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Effect of Additives and Selective Separators on Alkaline Zn-based Batteries

November 16th 2018, New York, New York

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Sandia National Laboratories



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Recent and Current Efforts at SNL



Electrocatalysts for ORR/OER/HER

- Catalysts for alkaline based electrocatalysis (Zn/Air)

Zn-based Alkaline Batteries

- Effect of Additives on limited DOD Zn/MnO₂ batteries
- Development of Separators for Selective Crossover [Na⁺/HO⁻ vs Zn(OH)₄²⁻]
- Increased Zn DOD
- Development of New Cathode Chemistries

Team



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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

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Electrocatalysts for ORR/OER/HER

- Numerous catalysts for alkaline based electrocatalysis (Zn/Air)

Alkaline Zn Batteries

- Use of Additives to Increase Lifetimes (limited DOD Zn/MnO₂)
- Development of Separators for Selective Crossover [Na⁺/HO⁻ vs Zn(OH)₄²⁻]
- Increased Zn DOD
- Development of new Cathode Chemistries

Drs.

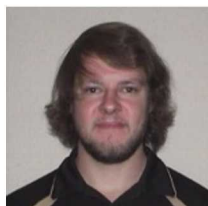
Students

SNL

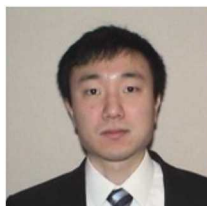
Team



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Alkaline Zn/MnO₂ Batteries



Two classes of rechargeable Zn/MnO₂ batteries:

One Electron

- 308 mAh/g-MnO₂
- 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)

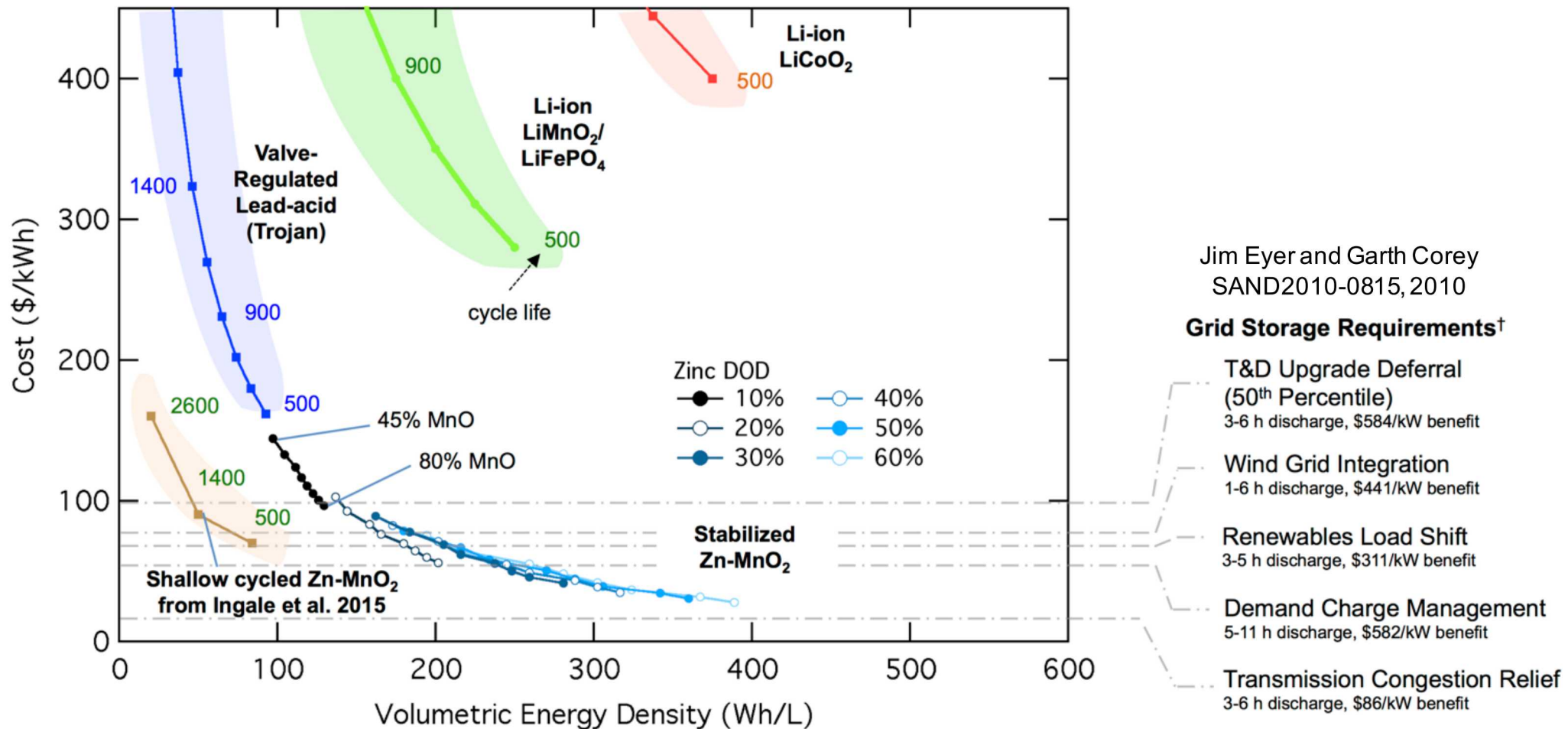
Two Electron

- 616 mAh/g-MnO₂
- 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

Alkaline Zn/MnO₂ Batteries



Opportunity exists to Increase Capacity and Decrease Costs



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

1. Continue to Support Limited Depth-of-Discharge (DOD) Efforts
2. Materials and Systems Development for Higher Capacity at Lower Cost

Improving Zn/MnO₂ Battery Performance

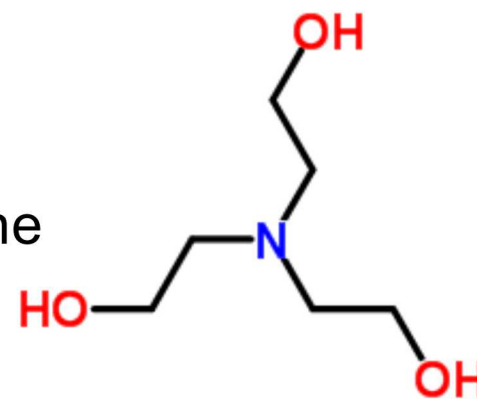


Chemical additives often used to improve battery performance

- Cathode Additives: Bi₂O₃, MgO, Sr-, Ba-, and Ti-based compounds
- Anode Additive: In, Bi, Pb, Ca(OH)₂, carboxymethyl cellulose

Triethanolamine (TEA)

- Known to form complexes with Mn²⁺ and Mn³⁺
- Previous work claimed triethanolamine binds solubilized Mn²⁺ and Mn³⁺, which could mitigate the formation of irreversible species

