

# Polysulfone-Based Zincate-Blocking Separators for Zn-MnO<sub>2</sub> Batteries

Igor V. Kolesnichenko,<sup>1</sup> David J. Arnot,<sup>1</sup> Matthew B. Lim,<sup>2</sup> Gautam G. Yadav,<sup>3</sup> Michael Nyce,<sup>4</sup> Jinchao Huang,<sup>3</sup> Sanjoy Banerjee,<sup>3,4</sup> Timothy N. Lambert<sup>1\*</sup>

<sup>1</sup>Department of Photovoltaics and Materials Technology, Sandia National Laboratories, Albuquerque, New Mexico 87185-0734, USA

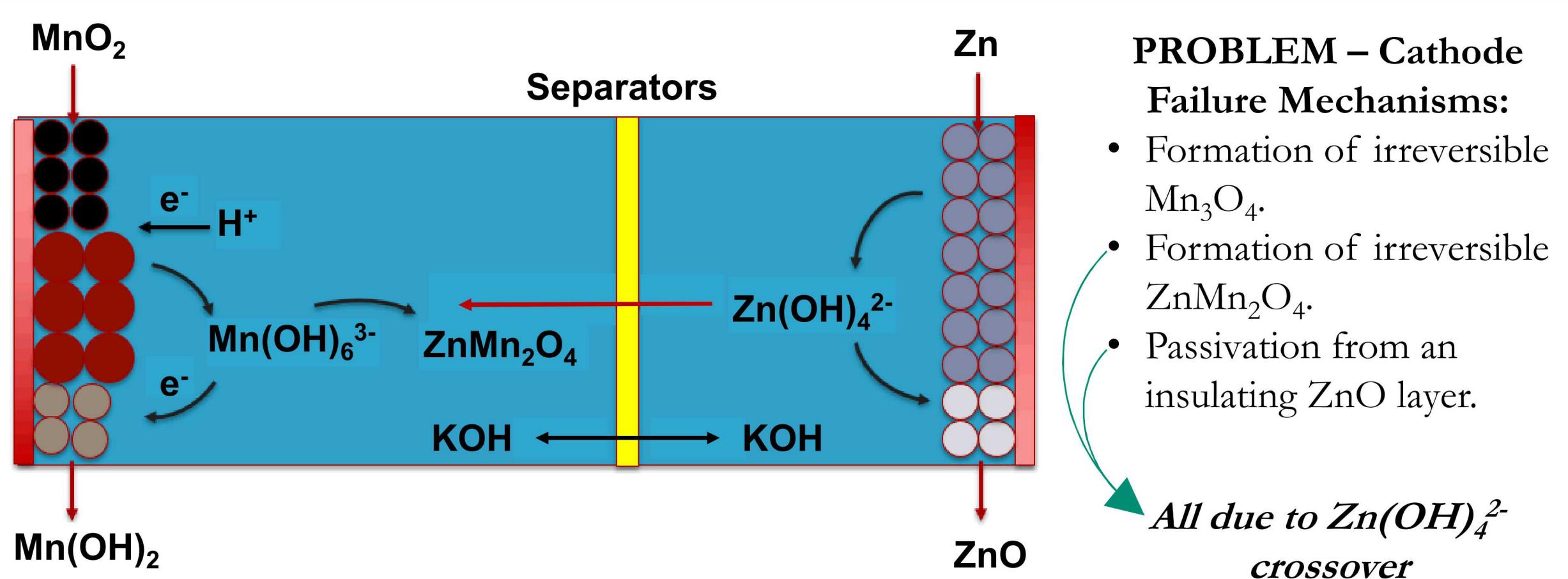
<sup>2</sup>Department of Energy Storage Technology and Systems, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

<sup>3</sup>Urban Electric Power, 401 N Middletown Rd, Pearl River, NY 10965, USA

