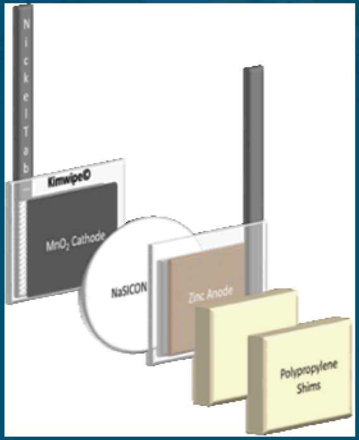
SAND2020-10554C

Improving Cycle Life and Active Materials Utilization for Rechargeable Alkaline Zn-MnO_2 Batteries

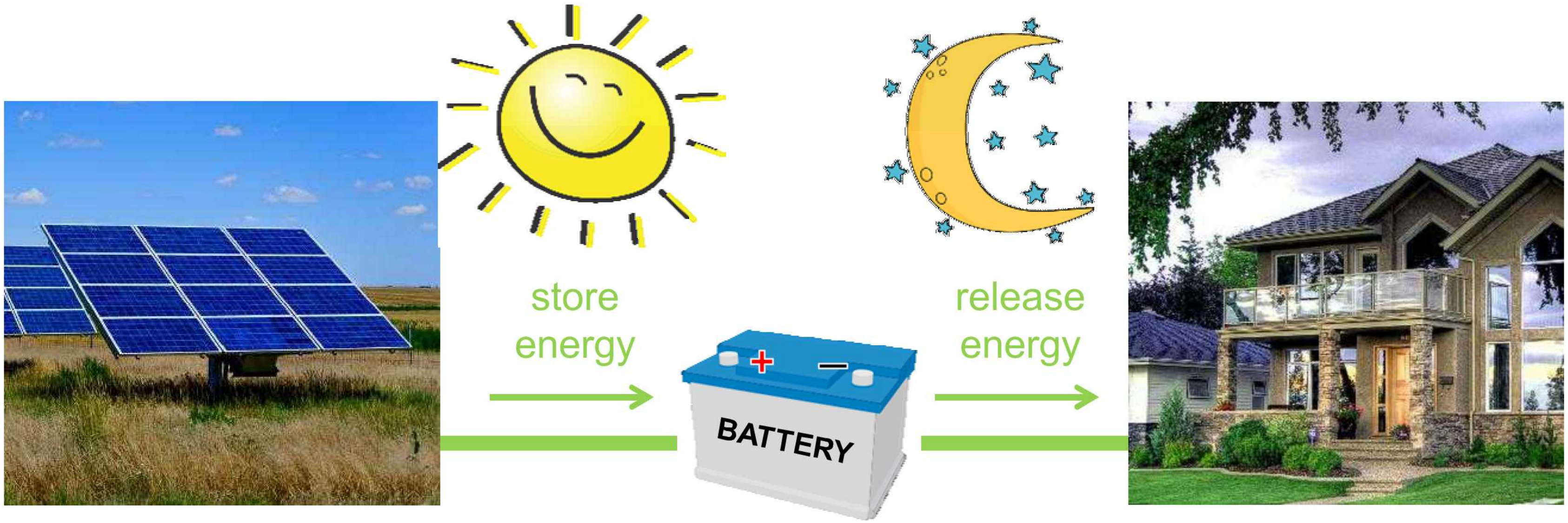


<u>Matthew B. Lim</u>, Maria Kelly, Jonathon Duay, Igor Kolesnichenko, Timothy N. Lambert

Sandia National Laboratories

235th ECS Meeting
May 28, 2019

Grid Energy Storage



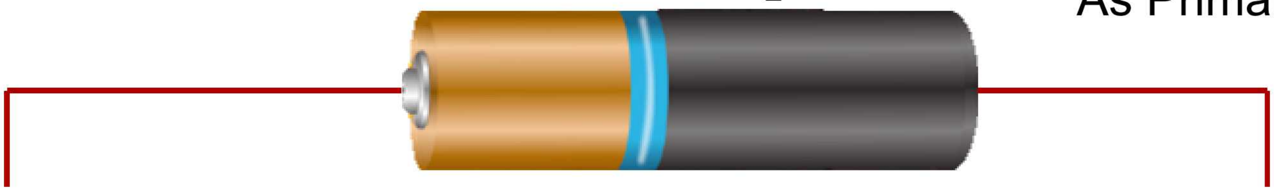
- Grid-level energy storage systems needed to enable intermittent renewables
- Li-ion, Pb-acid battery systems have been implemented but pose safety and environmental risks
- Successful grid storage must be safe, reliable, and low-cost

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.”

