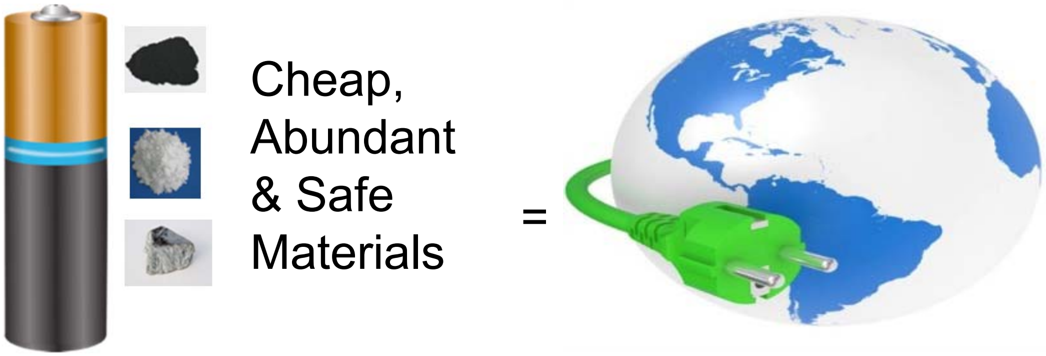
Exceptional service in the national interest

Sandia National Laboratories



Effect of Additives and Selective Separators on Alkaline Zn-based Batteries

November 16th 2018,
NAATBatt - Zn Battery Workshop
New York, New York

Timothy N. Lambert
Sandia National Laboratories

Recent and Current Efforts at SNL

Electrocatalysts for ORR/OER/HER

- Catalysts for alkaline based electrocatalysis (Zn/Air)

Zn-based Alkaline Batteries

- Effect of Additives on limited DOD Zn/MnO_2 batteries
- Development of Separators for Selective Crossover [Na^+/HO^- vs $Zn(OH)_4^{2-}$]
- Increased Zn DOD
- Development of new Cathode Chemistries

Team

Sandia National Laboratories — Dr. Timothy Lambert

CUNY The City University of New York Energy Institute — Prof. Sanjoy Banerjee

NM State University — Prof. Igor Vasiliev

Northeastern University — Prof. Joshua Gallaway

Acknowledgements

- Babu Chalamala, Manager, Energy Storage Technology & Systems, Sandia
- Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability (OE)
- Energy & Climate Investment Area, Laboratory Directed Research & Development (LDRD), Sandia

Recent and Current Efforts at SNL

Electrocatalysts for ORR/OER/HER

- Catalysts for alkaline based electrocatalysis (Zn/Air)

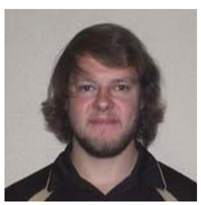
Zn-based Alkaline Batteries

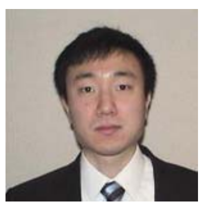
- Effect of Additives on limited DOD Zn/MnO_2 batteries
- Development of Separators for Selective Crossover [Na^+/HO^- vs $Zn(OH)_4^{2-}$]
- Increased Zn DOD
- Development of new Cathode Chemistries

SNL Team

Drs.


Jonathon Duay


Igor Kolesnichenko


Matthew Lim

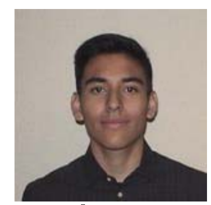
Students


Ruby Aidun


David Arnot


Maria Kelly


Kristen Maus


Ivan Pineda-Dominguez

Acknowledgements

- Babu Chalamala, Manager, Energy Storage Technology & Systems, Sandia
- Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability (OE)
- Energy & Climate Investment Area, Laboratory Directed Research & Development (LDRD), Sandia

Alkaline Zn/MnO_2 Batteries

Two classes of rechargeable Zn/MnO_2 batteries:

One Electron

- 308 mAh/g-MnO_2
- Historically limited cycle-ability
- > 3000 rechargeable cycles shown under limited depth of discharge conditions
- Technology has been commercialized by Urban Electric Power
- $100 per kWh (2019)

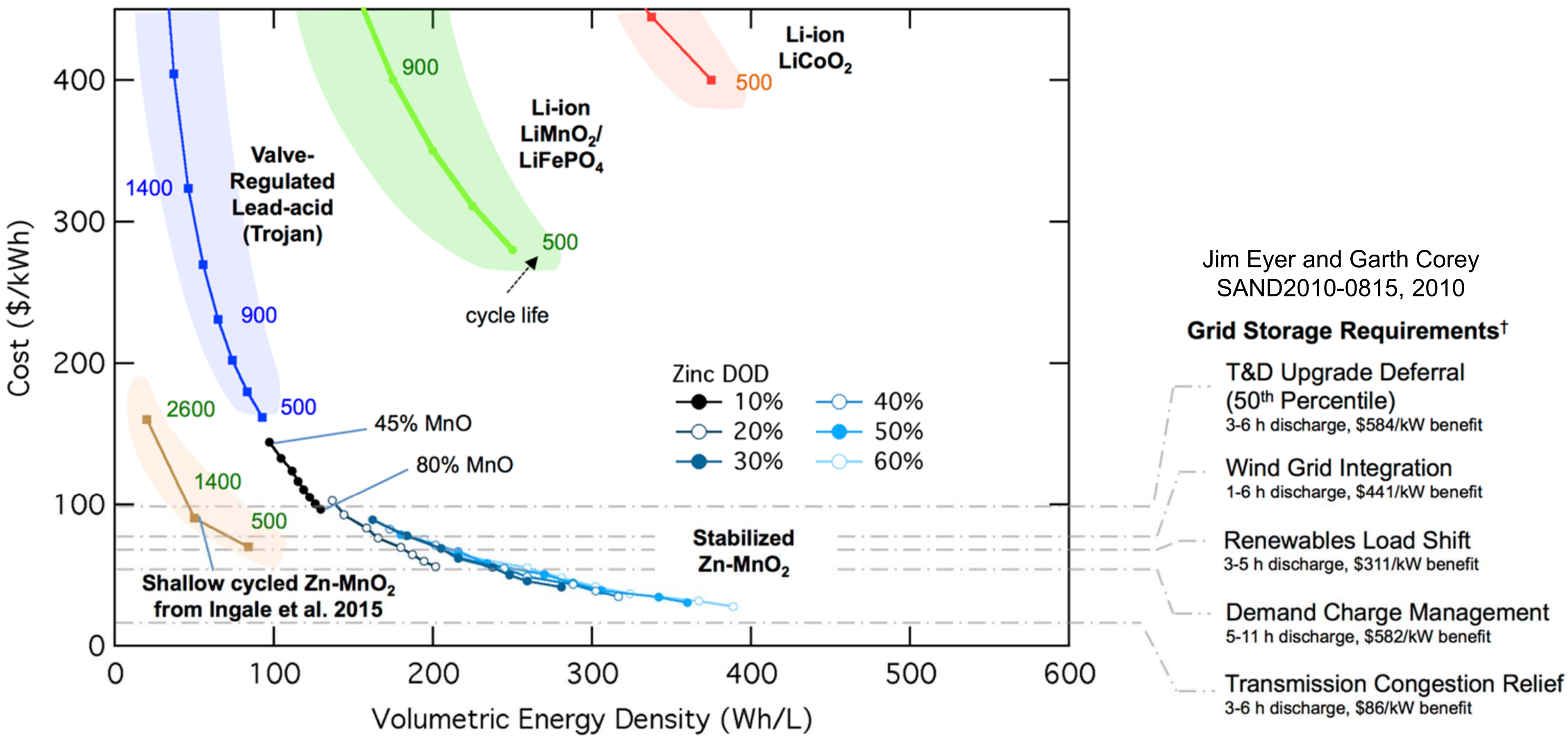
Two Electron

- 616 mAh/g-MnO_2
- Historically limited cycle-ability
- Recently stabilized with Cu, Bi, CNT additives to demonstrate > 3000 cycles vs. $Ni(OH)_2$
- 900 cycles vs. Zn reported with use of $Ca(OH)_2$ interlayer
- Projected ~ $50 per kWh

N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, *J. Power Sources*, **276**, 7 (2015).
G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nat. Commun., 8, 14424 (2017).

