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# Evaluation of a Ceramic Separator for use in Rechargeable Alkaline $Zn/MnO_2$ Batteries

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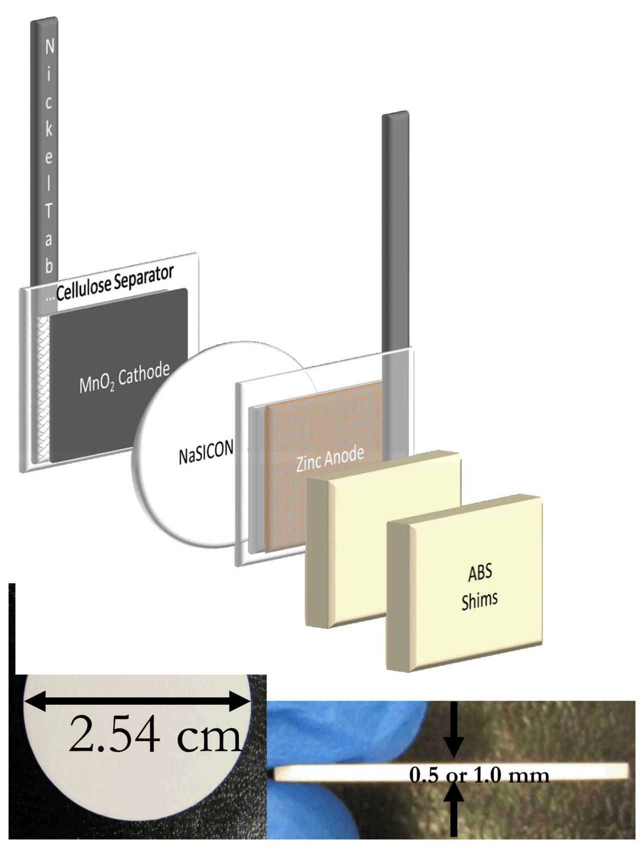
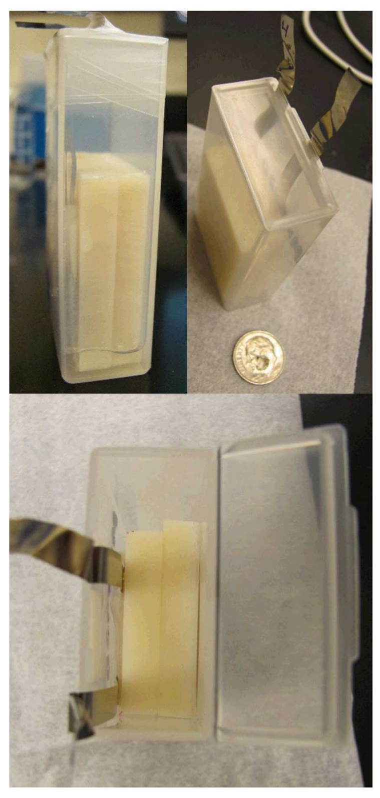
**ABSTRACT:** Rechargeable $Zn/MnO_2$ alkaline batteries are a promising technology for grid storage applications. Here, a commercial ceramic sodium ion conductor which is impervious to zincate [$Zn(OH)_4^{2-}$] a contributor to $MnO_2$ cathode failure, is evaluated as the battery separator. Reducing the thickness of the ceramic conductor to 0.5 mm by mechanical means provided a lower total resistance of 9.8 Ω. Analytical measurements failed to measure any $Zn(OH)_4^{2-}$ transport. For a 5% DOD at a C/5 rate, the cycle lifetime was increased by over 22% using the thinned ceramic separator compared to traditional Celgard and cellophane separators. Experiments showed limited amounts of zinc species on the cathode utilizing the ceramic separator, consistent with its prevention of $Zn(OH)_4^{2-}$ transport through the separator.

