

# Materials Chemistry to Advance Na-Batteries



## Erik D. Spoerke, Ph.D.

Sandia National Laboratories, Albuquerque, NM

DOE Na-Ion Battery Workshop  
Pacific Northwest National Laboratory, Richland, WA  
August 27th, 2019



**Martha Gross  
Stephen Percival,  
Leo Small,  
Amanda Peretti,  
Josh Lamb, and  
Babu Chalamala**

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



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.

SAND No.:

# “Really Cool Molten Sodium Batteries”



## Erik D. Spoerke, Ph.D.

Sandia National Laboratories, Albuquerque, NM

DOE Na-Ion Battery Workshop  
Pacific Northwest National Laboratory, Richland, WA  
August 27th, 2019



**Martha Gross  
Stephen Percival,  
Leo Small,  
Amanda Peretti,  
Josh Lamb, and  
Babu Chalamala**

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



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.

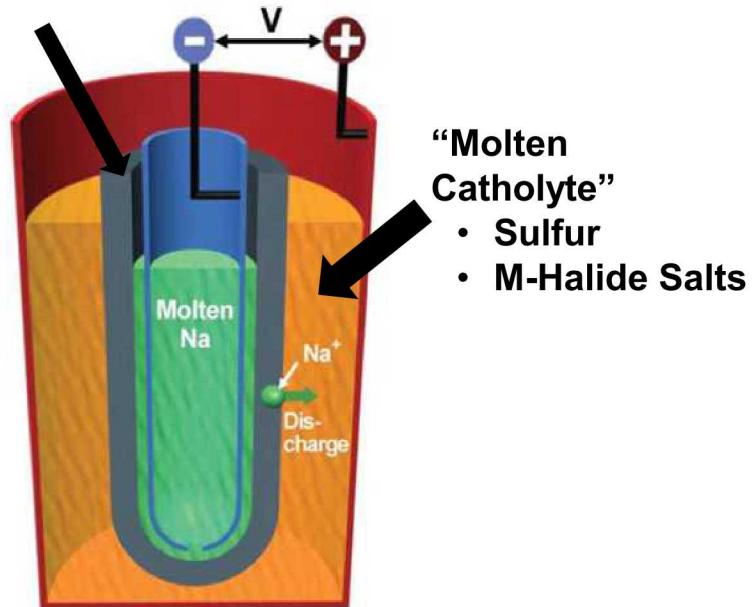
SAND No.:

# 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<sub>2</sub>) systems.
- Utilize zero-crossover solid state separators.
- Favorable battery voltages (>2V).

Ion Conducting Ceramic Separator



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

- Improves separator ionic conductivity
- Maintains molten phase chemistry

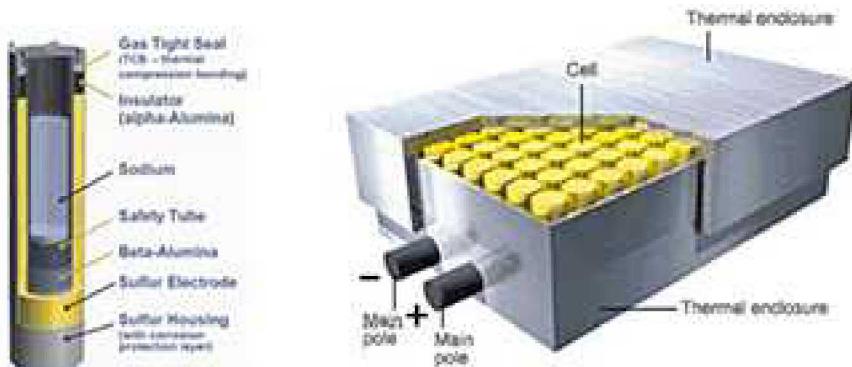
### Na-NiCl<sub>2</sub> ( $E_{cell} \sim 2.6V$ )



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



# 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<sub>2</sub> (“ZEBRA”) Batteries (FIAMM)

## FIAMM SoNick (Na-NiCl<sub>2</sub>) Batteries

- ~300°C operation, no cooling required
- 2-4 hour energy applications
- Operational from -20°C to +60°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-NiCl<sub>2</sub> 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)



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



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



“Behind the meter”

Grid Regulation

Renewable Integration

# Challenges with Existing Na Batteries

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



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

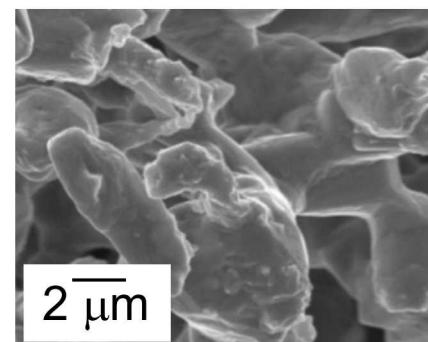
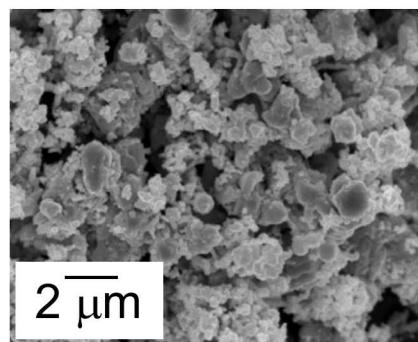


## Na-NiCl<sub>2</sub> ( $E_{cell} \sim 2.6V$ )



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

Particle Coarsening



# Promise in Molten Sodium Batteries

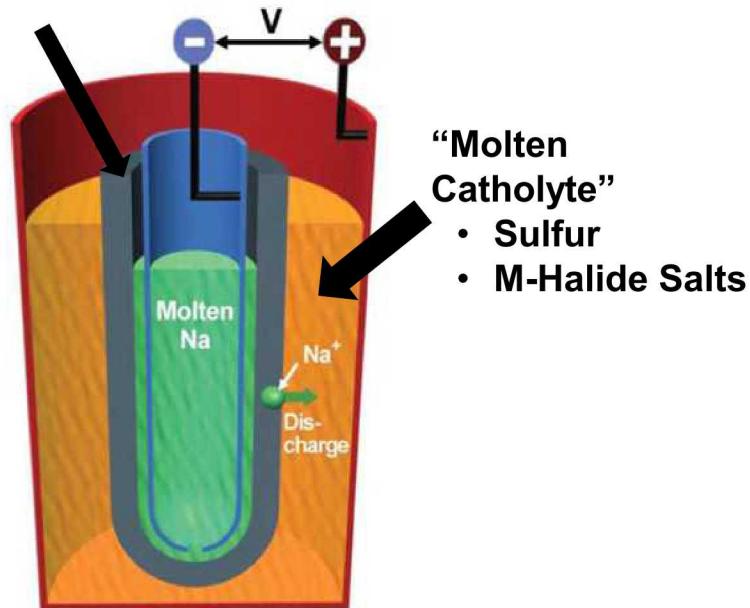
## Sodium-based batteries

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

## 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**

**Ion Conducting Ceramic Separator**



### Na-NiCl<sub>2</sub> ( $E_{cell} \sim 2.6V$ )

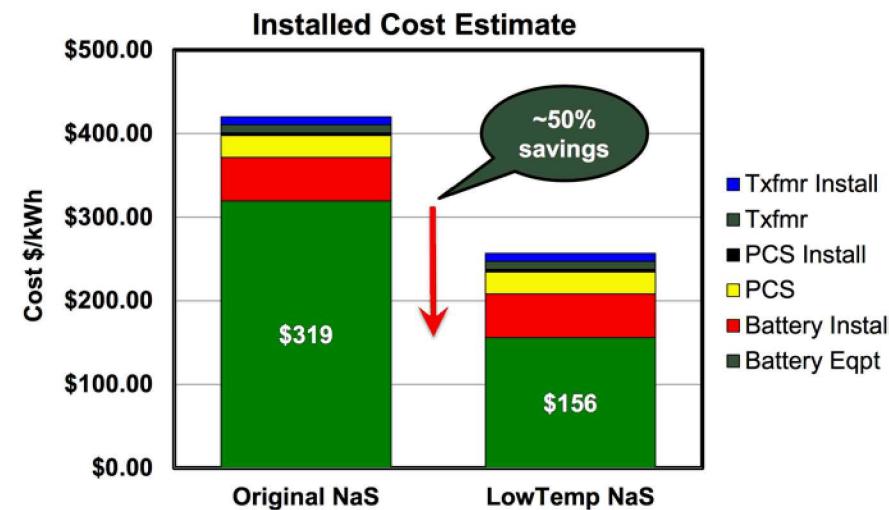


### Na-S ( $E_{cell} \sim 2V$ )

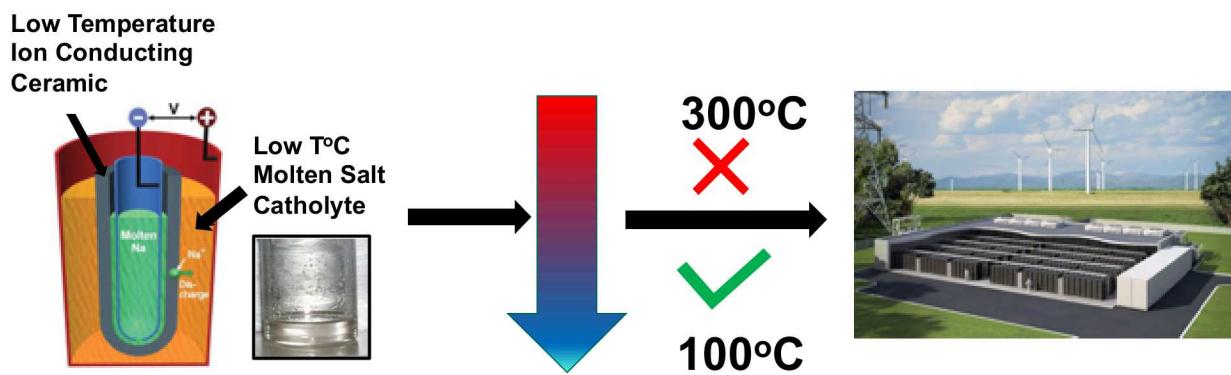


# Low Temperature Operation of a Molten Na Battery is Tremendously Enabling

- 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

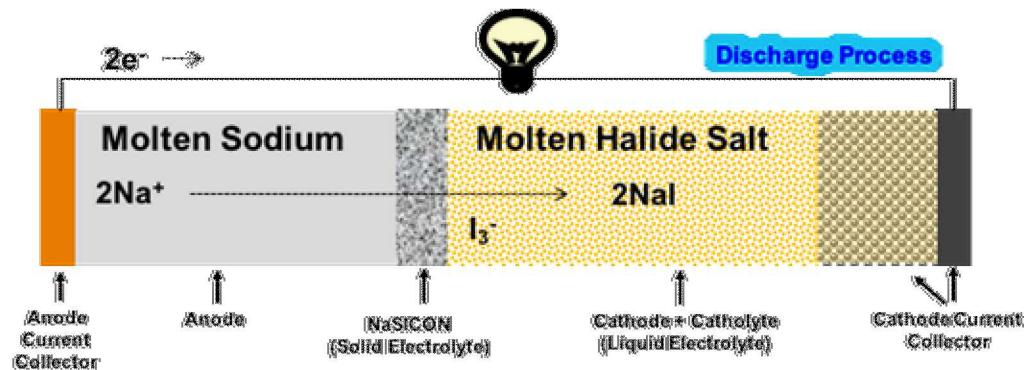


Gao Liu, et al. "A Storage Revolution." 12-Feb-2015 (online):  
<https://ei.haas.berkeley.edu/education/c2m/docs/Sulfur%20and%20Sodium%20Metal%20Battery.pdf>

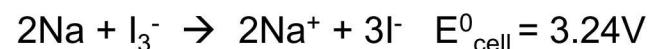
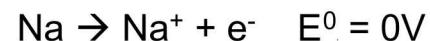


# Low Temperature Molten Na-Halide Batteries

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



## Na-NaI battery:

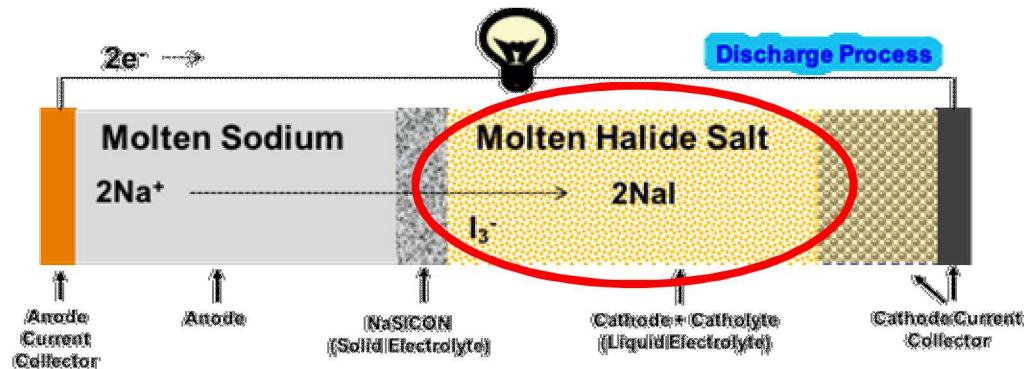


*Na-NaI batteries show promise as safe, low-cost, highly cyclable battery with functional energy density.*

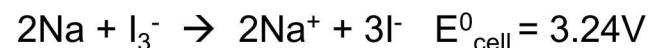
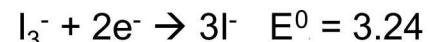
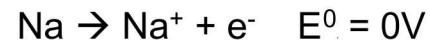
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

# Low Temperature Molten Na-Halide Batteries

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



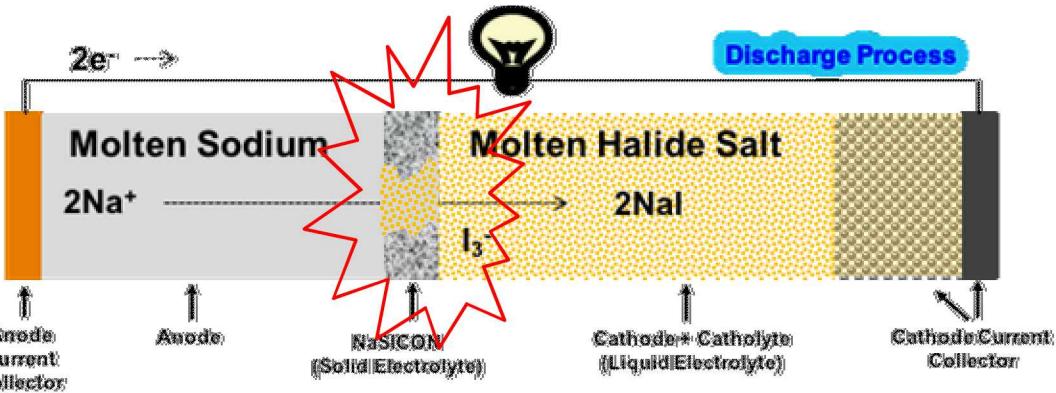
## Na-NaI battery:



Consider  $\text{NaI-AlX}_3$  catholyte...