Alkaline Zn/MnO_2 Batteries

Opportunity exists to Increase Capacity and Decrease Costs



Goals: Achieve Low Cost/High Energy Density Storage for the Grid

1. Continue to Support Limited Depth-of-Discharge (DOD) Efforts
2. Materials and Systems Development for Higher Capacity at Lower Cost

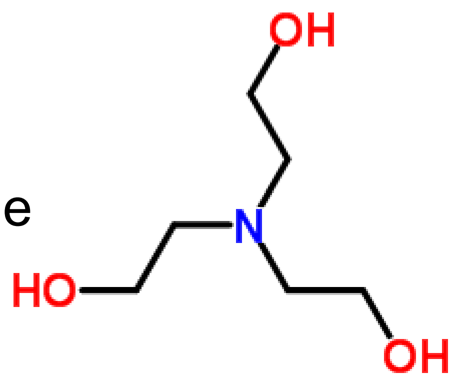
Improving Zn/MnO_2 Battery Performance

Chemical additives often used to improve battery performance

- Cathode Additives: Bi_2O_3, MgO, Sr-, Ba-, and Ti-based compounds
- Anode Additive: In, Bi, Pb, $Ca(OH)_2$, carboxymethyl cellulose

Triethanolamine (TEA)

- Known to form complexes with Mn^{2+} and Mn^{3+}
- Previous work claimed triethanolamine binds solubilized Mn^{2+} and Mn^{3+}, which could mitigate the formation of irreversible species

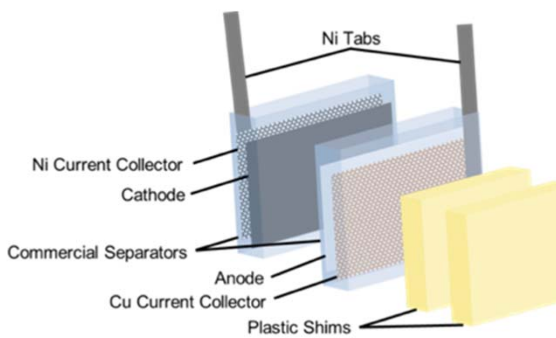


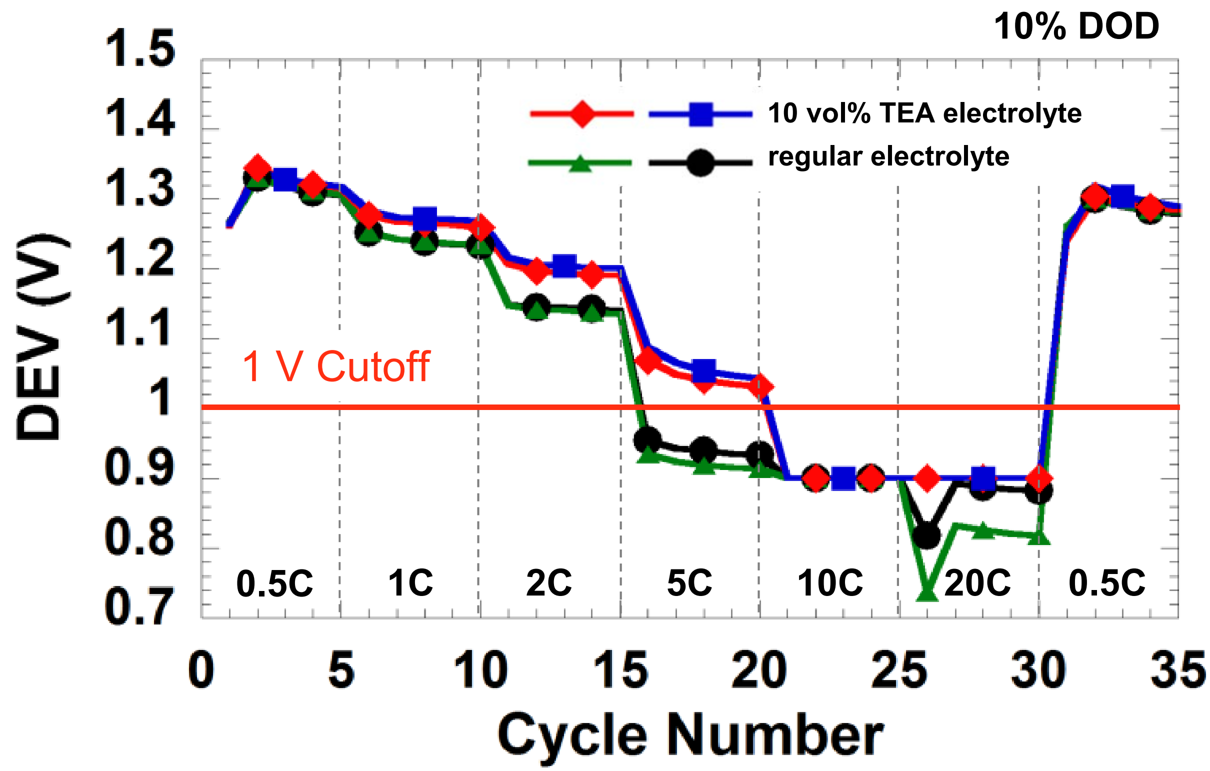
➡ Comprehensive analysis of TEA effect in limited DOD cells

A. Kozawa and R. A. Powers, *J. Electrochem. Soc.*, **113** 870 (1966).
A. Kozawa and J. F. Yeager, *J. Electrochem. Soc.*, **112**, 959 (1965).
M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

