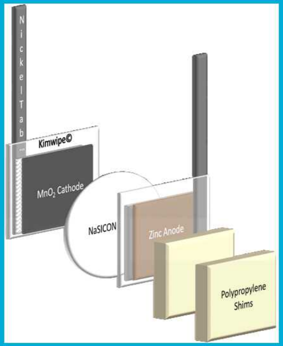
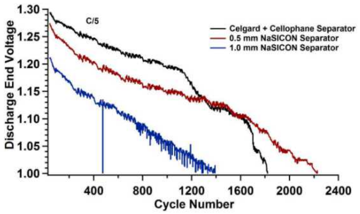
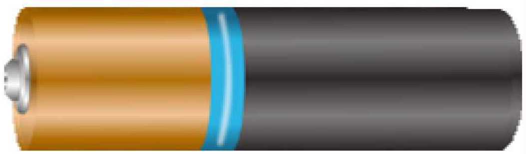
SAND2018-6979C

Evaluation of a Ceramic Separator for Use in Rechargeable Alkaline Zn/MnO_2 Batteries







PRESENTED BY

Jonathon Duay, Timothy Lambert, and Maria Kelly

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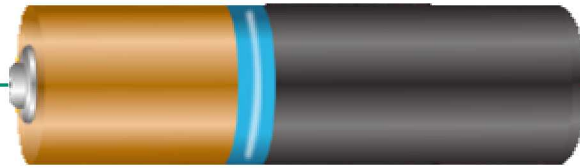
Rechargeable Alkaline Zn-MnO_2 Batteries

Zn-MnO_2



MnO_2

- ~ $1-2 per lb
- Mn, 12th most abundant
- 16,000,000 tons (2012)
- Safe

KOH

- Potash ~ $260 per ton
- Abundant
- Aqueous
- > Safety than Li-org

Zn

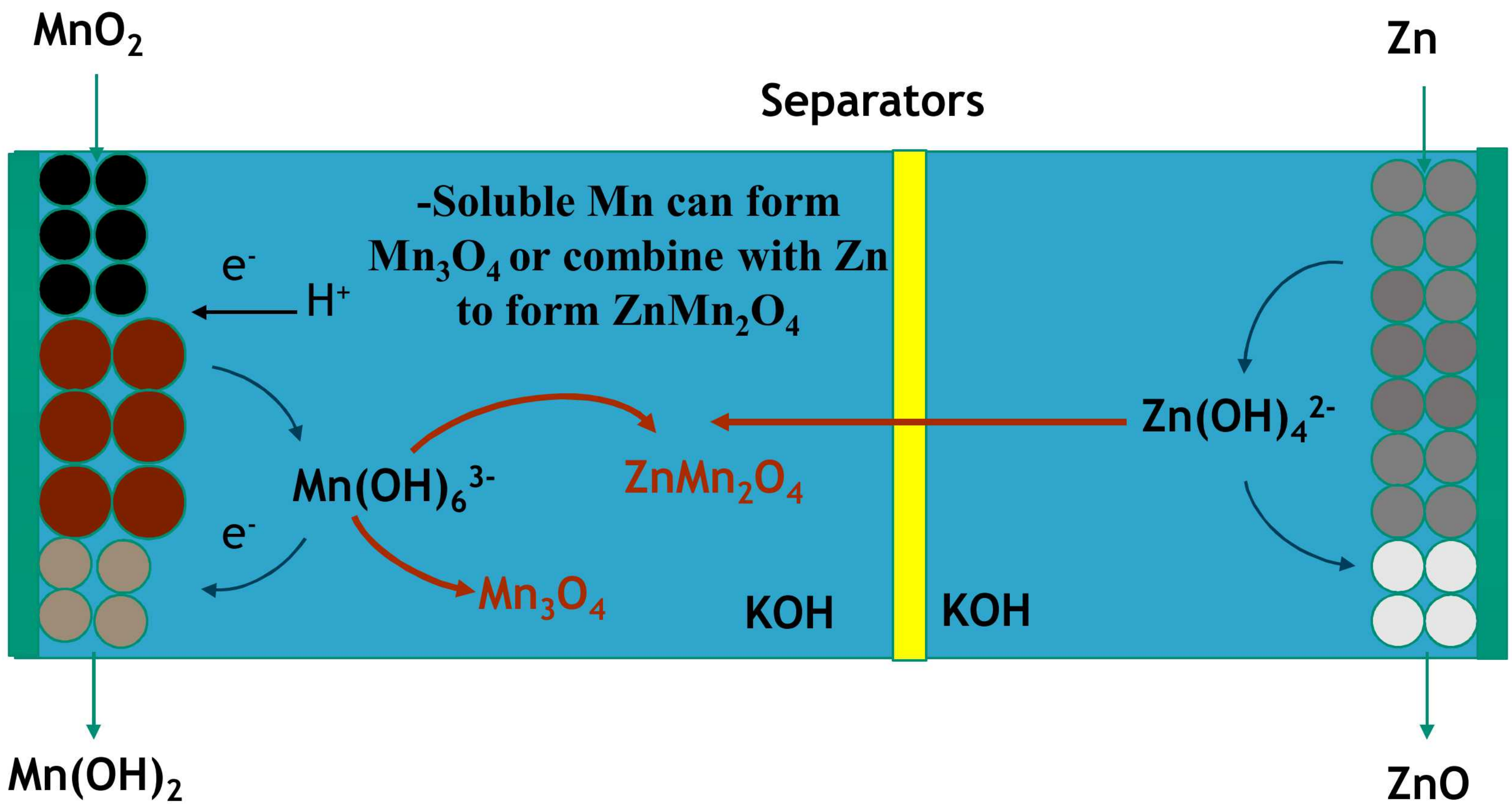
- ~ $1 per lb
- 25th most abundant
- 13,000,000 tons (2012)
- Safe

Co	$13-15/lb	**Li**	$2.5/lb
V	$11-12/lb	**Al**	$0.8-0.9/lb
Ni	$6-9/lb	**Cu**	$2.5-3.5/lb

$18/kWh
As Primary cell

The ultimate challenge in Zn/MnO_2 batteries is reversibility to increase cell lifetime