Alkaline Zn-MnO_2 Batteries

$18/kWh
As Primary cell

Zn-MnO_2



MnO_2

- ~ $1-2 per lb
- 16,000,000 tons (2012)
- Safe

KOH

- Potash ~ $260 per ton
- Aqueous
- Safer than Li-org

Zn

- ~ $1 per lb
- 13,000,000 tons (2012)
- Safe

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^- \quad [E^0 = +0.15\ V]$$

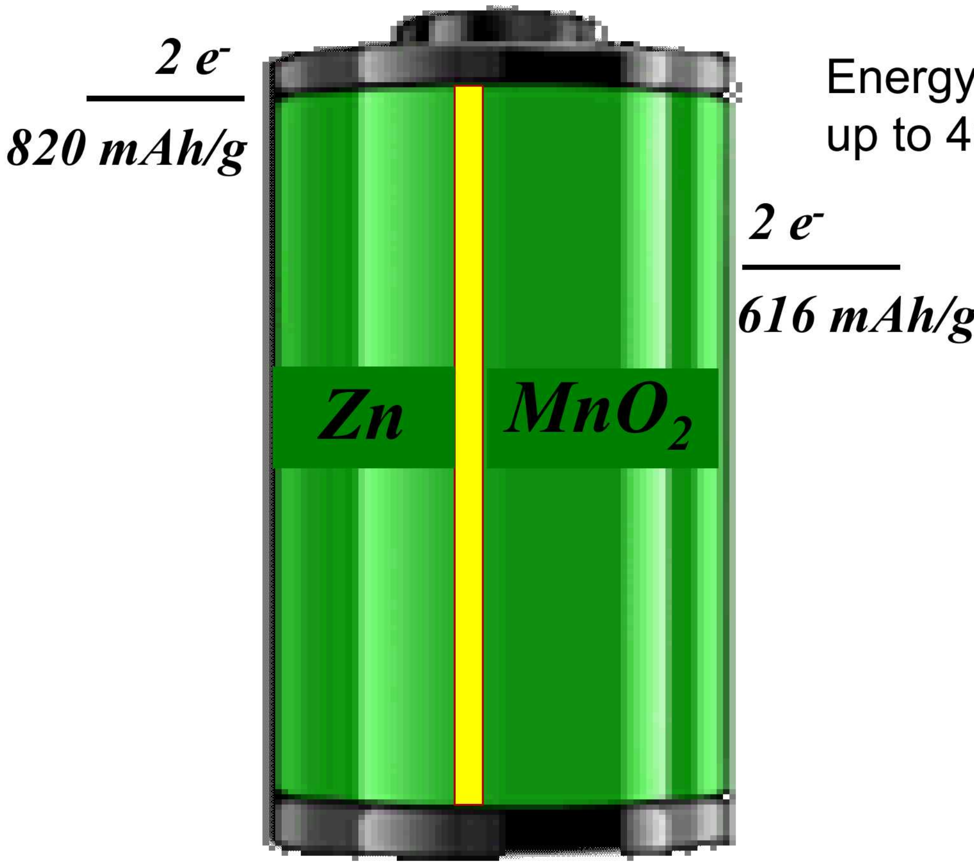
$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad [E^0 = +1.28\ V]$$

$$\mathbf{Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3} \quad [\mathbf{E^0 = +1.43\ V}]$$

Co	$13-15/lb	**Li**	$2.5/lb
V	$11-12/lb	**Al**	$0.8-0.9/lb
Ni	$6-9/lb	**Cu**	$2.5-3.5/lb

The ultimate challenge in rechargeable Zn/MnO_2 batteries is increasing energy density while maintaining reversibility

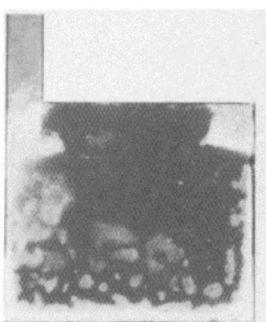
Rechargeable Alkaline Zn-MnO_2 Batteries



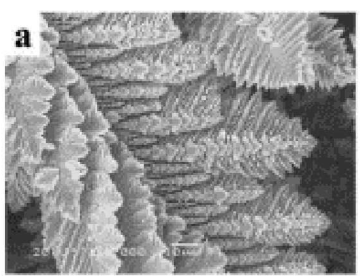
Energy density of primary cell: up to 400 Wh/L or 150 Wh/kg

Anode … Issues

- Passiva… …ructure breakdown
- Shape … …hase(s) formed
- Dendrit… …oning

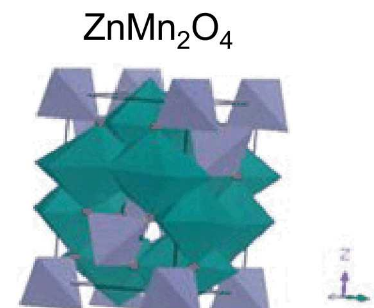


J. Electrochem. Soc., 138 (2), 645 (1991)



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

PNAS 115 (23), E5261 (2018)



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

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

- Technology has been commercialized by Urban Electric Power
  - 50-100 Wh/L, \$150-250/kWh