Rate Performance

- COTS materials
- Cathode-limited
- < 1.5% DOD on Zn

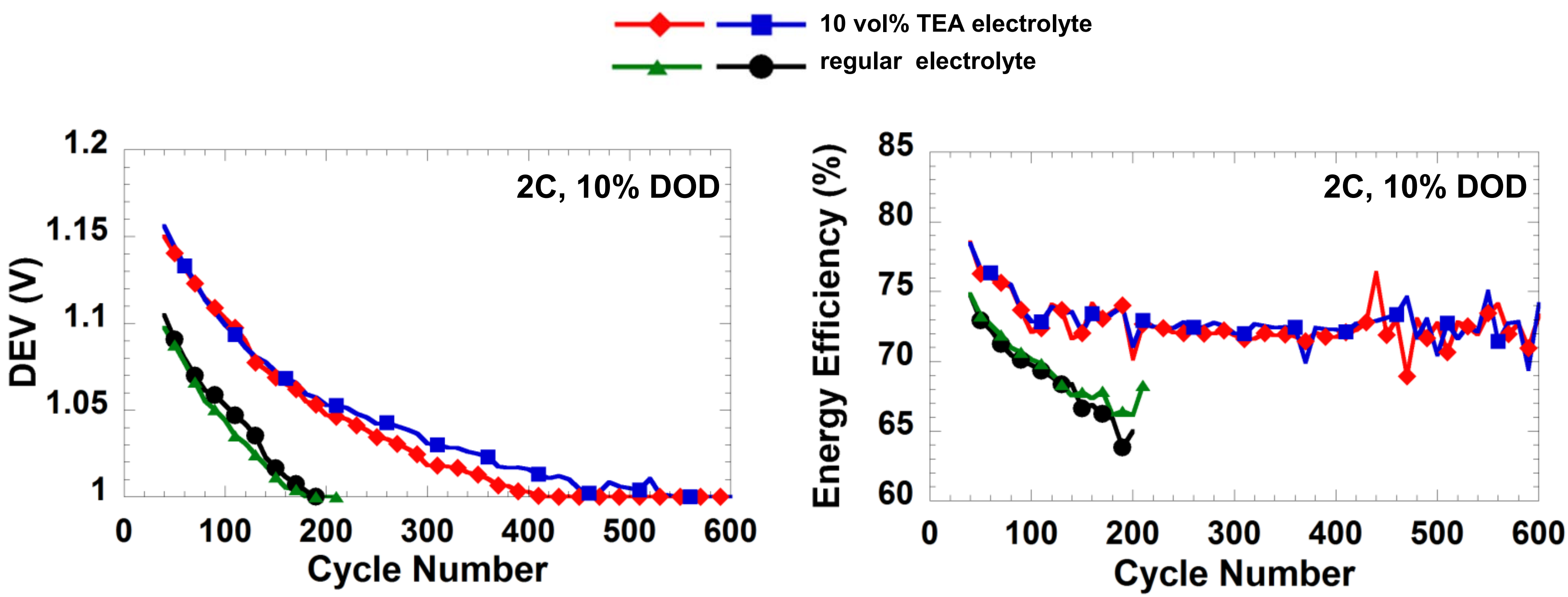




- 5 cycles each of C/2, 1C, 2C, 5C, 10C, 20C (based on cycled capacity)
- Cells prepared with TEA exhibit 29, 58, and 121 mV higher DEV at 1C, 2C, 5C
- All cells drop below 1V at 10C and 20C rates – high resistivity of MnO_2
- Cells prepared with TEA exhibit enhanced performance at higher rates

M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

Extended Cycling

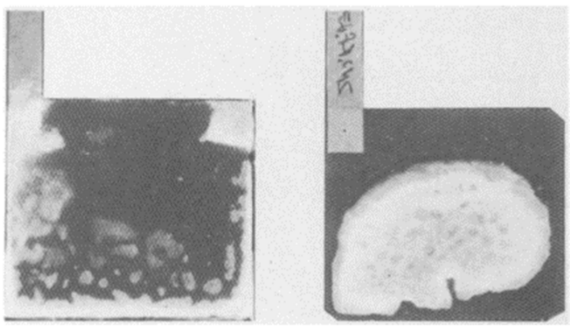


- Cycled at 2C rate, 10% DOD until failure (80% of cycled capacity remaining)
- Baseline Cells: 183 to 198 cycles, TEA Cells: 483 to 653 cycles
- TEA extends cycle lifetime by 297%
- Zn: harder to reduce, more soluble, less transport through separator, lower surface area

M. Kelly *et al. J. Electrochem. Soc.*, **113**, 870 (2017).

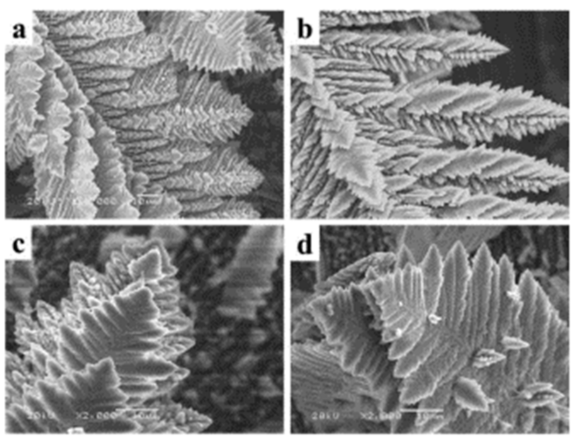
Zn Anode – Increasing DOD

Shape Change



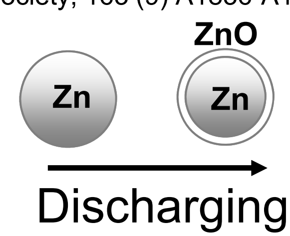
Journal of The Electrochemical Society, 138 (2) 645-664 (1991)

Dendrite Growth

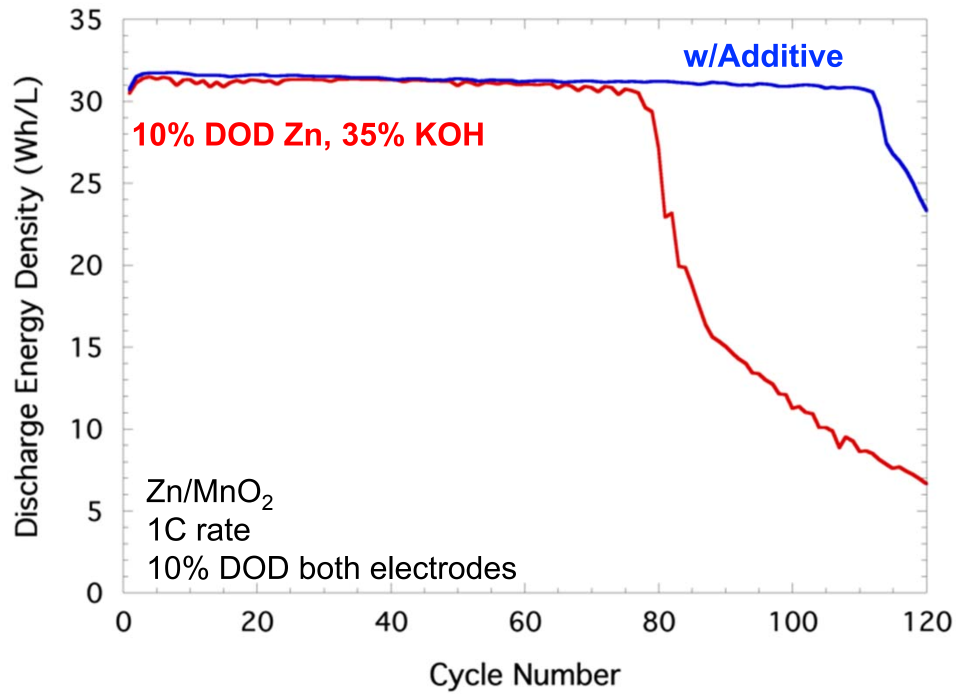


Journal of The Electrochemical Society, 163 (9) A1836-A1840 (2016)

Irreversible ZnO Passivation



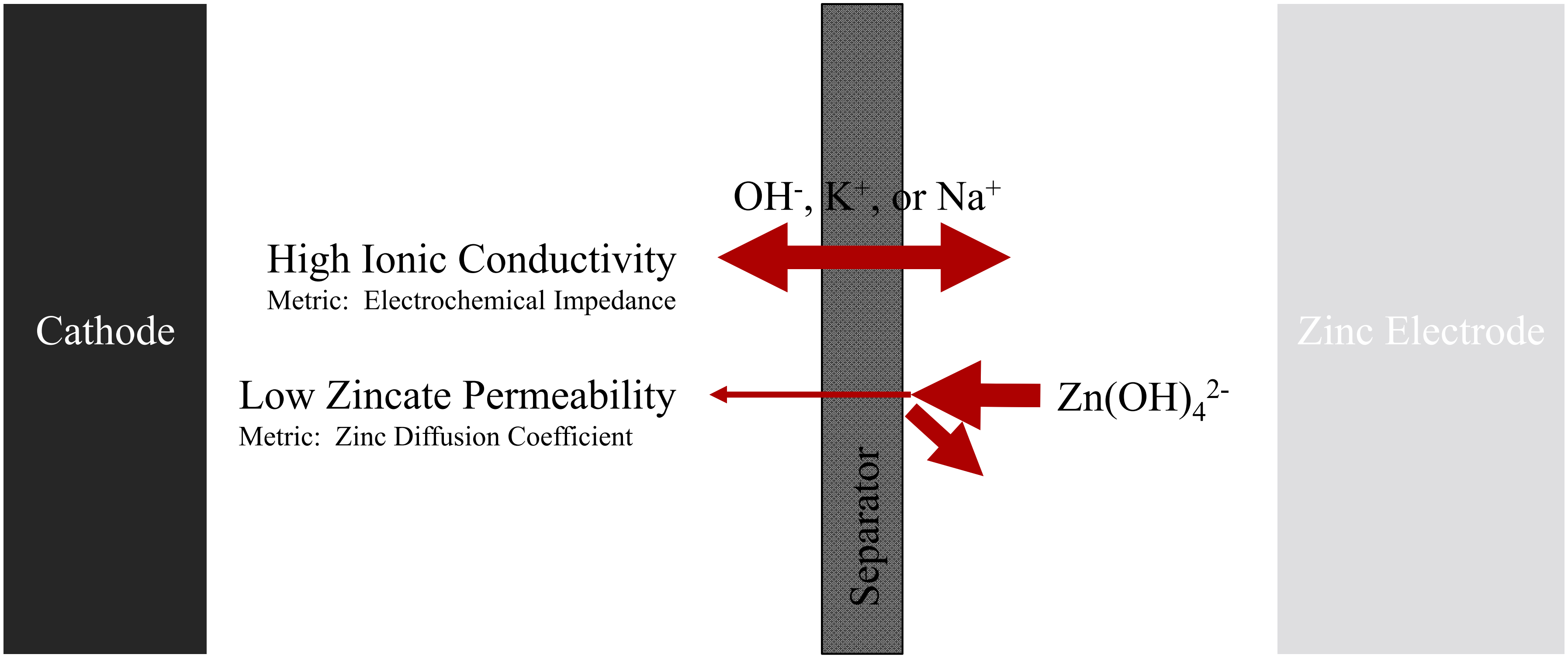
Effect of Electrolyte Additives on Zn DOD



