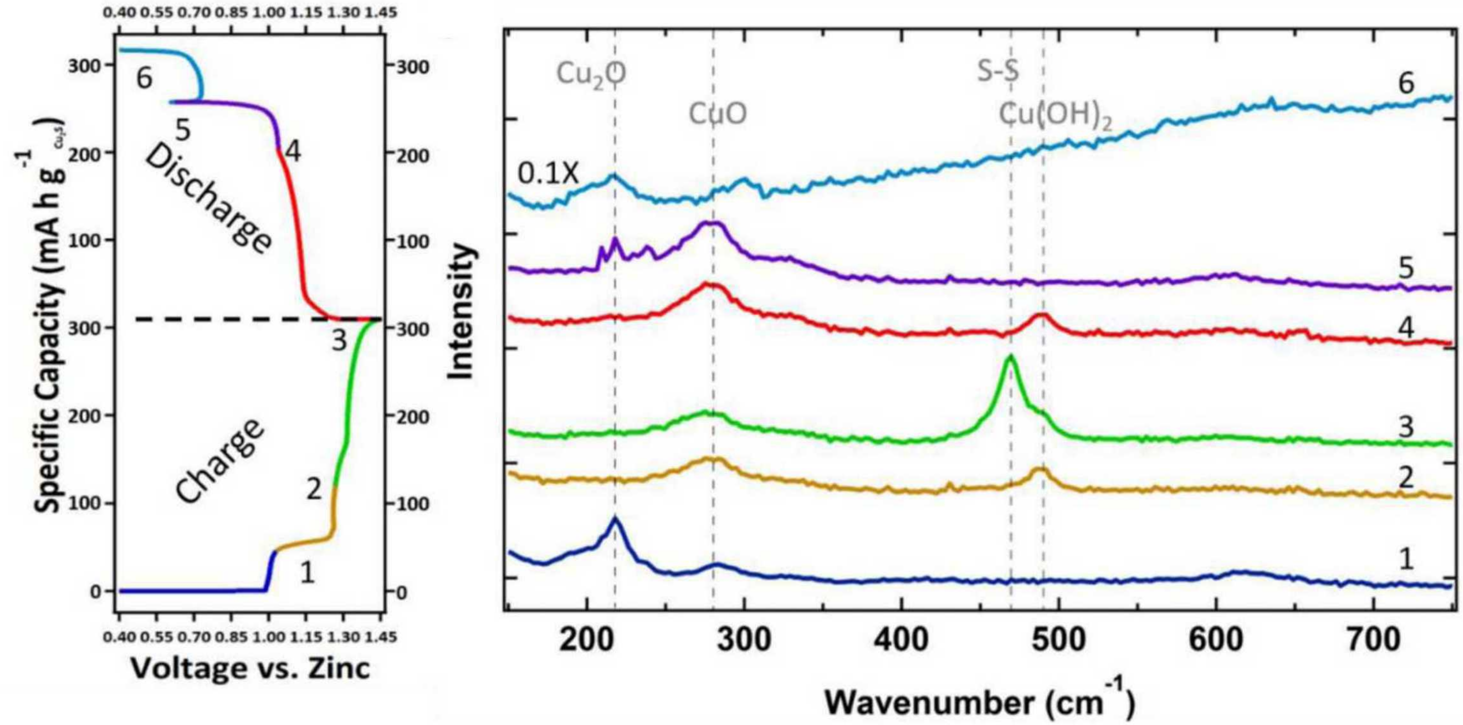
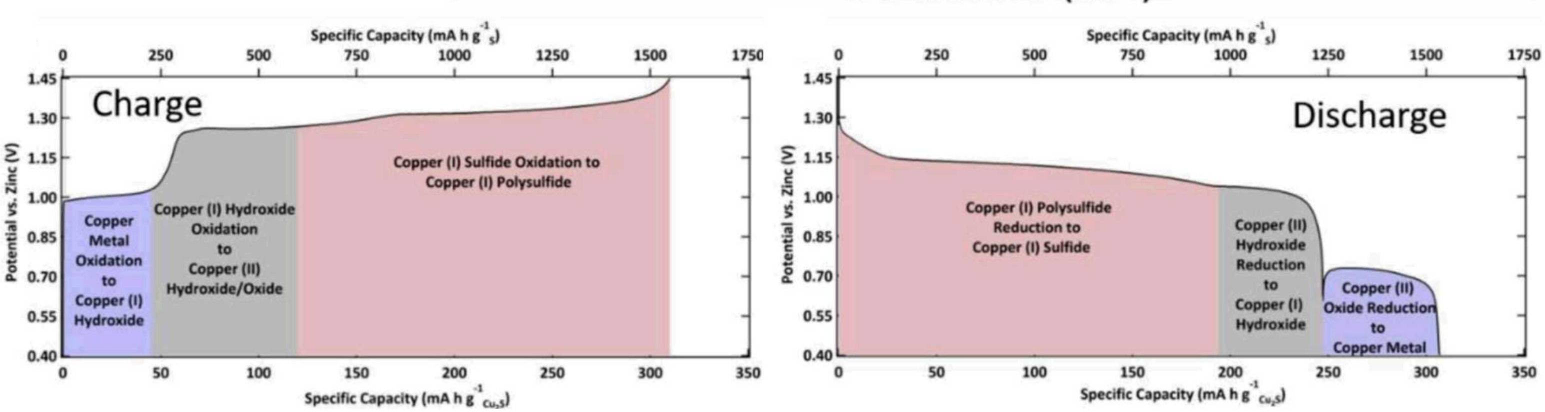
# Raman Analysis of $Cu_2S$ Charge Storage