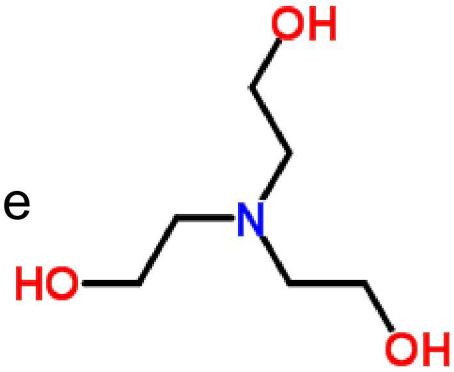
Improving Zn-MnO_2 Battery Performance

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

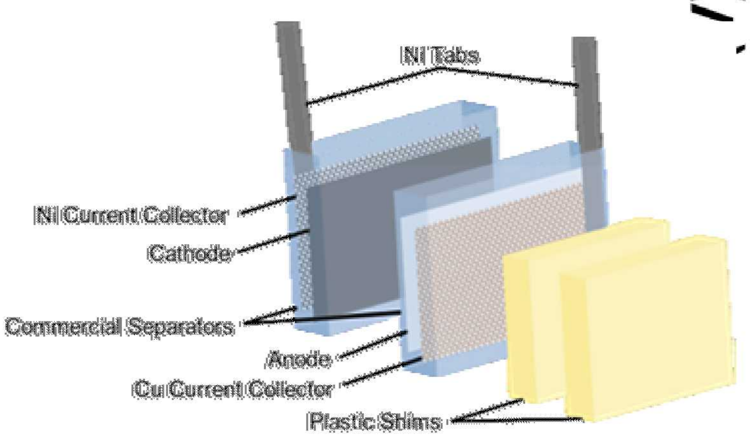


➡ Comprehensive analysis of TEA effect in limited DOD cells

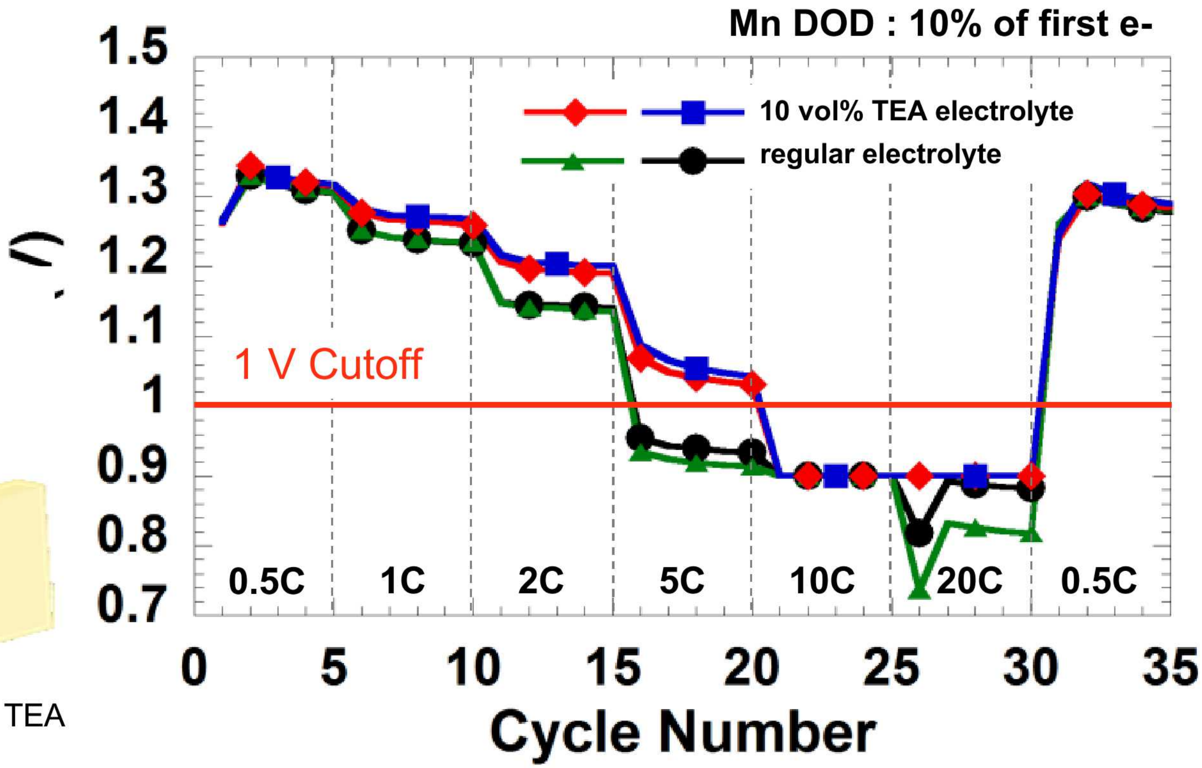
A. Kozawa and R. A. Powers, *J. Electrochem. Soc.*, **113** 870 (1966).
A. Kozawa and J. F. Yeager, *J. Electrochem. Soc.*, **112**, 959 (1965).
M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

