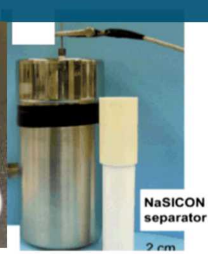
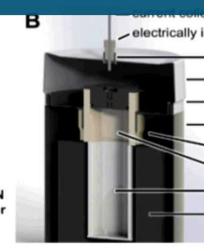
SAND2019-10905C

"Really Cool" Molten Sodium Batteries: Material Innovations to Enable Low Temperature Operation





Erik D. Spoerke, Ph.D.

Sandia National Laboratories, Albuquerque, NM

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

31st Rio Grande Symposium on Advanced Materials 2019
September 16th, 2019
Albuquerque, NM

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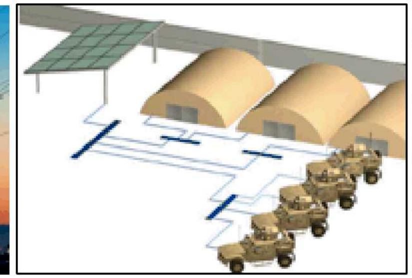
SAND No.:SAND2019-

A Need for Grid-Scale Energy Storage Research



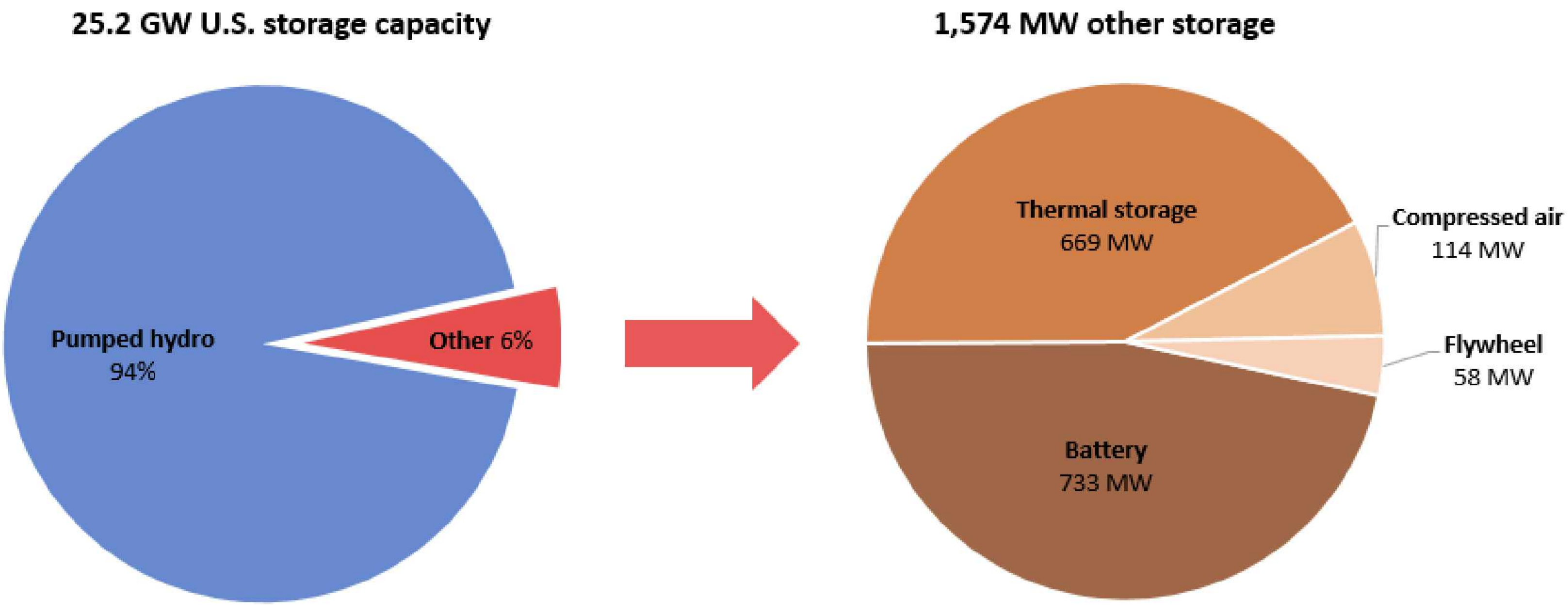
Renewable/Remote Energy


Grid Reliability


National Defense

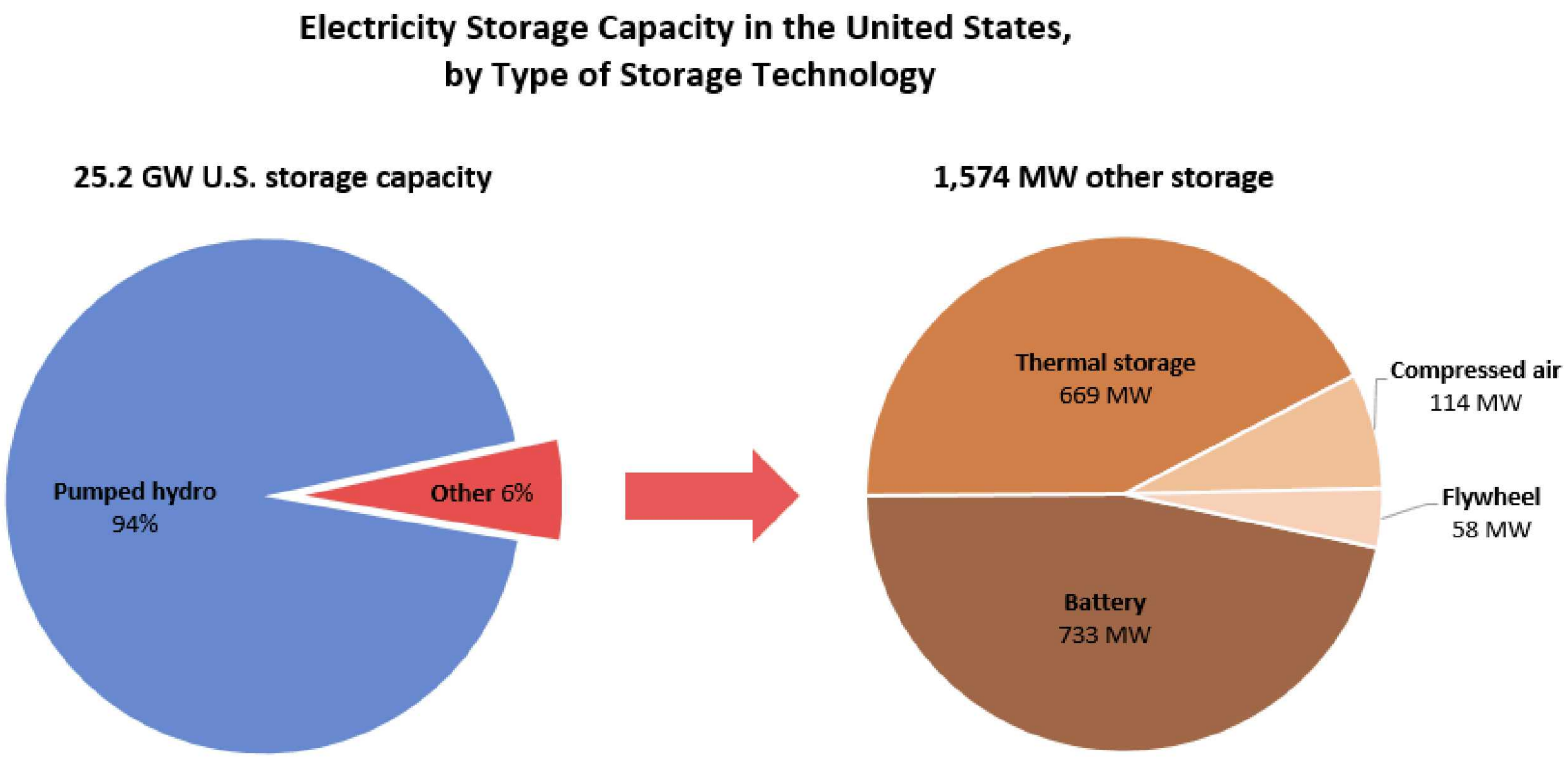

Emergency Aid

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*

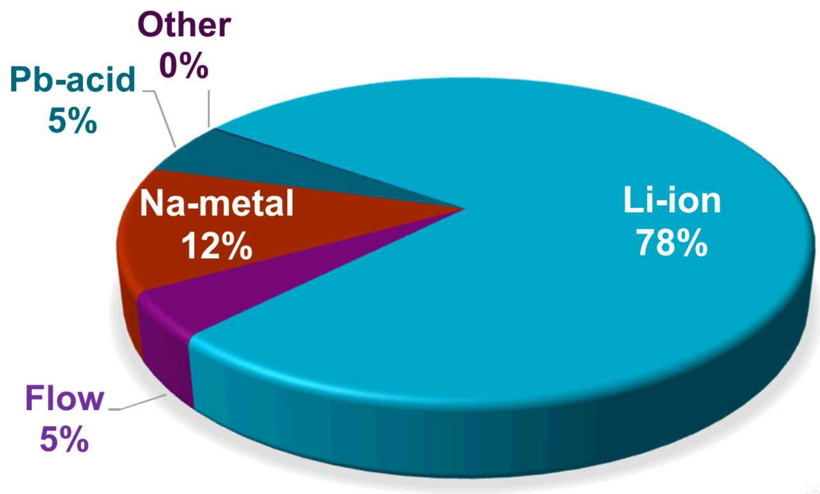
Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

