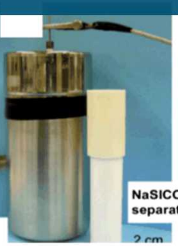
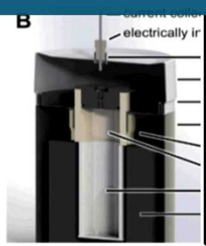
SAND2019-10800PE

# Materials Chemistry to Advance Na-Batteries





## Erik D. Spoerke, Ph.D.

Sandia National Laboratories, Albuquerque, NM


Materials Science & Engineering Department Seminar
University of North Texas, Denton, TX
September 13th, 2019

This work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the U.S. Department of Energy Office of Electricity.

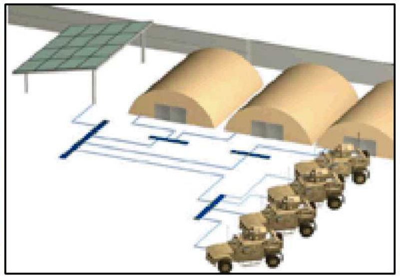


SAND No.:SAND2019-

# A Need for Grid-Scale Energy Storage Research

Renewable/Remote Energy

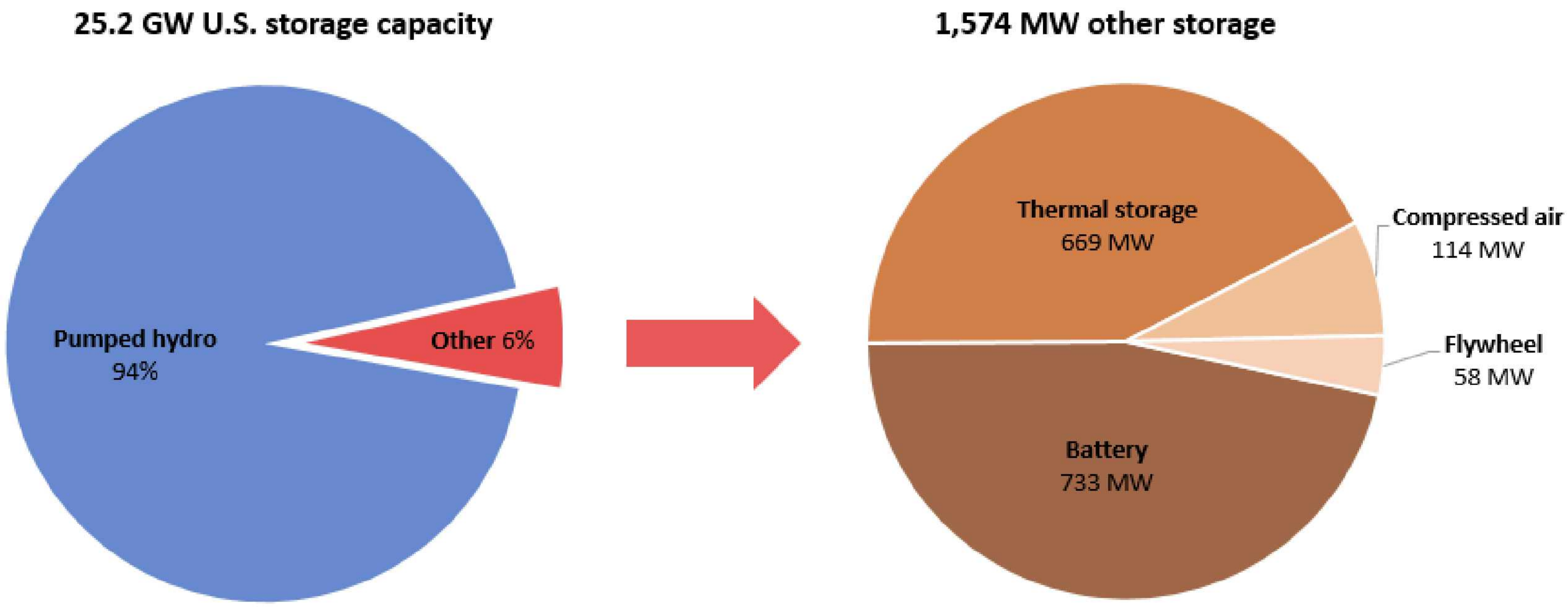
Grid Reliability



National Defense

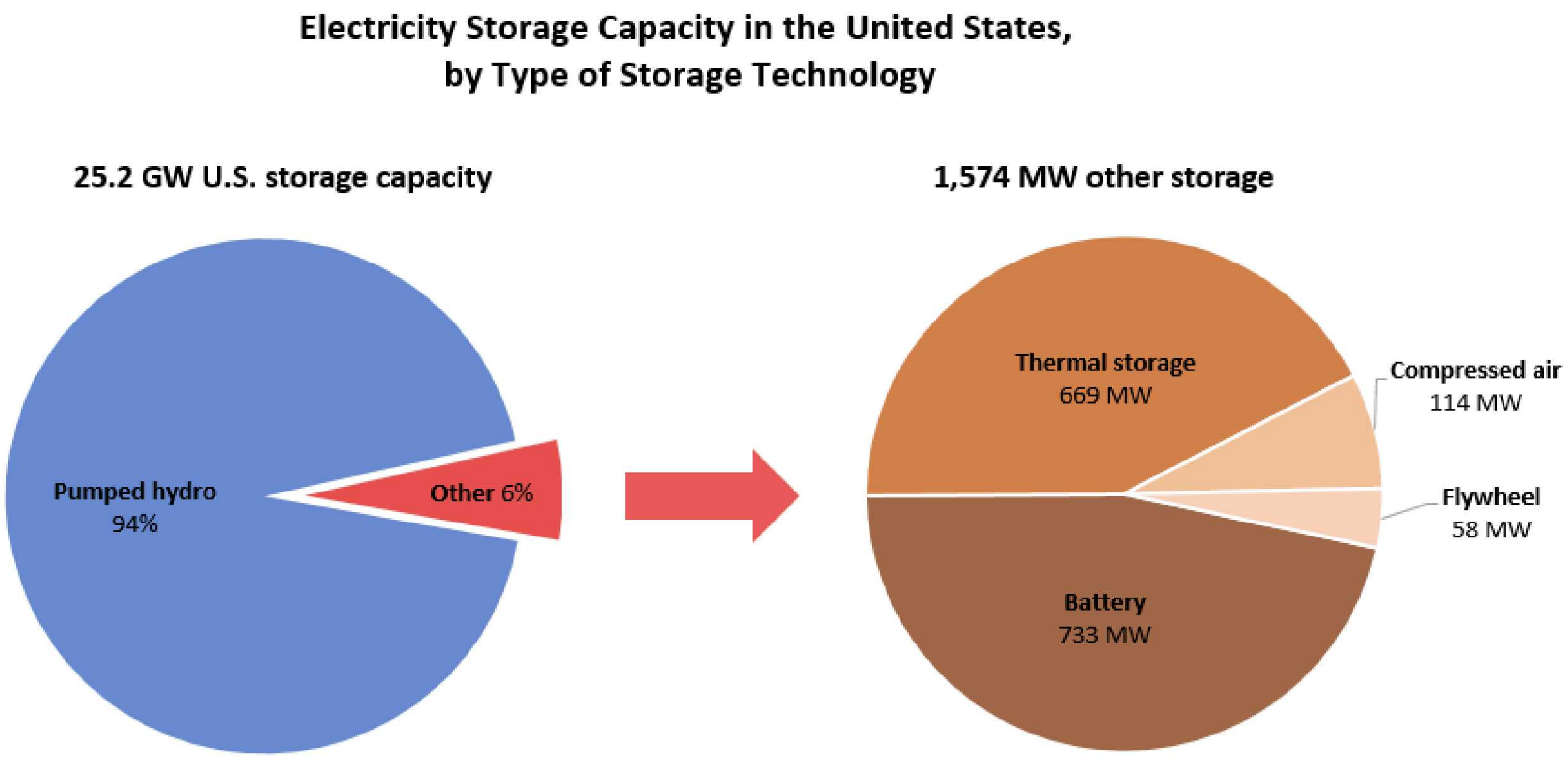
Emergency Aid

**Electricity Storage Capacity in the United States, by Type of Storage Technology**




***Source:*** *DOE Global Energy Storage Database http://www.energystorageexchange.org/ March, 2018*

# Battery-based Energy Storage: Room to Grow!




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

*0.07% Battery Energy Storage*

*2.2% Battery Energy Storage and Pumped Hydro Storage*

***Source:*** *DOE Global Energy Storage Database http://www.energystorageexchange.org/ March, 2018*

# Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

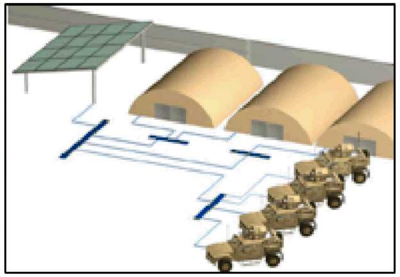
# Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

# A Need for Grid-Scale Energy Storage Research


Renewable/Remote Energy

Grid Reliability



National Defense

Emergency Aid

***U.S.***

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

***% of U.S. Generation Capacity***

- *0.07% BES*
- *2.2% BES + PHS*

***Globally***

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

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

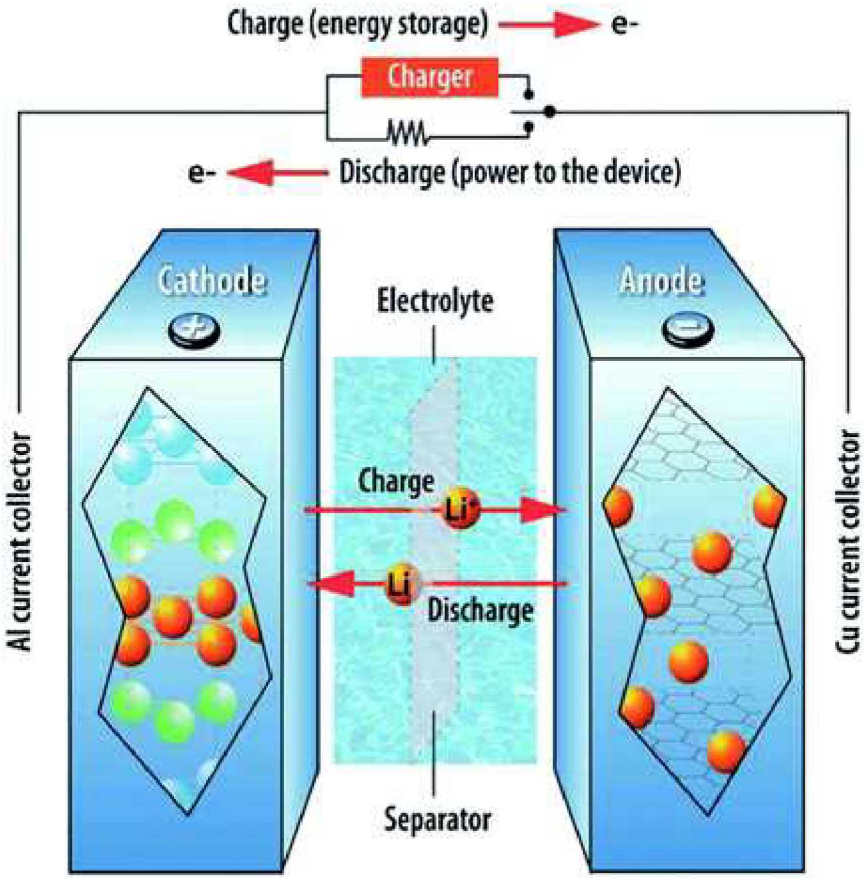
We will need much, much more storage on our grid to accommodate increasing renewable penetration and the transition to a clean energy economy.

- "Energy" applications – slower times scale, large amounts of energy
- "Power" applications – faster time scale, real-time control of the electric grid

Current Barriers:

- Expensive, especially in energy markets (need for continued R&D )
- Electricity markets do not have market mechanisms for services ES can provide (need to reduce regulatory and policy hurdles)

# Basic Battery Design




<u>Basic elements of all (most) batteries:</u>

- Current collectors
- Anode
- Cathode
- Electrolyte
- Ion-conducting, electronically insulating separator (may double as electrolyte)
- External circuit

***Not All Batteries are Equivalent!!***

# Considerations for Battery Selection

- How much energy storage is necessary?
- How quickly does that energy need to be stored/delivered?
- Does size/weight matter?
- Does the battery need to be mobile?
- Can the battery be heated?
- Will the battery be subjected to extreme temperatures or large temperature fluctuations?
- What are the consequences of battery failure or degradation?
- How much does it cost?

# Rechargeable Battery Technologies

Current Market drivers

- Consumer electronics, mobile devices and EVs – primarily Li-ion batteries
- Grid energy storage – growing market, currently modest size. Range of technologies

**Traditional Batteries**
**e.g. Lead-acid, Ni-Cd, Ni-MH, Zn-$MnO_2$**

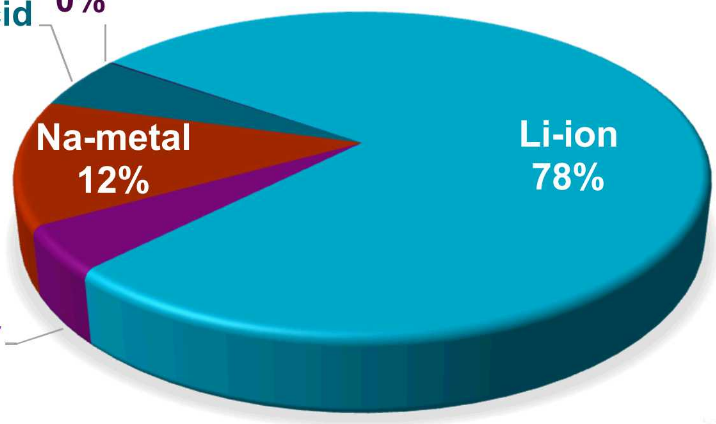
**Lithium Batteries**
**e.g. Li-ion, Li-polymer, Li-metal, Li-S**

**High-temperature Batteries**
**e.g. Na-S, Na-$NiCl_2$**

**Flow Batteries**
**e.g. Vanadium redox, Zn-Br**

| | World Wide Production Capacity | Cost and Performance Improvements |
|---|---|---|
| **Lead Acid Batteries** | 350 GWh | 2%/year (30 year data). $80-150/kWh |
| **Li-ion Batteries** | 220 GWh and growing rapidly | 5%/year (20 year data). Cell level price reaching $150/kWh |
| **NaS and NaNiCl** | 300 MWh | Mature, but no economy of scale |
| **Flow Batteries** | <200 MWh | Potential for lower cost. $400/kWh. Reach $270/kWh |
| **Alkaline chemistries (Zn-MnO2, Zn-air)** | <100 MWh | Not fully mature. Lowest cost BOM |

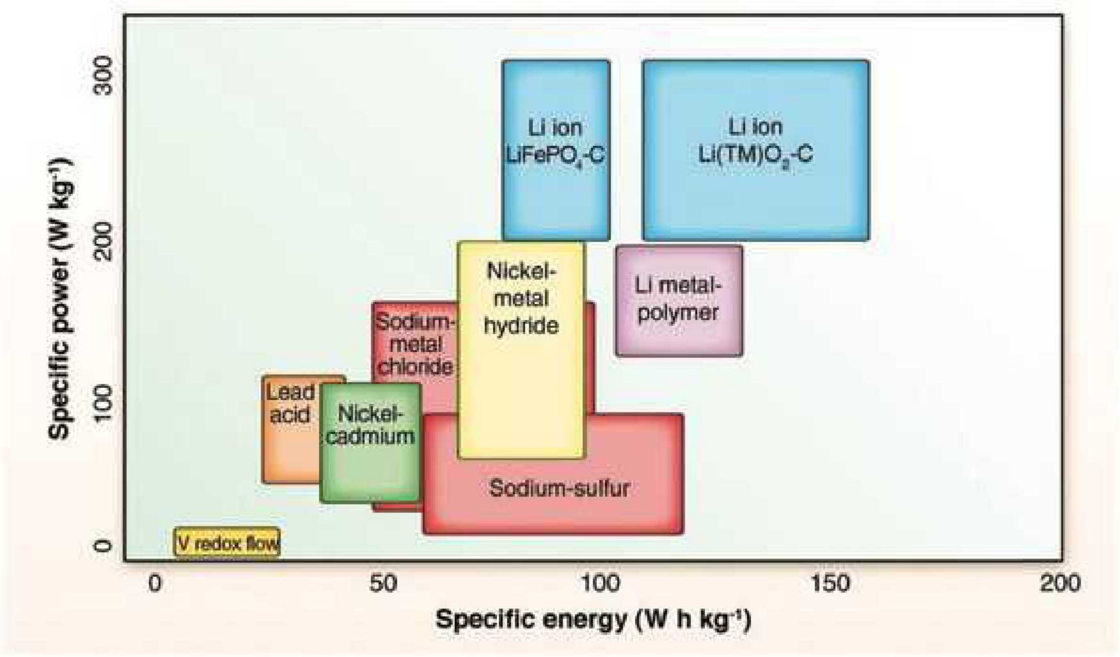
# Current Battery Storage Deployments




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

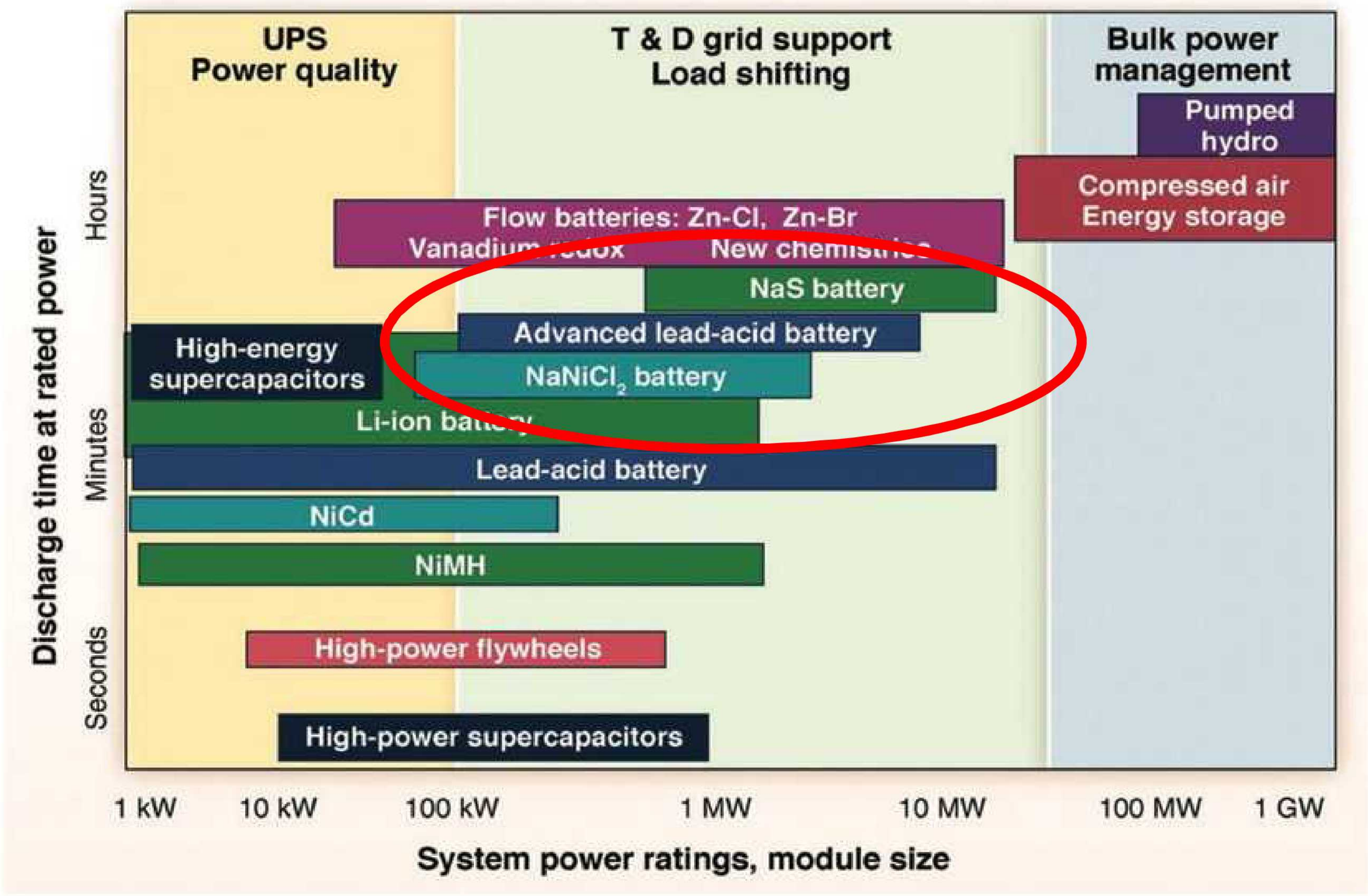
Li-ion batteries can not and should not become our singular grid-scale storage solution.

*Different batteries have variable energy densities and power densities….*

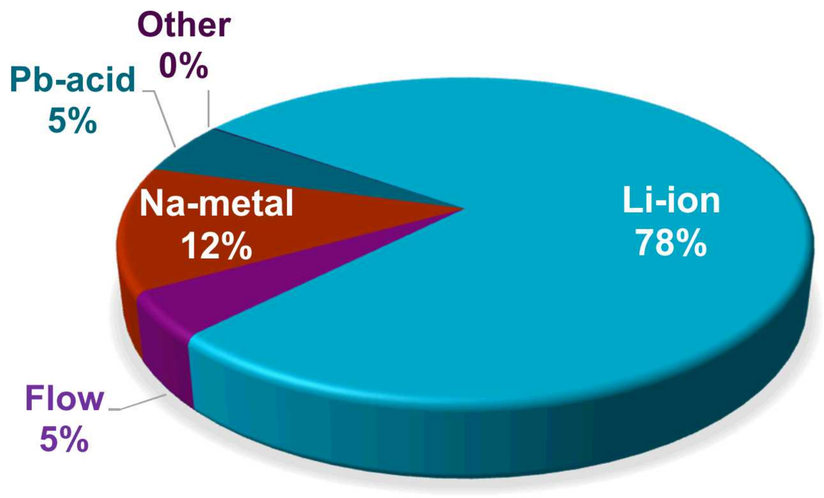



From: B. Dunn, *et al.*, *Science*, 2011, 334, 928–935.

# Variable Battery Utility Matches Variable Battery Capability



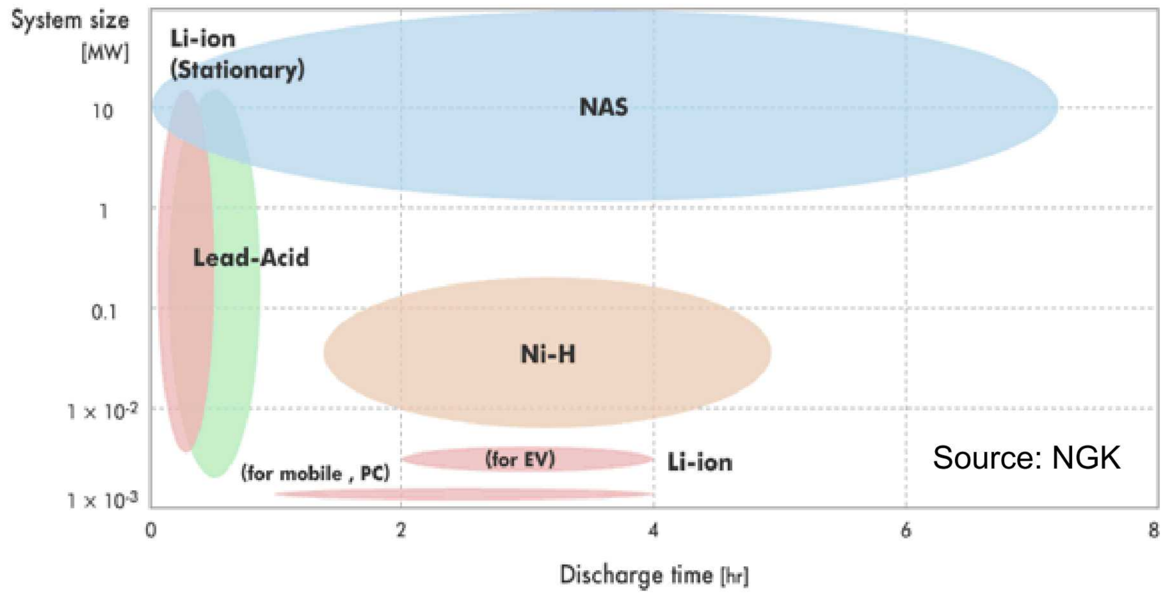
# Current Battery Storage Deployments




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

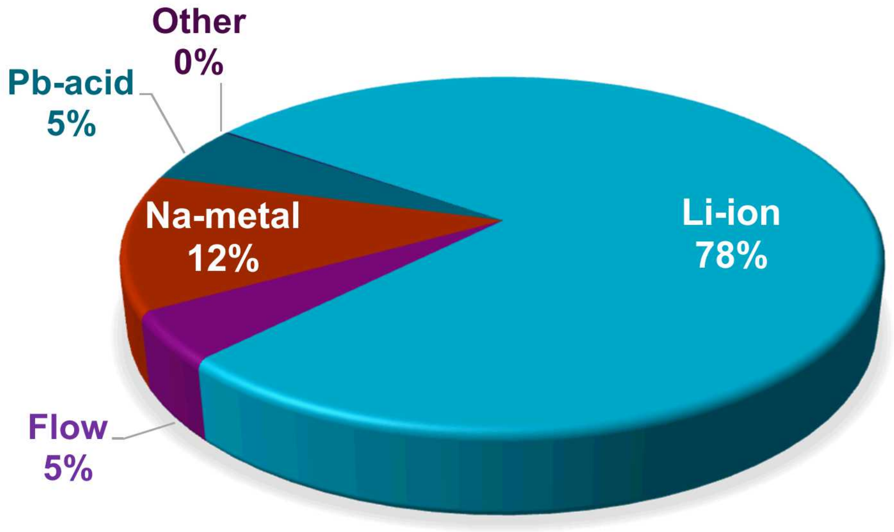
Li-ion batteries can not and should not become our singular grid-scale storage solution.