~ 20% increase in cycle life

M. Lim *et al. unpublished results.*

Features of a Good Zn Battery Separator

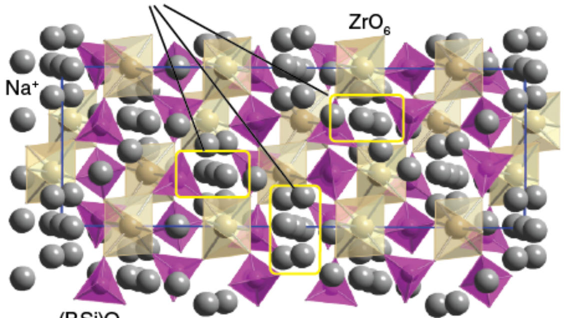


A selective membrane/separator is needed that allows charge carrying ions through but blocks or limits Zn (zincate)

Separators – Ceramic Separator

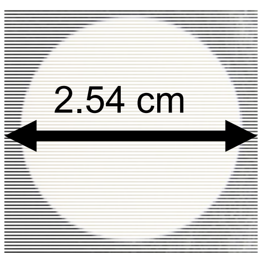
NaSuper **I**onic **CON**ductor

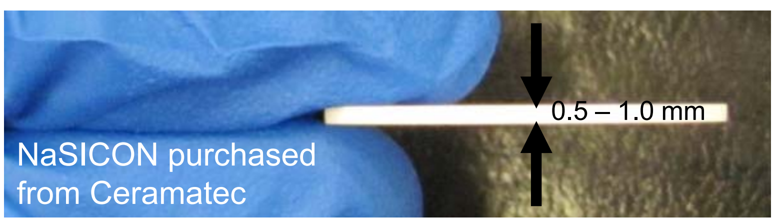
$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, 0 < x < 3



http://www.chemtube3d.com/solidstate/SSNASICON.htm

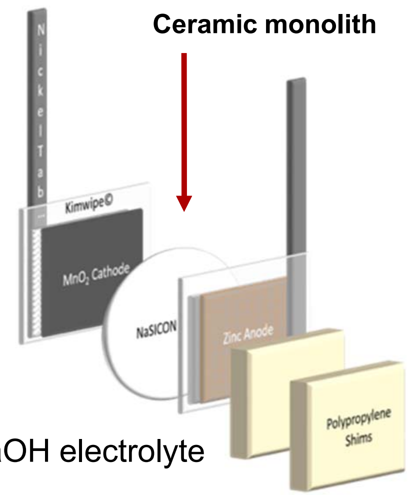
NaSICON





Provided by Dr. Erik Spoerke (SNL)

Battery Assembly Schematic

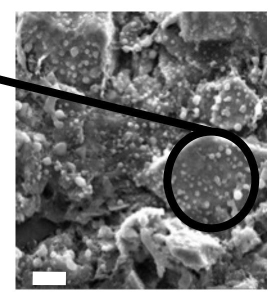


100% Selective Membrane

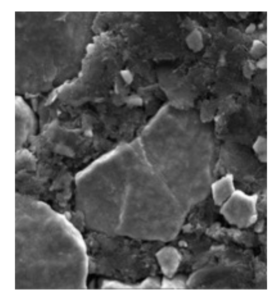
- **Na+ ions (~10^{-3} S/cm)**
- **No through separator Zn transport detected**

Cathode Post cycling

Zn w/ Celgard+Cellophane



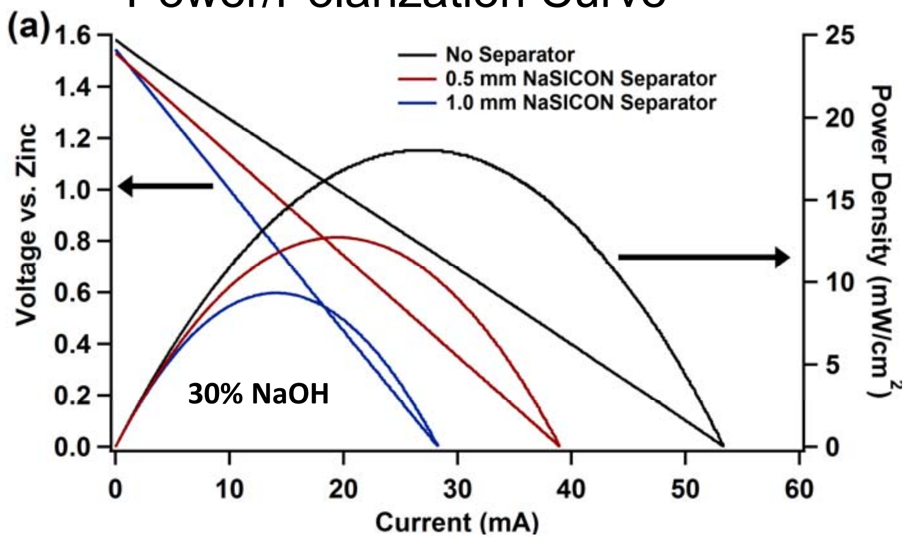
No Zn w/ NaSICON



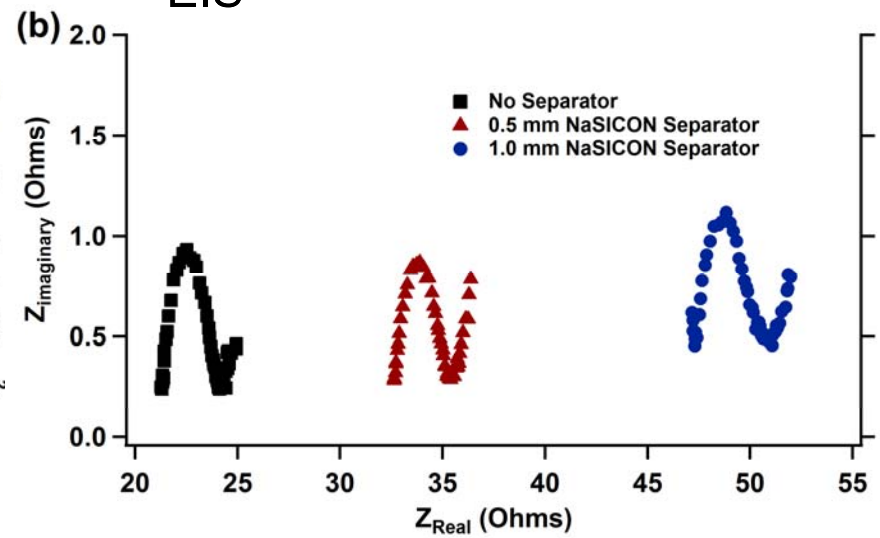
J. Duay, *et al. J. Power Sources* **2018**, *395*, 430–438. DOI:10.1016/j.jpowsour.2018.05.072.