<sup>4</sup>Department of Chemical Engineering, The CUNY Energy Institute at the City College of New York, Steinman Hall, 140<sup>th</sup> Street and 160 Convent Avenue, Room 316, New York, New York 10031, USA

\*Email: [tnlambe@sandia.gov](mailto:tnlambe@sandia.gov)

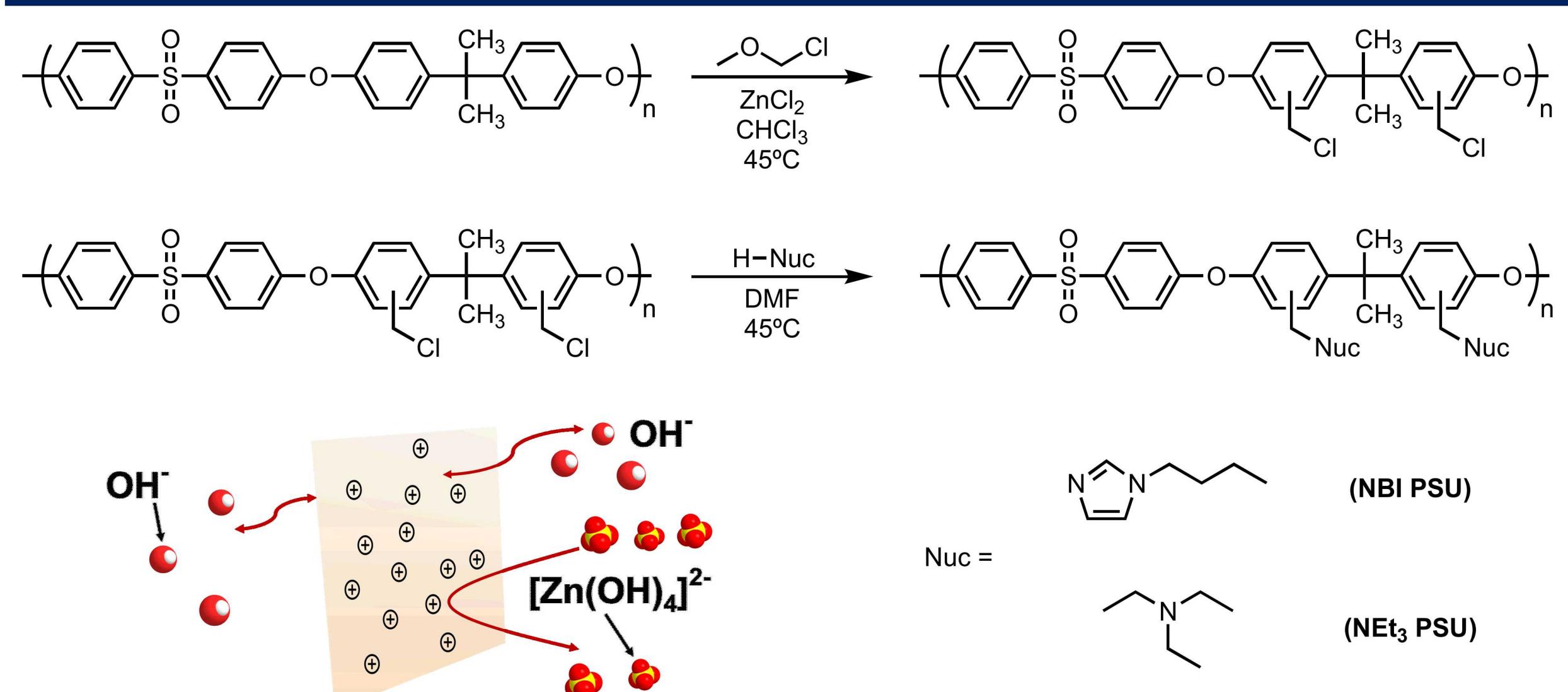
## Background and Objectives



### Objectives:

- Zn batteries are one of the core DOE-OE technologies – they are part of the push for resilient and safe energy storage
- Synthesize separators selective for blocking zincate, while allowing for crossover of hydroxide
- Cast membranes with thicknesses similar to those of commercial separators and establish the aforementioned selectivity outside of cells
- Implement into prototype cells and demonstrate an improvement in battery performance

