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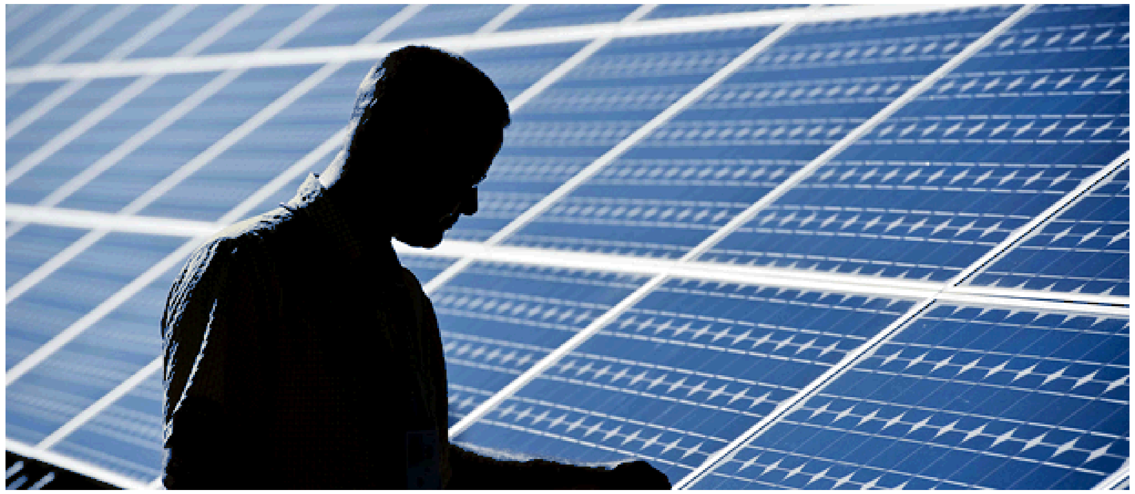
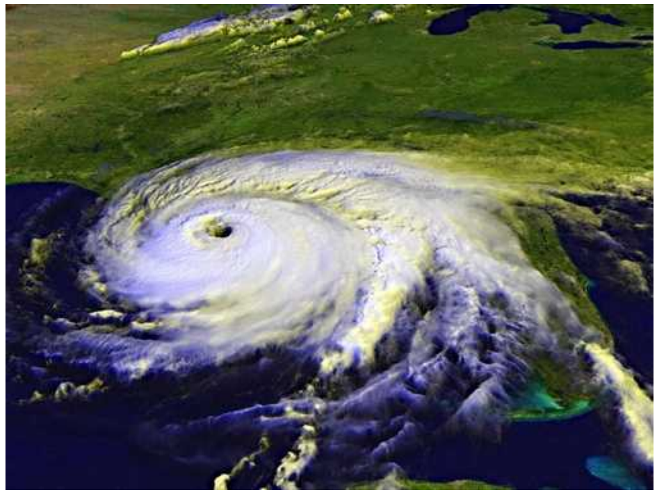
energy.sandia.gov


# Engineering Interfaces in Large Format Batteries for Grid Scale Energy Storage


Babu Chalamala

Travis Anderson, Leo Small, Harry Pratt, Cy Fujimoto, Erik Spoerke, Stephen Percival, Jill Wheeler, Eric Allcorn



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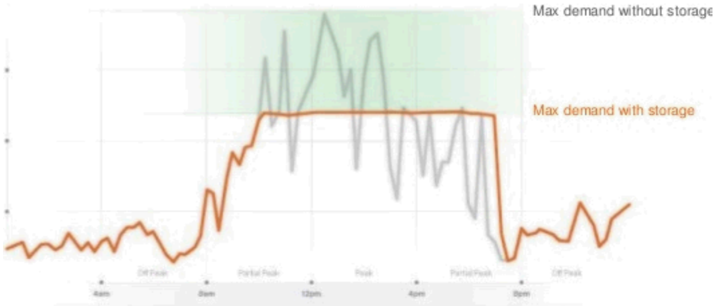
# Application Drivers for Grid Energy Storage

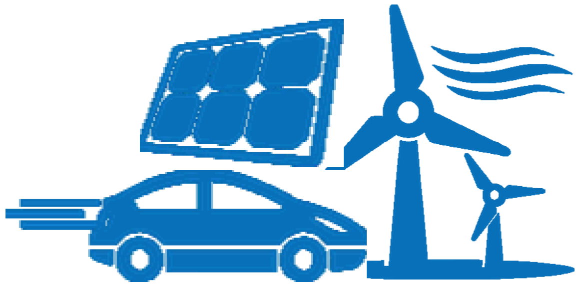
Grid-scale energy storage can enable significant cost savings to industry while improving infrastructure reliability and efficiency

- Renewable integration
- Grid resiliency and reliability
- Transmission & Distribution upgrade deferral
- Improving Power quality
- Improving the efficiency of existing generation fleet
- Demand management
- Off-grid applications

**Mitigate $79B/yr in commercial losses from outages**

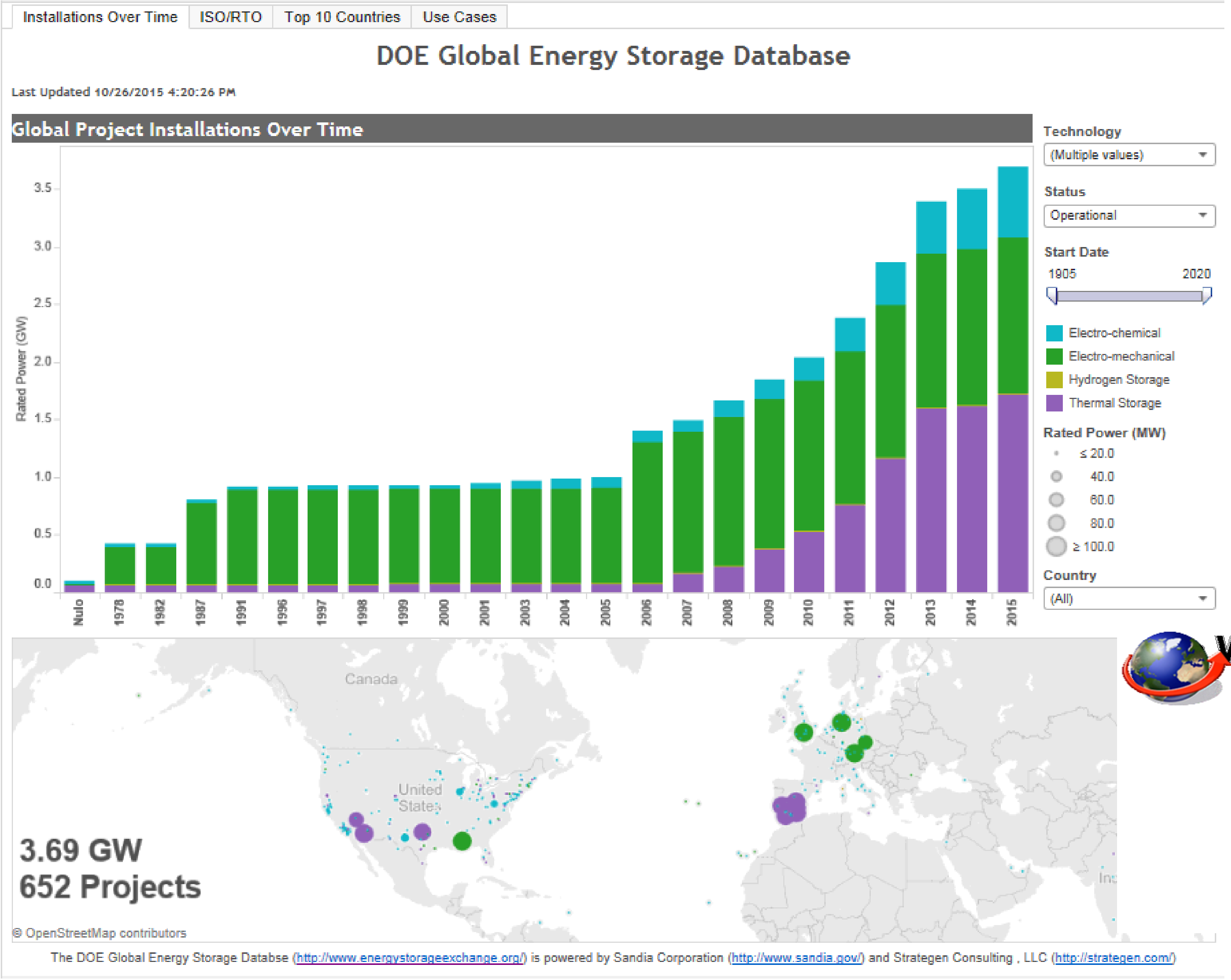



**Reduce commercial and industrial electrical bills through demand charge management. 7.5 million U.S. customers are enrolled in dynamic pricing (EIA 2015)**



**Balance the variability of 825 GW of new renewable generation while improving grid reliability and efficiency.**

# Energy Storage on the Grid Today




**World-wide 2.2%**

- **Japan 8.9%**
- **Europe 4.7%**
- **USA 2.2%**

**Source:** DOE Global Energy Storage Database

# Current Battery Energy Storage deployments (Operational as of Nov. 2017)

***Energy Storage Comparison***

***<u>Globally</u>***

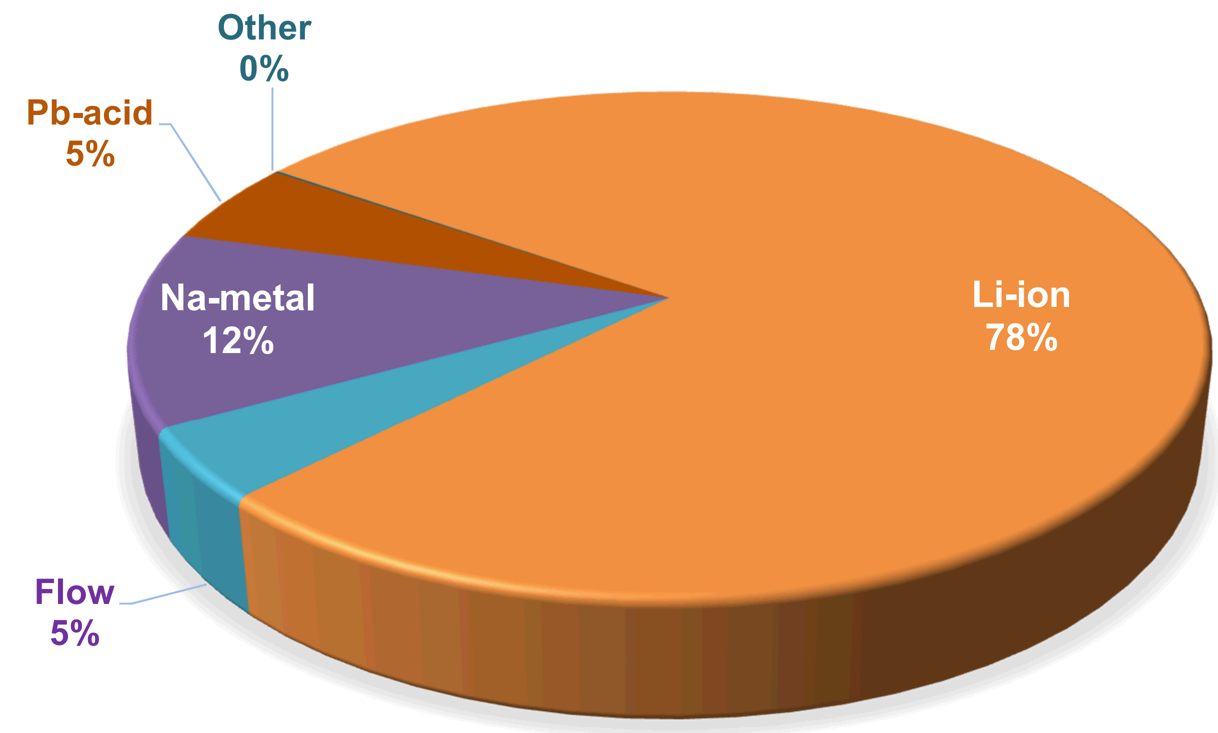
- *1.7 GW - Battery Energy Storage (BES)*
- *~170 GW - Pumped Hydro Storage (PHS)*