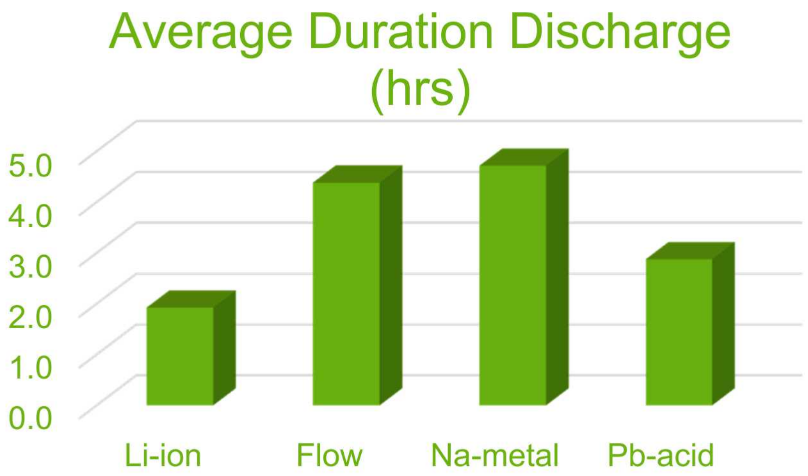
*Different batteries have variable discharge durations…*



# Current Battery Energy Storage Deployments

*(Operational as of Nov. 2017)




- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

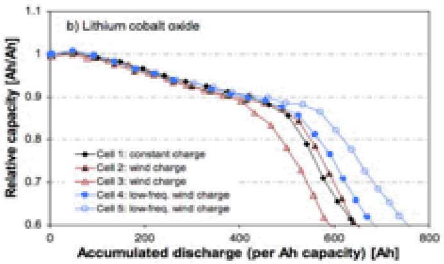
***Source:*** *DOE Global Energy Storage Database*
*http://www.energystorageexchange.org/ Nov. 2017*

# Challenges with Existing Batteries

**Li-ion (*$E_{cell}$* *~ 3.6V*)**

$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$

- Safety (flammable organic electrolytes
- Cycle lifetime limited
- Cost

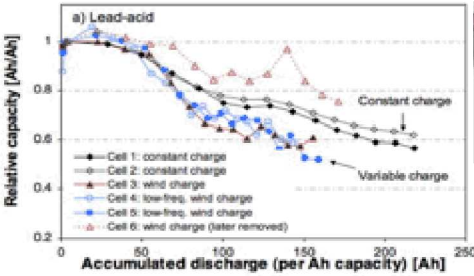



E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

**Pb-Acid (*$E_{cell}$* *~ 2.1V*)**

$Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$

- Capacity fades quickly (typically 200-300 cycles)
- Temperature-sensitive




E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

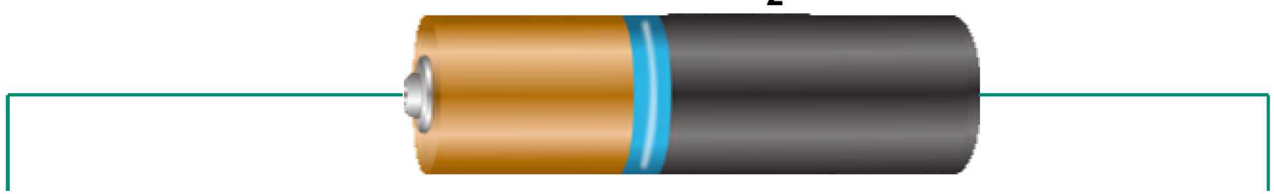
# Rechargeable Alkaline $Zn\text{-}MnO_2$ Batteries

## Promising large-scale storage candidate

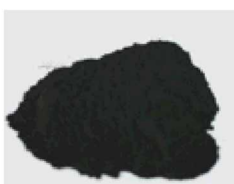
- Low cost: traditional primary batteries @ $18/kWh
- Long shelf life, lowest cost of materials, lowest manufacturing expenses, established supply chain
- Can be scaled to large form factors
- Limited thermal management required compared to Pb or Li
- Safer, environmentally friendly (EPA certified for landfill disposal, non flammable)

**Challenge**: Re-chargeability = Battery Lifetime & Cost

**$Zn\text{-}MnO_2$**



**$MnO_2$**



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

**KOH**

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

**Zn**

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

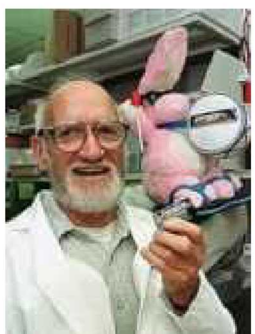
SNL Principal Investigator: Dr. Tim Lambert (tnlambe@sandia.gov)

# Historical Advances of Zn-$MnO_2$ Batteries

**1866** — Primary, Low Power
1[st] Zn-$MnO_2$ battery

Georges Leclanché

**1950** — Primary
Alkaline Zn-$MnO_2$ battery



Lewis Urry

**1970** — Limited Capacity, Poor Energy Density
5% Rechargeable Capacity

Karl Kordesch

**1980** — Potentiodynamic, Poor Cycle Life
60-80% Rechargeable Capacity

Halina Wroblowa

**2010–2016** — Stabilized full-cycling MnO2

2010-2014: CUNY Energy Institute shallow-cycle $MnO_2$

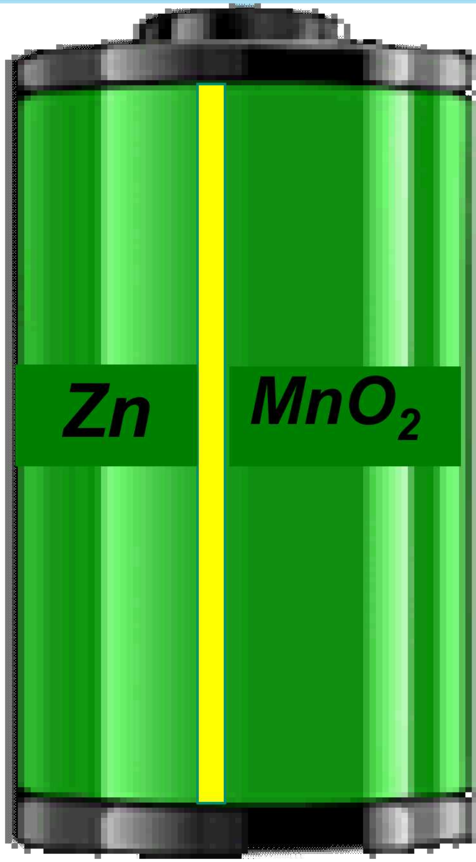
2014-2016: Stabilized full-cycling $MnO_2$

Sanjoy Banerjee

S. Banerjee, Symposium on Grid Energy Storage, MRS Spring Meeting, 2015; G. Yadav, CUNY Energy Institute, 2018

# Challenges Facing Secondary Zn-$MnO_2$ Batteries

*2 e⁻ / 820 mAh/g*

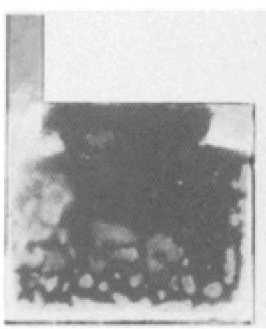



*2 e⁻ / 616 mAh/g*

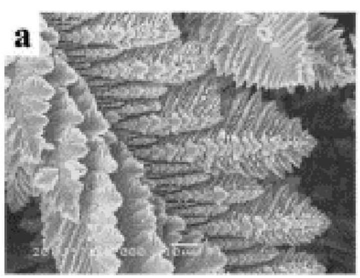
**Prospective Energy density of up to 400 Wh/L or 150 Wh/kg: equivalent to Li-ion**

## Anode … Issues

- Passiva… …ructure breakdown
- Shape … …hase(s) formed
- Dendrit… …oning

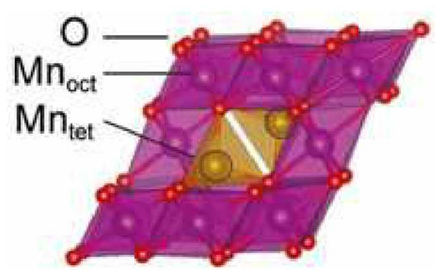


J. Electrochem. Soc., 138 (2), 645 (1991)



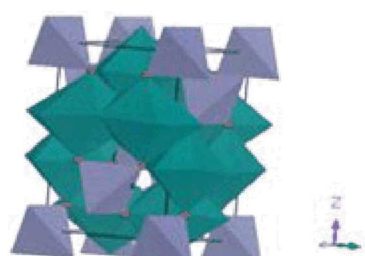

J. Electrochem. Soc., 163 (9), A1836 (2016)

α-$Mn_3O_4$




*PNAS* 115 (23), E5261 (2018)

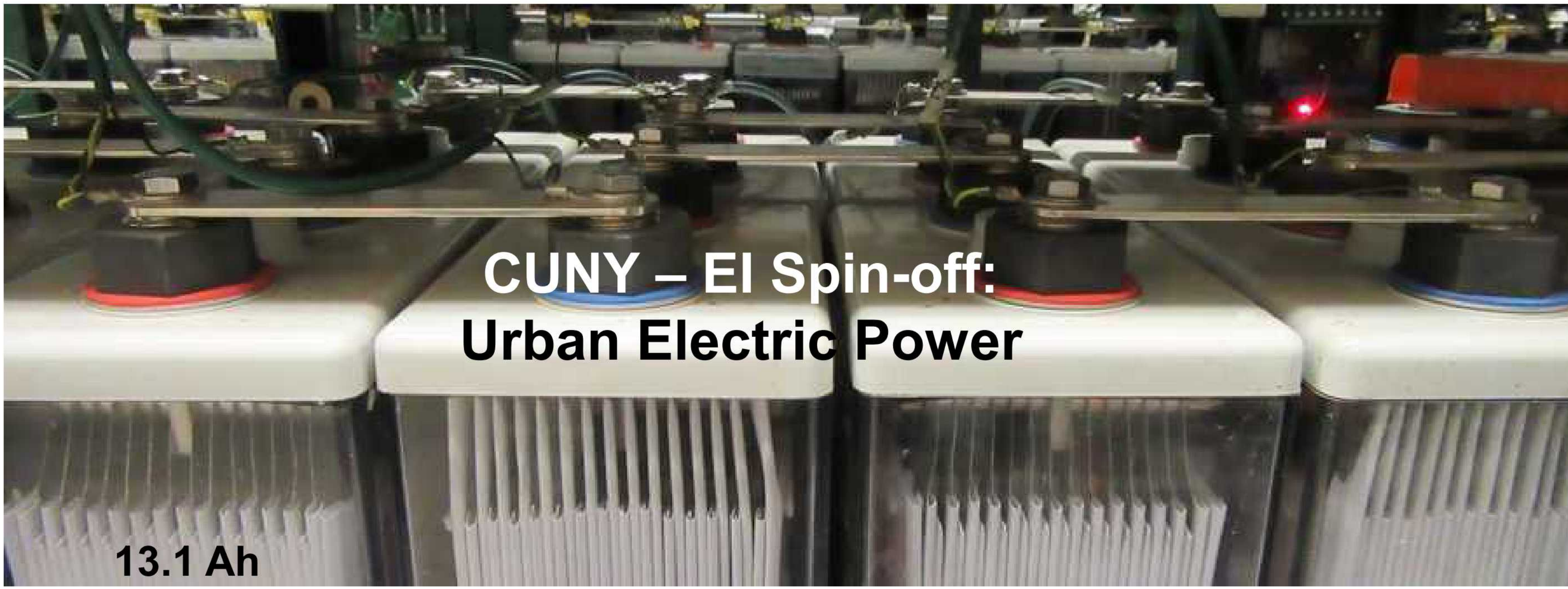
$ZnMn_2O_4$



Mater. Chem. Phys. 130, 39 (2011)

# CUNY-EI Development of Limited DOD Batteries

**Technology has been commercialized at ~20 Wh/L, $150-250/kWh**




- **1000+ cycles** shown under **limited depth-of-discharge (DOD)** conditions

N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, *J. Power Sources*, **276**, 7 (2015).

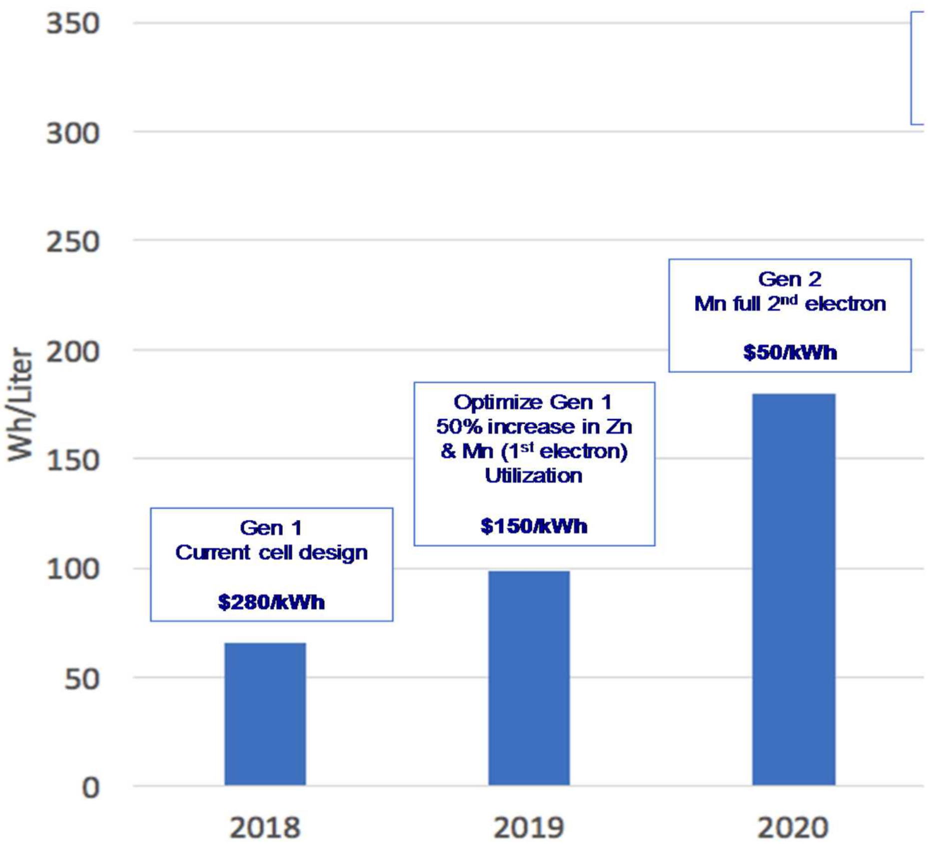
# Potential for Zn-$MnO_2$ Cells at $50/kWh

Potential for **$50/kWh** cells by controlling the following:

-Increasing the **full 2 $e^-$** recharge ability of $MnO_2$

-**Improve zinc utilization** to increase energy density and cost

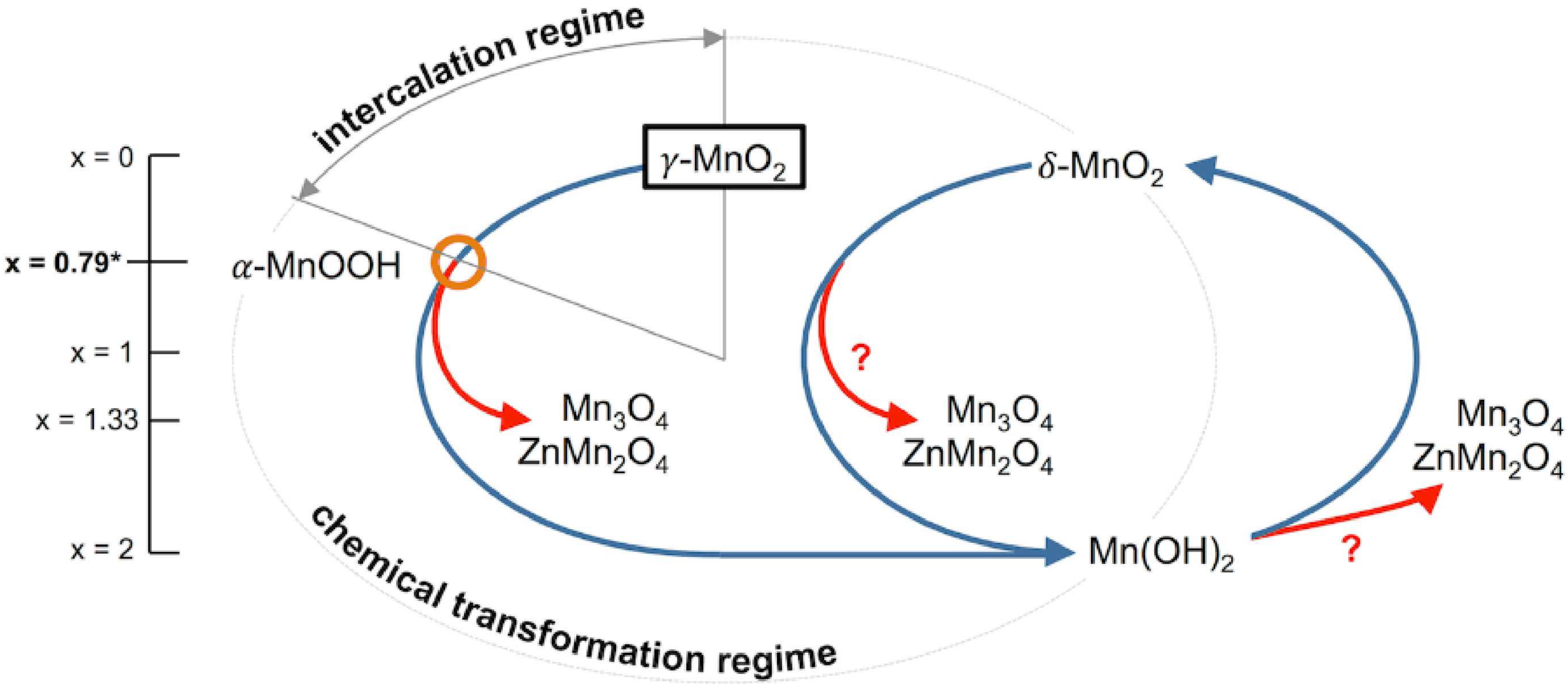
-**Mitigate cathode degradation** by controlling Zn migration across separator




Source: CUNY Energy Institute

**Cost equivalent to Pb acid with capacity equivalent of Li-ion with additional safety and toxicity merits**

# Full Utilization of 2e⁻ $MnO_2$ Cathode Challenges

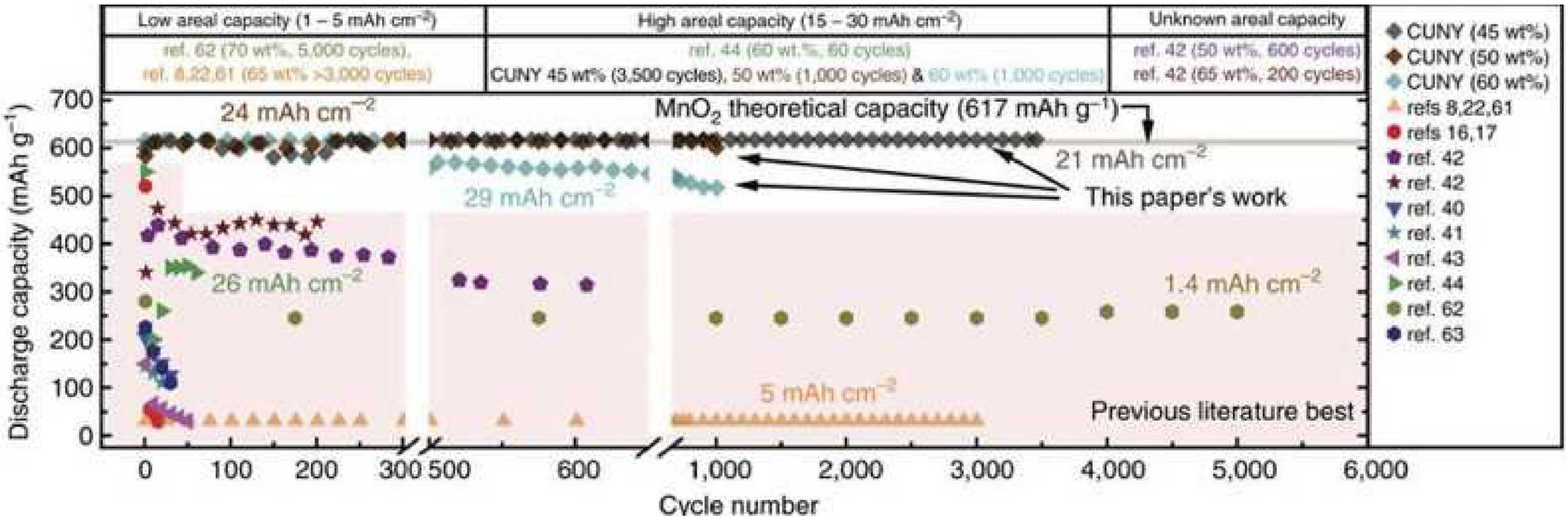


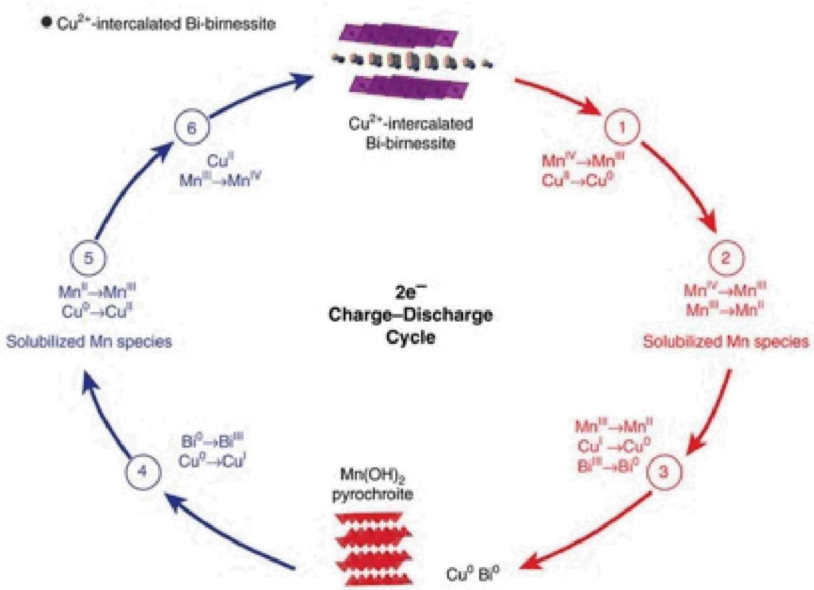

S. Banerjee, Symposium on Grid Energy Storage, MRS Spring Meeting, 2015; G. Yadav, CUNY Energy Institute, 2018

**Failure Mechanisms of Cathode**

**Instability of Mn(III)** resulting in formation of **irreversible $Mn_3O_4$** and/or Zn poisoning forming **irreversible $ZnMn_2O_4$**

# CUNY-EI Advances in $2e^-$ $MnO_2$ Cathode




- Chemistry relies on layered birnessite $MnO_2$ structure stabilized by Cu intercalation and Bi Doping
- $MnO_2$ goes through a complete conversion process from $MnO_2$ to $Mn(OH)_2$

**Note: Electrode cycled in Absence of Zn**

G.G. Yadav, J.W. Gallaway, D.E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, *Nature Communications*, vol. 8, 14424 (**2017**).
doi:10.1038/ncomms14424