## Polymer Synthesis/Membrane Fabrication



Synthesized polymers were blended with unmodified polysulfone (PSU) to lower the effective functional group content and study the relationship between functionalization and diffusion/selectivity. The unblended polymers were named 100-xxx PSU, the 1:1 blends 50-xxx PSU, and the 3:1 (unfunctionalized:functionalized) were labeled 25-xxx PSU.

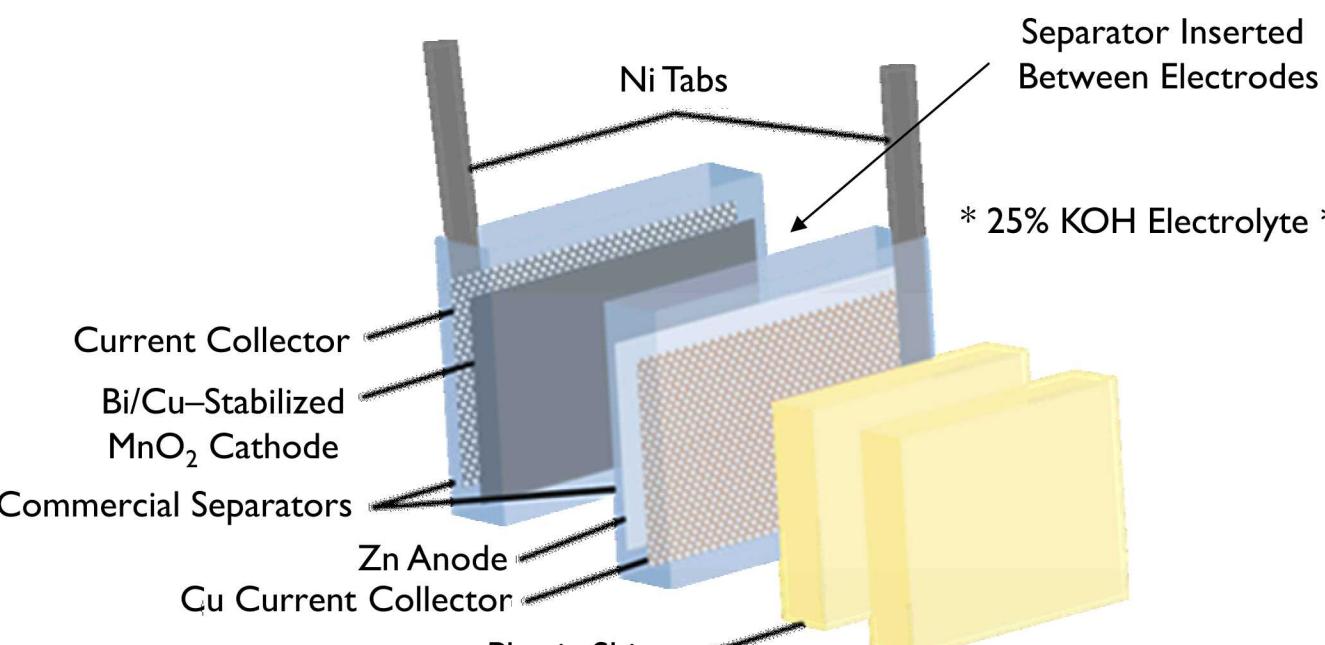
Separator	Hydroxide Diffusion Coefficient (cm <sup>2</sup> /min) *10 <sup>-6</sup>	Zincate Diffusion Coefficient (cm <sup>2</sup> /min) *10 <sup>-6</sup>	Selectivity R <sub>s</sub>	Water Uptake (%)	Thickness (μm) <sup>a</sup>	Conductivity (mS/cm)	Functionalization (groups/repeat unit) <sup>b</sup>
Celgard 3501	6.7 ± 0.6	5.7 ± 0.8	1.2 ± 0.2	72 ± 5	25 ± 1	12 ± 1.2	N/A
Cellophane 350P00	17 ± 0.5	2.0 ± 0.8	8.5 ± 3	98 ± 3	25 ± 1	14 ± 1.4	N/A
100-NEt <sub>3</sub> PSU	24 ± 4	1.4 ± 0.6	17 ± 8	76 ± 20	30 ± 5	7.4 ± 0.5	0.96
50-NEt <sub>3</sub> PSU	8.6 ± 0.1	0.34 ± 0.1	25 ± 7	37 ± 13	30 ± 5	4.3 ± 0.8	0.48
25-NEt <sub>3</sub> PSU	0.27 ± 0.07	0.019 ± 0.003	14 ± 4	15 ± 2	30 ± 5	0.91 ± 0.09	0.24
100-NBI PSU	15 ± 0.2	0.42 ± 0.02	36 ± 2	54 ± 9	30 ± 5	9.0 ± 1.4	0.98
50-NBI PSU	9.4 ± 0.1	0.17 ± 0.04	55 ± 10	26 ± 8	30 ± 5	7.2 ± 1.9	0.49
25-NBI PSU	2.5 ± 0.1	0.049 ± 0.002	51 ± 3	13 ± 3	30 ± 5	5.8 ± 0.4	0.25

