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Ion-Selective Polysulfone Separators for Alkaline Zn-MnO$_2$ Batteries

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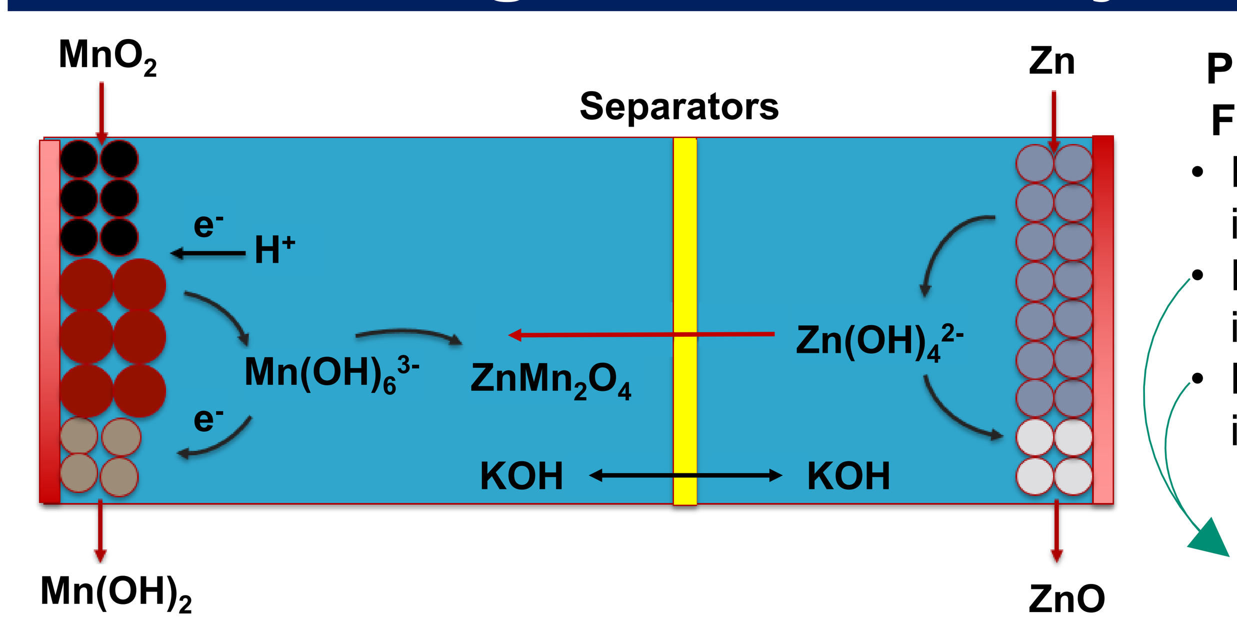
Background and Objectives



PROBLEM – Cathode Failure Mechanisms:

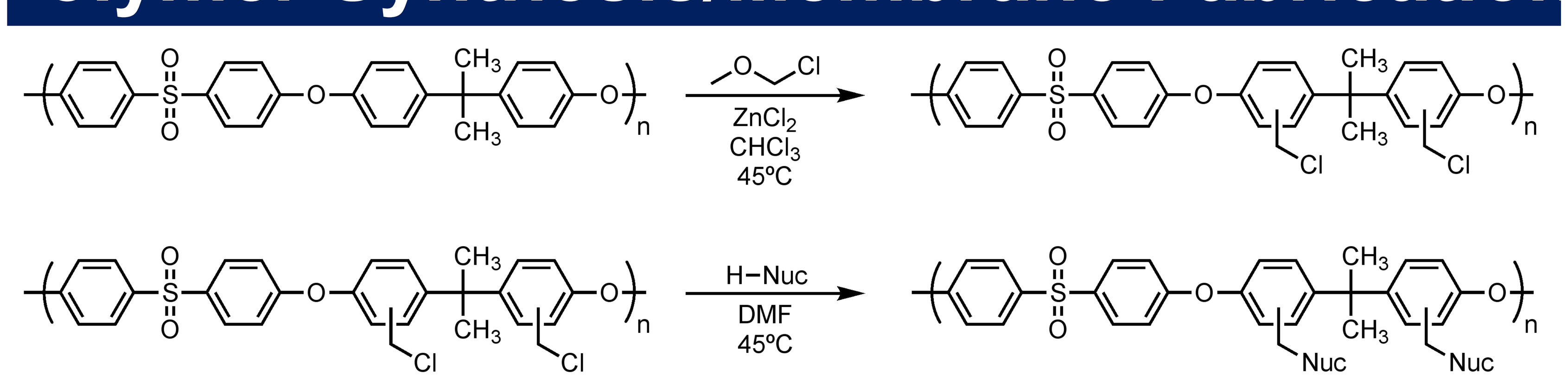
- Formation of irreversible Mn$_3$O$_4$.
- Formation of irreversible ZnMn$_2$O$_4$.
- Passivation from an insulating ZnO layer.