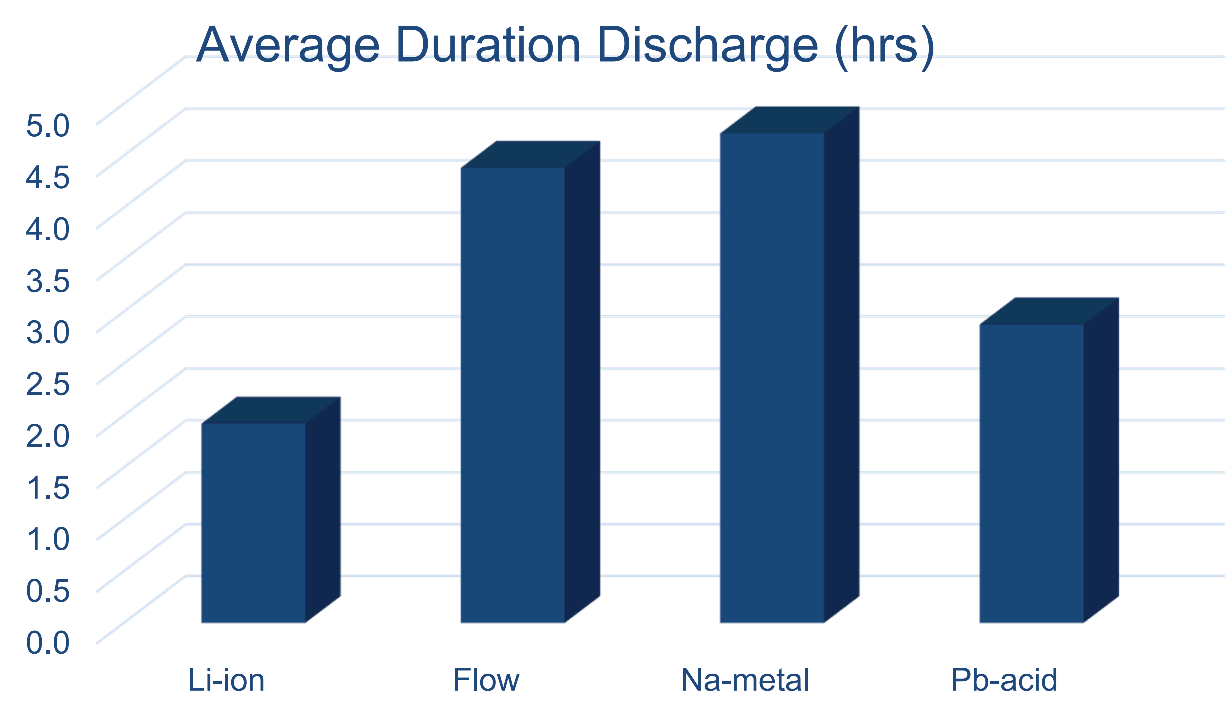
***<u>U.S.</u>***

- *0.33 GW BES*
- *22.7 GW PHS*

***<u>% of U.S. Generation Capacity</u>***

- *0.03% BES*
- *2.2% BES + PHS*




***Source:*** *DOE Global Energy Storage Database http://www.energystorageexchange.org/ Nov. 2017*

# Examples of recent installations


SD G&E 30 MW/120 MWh Li-ion Battery
Escondido, CA

3 MW/3 MWh Ultrabattery
East Lyons, PA

100kW/400kWh Flow Battery
EPB, Chattanooga, TN


SCE 20MW/80MWh Li-ion Battery
Mira Loma, CA

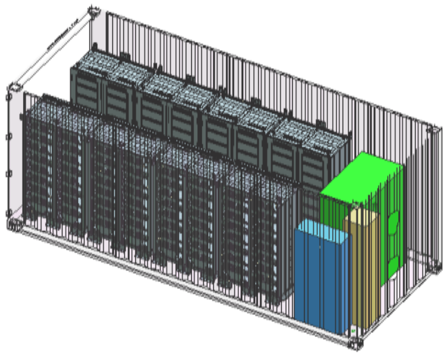
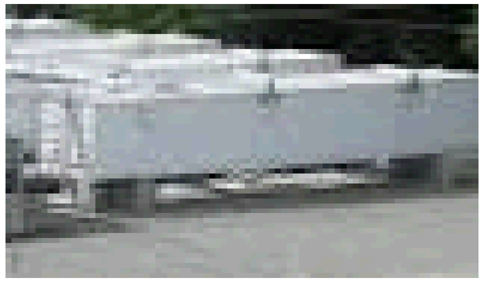
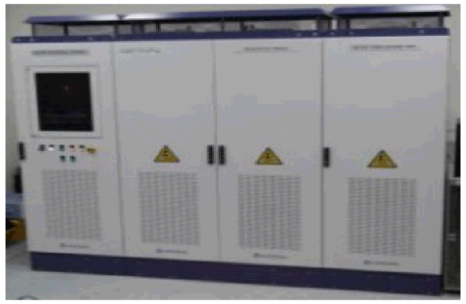
NGK 34MW/245 MWh NaS
Rokkasho, Japan

AVISTA 1 MW/3.2 MWh Flow Battery
Pullman, WA

# Elements of an Energy Storage System

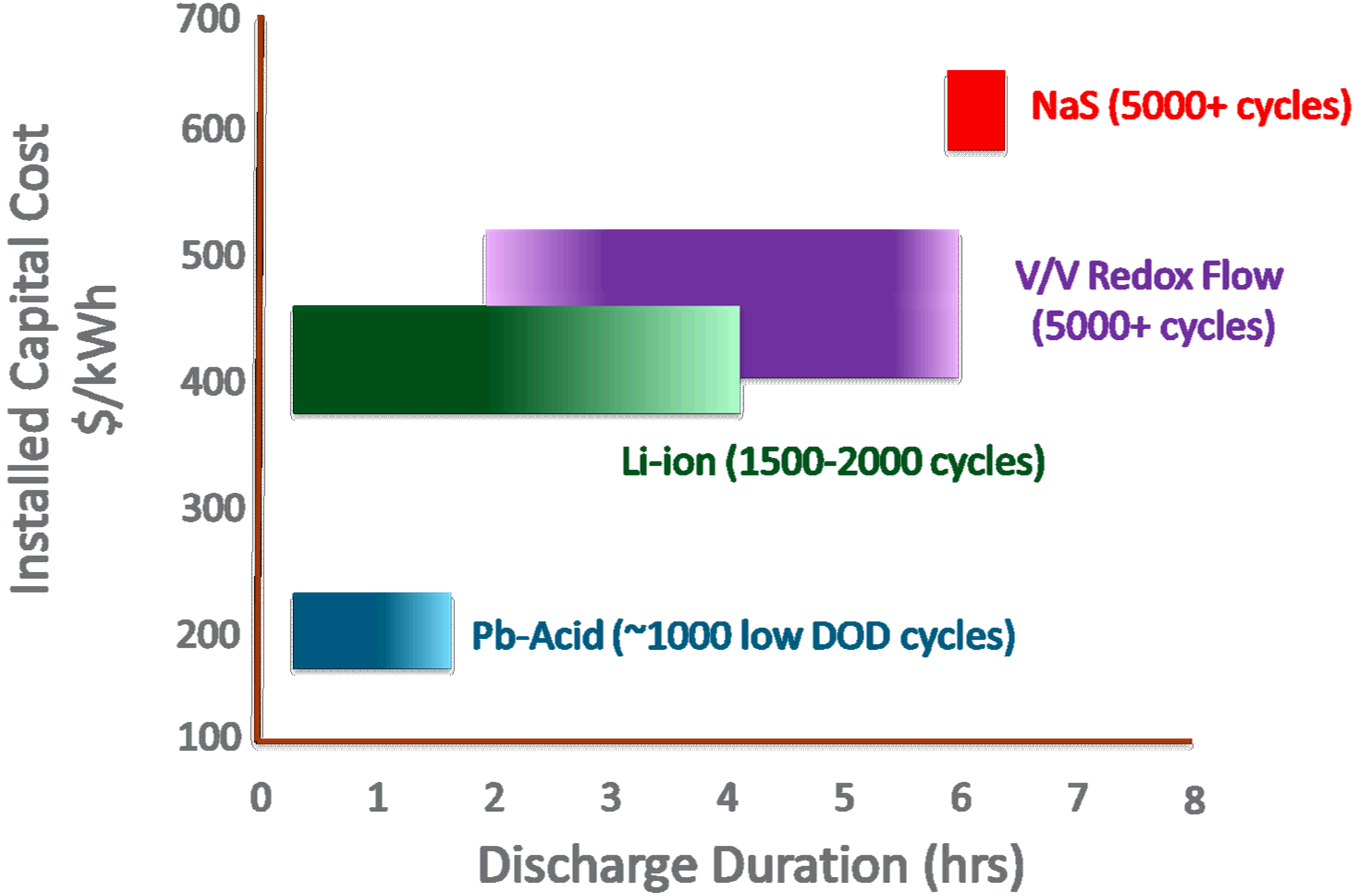
| Storage | Integration | PCS | EMS |
|---|---|---|---|
| • Cell<br>• Battery Management & Protection<br>• Racking | • Container / Housing<br>• Wiring<br>• Climate control | • Bi-directional Inverter<br>• Switchgear<br>• Transformer<br>• Skid | • Charge / Discharge<br>• Load Management<br>• Ramp rate control<br>• Grid Stability |

\+ Soft Costs

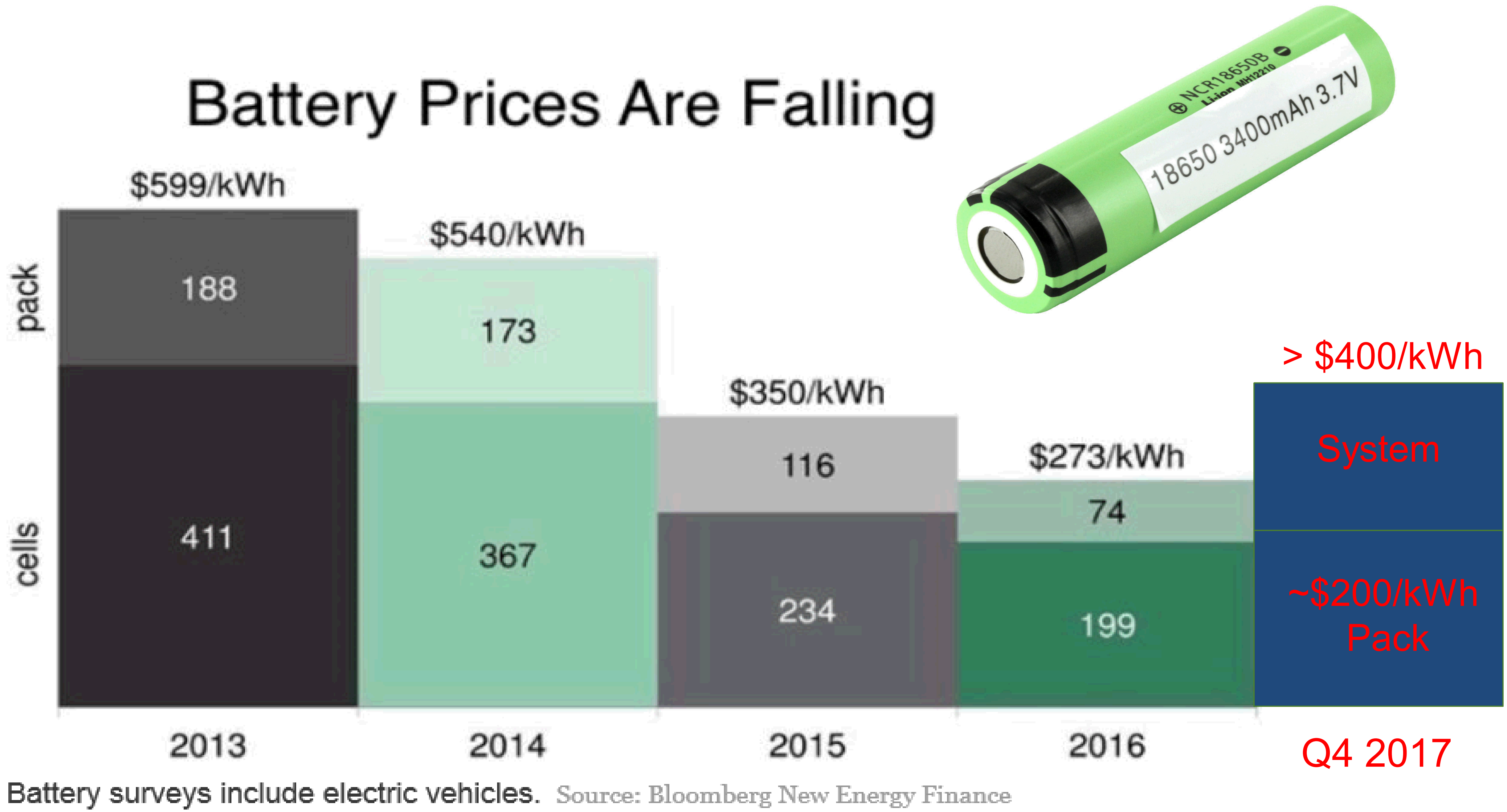

Cell to Battery to a Storage System
Doubling in cost, $250/kWh battery leads to $500-$700/kWh at the System level

# Grid Scale Batteries System Capital Cost (Q4'2017)



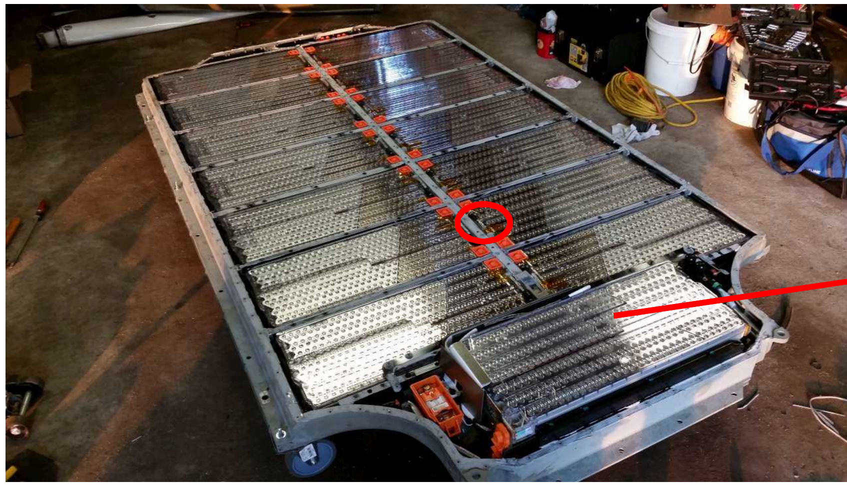

V. Sprenkle, PNNL, 2017

# Lithium Ion Battery Prices




V. Sprenkle, PNNL, 2017

# Need for Large Format Cells



**7,104 cells**


http://insideevs.com/look-inside-a-tesla-model-s-battery-pac/

http://club.dx.com/forums/forums.dx/threadid.457734

*18650 cell format used in 85 kWh Tesla battery*


*A system like 20MW -80MWh Mira Loma Battery Storage Facility would require in excess of 6 million of 18650 cells*