Room Temperature Resistance Measurements

Power/Polarization Curve



EIS

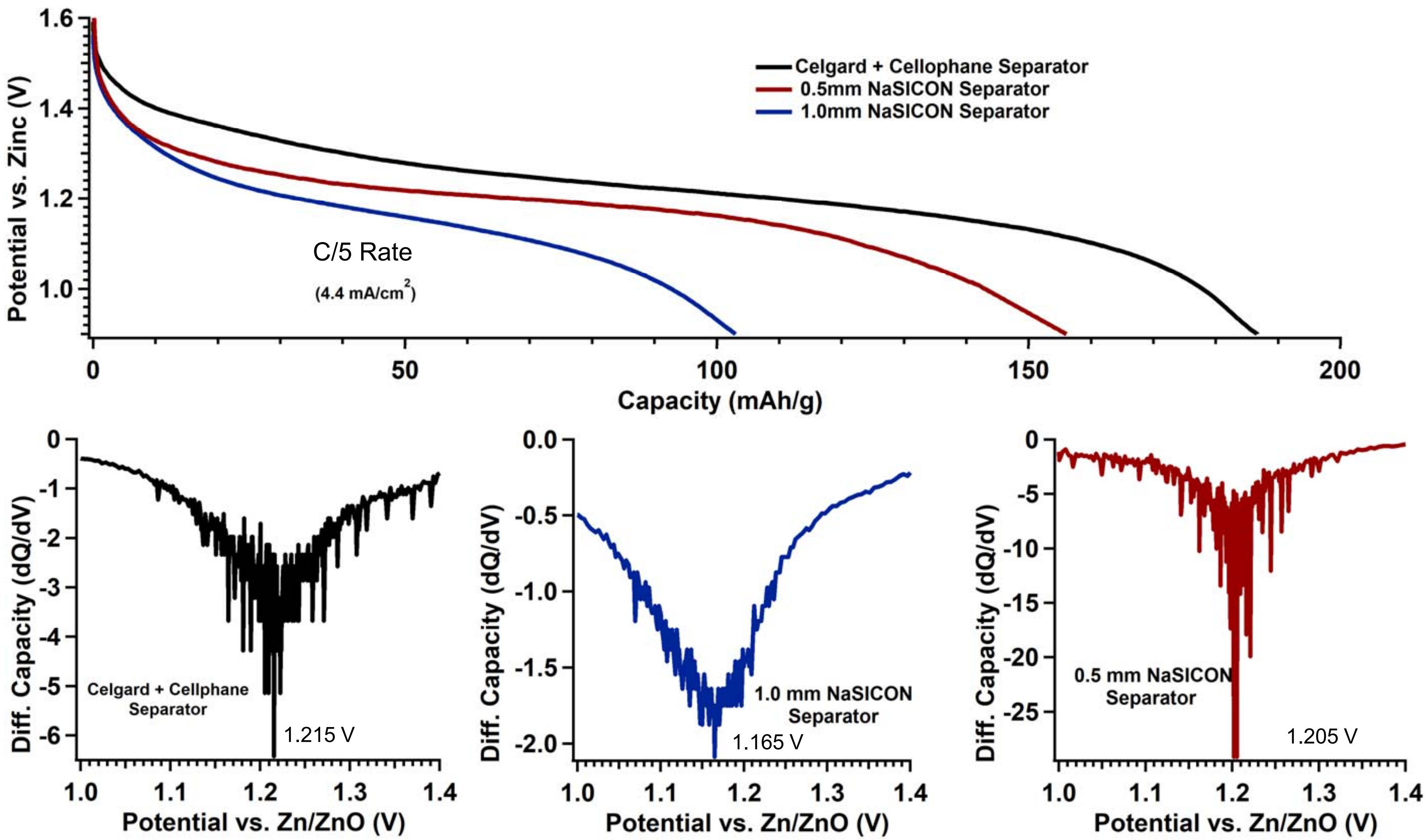


-NaSICON has significant effect on power curve due to its thickness
-NaSICON also increases total resistance of the battery
-However decreasing thickness can result in a usable separator

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

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

Effect of Membrane Resistance on Discharge

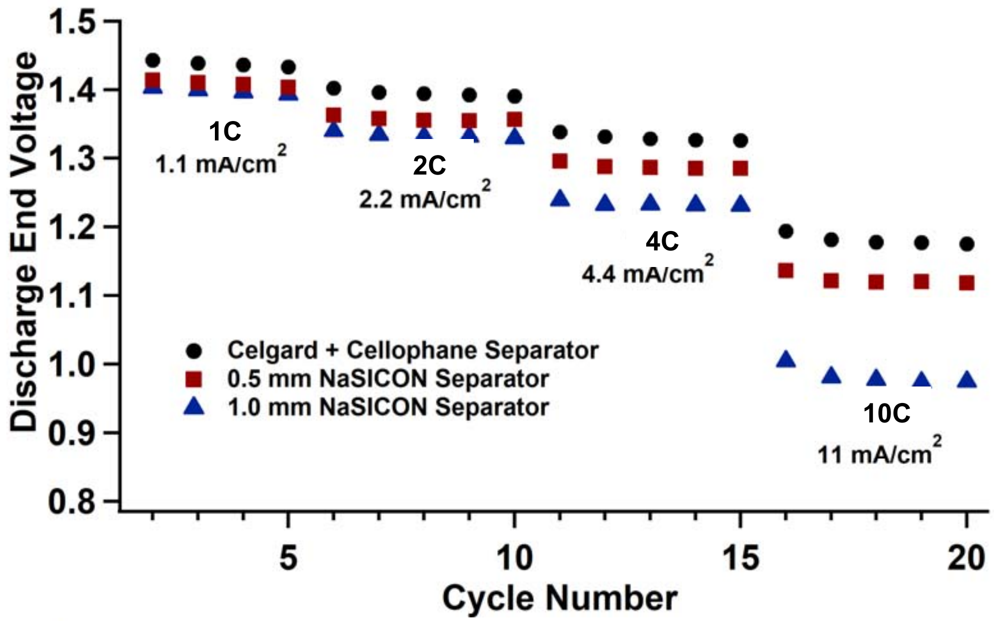


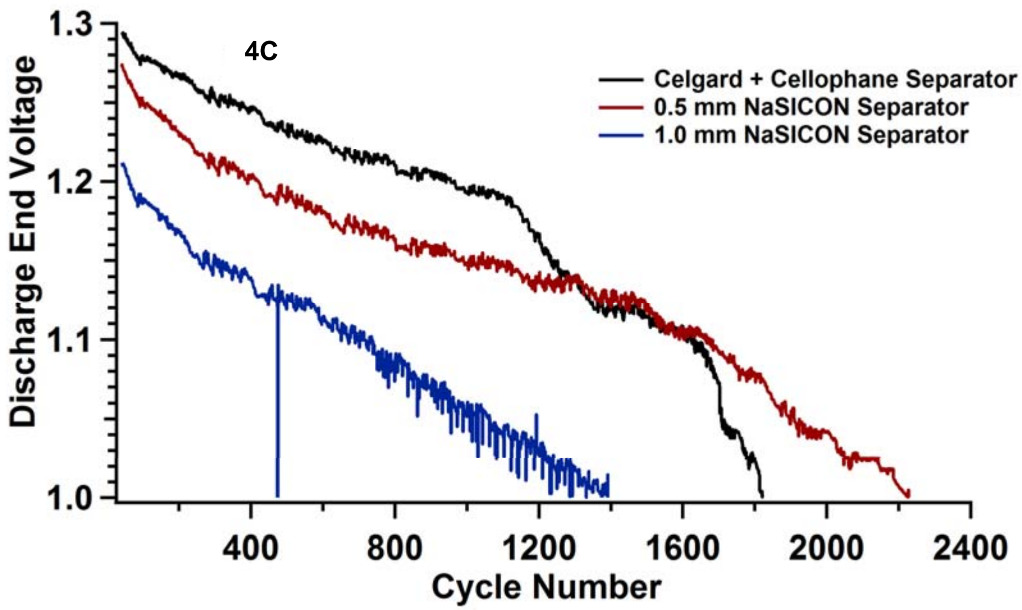
-NaSICON increases polarization of the cell