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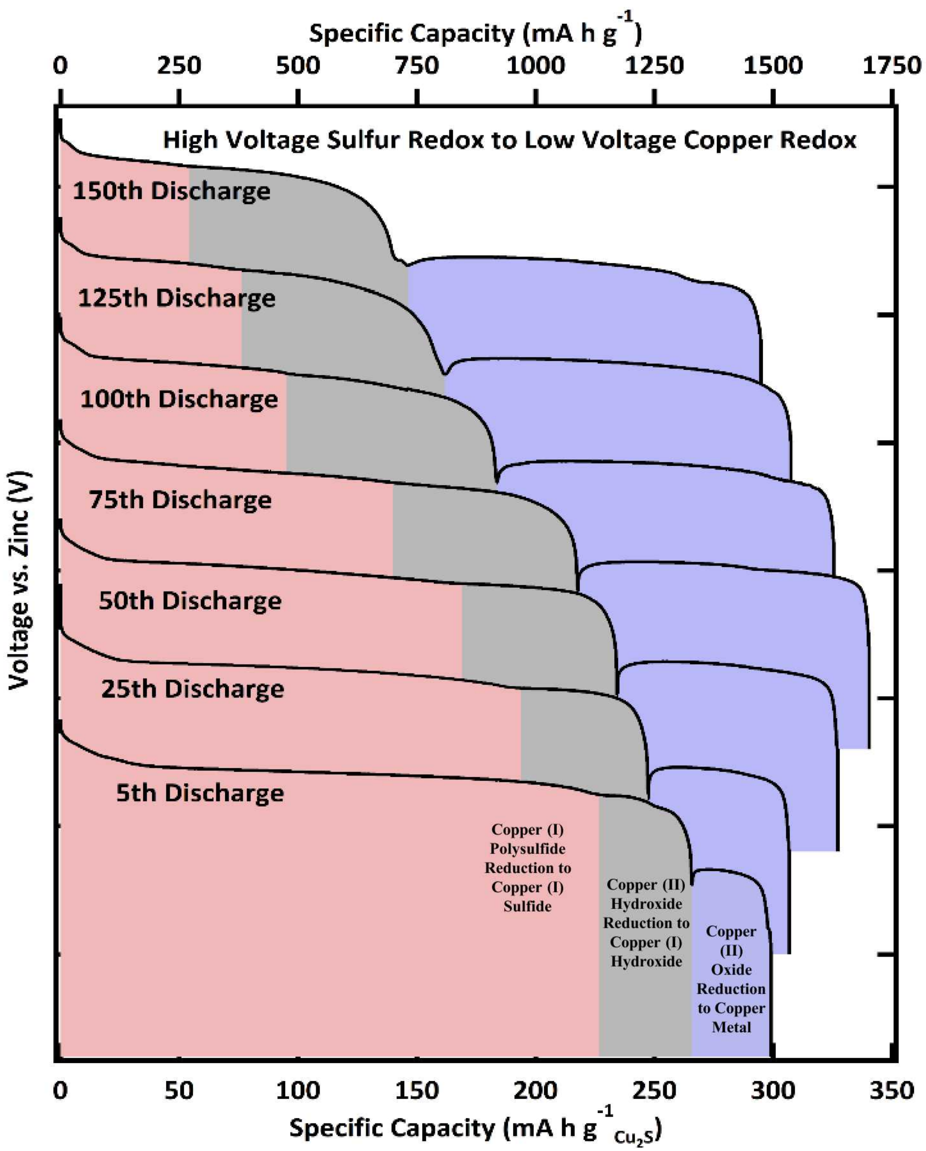
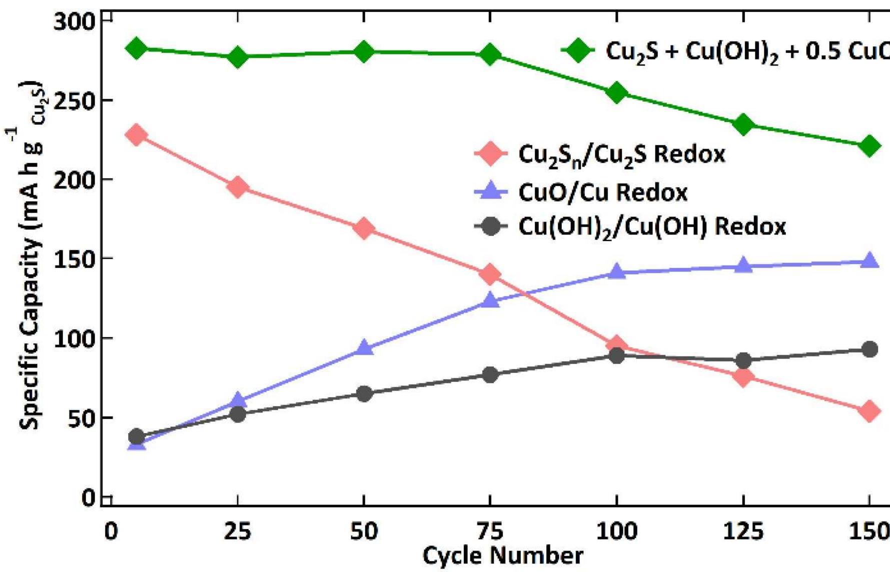
# $Cu_2S$ Failure Mechanism