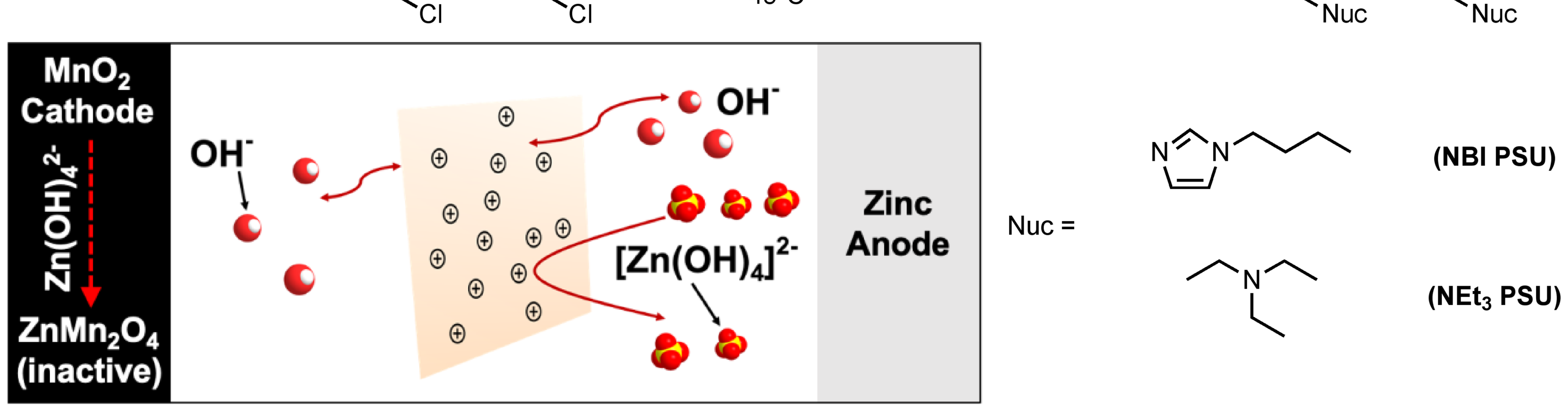
All due to Zn(OH)$_4^{2-}$ crossover

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^2/min) *10^{-6}	Zincate Diffusion Coefficient (cm^2/min) *10^{-6}	Selectivity R_s	Water Uptake (%)	Thickness (μm)^a	Conductivity (mS/cm)	Functionalization (groups/repeat unit)^b
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$_3$ PSU	24 ± 4	1.4 ± 0.6	17 ± 8	76 ± 20	30 ± 5	7.4 ± 0.5	0.96
50-NEt$_3$ PSU	8.6 ± 0.1	0.34 ± 0.1	25 ± 7	37 ± 13	30 ± 5	4.3 ± 0.8	0.48
25-NEt$_3$ 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$_3$ 