Flexible Ion-Selective Separators for Alkaline Zinc Batteries

Matthew B. Lim,[1] David J. Arnot,[2] Rachel L. Habing,[2] Igor V. Kolesnichenko,[2] Logan S. Ricketts,[2] Elijah I. Ruiz,[2] Timothy N. Lambert[2]*

[1]Department of Energy Storage Technology & Systems, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

[2]Department of Photovoltaics & Materials Technologies, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

***Email:** tnlambe@sandia.gov

Background and Objectives

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)
- Costs below $100/kWh at scale
- **High achievable energy density**
  - Zn/MnO_2 ~ 400 Wh/L
  - Zn/Ni ~ 300 Wh/L
  - Zn/Air ~ 1400 Wh/L

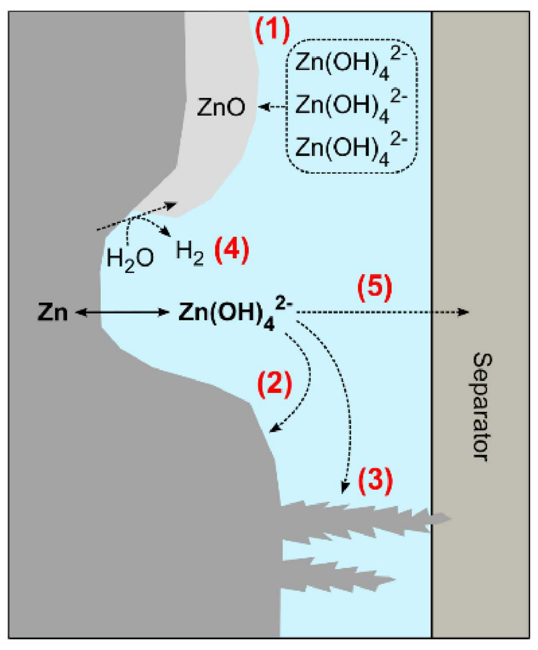
Zn

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

KOH

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

Primary challenge: Reversibility of zinc anode



Performance-Limiting Issues

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

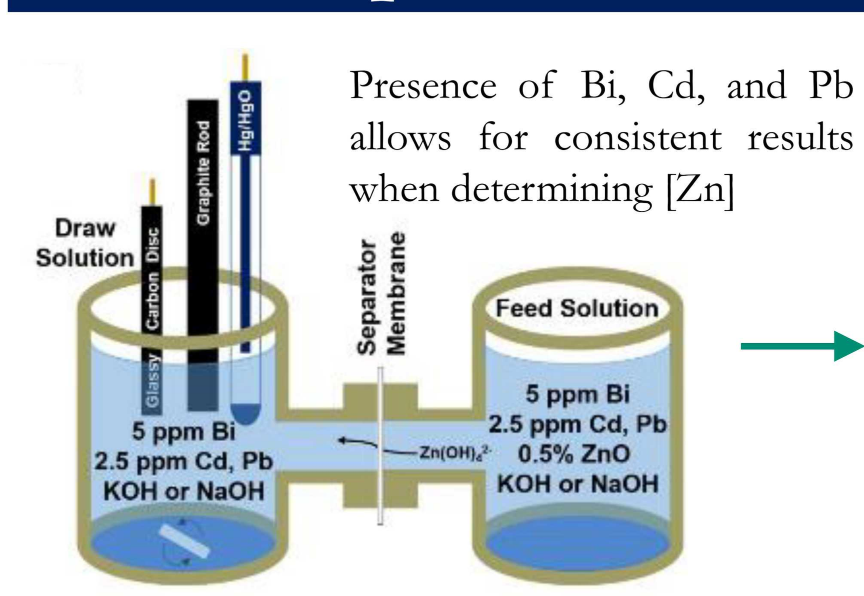
Caused by solubility of ZnO in KOH (as zincate, $Zn(OH)_4^{2-}$) and subsequent precipitation of ZnO and Zn

Restricting migration of zincate is key

Objectives

- **Fabricate and characterize a thin, flexible, scalable polymeric separator for alkaline zinc systems that selectively blocks zincate ions while allowing transport of hydroxide and cations**
- **Implement the separator into practical Zn/Ni cells cycled at high zinc utilization (≥ 20%) and demonstrate an improvement in performance compared to cells with commercial separators**