## Battery Assembly



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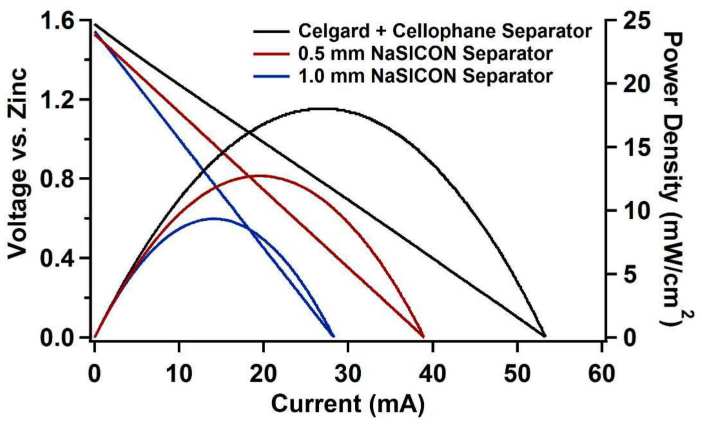
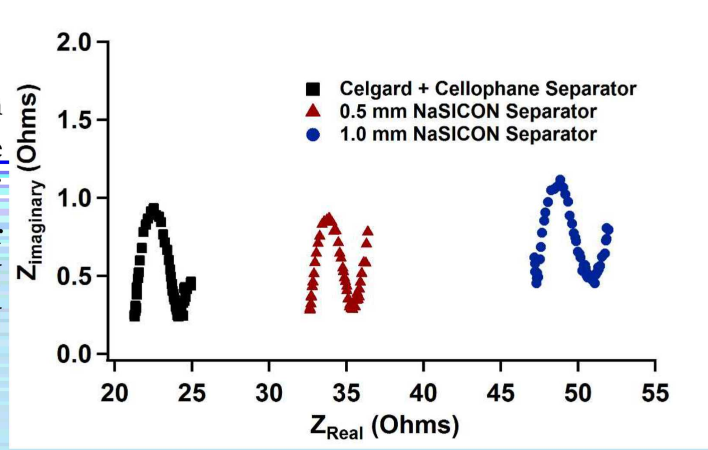
## Resistivity/Conductivity of NaSICON




Polarization and power curves of $Zn/MnO_2$ cells utilizing either a 0.5 mm NaSICON membrane, 1.0 mm NaSICON membrane separator or no separator

Nyquist plot obtained from electrochemical impedance spectroscopy (EIS) of $Zn/MnO_2$ cells utilizing either a 0.5 mm NaSICON membrane, 1.0 mm NaSICON membrane, or no separator




| | | From Polarization Curves | | From EIS | | |
|---|---|---|---|---|---|---|
| | Thickness (mm) | Resistance (Ω) | Conductivity (mS $cm^{-1}$) | Resistance (Ω) | Conductivity (mS $cm^{-1}$) | Zinc Diffusion Coefficient ($cm^2$ $min^{-1}$) |
| Celgard 3501 | 0.025 | N/A* | N/A* | 0.1 | 10.7 | $1.18 \times 10^{-6}$ |
| Cellophane 350P00 | 0.025 | N/A* | N/A* | 0.2 | 21.4 | $7.23 \times 10^{-7}$ |
| 0.5 mm NaSICON | 0.500 | 10.9 | 4.36 | 9.8 | 3.9 | $<5.12 \times 10^{-9}$ |
| 1.0 mm NaSICON | 1.060 | 25.8 | 3.58 | 25.3 | 3.5 | $<5.12 \times 10^{-9}$ |

**Resistance measurement results from polarization and EIS experiments as well as Zn diffusion coefficients from ICP-MS**