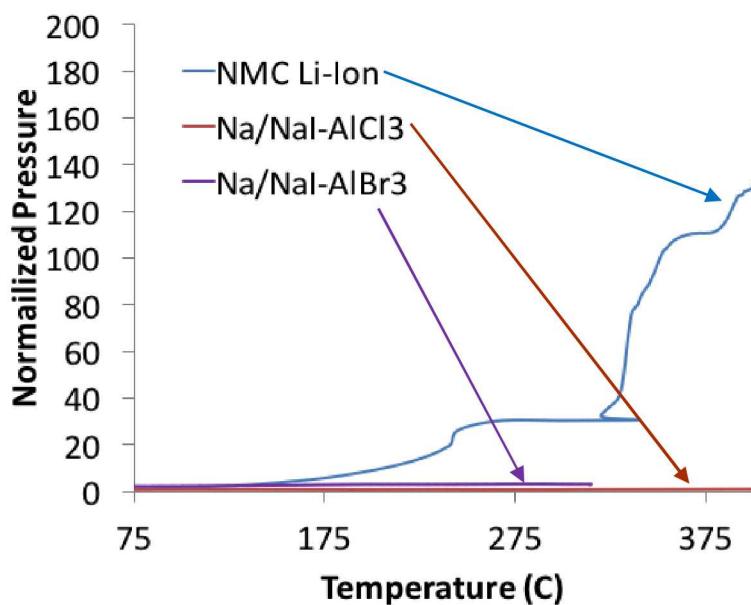
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

# Na-NaI Exhibits Inherent Improved Safety



Simulating separator failure, metallic Na and NaI/AlX<sub>3</sub> were combined and heated.

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

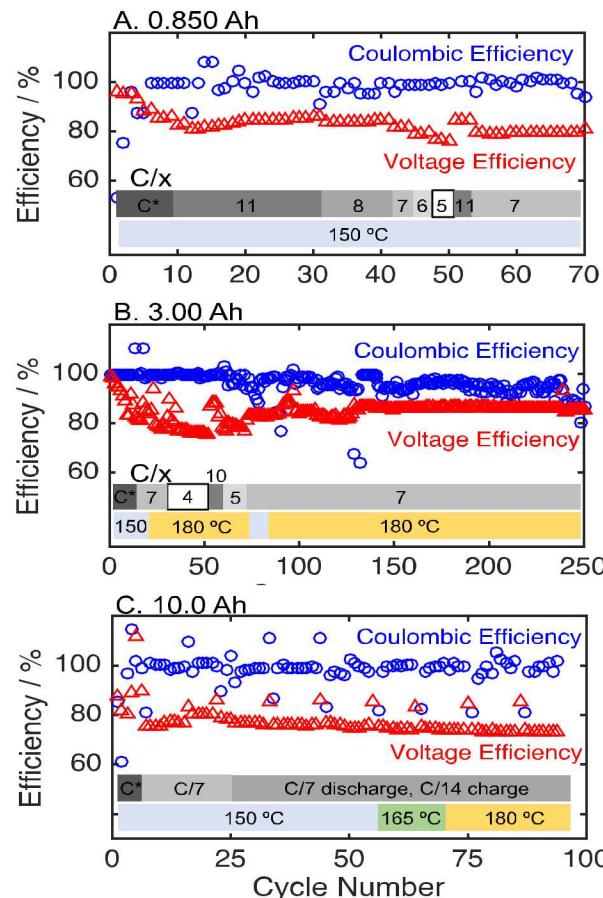
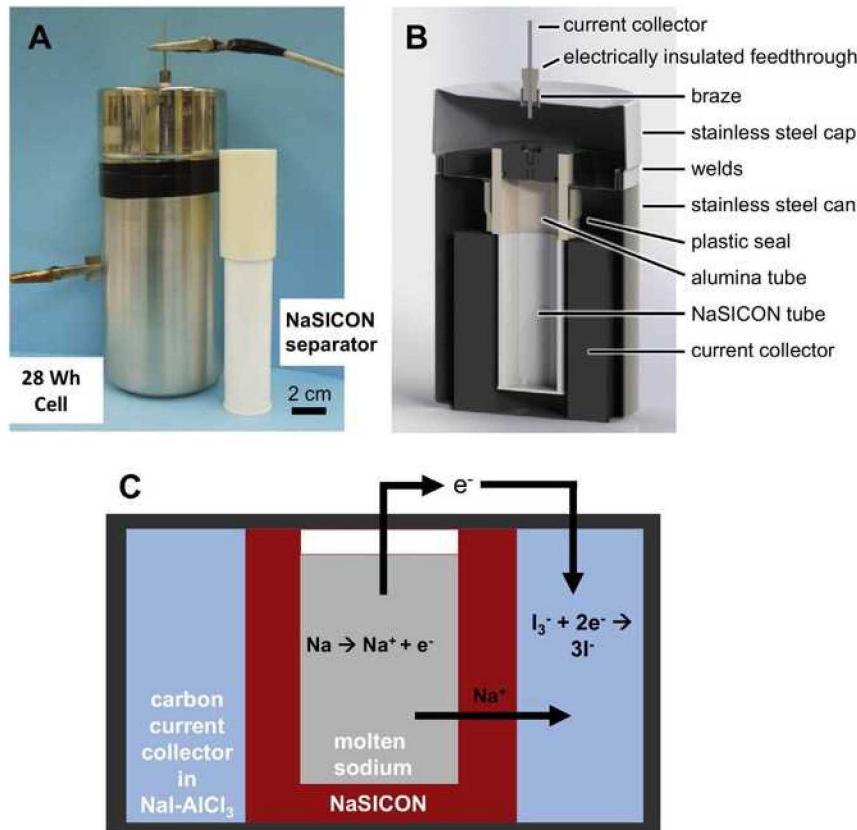


Accelerating rate calorimetry reveals that Na-NaI/AlX<sub>3</sub> mixtures exhibit:

- 1) *no significant exothermic behavior*
- 2) *no significant gas generation or pressurization*

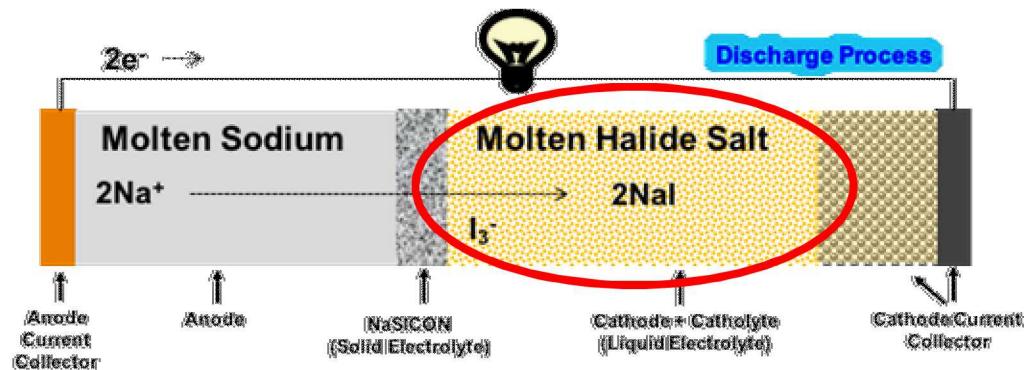
# An Intermediate Temperature Na-NaI Battery

Na-NaI battery was demonstrated across several scales at 150-180°C.

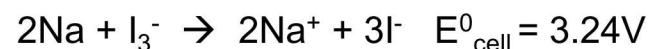
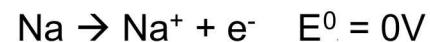


# Low Temperature Molten Na-NaI Batteries

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



## Na-NaI battery:

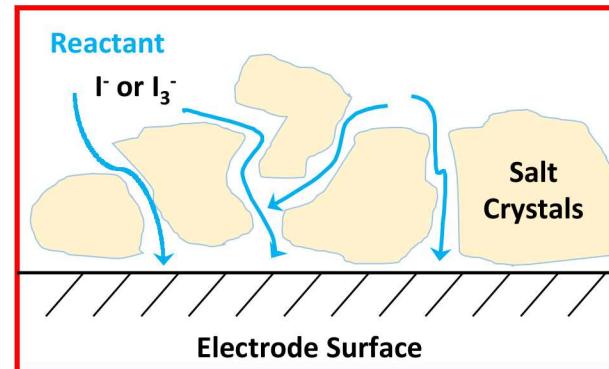


*How important is the molten character of the catholyte?*

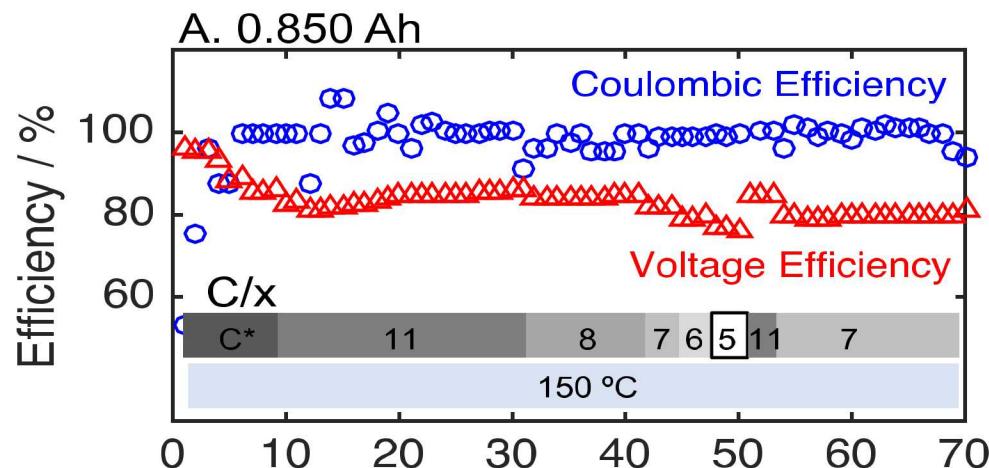
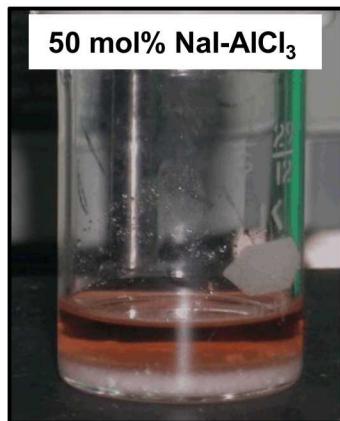
# Catholytes are Key to Low Temperature Operation

A fully molten catholyte avoids

- a) Particle-hindered electrochemical processes.
- b) Particle-related loss of capacity.



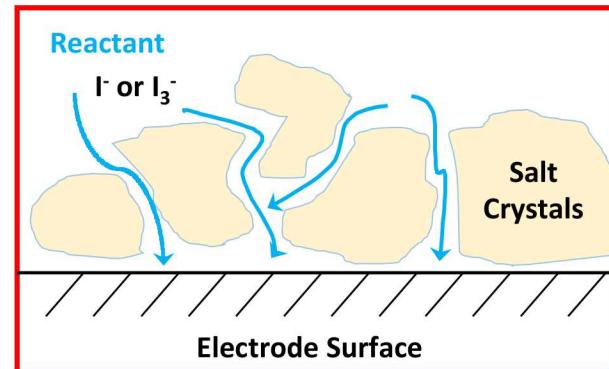
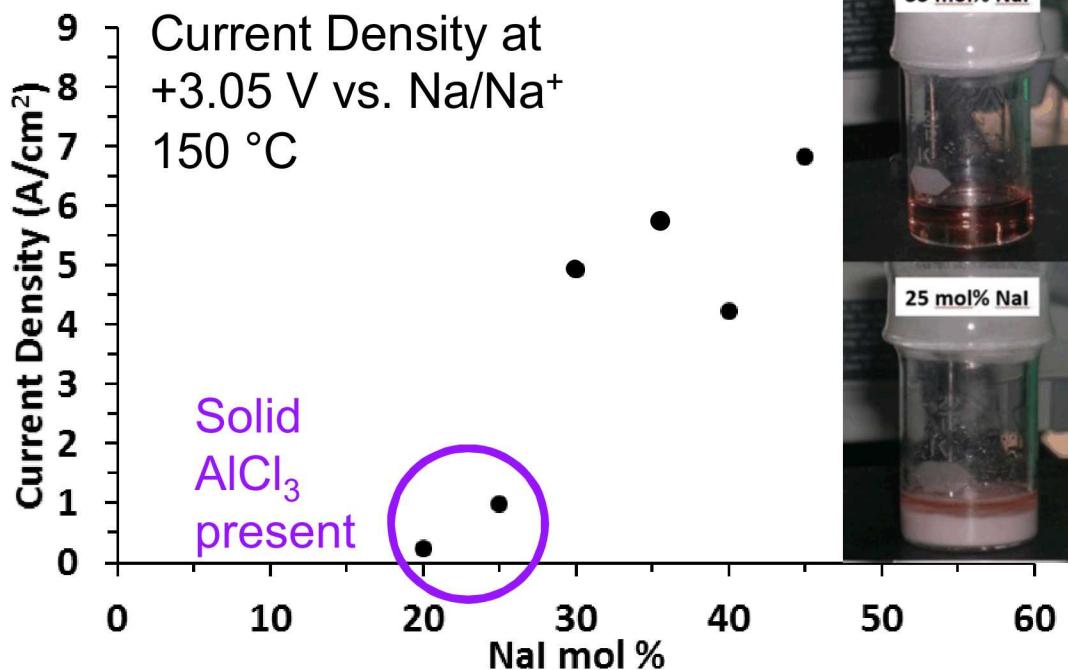
$NaI-AlCl_3$  at 150°C



# Catholytes are Key to Low Temperature Operation

A fully molten catholyte avoids

- a) Particle-hindered electrochemical processes
- b) Particle-related loss of capacity

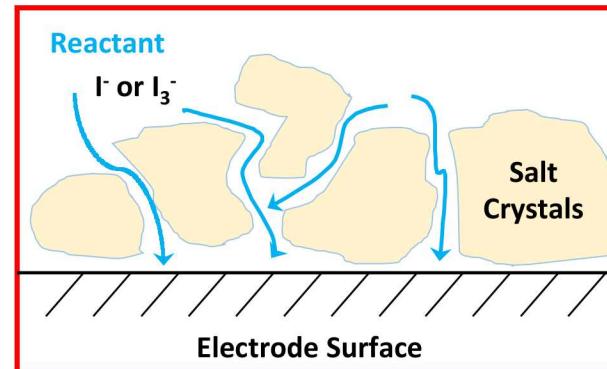


Current Density is significantly lower when solid secondary phases are present.