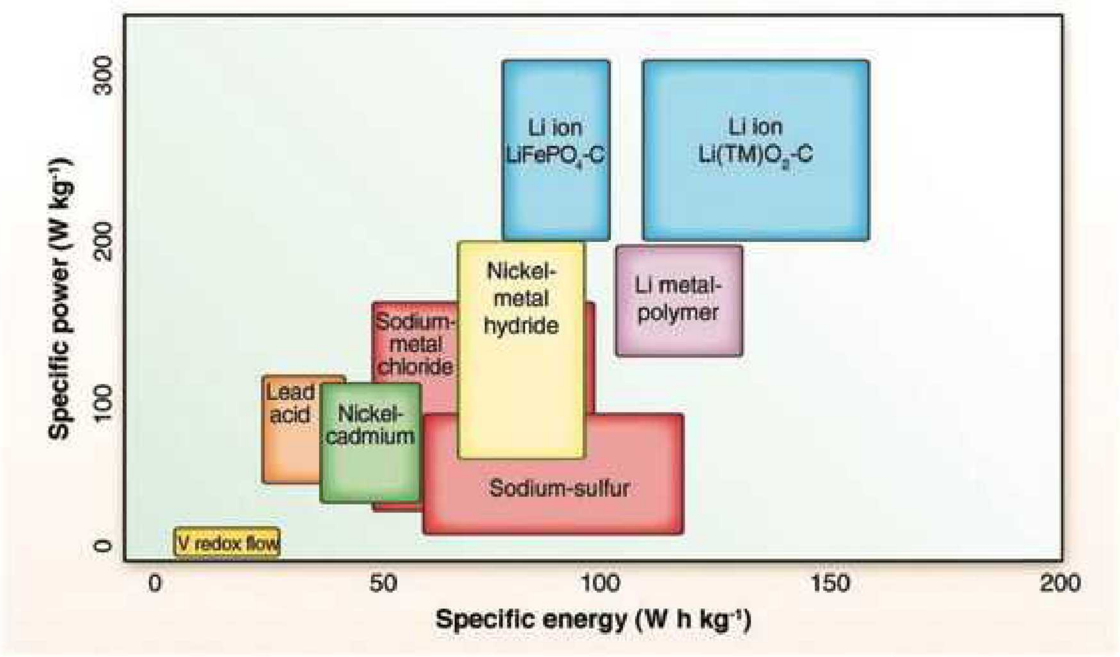
Current Battery Storage Deployments



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….



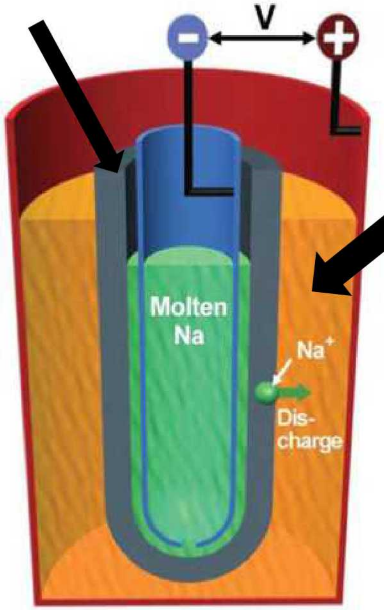
From: B. Dunn, *et al.*, *Science*, 2011, 334, 928–935.

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).

Ion Conducting Ceramic Separator



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

Traditional Na-Batteries operate at ~300^oC

- Improves separator ionic conductivity
- Maintains molten phase chemistry

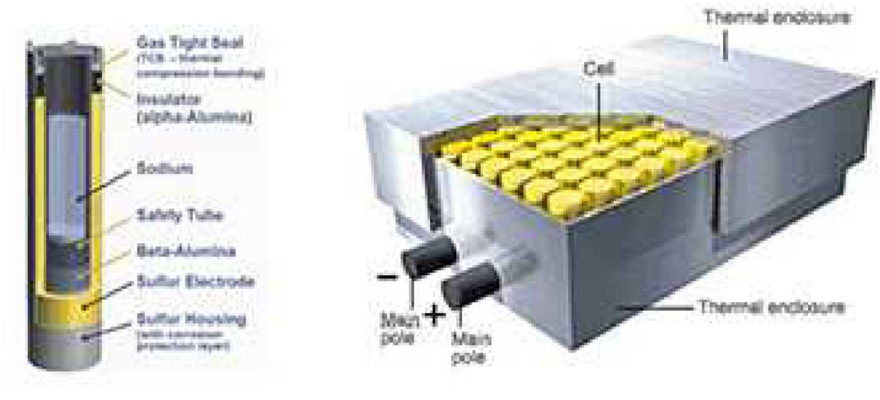
Na-$NiCl_2$ (E_{cell} ~ 2.6V)