***Large form factor cells are needed to further drive system cost lower***

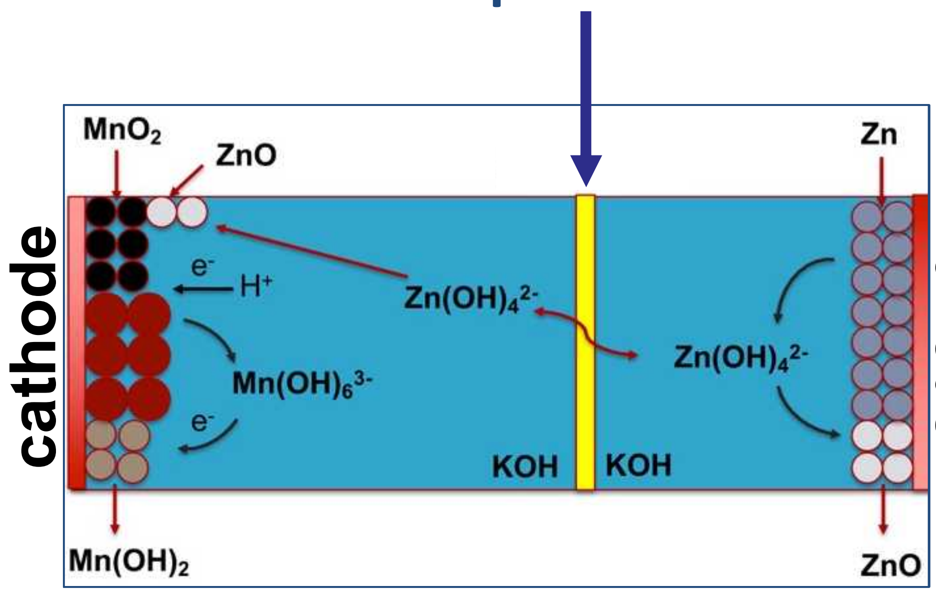
# Grid Storage and the Need for Large Format Batteries

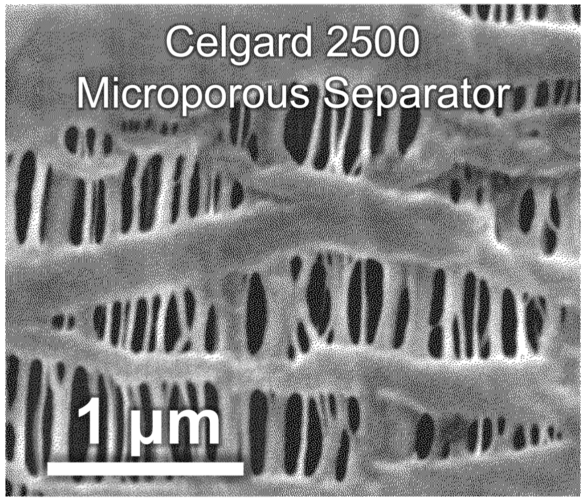
- Engineering costs are significant for small format cells. Large format cells are needed to reduce overall system costs.
- Large format cells also allow for tighter integration of power electronics, sensors, SOH monitoring at the cell level.

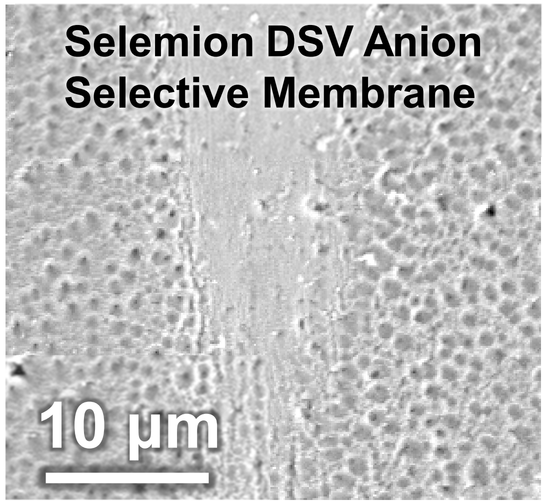
# Separators Define the Interface Between Anode and Cathode

- Fundamentally, a separator must
  - Prevent electronic shorting between anode and cathode
  - Enable facile ionic charge balancing (high ionic conductivity)
- Separators may be
  - Microporous - allows anything smaller than pore size through
  - Ion selective – only specific anions
    or cations transported

Separator

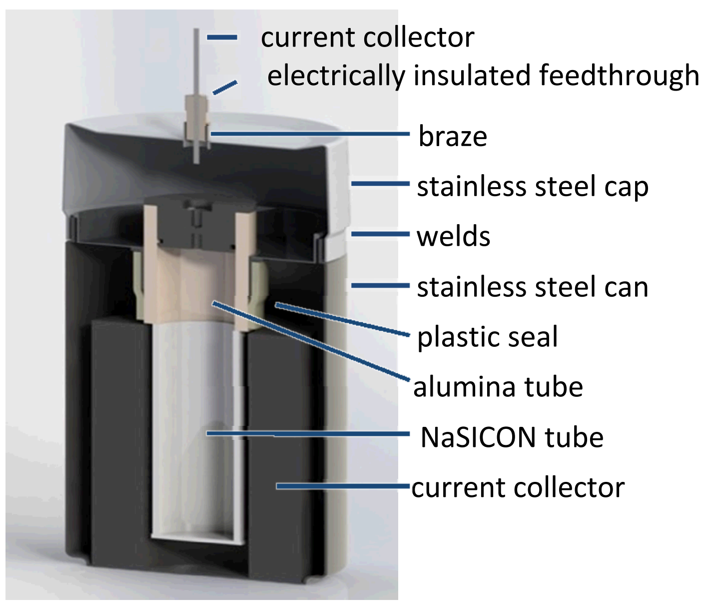


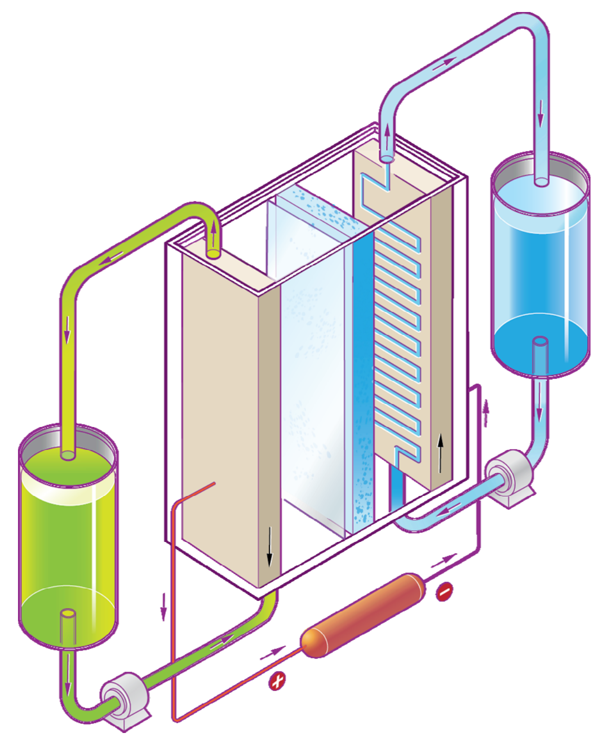
# Ion-Selective Separators for Large Format Batteries

## High Conductivity Separators for Low Temperature Molten Sodium Batteries



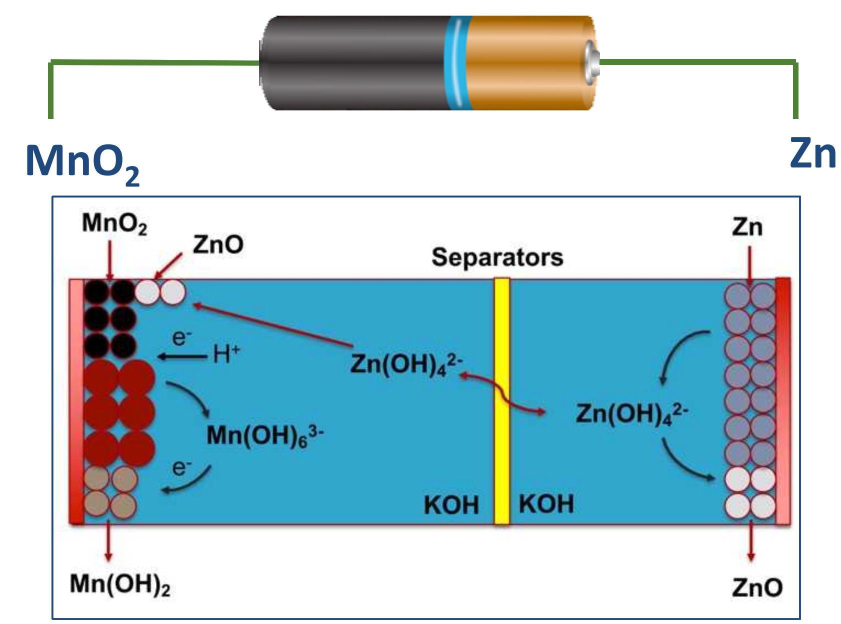

Robust ceramic separators exhibit low $Na^+$ conductivity at lower, more cost effective temperatures (<120 °C).

## Crossover in Redox Flow Batteries



Cross over of the electroactive species through the separator leads to severe capacity decay in flow battery systems.

## Zincate poisoning of $MnO_2$ in Zn/$MnO_2$ Batteries




Zincate diffusion and subsequent poisoning of $MnO_2$ impairs reversibility and significantly decreases lifetimes.

# NaS and NaNiCl2 Batteries

- Two primary chemistries
  - NaS, mature technology, deployed in grid applications
  - $NaNiCl_2$, mature, more stable than NaS
- NaS first developed by Ford Motor Co. in 1960's
  - Commercialized by NGK in Japan, over 1800 MWh of installed capacity
- NaNiCl2 (Zebra) developed in South Africa in 1980's
  - FIAMM in limited production, GE no longer in manufacturing
- Neither NaS nor NaNiCl2 are at high production volumes and the economies of scale needed

NGK 34MW - 245 MWh NaS
Rokkasho, Japan

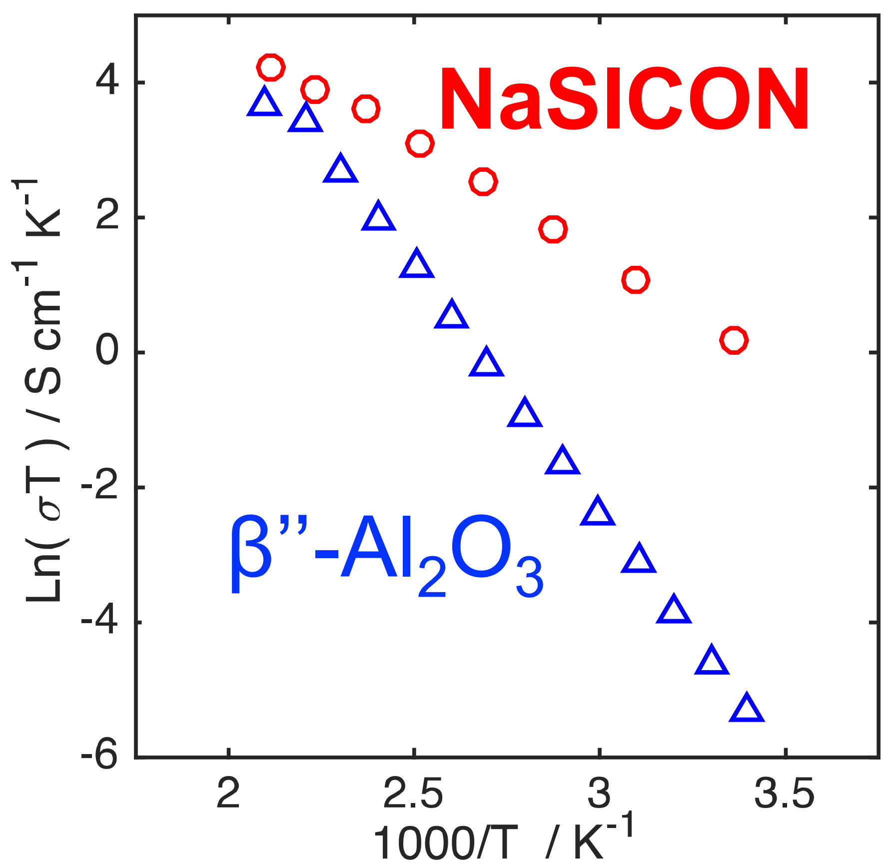
FIAMM 222-kWh System
Duke Energy Rankin Substation

# Molten Na Batteries - Engineering Challenges

- Low cost, earth abundant active materials, but challenging systems engineering
- Need for high temperature operation, kinetics driven by the solid ceramic electrolyte
  - Typical operating window 250-350 $^{o}$C. Need for continuous thermal management even when not in use. At lower T, Na metal freezes out, degree of distortion to cell dictated by SOC of battery
- Safety concerns related to membrane rupture. In NaS, failure can lead to exothermic reaction.
- Need hermetic seals.
- Charging/discharging limitations
- How to engineer cells that operate at lower T (150$^{o}$C or lower)

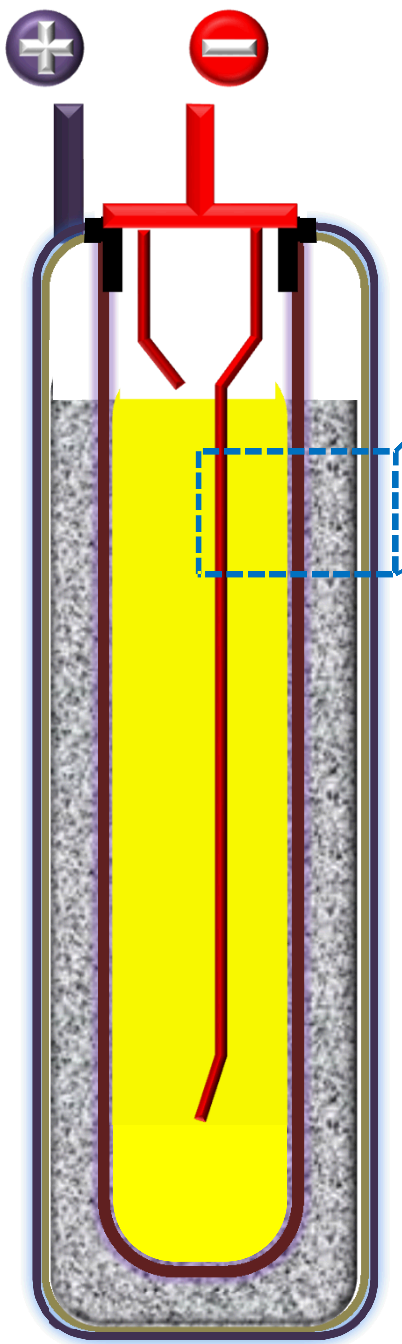
# Low Temperature NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