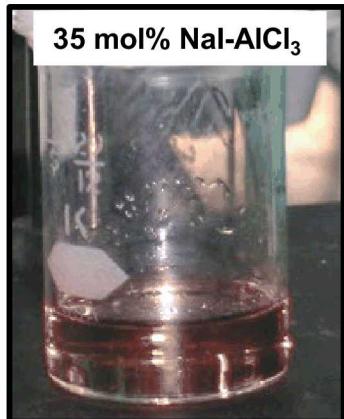
# Catholyte Composition is Especially Important at Lower Temperatures

A fully molten catholyte avoids

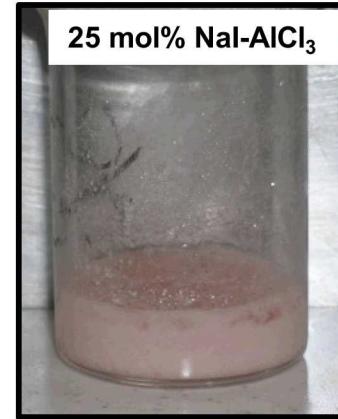
- a) Particle-hindered electrochemical processes
- b) Particle-related loss of capacity



NaI-AlCl<sub>3</sub> at 150°C



NaI-AlCl<sub>3</sub> and NaI-AlBr<sub>3</sub> salts at 90°C



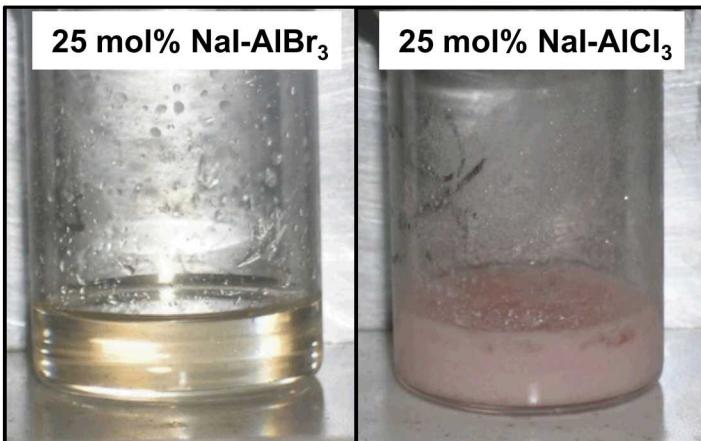
*Molten NaI-AlBr<sub>3</sub> composition range spans 5-25% NaI and cell voltage is near or above 3V.*

# Nal-AlBr<sub>3</sub>: An Electrochemically Promising Low Temperature Molten Catholyte

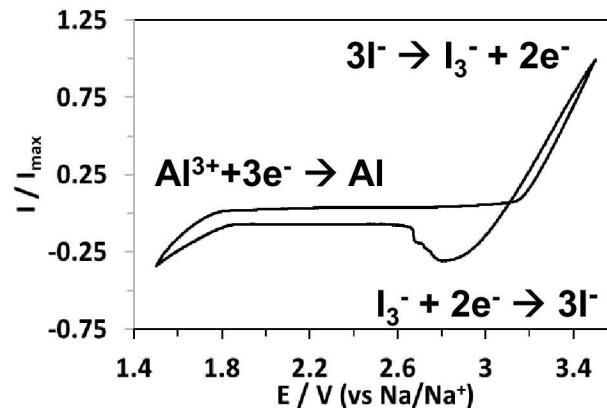
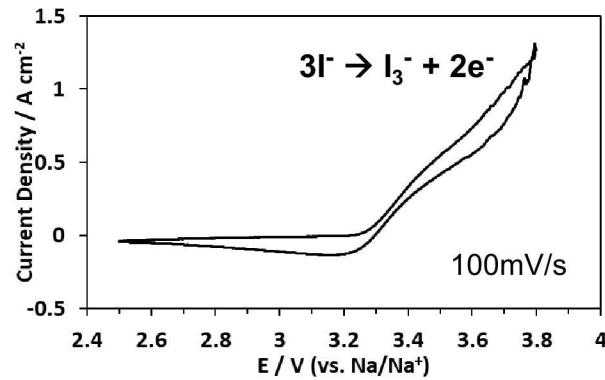
*The Nal-AlBr<sub>3</sub> catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures.*

- 25:75 Nal-AlBr<sub>3</sub> salt completely molten at 90 °C
- Larger fully molten capacity range (~5-25 mol% Nal)

Samples at 90°C



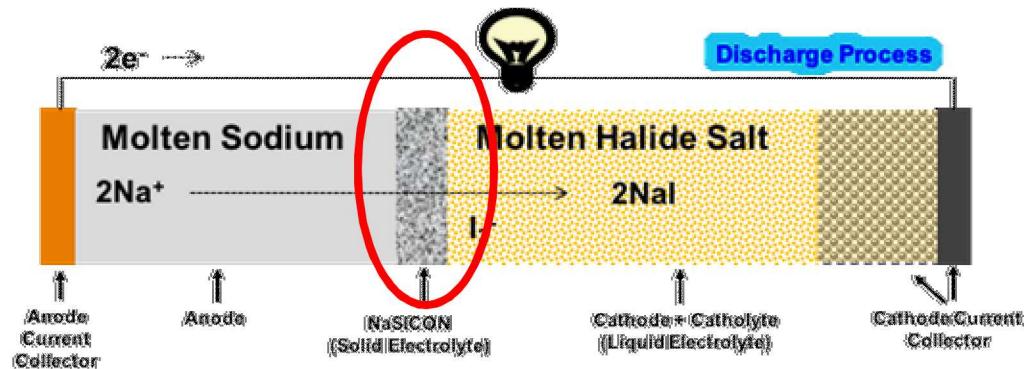
- Carbon Fiber microelectrode shows excellent electrochemical behavior of 25 mol% Nal-AlBr<sub>3</sub> at 90°C



- Nal-AlBr<sub>3</sub> system shows good iodide electrochemical reversibility.
  - AlBr<sub>3</sub> (20mol% Nal) system at 120 °C and 1V/s

# Low Temperature Solid State Separator

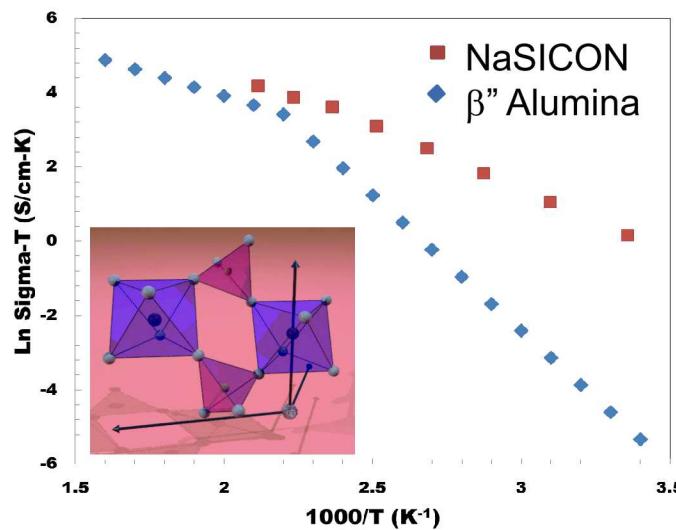
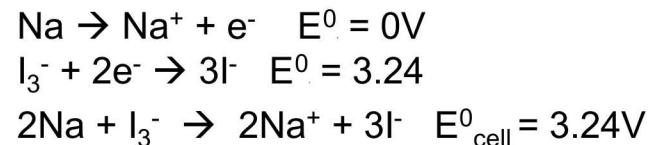
Our Vision: A molten sodium-based battery that comprises a robust, highly  $\text{Na}^+$ -conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.



## Key Qualities of NaSICON Ceramic Ion Conductors

- $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$
- High Na-ion conductivity ( $>10^{-3}$  S/cm at 25°C)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover

### Na-NaI battery:

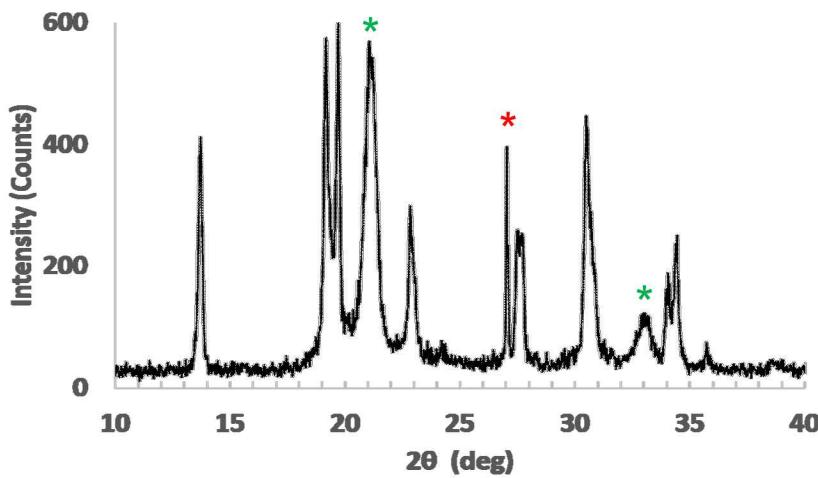


# Conventional Synthesis

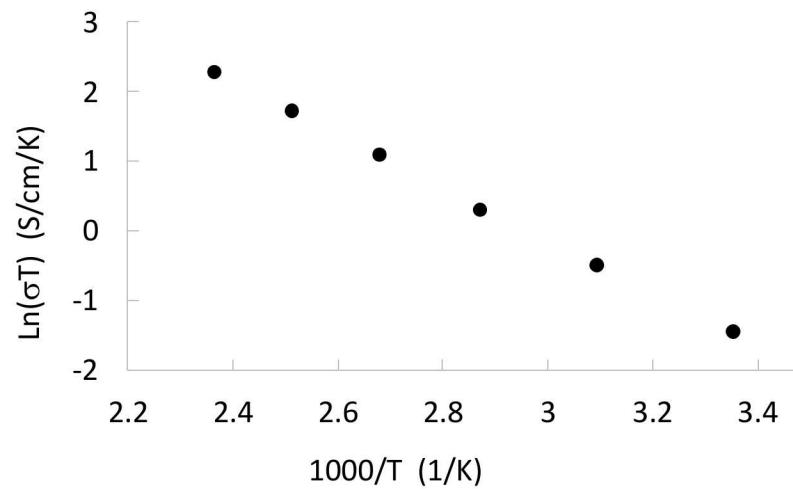
## Solid State Ceramic Synthesis (“Shake ‘n Bake”)



- Milled powders pressed and fired at 1200°C in air
- Pellet densities >95%
- X-ray diffraction confirms NaSICON synthesis with  $\text{ZrO}_2$  and  $\text{ZrSiO}_4$  secondary phases
- Conductivities reasonable, but slightly less than commercial NaSICON



\* Sample holder artifact



# Key Processing Variables

## Humidity

- Desired >92% theoretical density (3.2 g/cm<sup>3</sup>)
- 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.

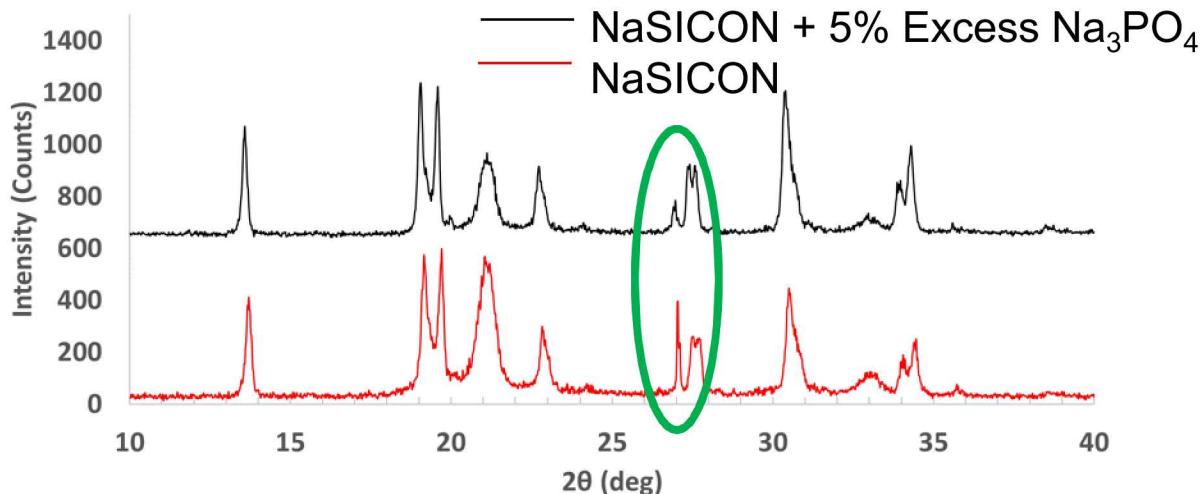
# Key Processing Variables

## Humidity

- Desired >95% theoretical density ( $3.2 \text{ g/cm}^3$ )
- During monsoon season (high humidity) pellet density dropped from 98% to ~70-80%
- Drying or calcining powder at  $600^\circ\text{C}$  immediately before pellet pressing returned density to >95% density.

## Secondary Phase Formation

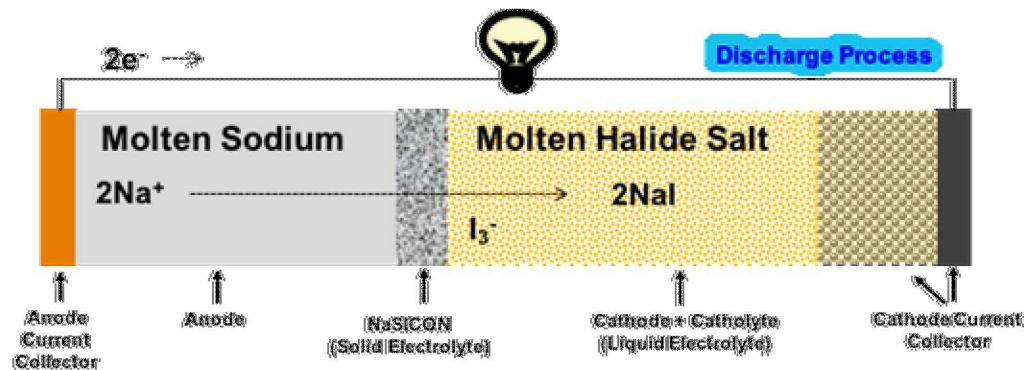
- Secondary phases, such as  $\text{ZrO}_2$  and  $\text{ZrSiO}_4$ , can degrade conductivity.
- “Na” and “ $\text{PO}_4$ ” volatility during sintering can lead to secondary phase formation.
- 5% Excess  $\text{Na}_3\text{PO}_4$  showed diminished secondary phases



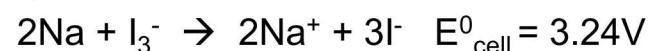
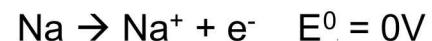
Conductivity  
increase by ~30%  
with excess  
 $\text{Na}_3\text{PO}_4$ !

# Low Temperature Molten Na-NaI Batteries

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



## Na-NaI battery:



# Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

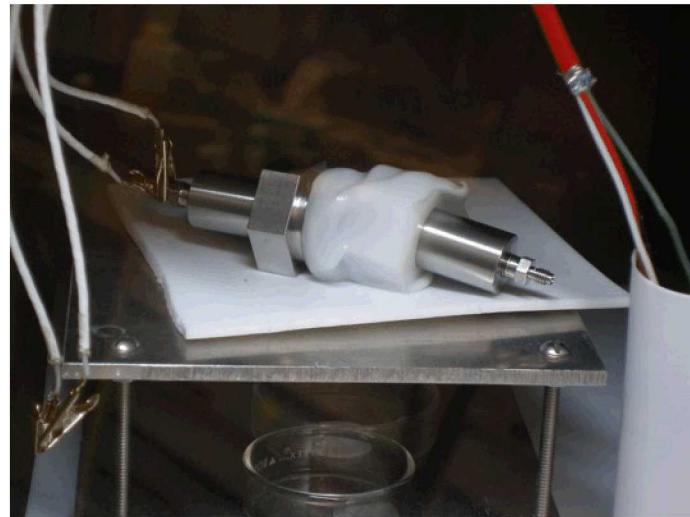
Compatibility must be considered for:

- 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

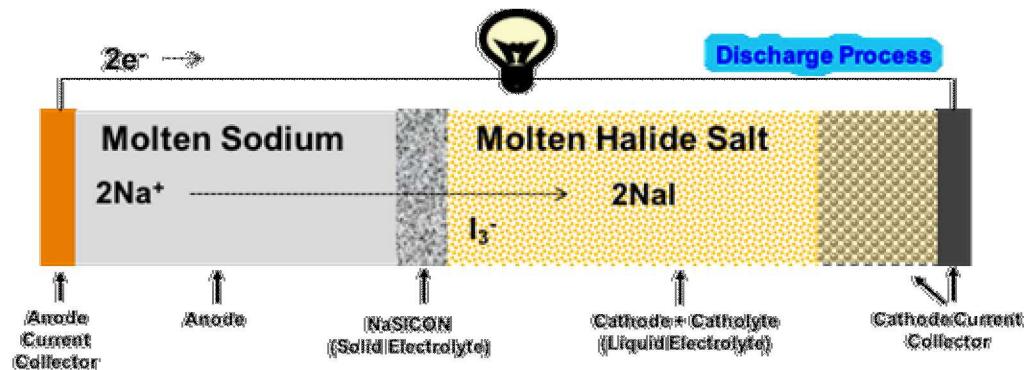


Chemical compatibility

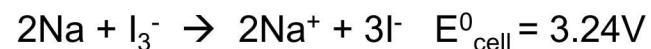
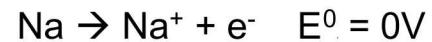