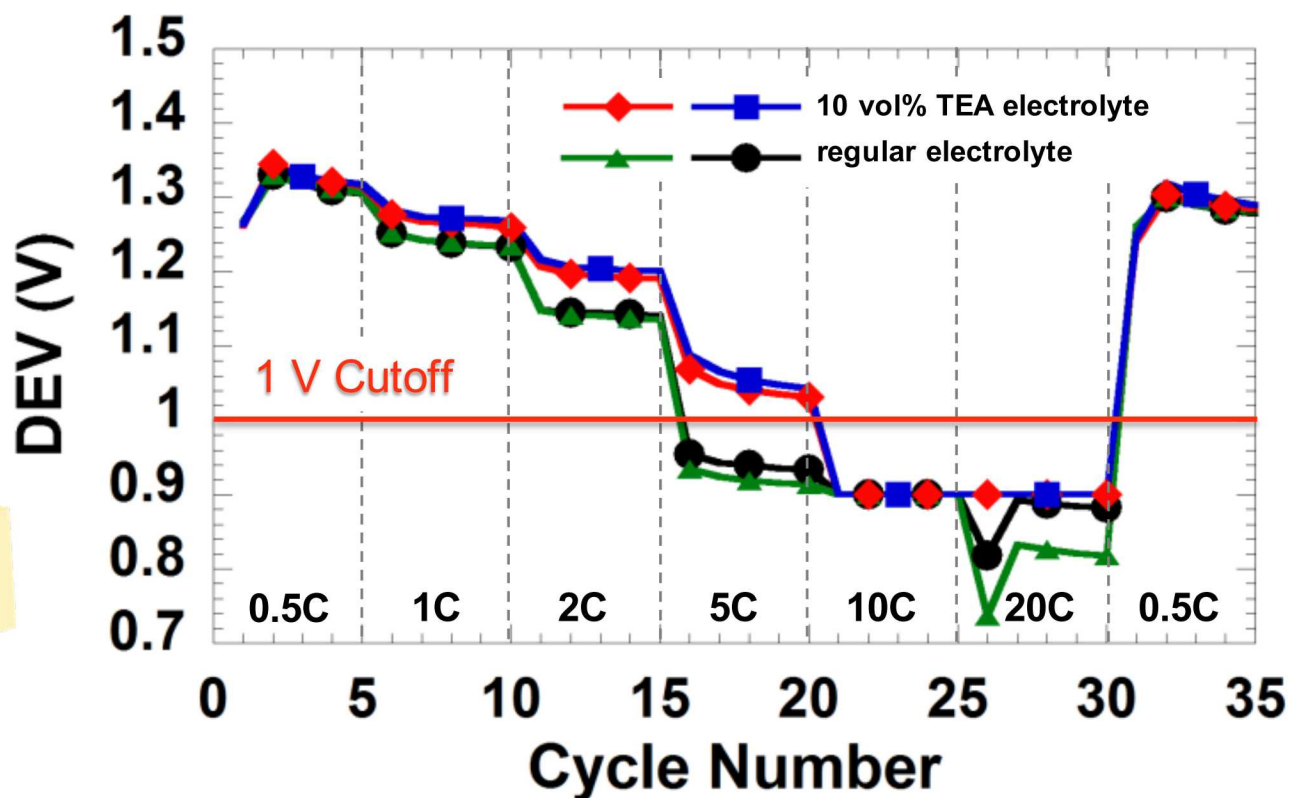
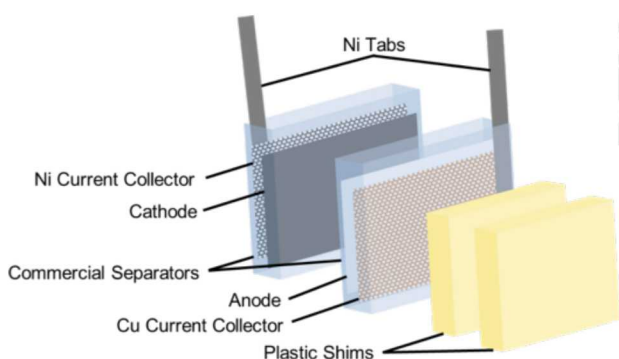


Comprehensive analysis of TEA effect in limited DOD cells

Rate Performance



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

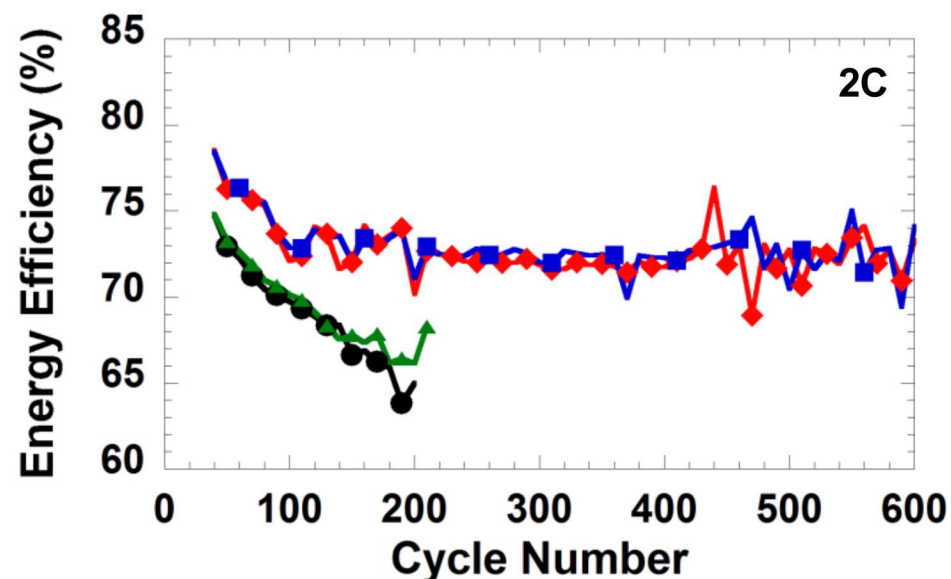
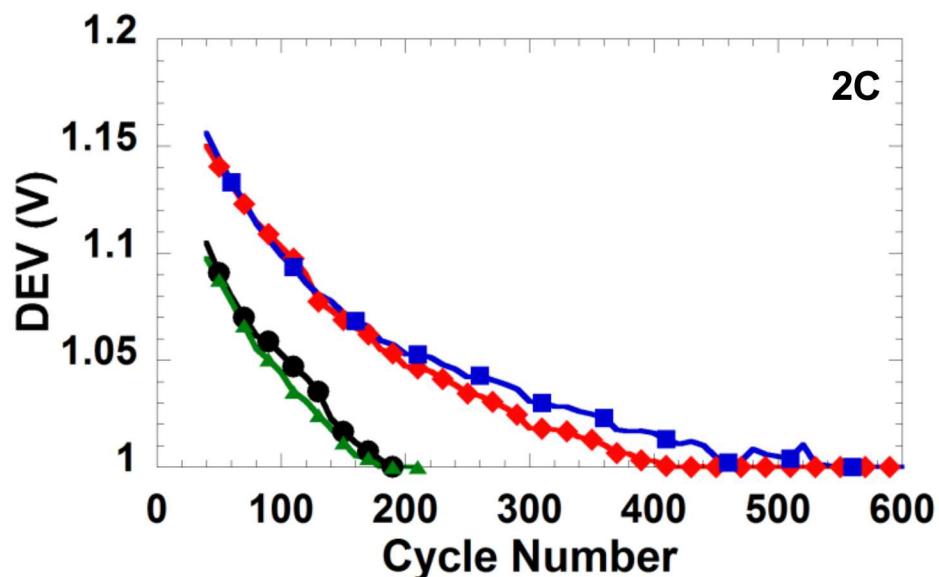


- 5 cycles each of C/2, 1C, 2C, 5C, 10C, 20C (based on cycled capacity)
- Cells prepared with TEA exhibit 29, 58, and 121 mV higher DEV at 1C, 2C, 5C
- All cells drop below 1V at 10C and 20C rates – high resistivity of MnO_2
- Cells prepared with TEA exhibit enhanced performance at higher rates

Extended Cycling



—◆— 10 vol% TEA electrolyte
—▲— regular electrolyte

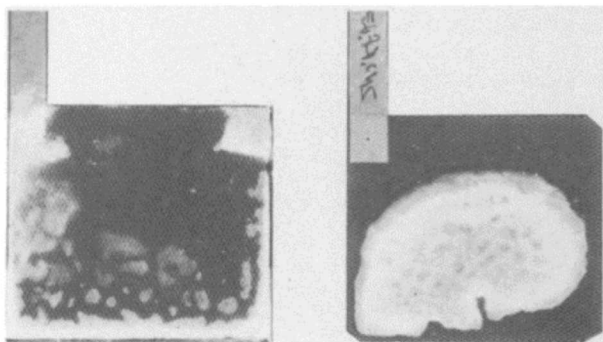


- Cycled at 2C rate, 10% DOD until failure (80% of cycled capacity remaining)
- Baseline Cells: 183 to 198 cycles, TEA Cells: 483 to 653 cycles
- TEA extends cycle lifetime by 297%
- Zn: harder to reduce, more soluble, less transport through separator