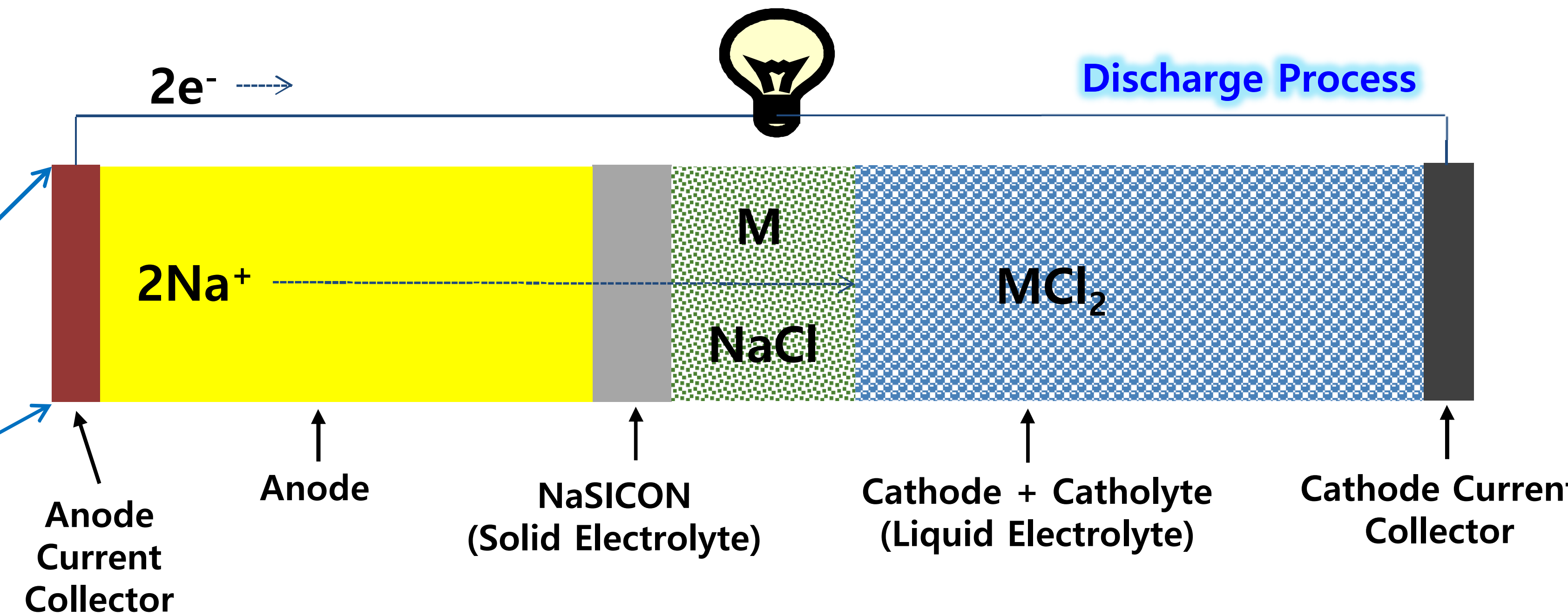
NaSICON (Na Super Ion CONductor): $Na_3Zr_2PSi_2O_{12}$




NaSICON a chemically/mechanically stable has high conductivity (>$10^{-3}$ S/cm @RT) at lower temperature. Opens the possibilities for a range of cell chemistries.

# Na-$NiCl_2$ Batteries






$$NiCl_2 + 2Na^+ + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Ni + 2NaCl$$

- Open-circuit Voltage: 2.58 V
- Lower Operating Temperature: 195°C
- Less metal corrosion compared to NaS
- Safer reaction between Na and $NaAlCl_4$ in case of solid electrolyte fracture

# Stable Na-$NiCl_2$ Cell Performance

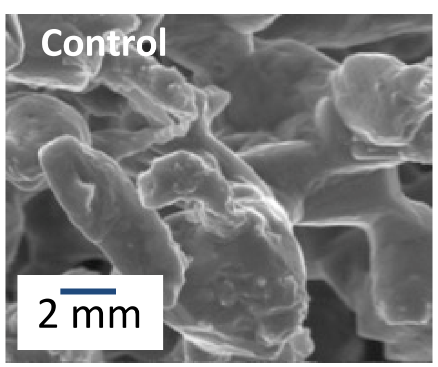
Sandia National Laboratories

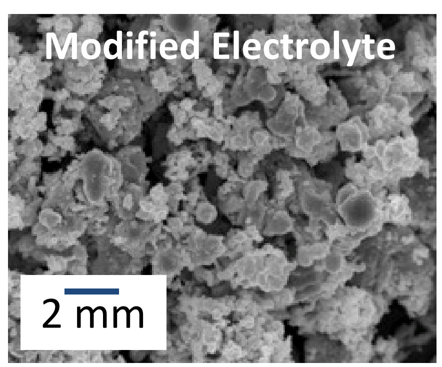
***Nickel grain growth at high temperatures during cycling limits cycle life and charge-discharge kinetics for Na-$NiCl_2$ batteries.***

**1 micrometer Ni Particle grows by more than 10X after multiple cycles**

Using a NaSICON electrolyte allows us to lower temperature below 200$^o$C and adding Ni metal growth inhibitors.

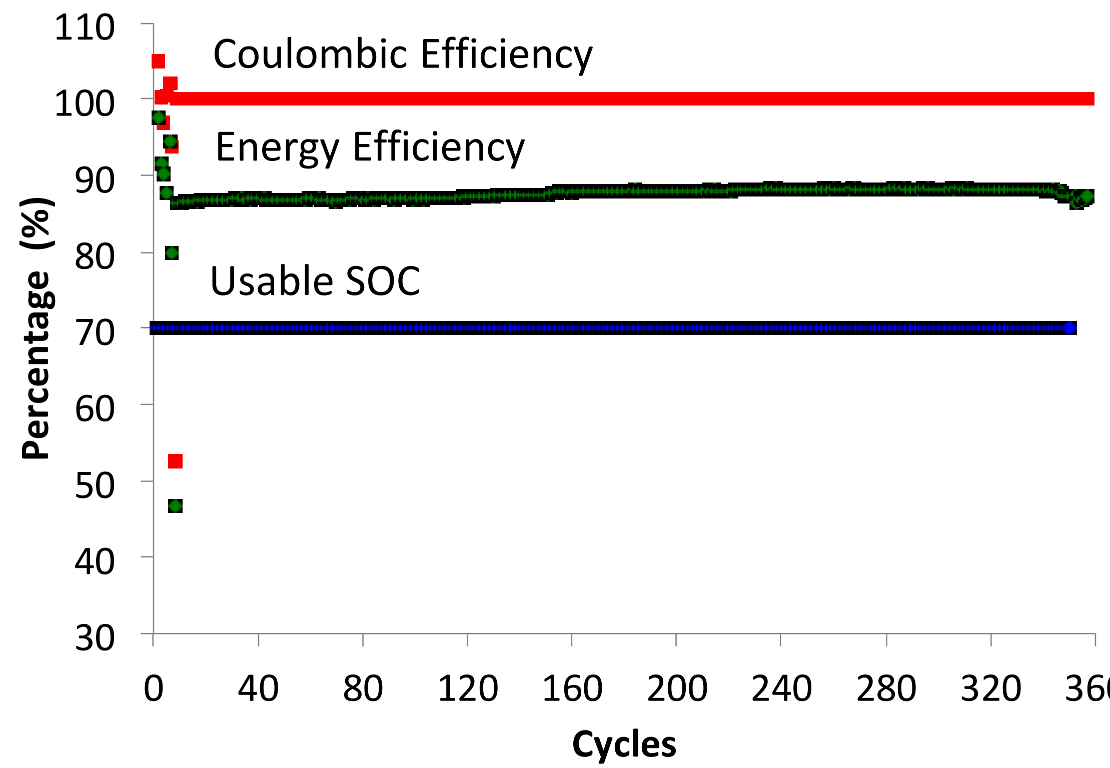
Together, these changes have allowed us to prevent Ni metal particle growth and preserve exceptional, stable battery performance over months (hundreds of cycles).




After electrochemical cycling, Ni-particle growth is suppressed using NaSICON and catholyte additives

**Cycle test (Prototype cell)**

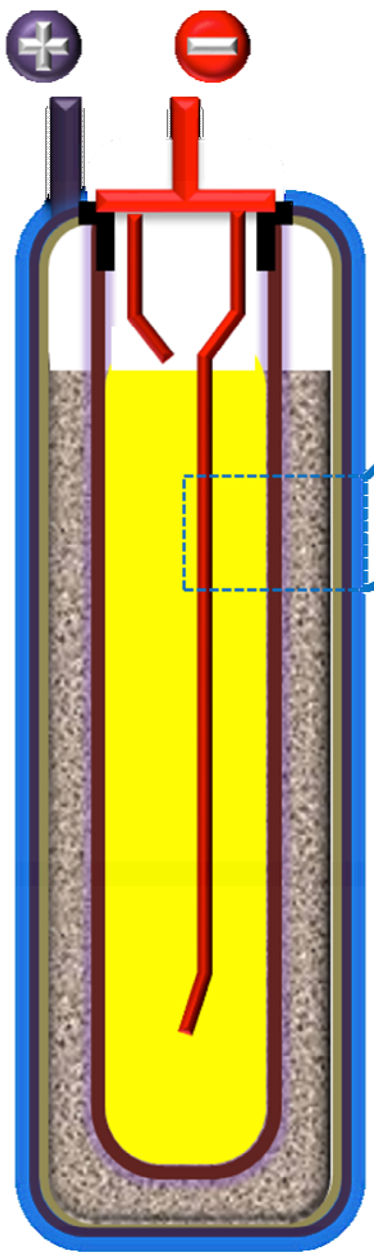


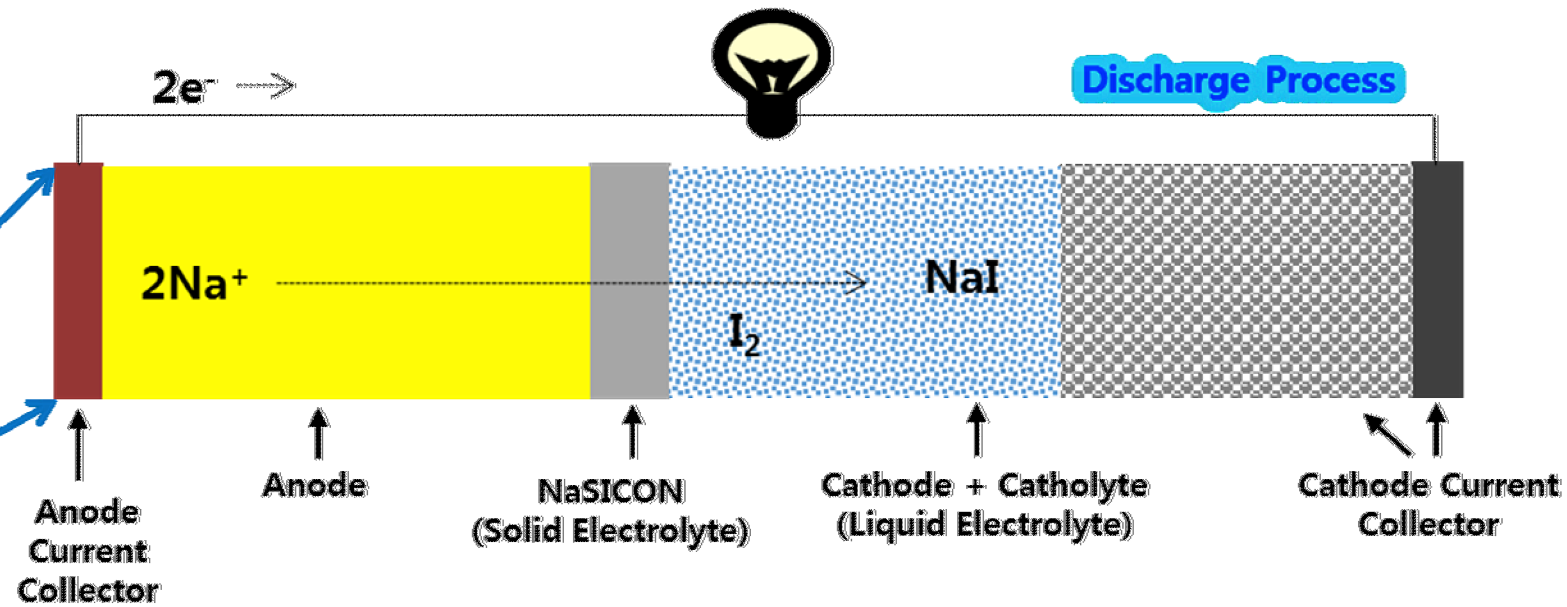

**13 Wh Na-$NiCl_2$ (NaX) Cell operation for 9+ months. 70% Depth of Discharge, >85% energy efficiency at 65 mA /$cm^2$ Charge/Discharge NaSICON current density**