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

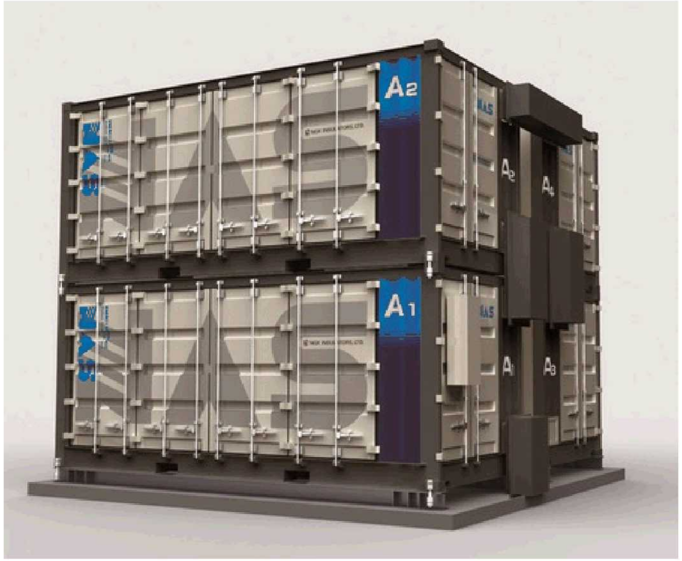
Na-S (E_{cell} ~ 2V)

$2Na + 4S \leftrightarrow Na_2S_4$

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-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

Challenges with Existing Na Batteries

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

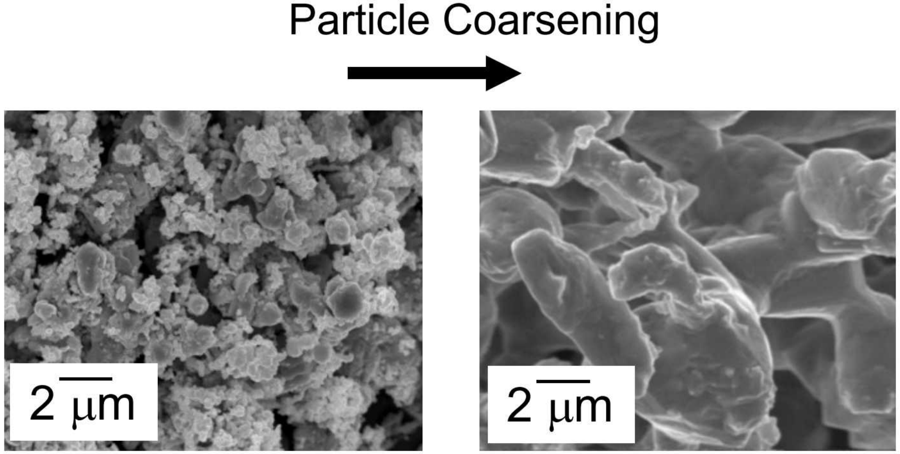
$2Na + 4S \leftrightarrow Na_2S_4$

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

Na-NiCl₂ (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)



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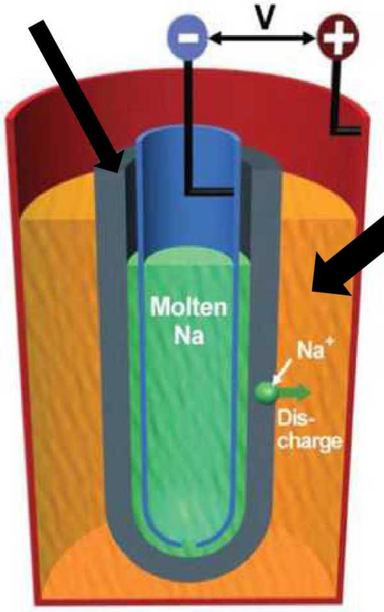


"Molten Catholyte"
- Sulfur
- M-Halide Salts

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)

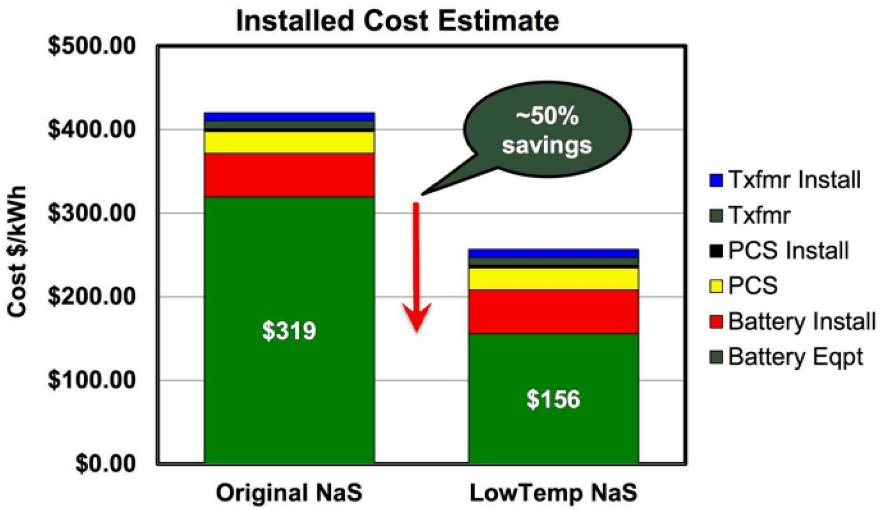
$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