# Sandia Advances in Zn Anode

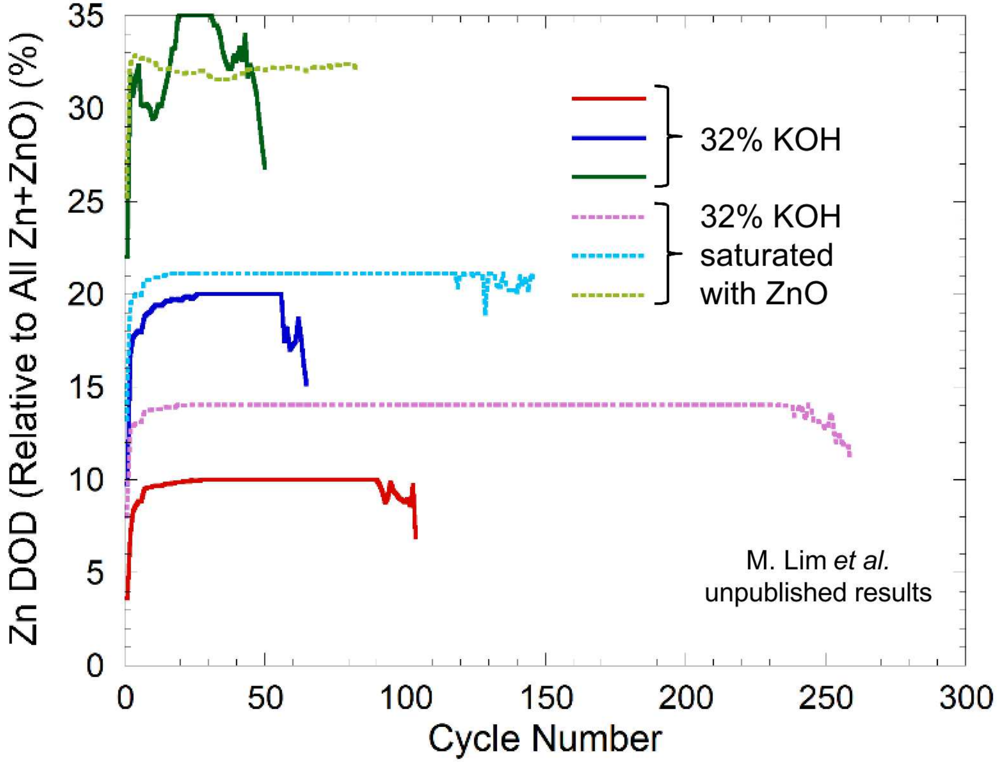
## ***Pre-saturating electrolyte*** *with ZnO can* ***minimize dissolution and migration*** *of zinc from the anode*

**Zn/Ni(OH)$_2$**

Anode capacity = 746 mAh/g

C/10 relative to full anode capacity ≈ 75 mA/g$_{anode}$

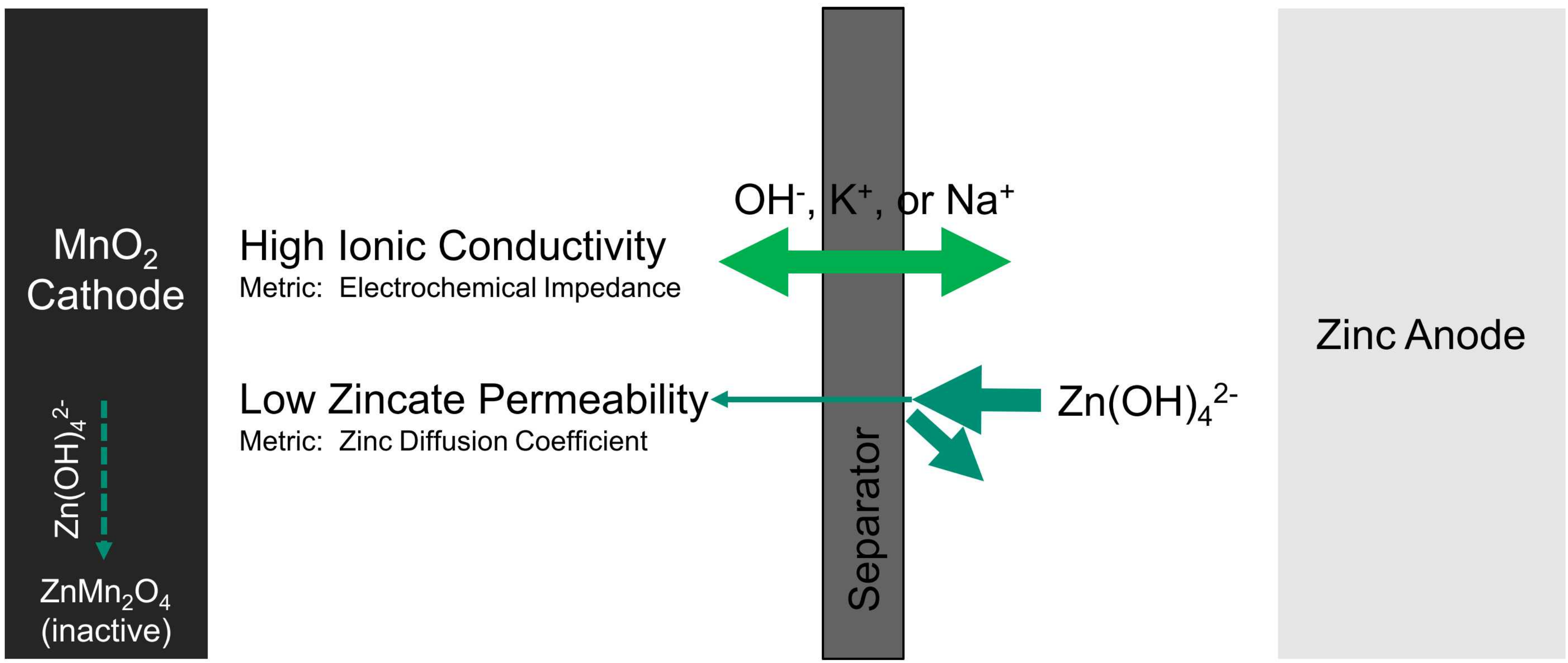
Excess Ni(OH)$_2$




- Cells tested at ~14% Zn DOD in saturated electrolyte show 149% longer cycle life than 10% Zn DOD cells in regular electrolyte
- Cells tested at ~21% Zn DOD in saturated electrolyte show 125+% longer cycle life than 20% Zn DOD cells in regular electrolyte

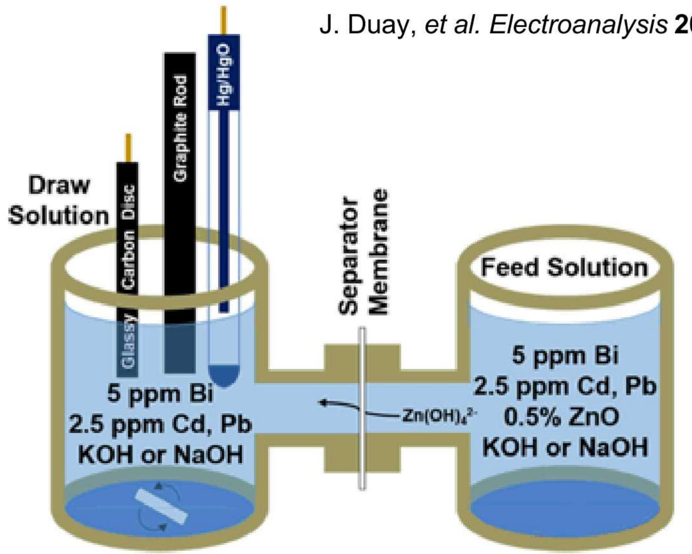
**Note: Electrode cycled vs. Ni(OH)$_2$ need for a good separator to cycle vs. MnO$_2$**

# Features of a Good $Zn\text{-}MnO_2$ Battery Separator

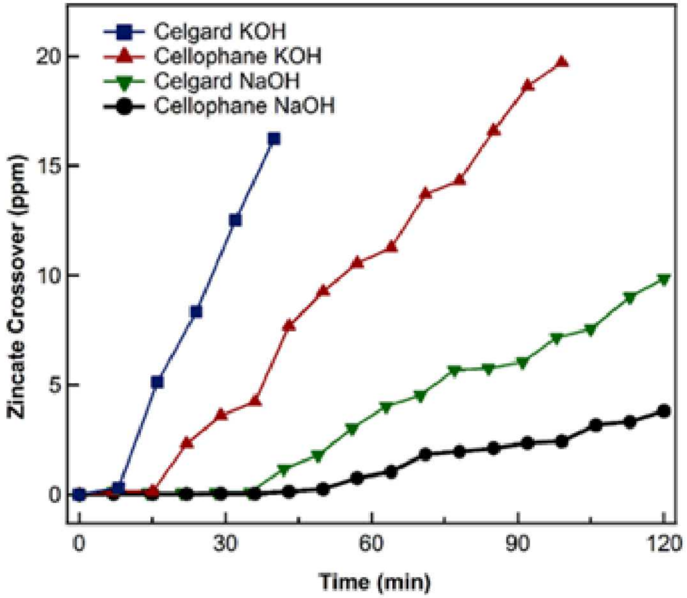



***A selective membrane/separator is needed that allows charge-carrying ions through but blocks or limits Zn (zincate)***

# Sandia Advance: Rapid Screening for Separators



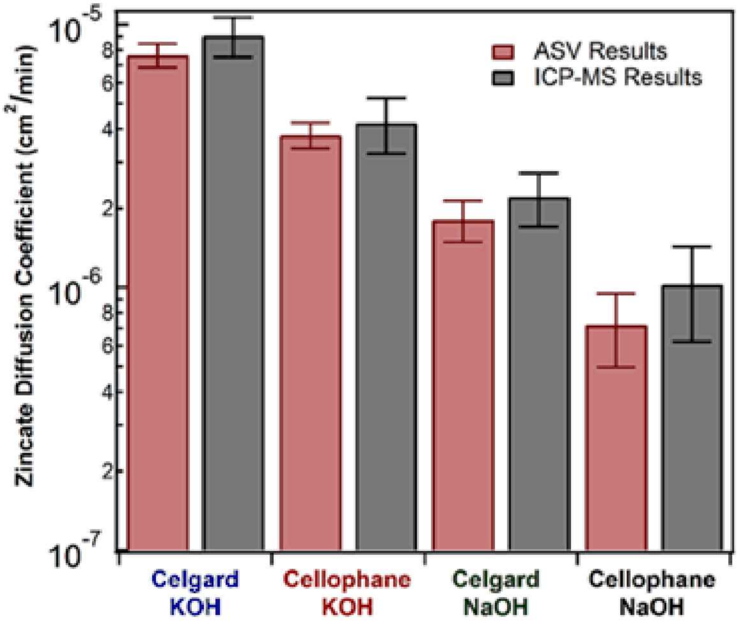

J. Duay, *et al.* *Electroanalysis* **2017**, *29*, 2261–2267




***ASV results are similar to ICP-MS with much shorter experimental times and no need for dilution or pH modification***

| Method | Dilution Factor | Experimental LOD | Timeframe of Experiment |
|---|---|---|---|
| **ASV (this work)** | **0** | **1.6 ± 0.6 ppm** | **Hours** |
| ICP-MS | >300x | 0.009 ppm<br>7.5 ± 2.4 ppm* | Days |
| Complexometric Titration | >20x | 1 ppm<br>96 ± 24 ppm* | Weeks |

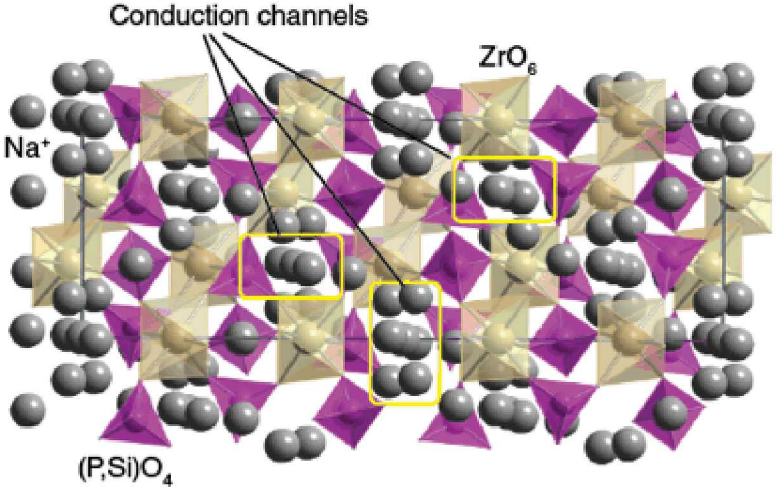
* LODs obtained in Lambert lab



# Utilization of a Solid State Separator

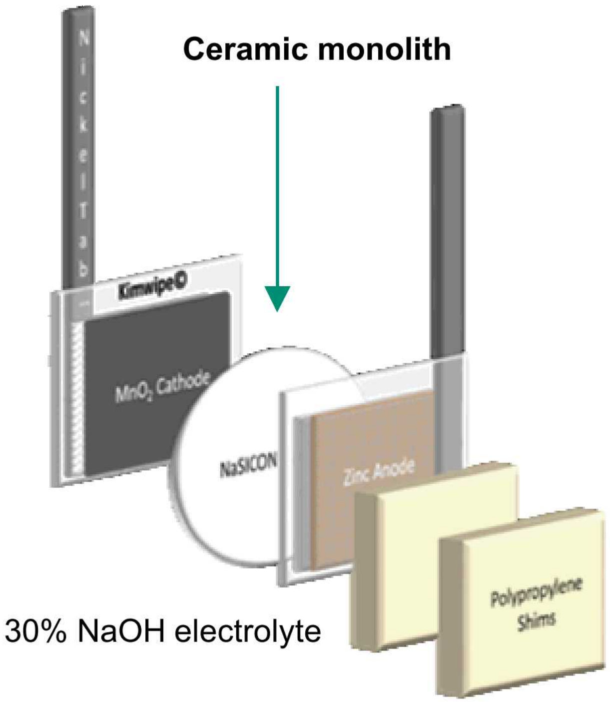
**Na S**uper **I**onic **CON**ductor

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

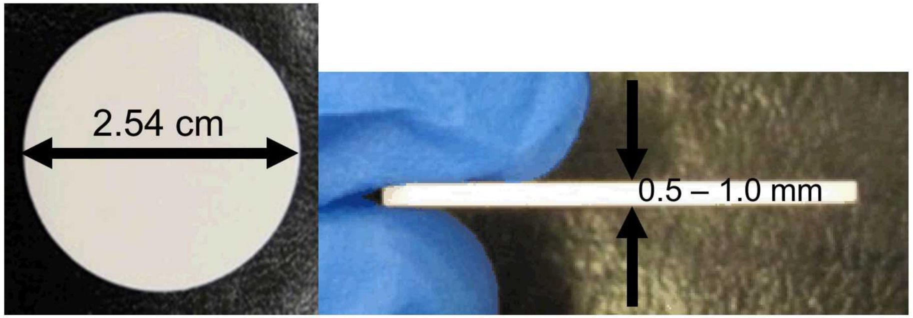



http://www.chemtube3d.com/solidstate/SSNASICON.htm

## Battery Assembly Schematic




## NaSICON purchased from Ceramatec

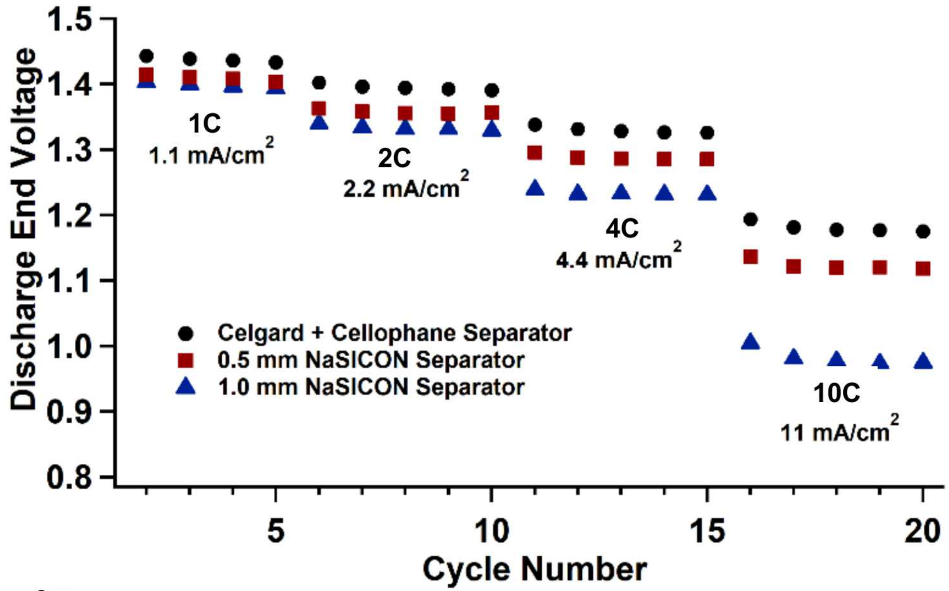



## 100% Selective Membrane

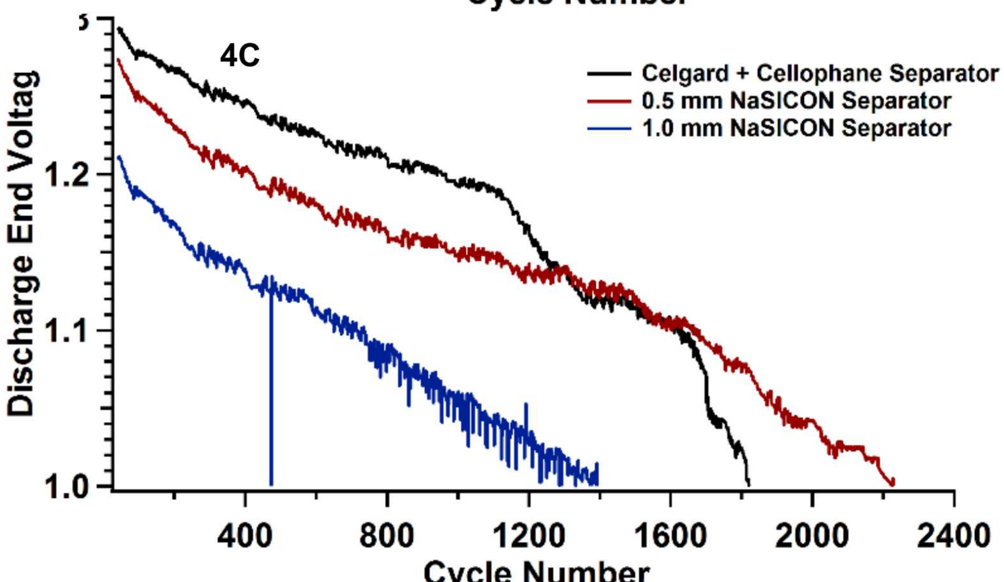
- **Conducts $Na^+$ ions (~$10^{-3}$ S/cm)**
- **No detectable through-separator Zn transport**

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

# Effect of NaSICON on 5% DOD Cells




At relevant discharge rates for grid storage, the thinner **0.5 mm NaSICON doesn't decrease DEV significantly** despite having >2.5x lower conductivity than conventional separators




As NaSICON is thinned and becomes less resistive, its advantages become more apparent, increasing cell lifetime by 22%

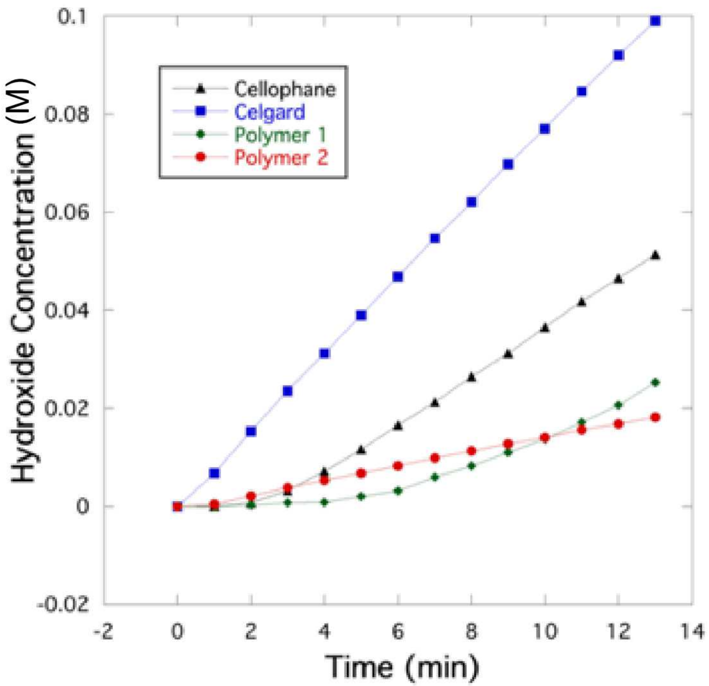
**NaSICON is currently not practical due to cost and brittleness upon thinning**

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

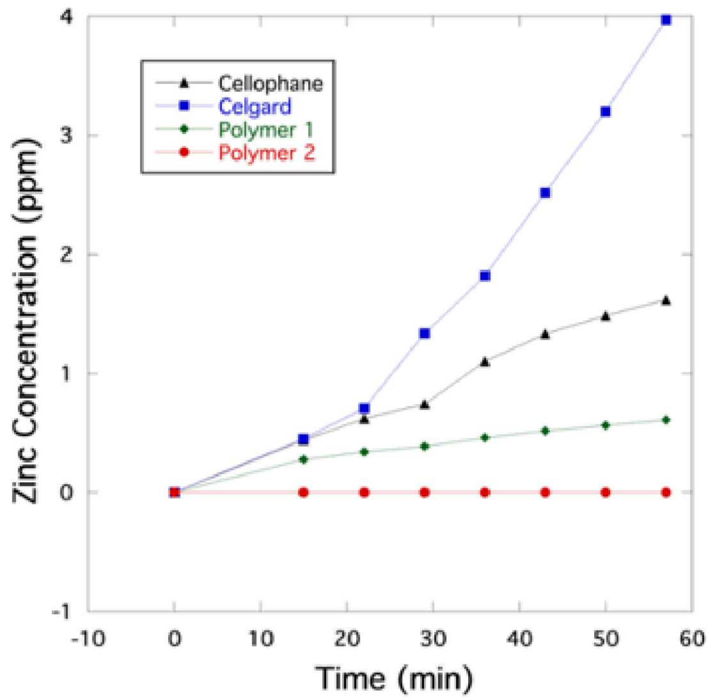
# Utilization of Flexible Polymeric Separators

*Development of flexible polymers that allow for selective ion transport (lower cost, higher volumetric energy density and more flexible battery assembly)*

## Hydroxide Diffusion




## Zincate Diffusion



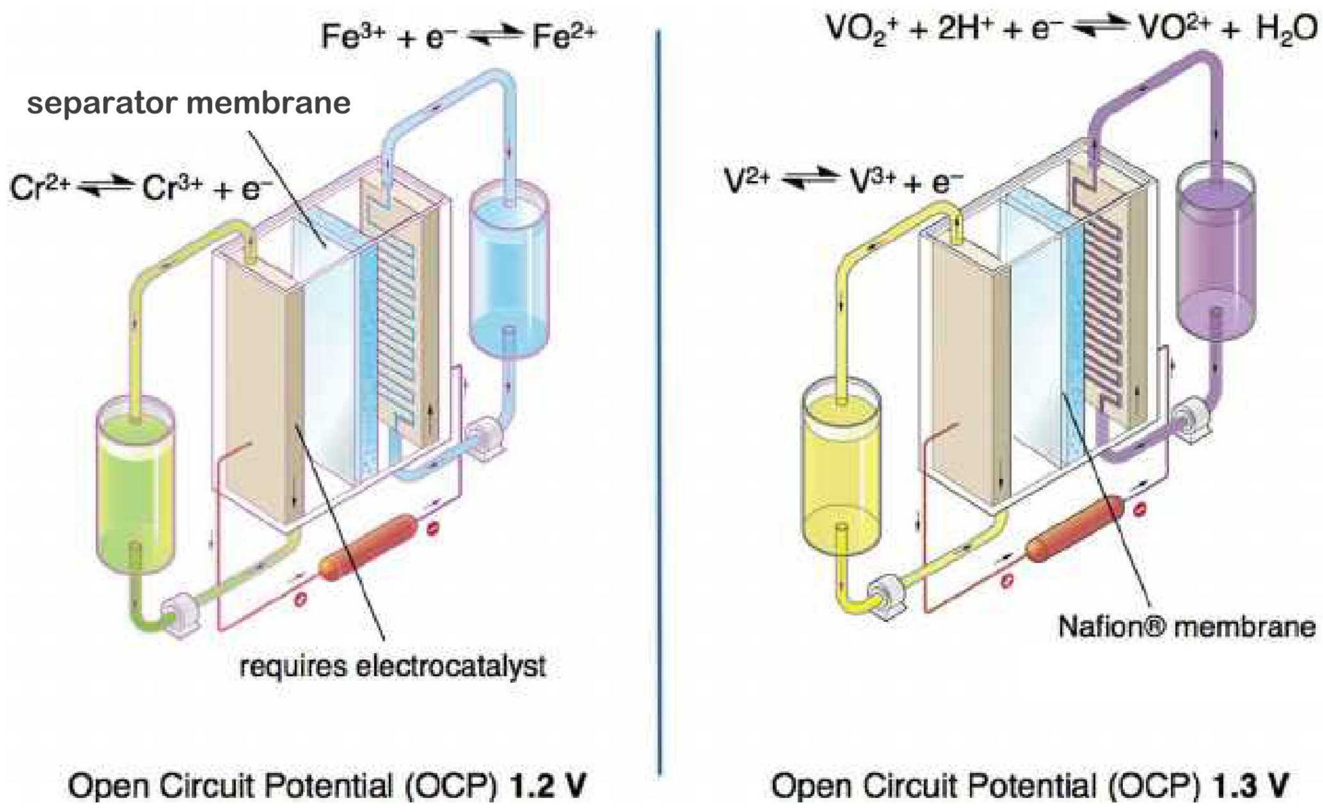

T.N. Lambert *et al.* unpublished results

| Separator | $D_{OH^-}$ ($cm^2/min$) | $D_{[Zn(OH)_4]^{2-}}$ ($cm^2/min$) | Selectivity Ratio |
|---|---|---|---|
| Cellophane | $1.74 \cdot 10^{-5}$ | $1.41 \cdot 10^{-6}$ | 12.3 |
| Celgard | $6.72 \cdot 10^{-6}$ | $1.58 \cdot 10^{-6}$ | 4.25 |
| Polymer 1 | $5.38 \cdot 10^{-6}$ | $5.56 \cdot 10^{-8}$ | 96.8 |
| **Polymer 2** | **$3.03 \cdot 10^{-6}$** | **$3.66 \cdot 10^{-11}$** | **$8.28 \cdot 10^{4}$** |

