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Zincate-Blocking Polymeric Separators for Zn/MnO_2 Batteries

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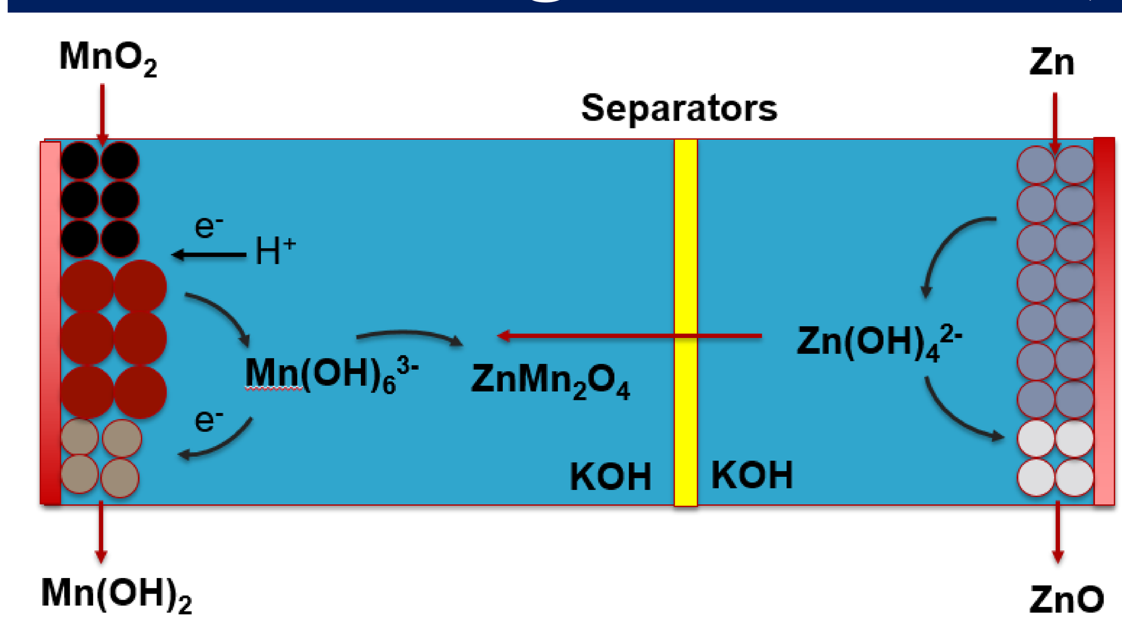
Background and Objectives



Cathode Failure Mechanisms:

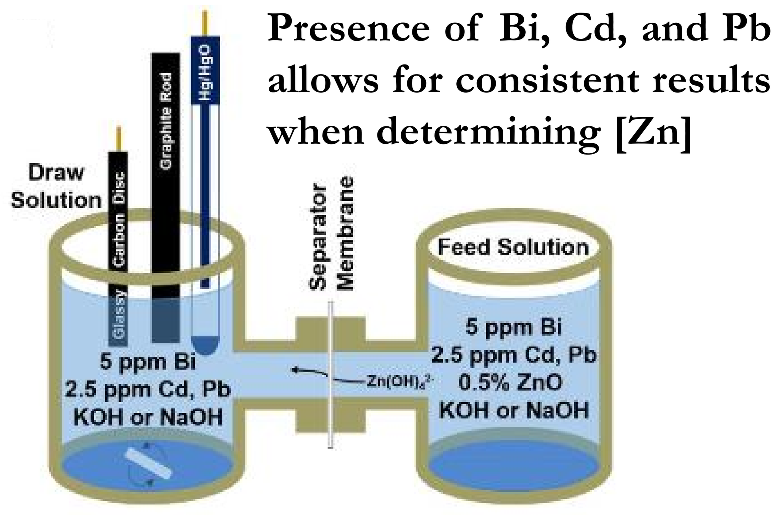
- Formation of irreversible Mn_3O_4.
- Formation of irreversible $ZnMn_2O_4$.
- Passivation from an insulating ZnO layer.