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

SK

# Na-$I_2$ Batteries





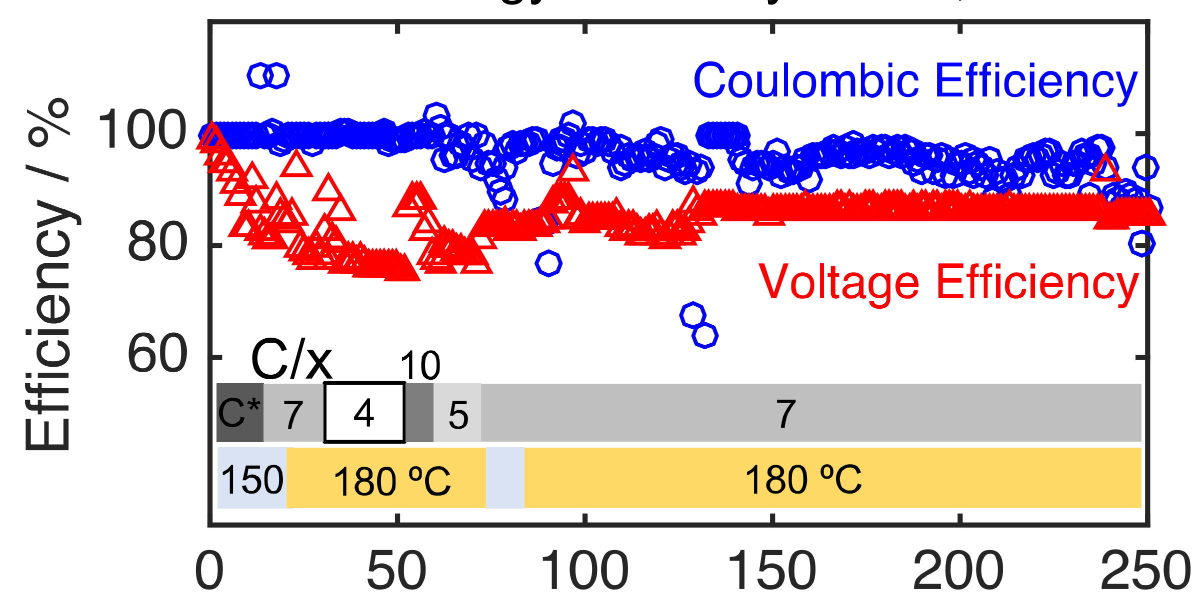

$$I_2 + 2Na^+ + \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} 2NaI$$

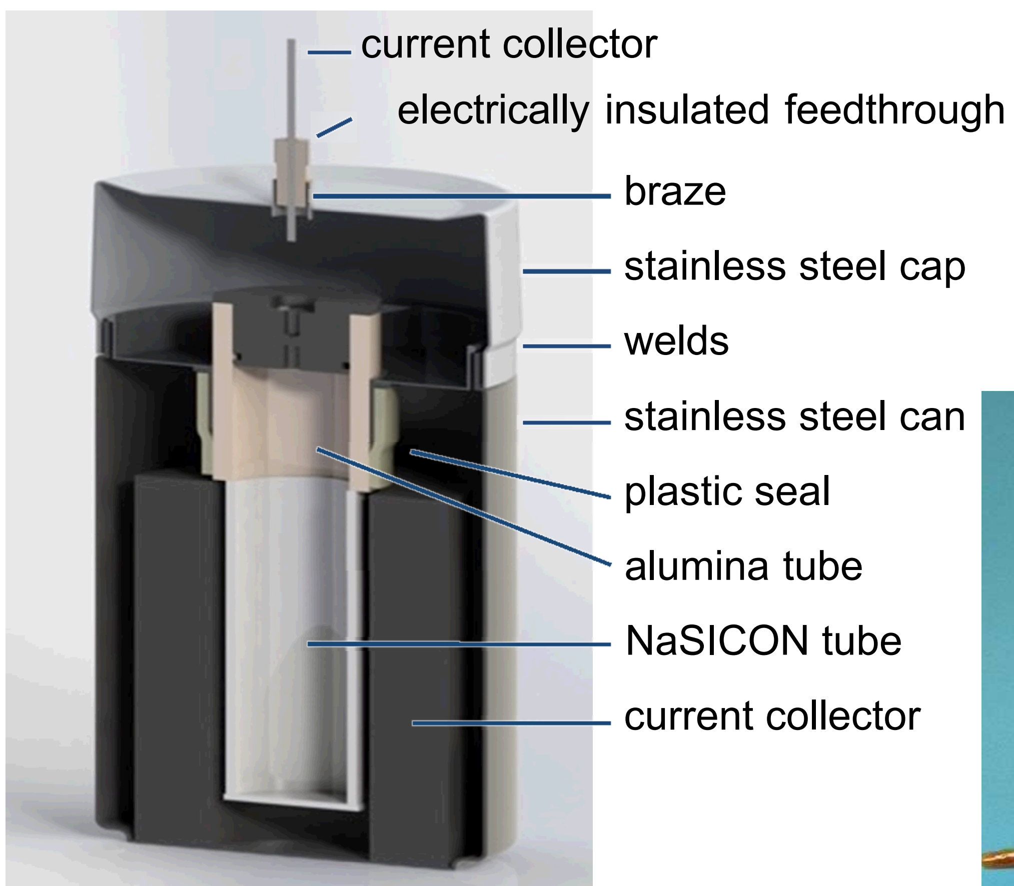
- Increased cell voltage (3.25V)
- Lower temperature (120-180$^o$C)
  - Lower cost materials/seals
  - Lower operational costs
  - New cathode chemistries
- *Liquid cathode increases feasible cycle life*

# Early Na-$I_2$ Prototypes Promising

- Graphite felt + tungsten wire current collectors
- NaI-$AlCl_3$ based molten salt catholyte
- 1" NaSICON tube glass sealed to α-alumina
- T = 150-180˚C

>80% energy efficiency over 3,000 h





**Demonstrated long term performance across multiple prototype scales**

- 0.75, 3, 10 Ah battery scales
- Functional C-rates
- Up to 50 mA/$cm^2$
- High energy efficiency of ~ 80%

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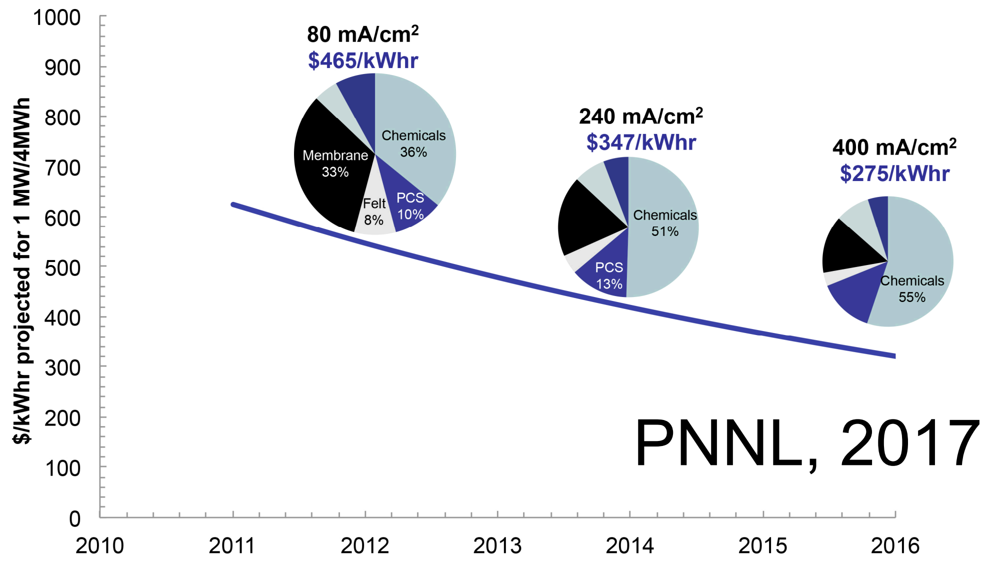
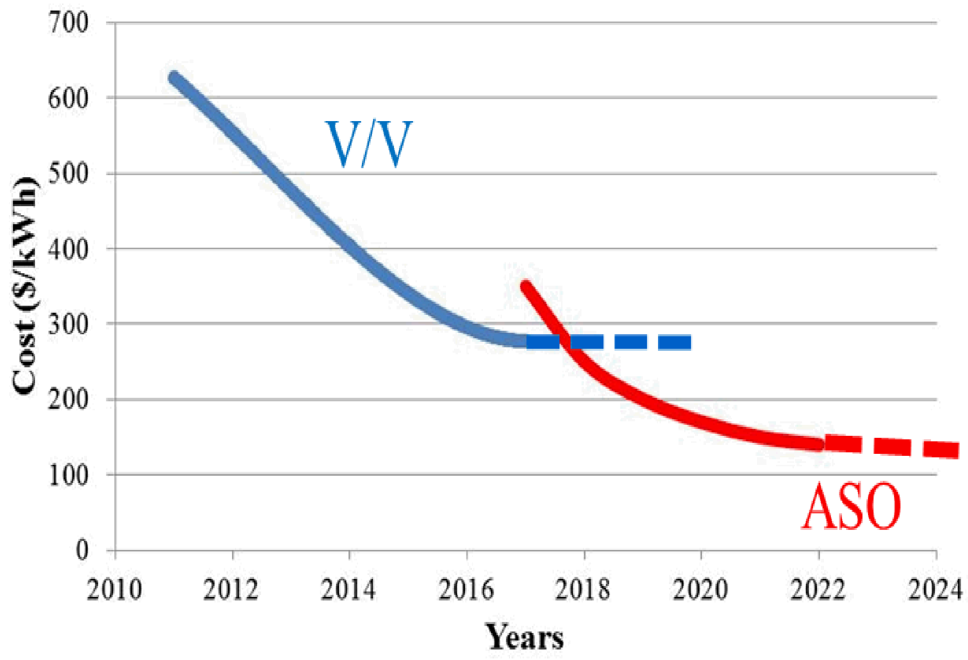
L.J. Small, E.D. Spoerke et al, *J. Power Sources* 360 (2017) 569-574.

# Flow Batteries – Challenges/Opportunities

- Significant materials challenges, and opportunities for improvement
  - Electrolytes relatively expensive (esp. Vanadium), need lower cost electrolytes
  - Low energy densities, limited solubility of V in aqueous electrolytes, need new materials
  - Electrolyte is temperature sensitive
  - Membranes are relatively expensive
- Potential opportunities to reduce materials cost
  - New redox chemistries, new electrolytes
  - Lower cost of membranes (beyond Nafion)
  - Increased current density and lower cost stack design




Major Opportunities for Improvement
Power Plant (Stack): Membranes
Energy: Electrolytes

# RFB stack sizes continue to grow

## Containerized Systems


UniEnergy Technologies, 1MW/4MWh

32 KW Stack
Rongke Power/UET
120 mA/cm2
Meter size stack

## Flow battery power plants

Sumitomo Electric, 15MW/60MWh

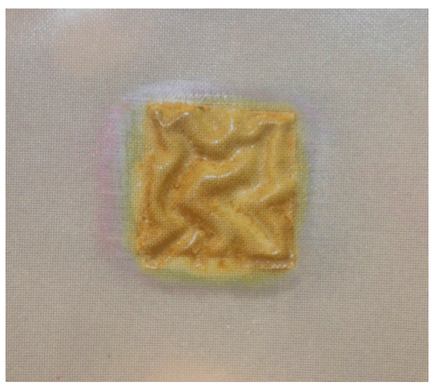
Stack room

# Low cost membranes for flow batteries

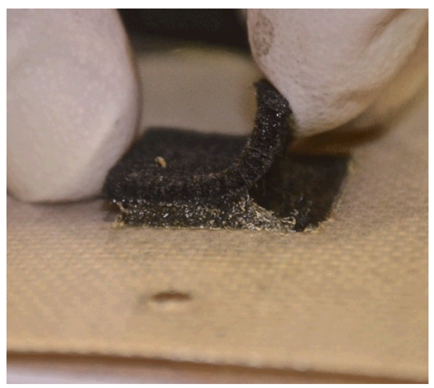
- Membranes are approximately 1/3 to 1/10 of the cost of materials in flow batteries
- Need lower cost alternatives to Nafion (Vanadium systems)
- New membranes for next generation non-aqueous systems