-However that polarization can be reduced by decreasing the thickness of the NaSICON

J. Duay, *et al. J. Power Sources* **2018**, *395*, 430–438.

Effect on 5% DOD Cells



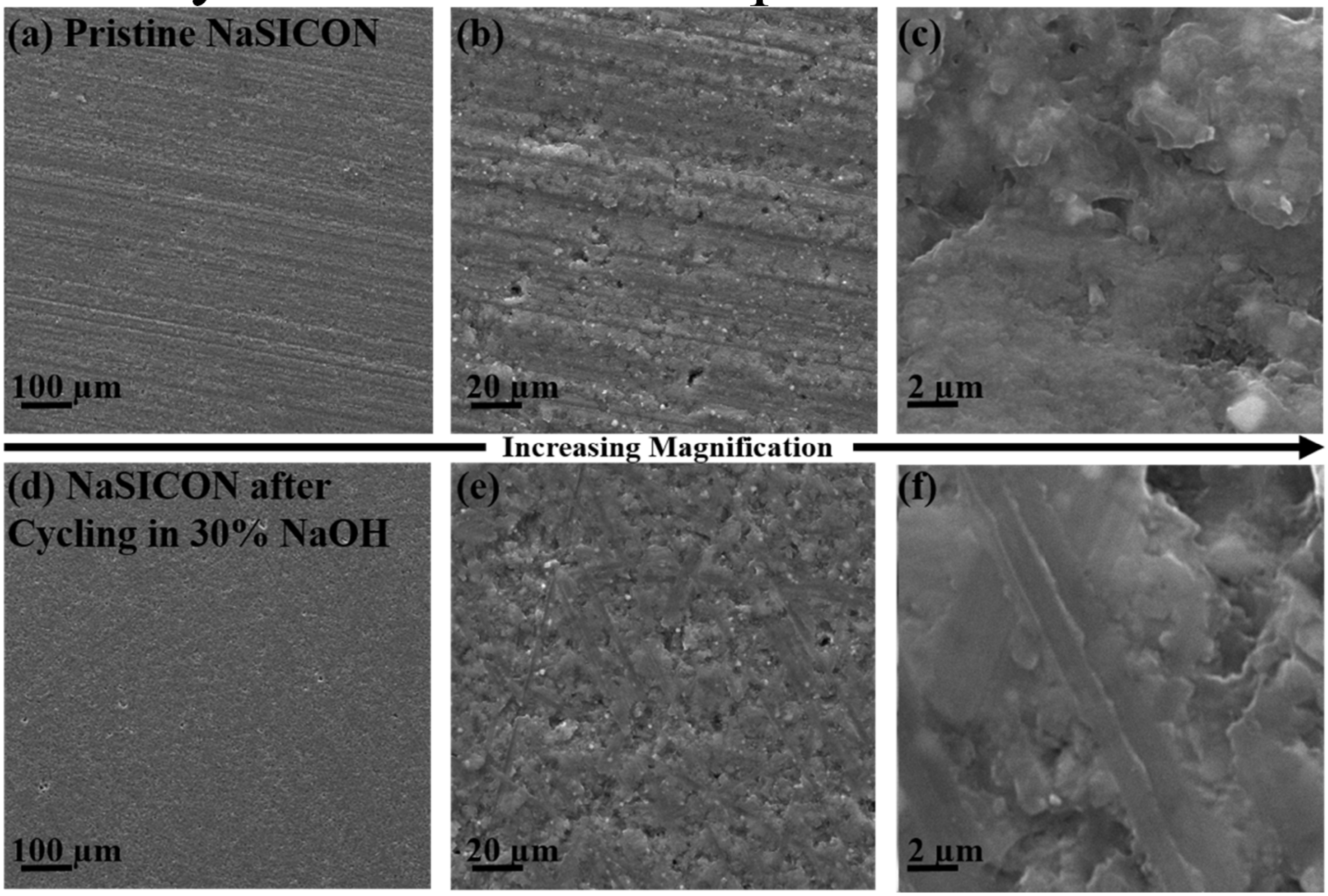


At relevant discharge rates for grid storage, the thinner **0.5 mm NaSICON doesn't decrease DEV significantly**

As NaSICON is thinned, it's advantages become more apparent increasing cell lifetime ~ 22%

J. Duay, *et al. J. Power Sources* **2018**, *395*, 430–438.

Stability of NaSICON Separator



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

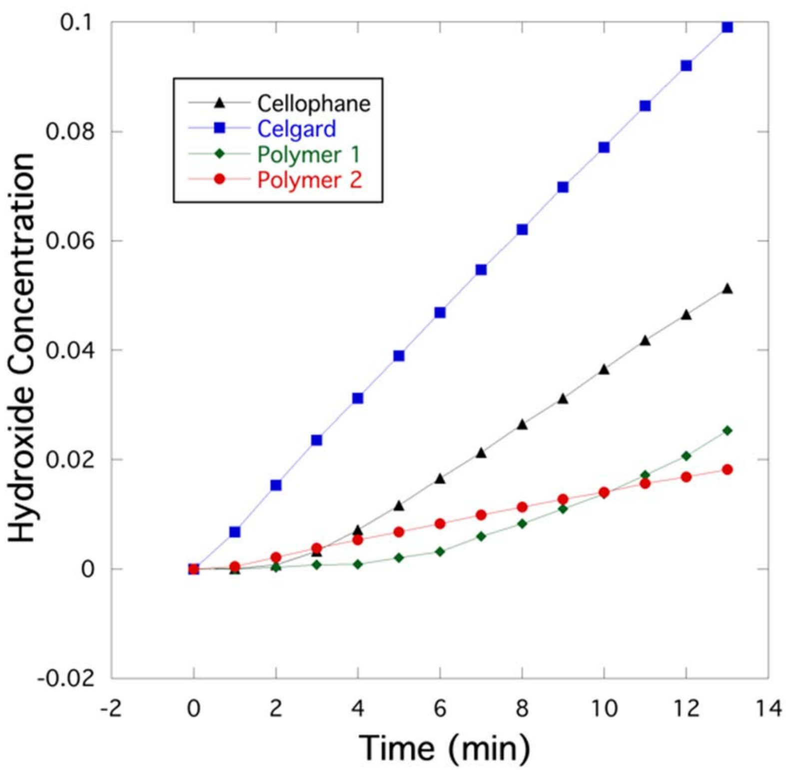
Thickness
Before: 0.503 ± 0.011 mm
After: 0.506 ± 0.013 mm

J. Duay, *et al. J. Power Sources* **2018**, *395*, 430–438.

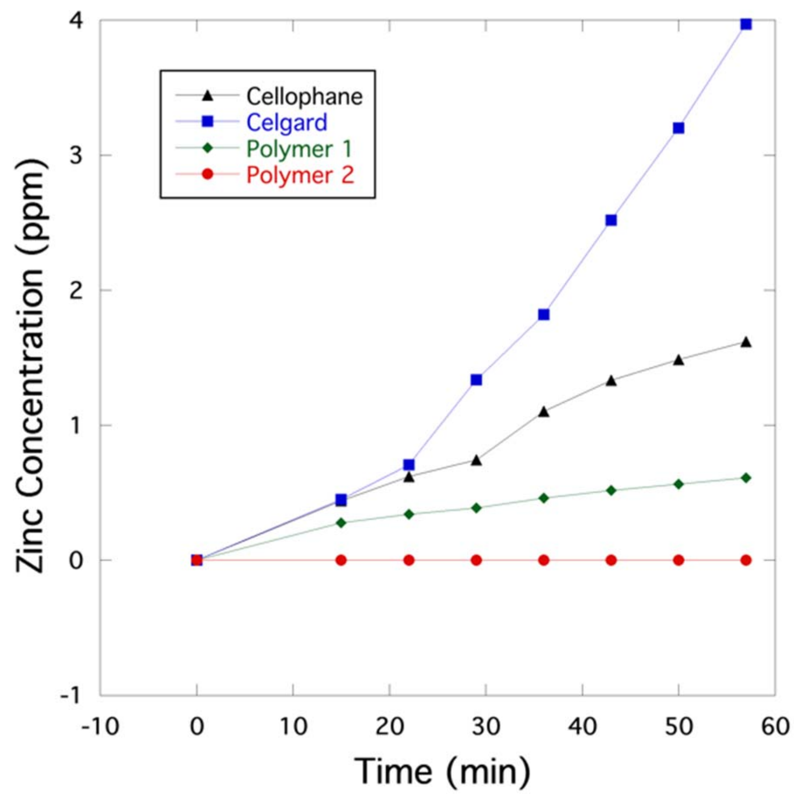
Separators – Polymeric Separators

Development of flexible polymers that allow for selective ion transport (lower cost and more flexible battery assembly)