Polymer 2 is effectively 100% selective for hydroxide

# Redox Flow Batteries

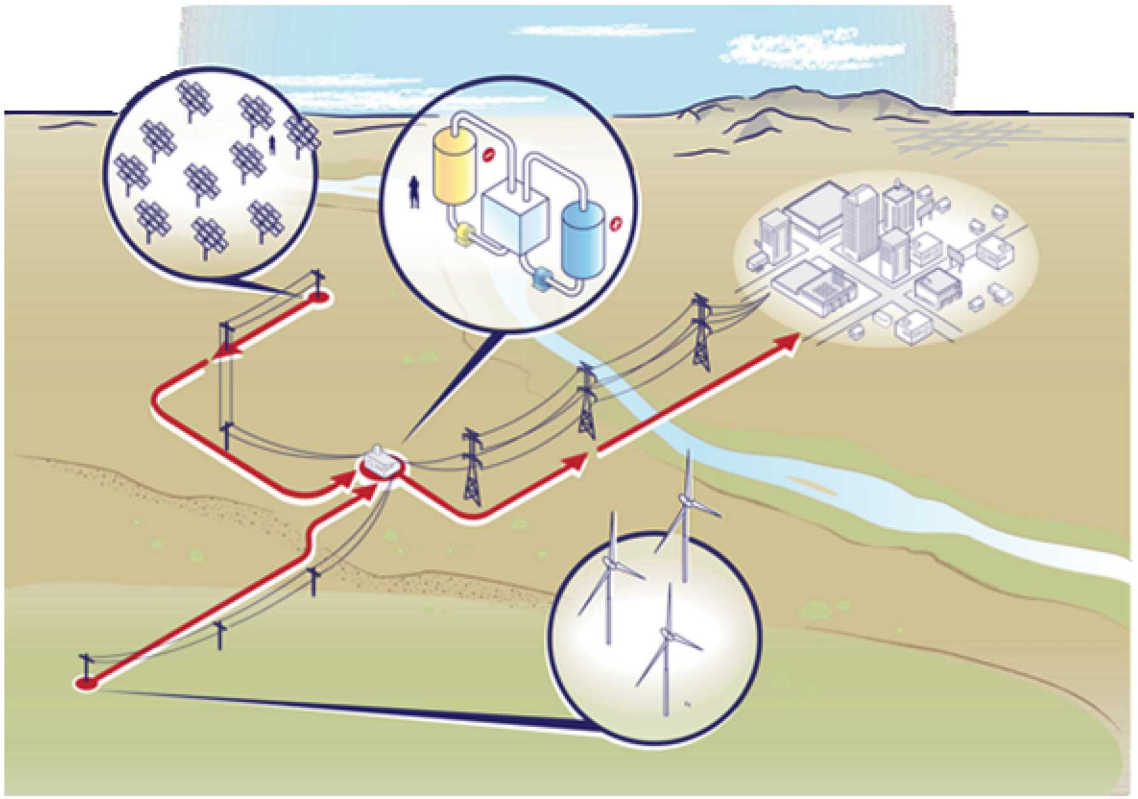
Redox flow batteries utilize dissolved redox-active species that are flowed through electrochemical cells. Anolytes and catholytes are separated by ion-conducting, but electronically-insulating, membranes. Critically, *energy and power are separated in this design.*

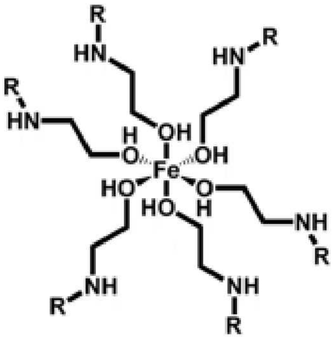



SNL Principal Investigator: Dr. Travis Anderson (tmander@sandia.gov)

# Ionic Liquid Flow Batteries

Metal ionic liquid (MetIL) flow batteries may offer **higher energy densities** due to **higher voltages** and increased active material concentrations.





Redox-active ionic liquids can be made from low-cost precursors.

SNL is developing and testing laboratory prototypes using *cost competitive electrolytes, novel cell designs, and tunable membranes.*


The differentiating technical approach of this work is to circumvent solubility issues by incorporating charge storage into the electrolyte.

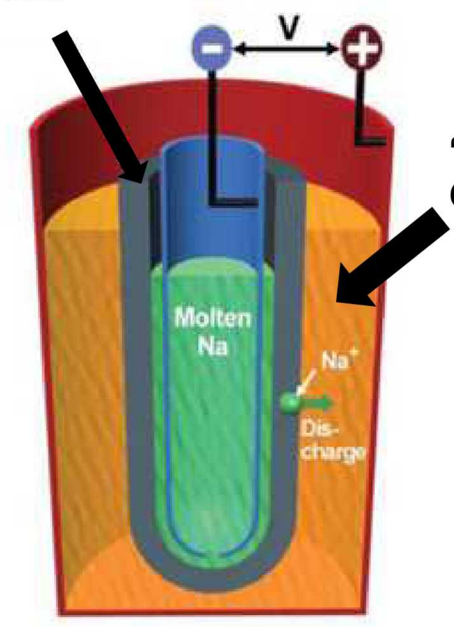
Dr. Leo Small, Harry Pratt, and Dr. Cy Fujimoto

SNL Principal Investigator: Dr. Travis Anderson (tmander@sandia.gov)

# Promise in Molten Sodium Batteries

## Sodium-based batteries

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium/Sulfur (NaS) and FzSoNick ZEBRA (Na-$NiCl_2$) systems.
- Utilize zero-crossover solid state separators.
- Favorable battery voltages (>2V).




## Traditional Na-Batteries operate at ~300°C

- Improves separator ionic conductivity
- Maintains molten phase chemistry

**Na-$NiCl_2$ ($E_{cell}$ ~ 2.6V)**

$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

**Na-S ($E_{cell}$ ~ 2V)**

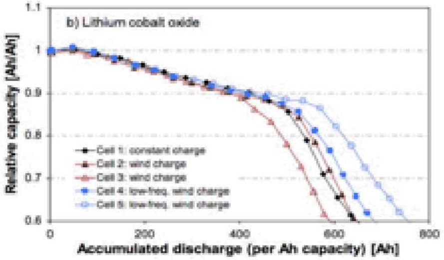
$2Na + 4S \leftrightarrow Na_2S_4$

# Challenges with Existing Batteries

## Li-ion ($E_{cell}$ ~ 3.6V)

$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$

- Safety (flammable organic electrolytes
- Cycle lifetime limited
- Cost

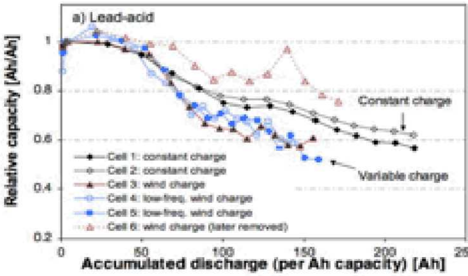



E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

## Pb-Acid ($E_{cell}$ ~ 2.1V)

$Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$

- Capacity fades quickly (typically 200-300 cycles)
- Temperature-sensitive

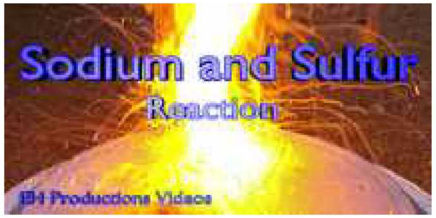



E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

## Na-S ($E_{cell}$ ~ 2V)

$2Na + 4S \leftrightarrow Na_2S_4$

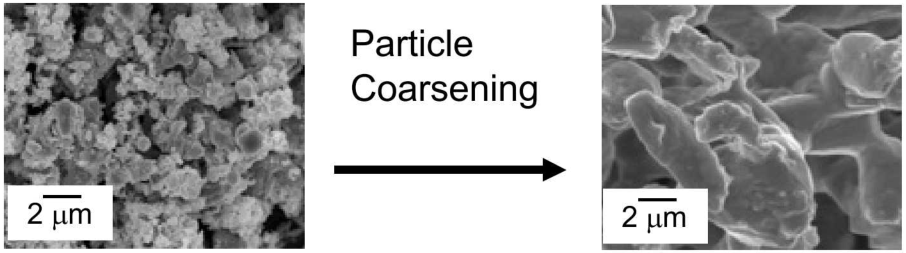
- Safety: Violent, toxic reactions between molten Na and molten S – cascading runaway!
- Corrosive, toxic chemistries
- High temperature operation (270-350$^{o}$C)



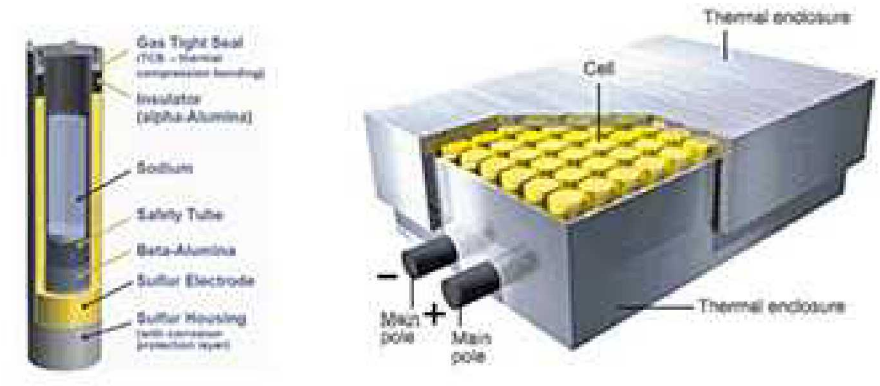

## Na-NiCl$_2$ ($E_{cell}$ ~ 2.6V)

$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

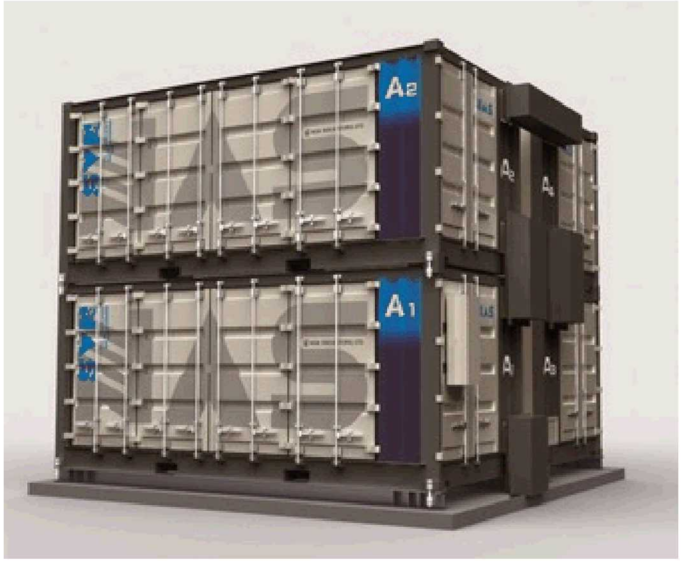
- Cycle lifetime (solid cathode phase)
- Cost (related to cycle lifetime and material costs)
- High temperature operation (typically > 200$^{o}$C)



# Sodium-Sulfur (NaS) Batteries (NGK)




Sodium-Sulfur (NaS) Batteries




Los Alamos, NM USA (1 MW)

Rokkasho village, Aomori, Japan (34 MW)

# NaS Battery Deployment (NGK)

**Approximately 560 MW / 4 GWh deployed in more than 200 locations globally.**

# Na-NiCl$_2$ ("ZEBRA") Batteries (FIAMM)

FIAMM SoNick (Na-NiCl$_2$) Batteries

- ~300$^{o}$C operation, no cooling required
- 2-4 hour energy applications
- Operational from -20$^{o}$C to +60$^{o}$C
- 20 year design life (3500-4500 cycles)
- Environmentally friendly and *recyclable*
- "No maintenance"

48 V (200Ah) module

620V module

620 V 90 kWh (25kW)


620 V 1.4 MWh (400 kW)

# $Na\text{-}NiCl_2$ Stationary Deployment (FIAMM)

Intended for On-Grid, Microgrid, and Off-Grid Applications

- Power Quality
- Frequency Regulation
- Load Shifting
- Peak Shaving
- Backup Power
- Renewable Resource Integration

**>100 MWh installed globally**

Sacramento, CA (USA)
190 kWh (50kW)

"Behind the meter"

Codrongianos, Sardinia (Italy)
4.15 MWh (1.2 MW)

Grid Regulation

French Guyanne (S. America)
4.5 MWh (1.5 MW)

Renewable Integration

SO|NICK

FIAMM Energy Storage Solutions

# Challenges with Existing Na Batteries

## Na-S ($E_{cell}$ ~ 2V)

$$2Na + 4S \leftrightarrow Na_2S_4$$

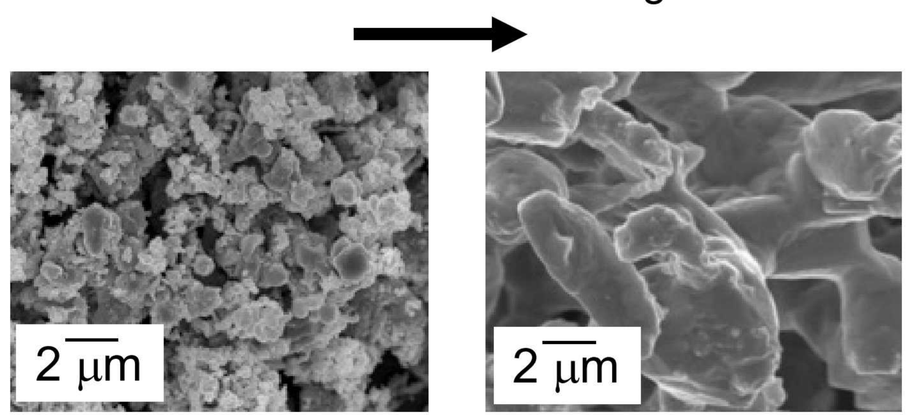
- Safety: Violent, toxic reactions between molten Na and molten S – cascading runaway!
- Corrosive, toxic chemistries
- High temperature operation (270-350°C)


## Na-NiCl$_2$ ($E_{cell}$ ~ 2.6V)

$$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$$

- Cycle lifetime (solid cathode phase)
- Cost (related to cycle lifetime and material costs)
- High temperature operation (typically > 200°C)

Particle Coarsening



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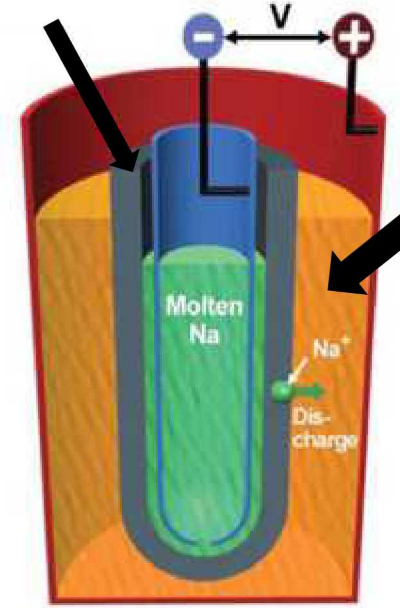
- Utilize zero-crossover solid state separators.
- Yield favorable battery voltages (>2V).

**Ion Conducting Ceramic Separator**




**"Molten Catholyte"**
- **Sulfur**
- **M-Halide Salts**

## Traditional Na-Batteries operate at ~300°C

- Improves separator ionic conductivity
- Maintains molten phase chemistry
- Increases cost
- Complicates material packaging
- Limits battery lifetime
- Introduces freeze-thaw hazards/costs

**Na-$NiCl_2$ ($E_{cell}$ ~ 2.6V)**

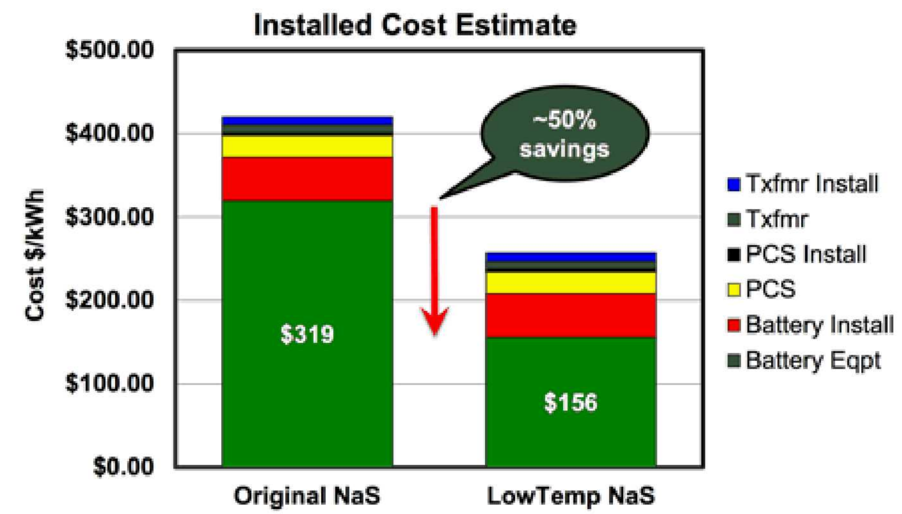
$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

**Na-S ($E_{cell}$ ~ 2V)**

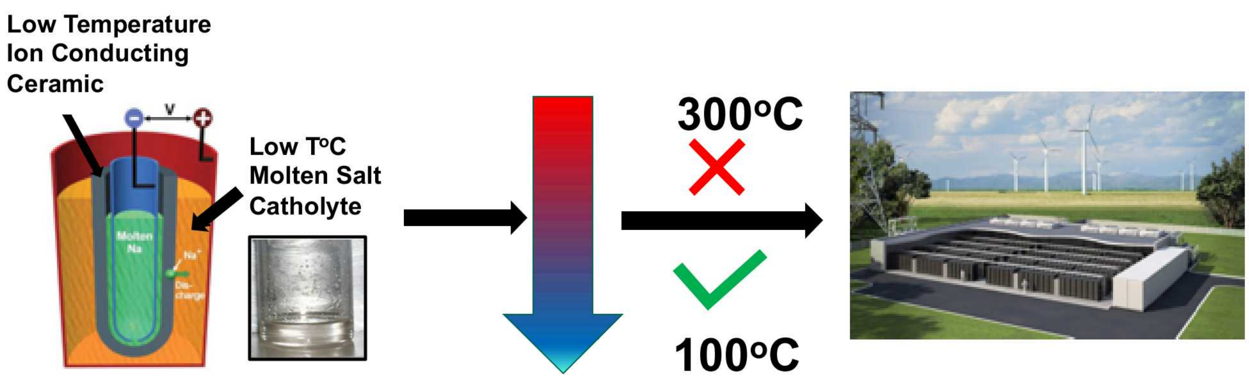
$2Na + 4S \leftrightarrow Na_2S_4$

# Low Temperature Operation of a Molten Na Battery is Tremendously Enabling

- Improved Lifetime
  - Reduced material degradation
  - Decreased reagent volatility
  - Fewer side reactions
- Lower material cost and processing
  - Seals
  - Separators
  - Cell body
  - Polymer components?
- Reduced operating costs
- Simplified heat management costs
  - Operation
  - Freeze-Thaw

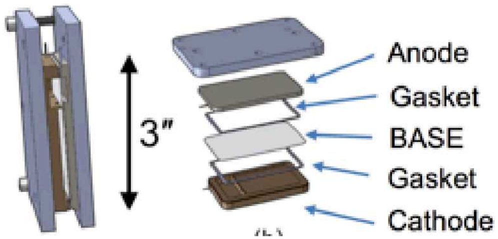


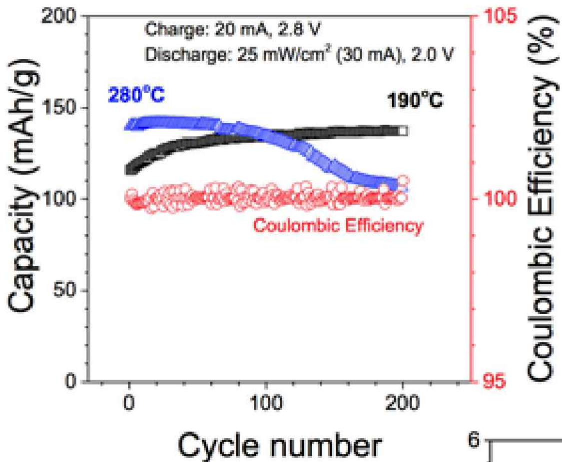

Gao Liu, et al. "A Storage Revolution." 12-Feb-2015 (online): https://ei.haas.berkeley.edu/education/c2m/docs/Sulfur%20and%20Sodium%20Metal%20Battery.pdf

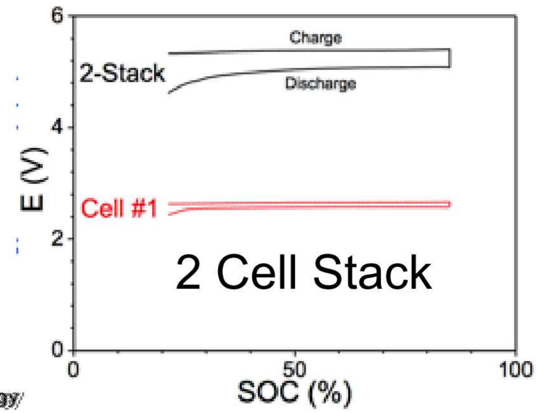


# Intermediate Temperature "ZEBRA" Batteries

## Planar Stack Configuration



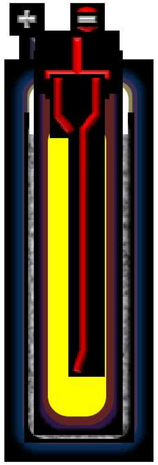




Pacific Northwest NATIONAL LABORATORY

RIST Research Institute of Industrial Science & Technology

## Tubular Configuration





## Multiscale Prototype Demonstrations

**13 Wh Na-$NiCl_2$ Cell**
- Operational for 9+ months.
- Energy efficiency >85%
- 65 mA /cm$^2$

**100 Wh Na-$NiCl_2$ Cell:**
- Operational for 4+ months.
- energy efficiency 81.5%
- 53 mA/cm$^2$

**250 Wh Na-$NiCl_2$ Cell:**
- operational for 3+ months
- energy efficiency 80%
- 53 mA/cm$^2$

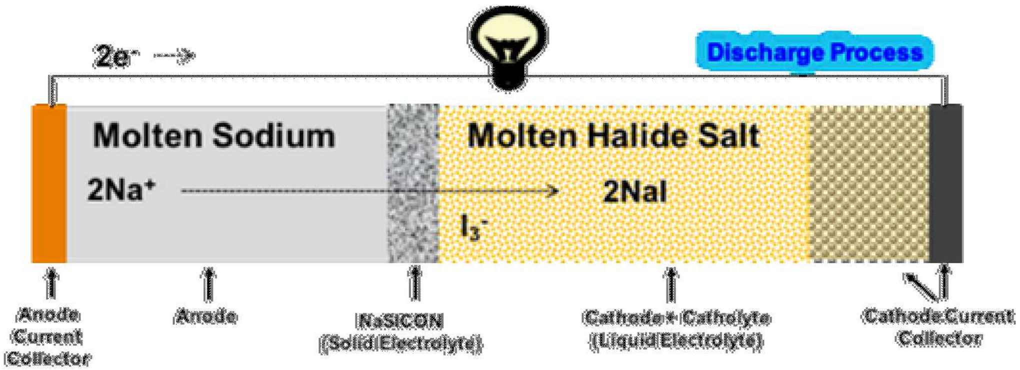
* All cycled to 70% DOD at C/7 rate.

SK

CERAMATEC TOMORROW'S CERAMIC SYSTEMS

# Low Temperature Molten Na-Halide Batteries

Our Vision: A molten sodium-based battery that comprises a robust, highly $Na^+$-conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.