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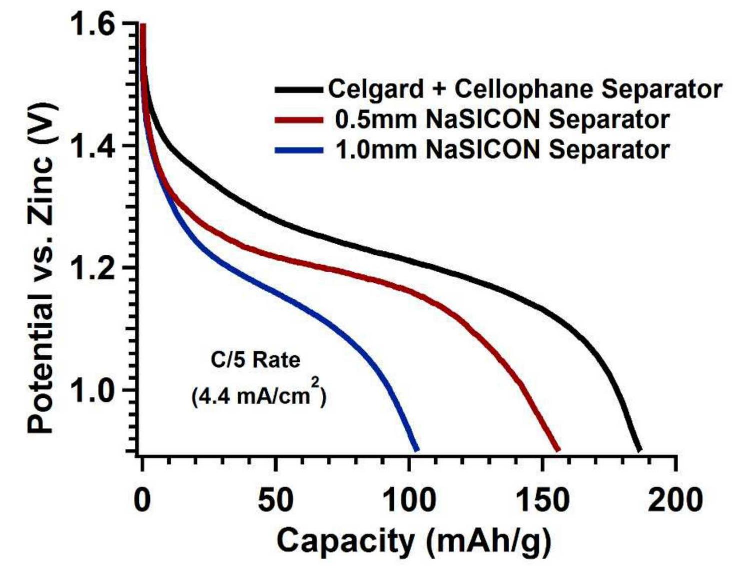
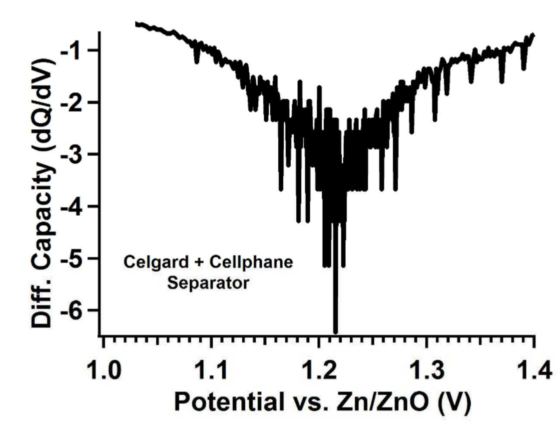
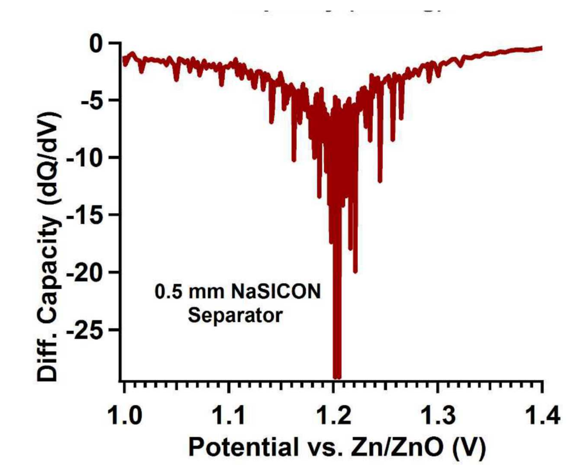
## Electrochemistry

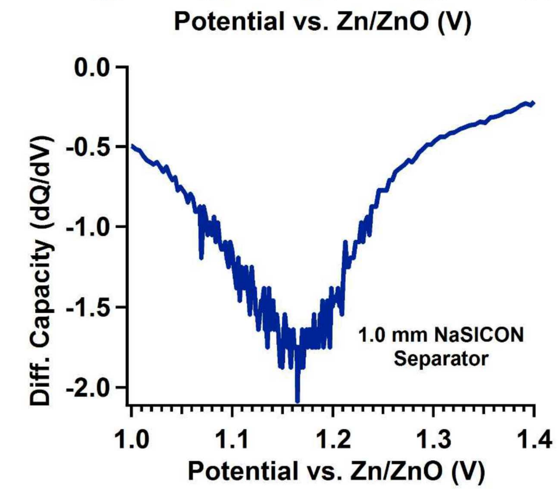


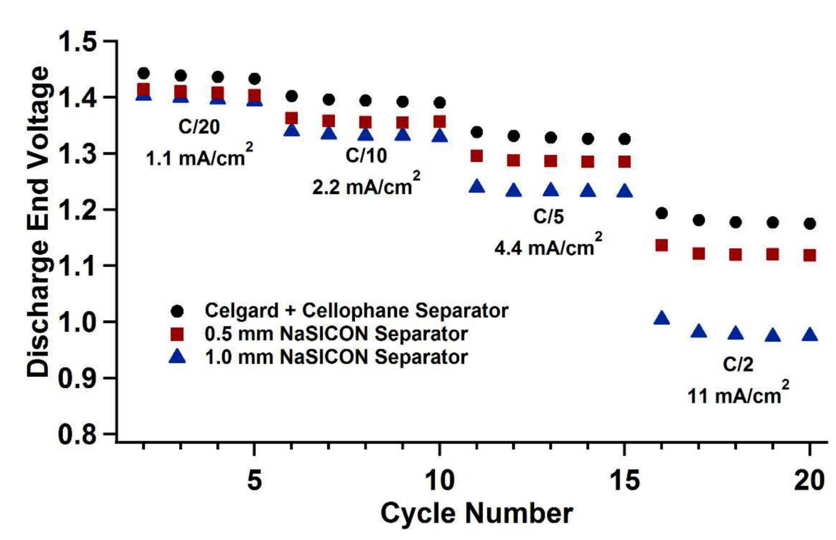

Discharge curves of a $Zn/MnO_2$ cell utilizing a Celgard + Cellophane layered separator, 0.5 mm NaSICON separator, or a 1.0 mm NaSICON separator.