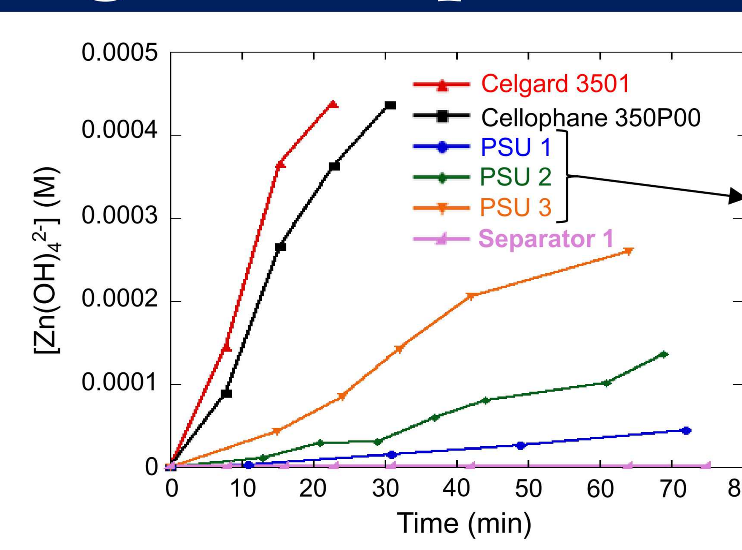
Separator Screening and Properties



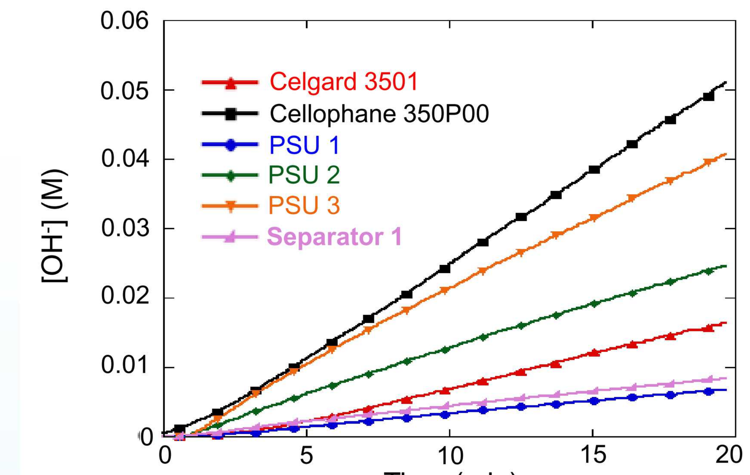
Presence of Bi, Cd, and Pb allows for consistent results when determining [Zn]

J. Duay, T.N. Lambert, R. Aidun, *Electroanalysis*, 29 (2017) 1-8. See also: Poster by D. Arnot *et al.* in this session.

Anodic stripping voltammetry (ASV) enables much faster screening of ion transport through separators compared to ICP-MS, with similar limits of detection and no need for dilution or pH modification.



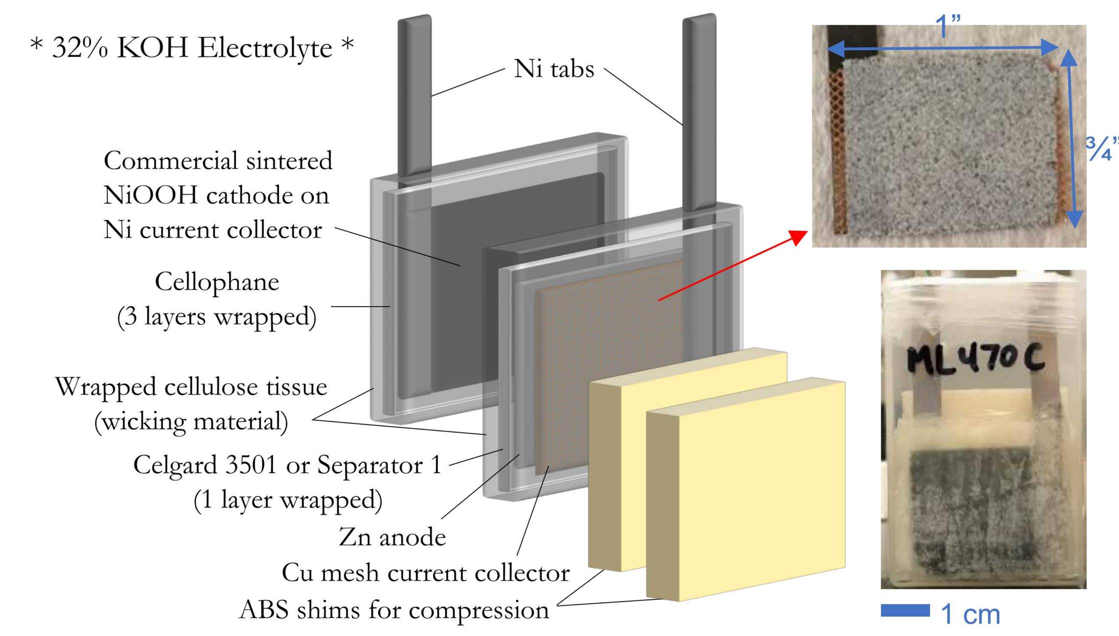
Functionalized polysulfone separators (see poster by I. Kolesnichenko *et al.* in this session)