Zn-MnO_2 Batteries Discharge Mechanism



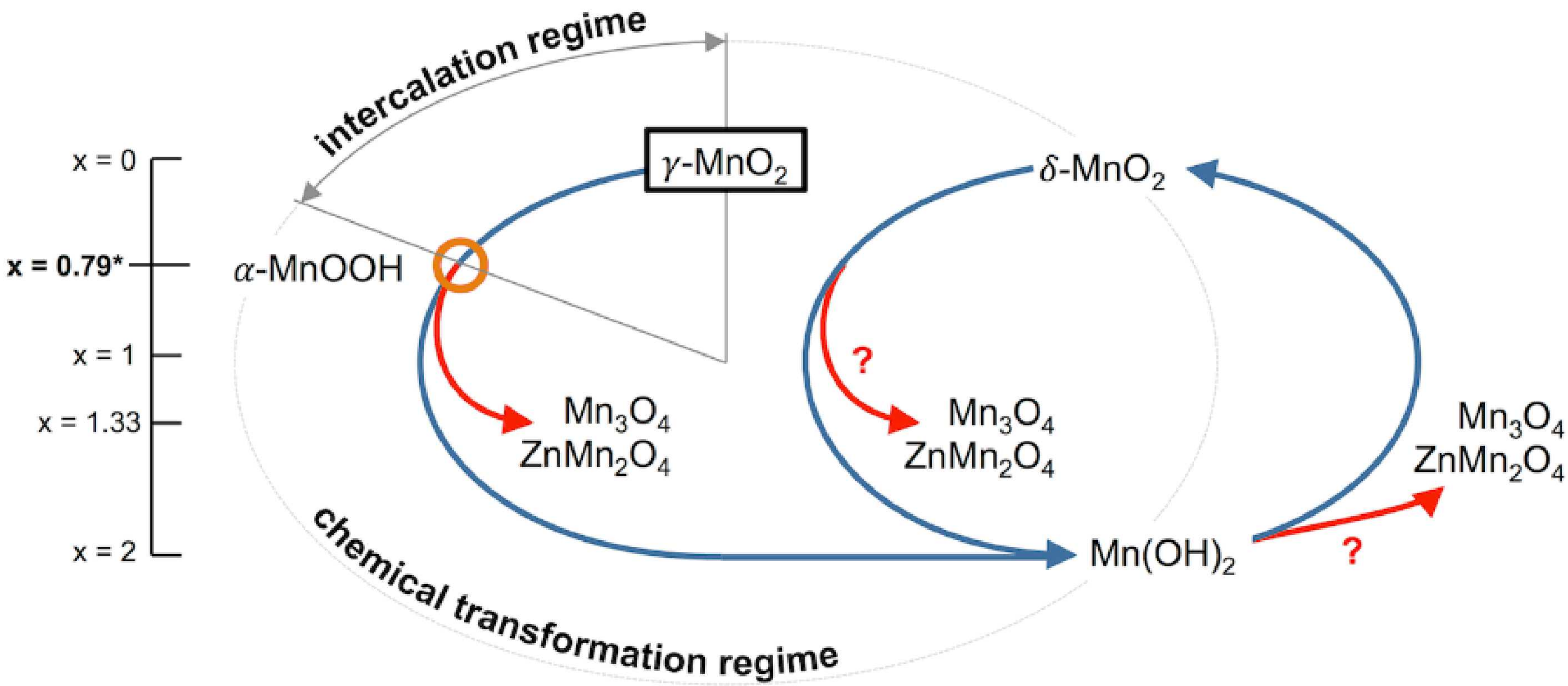
$$\mathbf{Mn^{IV}O_2} + H_2O + e^- \rightleftharpoons \mathbf{Mn^{III}OOH} + OH^- \quad E^0 = 0.26\ V\ (Hg/HgO)$$

$$\mathbf{Mn^{III}OOH} + H_2O + 3OH^- \rightleftharpoons \mathbf{Mn^{III}(OH)_6^{3-}}$$

$$\mathbf{Mn^{III}(OH)_6^{3-}} + e^- \rightleftharpoons \mathbf{Mn^{II}(OH)_2} + 4OH^-$$

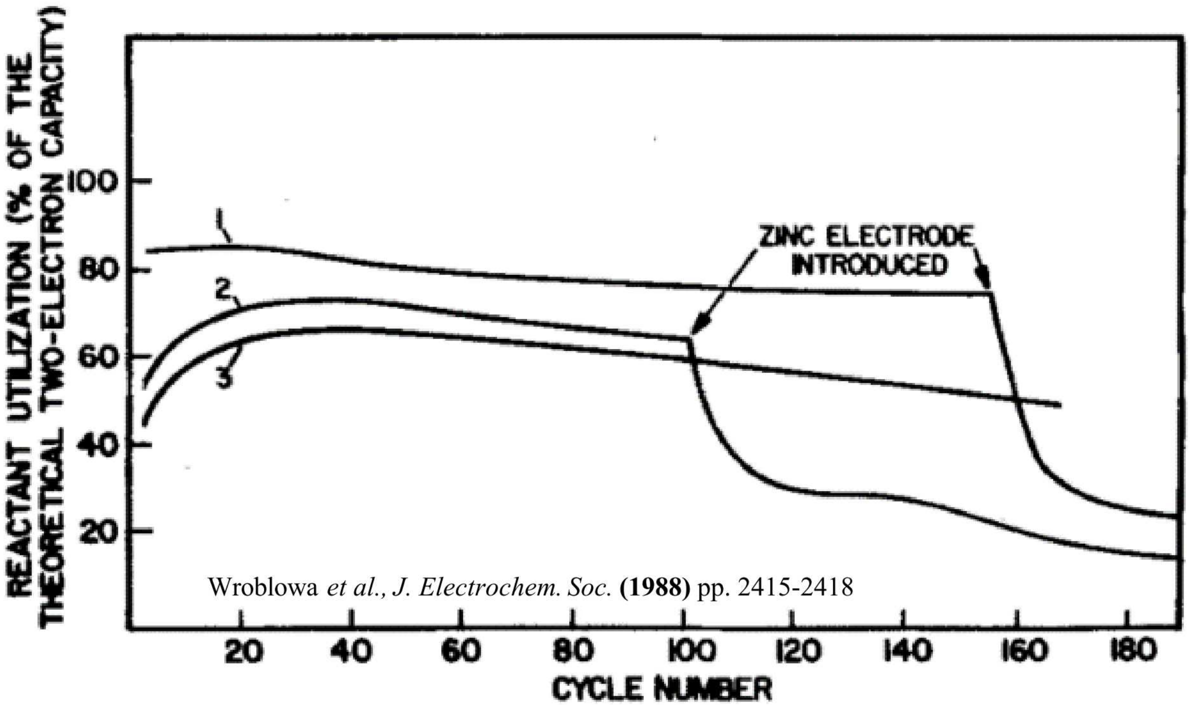
$E^0 = -0.38$ V (Hg/HgO)

Failure Mechanisms of MnO_2 Cathode



1. Instability of Mn(III) resulting in formation of irreversible $\mathbf{Mn_3O_4}$
2. Zn poisoning forming irreversible $\mathbf{ZnMn_2O_4}$

Need for Selective Separator



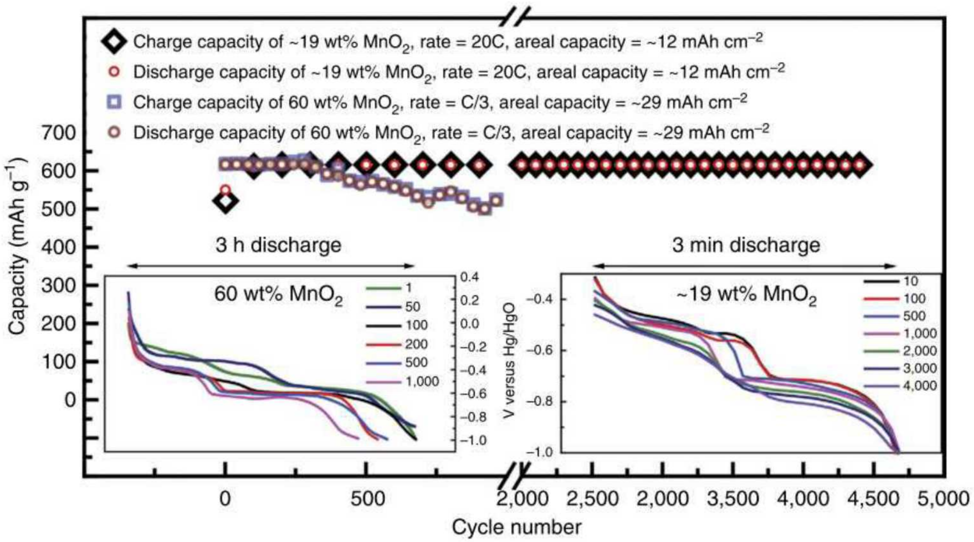
Wroblowa *et al., J. Electrochem. Soc.* **(1988)** pp. 2415-2418

Fig. 5. Effect of the introduction of zinc on capacity retention of modified MnO_2 electrodes: 1) chemically modified electrode; 2) physically modified electrode; 3) physically modified electrode in 9M KOH + 0.1M $Zn(OH)_4^{=}$.