Zn Anode – Increasing DOD

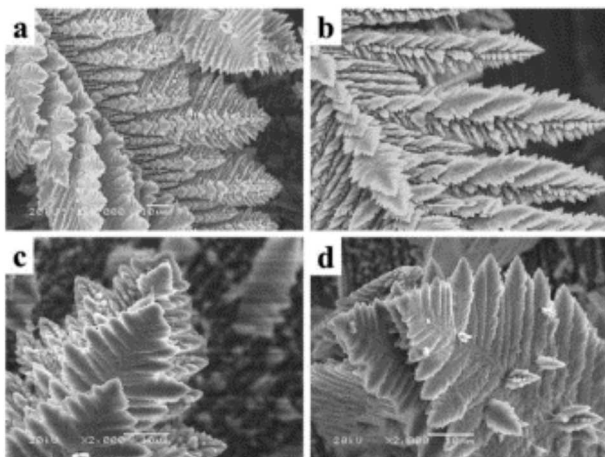


Shape Change



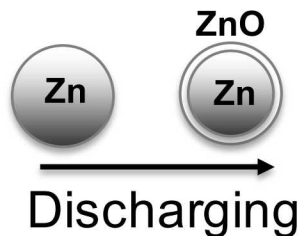
Journal of The Electrochemical Society, 138 (2) 645-664 (1991)

Dendrite Growth

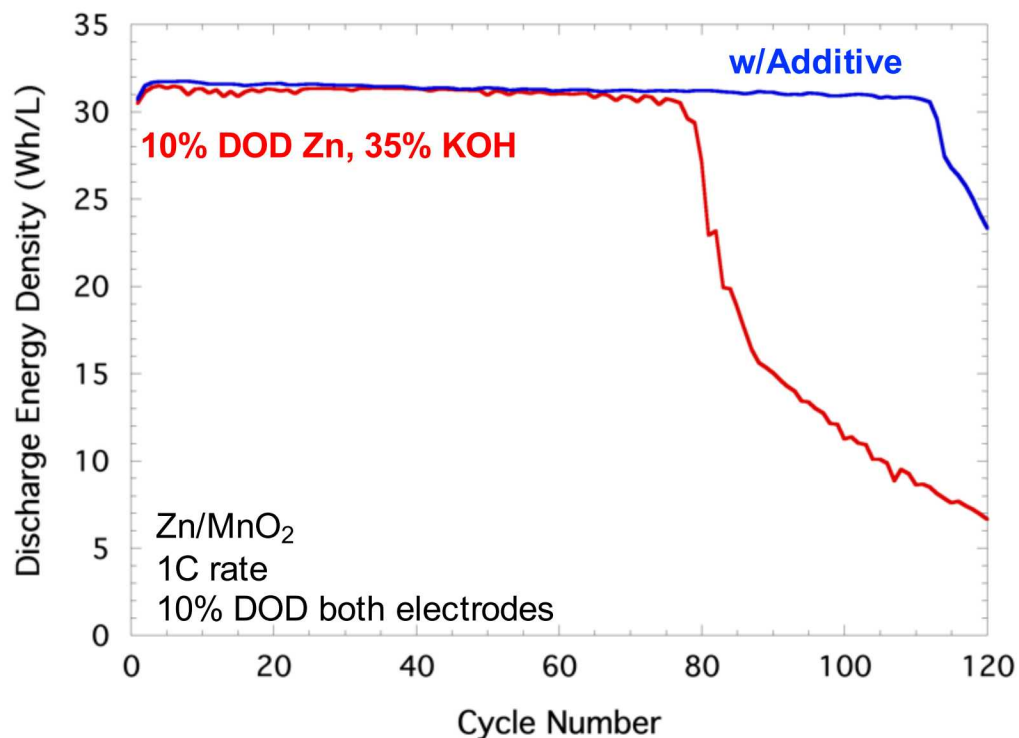


Journal of The Electrochemical Society, 163 (9) A1836-A1840 (2016)

Irreversible ZnO
Passivation

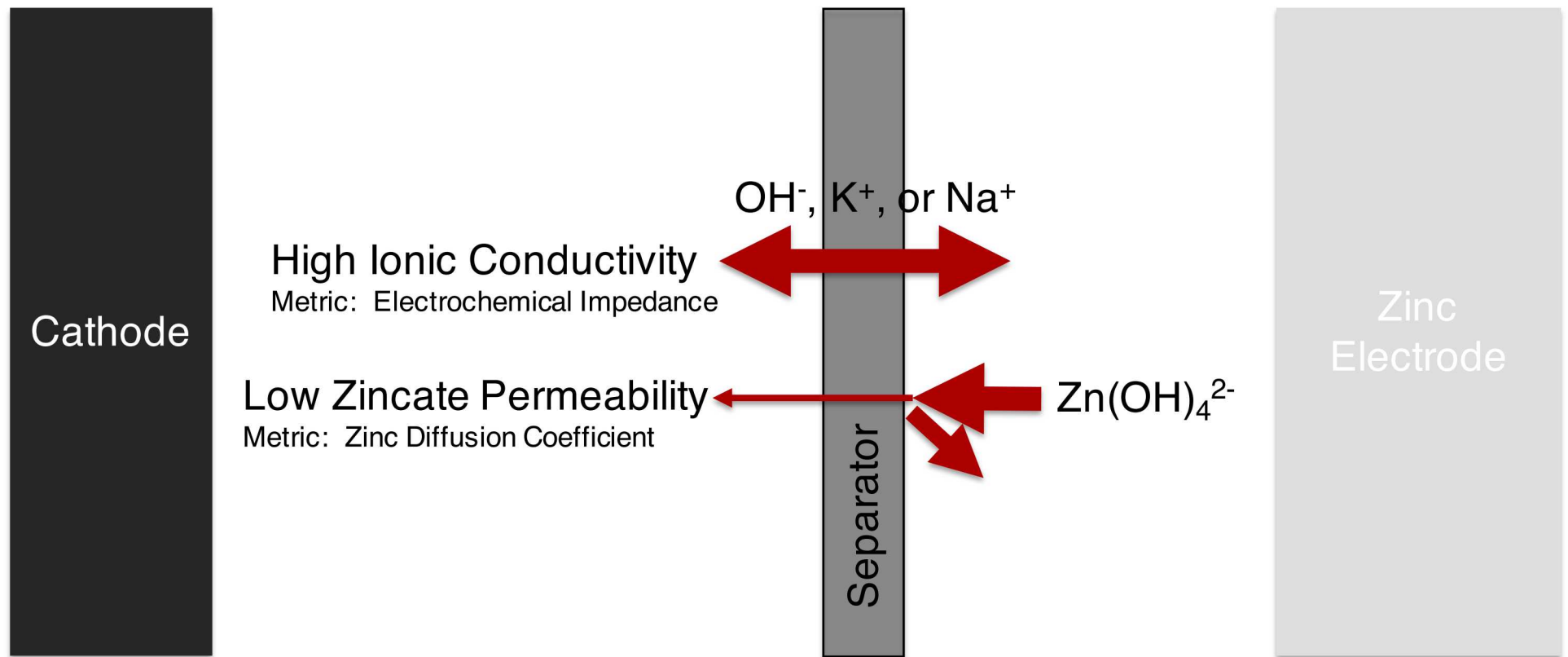


Effect of Electrolyte Additives on Zn DOD



~ 20% increase in cycle life
M. Lim *et al.* unpublished results.

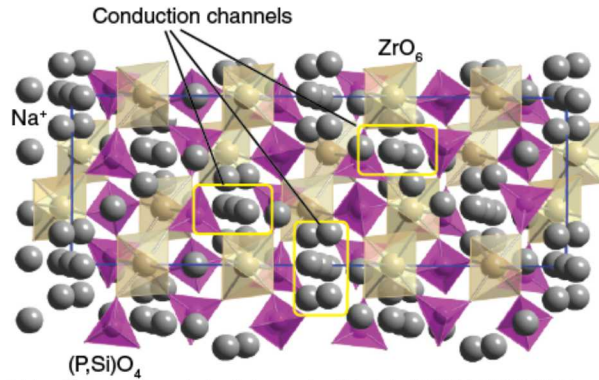
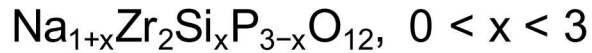
Features of a Good Zn Battery Separator



Separators – Ceramic Separator

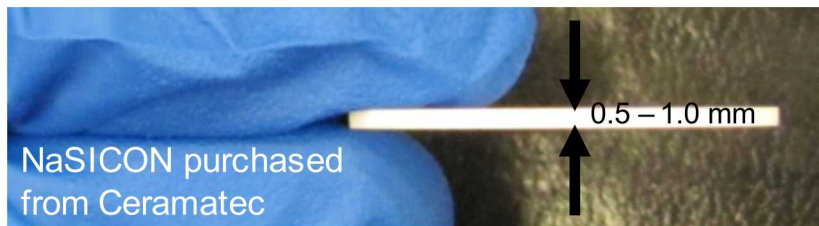
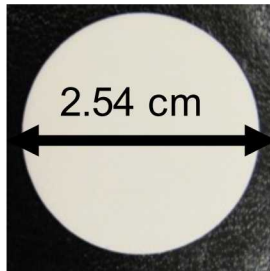