Separator	Hydroxide Diffusivity (cm^2/min) *10^{-6}	Zincate Diffusivity (cm^2/min) *10^{-6}	Selectivity (D_{OH-}/D_{Zn})	Water Uptake (%)	Thickness (µm)	Conductivity (mS/cm)
Celgard 3501	6.7 ± 0.6	5.7 ± 0.8	1.2 ± 0.2	72 ± 5	25 ± 1	12 ± 1.2
Cellophane 350P00	17 ± 0.5	2.0 ± 0.8	8.5 ± 3.0	98 ± 3	25 ± 1	14 ± 1.4
Separator 1	**2.2 ± 1.4**	**≤ 0.0001[a]**	**≥ 8,000**	**10 ± 3**	**25 ± 1**	**1.7 ± 0.2**

[a] No zinc crossover measured; value is calculated from the limit of detection after 25 days.

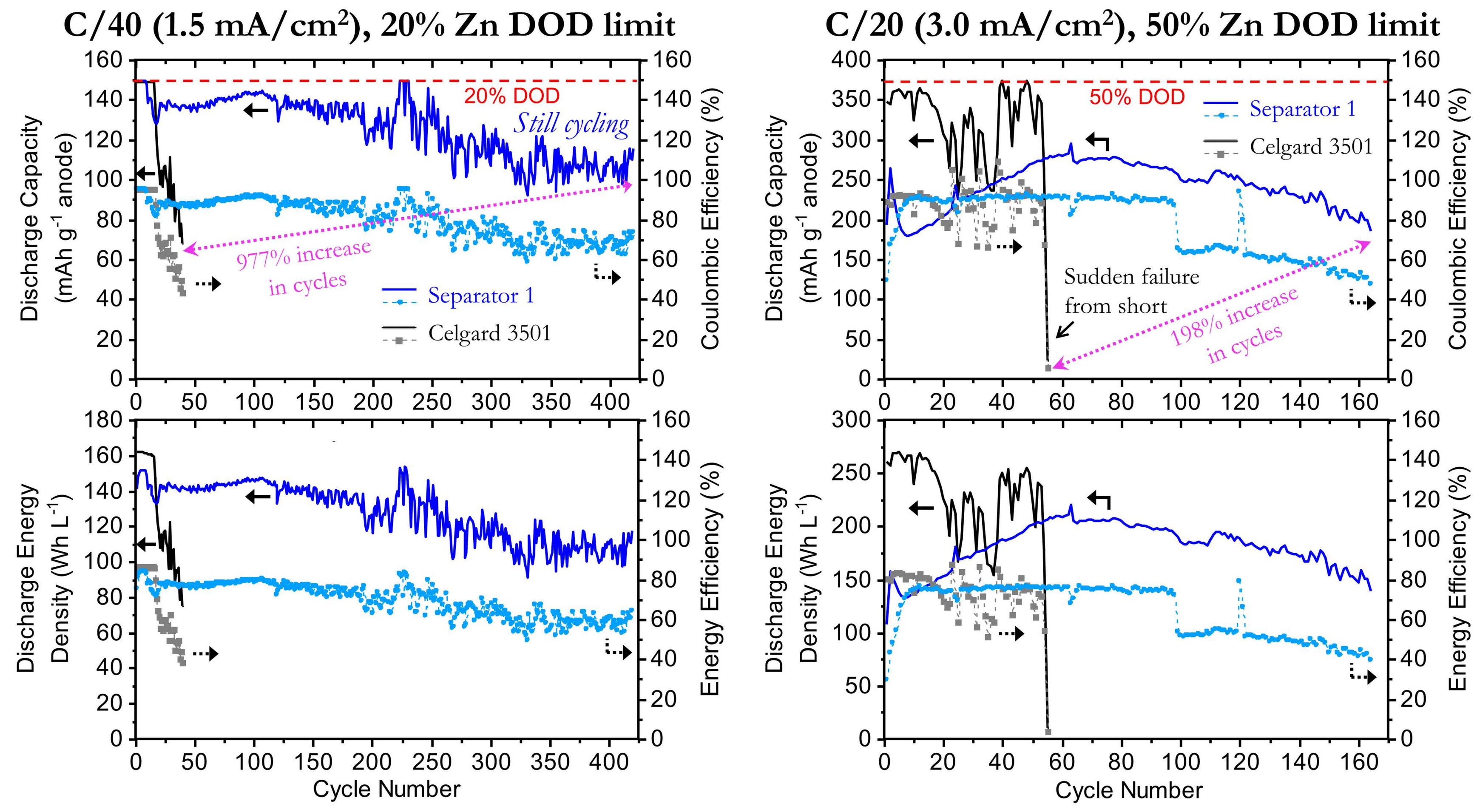
Zn/Ni Cell Assembly and Cycling



Scalable, powder-based anode formulation

83.1% Zn, 9.8% ZnO, 2.2% SDBS, 4.9% Teflon

Separator 1 has a thickness similar to COTS Celgard 3501 and is flexible, allowing the anode to be fully enclosed/wrapped without sacrificing pack volume

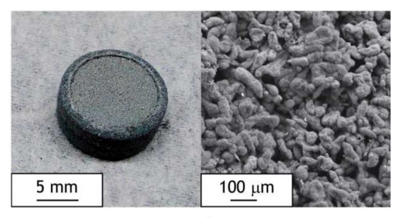


- At a 20% Zn DOD limit, Separator 1 mitigates rapid capacity fade, with the cell lasting 420+ cycles (and counting) while maintaining DOD >12%, average DOD of 16.9% (126 mAh/g_{anode}), and average energy density of 128 Wh/L (>100 Wh/L for 320 cycles).
- At a 50% DOD limit, Separator 1 stabilizes voltage behavior and prevents shorting from Zn growth that caused sudden failure in the controls, enabling much longer cycle life with a high average DOD of 32.4% (242 mAh/g_{anode}) and energy density of 180 Wh/L, despite initially showing lower capacity and energy due to the lower wettability of Separator 1.

Comparison to Literature

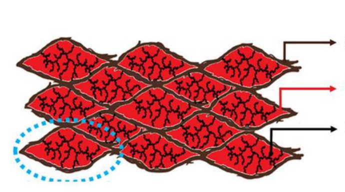
50% DOD cells with Separator 1 offer a high combination of cycle life, active material utilization, and areal capacity compared to other recent developments, along with less complex processing requirements.

- Parker et al., 2017
  - 3D Zn sponge
  - 111 cycles above 20% DOD (incl. 85 cycles at 40% DOD limit)