Research by Ford in the 1980s showed that the MnO_2 cathode could be stabilized at low loadings in the **absence of Zinc**

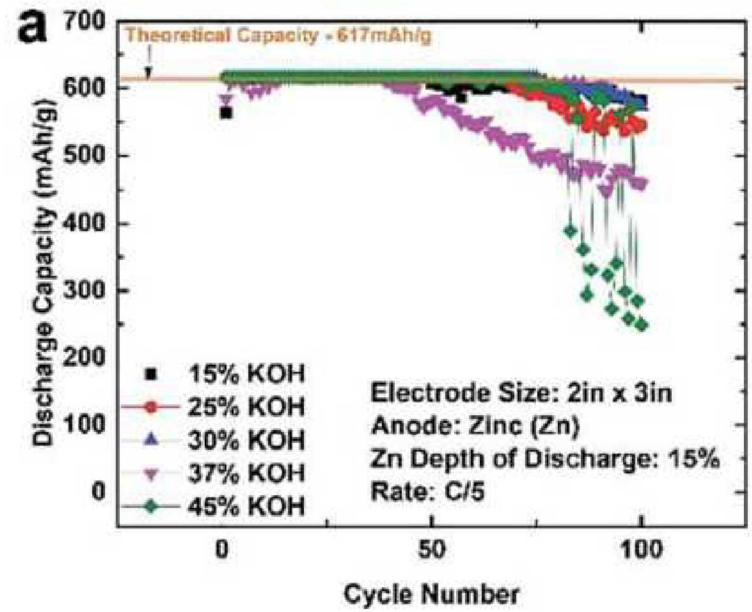
Cu^{2+} Stabilized MnO_2 Cathode

-Paired with Ni counter Electrode



Nat. Commun. **8,** 14424 doi: 10.1038/ncomms14424 (2017)

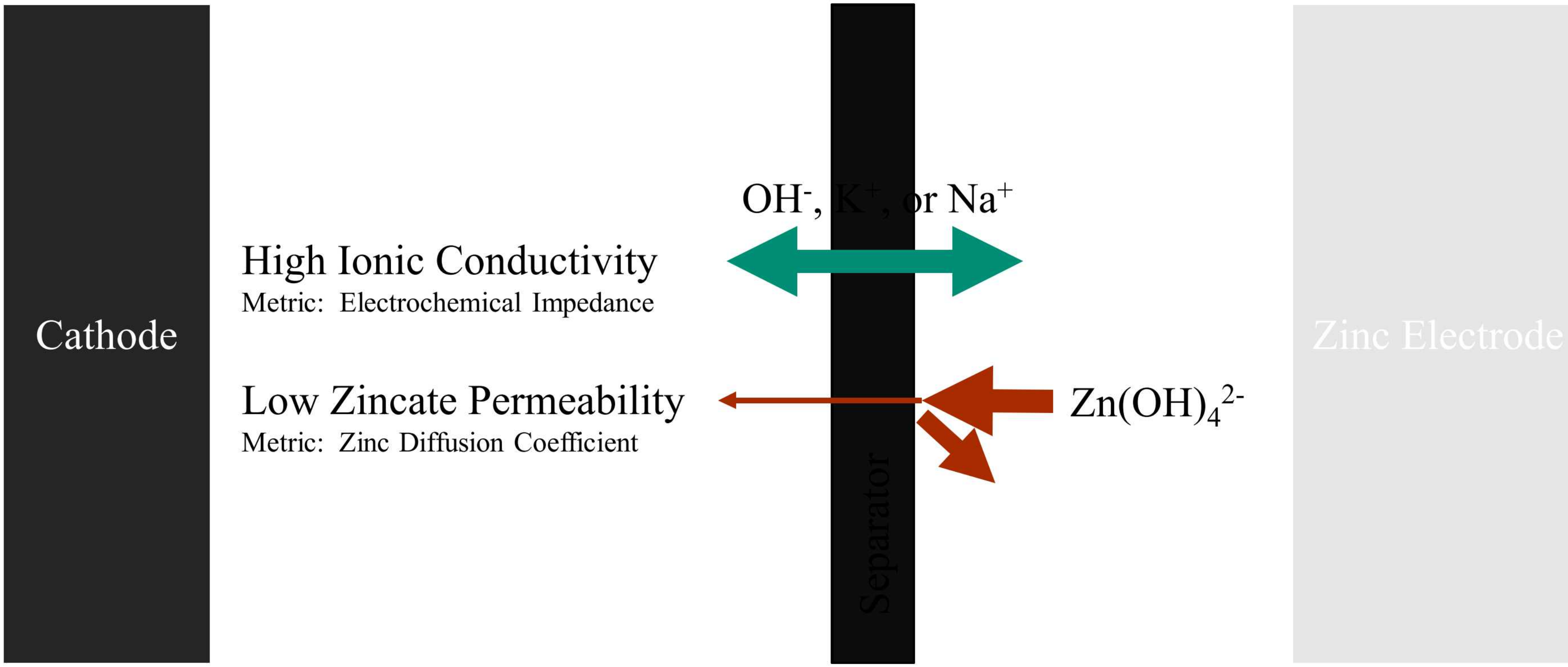
-Paired with Zn Electrode



J. Mater. Chem. A,2017, 5,15845–15854

Full 2e⁻ MnO_2 cathodes have been shown to be 100% reversible but only in the absence of Zinc thus there is an imperative need for Zinc/Zincate blocking separators

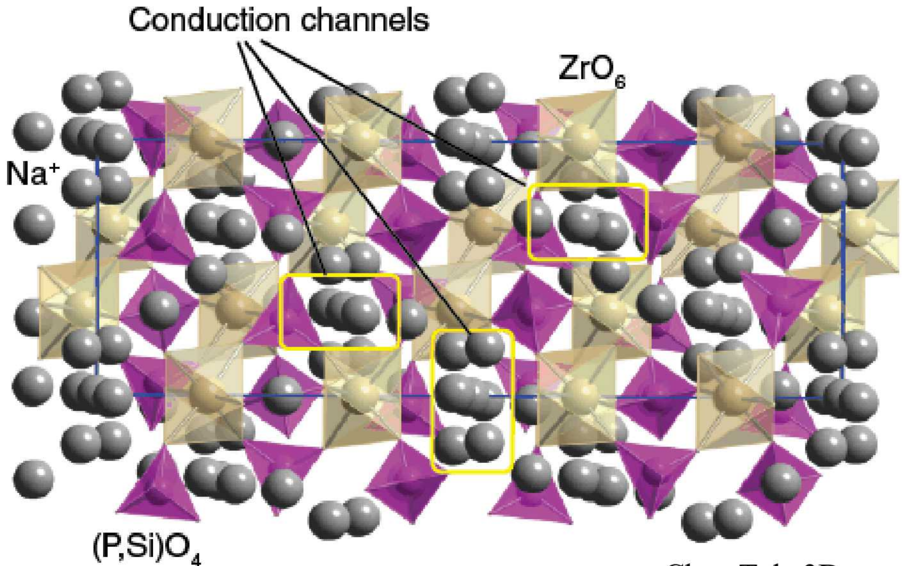
Features of a Good Zn Battery Separator



A selective membrane/separator is needed that allows charge carrying ions through but blocks or limits Zn (zincate)