# Low Temperature Molten Na-NaI Batteries

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

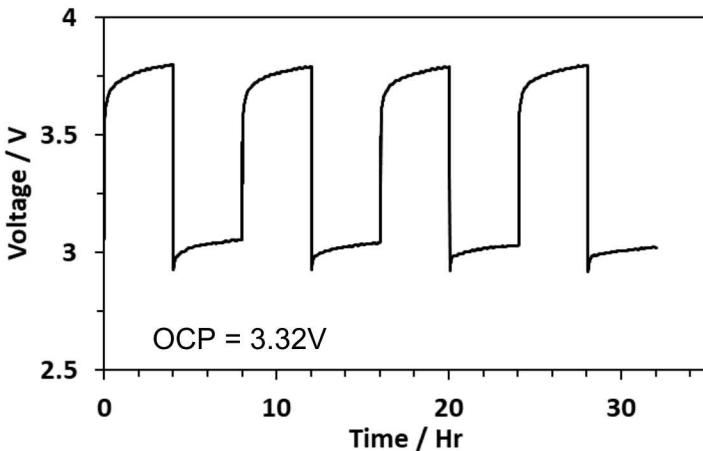
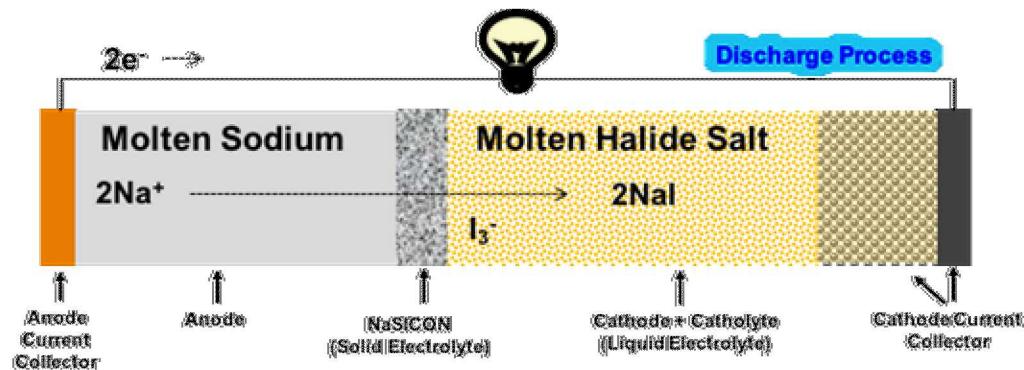


## Na-NaI battery:



# Low Temperature Molten Na-NaI Batteries

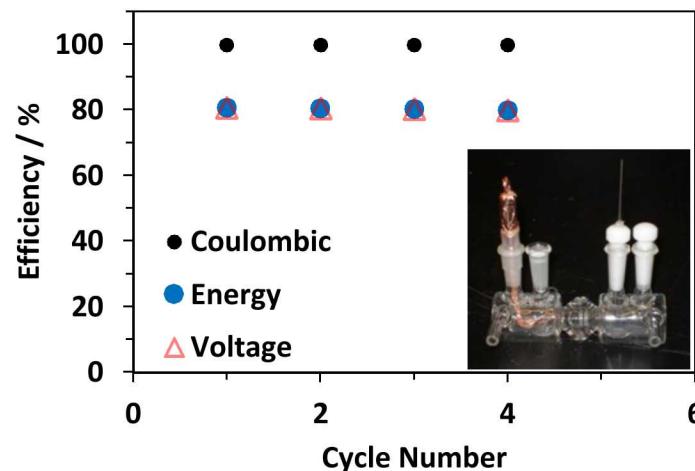
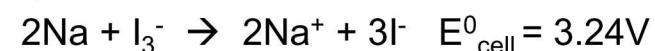
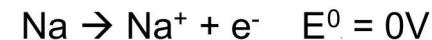
Our Vision: A molten sodium-based battery that comprises a robust, highly  $\text{Na}^+$ -conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.



Battery cycling  
at 110°C!

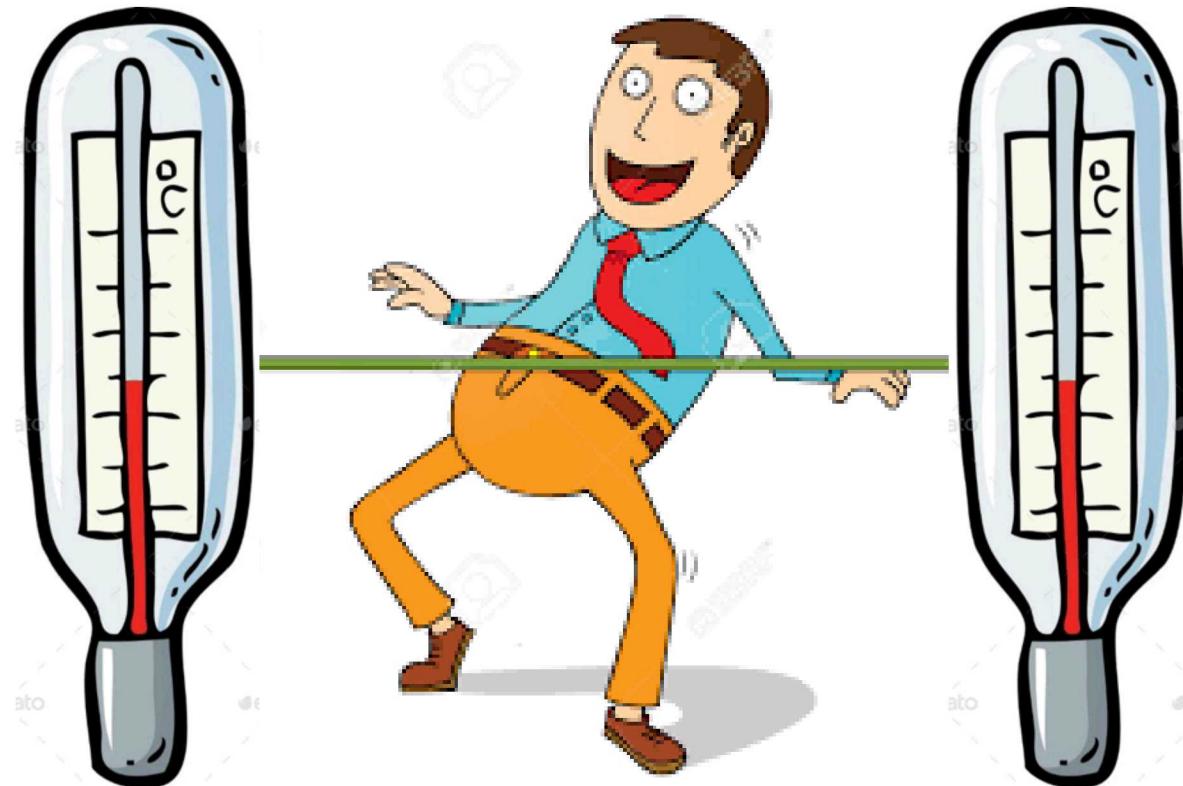
25 mol%  $\text{NaI-AlBr}_3$   
with NaSICON  
separator.

## Na-NaI battery:



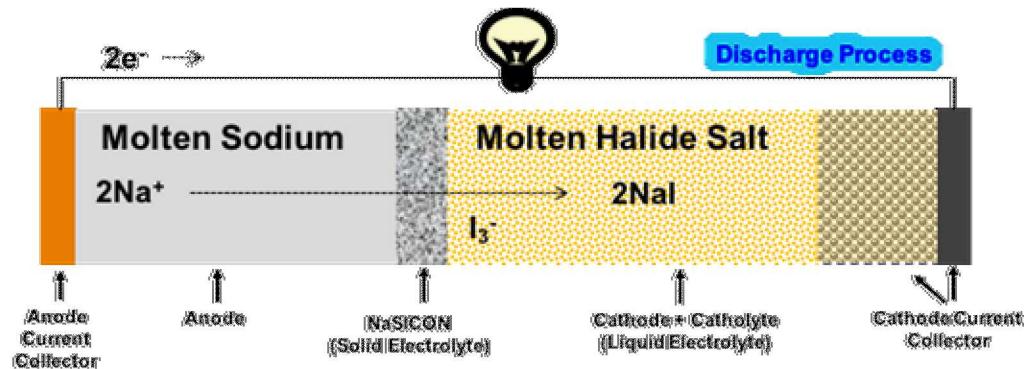


# How low can we go?

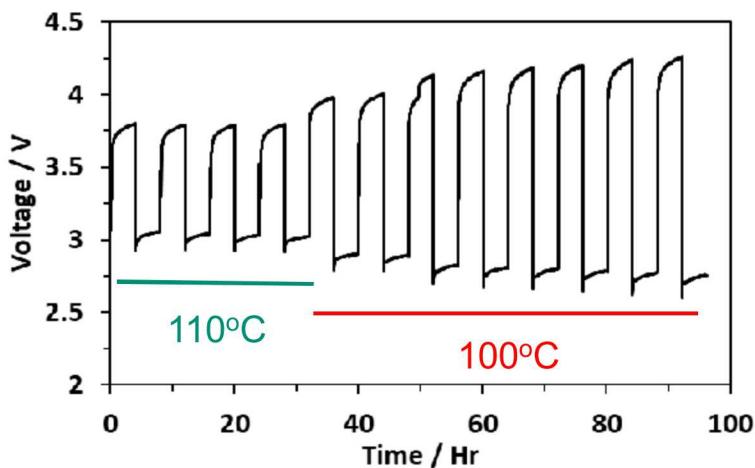
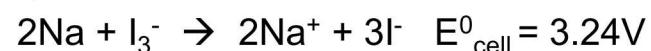
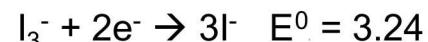
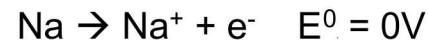


# Lowest Temperature Molten Na-NaI Batteries

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

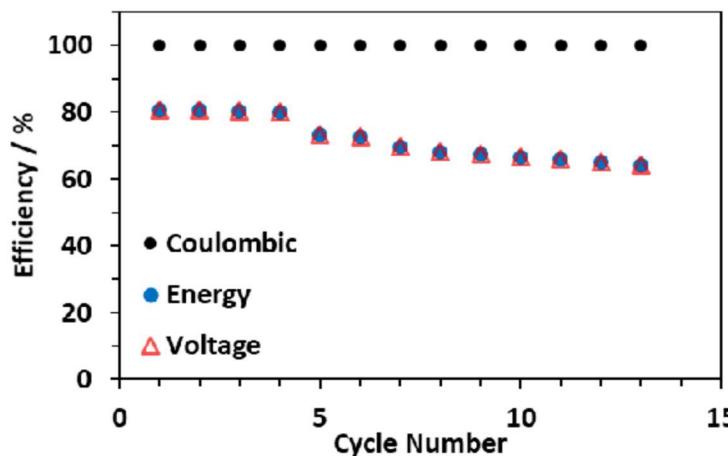


## Na-NaI battery:



Battery cycling  
at 100°C!

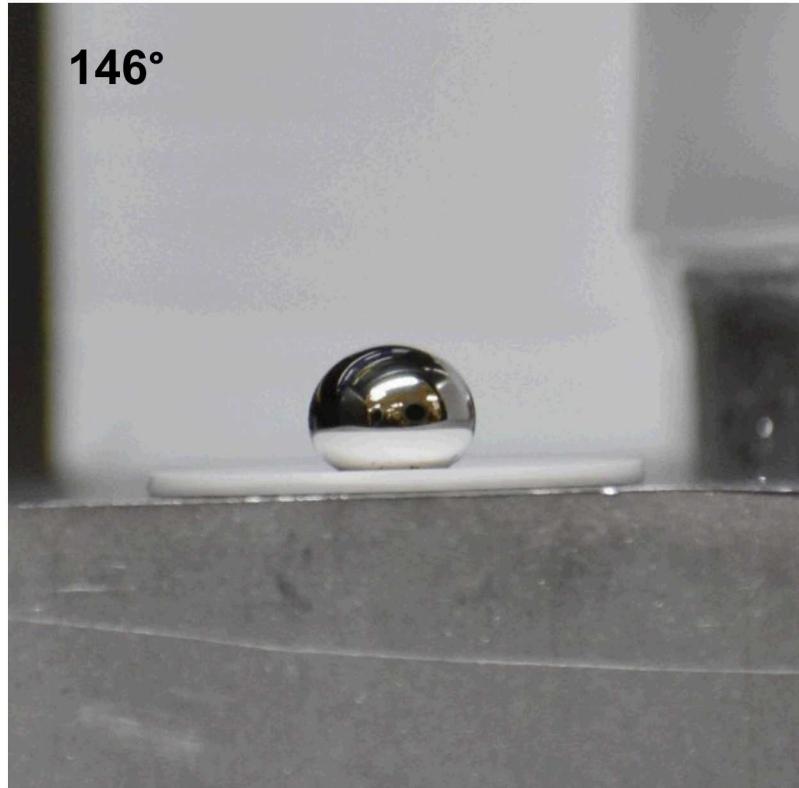
25 mol%  $\text{NaI-AlBr}_3$   
with NaSICON  
separator.



# NaSICON Surface Treatment Affects Na-Wetting

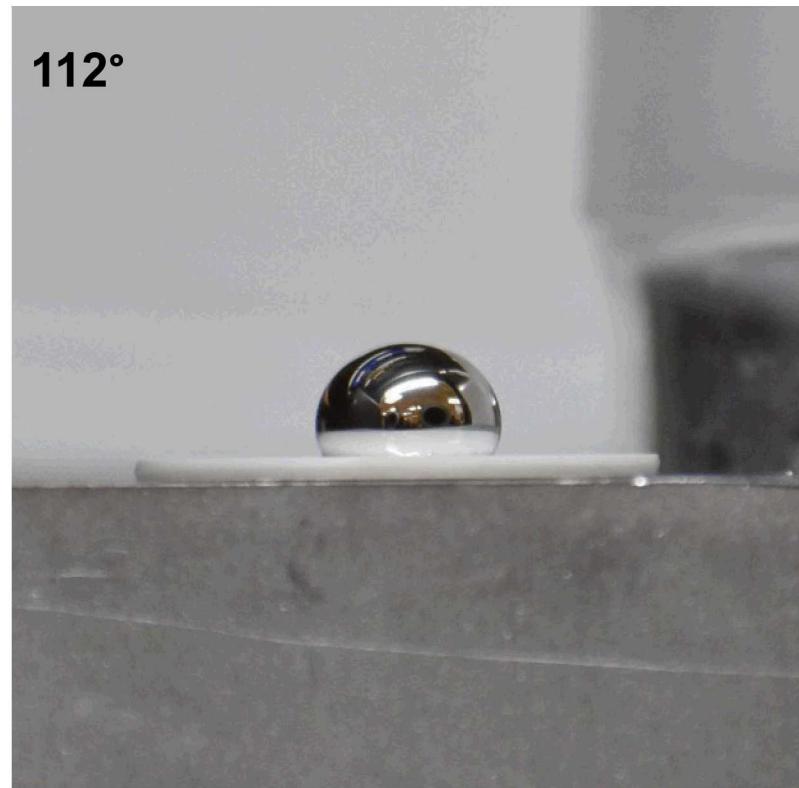
*Polishing NaSICON surface significantly improves Na-wetting at 110°C.*