NaSuper Ionic CONductor

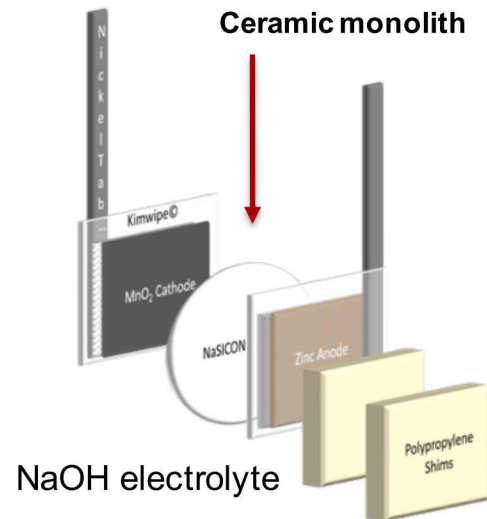


<http://www.chemtube3d.com/solidstate/SSNASICON.htm>

NaSICON



Battery Assembly Schematic



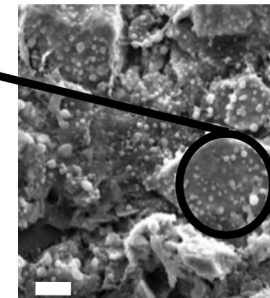
100% Selective Membrane

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

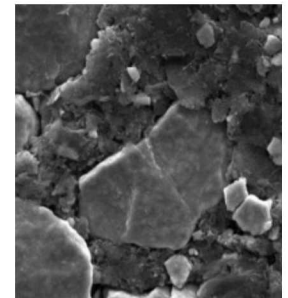
Cathode Post cycling

Zn w/ Celgard+Cellophane

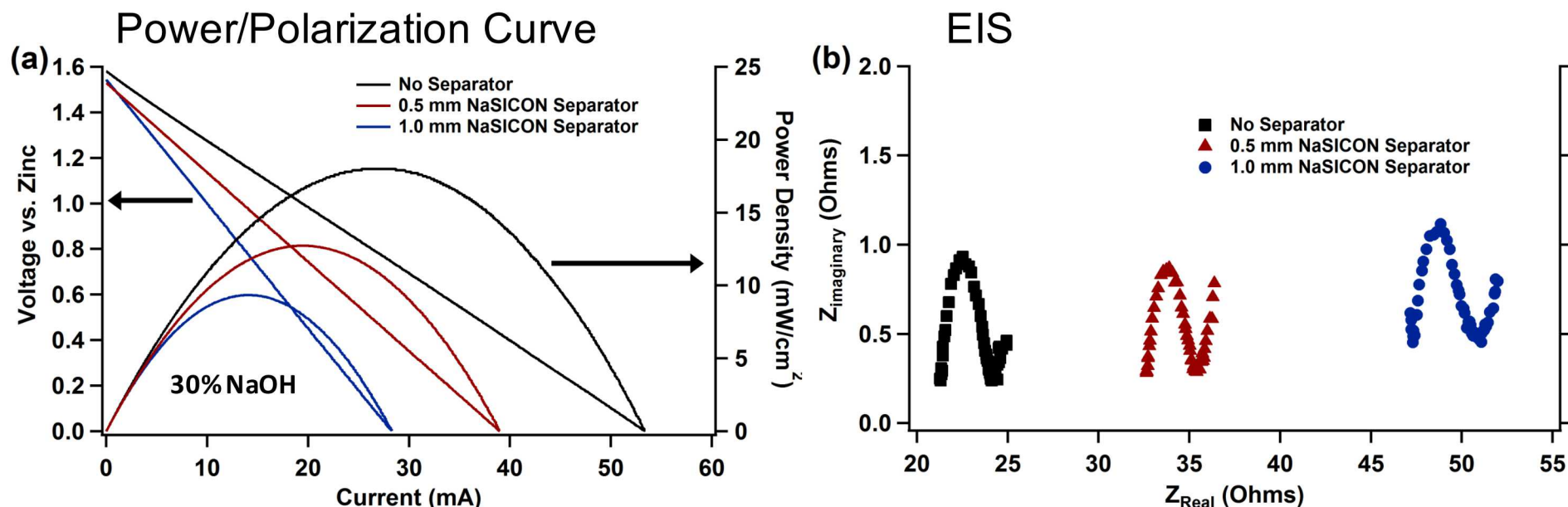
Zn-based particles



No Zn w/ NaSICON



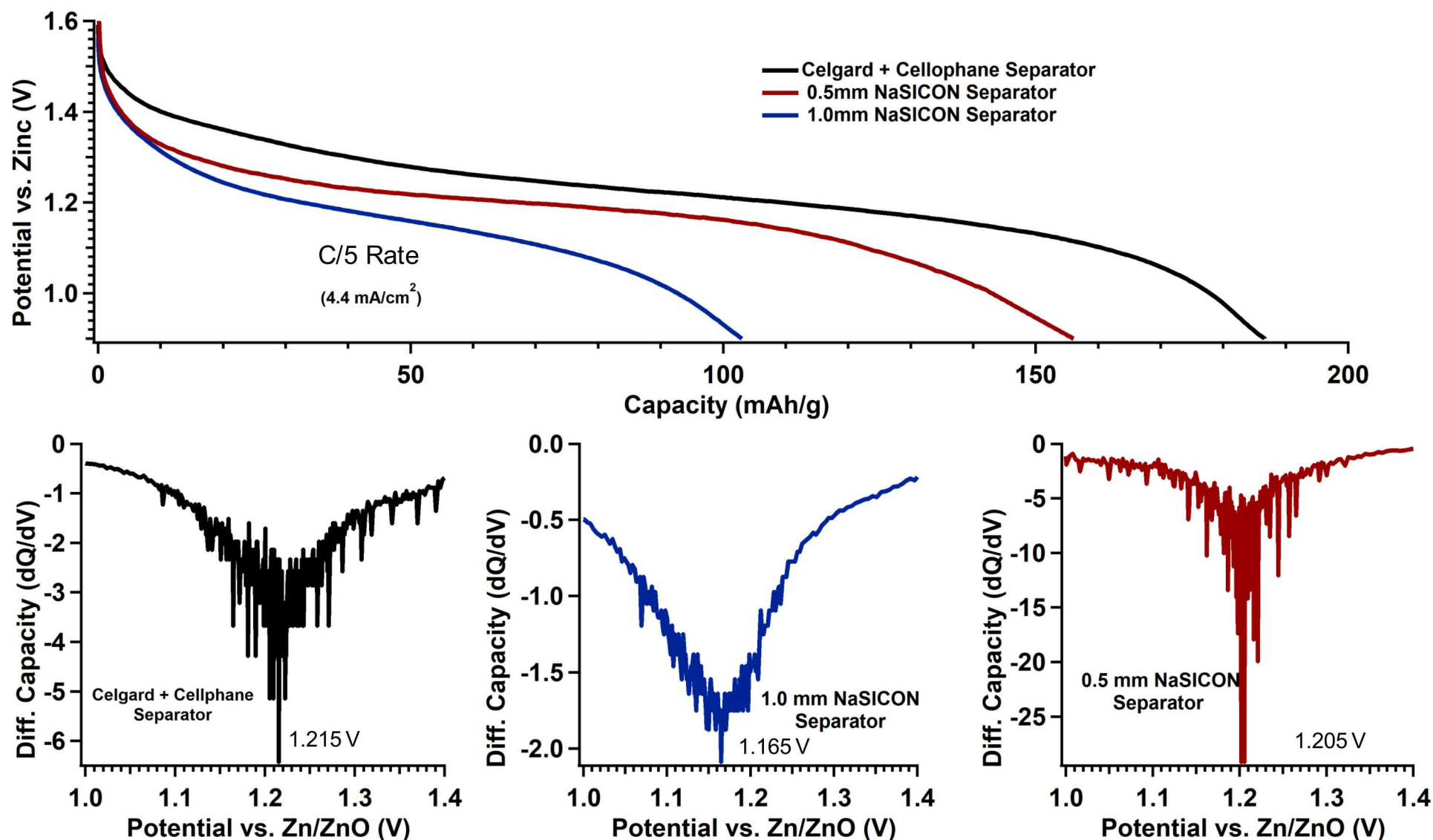
Room Temperature Resistance Measurements