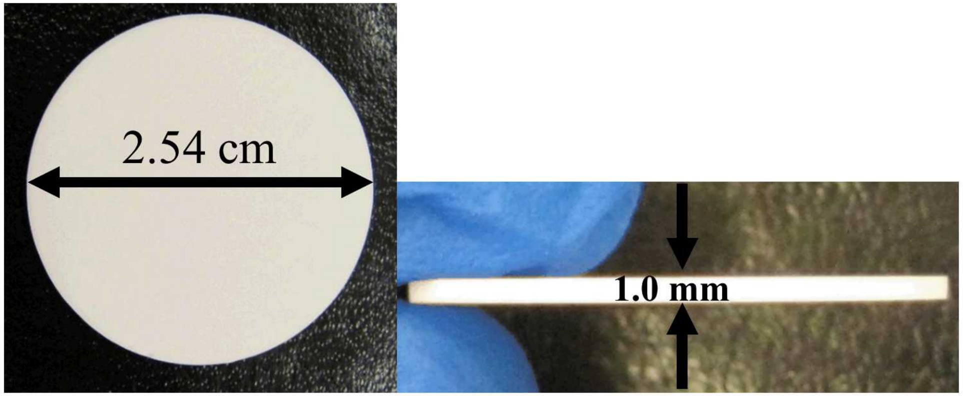
NaSICON as Separator

Nominal Composition:
$Na_3Zr_2Si_2PO_{12}$



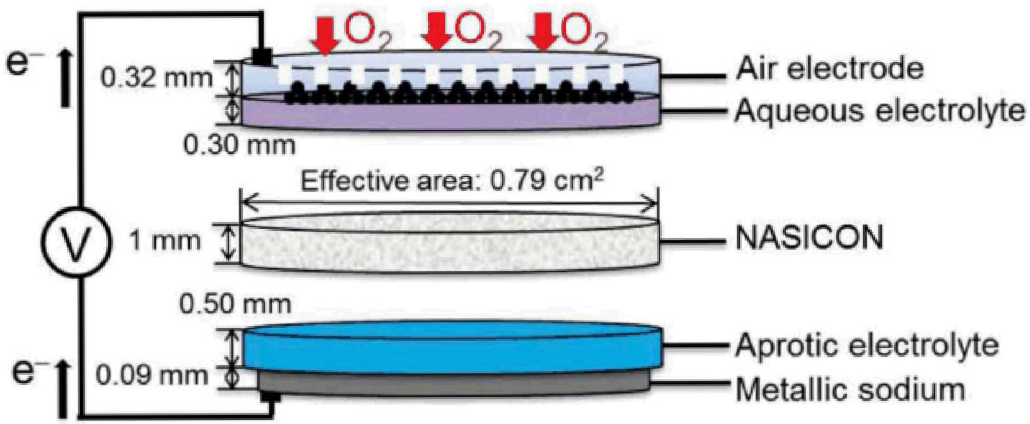
ChemTube3D

Disc form factor from Ceramatec

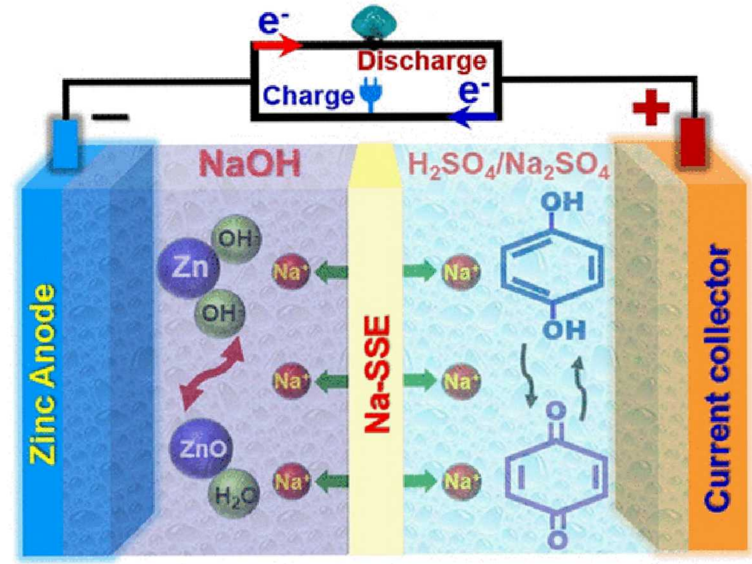


100% Selective Membrane
-Conducts sodium ions (~10^{-3} S/cm)
-Ceramic Nature should eliminate zincate crossover

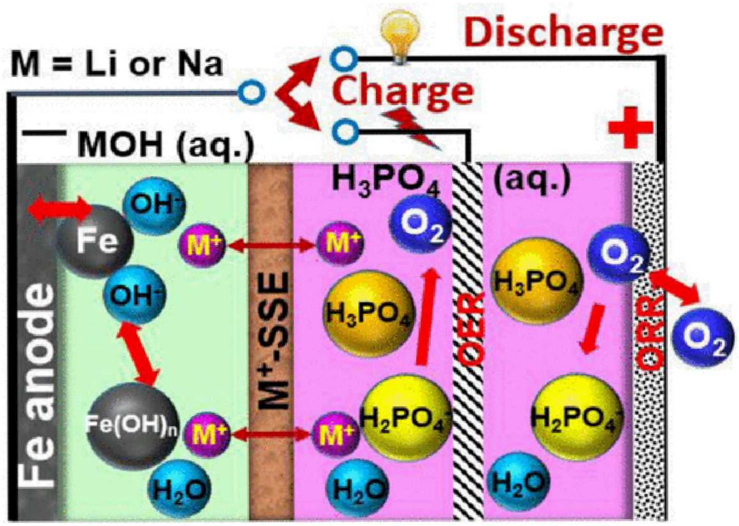
NaSICON Separator Work in the Literature



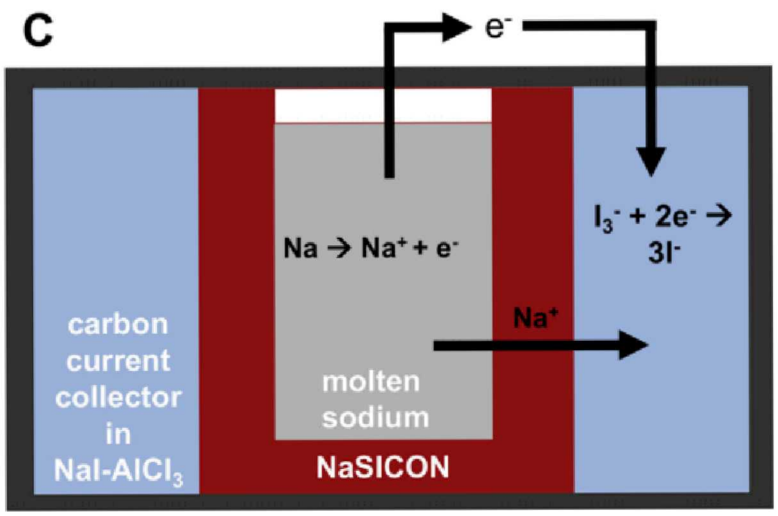
Journal of The Electrochemical Society, 162 (7) A1215-A1219 (2015)