Unpolished



146°

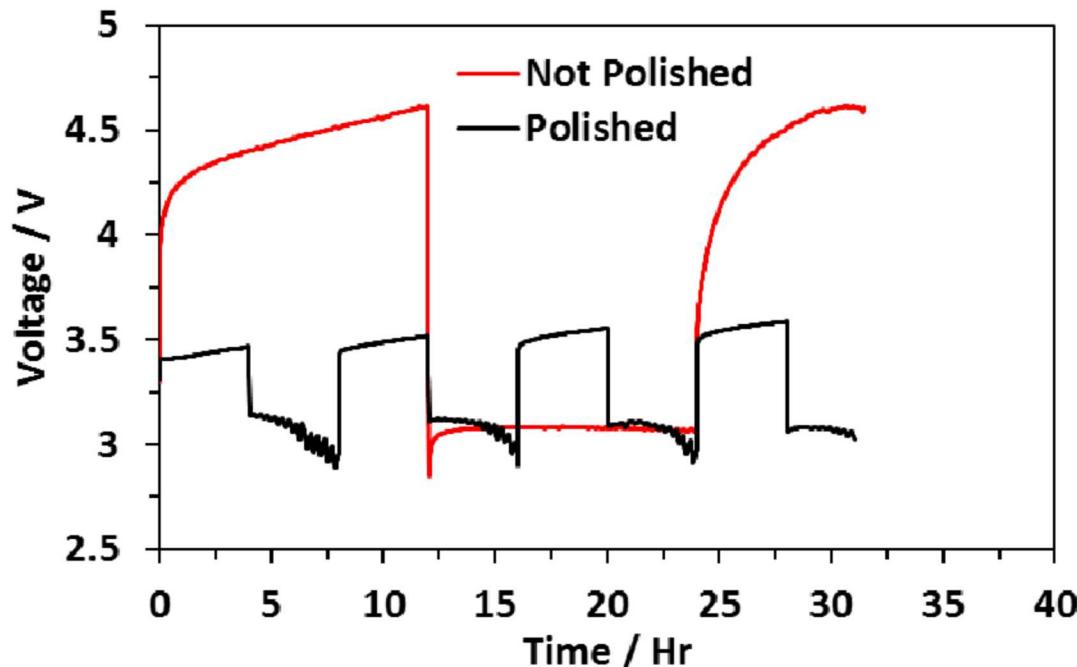
Polished



112°

# Separator Treatment Affects Cell Performance

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



- Not polished NaSICON battery operated at  $\pm 0.299$  mA current C/12 1% DOD
- Polished NaSICON battery operated at  $\pm 0.897$  mA C/4 1% DOD

# Separator Treatment Affects Cell Performance

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

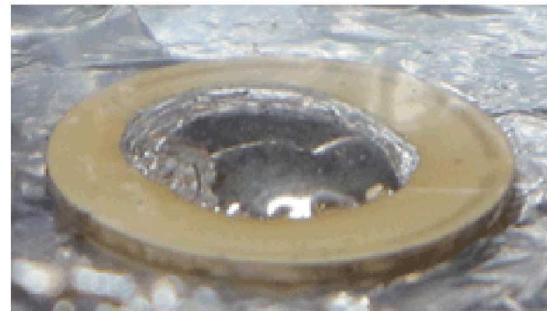
Heated at  
100-200°C for  
30 minutes



# 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.

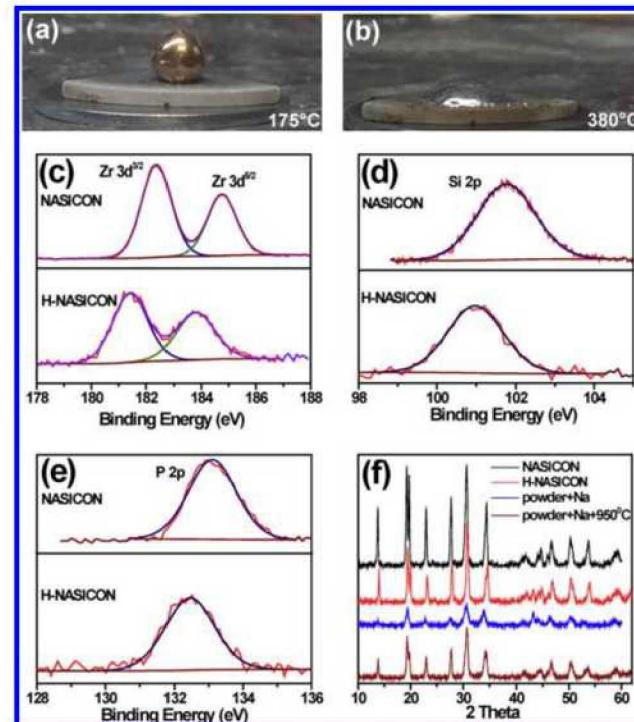
Heated at  
100-200°C for  
30 minutes



Heated above  
380°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.



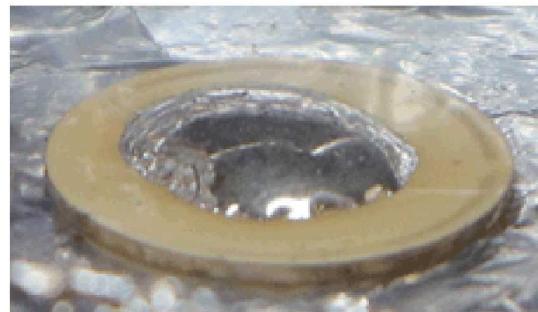
# Separator Treatment Affects Cell Performance

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

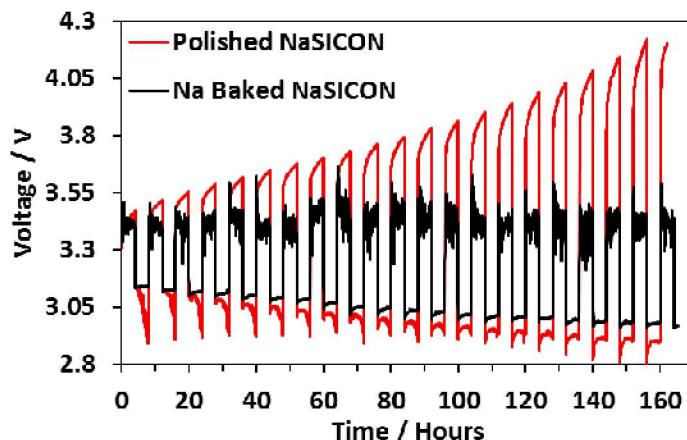
Heated below 200°C for 30 minutes



Heated above 380°C for 30 minutes

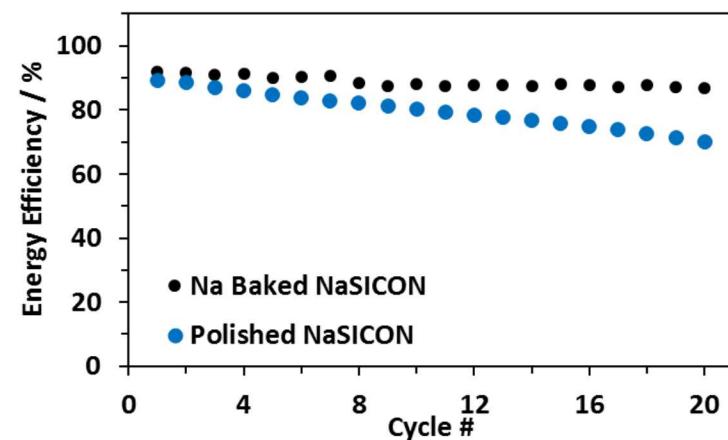


Na-treated NaSICON shows lower overpotentials on battery cycling.



Battery cycling at 110°C!

25 mol% NaI-AlBr<sub>3</sub> with NaSICON separator.



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

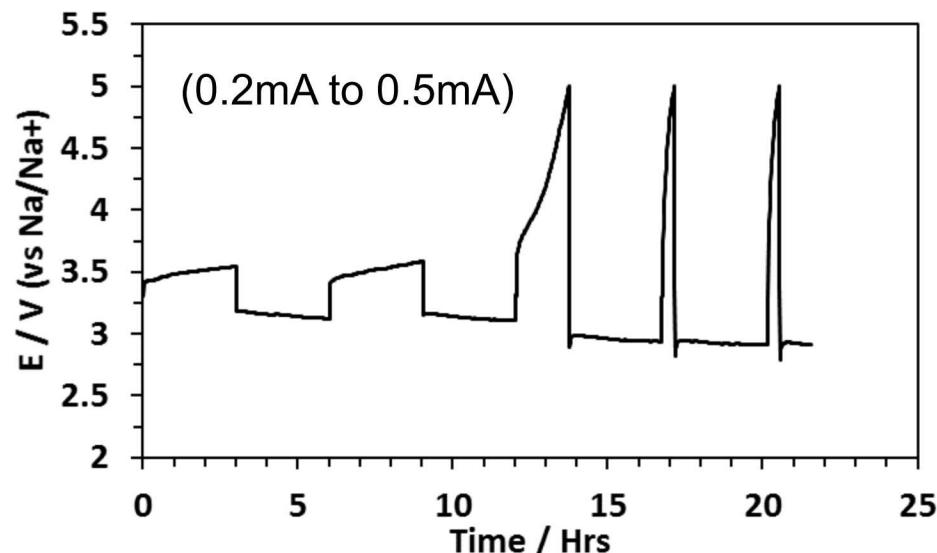
# Carbon Coating NaSICON

5nm of carbon coating enhances Na-wetting on NaSICON



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

Cathode – small area of carbon accidentally removed while taking salt off with toluene

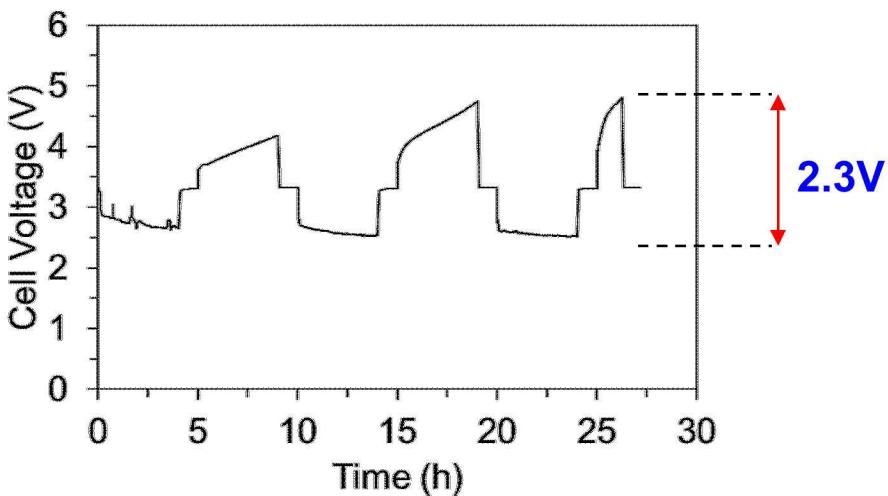


Even in thin layers, carbon can serve as a sodium blocking layer. Further work is needed if this is to be an option.

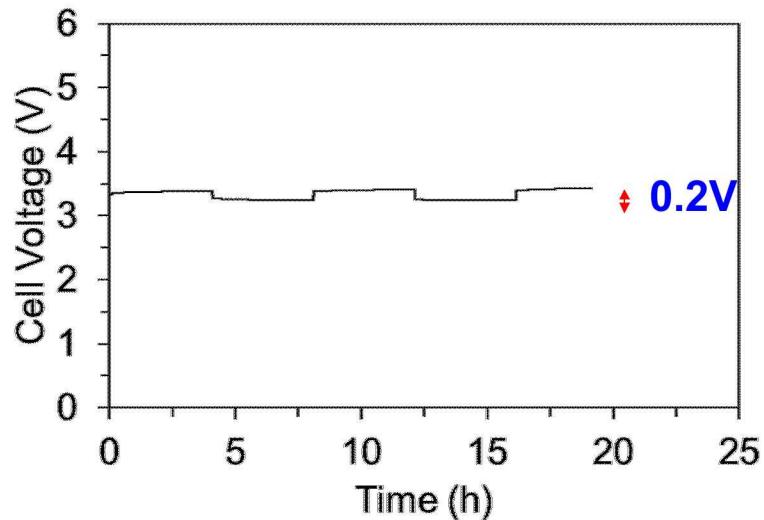
# Cathode Current Collector

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

Without carbon felt current collector



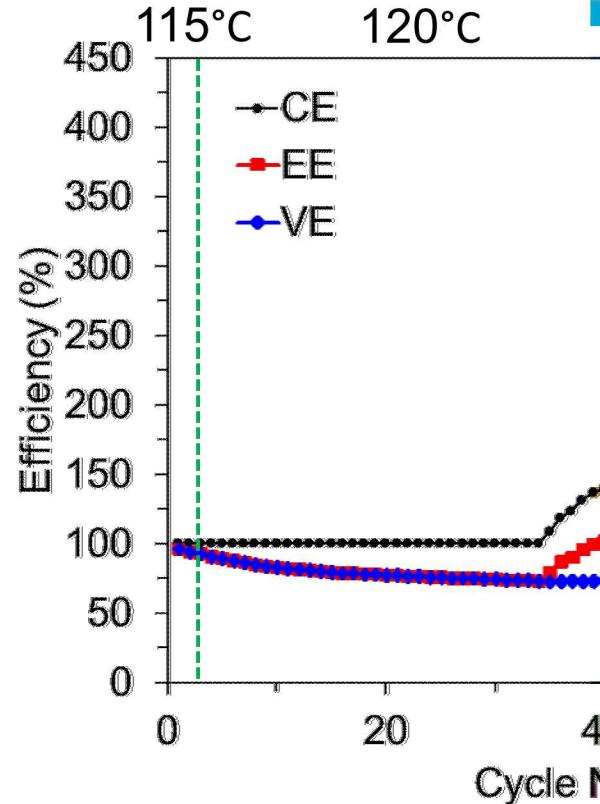
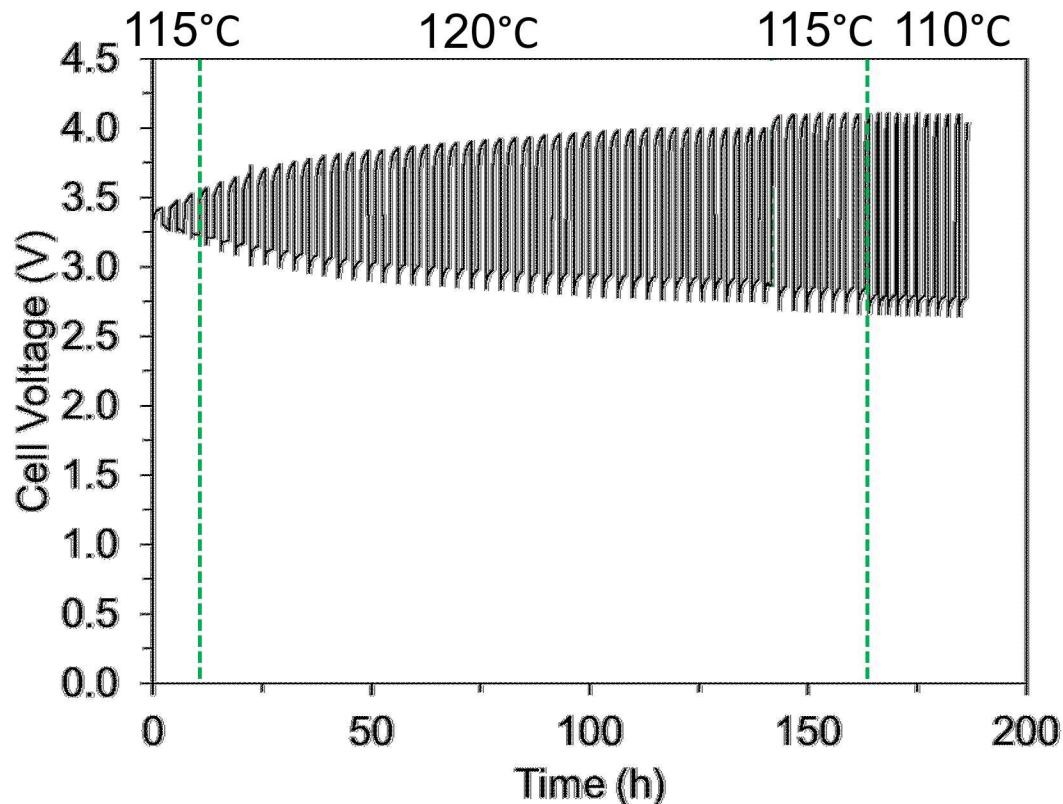
With carbon felt, treated with 0.1M HCl overnight