- NaSICON has significant effect on power curve due to its thickness
- NaSICON also increases total resistance of the battery
- However decreasing thickness can result in a usable separator

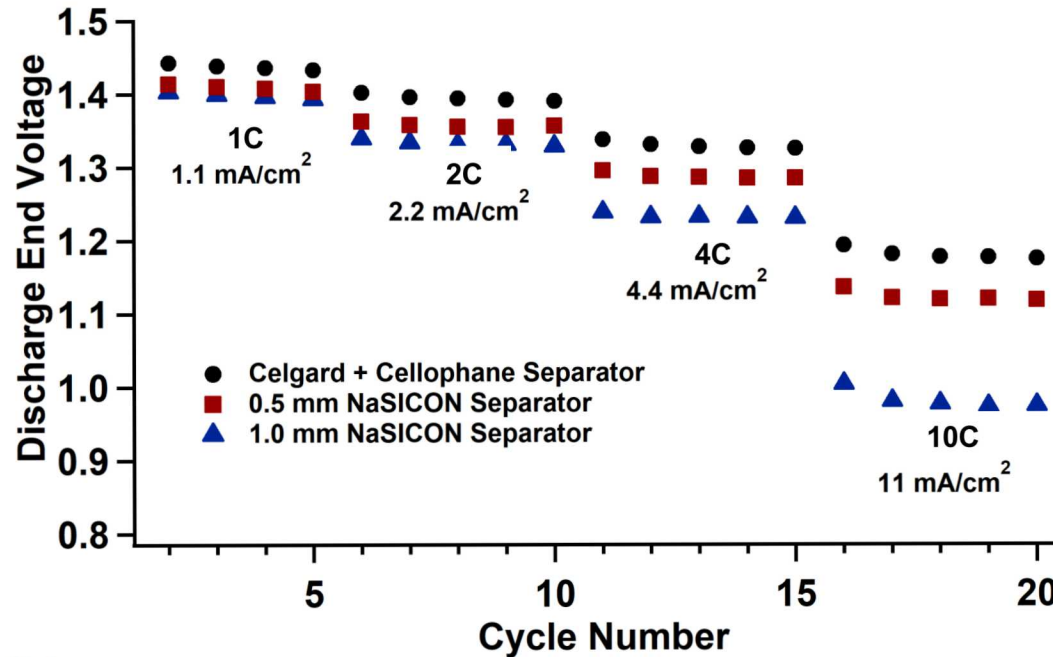
	Thickness (mm)	From EIS		Zinc Diffusion Coefficient ($\text{cm}^2 \text{min}^{-1}$)
		Room Temperature Resistance (Ω)	Room Temperature Conductivity (mS cm^{-1})	
Celgard 3501	0.025	0.1	10.7	1.18×10^{-6} *
Cellophane 350P00	0.025	0.2	21.4	7.23×10^{-7} *
0.5 mm NaSICON	0.500	9.8	3.9	$< 5.12 \times 10^{-9}$
1.0 mm NaSICON	1.060	25.3	3.5	$< 5.12 \times 10^{-9}$

Effect of Membrane Resistance on Discharge

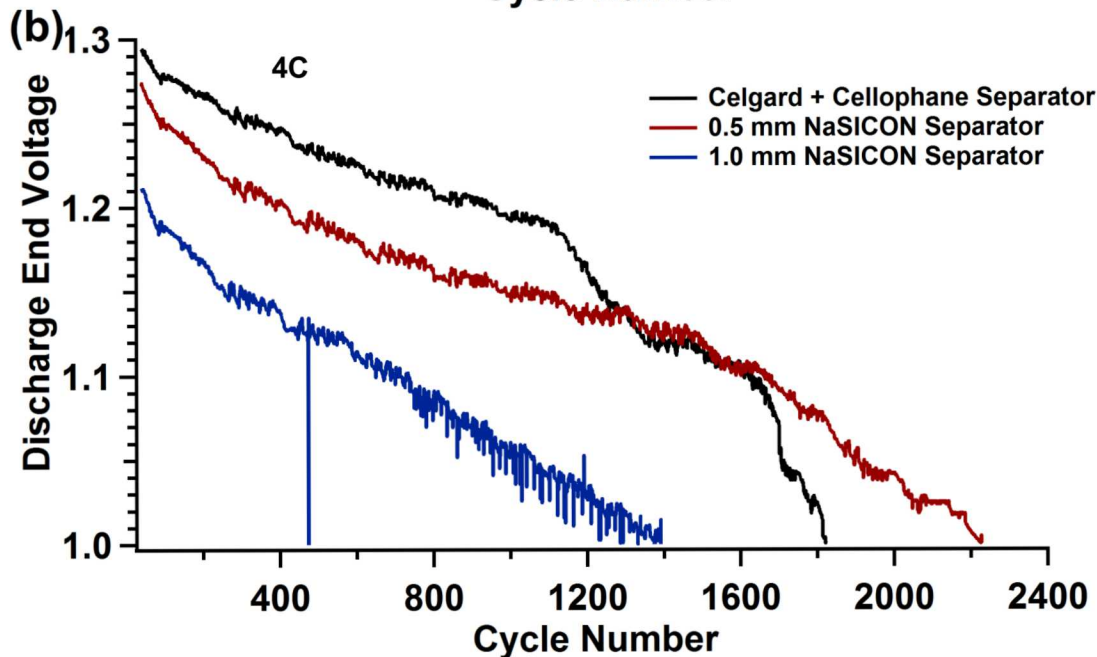


-NaSICON increases polarization of the cell
 -However that polarization can be reduced by decreasing the thickness of the NaSICON