ACS Appl. Energy Mater., **2018**, *1* (2), pp 273–277

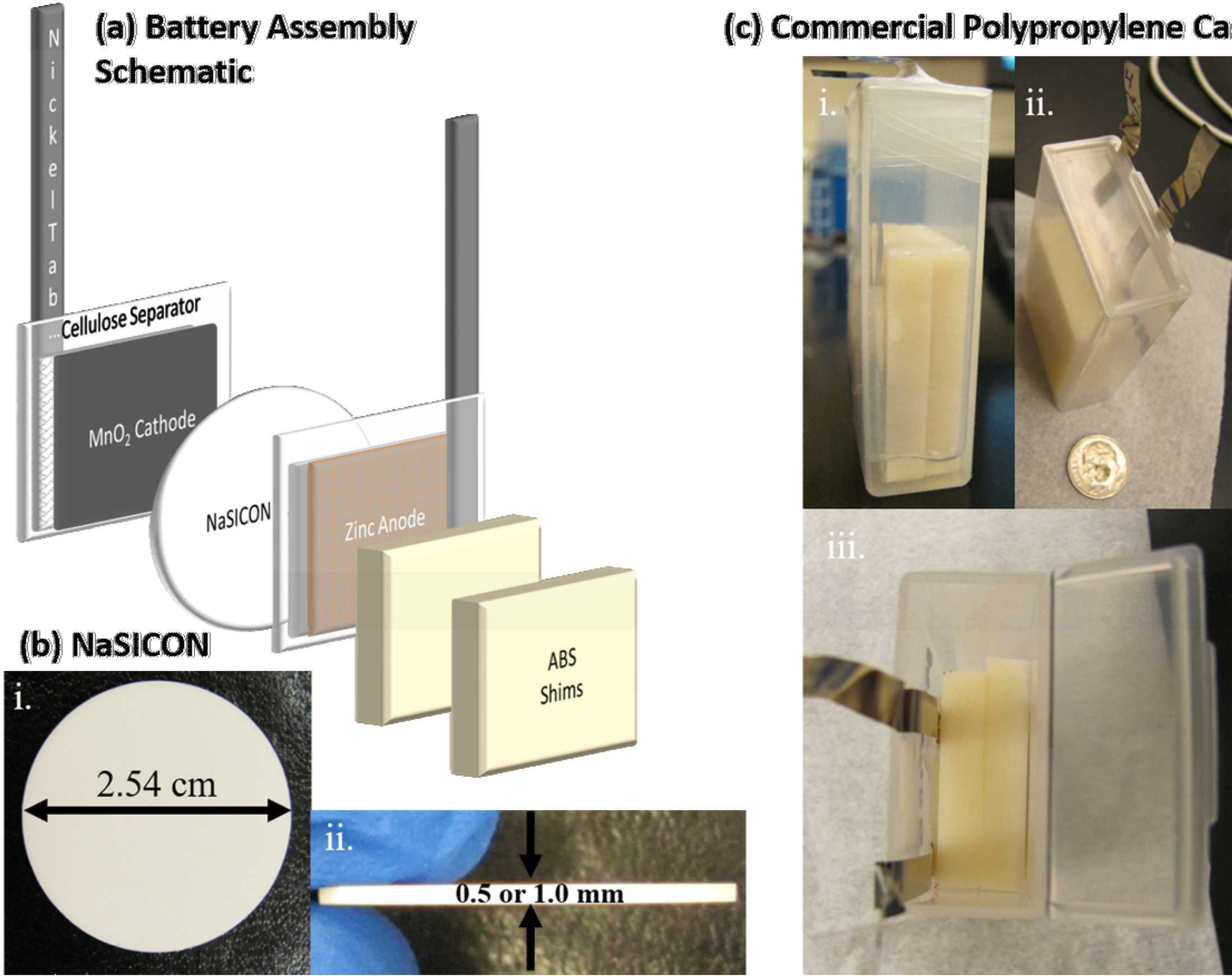


ACS Energy Lett., **2017**, *2* (5), pp 1050–1055



L.J. Small et al. / Journal of Power Sources 360 (2017) 569e574

Our Cell Design using NaSICON Disc



- NaSICON is positioned between the electrodes
- Zincate does have ability to go around
- However most ion flux occurs between electrodes

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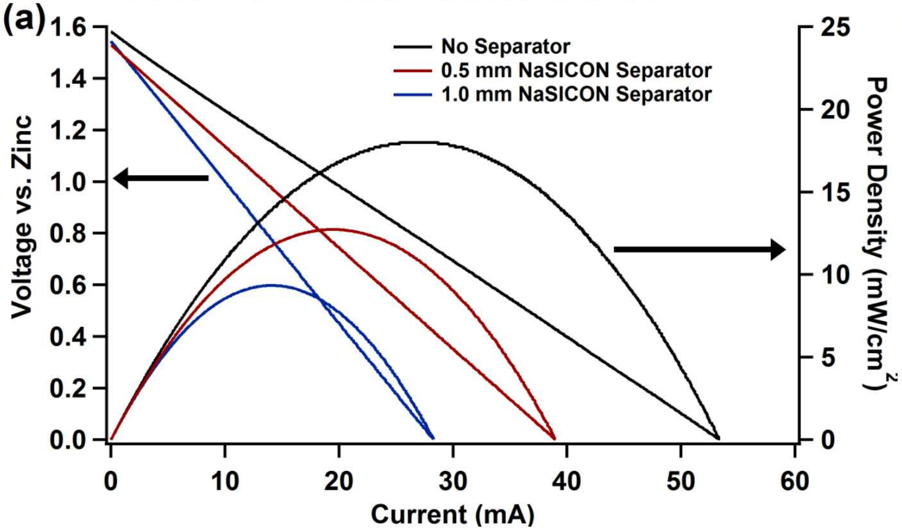
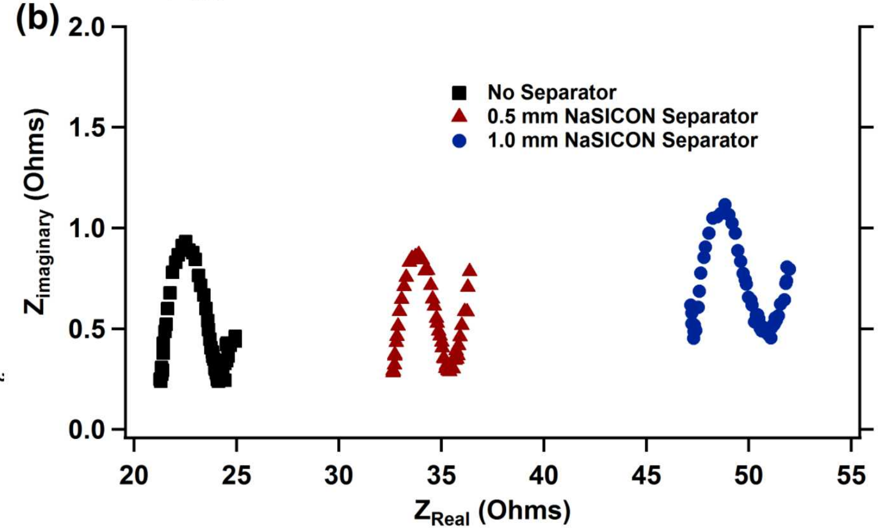
Room Temperature Resistance Measurements



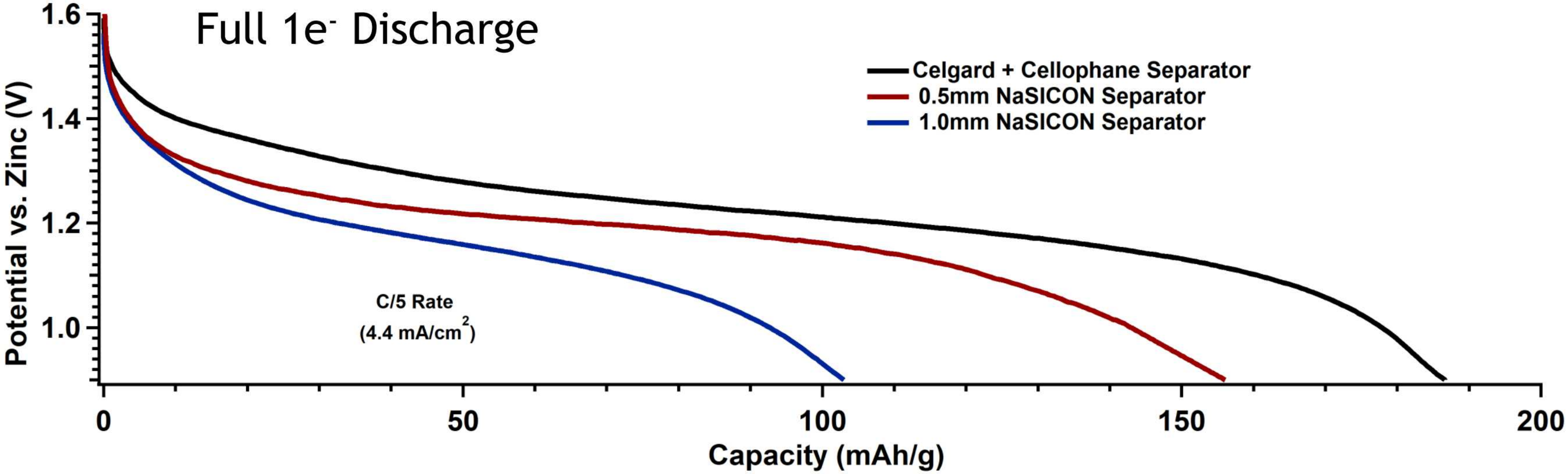


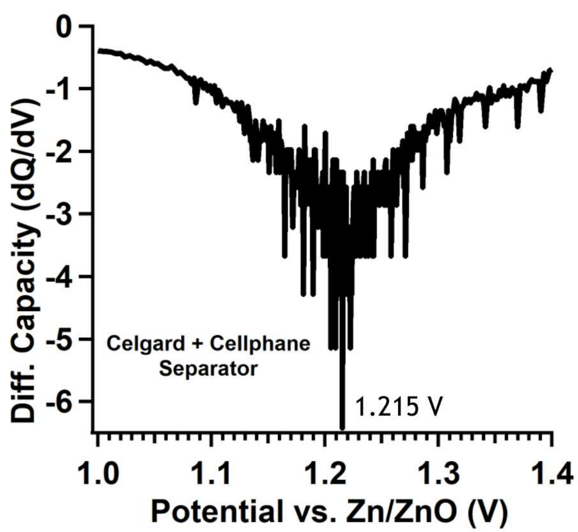
- NaSICON has significant effect on power curve due to its thickness
- NaSICON also increases total resistance of the battery
- However decreasing thickness can result in a usable separator