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

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

## Title

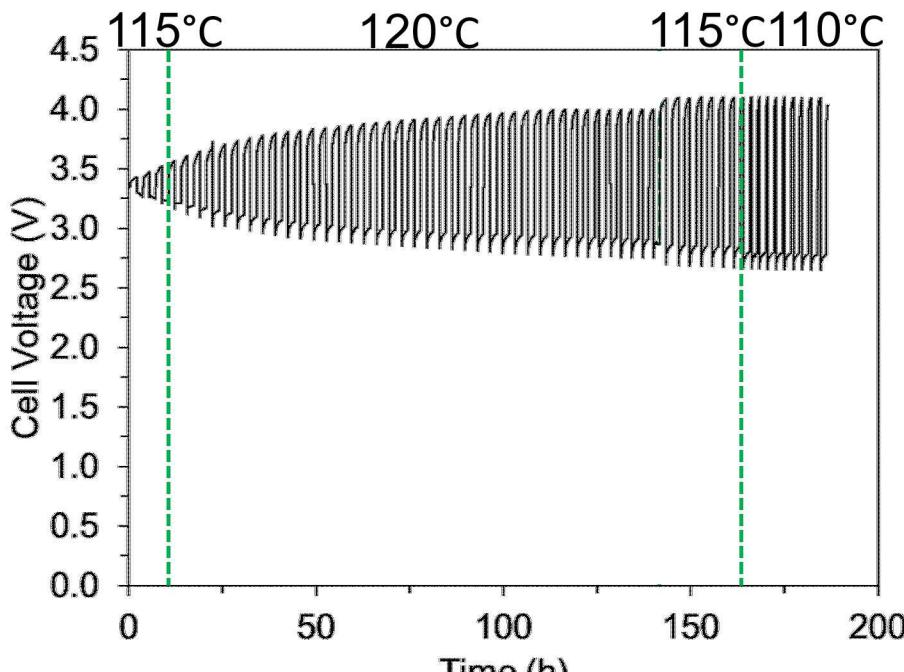
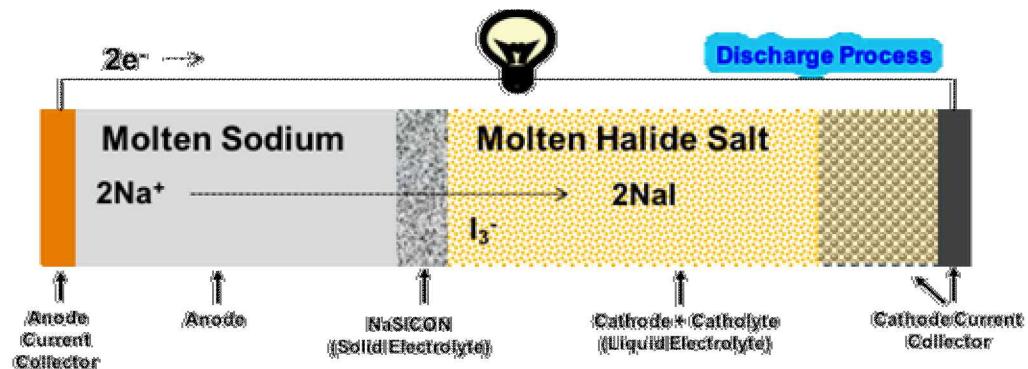
Partial Charge Assembly 120 $\rightarrow$ 115 $\rightarrow$ 110°C

## Cell Conditions:

- Cycling at 120°C
- 25-26% DOD
- 18.75 mol% NaI + 6.25 mol% I<sub>2</sub> in AlBr<sub>3</sub> (25% SOC)
- Amanda's NaSICON, Sn-coated on anode side
- 0.89 mA current = 0.5mA cm<sup>-2</sup> current density
- Mini bobble cell parts

# Put it all together

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

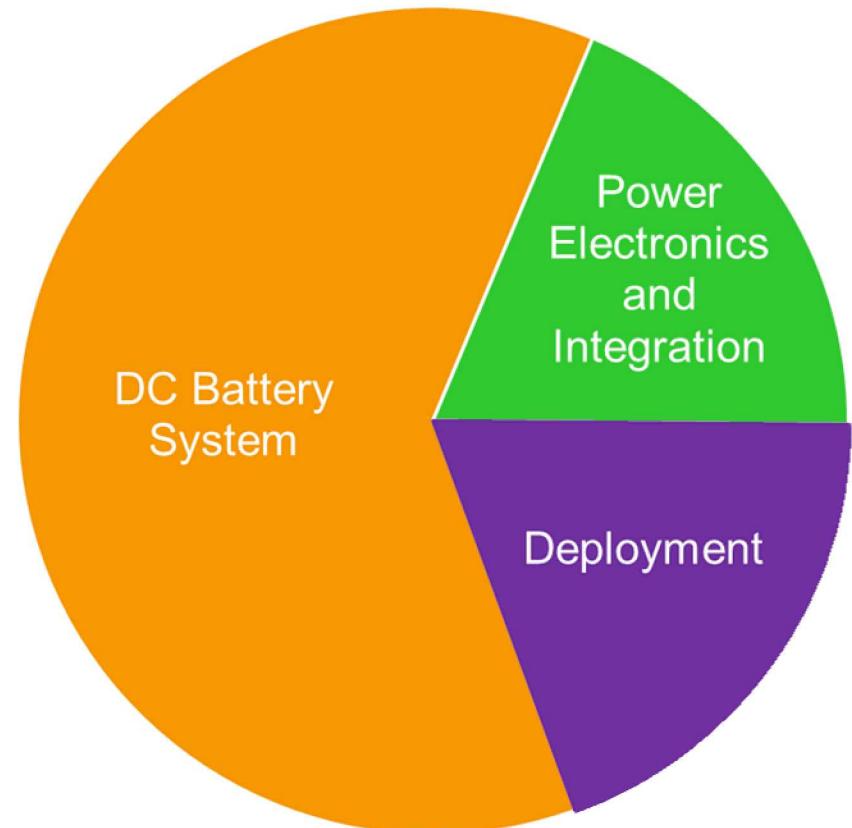


## Cell Conditions:

- Cycling at 120°C
- 25-26% DOD
- 18.75 mol% NaI + 6.25 mol% I<sub>2</sub> in AlBr<sub>3</sub> (25% SOC)
- 0.89 mA current = 0.5mA cm<sup>-2</sup> current density
- Mini bobble cell parts

# 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 Away Messages

- Low temperature sodium batteries, enabled by new materials chemistries, may help address a huge need for increased grid-scale energy storage.
- Molten salt catholyte chemistry must be carefully considered.
- Solid State NaSICON can be successfully synthesized with high density and reasonable conductivity
  - Humidity and secondary phase formation can affect NaSICON ceramic properties (can be managed through synthetic modifications?)
- Surface preparation of NaSICON will affect battery performance
  - Cleaning/polishing
  - High temperature Na-treatment
  - Carbon coating?
  - **Seek new, non-blocking NaSICON treatments**
- Chemical compatibility of composite components is **IMPORTANT!**

*Continued materials development, and specific emphasis on interfaces, will be key to developing a new generation of molten-sodium batteries!*

# Acknowledgements

## SNL Team

Dr. Martha Gross

Dr. Stephen Percival

Dr. Leo Small

Amanda Peretti

Dr. Josh Lamb

Dr. Eric Allcorn

Sara Dickens

Dr. Babu Chalamala



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

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](mailto:edspoer@sandia.gov)



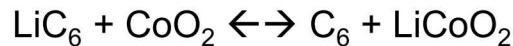
Work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity Delivery and Energy Reliability.

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.

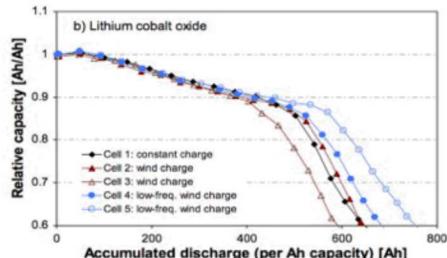
# Backup Slides

# Challenges with Existing Batteries

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



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

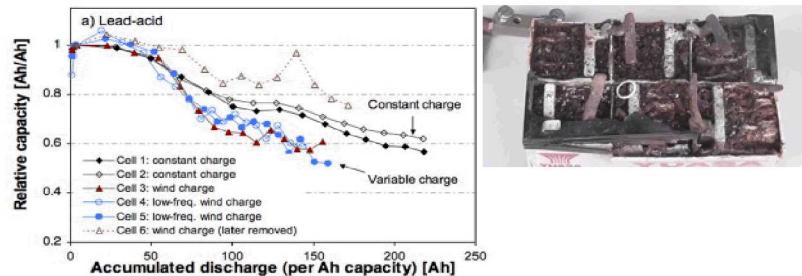


E. Krieger, et al. (2013) *Energy* **60**. 492-500.

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



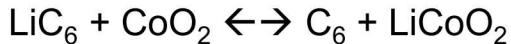
- Capacity fades quickly (typically 200-300 cycles)
- Temperature-sensitive



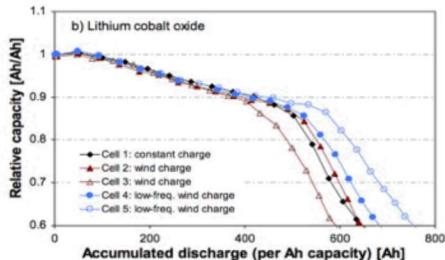
E. Krieger, et al. (2013) *Energy* **60**. 492-500.

# Challenges with Existing Batteries

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



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



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

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



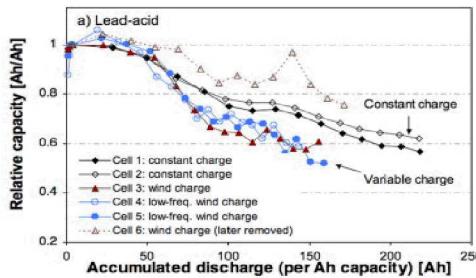
- Safety: Violent, toxic reactions between molten Na and molten S – cascading runaway!
- Corrosive, toxic chemistries
- High temperature operation (270-350°C)



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



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

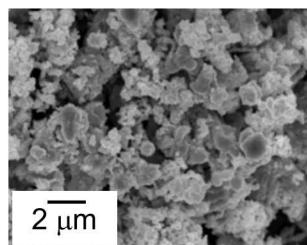


E. Krieger, *et al.* (2013) *Energy* **60**, 492-500.

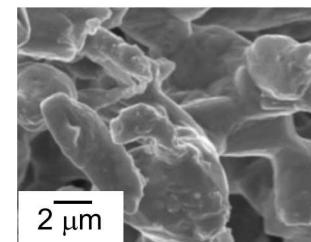
## Na-NiCl<sub>2</sub> ( $E_{cell} \sim 2.6V$ )



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



Particle Coarsening



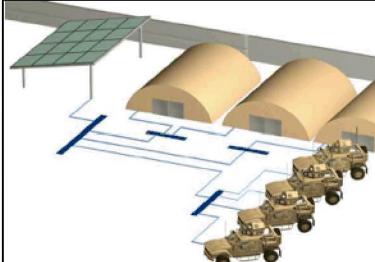
# A Need for Grid-Scale Energy Storage Research



Renewable/Remote Energy



Grid Reliability



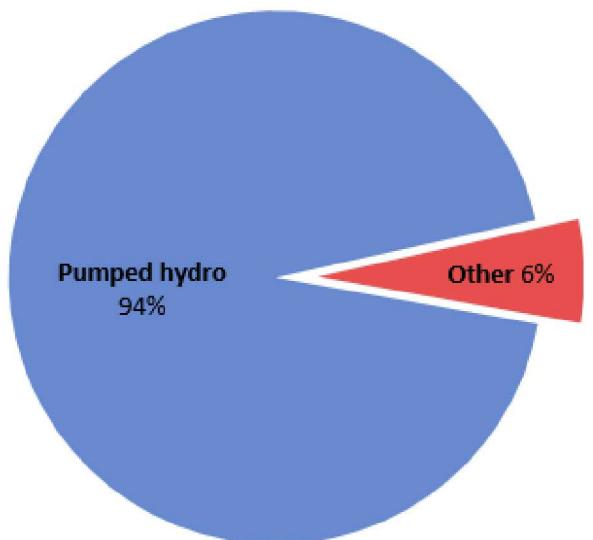
National Defense



Emergency Aid

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

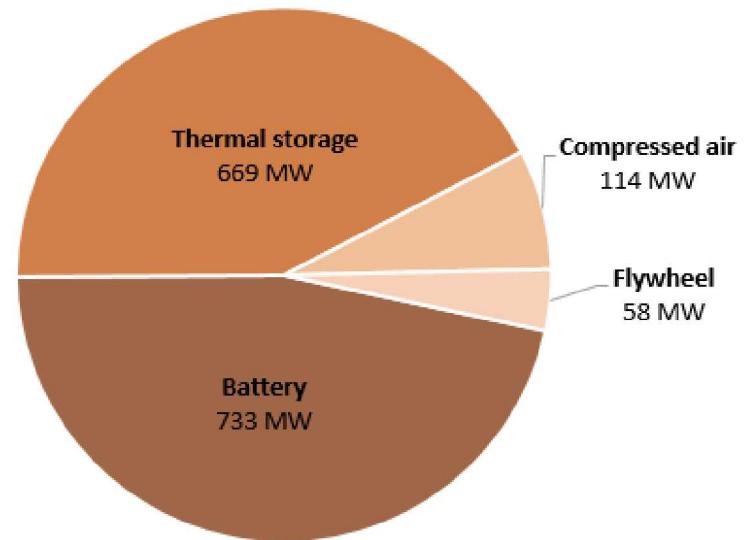
25.2 GW U.S. storage capacity



Other 6%

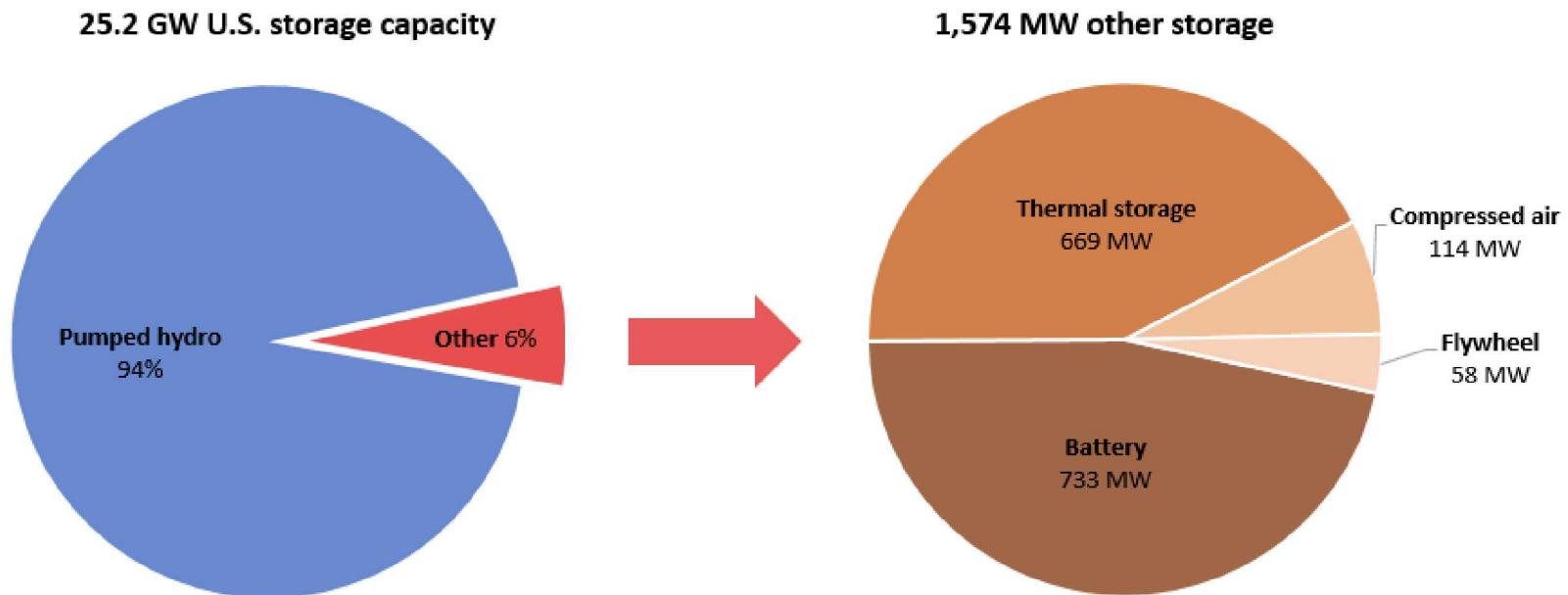


1,574 MW other storage



# Battery-based Energy Storage: Room to Grow!

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



## % of in service U.S. Generation Capacity

0.07% Battery Energy Storage

2.2% Battery Energy Storage and Pumped Hydro Storage

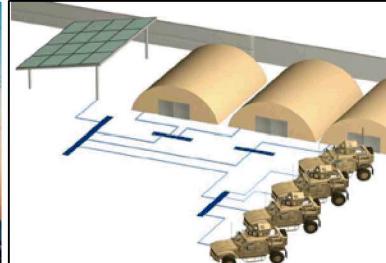
# A Need for Grid-Scale Energy Storage Research