Effect on 5% DOD Cells

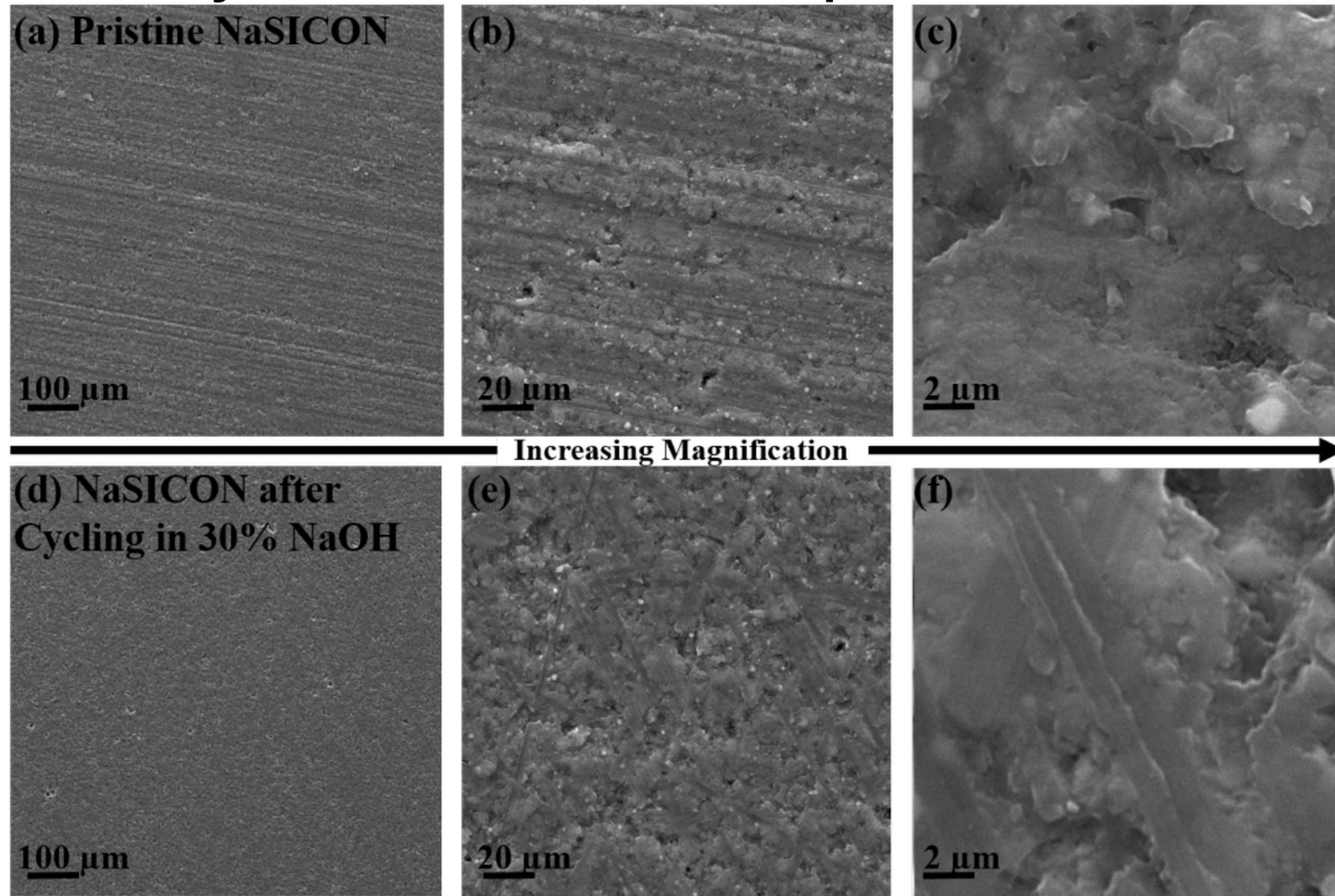


At relevant discharge rates for grid storage, the thinner **0.5 mm NaSICON doesn't decrease DEV significantly**



As NaSICON is thinned, it's advantages become more apparent increasing cell lifetime ~ 22%

Stability of NaSICON Separator



No dissolution or pitting observed after two months in 30% NaOH

Thickness

Before: 0.503 ± 0.011 mm

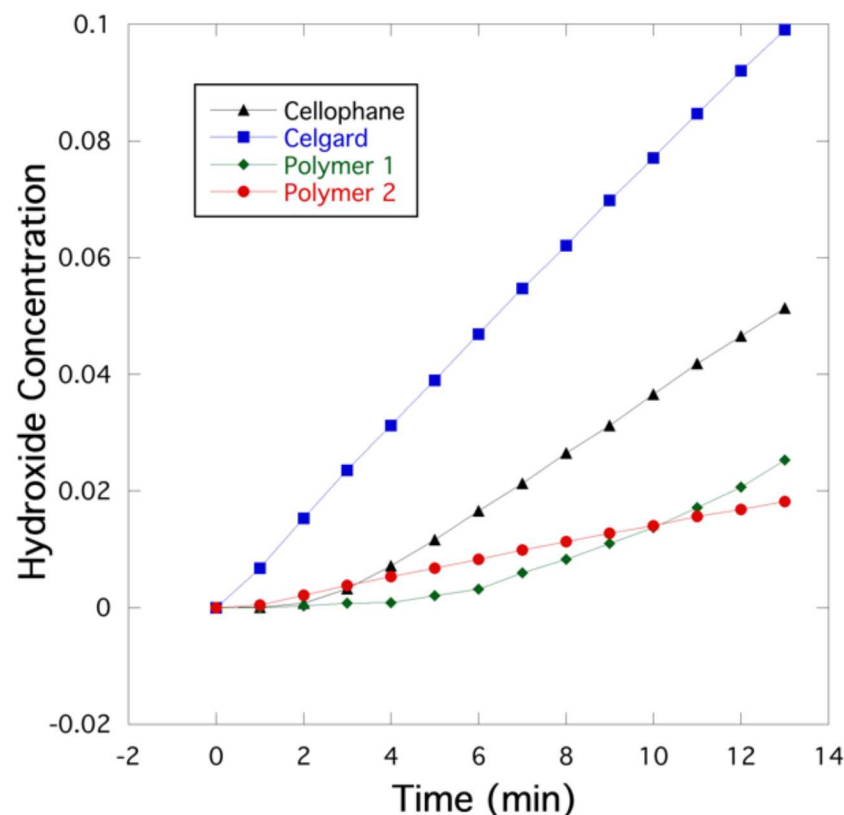
After: 0.506 ± 0.013 mm

Separators – Polymeric Separators

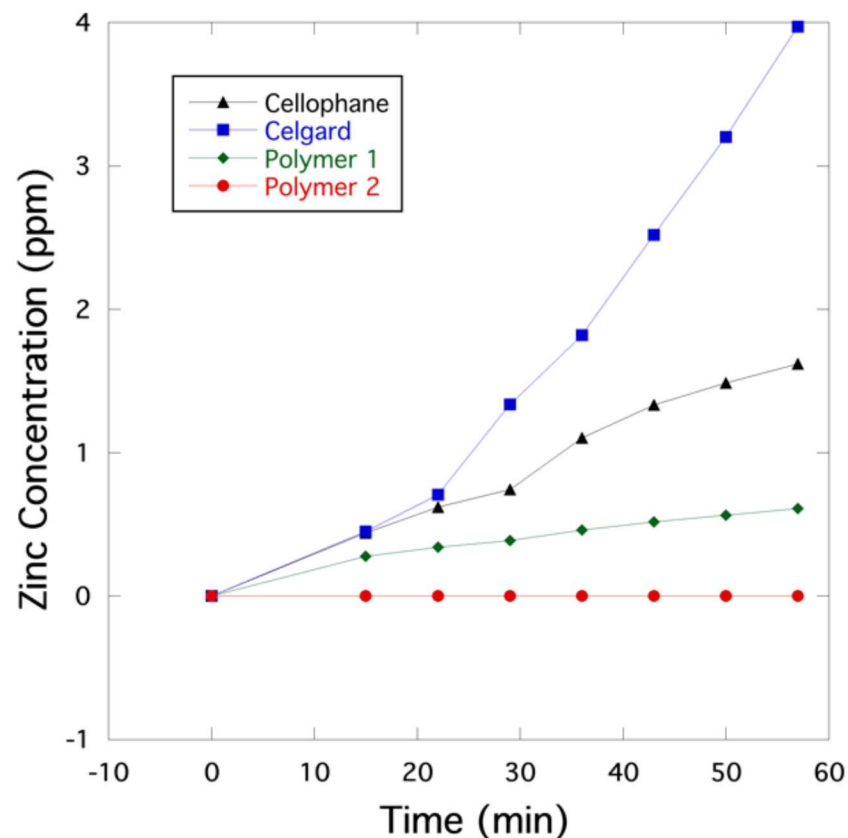
*Development of flexible polymers that allow for selective ion transport
(lower cost and more flexible battery assembly)*



Hydroxide Diffusion



Zincate Diffusion



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

Polymer 2 appears to be 100% selective for hydroxide

D. Arnot et al. unpublished results.

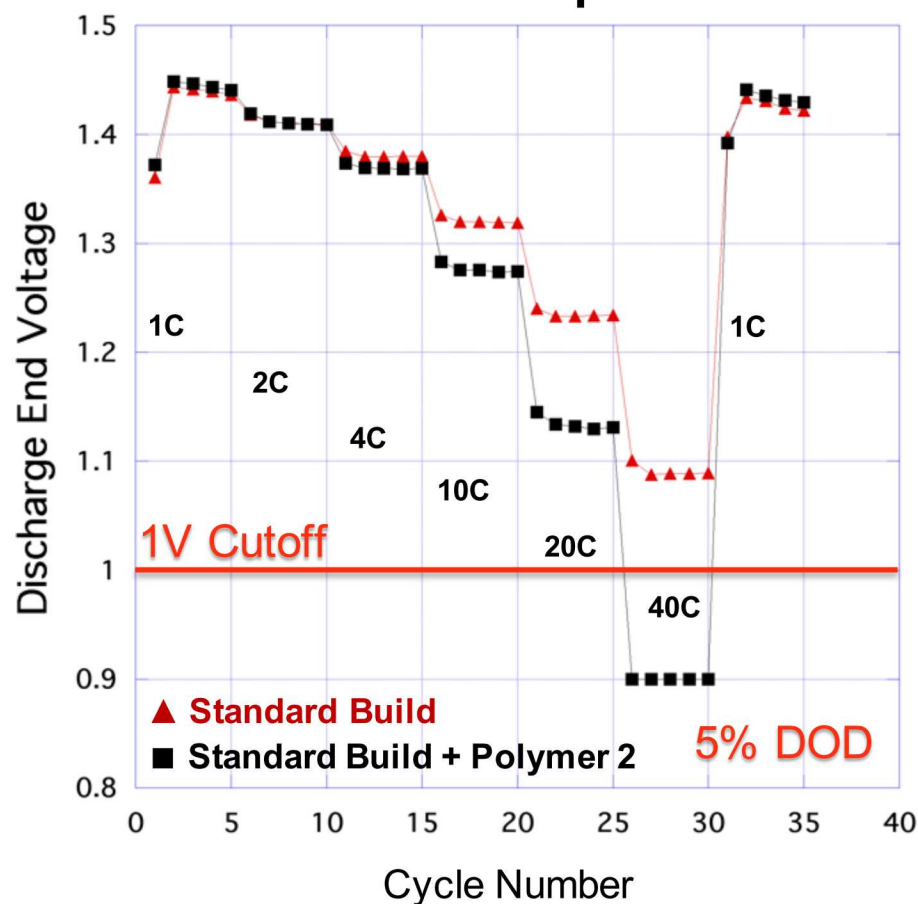
ASV Analysis for Diffusion coefficients: J. Duay *et al.*, *Electroanalysis* (2017) 29, 2261-2267 DOI:10.1002/elan.201700337.