Differential capacity curves for the discharge curves found above



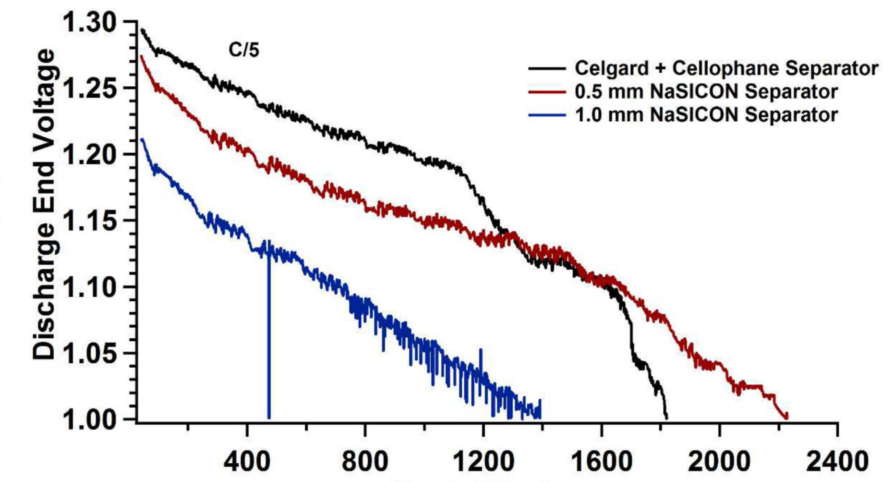




Discharge end voltage of cells cycled at 5% DOD at different discharge rates for a Celgard + Cellophane, 0.5 mm NaSICON, and 1.0 NaSICON cell.

Discharge end voltage versus cycle number for cells discharged at a C/5 rate at 5% DOD for a Celgard + Cellophane, 0.5 mm NaSICON, and 1.0 mm NaSICON cell.

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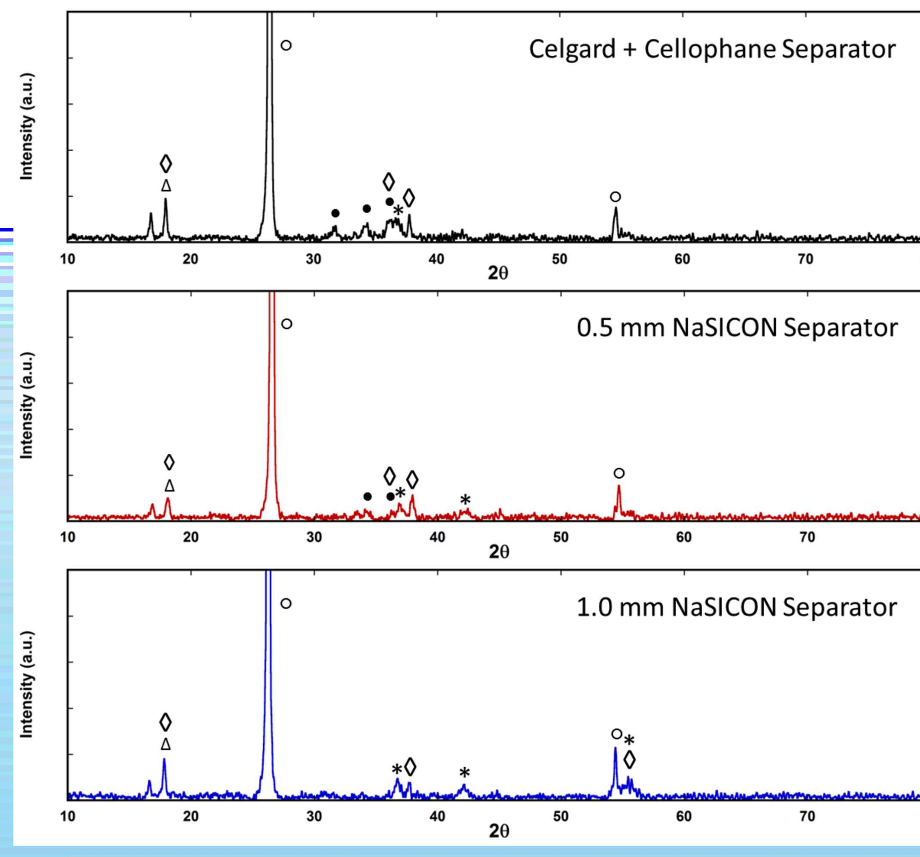
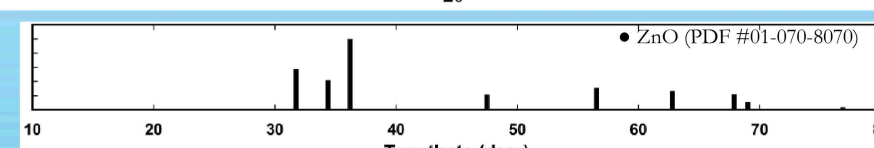
## Post-Mortem Analysis