Renewable/Remote Energy



Grid Reliability



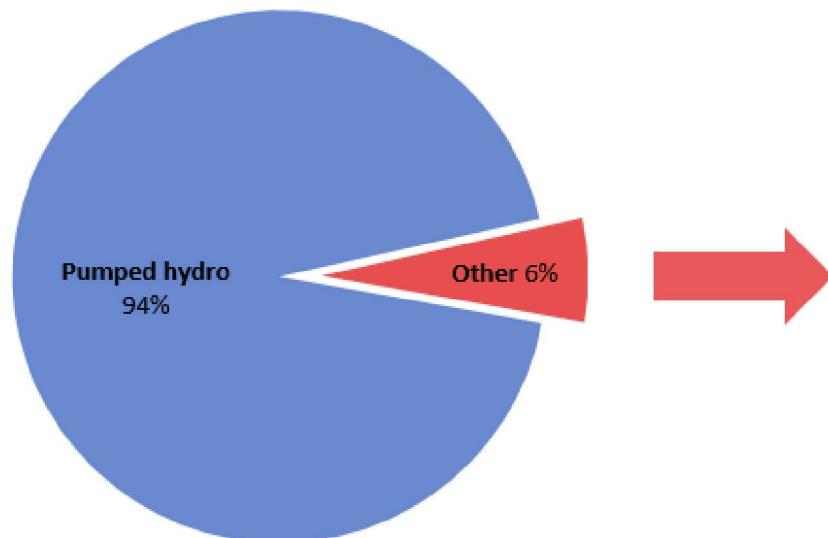
National Defense



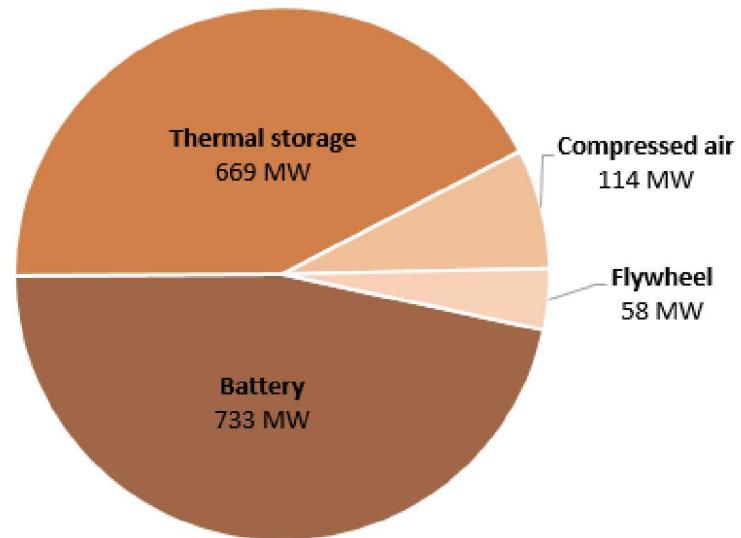
Emergency Aid

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

25.2 GW U.S. storage capacity



1,574 MW other storage



# Battery-based Energy Storage: Room to Grow!



Image from Can Stock Photo

# Battery-based Energy Storage: Room to Grow!



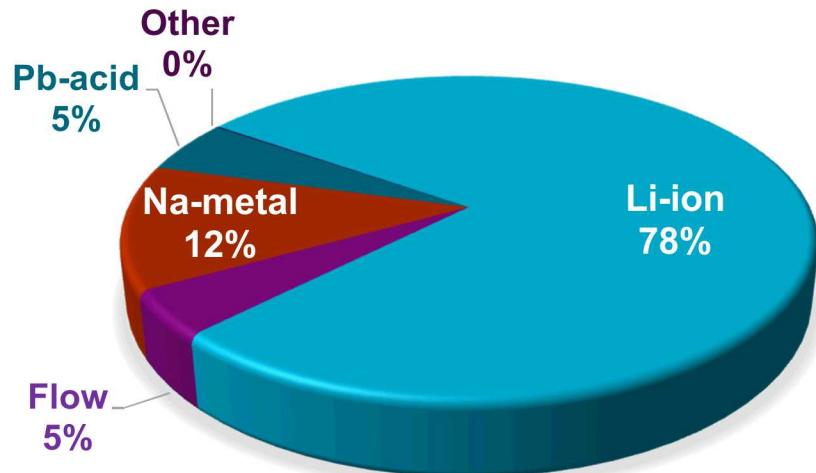
# Alternative Summary

- 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<sub>2</sub> (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!**

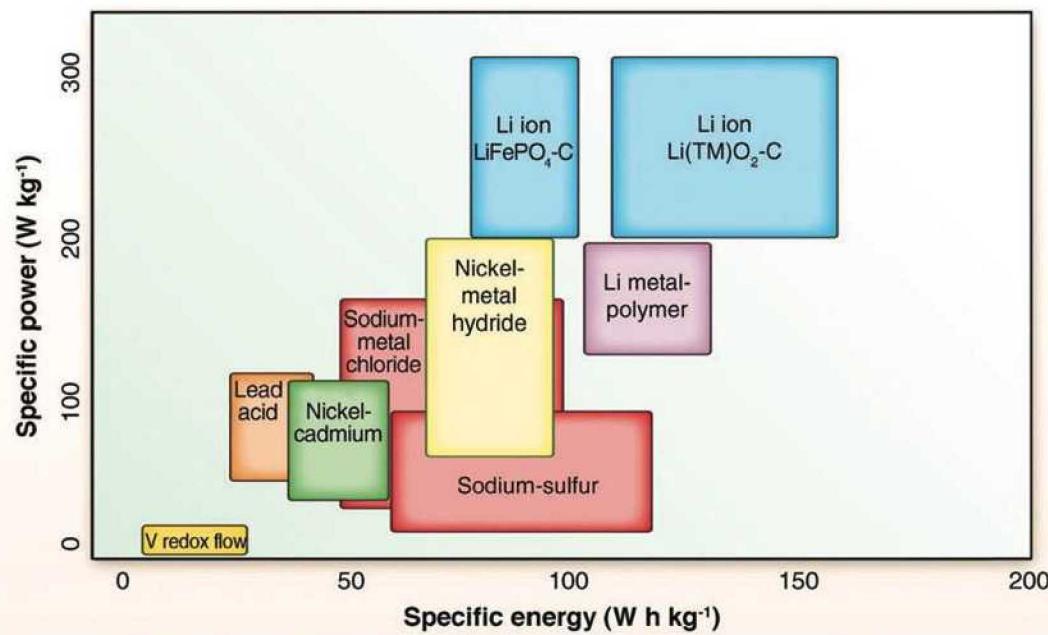
# Current Battery Storage Deployments



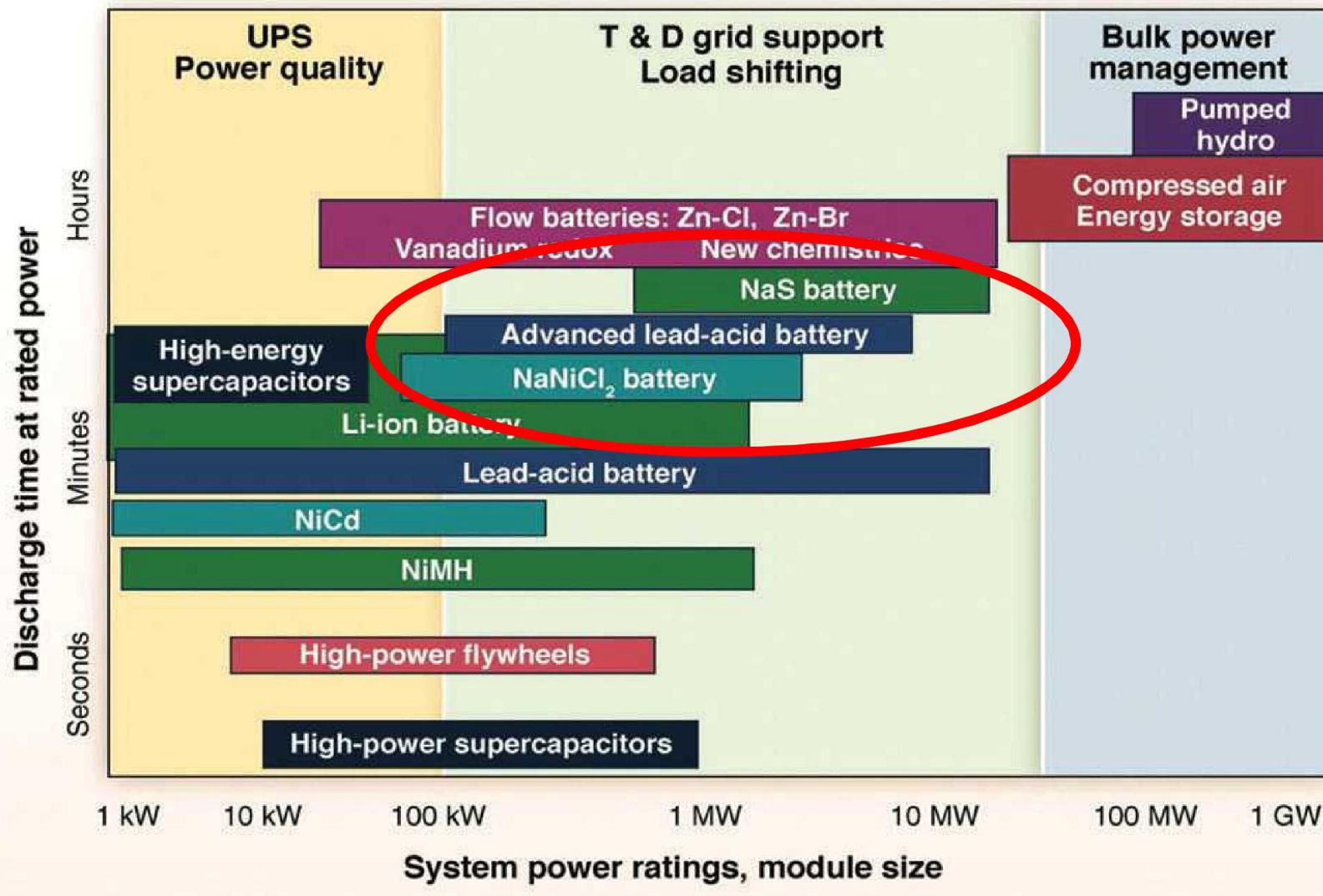
DOE Global Energy Storage Database:  
<http://www.energystorageexchange.org/> Nov. 2017

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

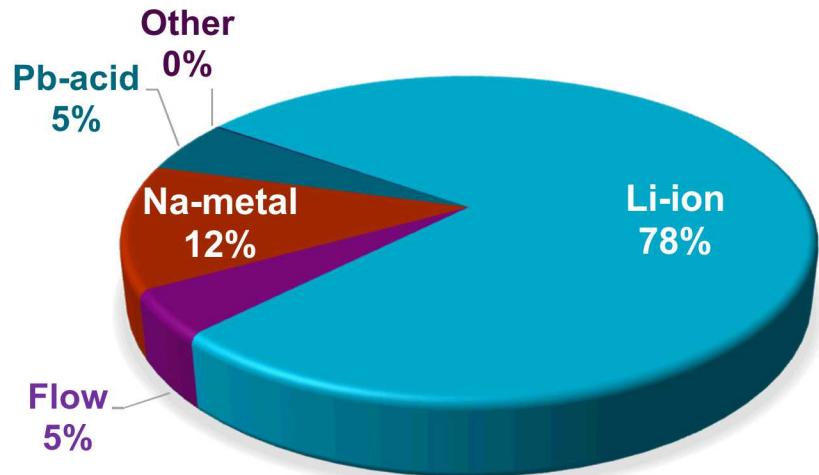
Li-ion batteries can not and should not become our singular grid-scale storage solution.



# Variable Battery Utility Matches Variable Battery Capability



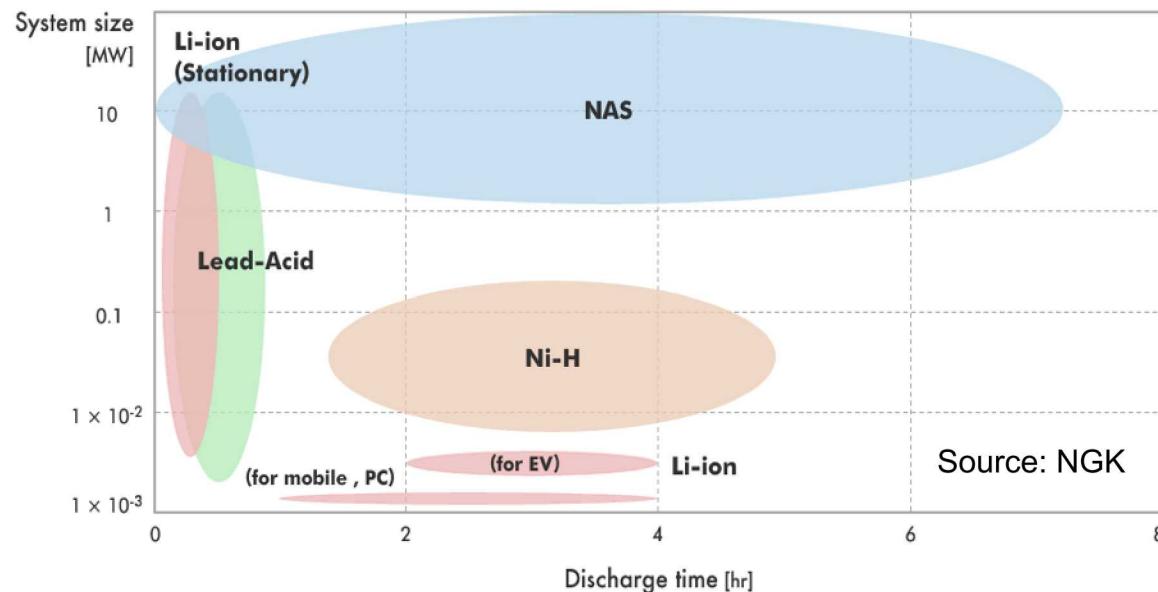
# Current Battery Storage Deployments



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

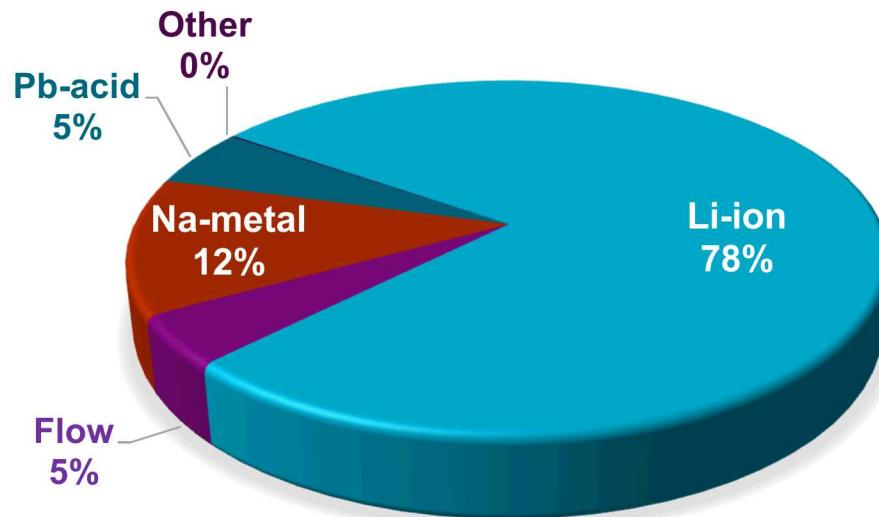
*Different batteries have variable discharge durations...*