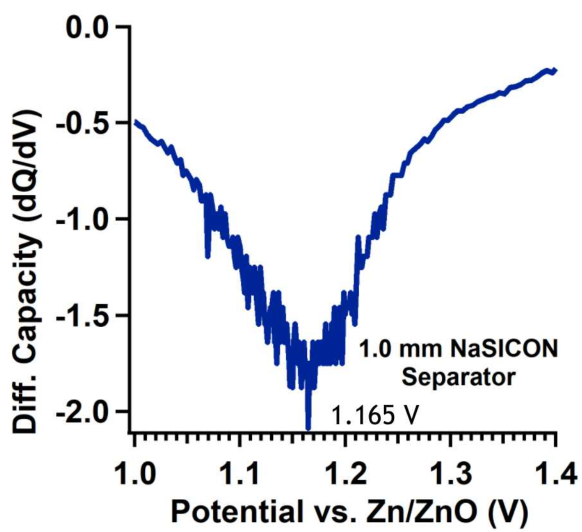
		From Polarization Curves		From EIS		
	Thickness (mm)	Room Temperature (RT) Resistance (Ω)	RT Conductivity (mS cm^{-1})	RT Resistance (Ω)	RT Conductivity (mS cm^{-1})	Zinc Diffusion Coefficient (cm^2 min^{-1})
Celgard 3501	0.025	N/A	N/A	0.1	10.7	1.18 x 10^{-6}^
Cellophane 350P00	0.025	N/A	N/A	0.2	21.4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

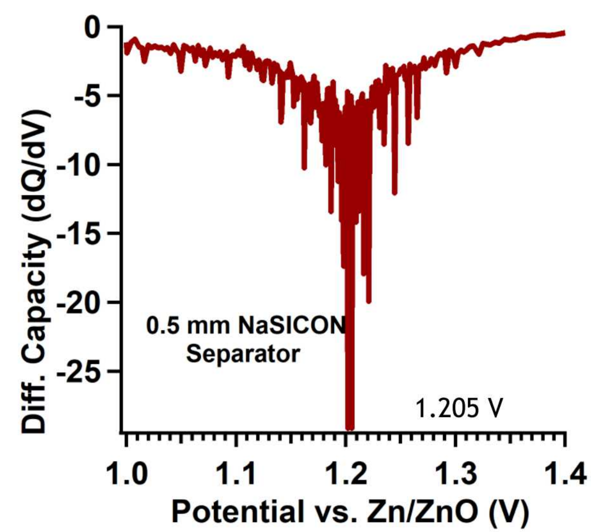
^Duay *et al., Electroanalysis* (**2017**) 29, 2261-2267 DOI:10.1002/elan.201700337

Effect of Membrane Resistance on Discharge







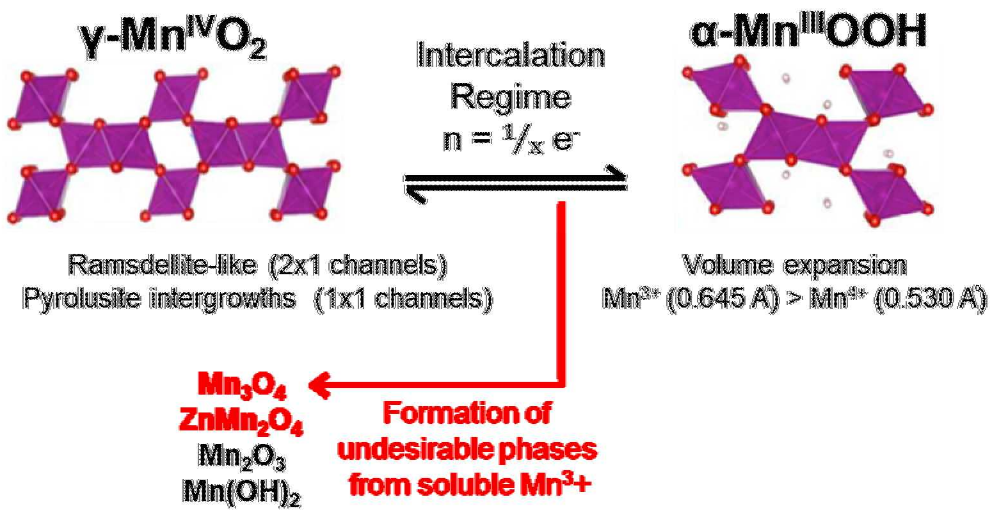


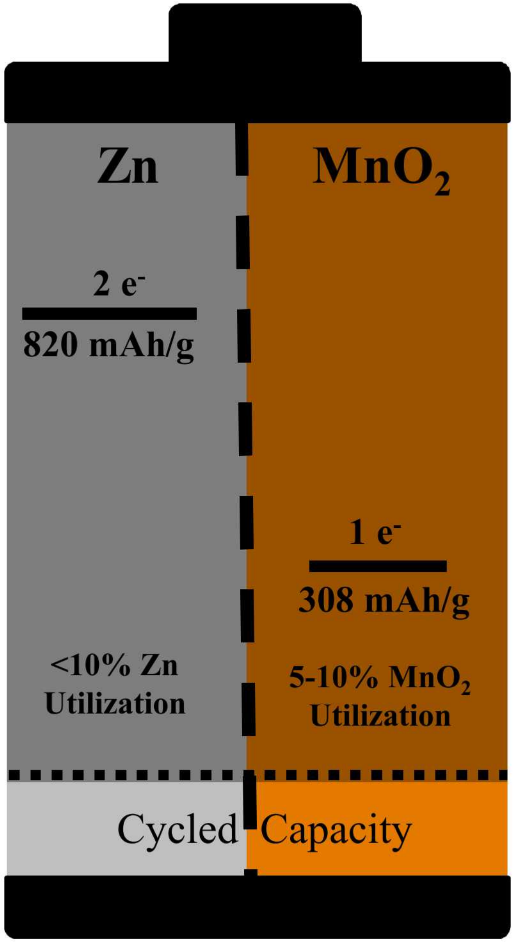
-NaSICON increases overpotential of the battery
-However that can be reduced by decreasing the thickness of the NaSICON