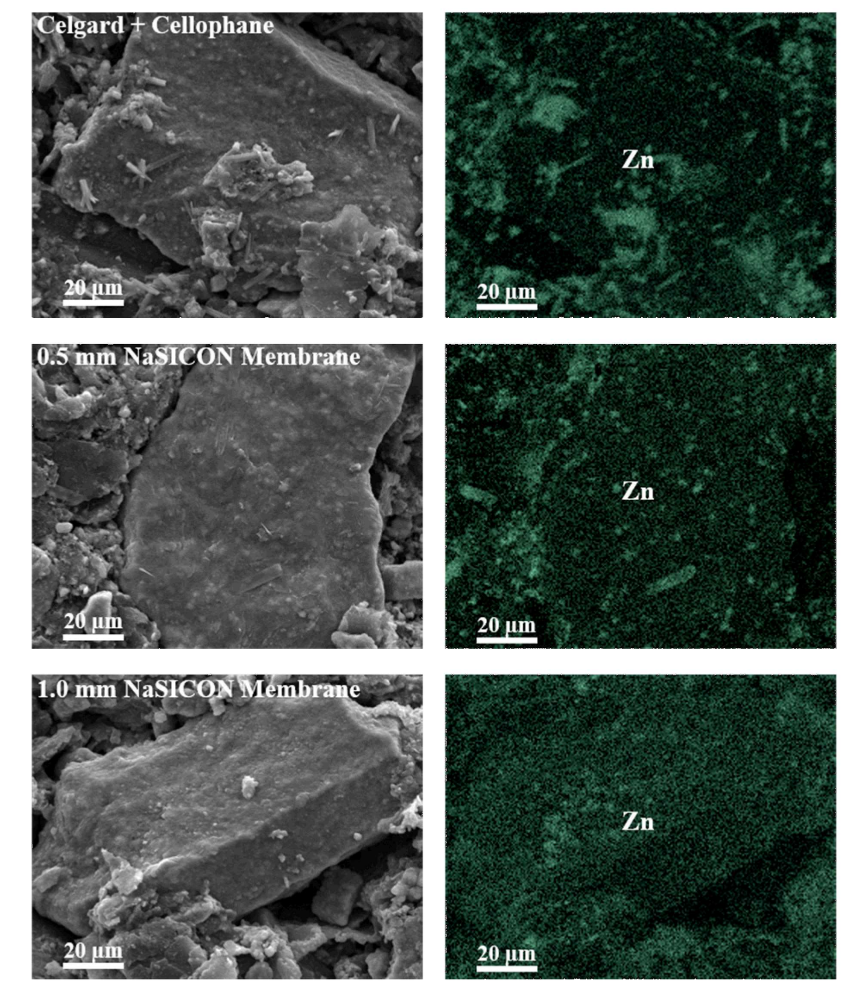



XRD spectra of EMD cathodes cycled to failure utilizing Celgard + Cellophane layered, 0.5 mm NaSICON, and 1.0 mm NaSICON membranes.