# Most commercially available, ion Selective membranes are not designed for non-aqueous use

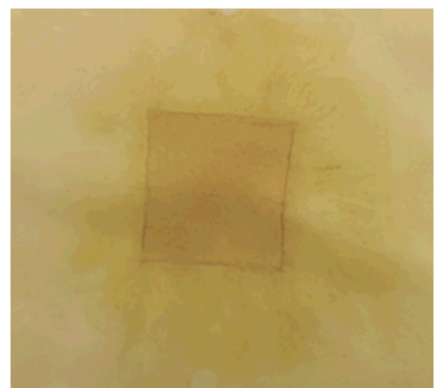
**Commercial**



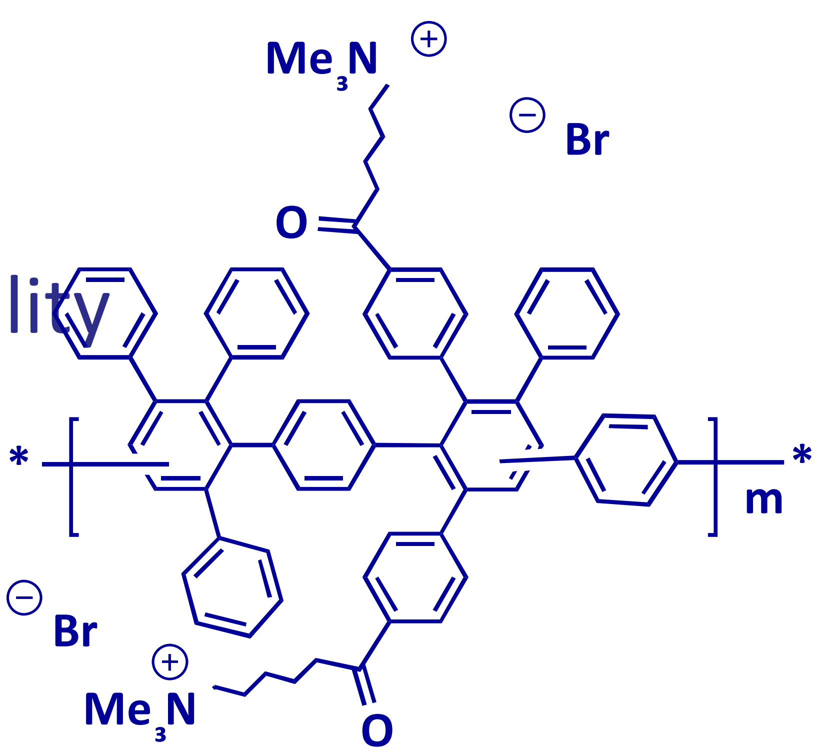
**1st Generation SNL***



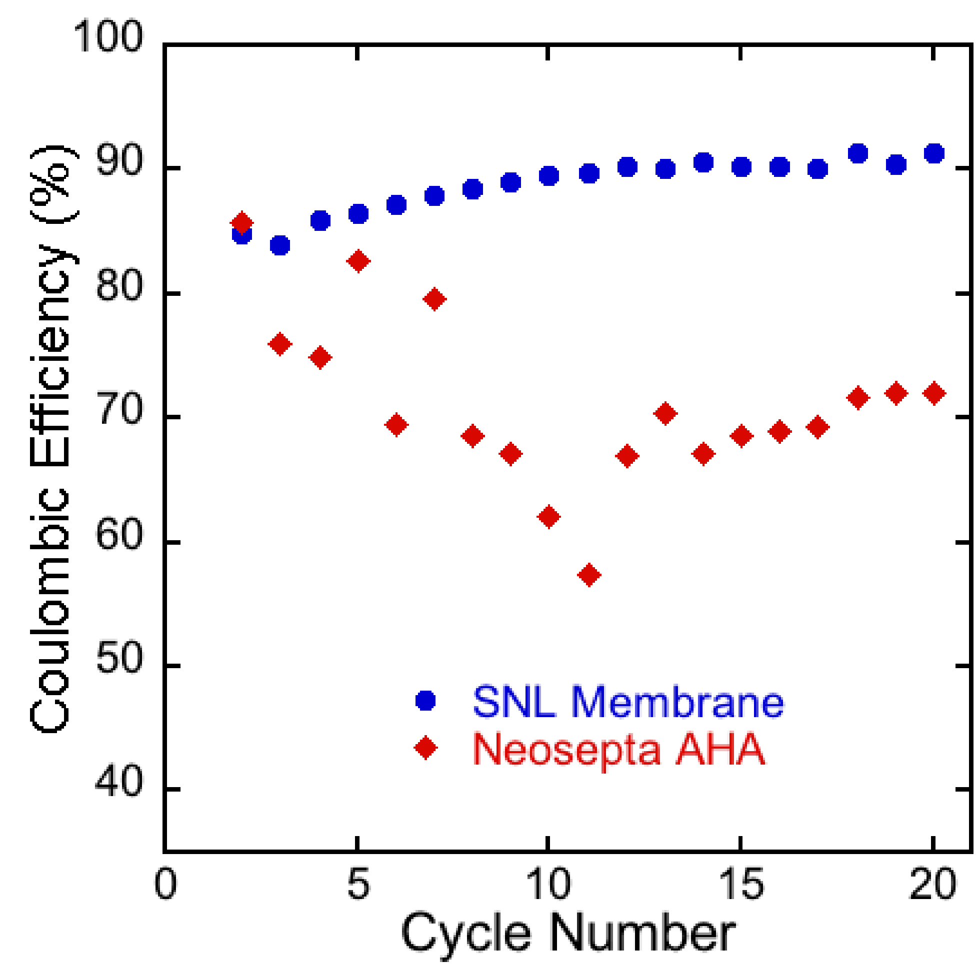
**2nd Generation SNL***



New membranes have increased chemical and temperature stability over commercial materials.

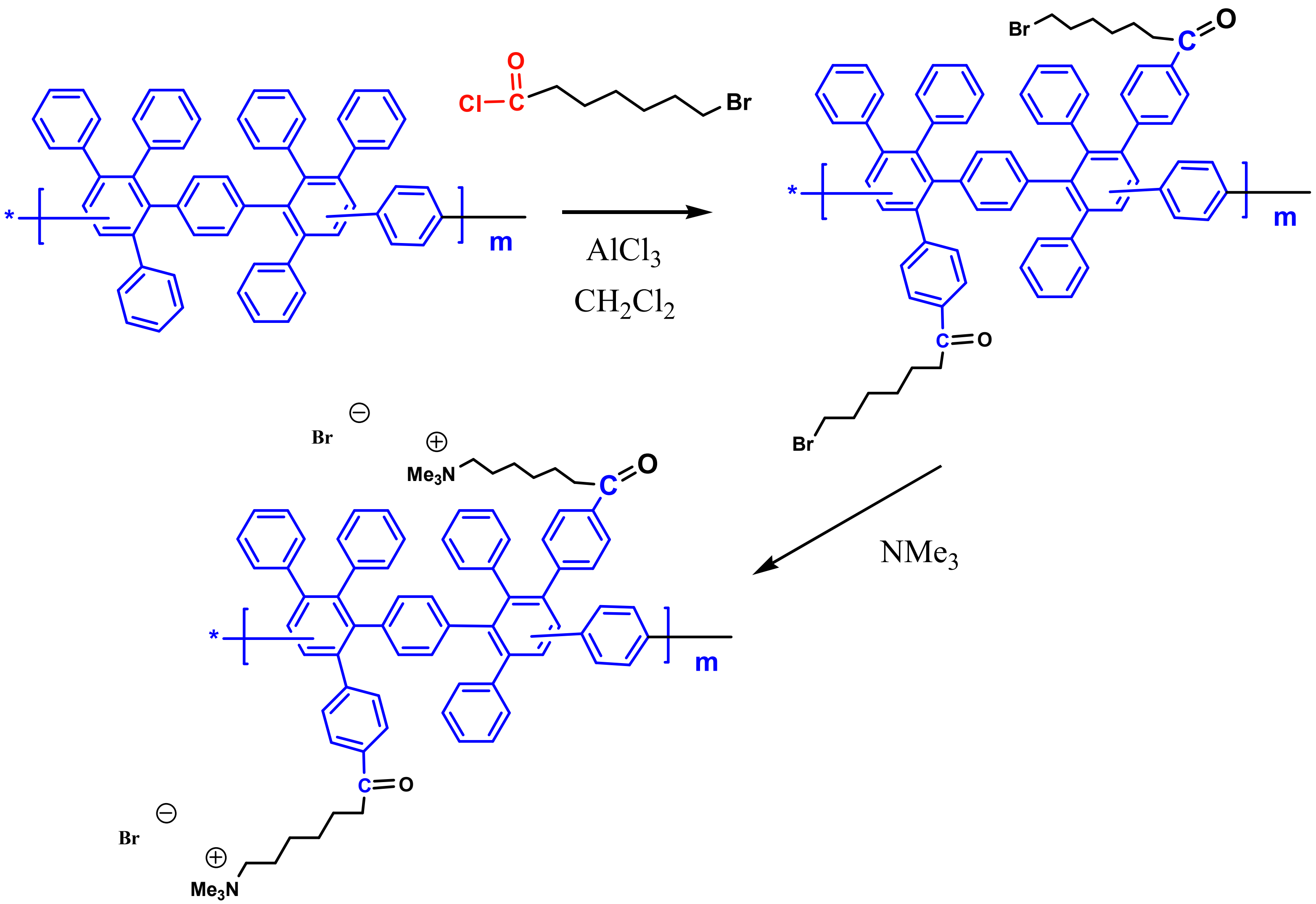



- Coulombic efficiency increased from 70% to 90%.
- Current density increased from 0.5 to 10 mA/cm$^2$.



# Membrane Ion Content

Membranes contain a polyphenylene backbone with pendant ionic groups; ionic content was varied qualitatively high, medium, and low.




**Low Ion Content**

Very brittle sample–no data

**Medium Ion Content**

Best Coulombic efficiency

Best electrochemical yield

Least crossover

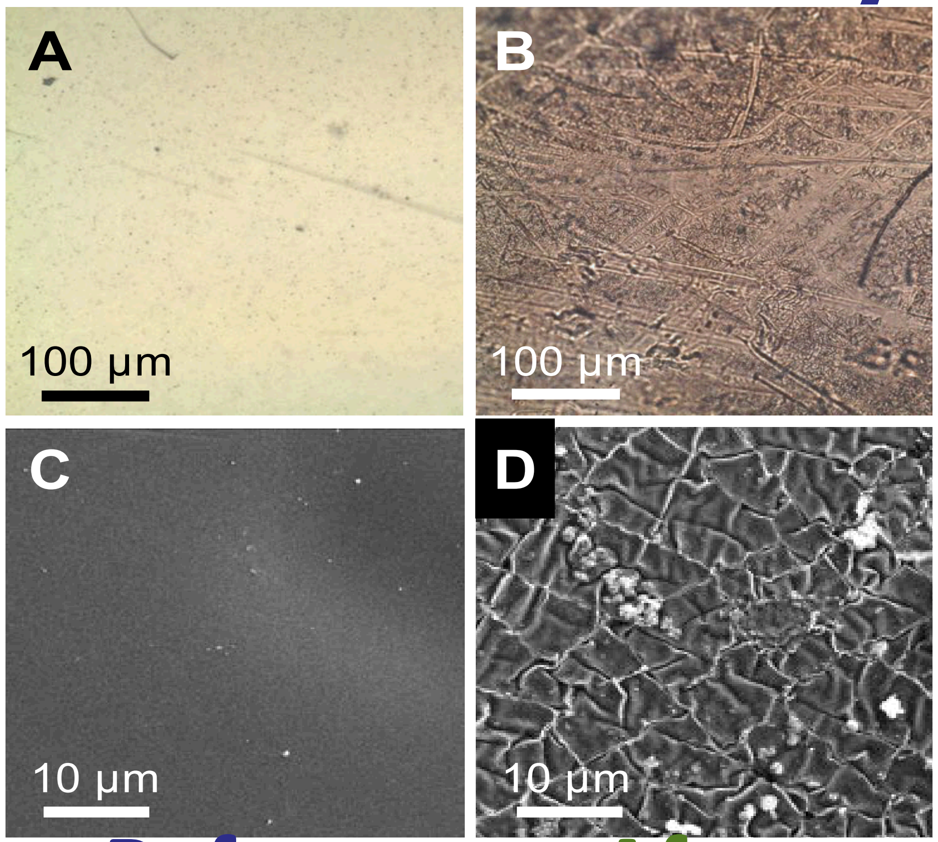
**High Ion Content**

Good Coulombic efficiency

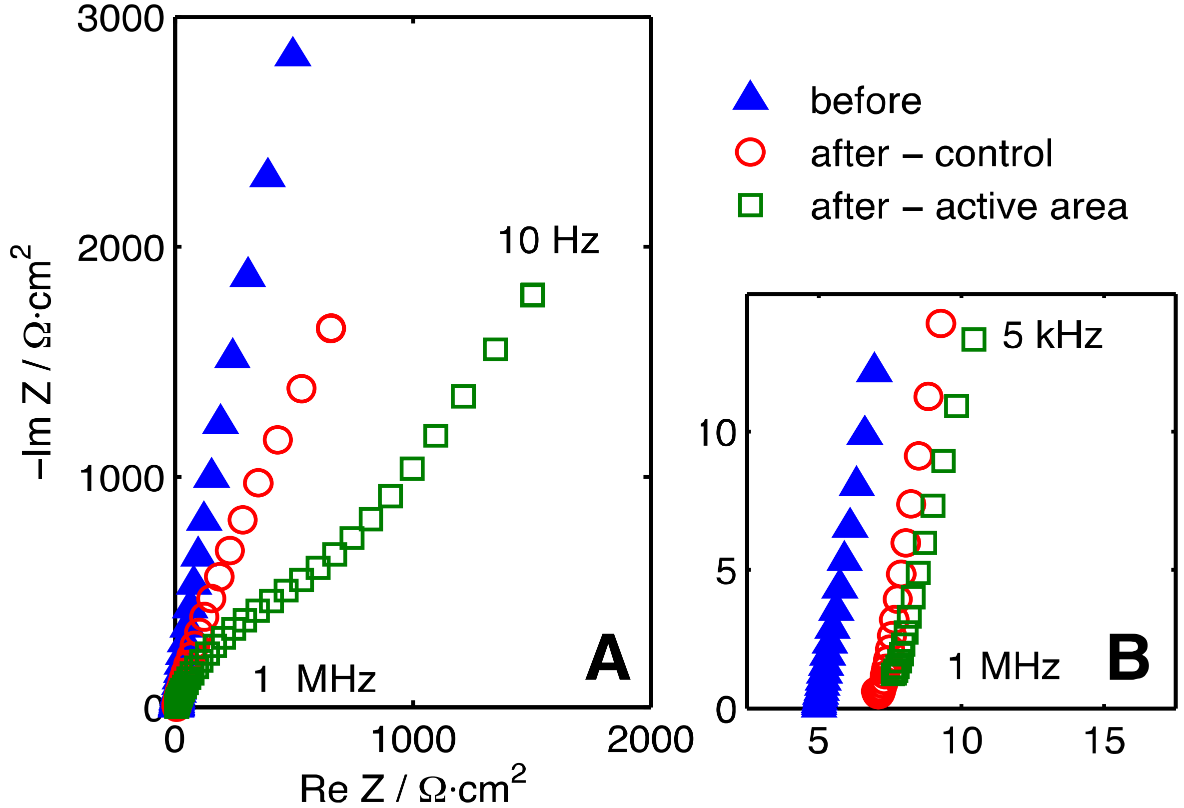
High crossover

The membranes are prepared by a propriety process using Friedel Crafts acylation with a ketone to add pendant ammonium groups and simultaneously lightly crosslink the polymer backbone.