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

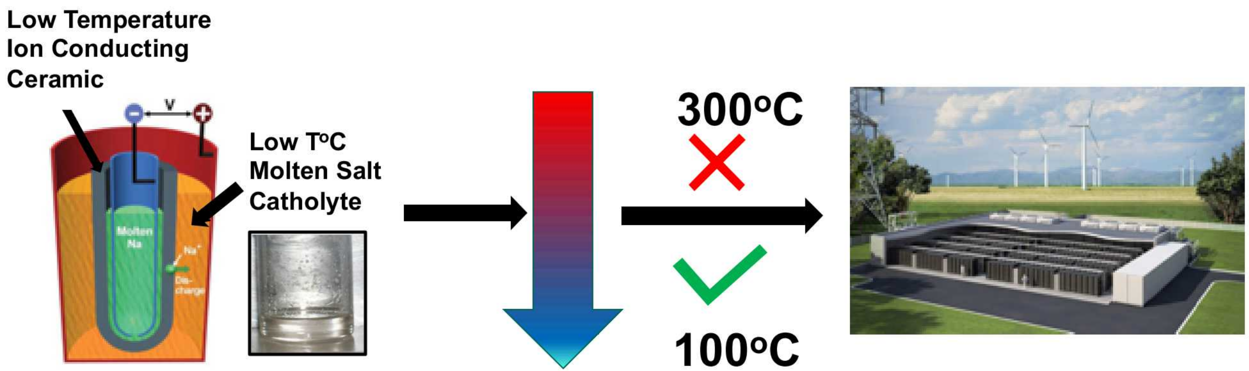
$2Na + 4S \leftrightarrow Na_2S_4$

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

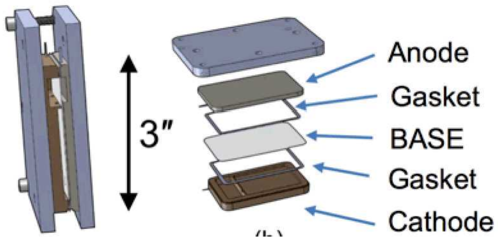


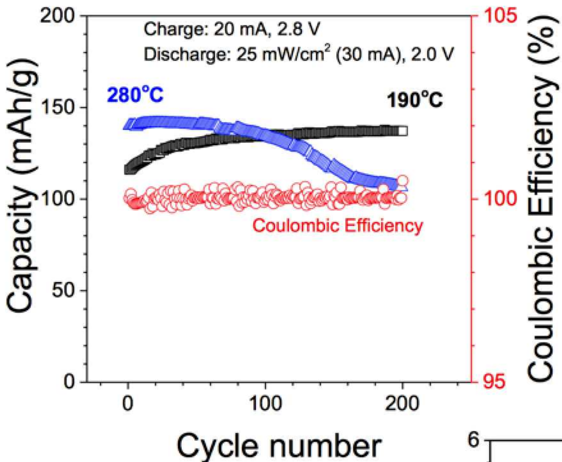
Gao Liu, et al. "A Storage Revolution." 12-Feb-2015 (online): https://ei.haas.berkeley.edu/education/c2m/docs/Sulfur%20and%20Sodium%20Metal%20Battery.pdf