**Na-NaI battery:**

$Na \rightarrow Na^+ + e^-$ $E^0 = 0V$

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

*Na-NaI batteries show promise as safe, low-cost, highly cyclable battery with functional energy density.*

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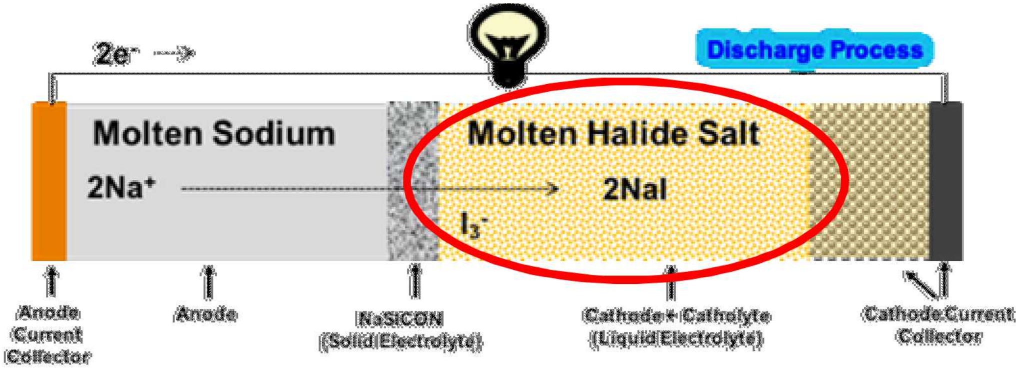


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$I_3^- + 2e^- \rightarrow 3I^- \quad E^0 = 3.24$

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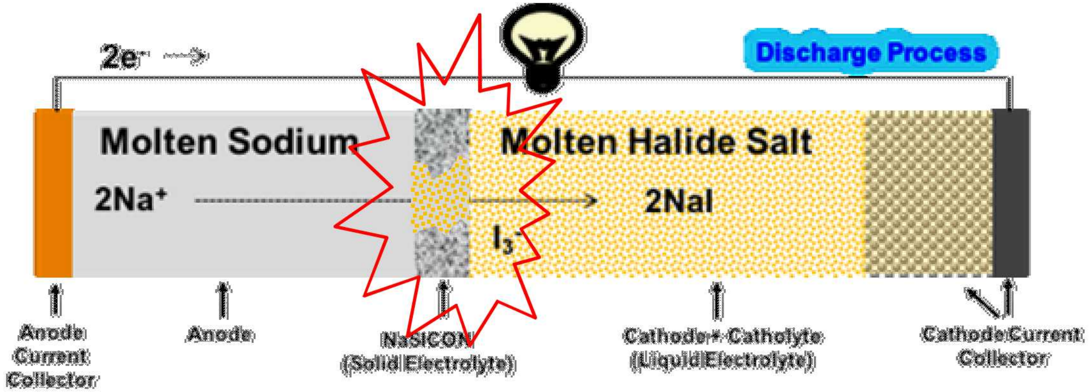
*Consider NaI-AlX$_3$ catholyte…*

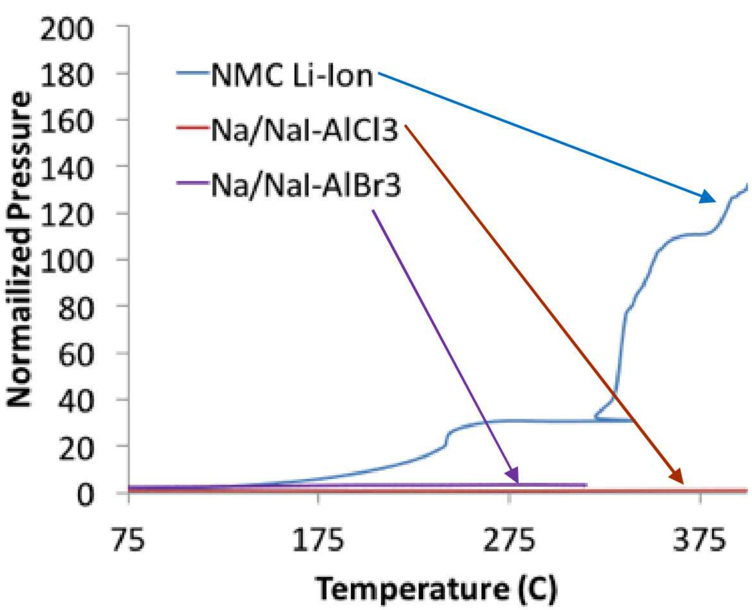
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

# Na-NaI Exhibits Inherent Improved Safety




Simulating separator failure, metallic Na and NaI/$AlX_3$ were combined and heated.

Byproducts of reaction are aluminum metal and harmless sodium halide salts.

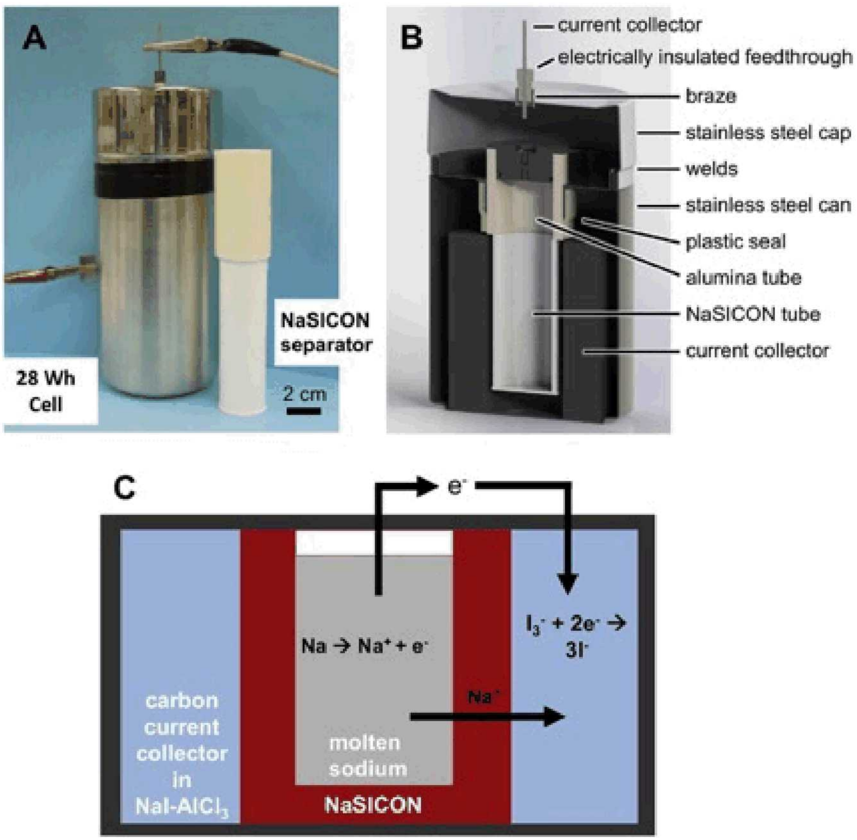


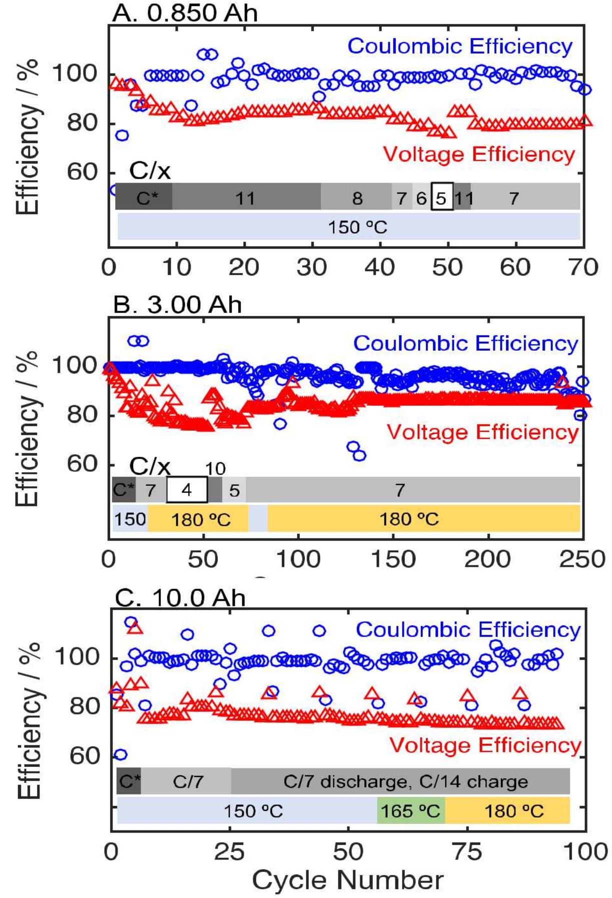

Accelerating rate calorimetry reveals that Na-NaI/$AlX_3$ mixtures exhibit:

1) *no significant exothermic behavior*
2) *no significant gas generation of pressurization*

# An Intermediate Temperature Na-NaI Battery

*Na-NaI battery was demonstrated across several scales at 150-180$^{o}$C.*




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

# Low Temperature Molten Na-NaI Batteries

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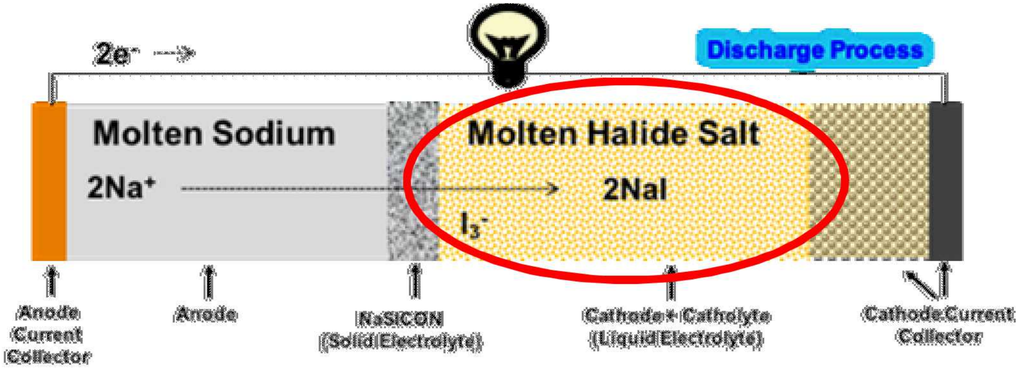


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$Na \rightarrow Na^+ + e^-$ $E^0 = 0V$

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

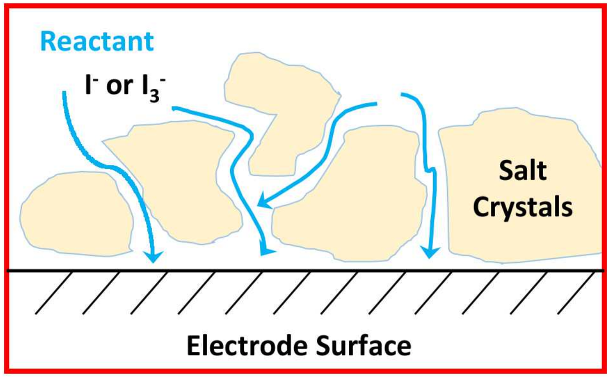
*How important is the molten character of the catholyte?*

# Catholytes are Key to Low Temperature Operation

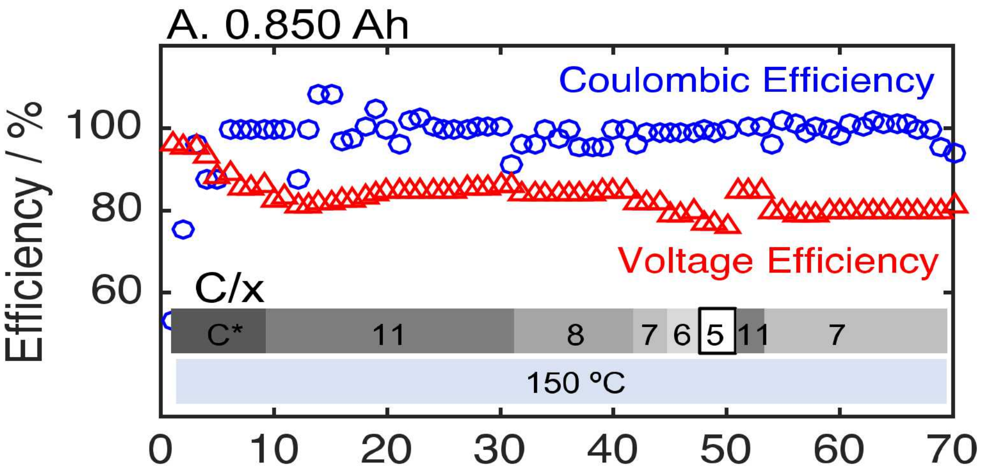
A fully molten catholyte avoids

a) Particle-hindered electrochemical processes.

b) Particle-related loss of capacity.




$NaI$-$AlCl_3$ at 150°C


Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

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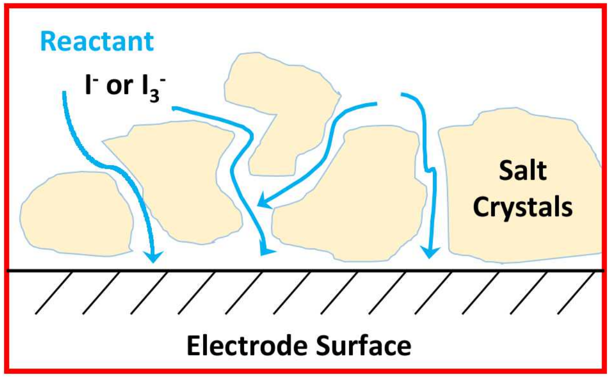
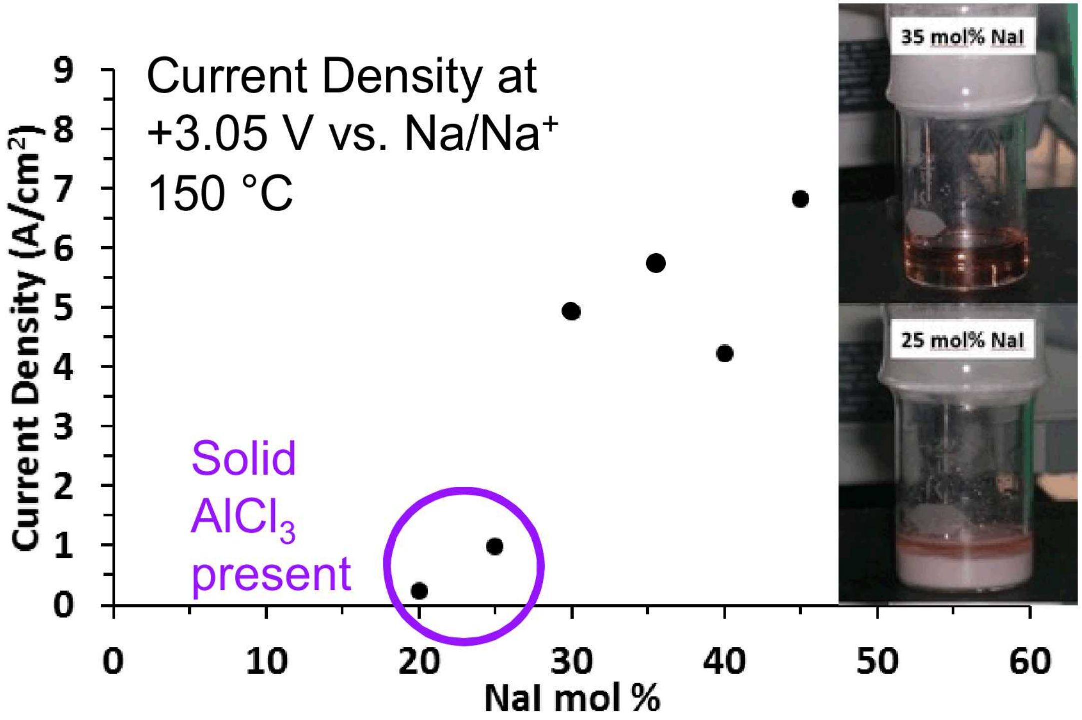



Current Density is significantly lower when solid secondary phases are present.

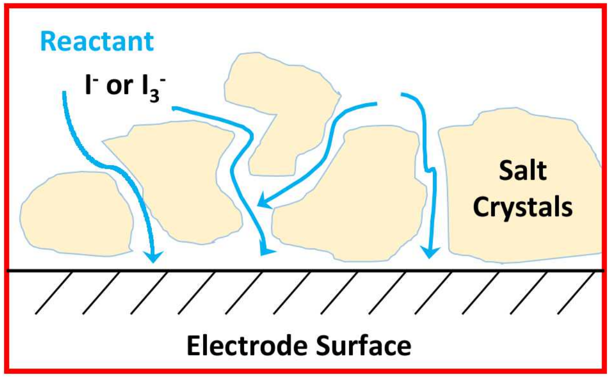
Percival, Small, and Spoerke. *J. Electrochem. Soc.*, **165** (14) A3531-A3536 (2018)

# Catholyte Composition is Especially Important at Lower Temperatures

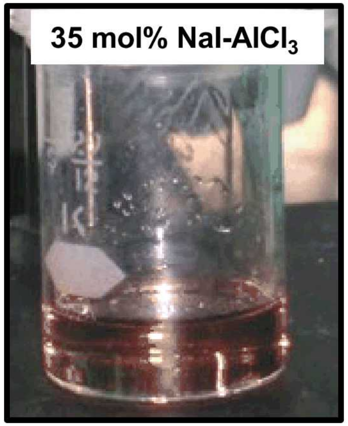
A fully molten catholyte avoids

a) Particle-hindered electrochemical processes

b) Particle-related loss of capacity




$NaI\text{-}AlCl_3$ at 150°C




$NaI\text{-}AlCl_3$ and $NaI\text{-}AlBr_3$ salts at 90°C




*Molten $NaI\text{-}AlBr_3$ composition range spans 5-25% NaI and cell voltage is near or above 3V.*

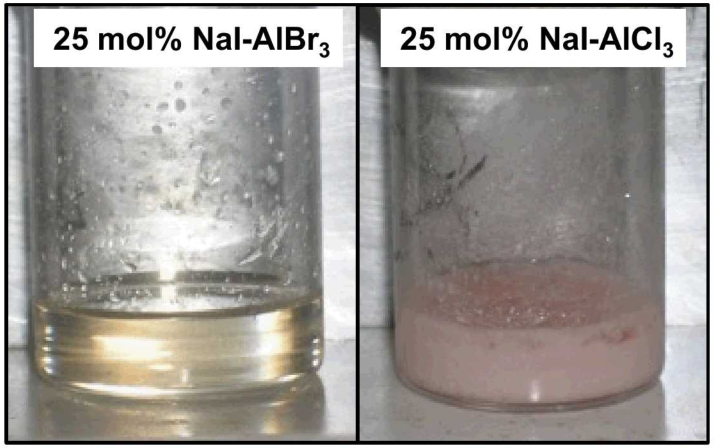
Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

# NaI-$AlBr_3$: An Electrochemically Promising Low Temperature Molten Catholyte

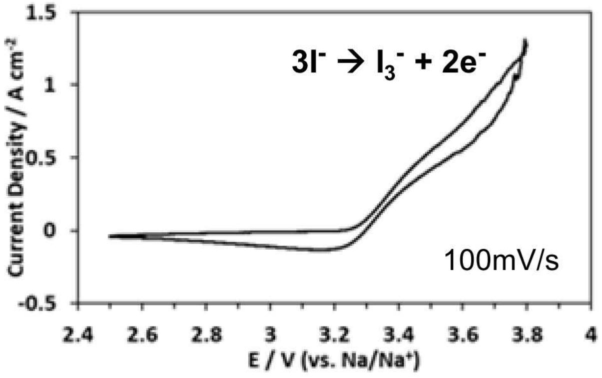
*The NaI-$AlBr_3$ catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures.*

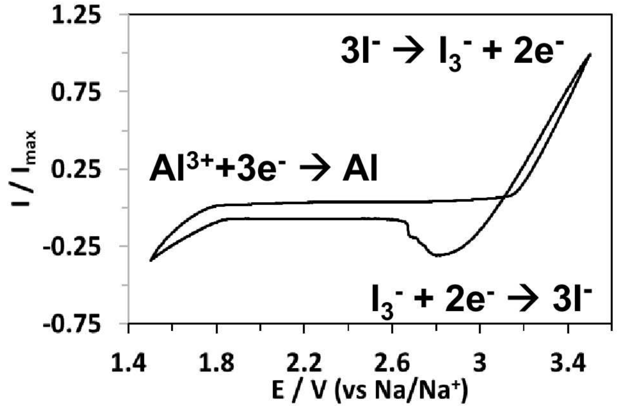
- 25:75 NaI-$AlBr_3$ salt completely molten at 90 °C
- Larger fully molten capacity range (~5-25 mol% NaI)

Samples at 90°C




- Carbon Fiber microelectrode shows excellent electrochemical behavior of 25 mol% NaI-$AlBr_3$ at 90°C




- NaI-$AlBr_3$ system shows good iodide electrochemical reversibility.
  - $AlBr_3$ (20mol% NaI) system at 120 °C and 1V/s

# Low Temperature Solid State Separator

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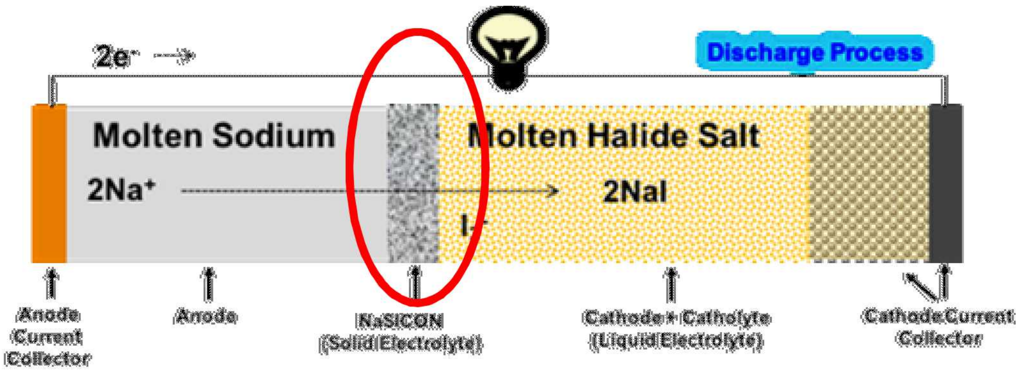


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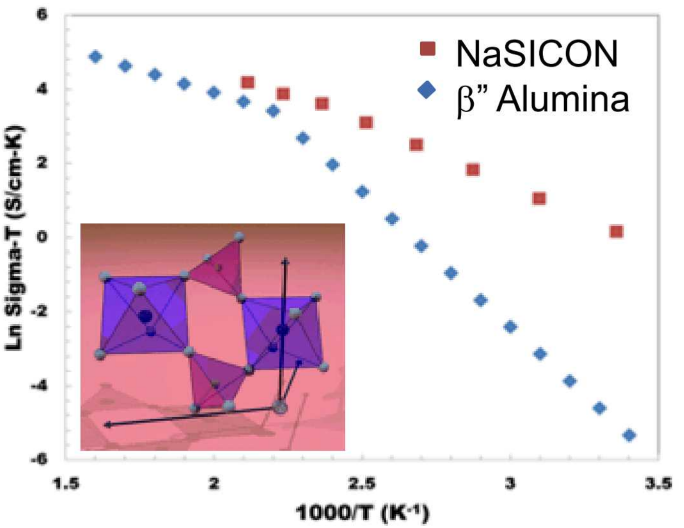
## Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity (>$10^{-3}$ S/cm at 25°C)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover



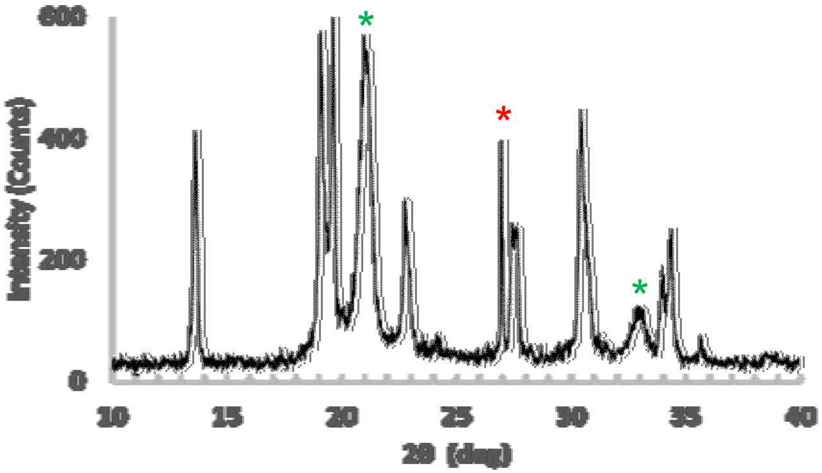

Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

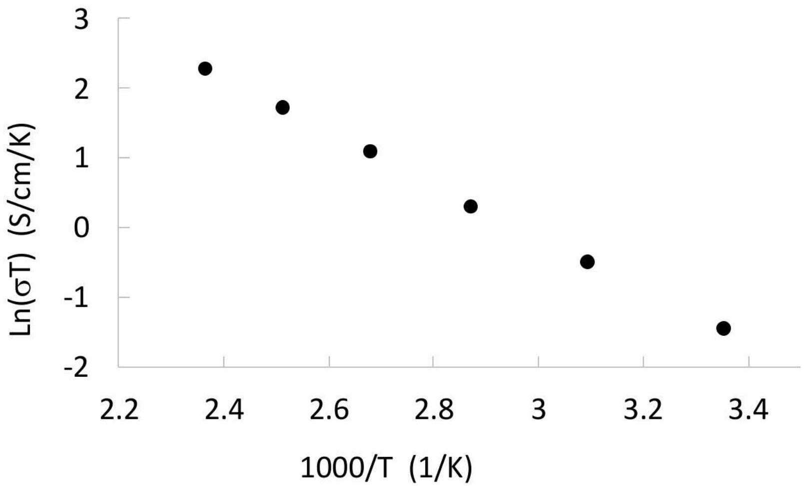
# Conventional Synthesis

<u>Solid State Ceramic Synthesis ("Shake 'n Bake")</u>

**$2ZrSiO_4 + Na_3PO_4 \rightarrow Na_3Zr_2PSi_2O_{12}$**

- Milled powders pressed and fired at 1200$^o$C in air
- Pellet densities >95%
- X-ray diffraction confirms NaSICON synthesis with $ZrO_2$ and $ZrSiO_4$ secondary phases
- Conductivities reasonable, but slightly less than commercial NaSICON




* Sample holder artifact

# Low Temperature Seals

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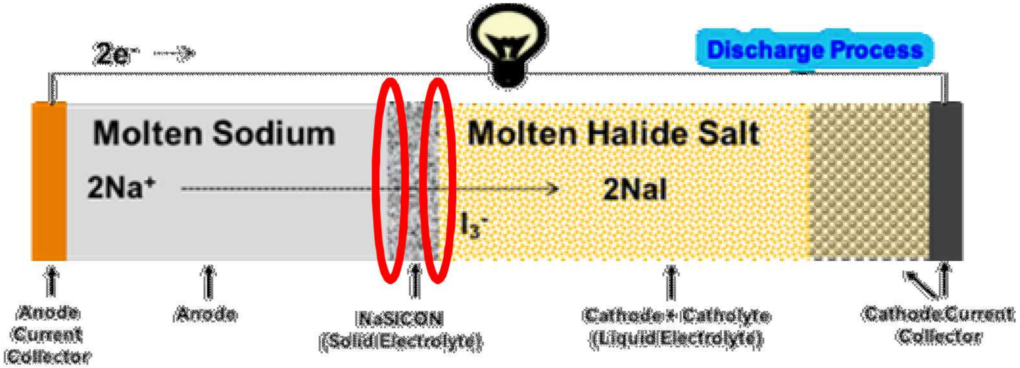


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$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

# Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

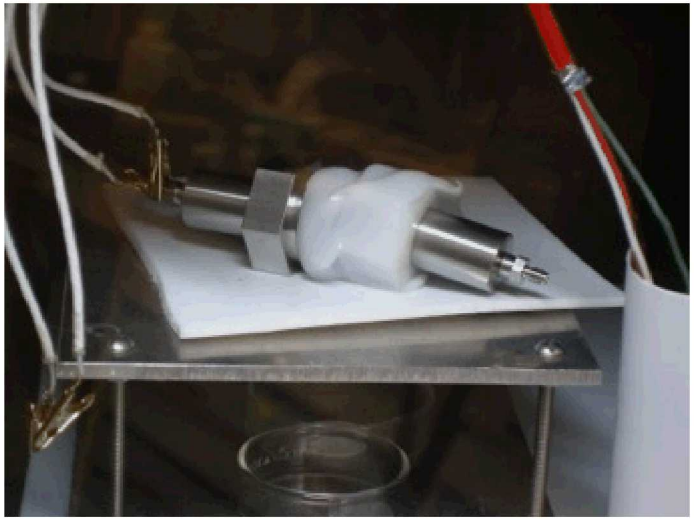
Compatibility must be considered for:

- Molten sodium
- Molten halide catholyte salts
- Non-ambient temperatures
- Electrochemical reactions
- Temperature
- Mechanical Properties (toughness, compliance, hermeticity, etc.)