Caused by $Zn(OH)_4^{2-}$ crossover

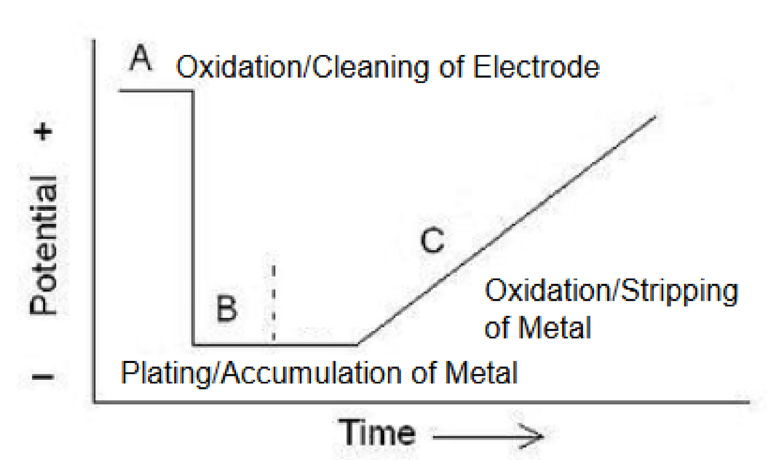
Objectives:

- 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

Zinc Diffusion Analysis



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



A. J. Bard, L. R. Faulkner, Electrochemical Methods, (2001) 458–466.

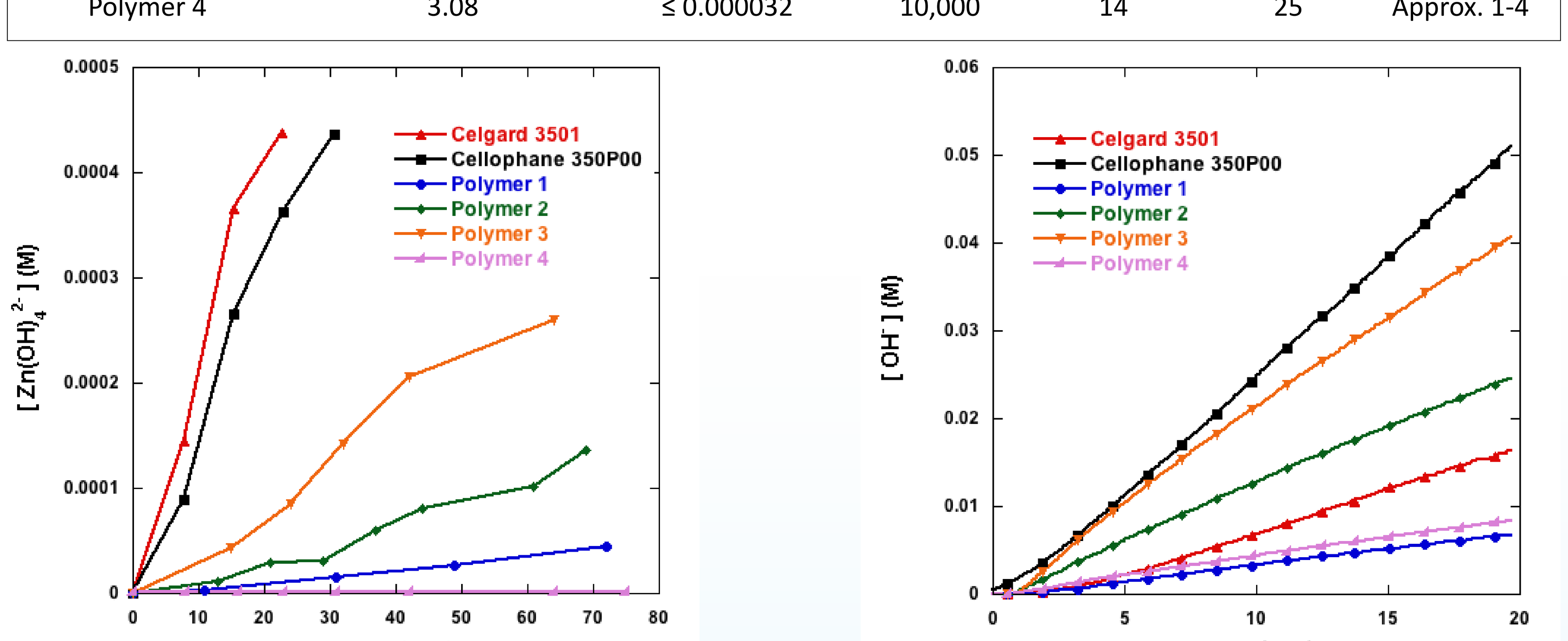
Anodic stripping voltammetry (ASV) allows for much faster screening of separators compared to ICP-MS, with similar limits of detection.