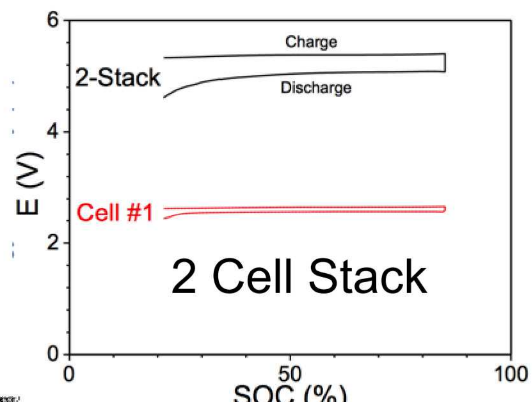


Intermediate Temperature "ZEBRA" Batteries

Planar Stack Configuration







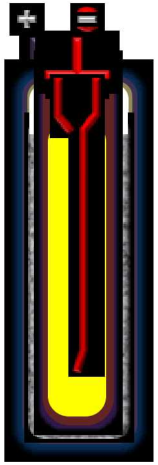
Pacific Northwest NATIONAL LABORATORY

RIST Research Institute of Industrial Science & Technology

Tubular Configuration

100Wh

250Wh



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

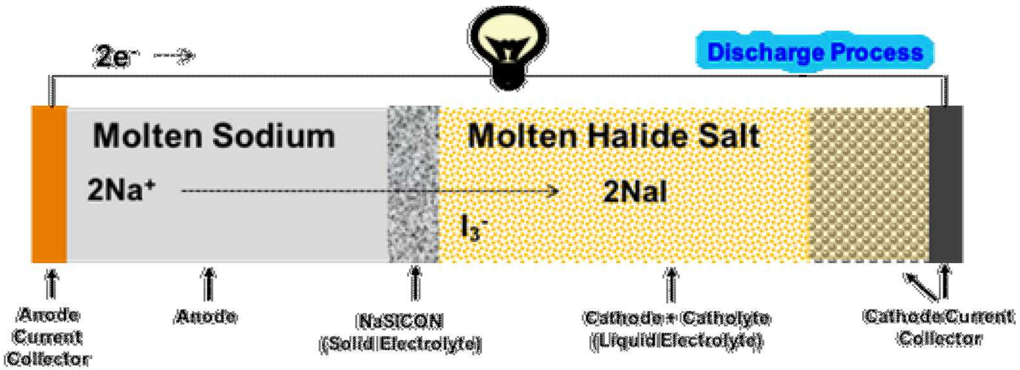
* All cycled to 70% DOD at C/7 rate.

SK

CERAMATEC TOMORROW'S CERAMIC SYSTEMS

Low Temperature Molten Na-Halide Batteries

<u>Our Vision:</u> 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.



<u>Na-NaI battery:</u>

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

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

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

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

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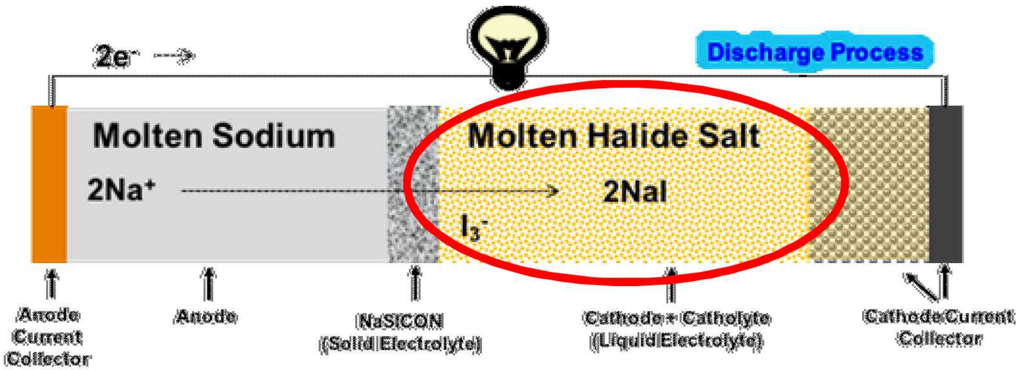

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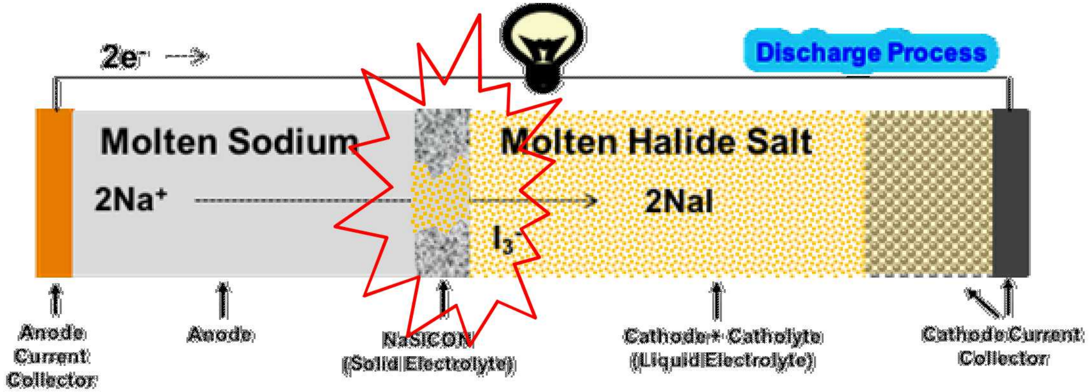
Consider NaI-AlX$_3$ catholyte…

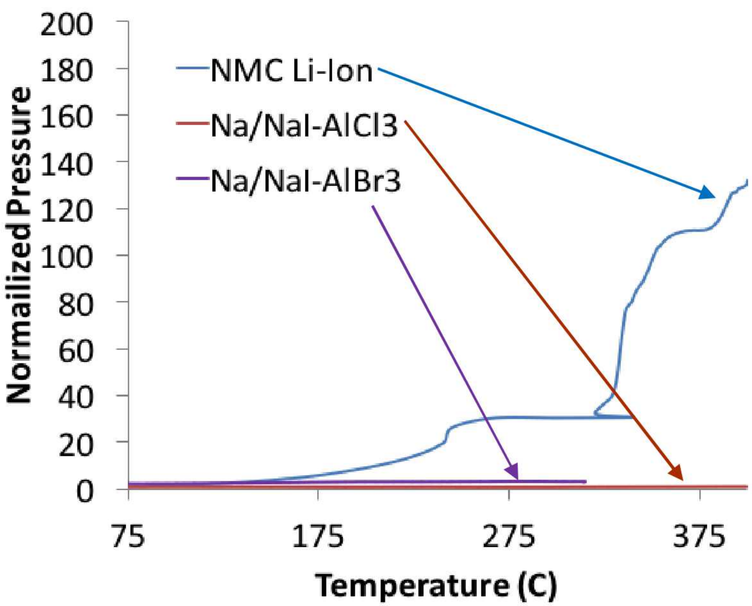
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