Rate Performance

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



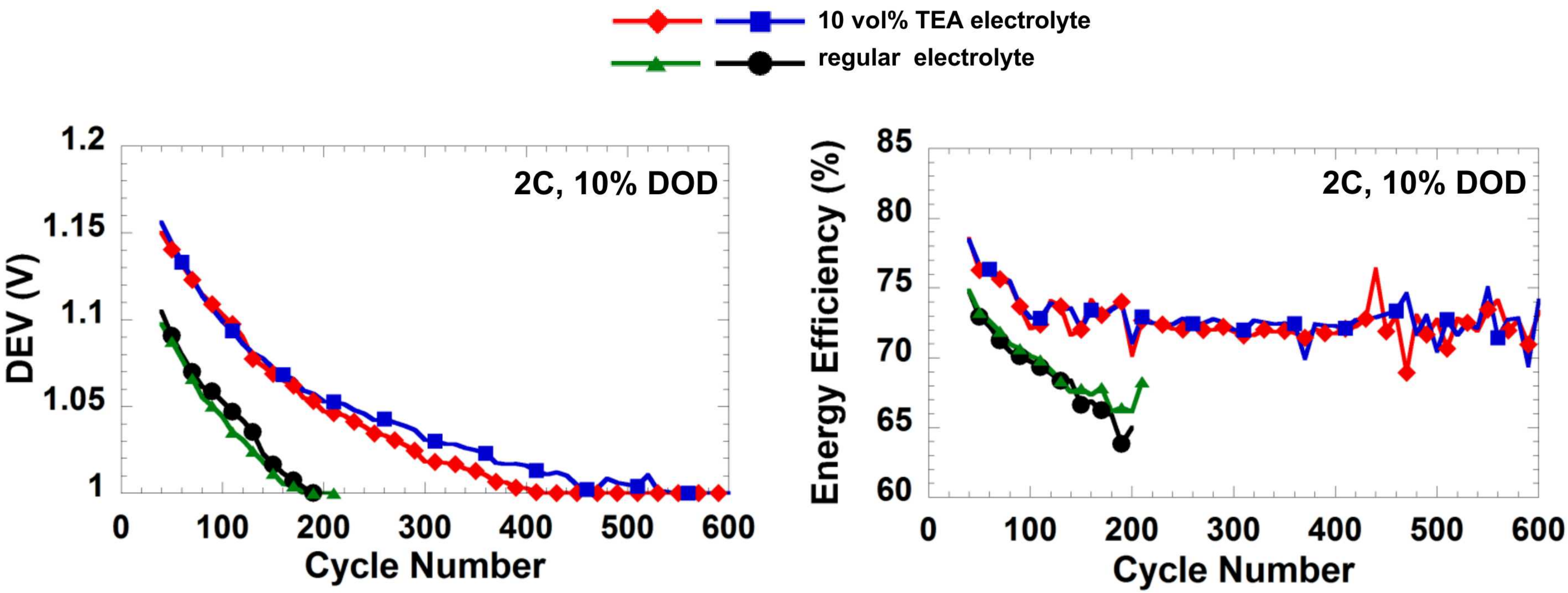
Electrolyte: 32 wt% KOH with/without 10 vol% TEA



- 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, more soluble, less transport through separator, lower surface area

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

Zn Anode – Increasing Cycle Life at High DOD

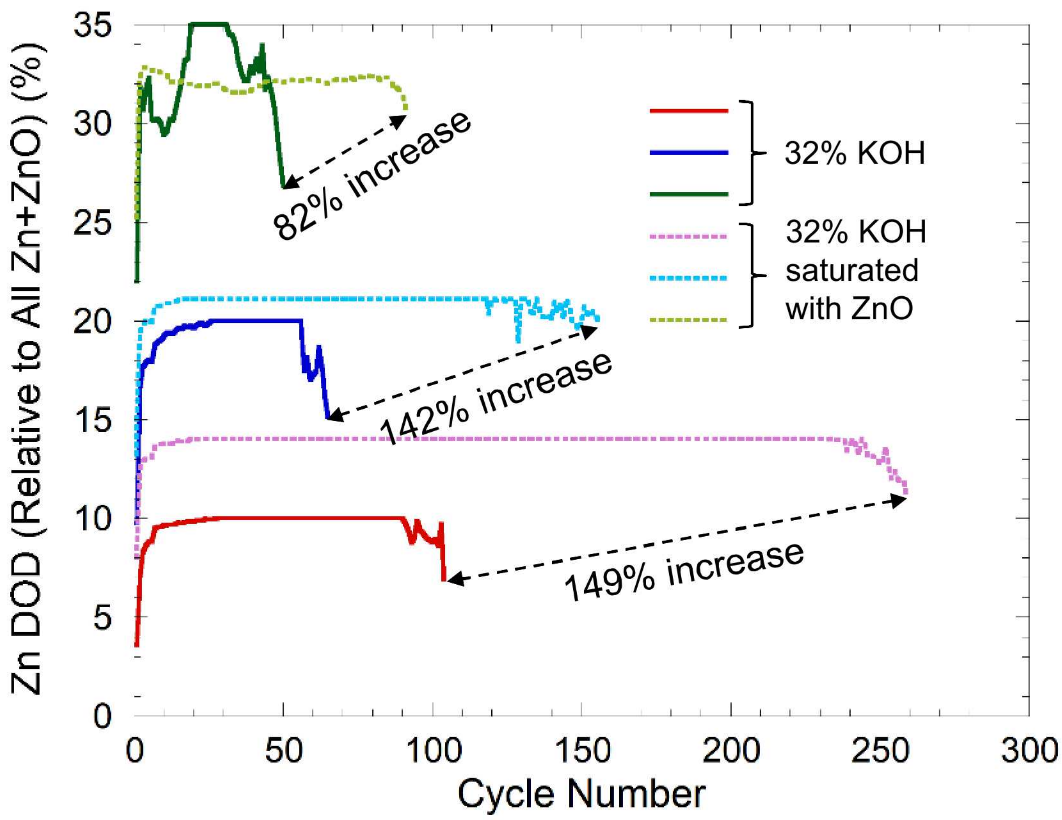
Pre-saturating electrolyte with ZnO can minimize dissolution and migration of zinc from the anode