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

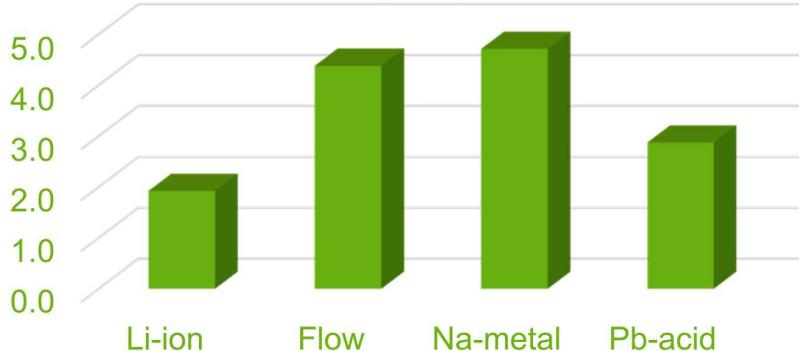


# Current Battery Energy Storage Deployments

\*(Operational as of Nov. 2017)



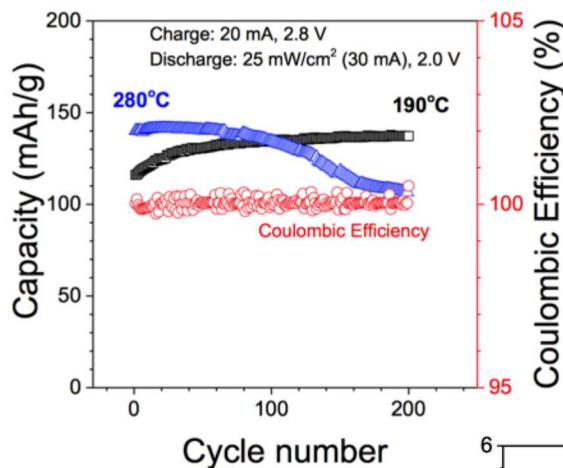
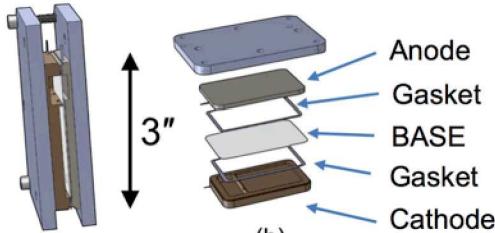
## Average Duration Discharge (hrs)



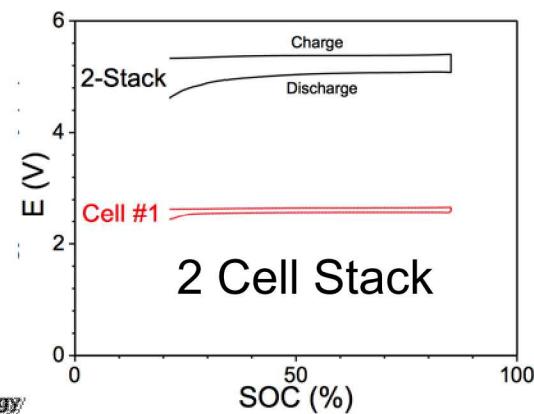
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

# Intermediate Temperature “ZEBRA” Batteries

## Planar Stack Configuration



Pacific Northwest  
NATIONAL LABORATORY



## Tubular Configuration



100Wh

250Wh



## Multiscale Prototype Demonstrations

### **13 Wh Na-NiCl<sub>2</sub> Cell**

- Operational for 9+ months.
- Energy efficiency >85%
- 65 mA /cm<sup>2</sup>

### **100 Wh Na-NiCl<sub>2</sub> Cell:**

- Operational for 4+ months.
- energy efficiency 81.5%
- 53 mA/cm<sup>2</sup>

### **250 Wh Na-NiCl<sub>2</sub> Cell:**

- operational for 3+ months
- energy efficiency 80%
- 53 mA/cm<sup>2</sup>



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

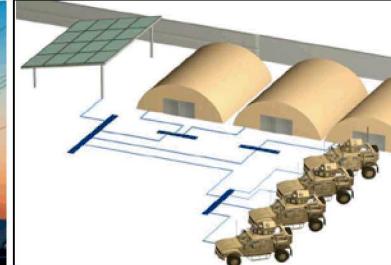
# A Need for Grid-Scale Energy Storage Research



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)*

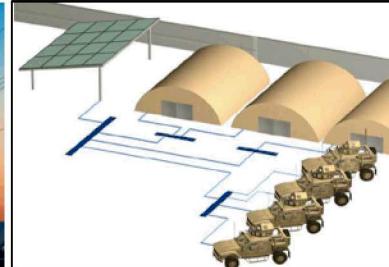
# A Need for Grid-Scale Energy Storage Research



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)



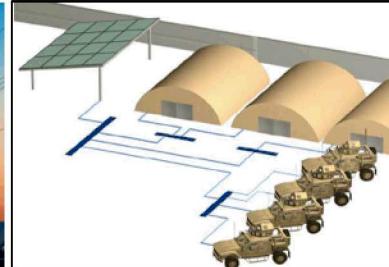
# A Need for Grid-Scale Energy Storage Research



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)



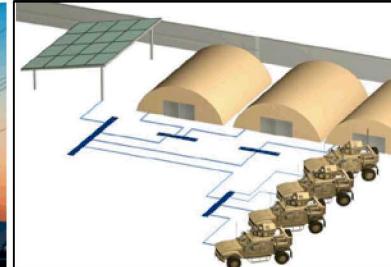
# A Need for Grid-Scale Energy Storage Research



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)*

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

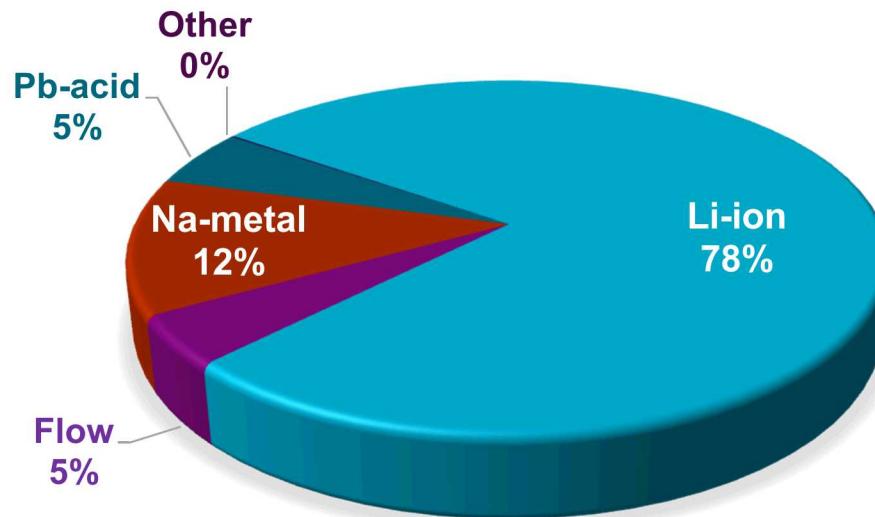
- “Energy” applications – slower times scale, large amounts of energy
- “Power” applications – faster time scale, real-time control of the electric grid

## Current Barriers:

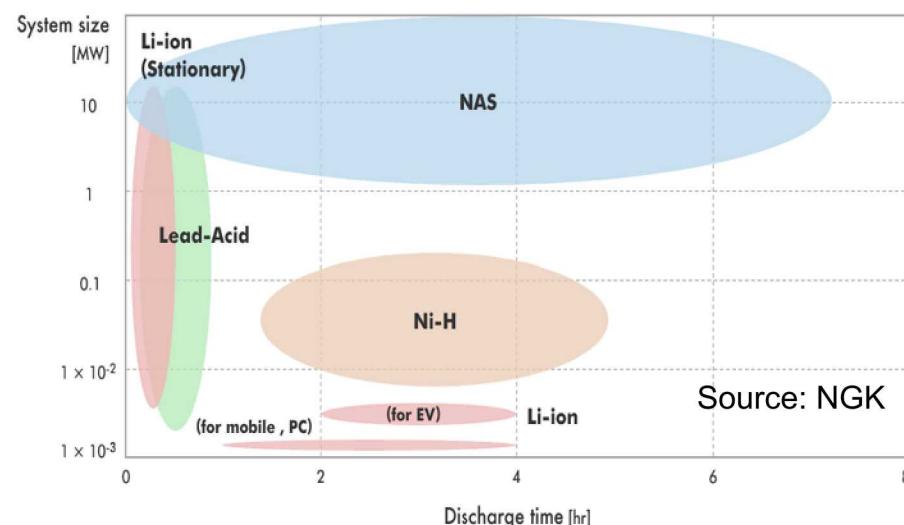
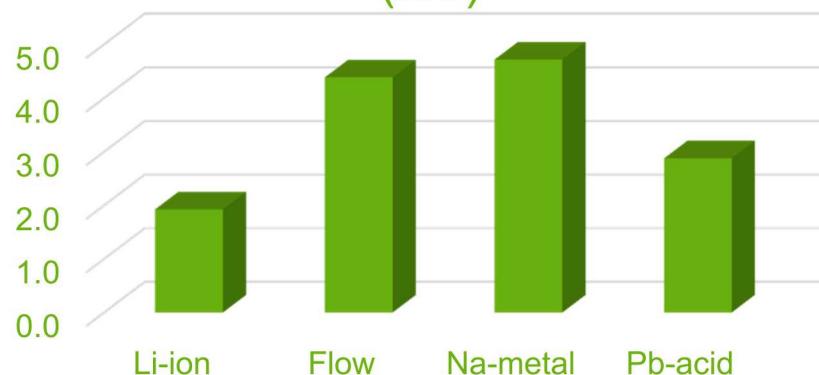
- Expensive, especially in energy markets (**need for continued R&D** )
- Electricity markets do not have market mechanisms for services ES can provide (**need to reduce regulatory and policy hurdles** )

# Current Battery Energy Storage Deployments

\*(Operational as of Nov. 2017)



## Average Duration Discharge (hrs)



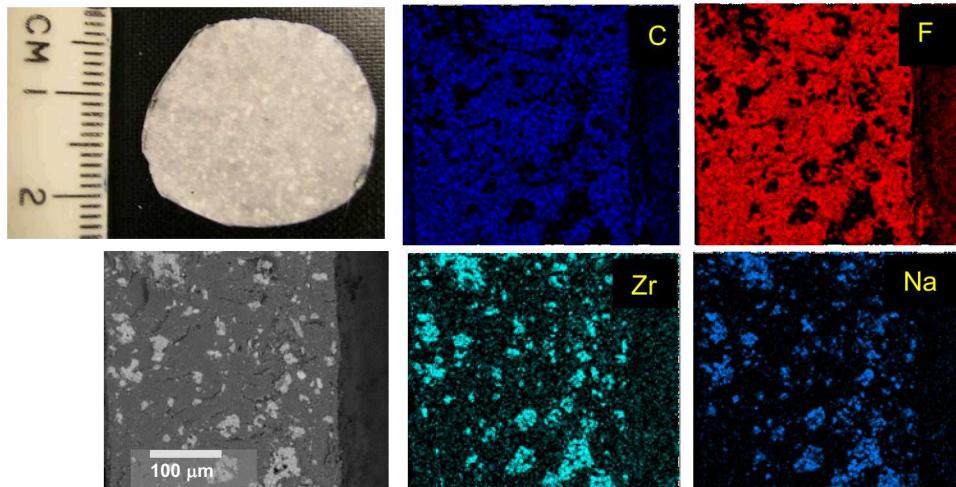
# Composite Separator Innovation

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 ( $4 \times 10^{-10}$ ). Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.**

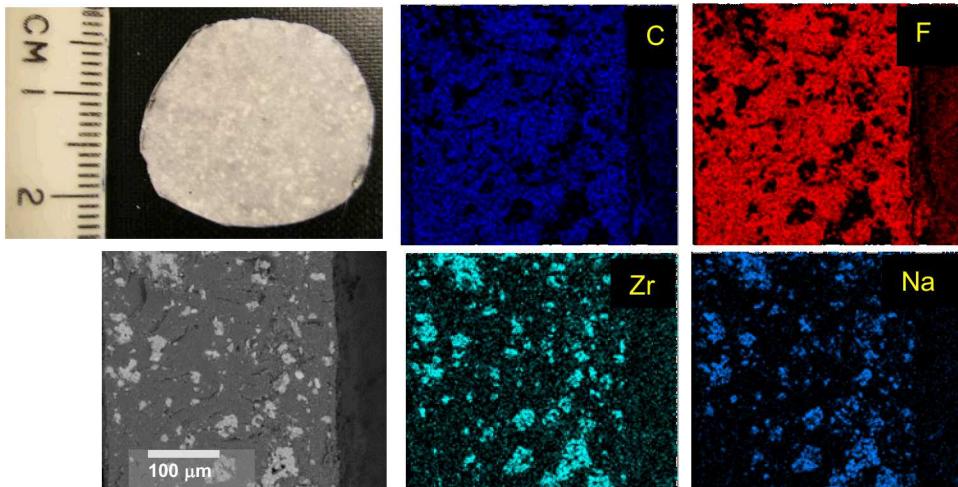


# Composite Separator Innovation

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

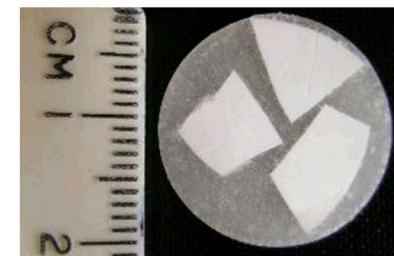
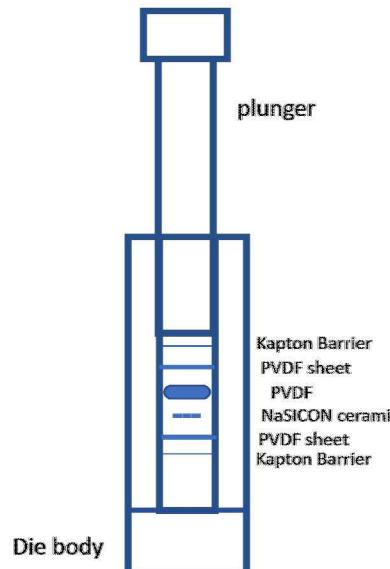
## Initial Approach

- 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 ( $4 \times 10^{-10}$ ). Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.**



## 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.

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