Duay, J.; Kelly, M.; and Lambert, T.L. *Manuscript Under Review*

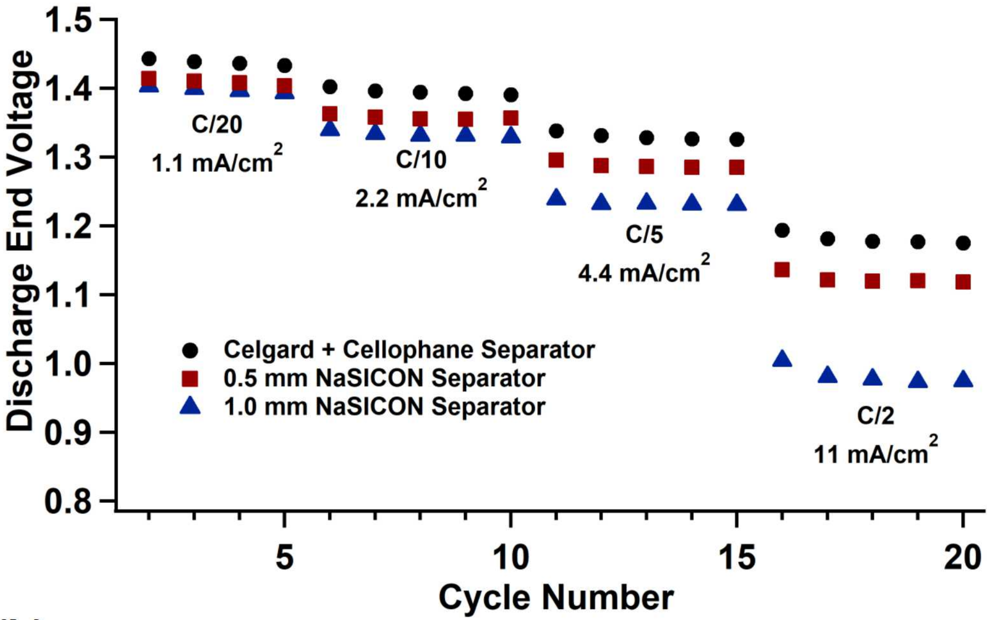
Limited Depth of Discharge (DOD) Cycling

Reversibility can be maintained when only **a fraction of the first e⁻ step is cycled.**

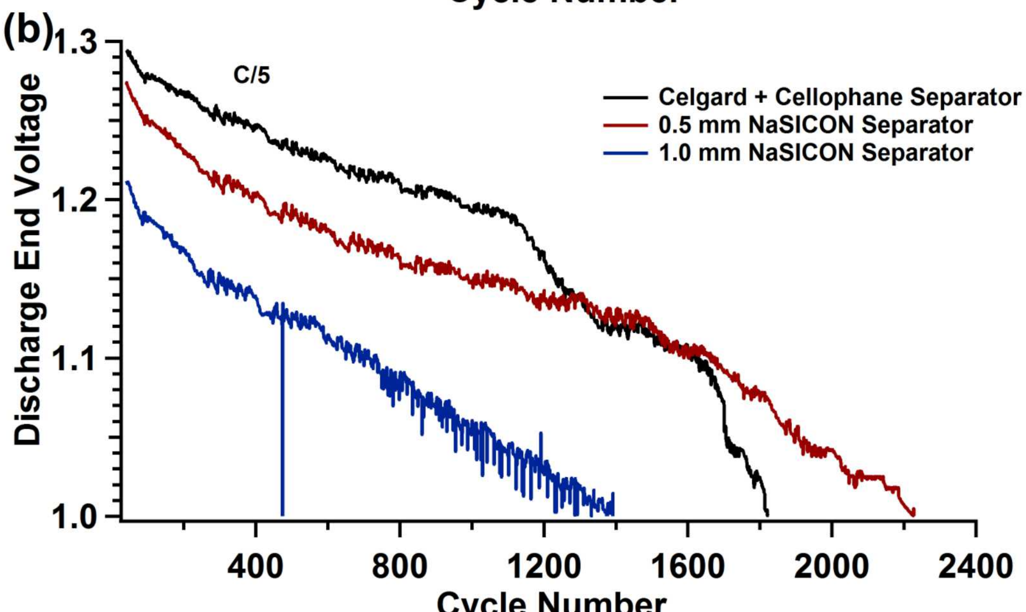




Effect on Limited 5% DOD Cells



-at relevant discharge rates for grid storage, the thinner **0.5 mm NaSICON doesn't decrease DEV significantly**



-As NaSICON is thinned, it's advantages become more apparent increasing cell lifetime

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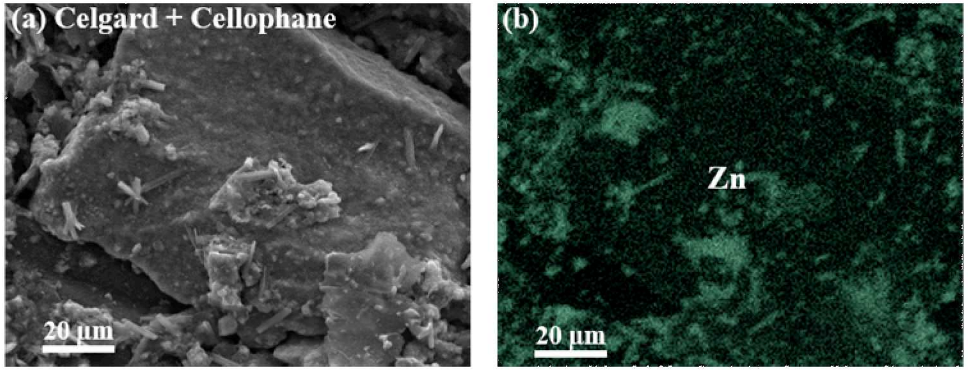
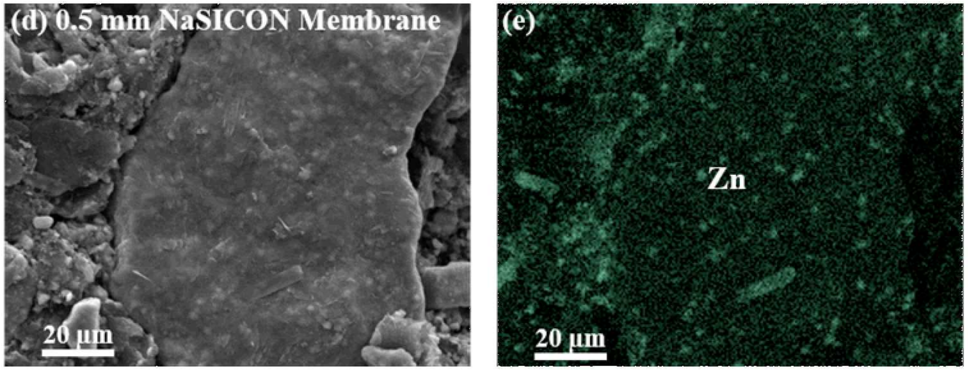
Failure Analysis by SEM/EDS



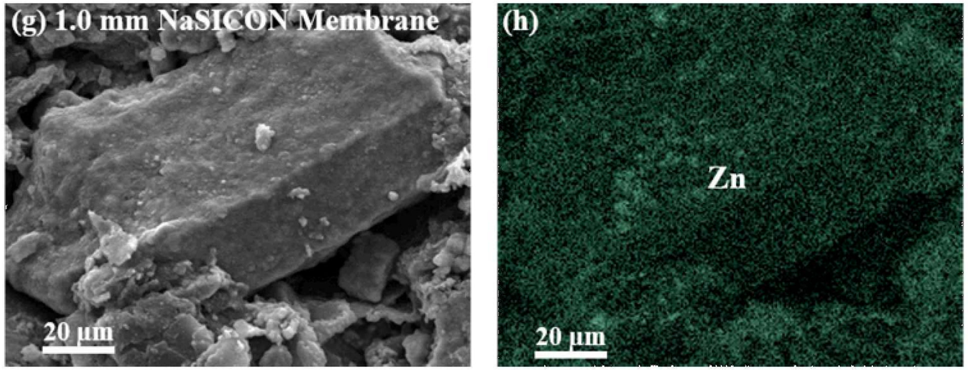
(c)

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**



(f)

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**



(i)