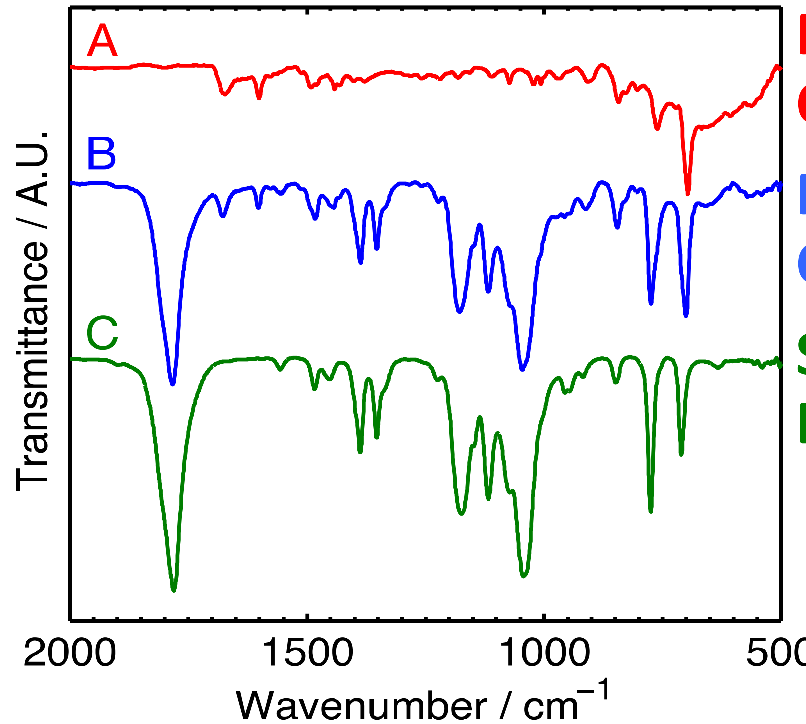
# Chemical Stability




**Before Cycling** | **After Cycling**




- SEM and EDS data suggest that there was some decomposition of the ionic liquid.
- The increased resistance after cycling is attributed to the formation of a film on the surface of the membrane.




**Membrane Before Cycling**

**Membrane After Cycling**

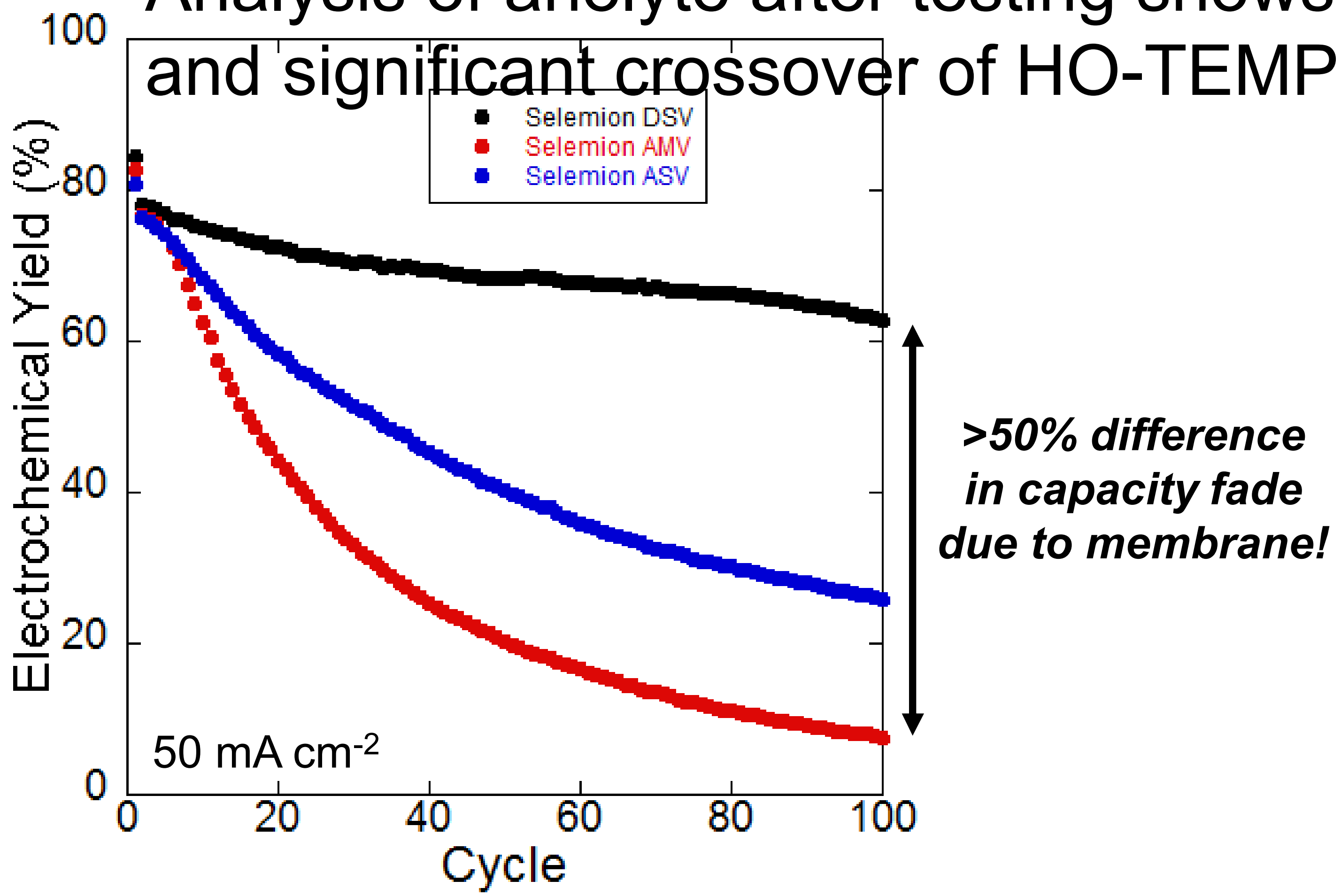
**Supporting Electrolyte**

**Infrared data shows membrane is stable.**

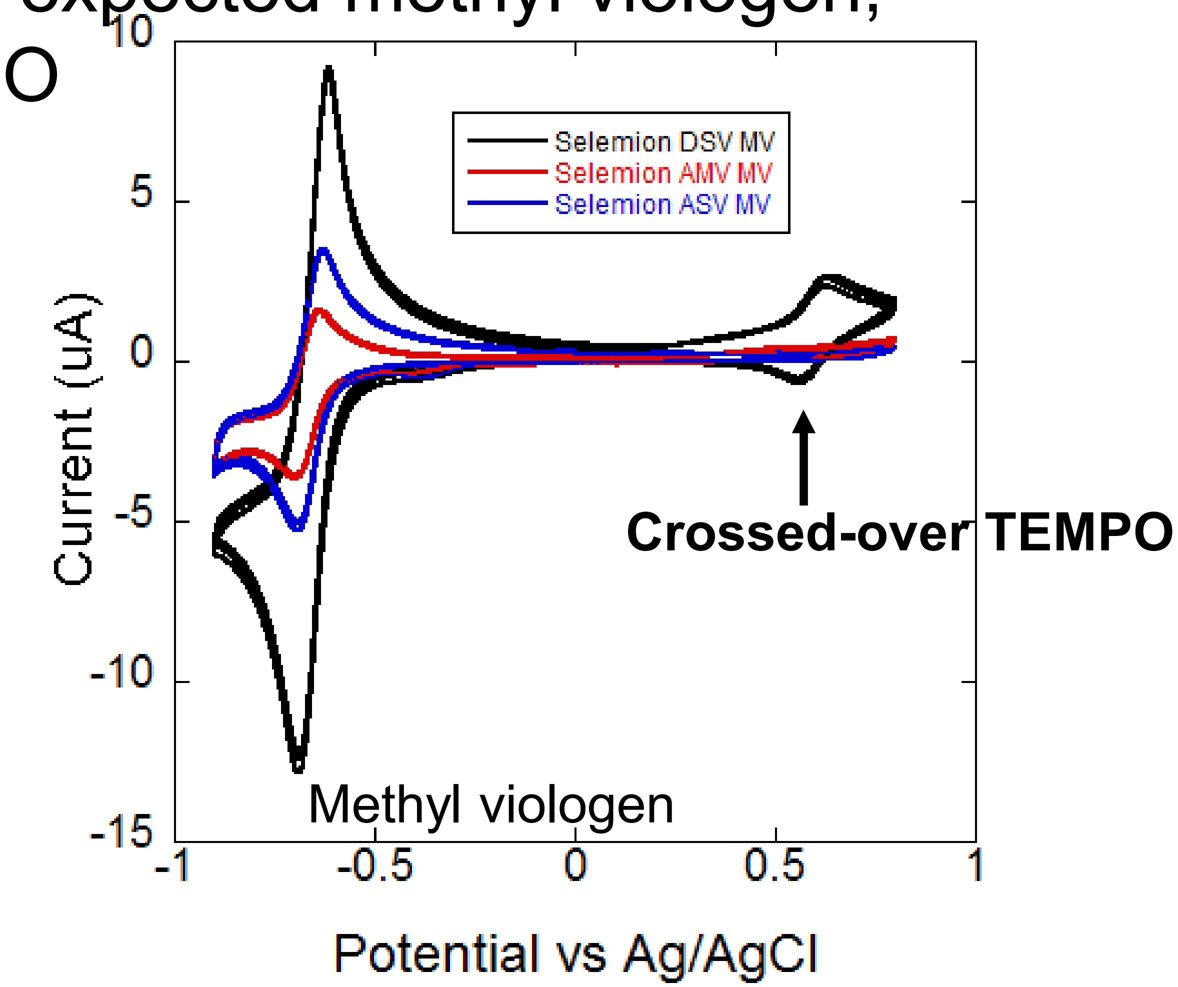
# Membranes Control Aqueous-Organic RFB Performance

***Membranes significantly influence capacity loss in aqueous organic RFB***

- Aqueous-organic RFB, 100 cycles at 50 mA $cm^{-2}$
  - Anolyte: 0.5 M methyl viologen in 1.5 M NaCl
  - Catholyte: 0.5 M HO-TEMPO in 1.5 M NaCl
- Analysis of anolyte after testing shows expected methyl viologen, and significant crossover of HO-TEMPO




Three anion exchange membranes from same manufacturer show markedly different capacity fade.




Cyclic voltammetry confirms crossover of HO-TEMPO into anolyte.

# Alkaline Zn-$MnO_2$ Batteries

- **Cost**
  - Traditional primary batteries, low cost ($18-20/kWh primaries)
  - Low-cost materials and manufacturing
  - Established supply chain
- **Safety**
  - Aqueous chemistry
  - Non-flammable
  - EPA certified for landfill disposal
- **Reliability**
  - Long shelf-life
  - Limited thermal management required
- **Reversibility and Cycle life are the Challenges**

# Zn-MnO2 Batteries – Critical Issues

**Cathode**

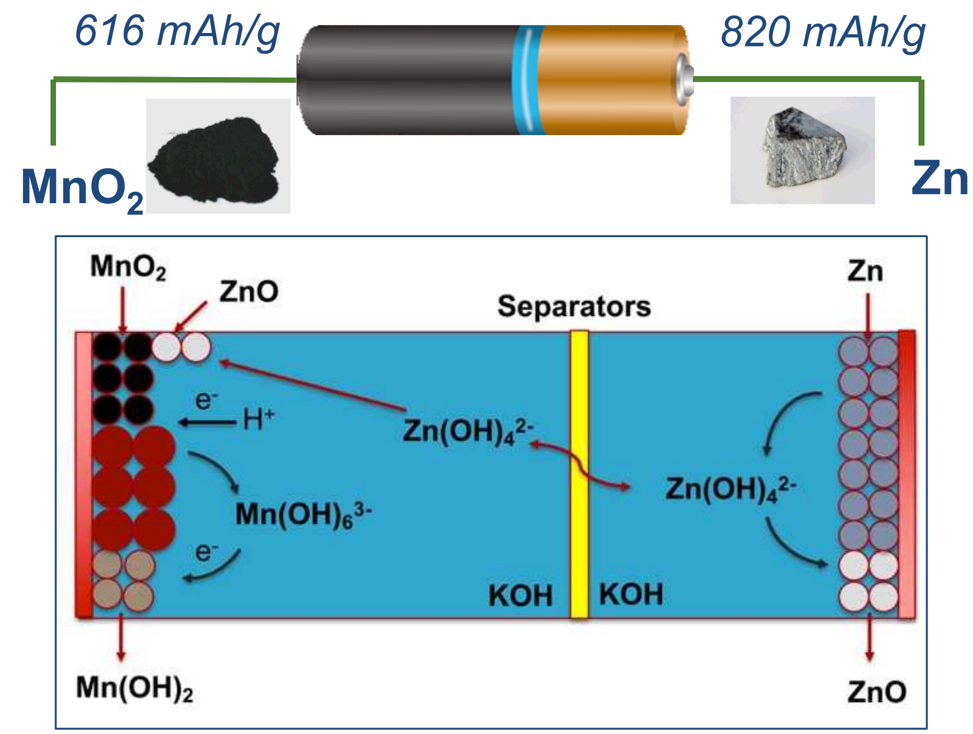
- Irreversibility of Cathode
- Susceptibility to Zinc poisoning

**Separator**

- Zincate crossover

**Anode**

- Shape Change
- Dendrite Growth
- Irreversible ZnO Passivation

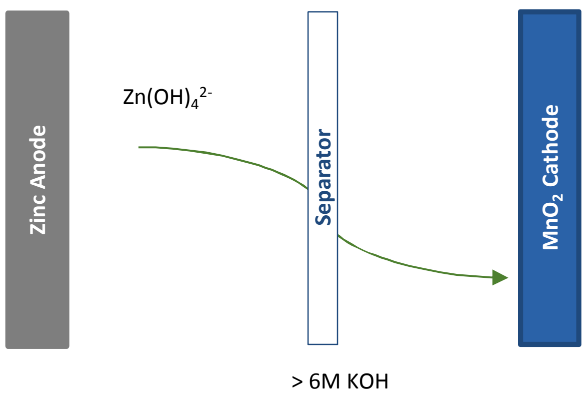



*Limiting Depth of Discharge has been shown to be a viable approach*
N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

*Full 2e⁻ can be stabilized but is still susceptible to zinc poisoning*
G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nat. Commun., 8, 14424 (2017).