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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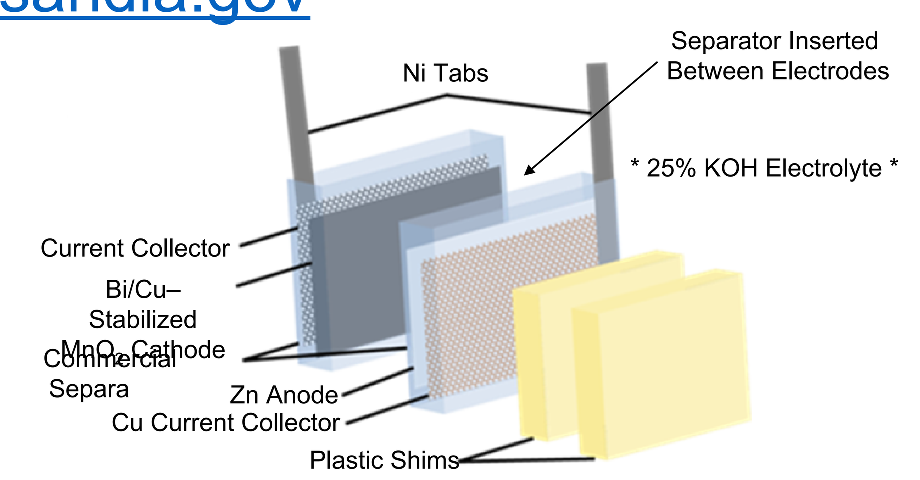
Battery Assembly and Cycling



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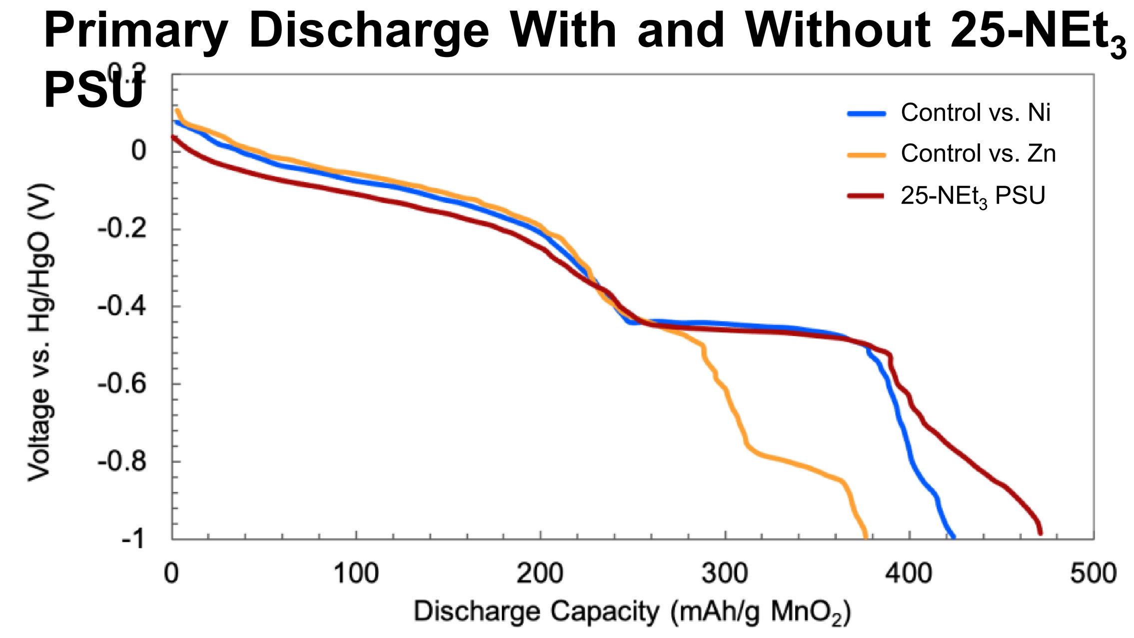
Secondary control cells were assembled by wrapping both the anode and cathode in 3 layers of Cellophane, while the secondary cells containing 50-NBI PSU were assembled by wrapping only the anode in 3 layers of Cellophane, inserting 50-NBI PSU between the electrodes (as shown to the left) and using the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