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**

-NaSICON reduced Zinc species crossover and deposition/reaction with EMD

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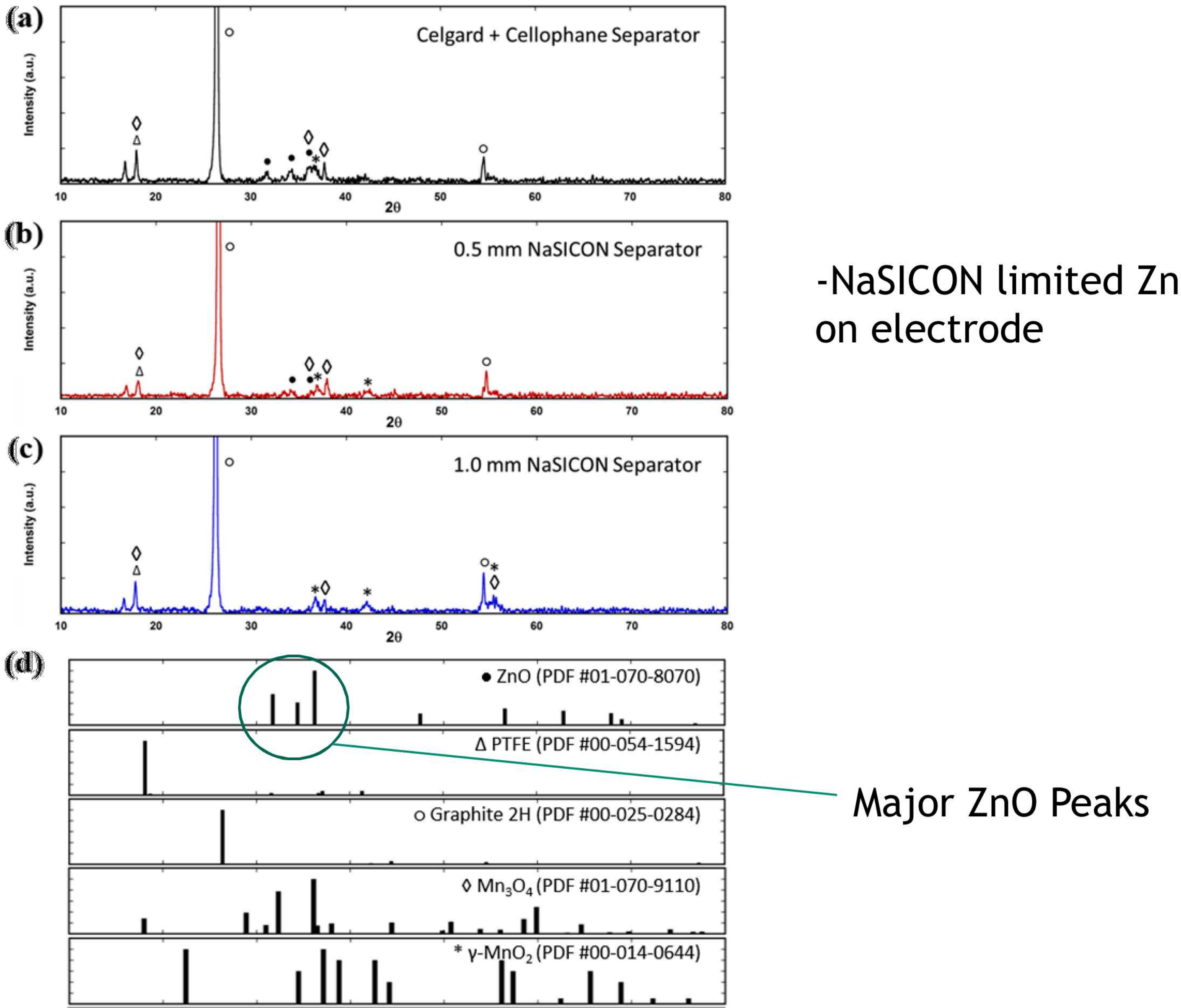
Failure Analysis by XRD



-NaSICON limited ZnO buildup on electrode

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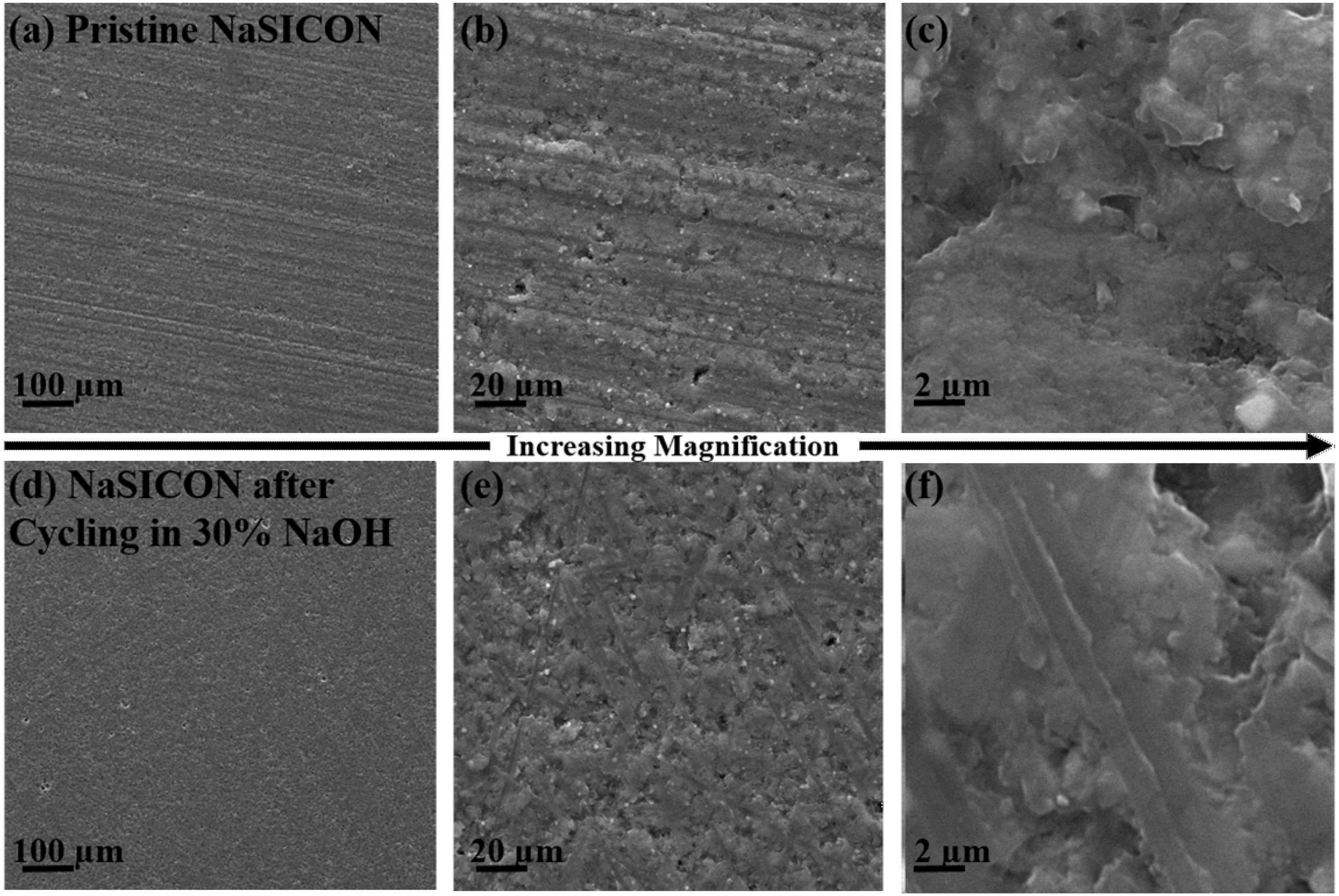
Stability of NaSICON



-No dissolution or pitting observed after two months in 30% NaOH

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Conclusions

-NaSICON used here for **first time as Zn/MnO_2 Battery Separator**
-NaSICON was found to be **too resistive at 1.0 mm thickness**
-Reducing **thickness of NaSICON to 0.5 mm was found to be sufficient** for extending lifetime in 5% DOD cells
-NaSICON **reduced the amount of Zn Crossover** based on EDS and XRD
-NaSICON was found to be **stable over two months in 30% NaOH**
-Ultimate **failure of cell could still be from Zn poisoning** due to cell design

Future Work

-Design of **Hermetically Separated Electrodes** to prevent Zn going around NaSICON
-Continued **reduction in thickness/resistance** of NaSICON
-Possible NaSICON/**polymer composites** to help reduce thickness/resistance of membrane
-**Filtration of suspended NaSICON powder** onto commercial battery separator

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Questions?