Zn/Ni(OH)$_2$

Anode capacity = 746 mAh/g

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

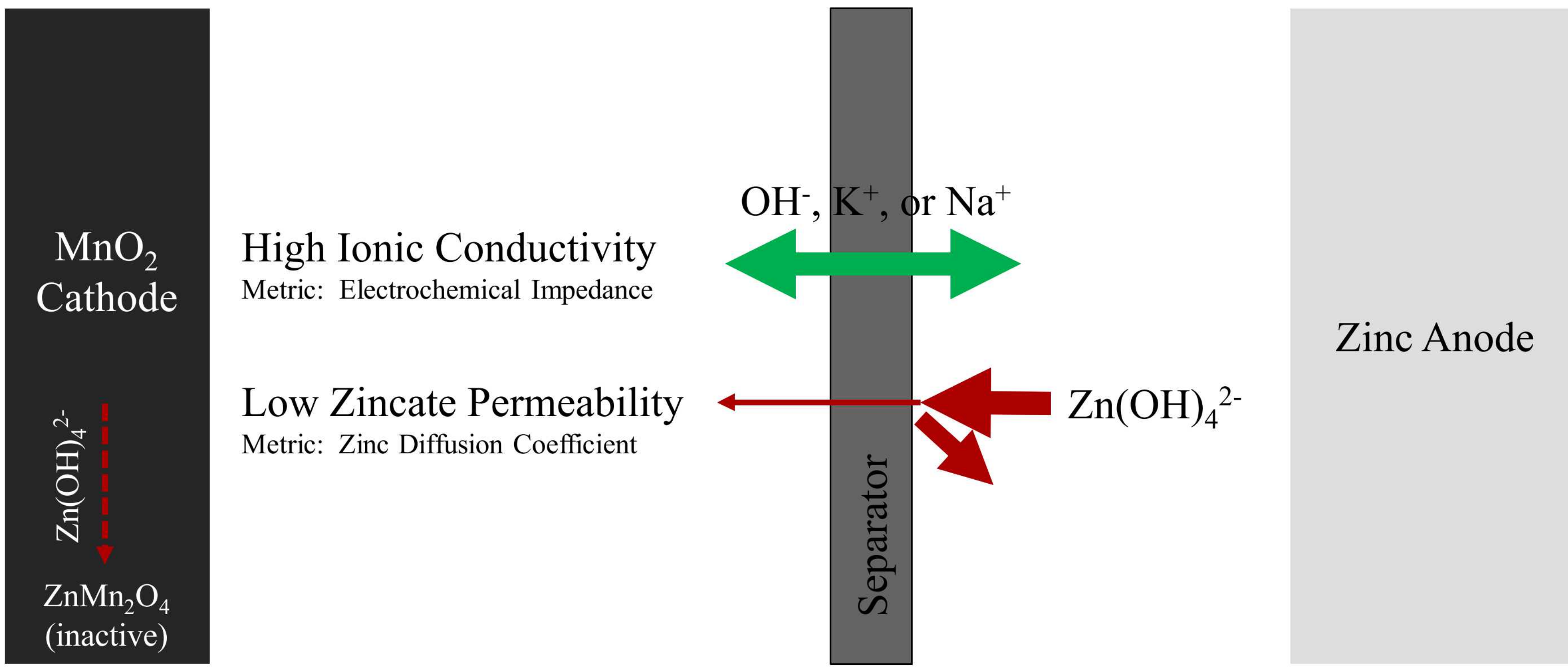
Excess Ni(OH)$_2$



M. Lim *et al.* unpublished results

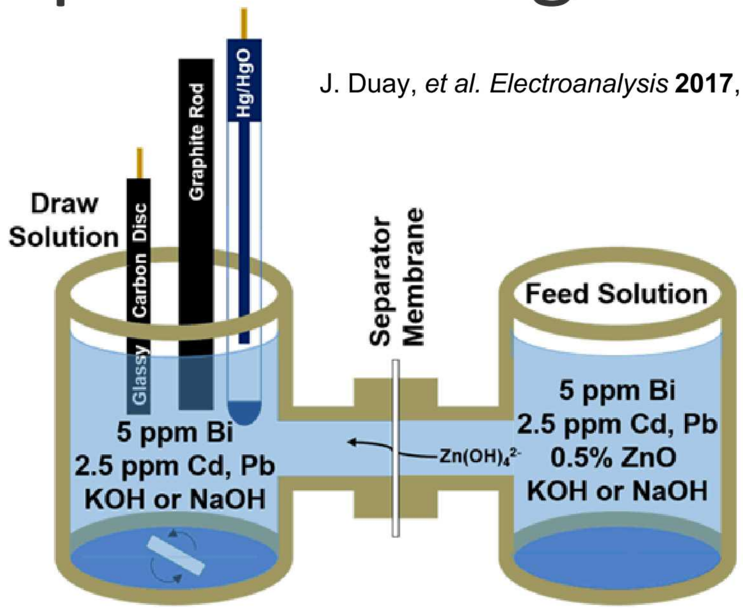
Cells with saturated electrolyte last significantly longer than cells with regular electrolyte cycled at comparable or lower DOD, *even when including dissolved ZnO in capacity*