Hydroxide Diffusion



Zincate Diffusion



$$D = \frac{V_b L}{At} ln\left(\frac{C_A}{C_A - C_B}\right)$$

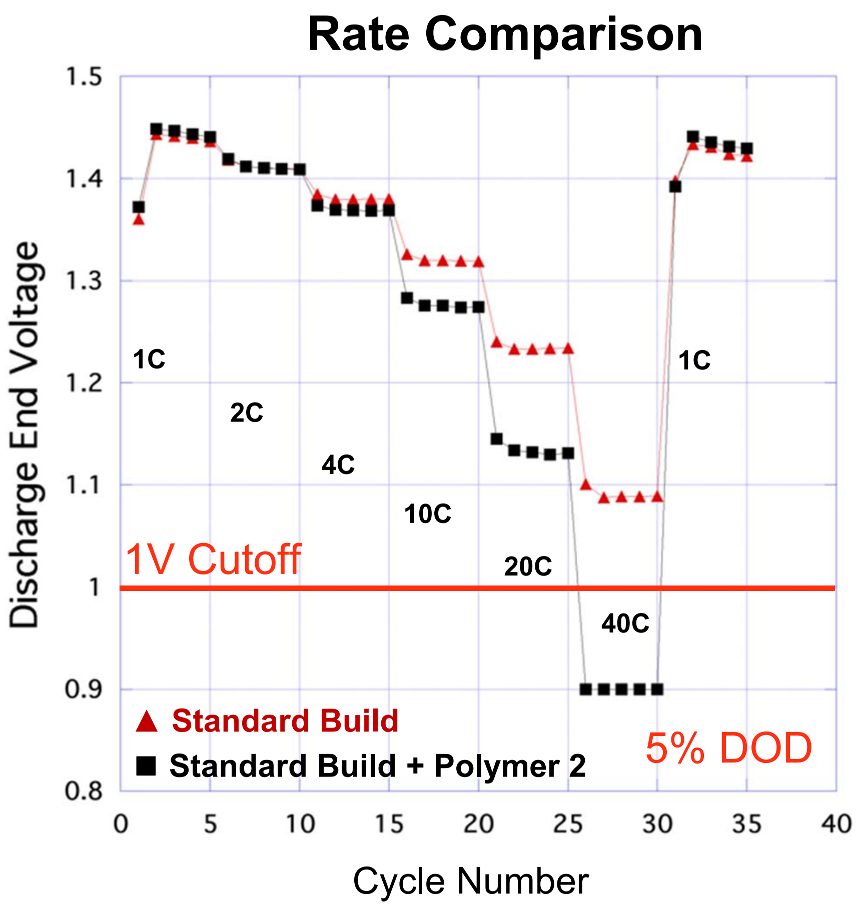
Polymer 2 appears to be 100% selective for hydroxide

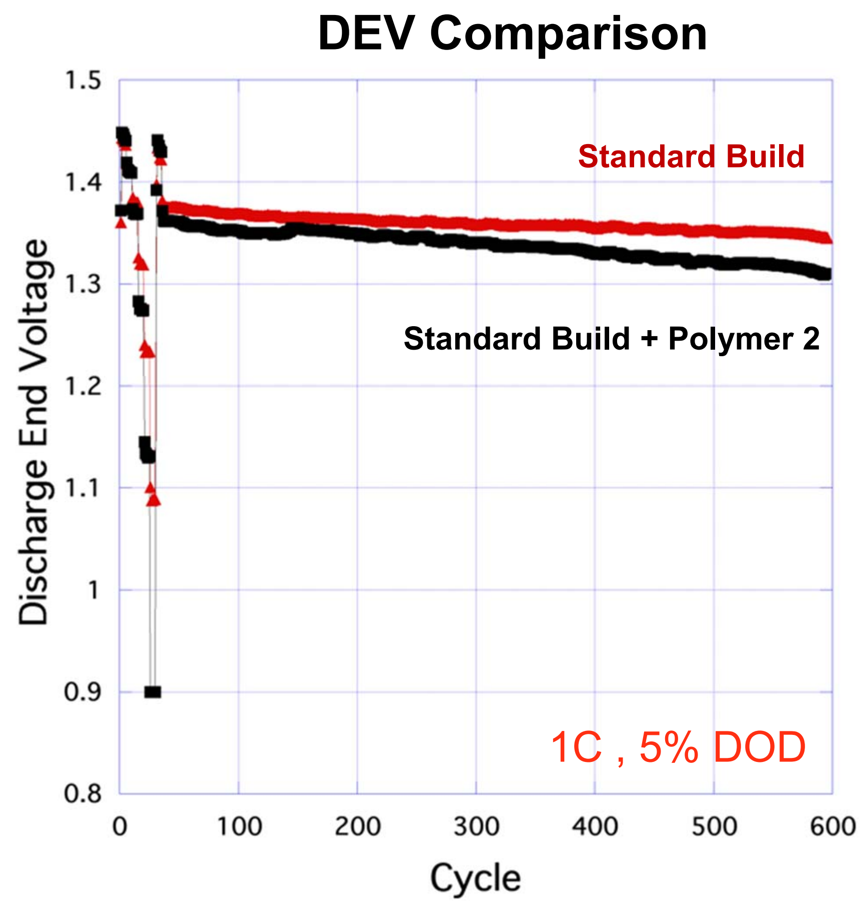
D. Arnot *et al. unpublished results*.

ASV Analysis for Diffusion coefficients: J. Duay *et al.*, *Electroanalysis* (**2017**) 29, 2261-2267 DOI:10.1002/elan.201700337.