ASV Analysis of Zn performed for the first time in alkaline conditions.

J. Duay, T.N. Lambert, R. Aidun, *Electroanalysis,* 29 (2017) 1-8.

Polymeric Separators

Separator	Hydroxide Diffusion Coefficient (cm²/min) *10⁻⁶	Zincate Diffusion Coefficient (cm²/min) *10⁻⁶	Selectivity	Water Uptake (%)	Thickness (µm)	Conductivity (mS/cm)
Celgard 3501	6.74	5.7	1.18	68	25	12.2
Cellophane 350P00	17.4	2.0	8.70	96	25	13.8
Polymer 1	2.48	0.049	50.6	11	30	5.83
Polymer 2	9.43	0.17	55.5	17	30	7.19
Polymer 3	15.4	0.42	36.7	47	30	8.79
Polymer 4	3.08	≤ 0.000032	10,000	14	25	Approx. 1-4

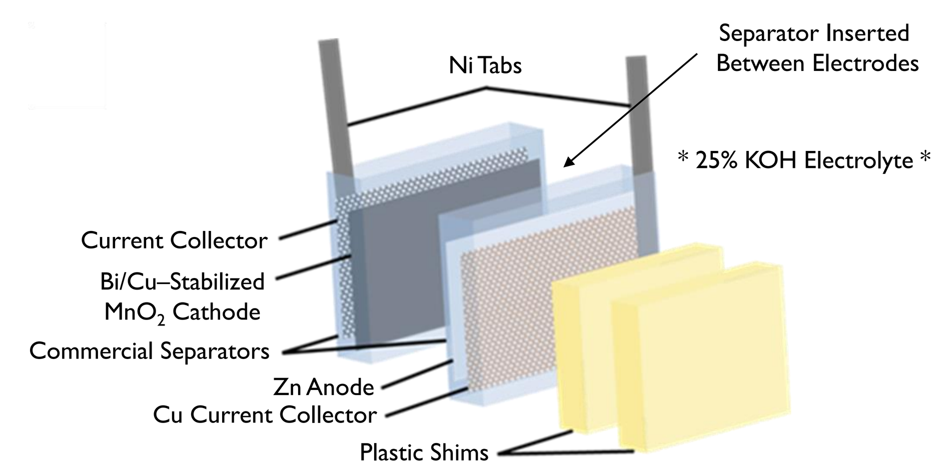


Polymers 1-3 show a greatly improved selectivity ratio over commercial separators for screening out zincate, while allowing for hydroxide crossover. Polymer 4 has an even higher selectivity ratio, but is also far less conductive, resulting in lower practical cycling rates.

Future Goal:

Attain a selectivity ratio on par with Polymer 4, while retaining a conductivity similar to those of commercial separators