Separators – Polymeric Separators

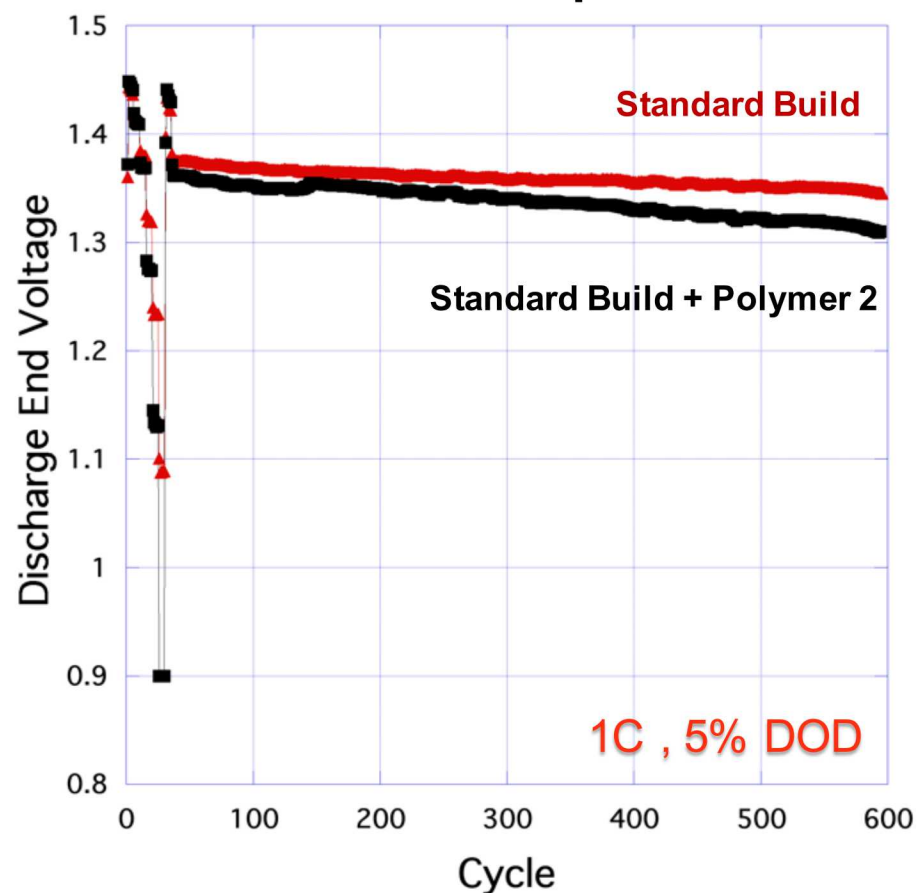


Application to Limited DOD Zn/MnO₂ cells

Rate Comparison



DEV Comparison

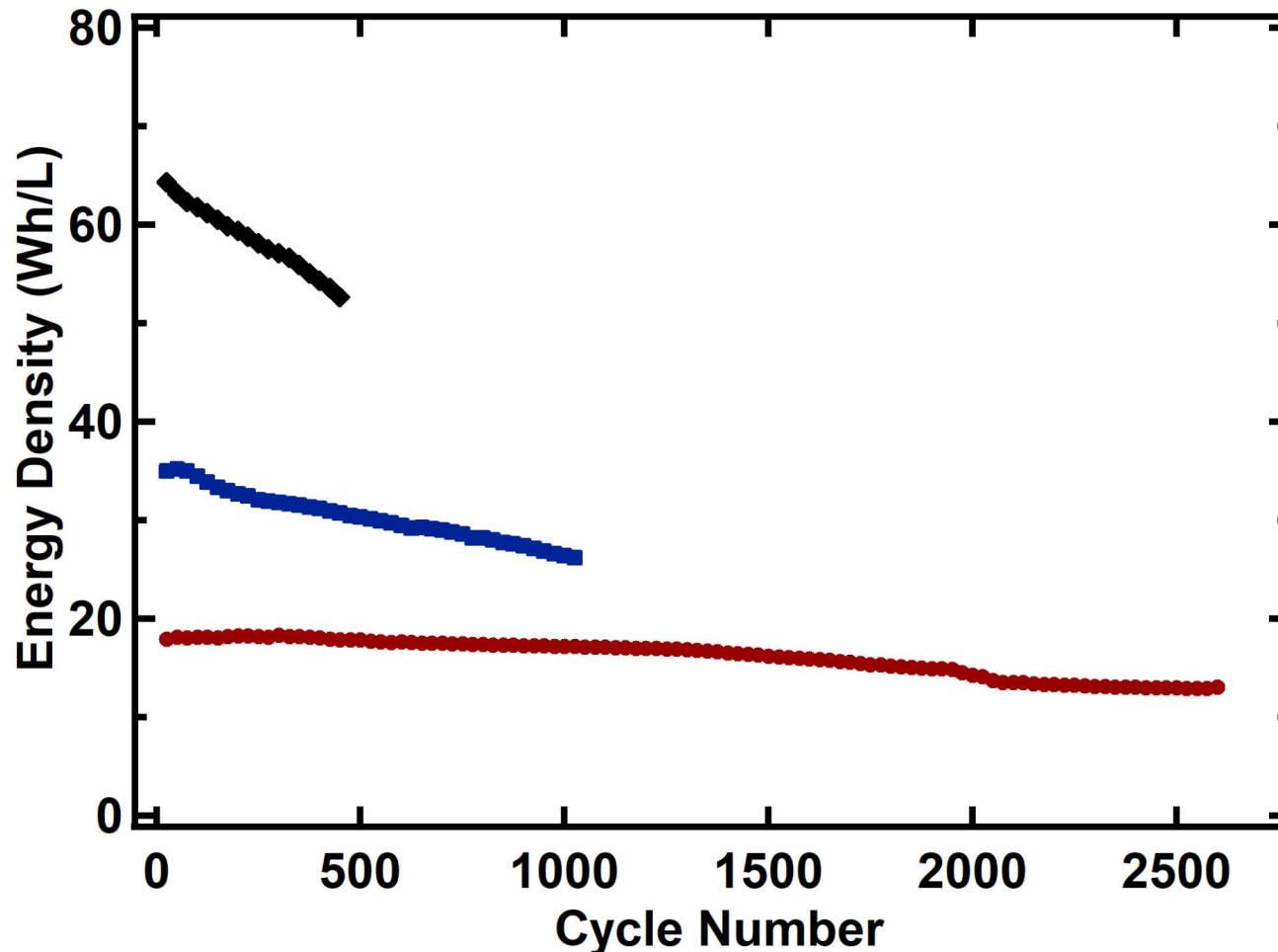


Polymer 2 appears to be a promising hydroxide selective separator

New Cathodes for Alkaline Zn Battery



- Cathode limited batteries with Zn anode, alkaline electrolyte
- Long cycle life with energy densities similar to limited DOD Zn/MnO₂ achieved