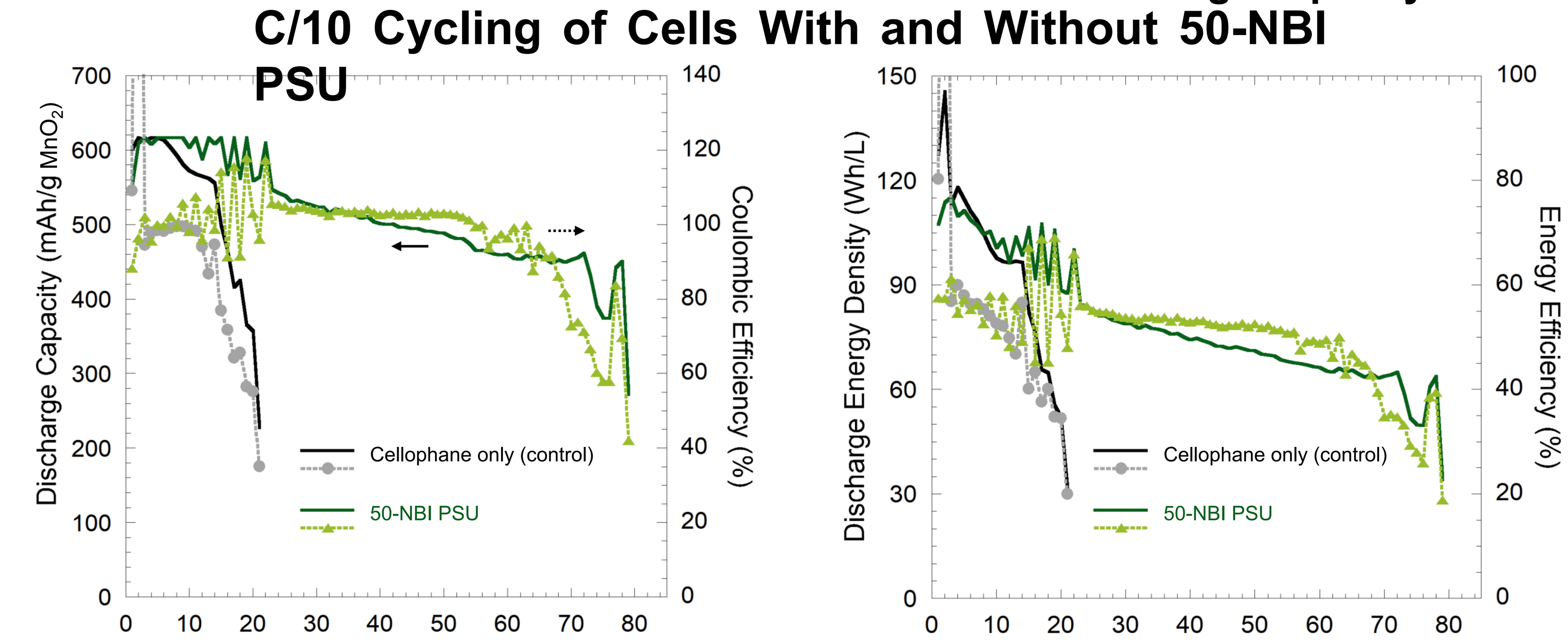
The primary discharge cell with 25-NEt$_3$ PSU was assembled similarly to the 50-NBI PSU-containing one, but instead of inserting the separator between electrodes it was used to wrap the cathode.

Primary Discharge With and Without 25-NEt$_3$ PSU



Discharge of MnO$_2$ in the absence of Zn (using a Ni anode) reveals a large plateau near -0.4 V, corresponding to the 2nd e⁻ of the cathode. When the 25-NEt$_3$ 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$_2$ cell containing 25-NEt$_3$ 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$_2$ 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-MnO2 Batteries" *ACS Appl. Mater. Interfaces*, **2020**, *12*, 50406-50417.
- 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*

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