  - Anode capacity ~ 100 mAh/cm²



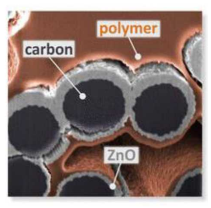
Science **356**, 415

- Yan et al., 2018
  - ZnO nanoparticles in "lasagna-like" GO matrix
  - 150 cycles with 82.2% avg. DOD
  - Anode capacity ~ 0.66 mAh/cm²



ACS Appl. Energy Mater. **1**, 6345

- Stock et al., 2018
  - C mesh/ZnO/anion-exchange ionomer core-shell structure
  - 67 cycles with 40.5% avg. DOD
  - Anode capacity ~ 5.7 mAh/cm²



ACS Appl. Energy Mater. **1**, 5579

- **This work**
  - **Scalable Zn/ZnO powder-based anode and flexible separator**
  - **164 cycles above 25% DOD with 32.4% avg. DOD**
  - **Anode capacity ~ 60 mAh/cm²**

Conclusions and Research Output

- Prepared flexible polymeric membranes that are effectively impervious to zincate, while maintaining hydroxide transport on par with commercial separators
- Zn/Ni cells with anodes wrapped in our separator show substantial cycle life improvement at high Zn utilization (≥20%) over cells with commercial separators only—*among the best performers in recent literature*
- Our separator mitigates the fundamental problems of Zn redistribution and shorting and can be easily adapted to any alkaline Zn battery
- Future studies to incorporate our separator into Zn/MnO_2 cells with **Bi/Cu-modified cathodes that can reversibly deliver the full 617 mAh/g capacity of MnO_2 → prevent or delay inactivation of MnO_2 by zincate**

Publication:

- DJ Arnot, MB Lim, NS Bell, RL Habing, IV Kolesnichenko, LS Ricketts, EI Ruiz, TN Lambert. *To be Submitted* (2020).

Presentation:

- DJ Arnot, IV Kolesnichenko, MB Lim, TN Lambert. "Permselective Separators for Grid Storage Alkaline Zn/MnO_2 Batteries." Poster, 2019 Annual AIChE Student Conference, Orlando, FL (Nov 11, 2019).

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