TN Lambert

# Need for Selective Separators



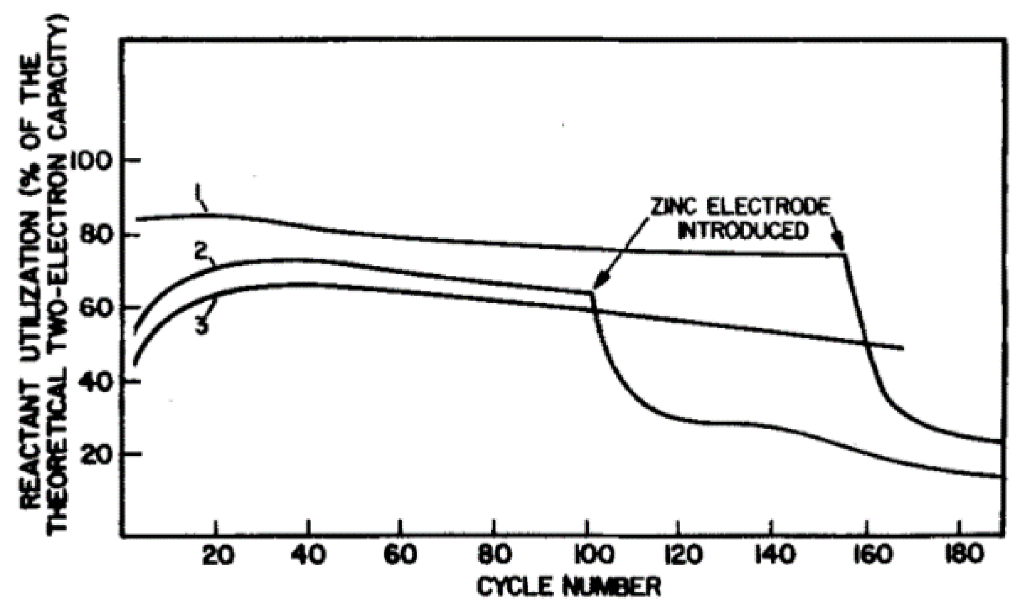
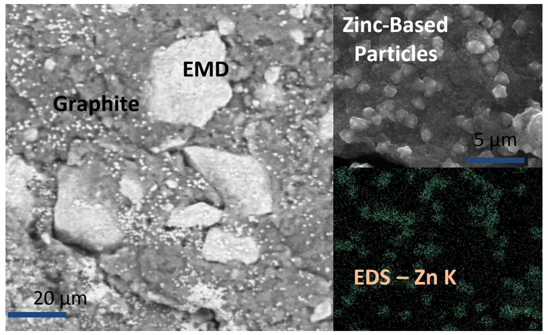




Fig. 5. Effect of the introduction of zinc on capacity retention of modified $MnO_2$ electrodes: 1) chemically modified electrode; 2) physically modified electrode; 3) physically modified electrode in 9M KOH + 0.1M $Zn(OH)_4^{=}$.

## $MnO_2$ Cathode After Cycling




Zinc-Based Particles
-Insulating
-Combine with cathode material to form irreversible compounds

- Research by Ford in the 1980s showed that the $MnO_2$ cathode could be stabilized at low loadings ***in the absence of Zinc***
- New stabilized 2e- cathodes are 100% reversible ***in the absence of Zinc***

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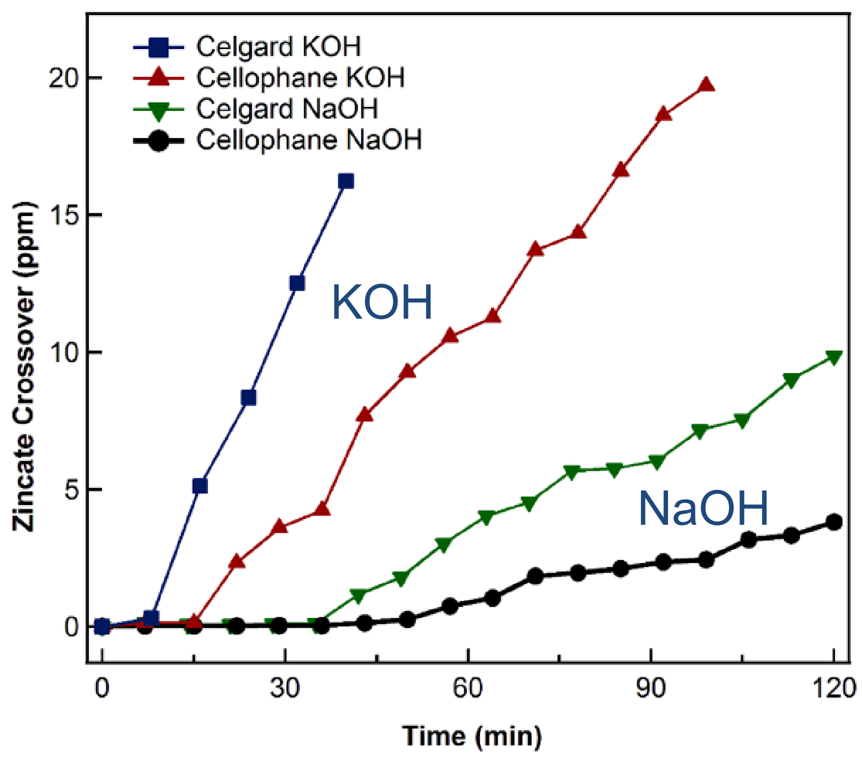
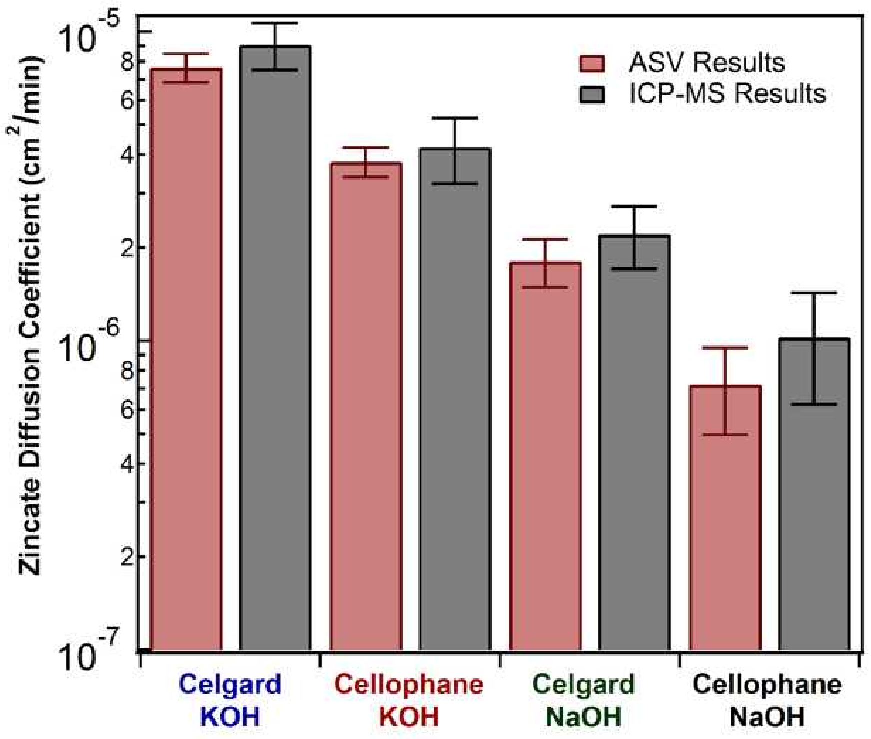
***Imperative need for zincate blocking separators***

# Rapid screening of separators




- Compares favorably *vs.* ICP and Complexometric methods
- Faster experiment times, very reproducible, low limit of detection
- First demonstration of ASV measurement of Zinc in alkaline
- Will allow for rapid screening of newly developed membranes

J. Duay *et al.* *"Stripping Voltammetry for the Real Time Determination of Zinc Membrane Diffusion Coefficients in High pH: Towards Rapid Screening of Alkaline Battery Separators" Electroanalysis 2017, http://dx.doi.org/10.1002/elan.201700337.*

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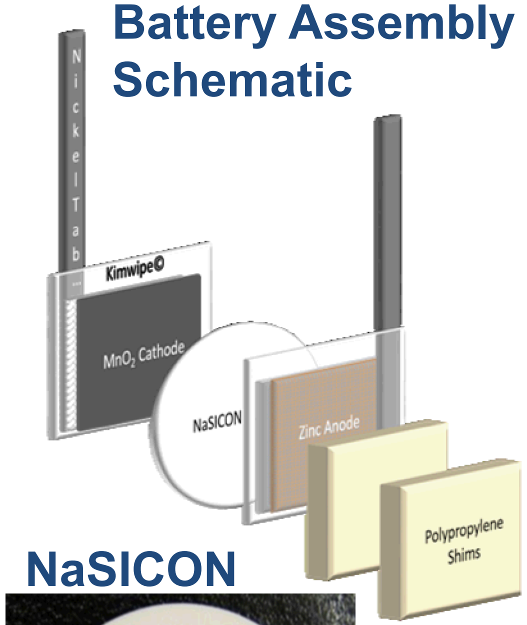
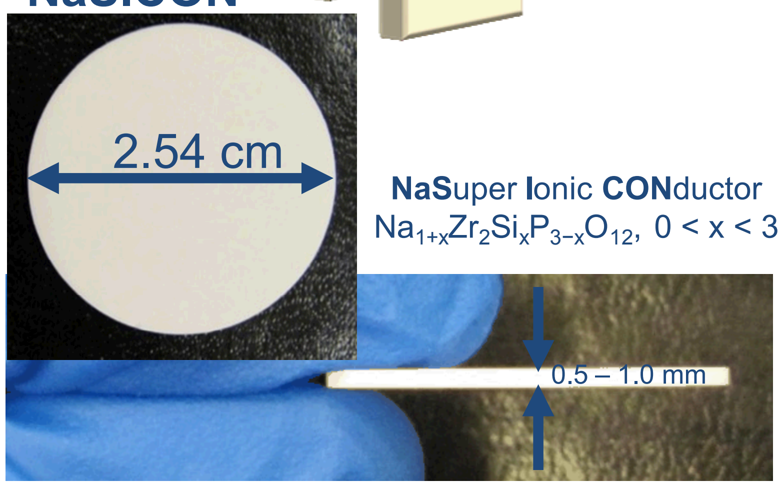
# Initial Studies on Stopping Zincates

## Battery Assembly Schematic




## NaSICON



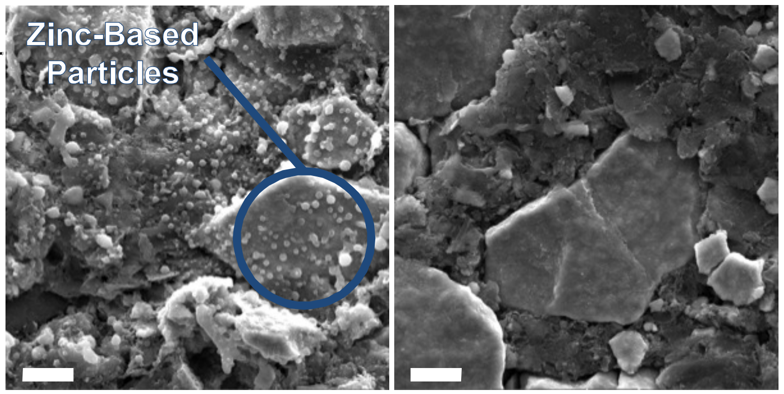

**Na**Super **I**onic **CON**ductor
$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, 0 < x < 3

NaSICON purchased from Ceramatec

## SEM/EDS analysis after cycling

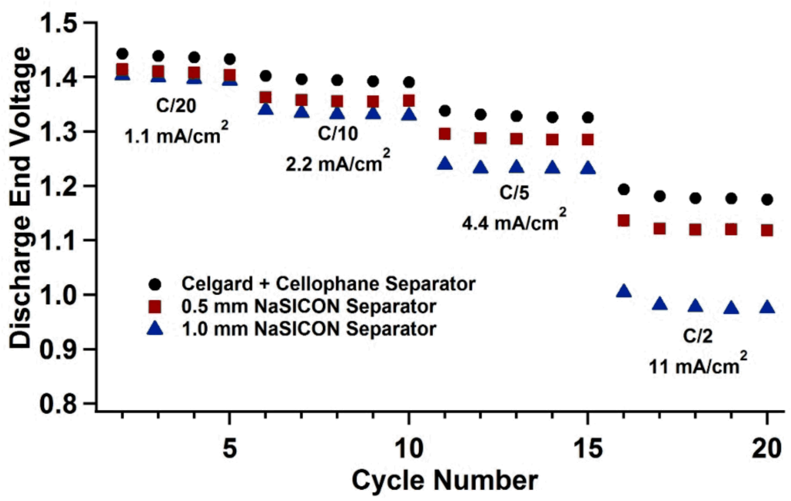
**Celgard + Cellophane Separators** | **1.0 mm NaSICON Separator**

| Element | Atomic % |
|---|---|
| Au K | 0.2 |
| C K | 43.9 |
| F K | 10.7 |
| Mn K | 9.8 |
| Na K | 1.5 |
| O K | 32.3 |
| **Zn K** | **1.6** |




| Element | Atomic % |
|---|---|
| Au K | 0.1 |
| C K | 43.6 |
| F K | 11.3 |
| Mn K | 10.8 |
| Na K | 0.9 |
| O K | 33.3 |
| **Zn K** | **0.0** |

**Ceramic Separators in NaOH electrolyte are viable at low rates**




J. Duay *et al. manuscript in preparation.*

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# Summary

- Engineering costs are significant for small format cells. Large format cells are needed to reduce overall system costs.
- Large format cells also allow for tighter integration of power electronics, sensors, SOH monitoring at the cell level.

# Acknowledgements

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