Separators – Polymeric Separators

Application to Limited DOD Zn/MnO_2 cells



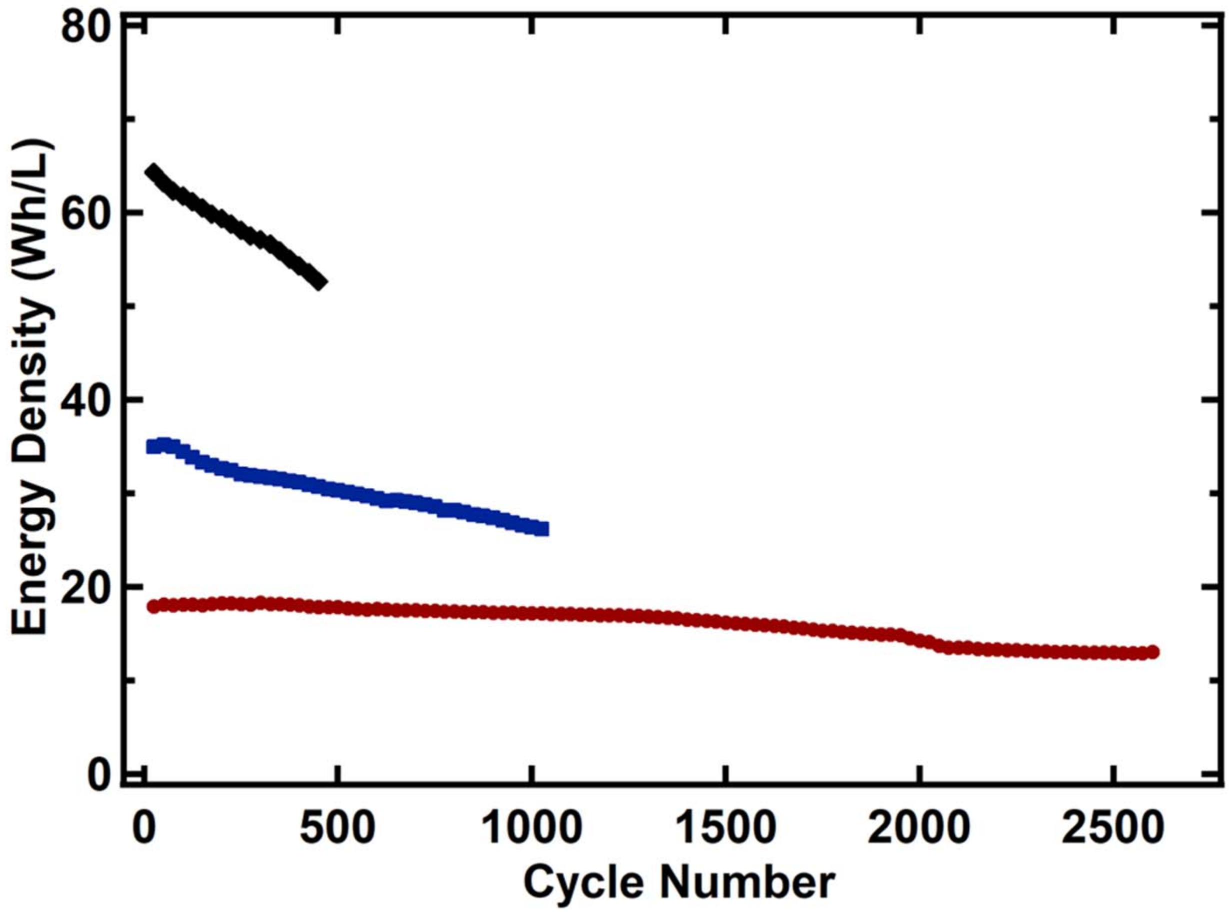


Polymer 2 appears to be a promising hydroxide selective separator

D. Arnot *et al. unpublished results.*

New Cathodes for Alkaline Zn Battery

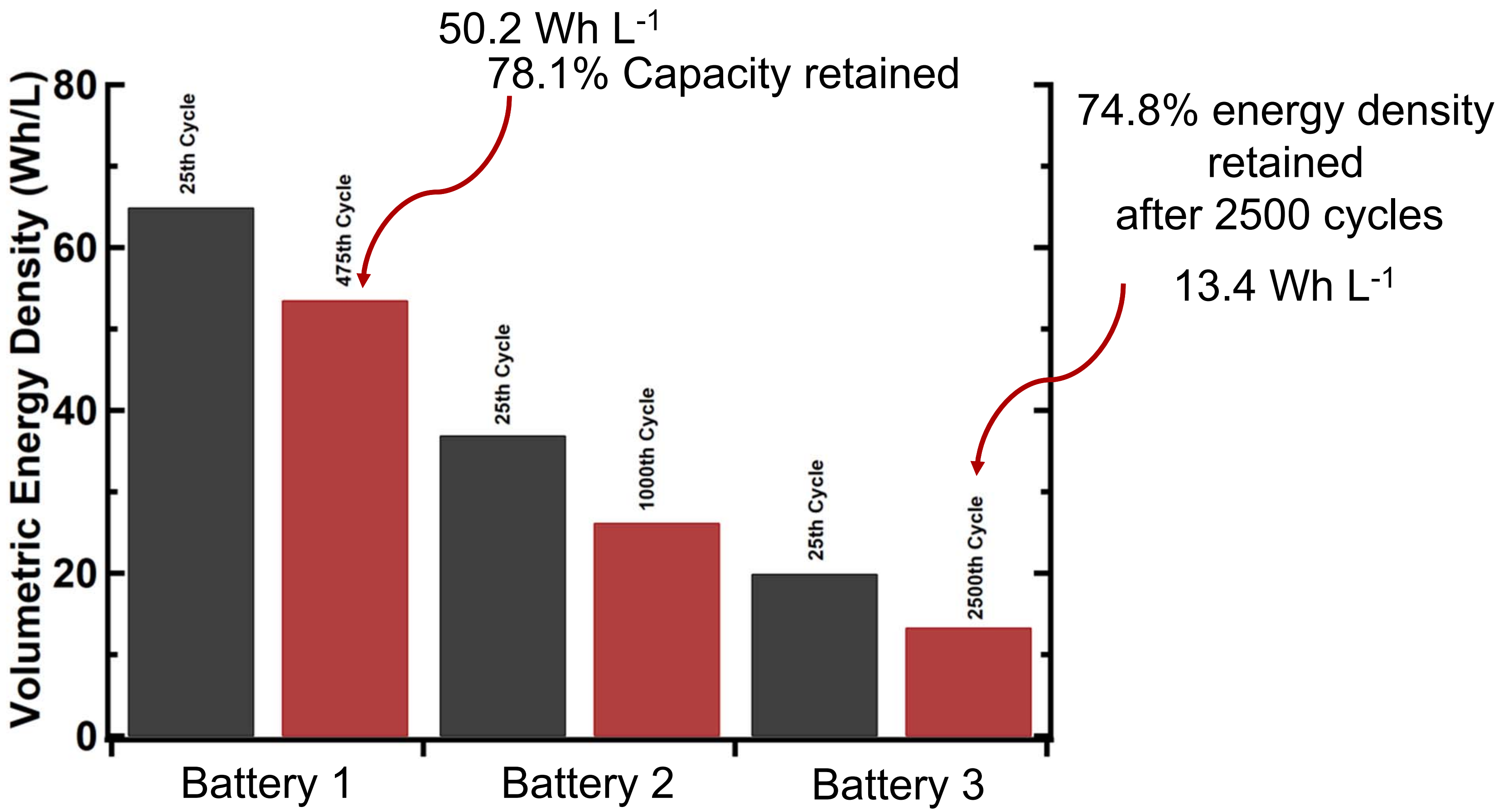
- Cathode limited batteries with Zn anode, alkaline electrolyte
- Long cycle life with energy densities similar to limited DOD Zn/MnO_2 achieved



T. N. Lambert and J. Duay, United States of America Patent Application, 15/669,587, 2017 - PCT/US17/45629, 2017.
T. N. Lambert and J. Duay, United States of America Patent Application, 16/054,114, 2018 - PCT/US18/45187, 2018.

New Cathodes for Alkaline Zn Battery

- Cathode limited batteries with Zn anode, alkaline electrolyte
- Long cycle life with energy densities similar to limited DOD Zn/MnO_2 achieved
- High volumetric energy densities have been obtained but with lower cycle life
- Optimization is ongoing - looking for partners to develop further



T. N. Lambert and J. Duay, United States of America Patent Application, 15/669,587, 2017 - PCT/US17/45629, 2017.
T. N. Lambert and J. Duay, United States of America Patent Application, 16/054,114, 2018 - PCT/US18/45187, 2018.

Summary

- Electrolyte additives can increase cycle life and rate performance in limited DOD Zn/MnO_2 batteries
- NaSICON separators block zincate crossover and can be effective at rates relevant to grid storage despite their high resistance
- Polymeric selective separators are under development at SNL and several promising leads have been developed – applicable to $1e^-$ and $2e^-$ MnO_2
- New ‘low cost’ cathodes with grid storage relevant energy densities are under development

Acknowledgements

U.S. DEPARTMENT OF ENERGY

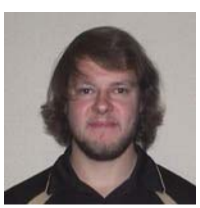

Imre Gyuk

Sandia National Laboratories

LDRD Laboratory Directed Research and Development


Babu Chalamala


Jonathon Duay


Igor Kolesnichenko

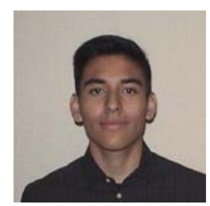

Matthew Lim


Ruby Aidun


David Arnot


Maria Kelly


Kristen Maus


Ivan Pineda-Dominguez

Thank you