Features of a Good Zn-MnO_2 Battery Separator

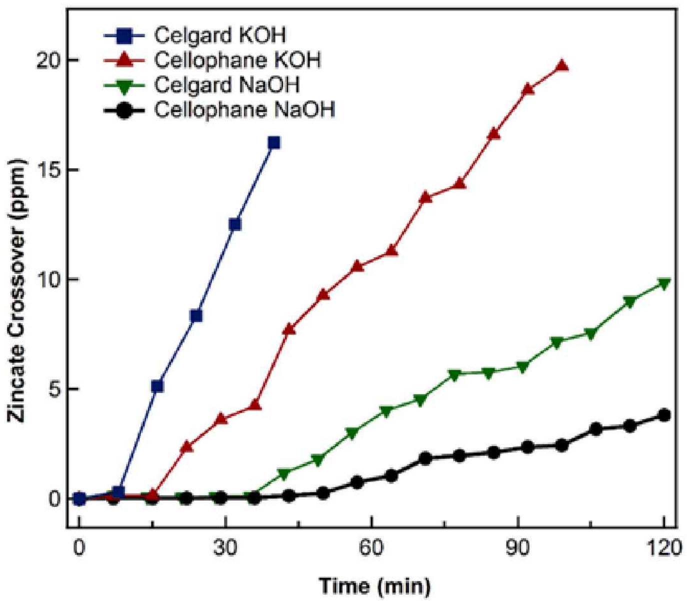


A selective membrane/separator is needed that allows charge-carrying ions through but blocks or limits Zn (zincate)

Rapid Screening Assay for Separators



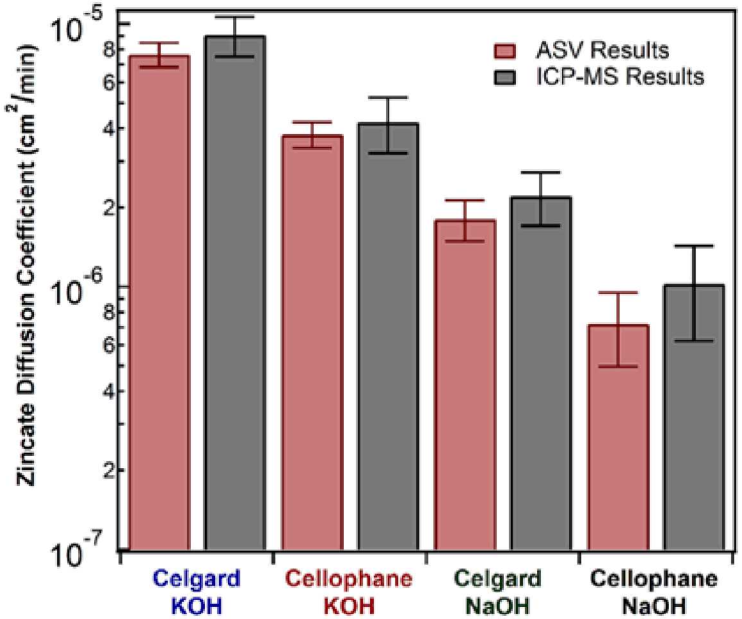
J. Duay, *et al. Electroanalysis* **2017**, *29*, 2261–2267



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 7.5 ± 2.4 ppm*	Days
Complexometric Titration	>20x	1 ppm 96 ± 24 ppm*	Weeks