Magnesium metal and Teflon (PTFE) are elements of decoy flares…Sodium has a similar reactivity.

Molten sodium and fluoropolymers should not be considered stable, especially for long-term use.

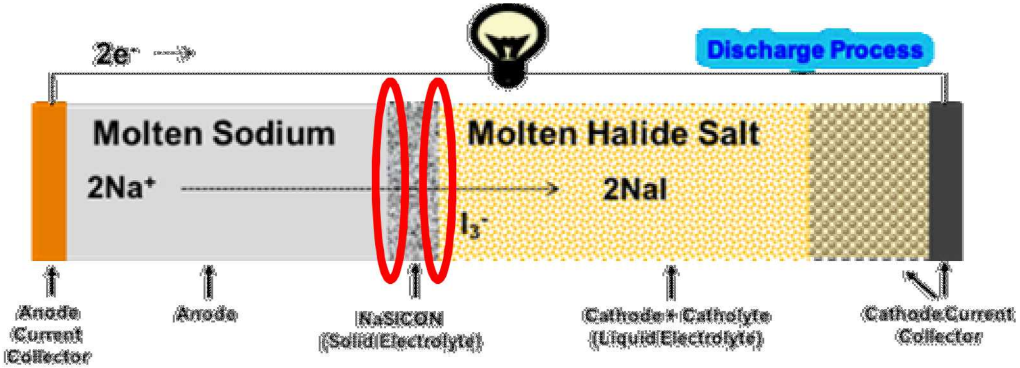
Thermal and mechanical stability



Chemical compatibility

# Low Temperature Molten Na-NaI Batteries

Our Vision: A molten sodium-based battery that comprises a robust, highly $Na^{+}$-conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.




**Na-NaI battery:**

$Na \rightarrow Na^{+} + e^{-}$ $E^{0} = 0V$

$I_3^{-} + 2e^{-} \rightarrow 3I^{-}$ $E^{0} = 3.24$

$2Na + I_3^{-} \rightarrow 2Na^{+} + 3I^{-}$ $E^{0}_{cell} = 3.24V$

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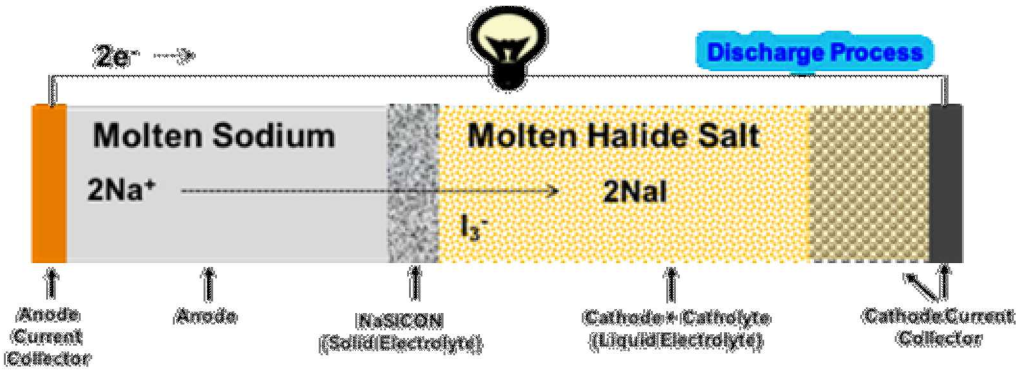


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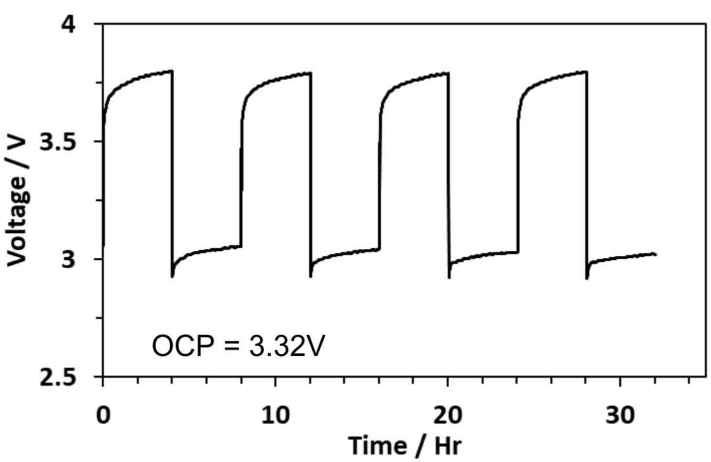
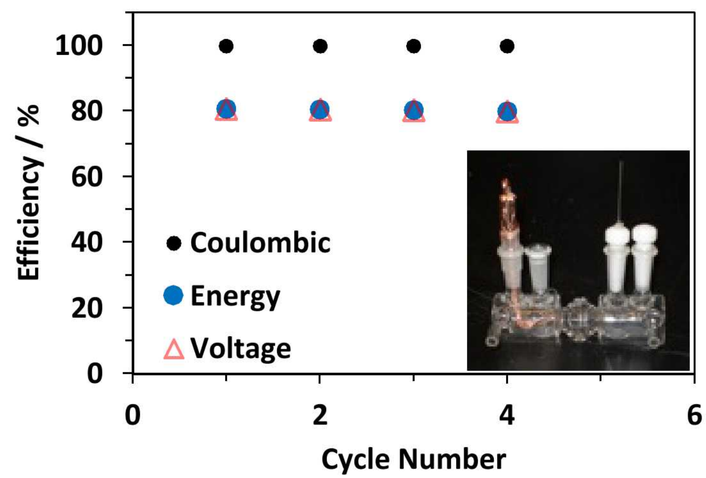
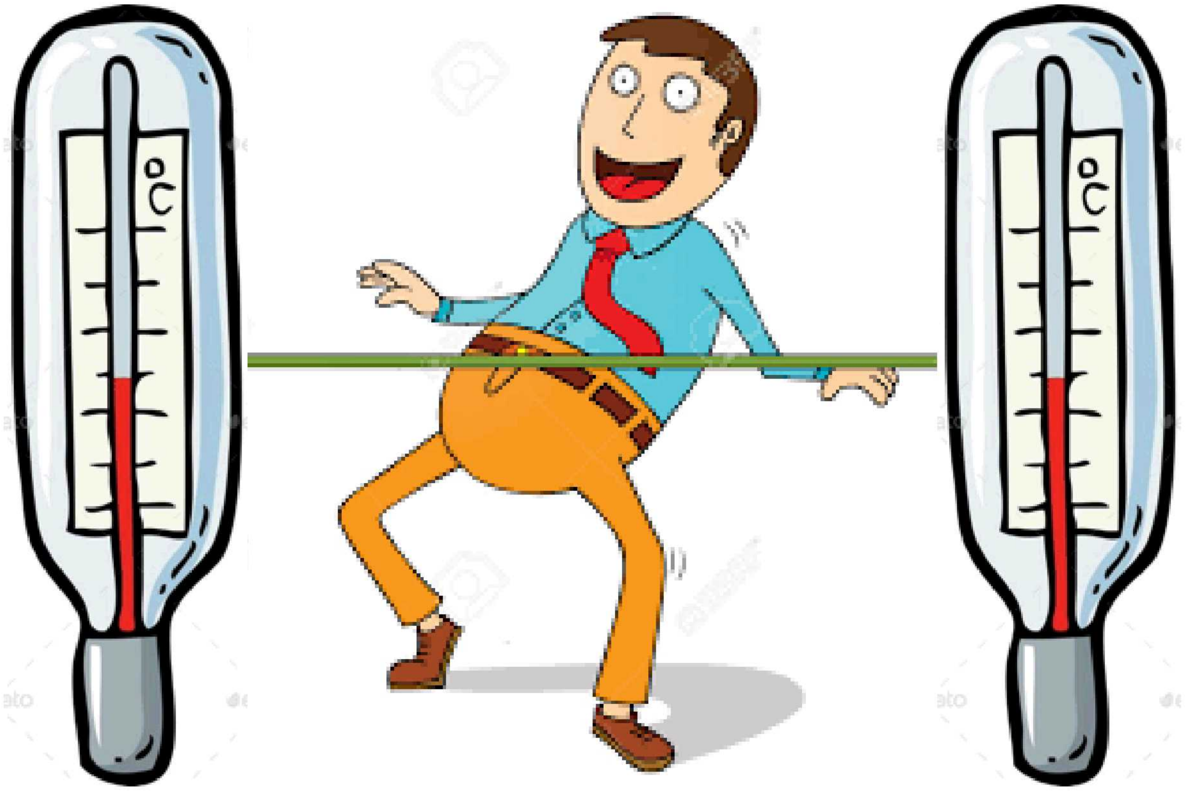



Battery cycling at 110$^{o}$C!

25 mol% NaI-$AlBr_3$ with NaSICON separator.



# How low can we go?



# Low*est* Temperature Molten Na-NaI Batteries

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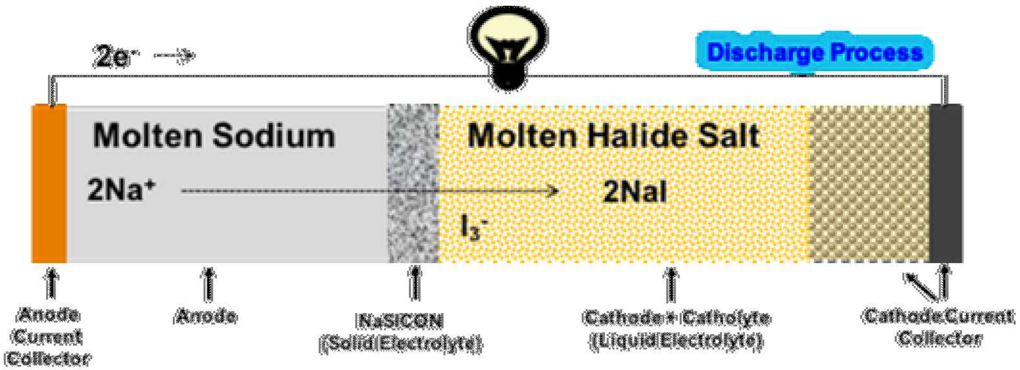


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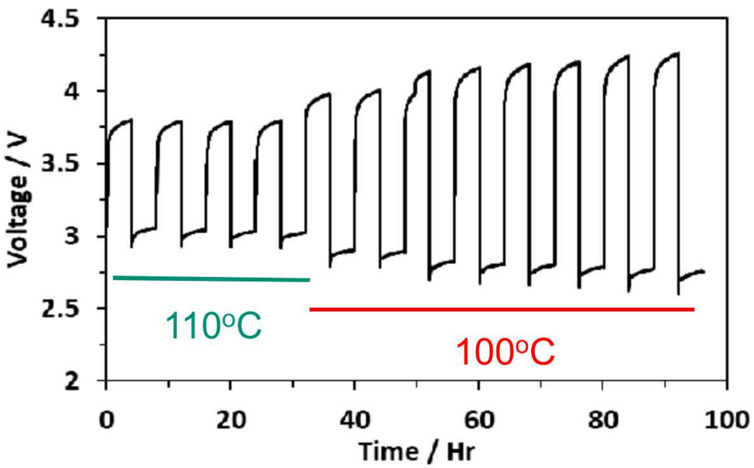
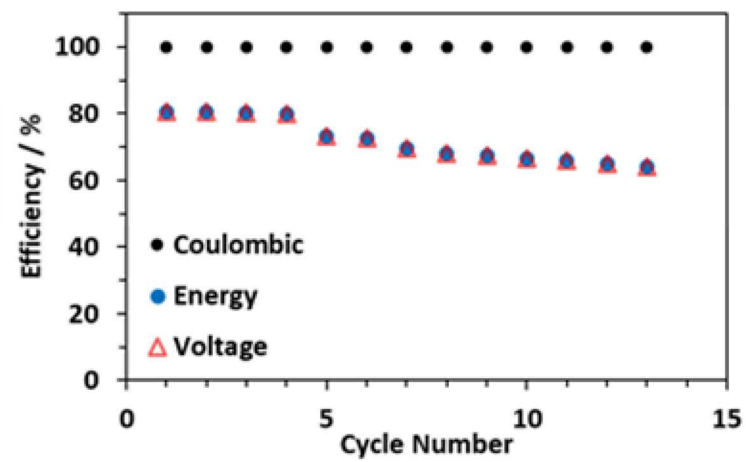



Battery cycling at **<u>100°C</u>**!

25 mol% $NaI\text{-}AlBr_3$ with NaSICON separator.



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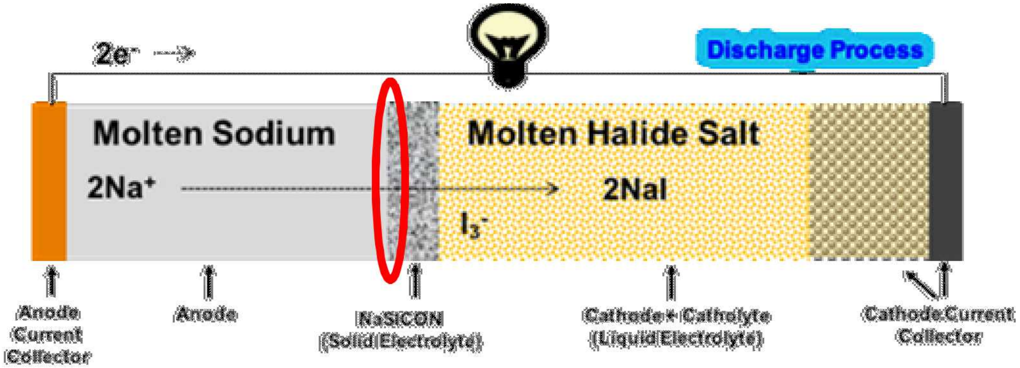


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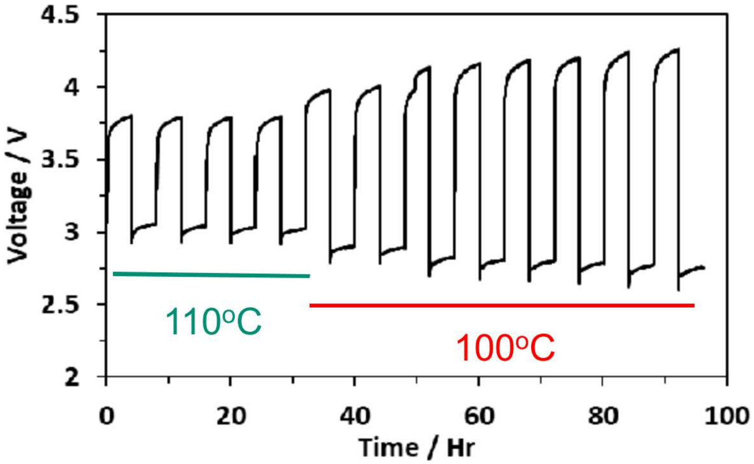


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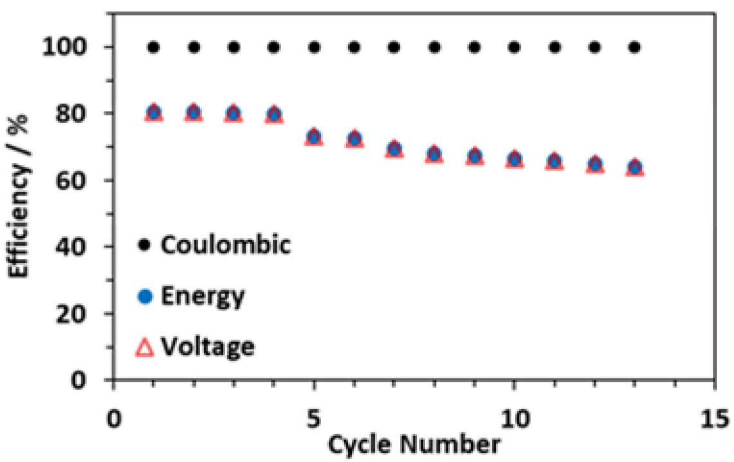
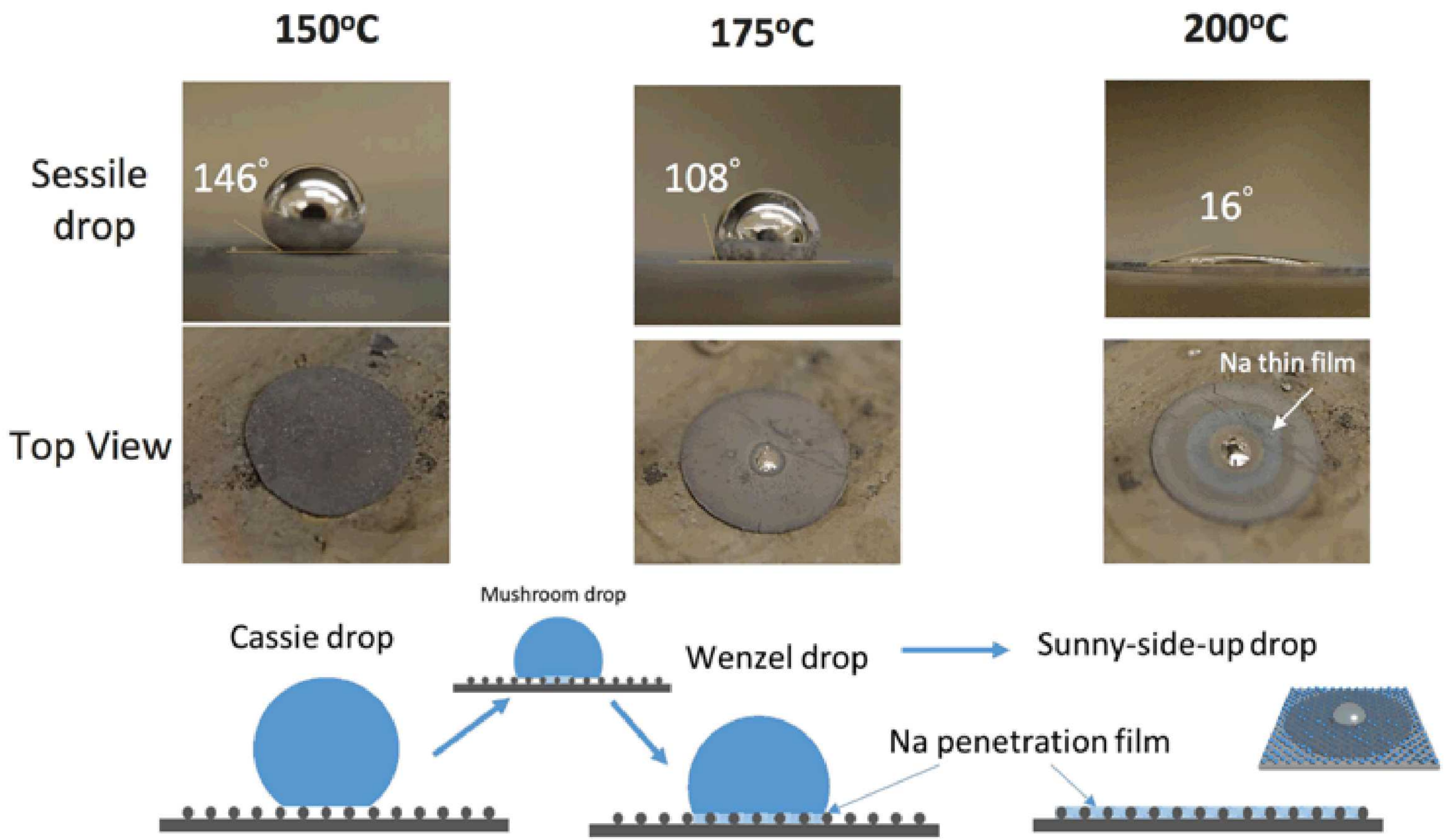


# Follow the Bouncing…Sodium!

**110°C**

# Molten Na-Wetting is Temperature Dependent



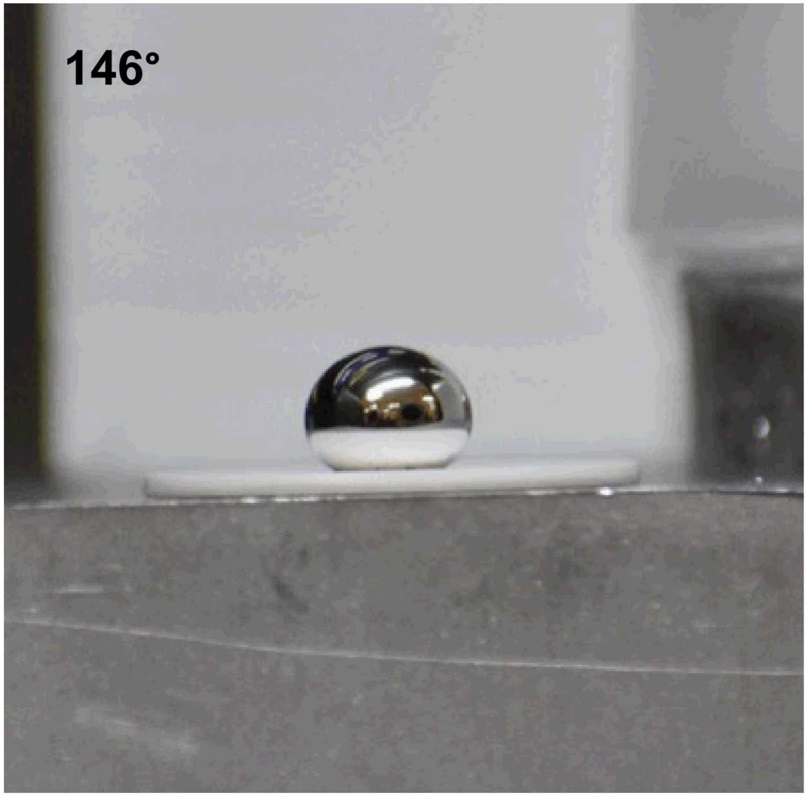

- ❑ Na wetting in "sunny-side-up" shape is responsible for high battery performances