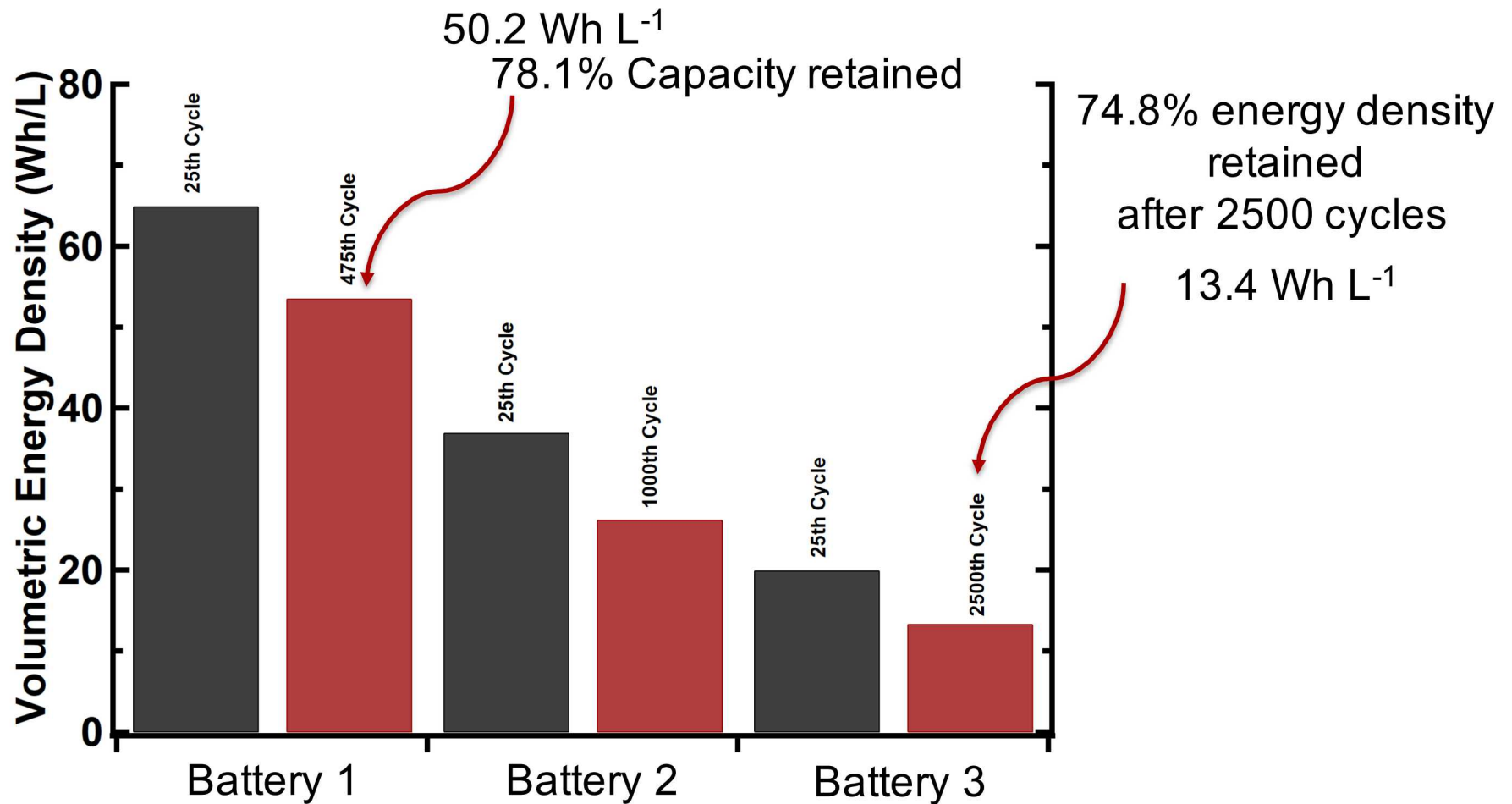
T. N. Lambert and J. Duay, United States of America Patent, 15/669,587, 2017 - PCT/US17/45629, 2017.

T. N. Lambert and J. Duay, United States of America Patent, 16/054,114, 2018 - PCT/US18/45187, 2018.

New Cathodes for Alkaline Zn Battery



- Cathode limited batteries with Zn anode, alkaline electrolyte
- Long cycle life with energy densities similar to limited DOD Zn/MnO₂ achieved
- High volumetric energy densities have been obtained but with lower cycle life
- Work is ongoing - looking for commercial partners to develop further



T. N. Lambert and J. Duay, United States of America Patent, 15/669,587, 2017 - PCT/US17/45629, 2017.

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Summary



- Electrolyte additives can increase cycle life and (cathode) rate performance in limited DOD Zn/MnO₂ batteries
- NaSICON separators block 100% zincate crossover and can be effective at rates relevant to grid storage despite their high resistance
- Polymeric selective separators are under development at SNL and several promising leads have been developed – applicable to 1e⁻ and 2e⁻ MnO₂
- New 'low cost' cathodes with grid storage relevant energy densities are under development

Acknowledgements



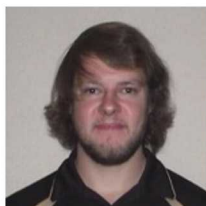
Imre Gyuk



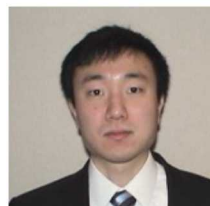
Babu Chalamala



Jonathon Duay



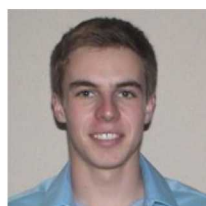
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Kristen Maus

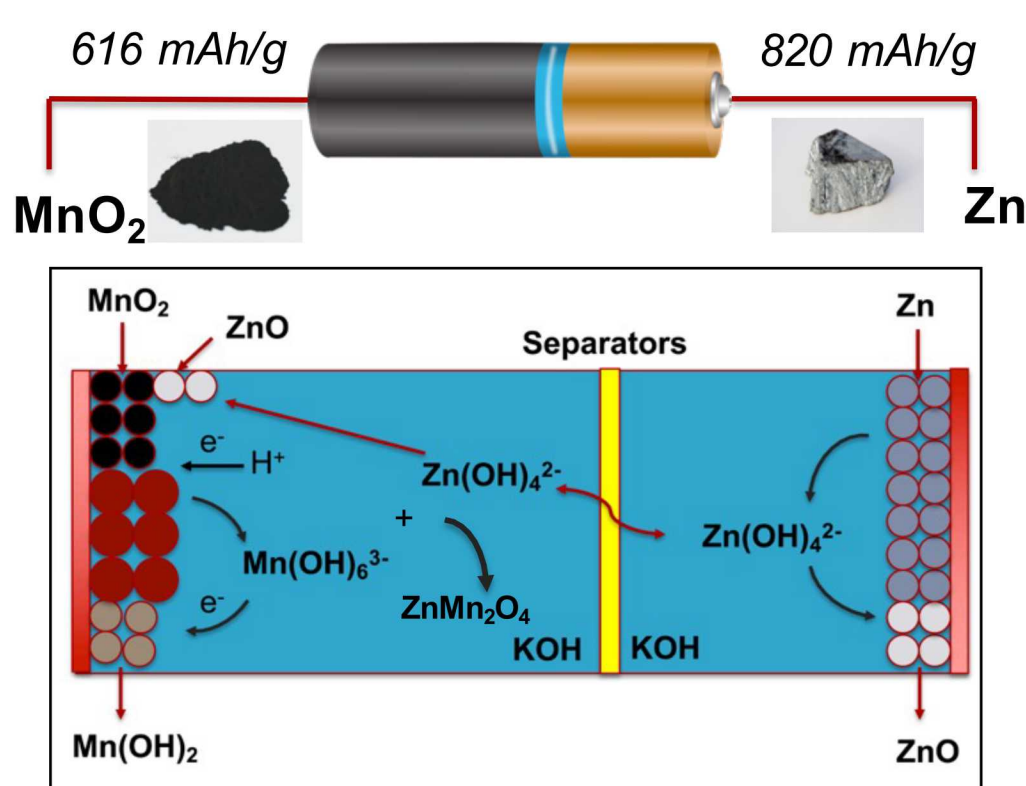


Ivan
Pineda-Dominguez



Thank you

Alkaline Zn/MnO₂ Batteries



Issues to be addressed

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).