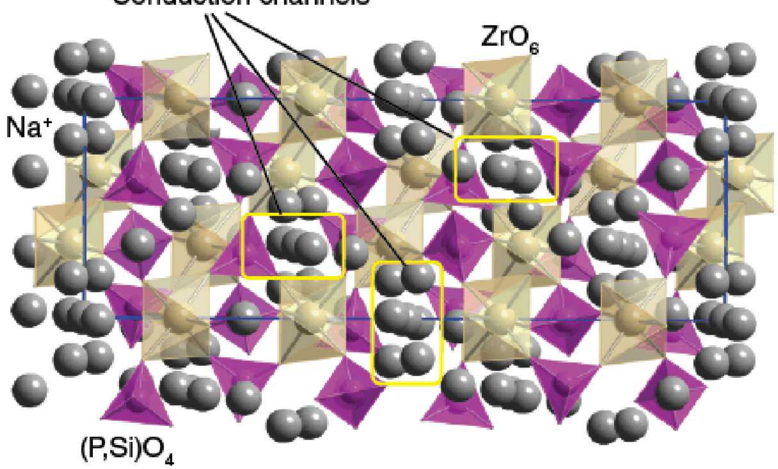
* LODs obtained in our lab



NaSICON Ceramic Separator

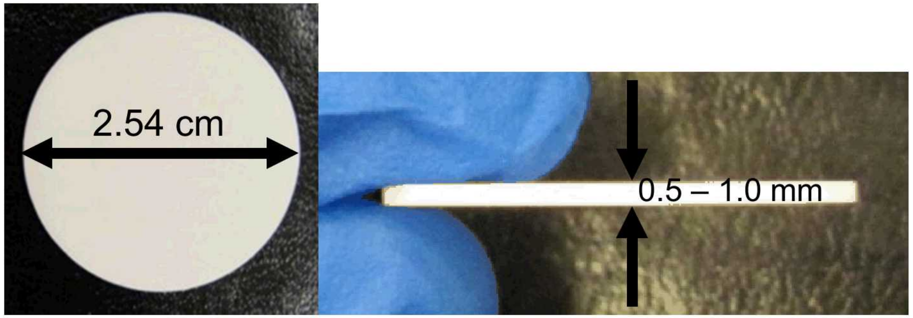
NaSuper **I**onic **CON**ductor

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

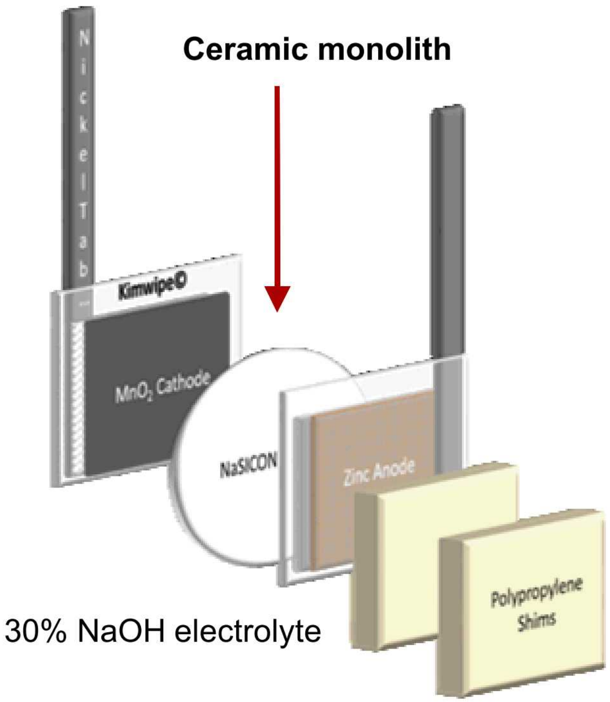


http://www.chemtube3d.com/solidstate/SSNASICON.htm

NaSICON purchased from Ceramatec



Battery Assembly Schematic

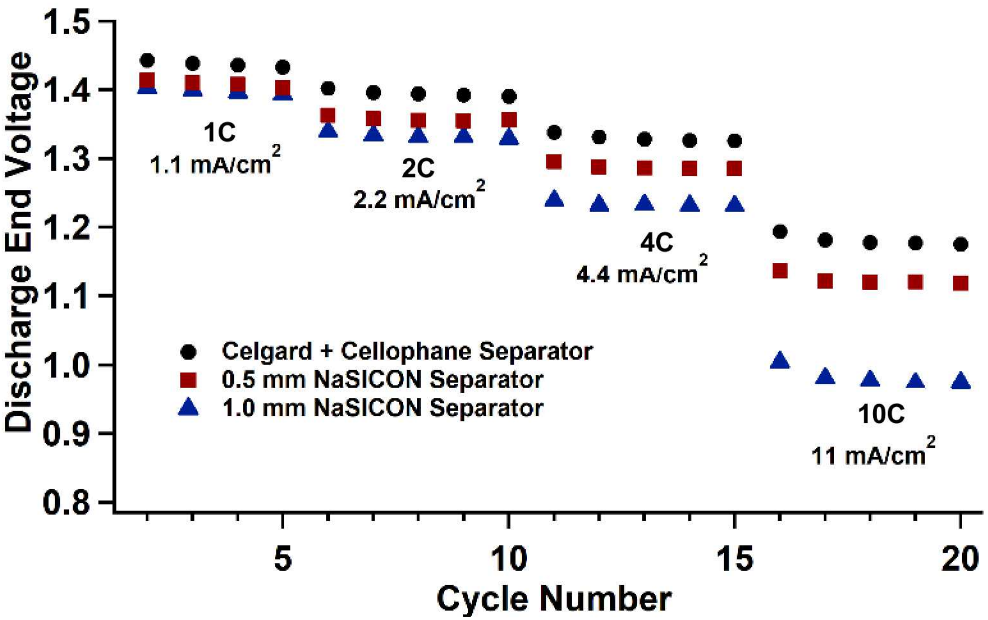


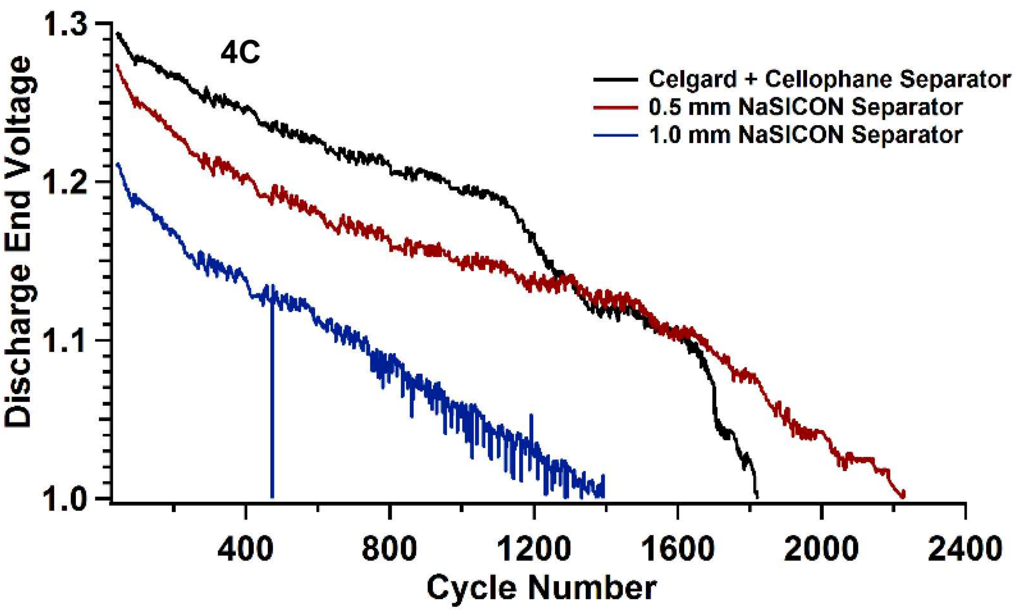
100% Selective Membrane

- **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

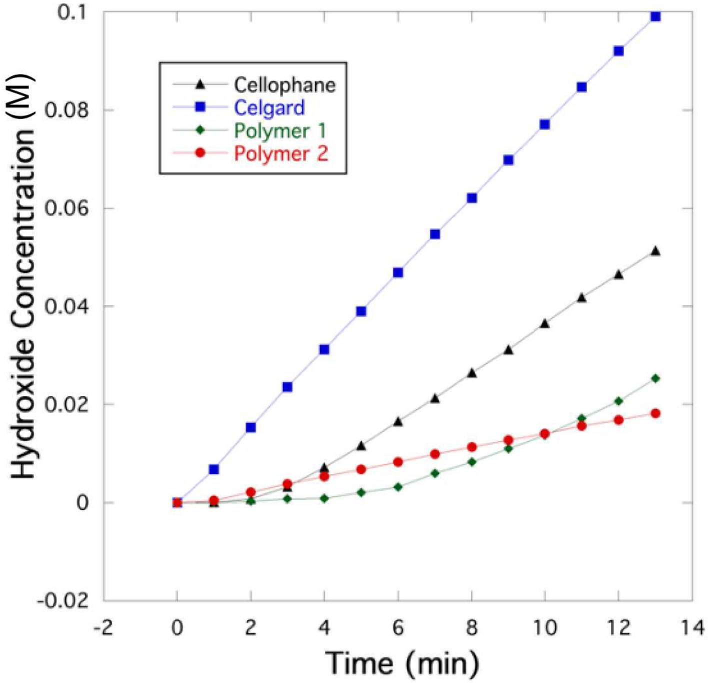
As NaSICON is thinned and becomes less resistive, its advantages become more apparent, increasing cell lifetime by 22%

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

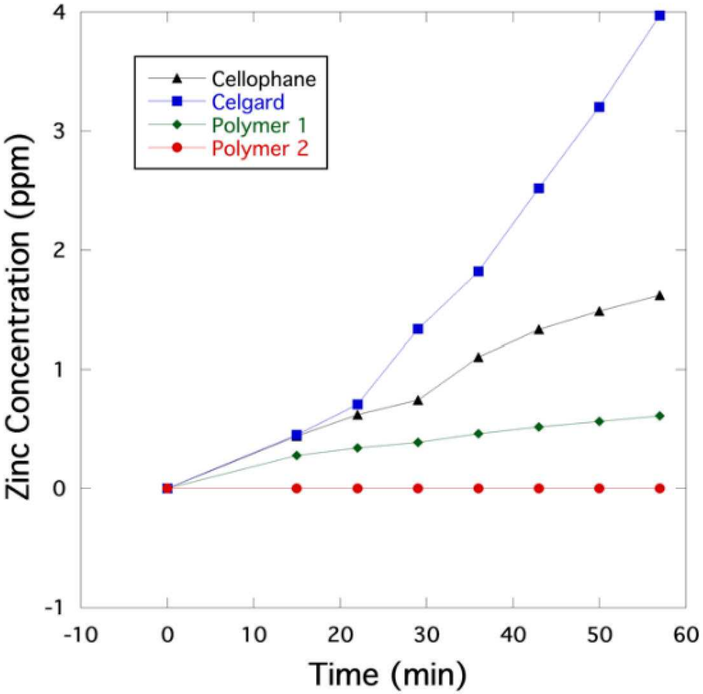
Flexible Polymeric Separators

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



D. Arnot *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	**$3.03 \cdot 10^{-6}$**	**$3.66 \cdot 10^{-11}$**	**$8.28 \cdot 10^{4}$**

Polymer 2 is effectively 100% selective for hydroxide

Summary

- Electrolyte additives can increase cycle life, active material utilization and rate performance in limited DOD Zn/MnO_2 batteries
- ASV technique can be used to rapidly evaluate separators for zincate permeability
- NaSICON separators block zincate and can be effective at rates relevant to grid storage despite their high resistance
- Flexible polymeric selective separators are under development

Future Work

- Combining electrode/electrolyte improvements and selective separators with **reversible 2e$^-$ MnO_2 cathode**
  - Recently stabilized with Cu, Bi, CNT additives to achieve 3000+ cycles vs. $Ni(OH)_2$, but still sensitive to the presence of zinc
  - Ongoing collaboration with CUNY
  - Potential for >250 Wh/L and <$100/kWh

G. Yadav *et al.*, *Nat. Commun.* 8:14424 (2017).
G. Yadav *et al.*, *J. Mater. Chem. A* **5**, 15845 (2017).
G. Yadav *et al.*, *Mater. Today Energy* **6**, 198 (2017).
G. Yadav *et al.*, *Int. J. Hydrog. Energy* **43**, 8480 (2018).

Acknowledgments

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