Pacific Northwest NATIONAL LABORATORY

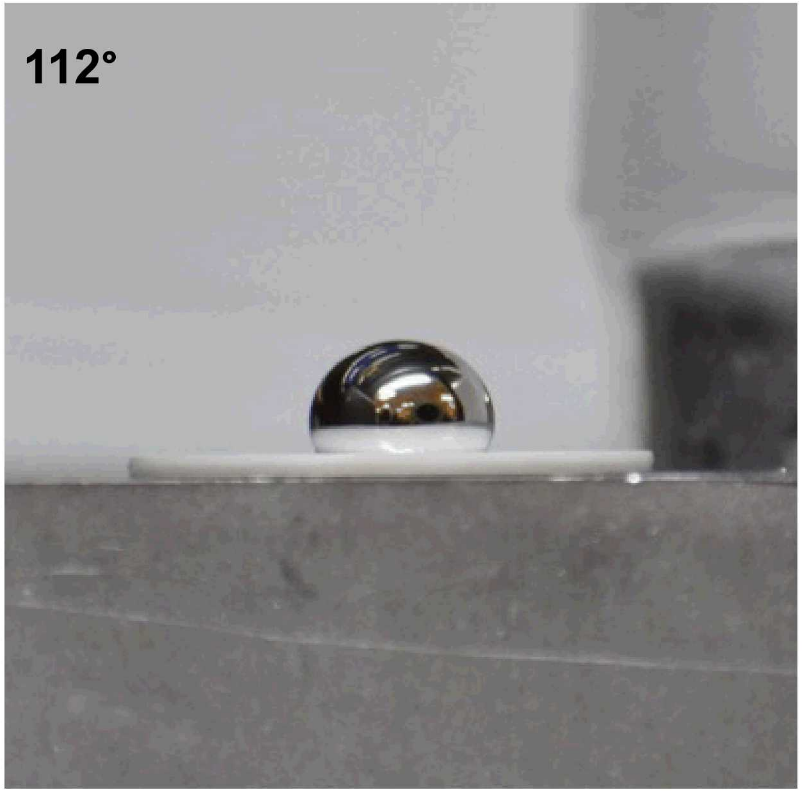
# NaSICON Surface Treatment Affects Na-Wetting

*Polishing NaSICON surface significantly improves Na-wetting at 110°C.*

Unpolished

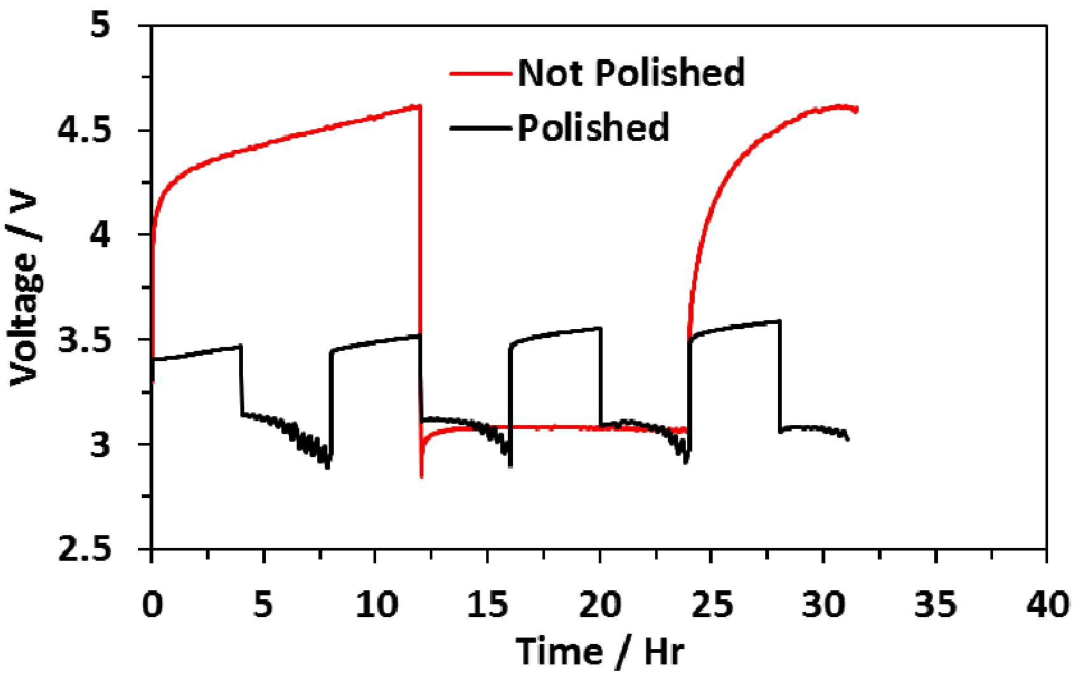



Polished



# Separator Treatment Affects Cell Performance

First, clearing roughening the NaSICON surface with a surface polish allowed higher operating current density and lower overpotentials.




- **Un**polished NaSICON battery operated at ± 0.299 mA current C/12 1% DOD
- Polished NaSICON battery operated at ±0.897mA C/4 1% DOD

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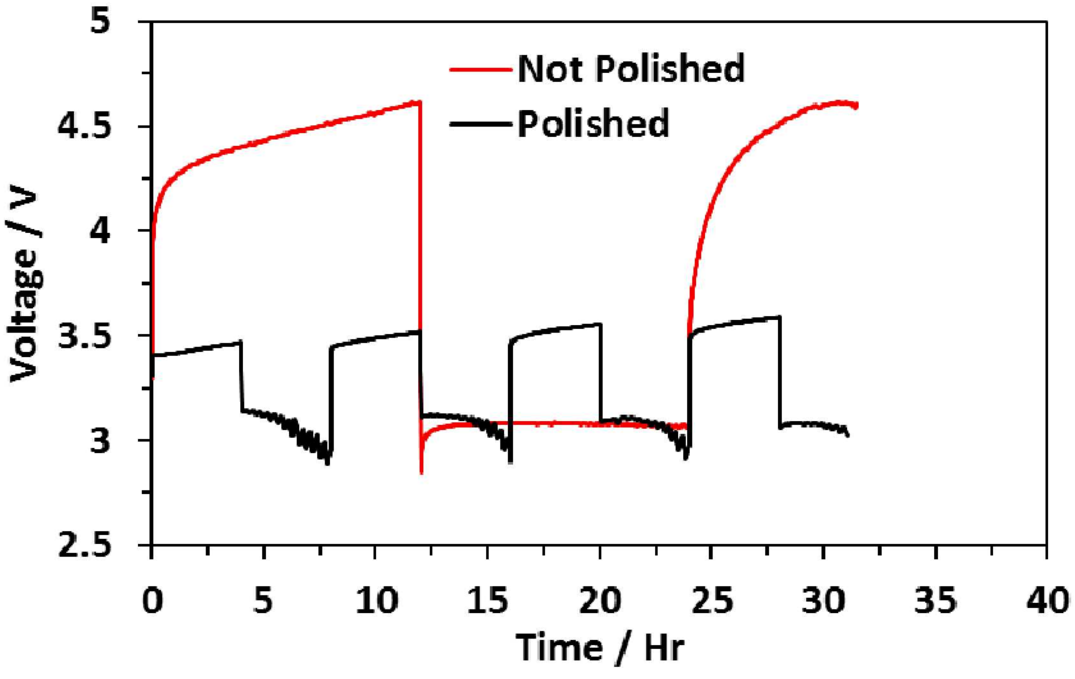
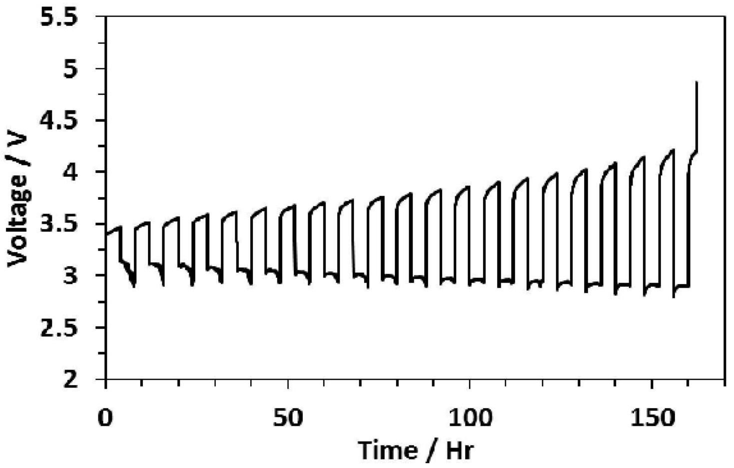
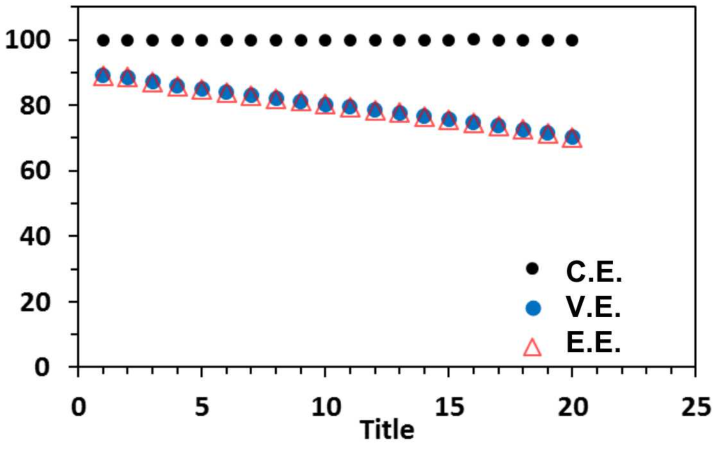
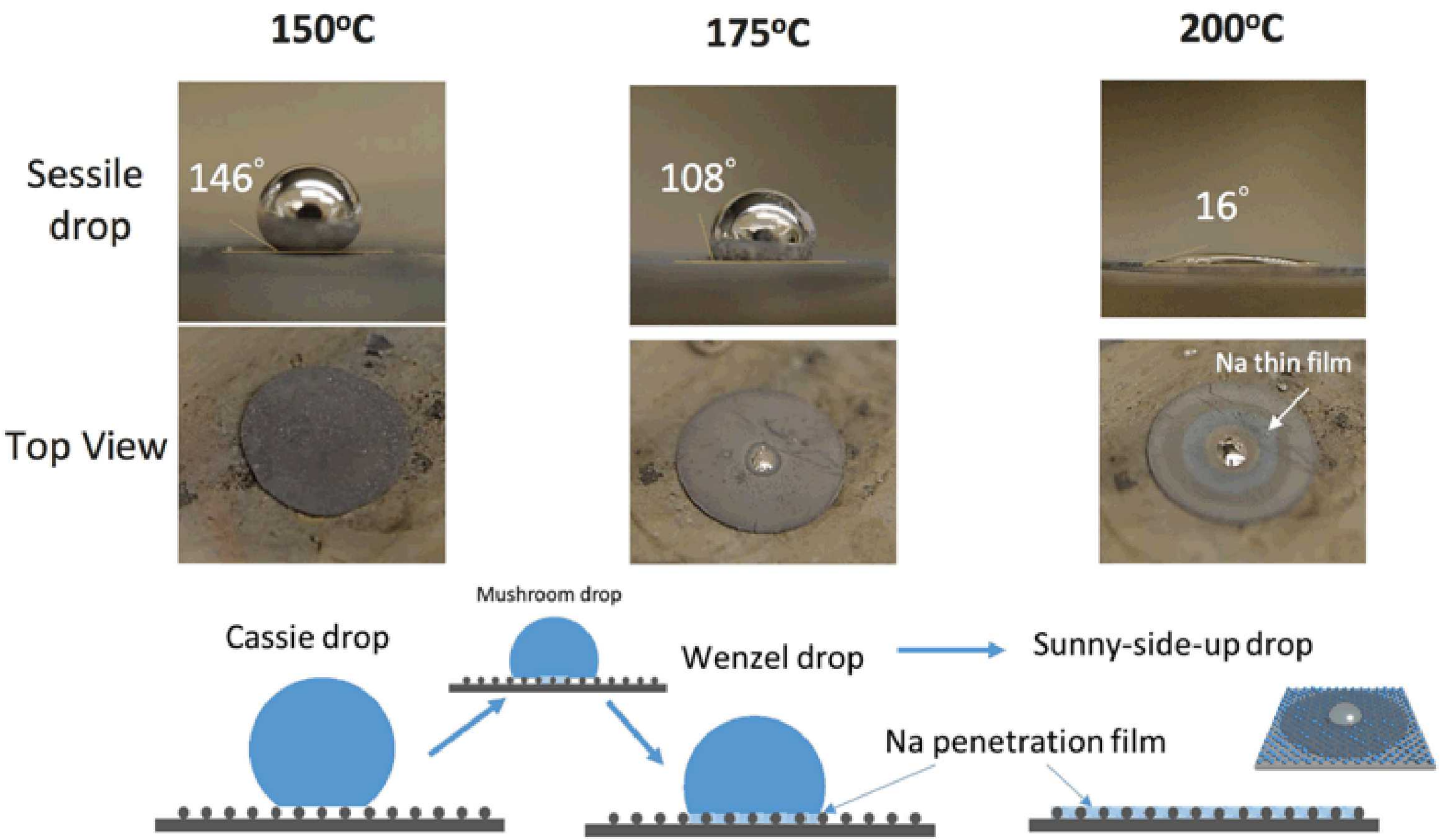



Polished NaSICON alone still shows relatively rapid performance fade.

# What about PbO?



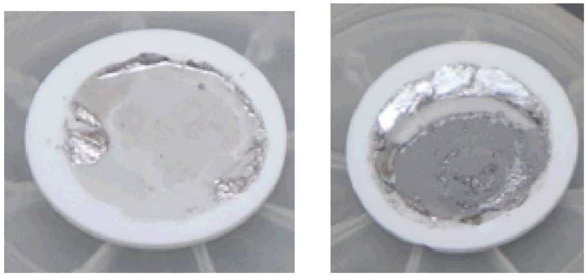

- ❑ Na wetting in "sunny-side-up" shape is responsible for high battery performances



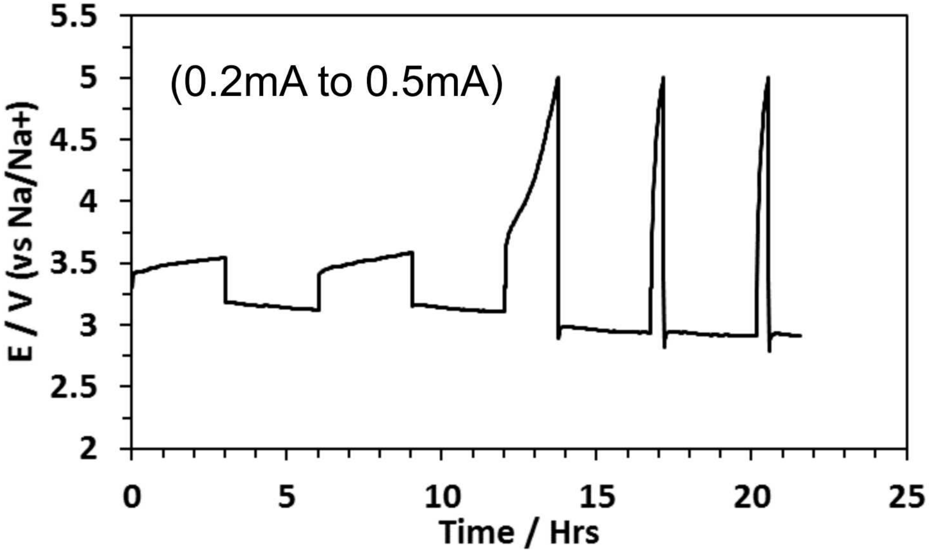
G. Li, 2018 DOE OE Peer Review

# Carbon Coating NaSICON

5nm of carbon coating (evaporated) enhances Na-wetting on NaSICON



Even at low current densities, the carbon coating does not facilitate adequate Na-conductivity across separator interfaces.




Even in thin layers, carbon can serve as a sodium blocking layer. Further work is needed if this is to be an option.

# Separator Treatment Affects Cell Performance

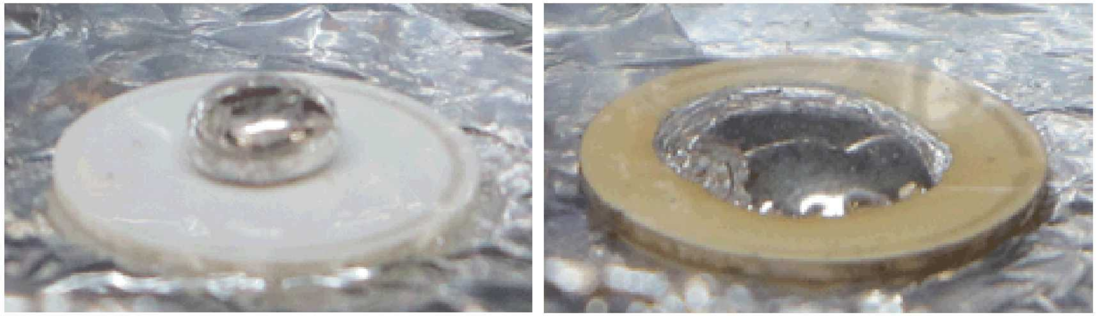
At reduced temperatures, sodium wetting on NaSICON is not adequate.

Heated at 100-200$^{o}$C for 30 minutes

# Separator Treatment Affects Cell Performance

A high temperature soak of Na metal on the NaSICON modifies interfacial wetting.

Heated at 100-200°C for 30 minutes

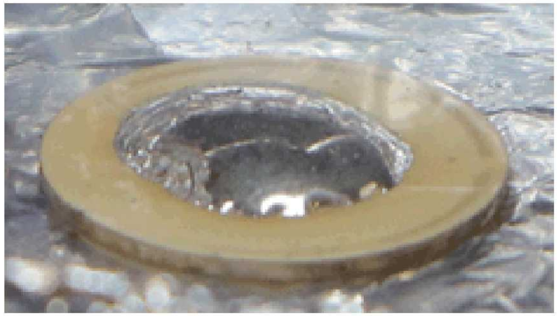


Heated above 380°C for 30 minutes

# Separator Treatment Affects Cell Performance

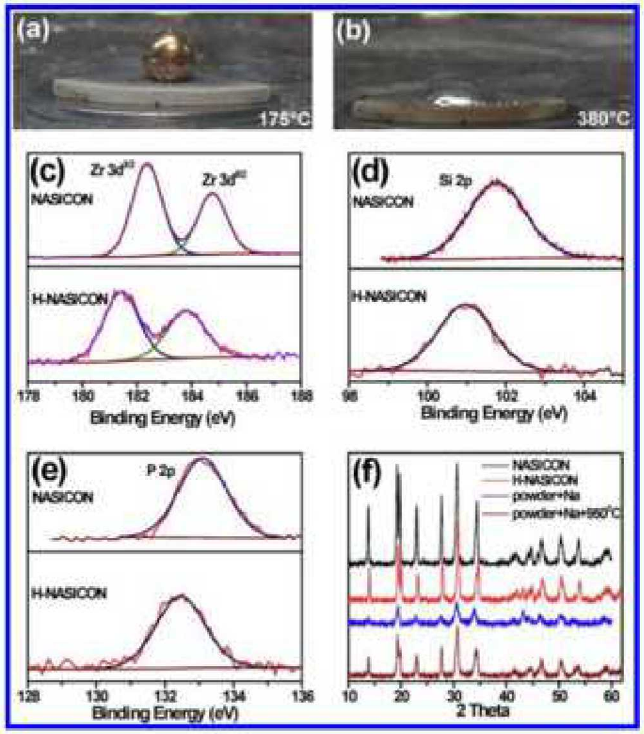
A high temperature soak of Na metal on the NaSICON modifies interfacial wetting.

Heated at 100-200$^{o}$C for 30 minutes



Heated above 380$^{o}$C for 30 minutes

Based on treatments applied to NaSICON in a solid-state system, the change in pellet surface is believed due to formation of an amorphous, reduced NaSICON surface.

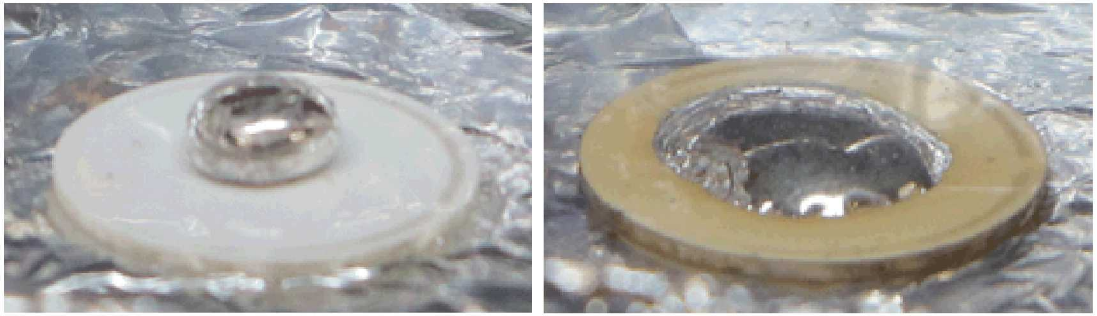



W. Zhou, *et al. ACS Cent. Sci.* (2017) **3**, 52-57.

# Separator Treatment Affects Cell Performance

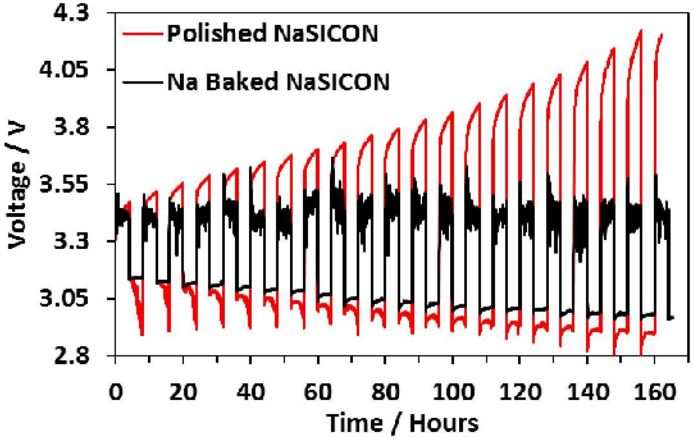
A high temperature soak of Na metal on the NaSICON modifies interfacial wetting.

Heated below 200°C for 30 minutes



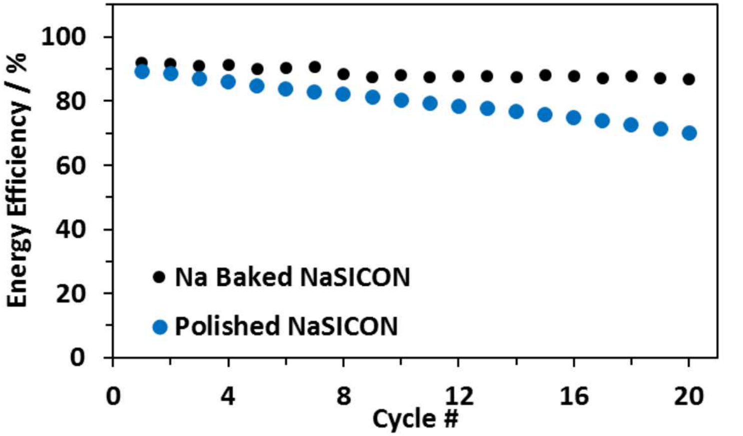
Heated above 380°C for 30 minutes

Na-treated NaSICON shows lower overpotentials on battery cycling.



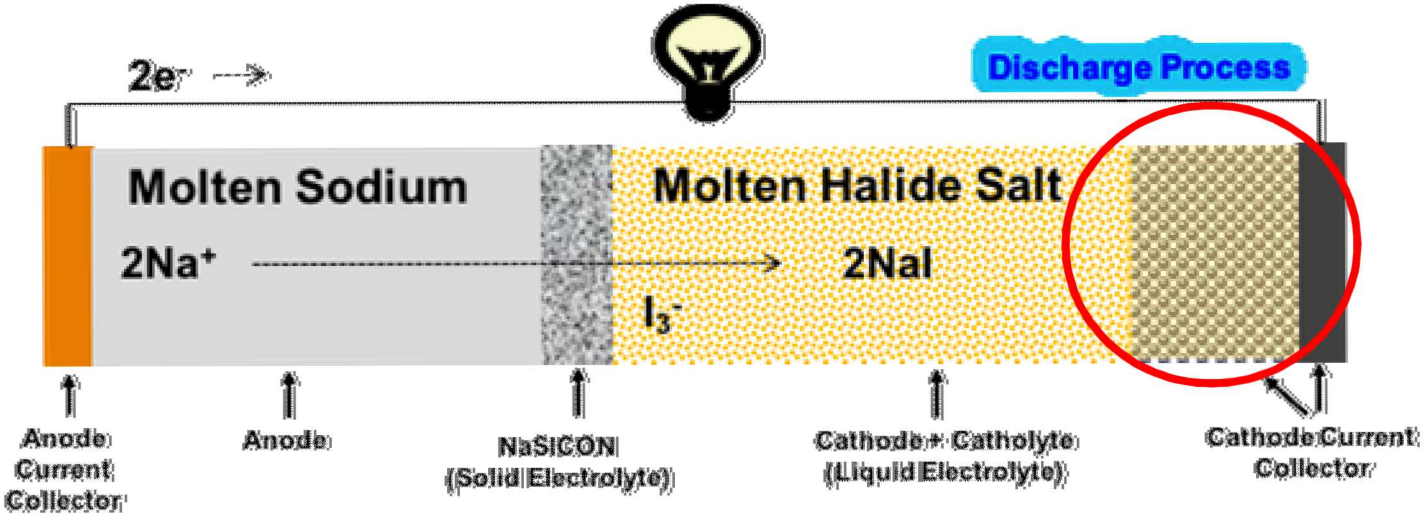

Battery cycling at 110°C!