All synthesized polymers show a better selectivity ratio for hydroxide diffusion over zincate than commercial separators, with the 50-NBI PSU demonstrating a 45-fold improvement over Celgard. Aside from 25-NEt<sub>3</sub> PSU, the water uptake and conductivity values also remain in a same range, suggesting a likely overall improvement in battery cycle life.

## Acknowledgements

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## Battery Assembly and Cycling

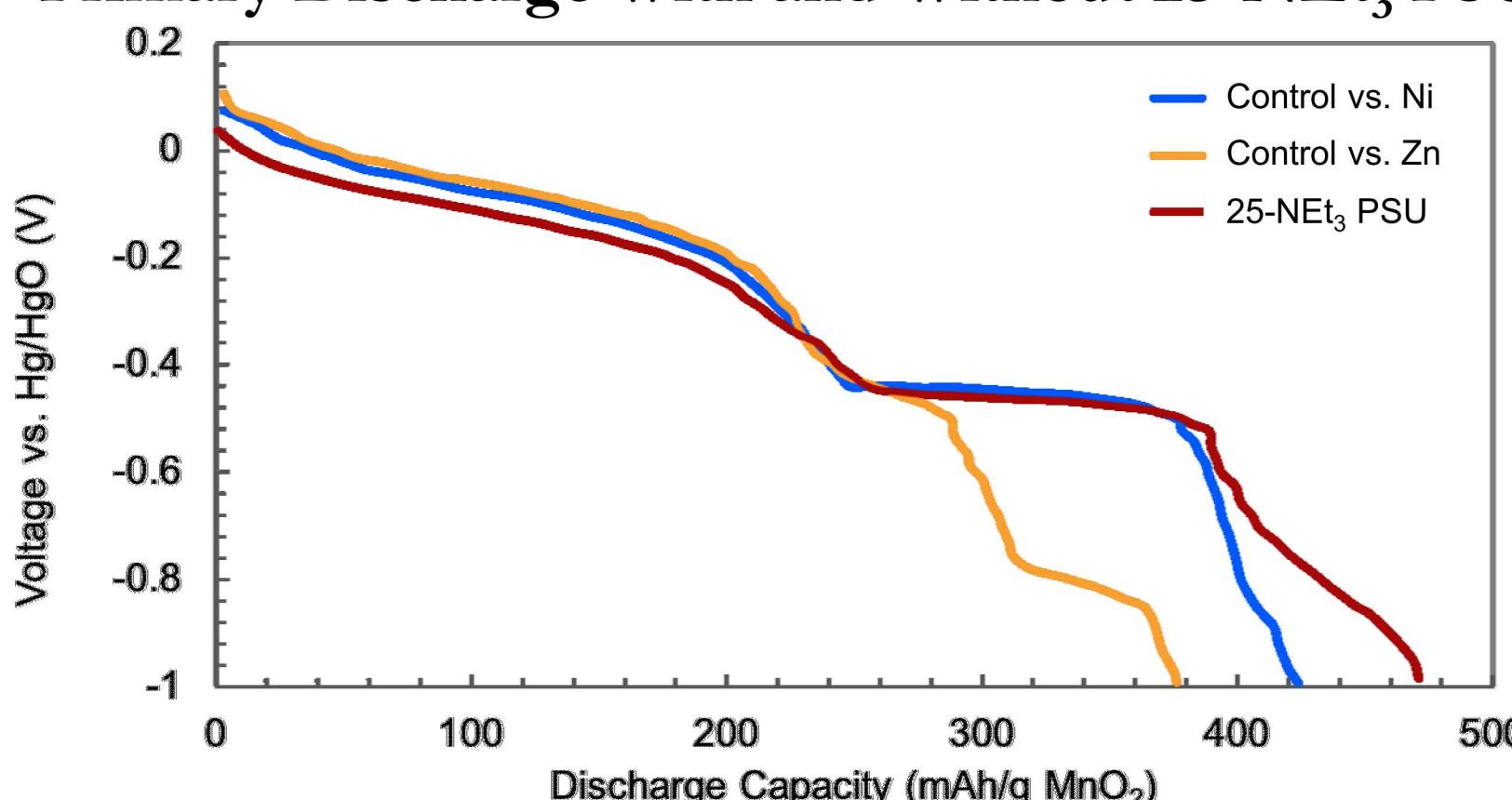


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Secondary control cells were assembled by wrapping both the anode and cathode in 3 layers of Cellophane, while the secondary cells containing 50-NBI PSU were assembled by wrapping only the anode in 3 layers of Cellophane, inserting 50-NBI PSU between the electrodes (as shown to the left) and using the cathode as received from CUNY, with no additional wrapping.