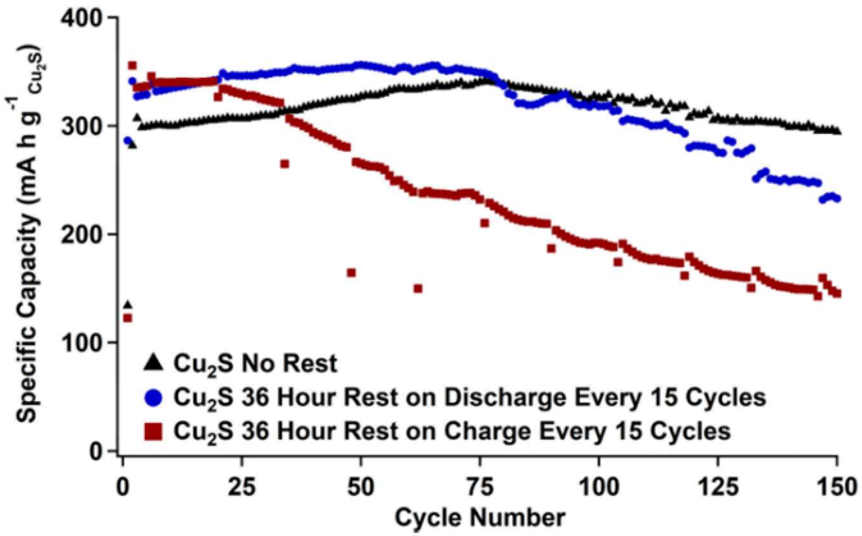



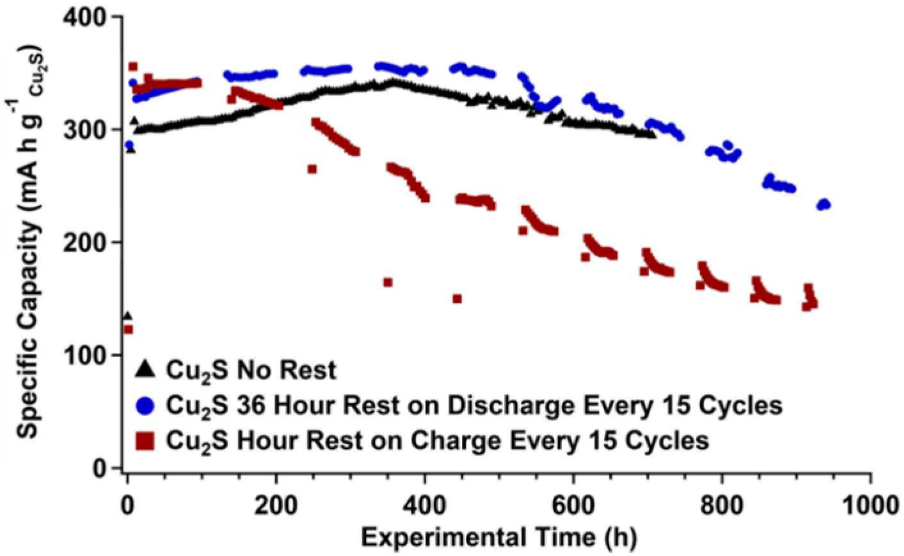

***Raman Results suggest a Slow degradation from $Cu_2S$ electrochemistry to $CuO/Cu(OH)_2$ electrochemistry***

Lambert, T.L.; Duay, J. Rechargeable Copper Sulfide Electrodes for Electrochemical Applications. U.S. Patent Application No. 16/054,114, filed **August 2018**.
J. Duay, T.N. Lambert *et al.* ***J. Electrochem. Soc.*** **2019** volume 166, issue 4, A687-A694

# Chemical or Electrochemical Degradation?

Pausing on Charge or Discharge for 36 hours every 15 cycles




***Slow degradation from $Cu_2S$ to $CuO/Cu(OH)_2$ electrochemistry is most likely chemical and not electrochemical***

***Faster Degredation on charge rest suggests sulfur disproportionation:***

$$(2n+1)S^0 + 6OH^- \rightarrow 2S_n^{2-} + SO_3^{2-} + 3H_2O$$


Lambert, T.L.; Duay, J. Rechargeable Copper Sulfide Electrodes for Electrochemical Applications. U.S. Patent Application No. 16/054,114, filed **August 2018**.