25 mol% NaI-$AlBr_3$ with NaSICON separator.




- Polished NaSICON battery operated at ±0.897 mA C/4 1% DOD
- Na Baked NaSICON battery operated at ±0.894 mA C/4 1% DOD

# Is this “Good Enough?”

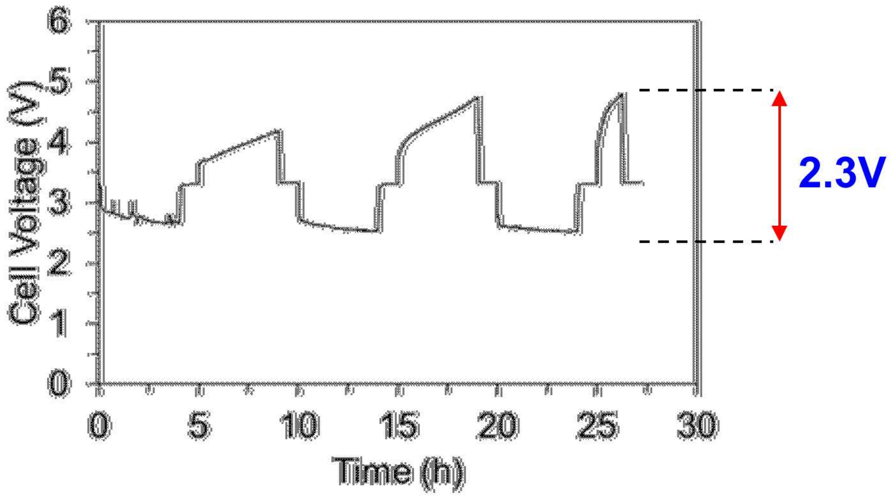


2e-
Discharge Process
Molten Sodium
Molten Halide Salt
2Na+
2NaI
I3-
Anode Current Collector
Anode
NaSICON (Solid Electrolyte)
Cathode + Catholyte (Liquid Electrolyte)
Cathode Current Collector

# Cathode Current Collector

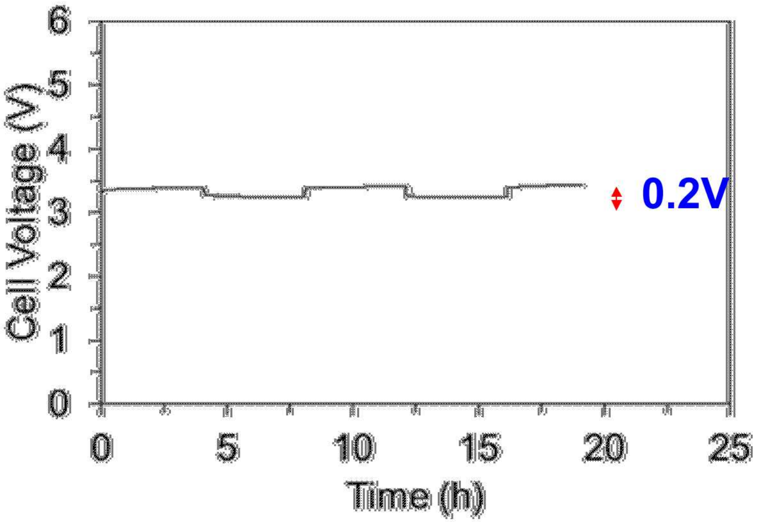
*Proper cathodic current collector surface area and wetting also drastically impacts battery performance.*

Without carbon felt current collector




- 0.5mA current, 4h charge & discharge
- 1 hour rest between charge and discharge

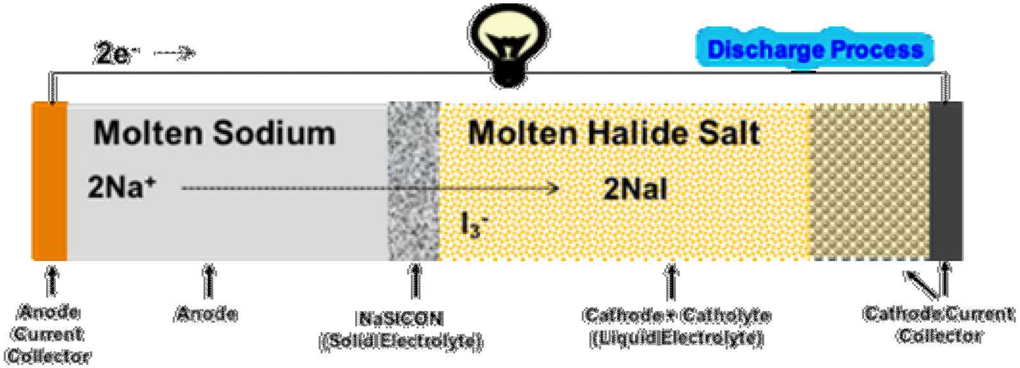
With carbon felt, treated with 0.1M HCl overnight

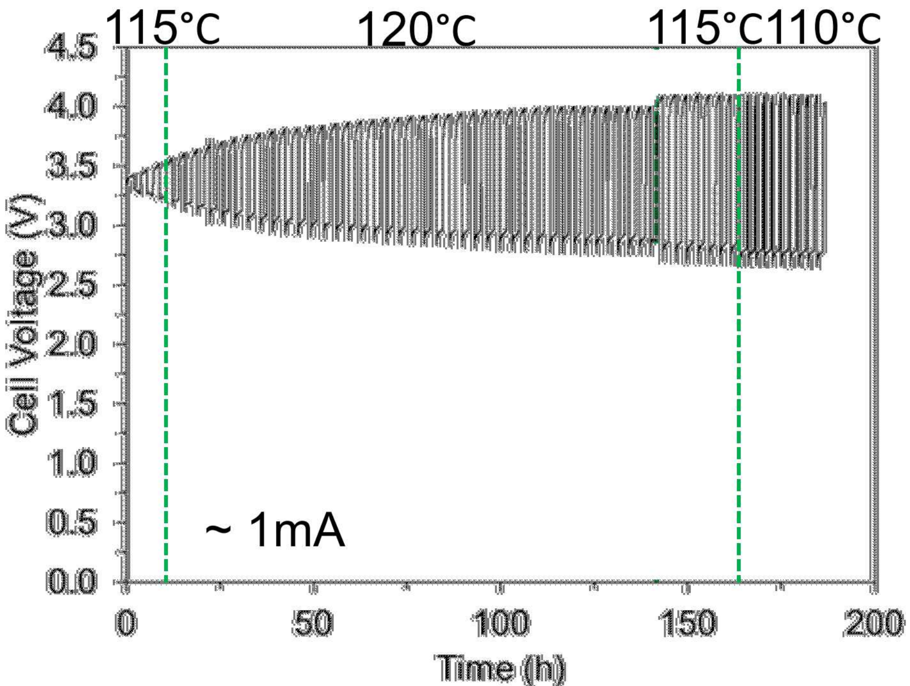



- 0.5mA current, 4h charge & discharge
- **Substantial improvement in cycling overpotential**

# Putting it all together

- Na-wetting NaSICON
- Effective low temperature seals
- Activated C-current collector
- Low Temperature catholyte salt

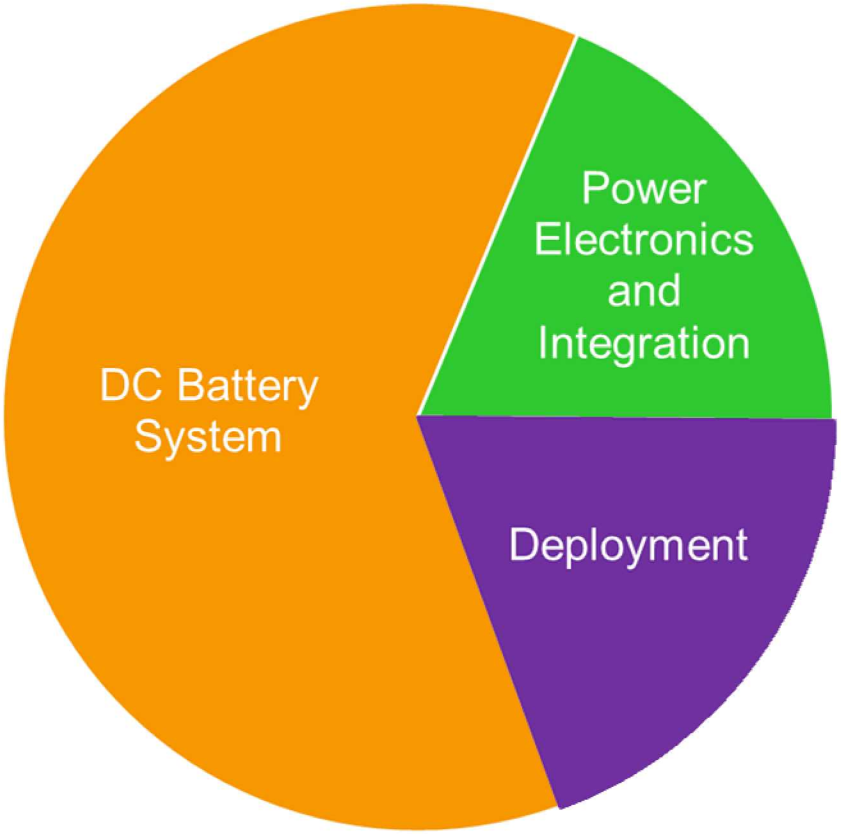



*The right materials allow for high cyclability at low temperatures!*

# Still Work to Do…

- Improve high performance, zero-crossover solid state separator technology
  - Low temperature conductance
  - Mechanical properties
  - Chemical compatibility
- Optimize cost-effective catholyte and cathode current collectors
- Identify lower cost battery packaging materials
- Demonstrate extended battery lifetime
- Improve understanding of emerging electrochemistries and interfaces
- Integrate batteries with power electronics
- Engineer effective deployment strategies



# Take Home Messages

- ✓ Grid scale energy storage will continue to be a critical national priority, important for both civilian and defense-based utilities.
- ✓ Specific performance requirements are important in determining what types of batteries will be best suited to an application – not all batteries are the same!
- ✓ There remains a need for *safe, low-cost,* large scale energy storage technologies with *reliable, long-term* performance.
  - ✓ Na-based batteries
  - ✓ Redox flow batteries
  - ✓ Rechargeable alkaline batteries

- ✓ Research across the DOE National Laboratory complex is aimed at meeting the challenge to create truly enabling next generation energy storage technologies.

# Acknowledgements


**SNL Team**

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Dr. Stephen Percival

Dr. Leo Small

Amanda Peretti

Dr. Josh Lamb

Dr. Eric Allcorn

Sara Dickens

Dr. Babu Chalamala

Dr. Tim Lambert

Dr. Jon

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Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

# Acknowledgements

Thank you!

Please contact me with questions: edspoer@sandia.gov

Work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity.

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# Backup Slides

# Title

# Alternative Summary

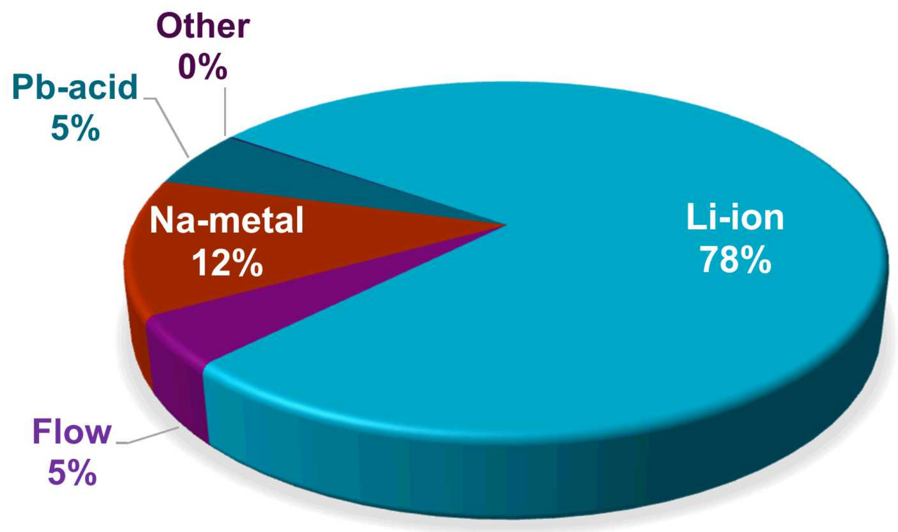
- Growing grid-scale energy storage demands are expected to exceed the scale and capability of Li-ion batteries.
- Sodium-based batteries offer the potential for safe, cost-effective storage with long cycle life.
- NaS (NGK) and Na-$NiCl_2$ (FIAMM) batteries are currently being manufactured and deployed globally for grid-scale applications.
  - ✓ On-Grid
  - ✓ Off-Grid
  - ✓ Microgrid
  - ✓ Grid regulation
  - ✓ Renewables integration
- Current research into safe, new sodium battery chemistries is expected to lead to reduced cost and increased utility.

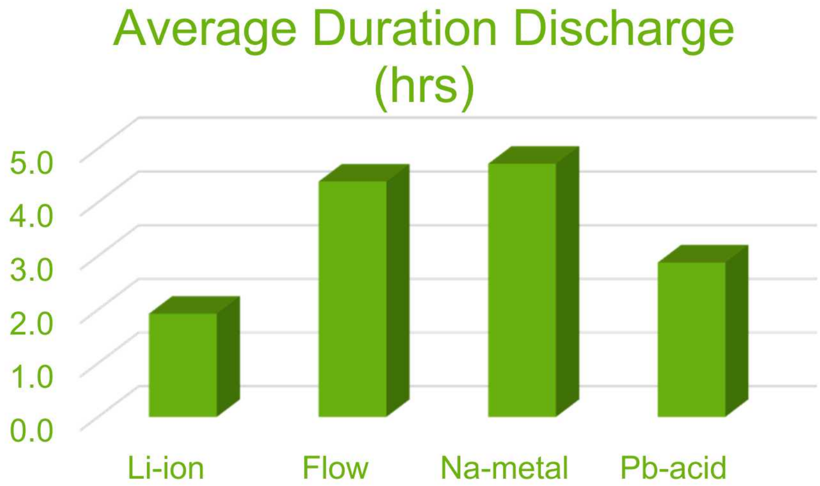
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

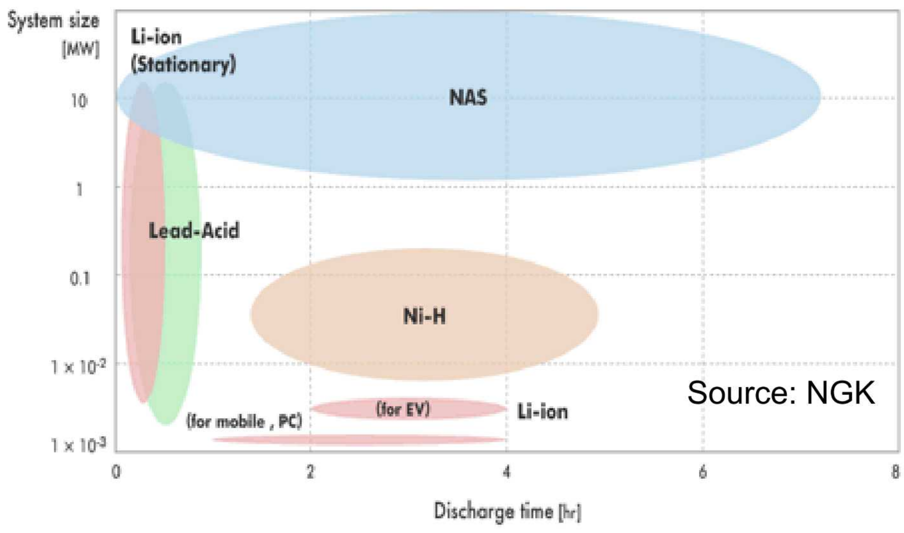
Sodium-based batteries *are* viable and promising candidates for grid-scale energy storage!

# Current Battery Energy Storage Deployments

*(Operational as of Nov. 2017)




Source: NGK

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

# Key Processing Variables

**Humidity**

- Desired >92% theoretical density (3.2 g/cm$^3$)
- During monsoon season (high humidity) pellet density dropped from 98% to ~70-80%
- Drying or calcining powder at 600°C immediately before pellet pressing returned density to >92% density.

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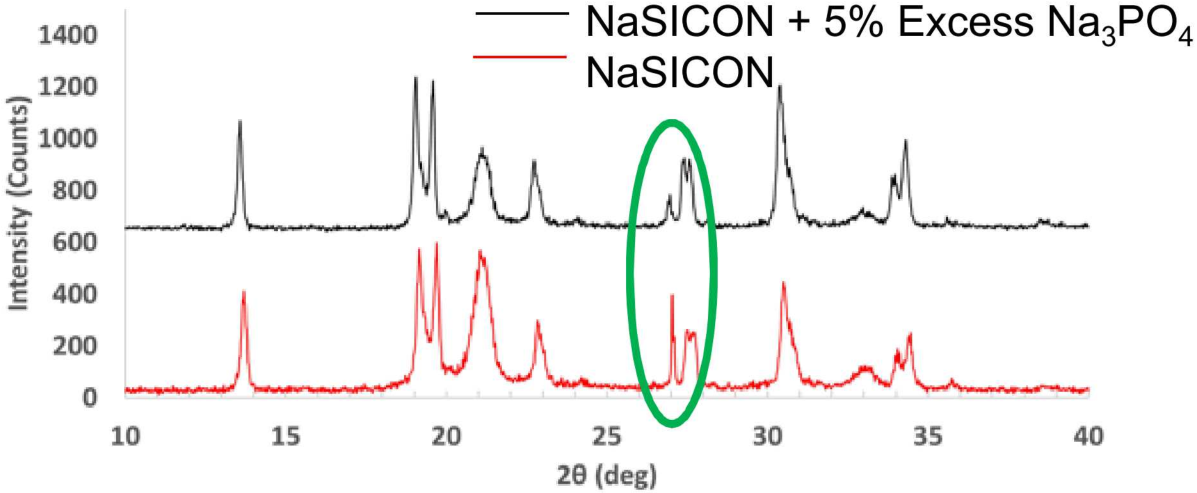
**Secondary Phase Formation**

- Secondary phases, such as $ZrO_2$ and $ZrSiO_4$, can degrade conductivity.
- "Na" and "$PO_4$" volatility during sintering can lead to secondary phase formation.
- 5% Excess $Na_3PO_4$ showed diminished secondary phases




Conductivity increase by ~30% with excess $Na_3PO_4$!

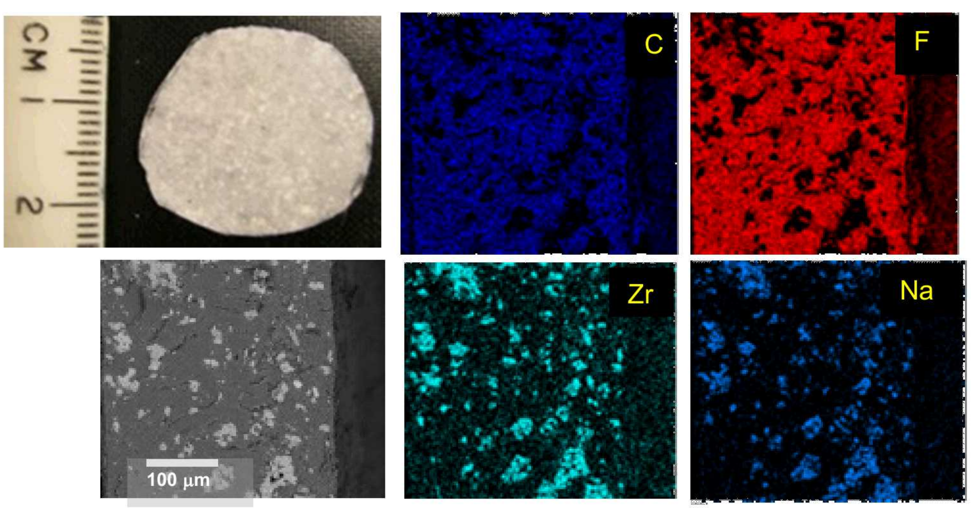
# Composite Separator Innovation

Composite separators could enable thinner (higher conductance), *mechanically robust* separators.

## Initial Approach

- Powdered NaSICON and powdered polymer (polyvinylidene difluoride: PVDF) were warm-pressed together
- Tough composite with reasonable distribution of NaSICON
- Good interfaces between NaSICON and polymer

➢ Impractically low ionic conductivity ($4x10^{-10}$). Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.



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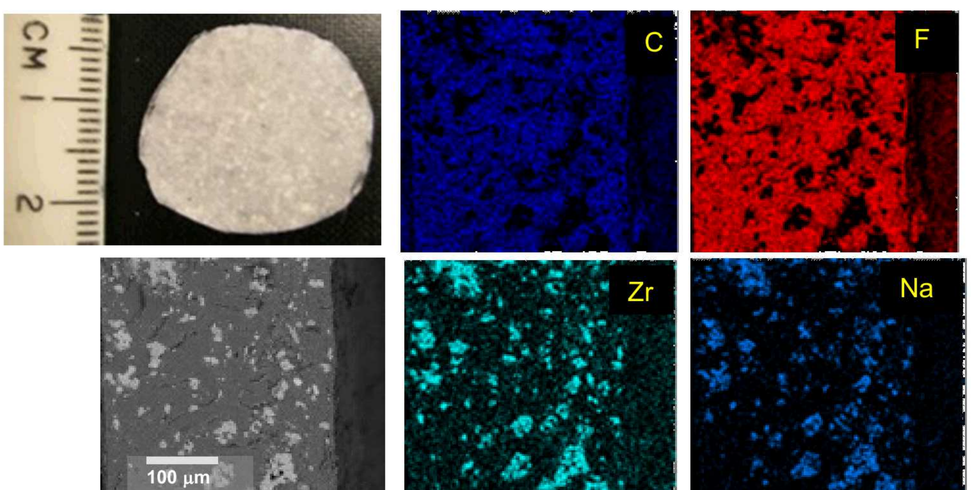
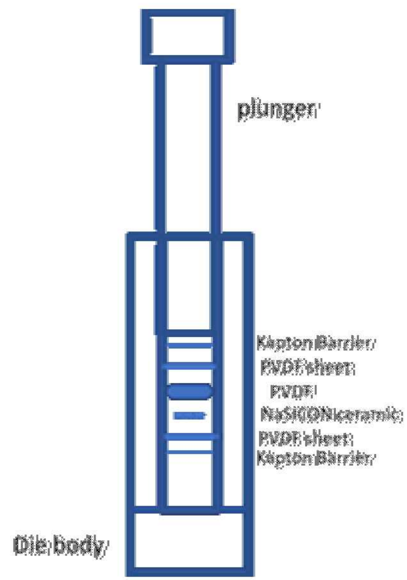
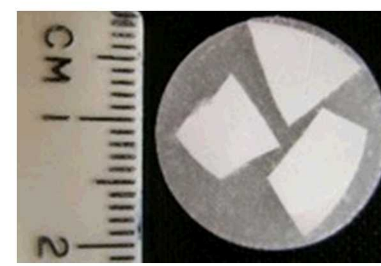



## An alternative approach

- NaSICON chips (1mm thick) enveloped in PVDF powder and warm-pressed
- NaSICON chips provide continuous conductive path through separator



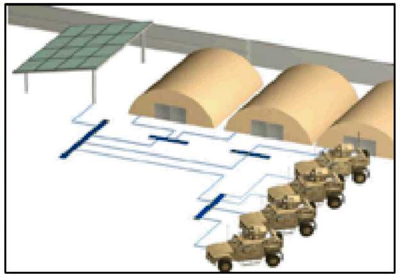

Conductivity is determined by NaSICON ceramic.

$\sigma_{RT}$ ~0.5 mS/cm for composite!

# A Need for Grid-Scale Energy Storage Research


Renewable/Remote Energy

Grid Reliability



National Defense

Emergency Aid

***U.S.***

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

***% of U.S. Generation Capacity***

- *0.07% BES*
- *2.2% BES + PHS*

***Globally***

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

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

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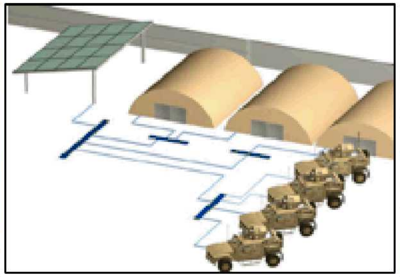

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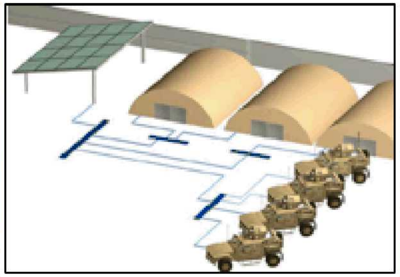
***Source:*** *DOE Global Energy Storage Database*
*http://www.energystorageexchange.org/ Nov. 2017*

# A Need for Grid-Scale Energy Storage Research


Renewable/Remote Energy

Grid Reliability



National Defense

Emergency Aid

***U.S.***

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

***% of U.S. Generation Capacity***

- *0.07% BES*
- *2.2% BES + PHS*

***Globally***

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

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