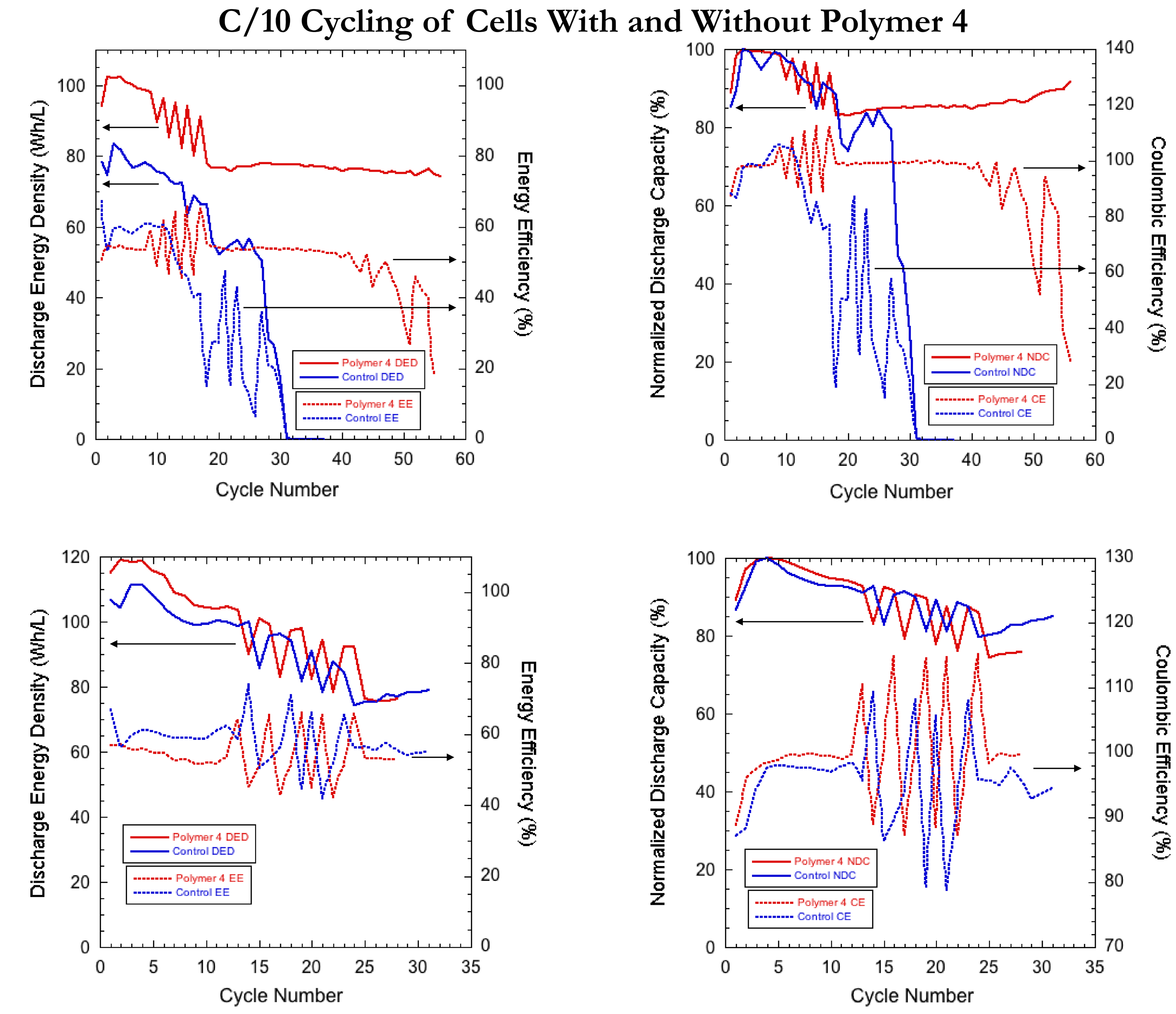
Battery Assembly and Cycling



Journal of Power Sources, 395 (**2018**) 430-438

Control cells are assembled by wrapping both the anode and cathode in 3 layers of Cellophane, while the cells containing Polymer 4 are assembled by wrapping only the anode in 3 layers of Cellophane, inserting Polymer 4 between the electrodes (as shown to the left) and using the cathode as received from CUNY, with no additional wrapping.

C/10 Cycling of Cells With and Without Polymer 4



Conclusions and Research Output

- Prepared flexible polymeric membranes that are resistant to zincate, while maintaining hydroxide permeability on par with commercial separators
- Conductivity constraints limit the rates at which functional batteries containing the fabricated separators can be cycled → **Need to improve upon conductivity**
- Preliminary data from Zn–MnO_2 cells shows cycling at C/10 rates that is on par with cells using commercial separators

Publications

- Kolesnichenko, I. V.; Arnot, D. A.; Lim, M. B.; Lambert, T. N. "Zincate–Blocking Functionalized Separators for Secondary Zn/MnO_2 Batteries" *in final preparation*
- 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 preparation*

Acknowledgements

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