Peaks for ZnO (PDF #01-070-8070)

## Post-Mortem (cont'd)

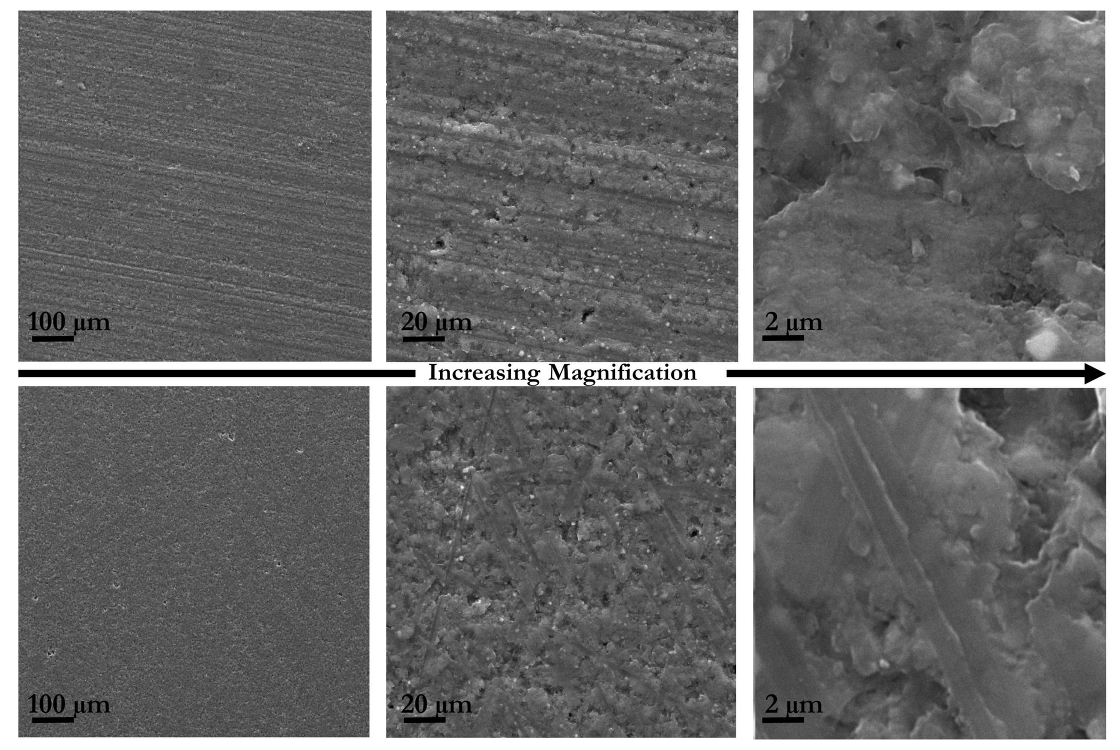



| Element | Atomic % |
|---|---|
| C K | 29.1 |
| F K | 5.3 |
| Mn K | 17.0 |
| Na K | 3.14 |
| O K | 36.1 |
| Zn K | 9.3 |

| Element | Atomic % |
|---|---|
| C K | 27.0 |
| F K | 5.33 |
| Mn K | 16.6 |
| Na K | 2.4 |
| O K | 43.7 |
| Zn K | 4.2 |

| Element | Atomic % |
|---|---|
| C K | 33.1 |
| F K | 4.9 |
| Mn K | 20.6 |
| Na K | 2.5 |
| O K | 24.5 |
| Zn K | 1.4 |

**(LEFT) SEM image of EMD cathode after cycling with Celgard + Cellophane separator, 0.5 mm NaSICON membrane, or 1.0 mm NaSICON membrane. EDX mapping Zn for EMD cathode on left. EDX survey for the atomic % of elements found in EDX mass.**




**SEM images of a pristine NaSICON disc and NaSICON membrane cycled in 30% NaOH with increasing magnification from left to right**

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## Conclusion

This work suggests that a decrease in the NaSICON membrane thickness (and hence resistance) will make this work more practical. However further decrease in NaSICON membrane thickness will result in brittle membranes that may break at low stress levels. Thus a new research space is needed that can focus on hybrid materials that incorporate NaSICON or a ceramic analogue with soft flexible materials that can be reduced to thicknesses/resistance values necessitated by $Zn/MnO_2$ batteries for grid storage and still impede the transport of $Zn(OH)_4^{2-}$.

## Acknowledgements

Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability is thanked for his financial support of this project. The authors also thank Dr. Erik Spoerke for the procurement of the NaSICON discs, Dr. Eric Allcorn for help with the design and 3D-Printing of the H-cell, and Alice Kilgore for mechanically thinning the NaSICON discs used here.

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