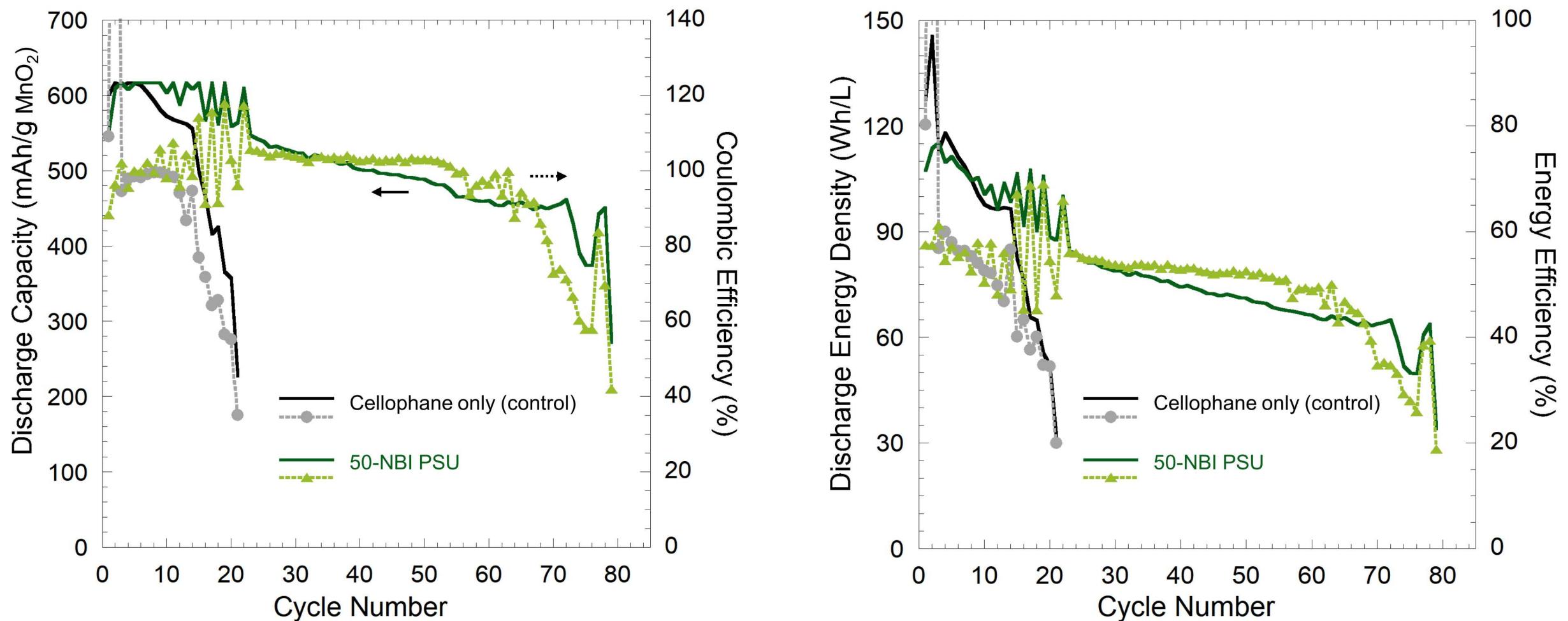
The primary discharge cell with 25-NEt<sub>3</sub> PSU was assembled similarly to the 50-NBI PSU-containing one, but instead of inserting the separator between electrodes it was used to wrap the cathode.

### Primary Discharge With and Without 25-NEt<sub>3</sub> PSU



Discharge of MnO<sub>2</sub> in the absence of Zn (using a Ni anode) reveals a large plateau near -0.4 V, corresponding to the 2<sup>nd</sup> e<sup>-</sup> of the cathode. When the 25-NEt<sub>3</sub> PSU separator is implemented into the Zn system this effect is observed due to zincate blocking, along with a much higher discharge capacity.

### C/10 Cycling of Cells With and Without 50-NBI PSU



The above C/10 cycling data demonstrates a cell lifetime enhancement from 21 cycles when using only Cellophane as a separator to 79 cycles when using 50-NBI PSU.

### Future Goal:

Continue improvement of selectivity for hydroxide permeability over zincate, while maintaining similar water uptake and conductivity numbers to those of Celgard and Cellophane to enhance cell capacities and cycle lives.

## Conclusions and Research Output

- Prepared flexible polymeric membranes that are more selective than commercial separators for hydroxide over zincate crossover
- Primary discharge of Zn-MnO<sub>2</sub> cell containing 25-NEt<sub>3</sub> PSU demonstrates a much higher capacity than that of a cell without our membrane due to blocking zincate
- C/10 cycling data from Zn-MnO<sub>2</sub> cells containing 50-NBI PSU membrane shows a 4-fold improvement in cycle life over cells using commercial separators

### Publications

- Kolesnichenko, I. V.; Arnot, D. A.; Lim, M. B.; Yadav, G. G.; Nyce, M.; Huang, J.; Banerjee, S.; Lambert, T. N. "Zincate-Blocking Functionalized Polysulfone Separators for Secondary Zn-MnO<sub>2</sub> Batteries" *submitted to ACS Applied Materials and Interfaces*
- Arnot, D. A.; Lim, M. B.; Kolesnichenko, I. V.; Lambert, T. N. "Development of Zincate-Blocking Separators and Their Application in Zinc-Manganese Oxide Batteries" *in final preparation*