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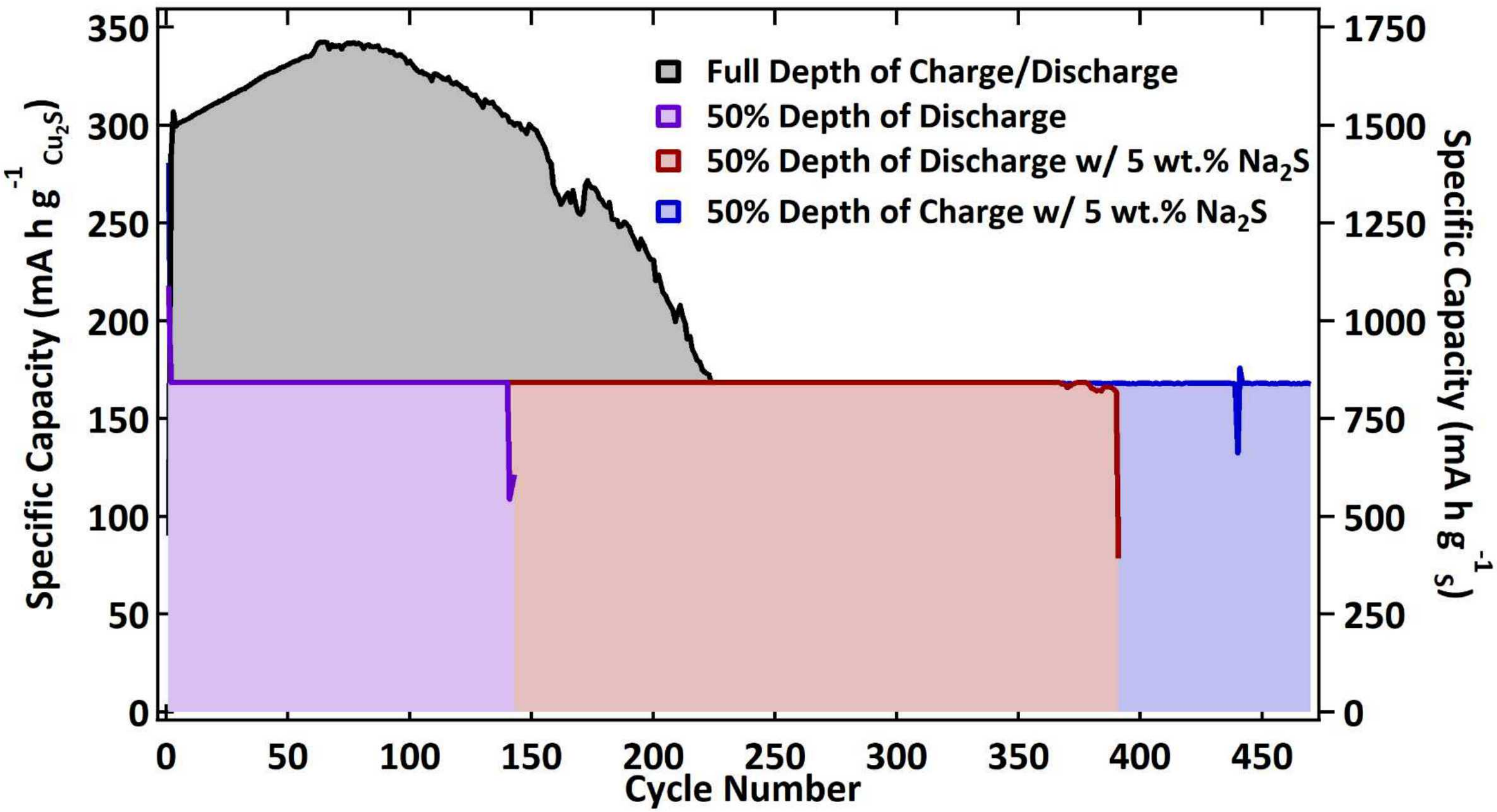
# Limiting the Depth of Discharge/Charge




-Limiting the DOD **does not improve** cycle life
-Addition of Sulfide **slows Sulfur to Oxide redox** chemistry
-Limiting the DOC **does improve** cycle life

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# Summary



-Need for battery production on the order of steel for use in grid storage
-Zn/$MnO_2$ primary batteries are currently produced cheaply at large volumes
-Zincate Concentration can extend Zinc anode cycle life for secondary Zn batteries
-Need for separator to block Zincate from $MnO_2$ cathode
-Polysulfide/Zn Solid-State Batteries as alternative cheap large format Battery

# Acknowledgments

**Dr. Imre Gyuk** – Office of Electricity Delivery and Energy Reliability (OE) Energy Storage Program Manager

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Thank you