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.

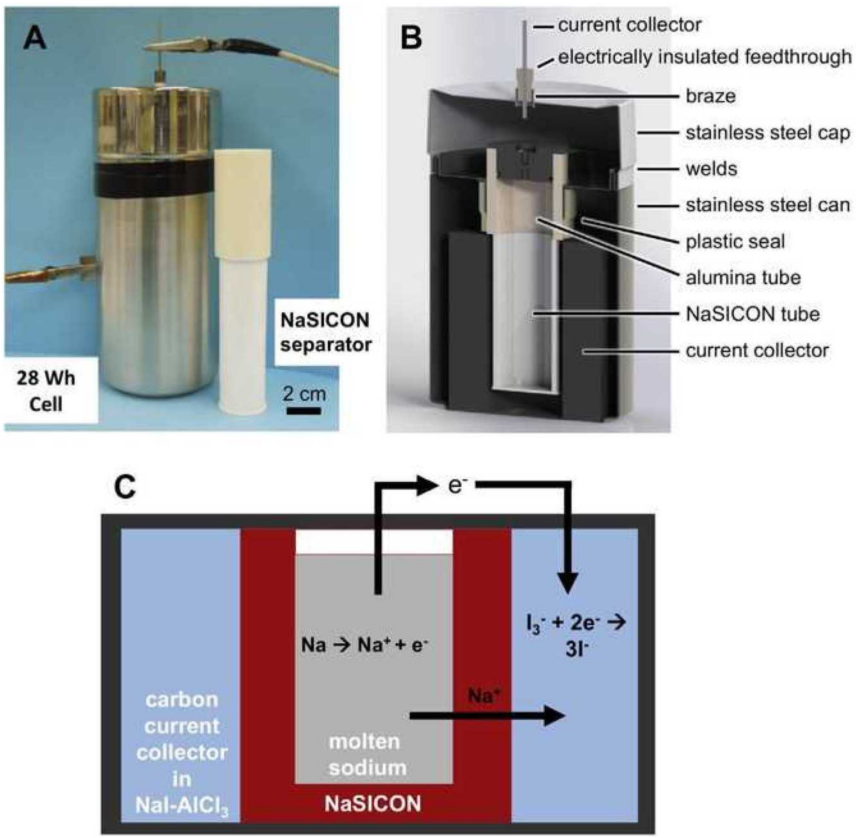


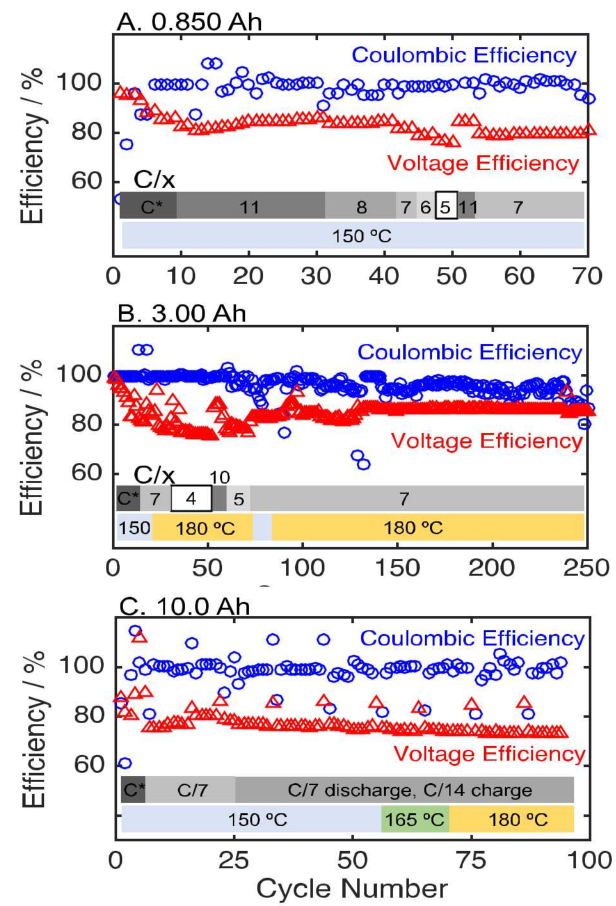
Accelerating rate calorimetry reveals that Na-NaI/AlX_3 mixtures exhibit:

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°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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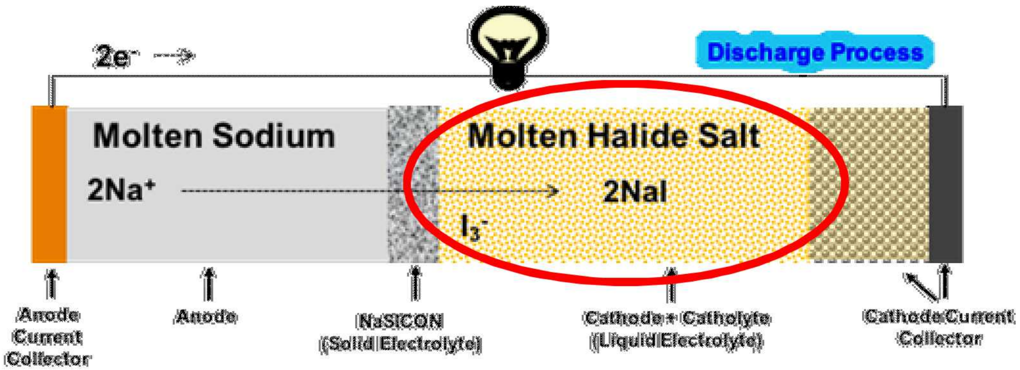

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$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

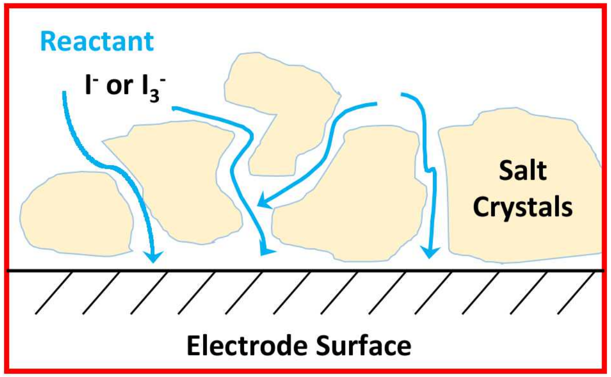
How important is the molten character of the catholyte?

Catholytes are Key to Low Temperature Operation

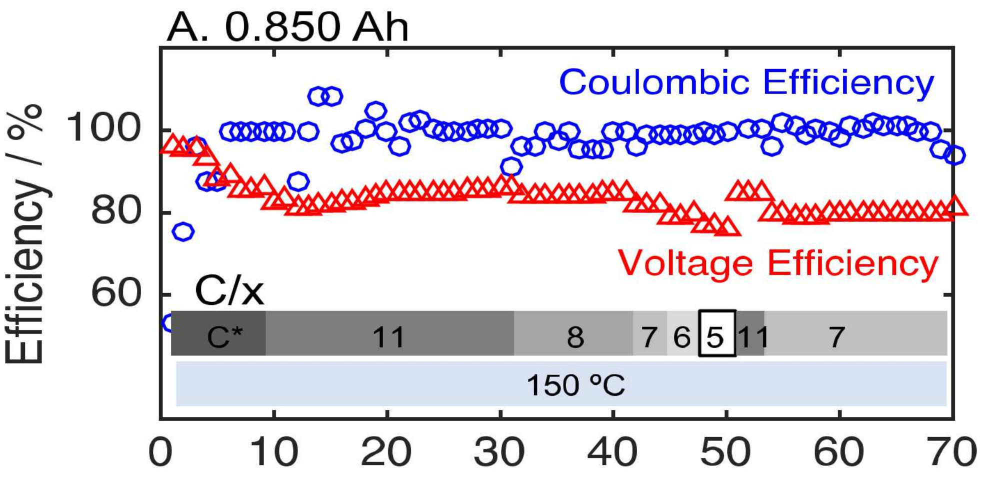
A fully molten catholyte avoids

a) Particle-hindered electrochemical processes.

b) Particle-related loss of capacity.



NaI-AlCl$_3$ at 150^{o}C



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

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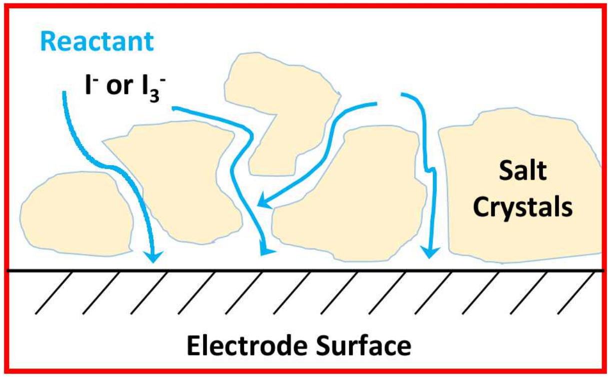
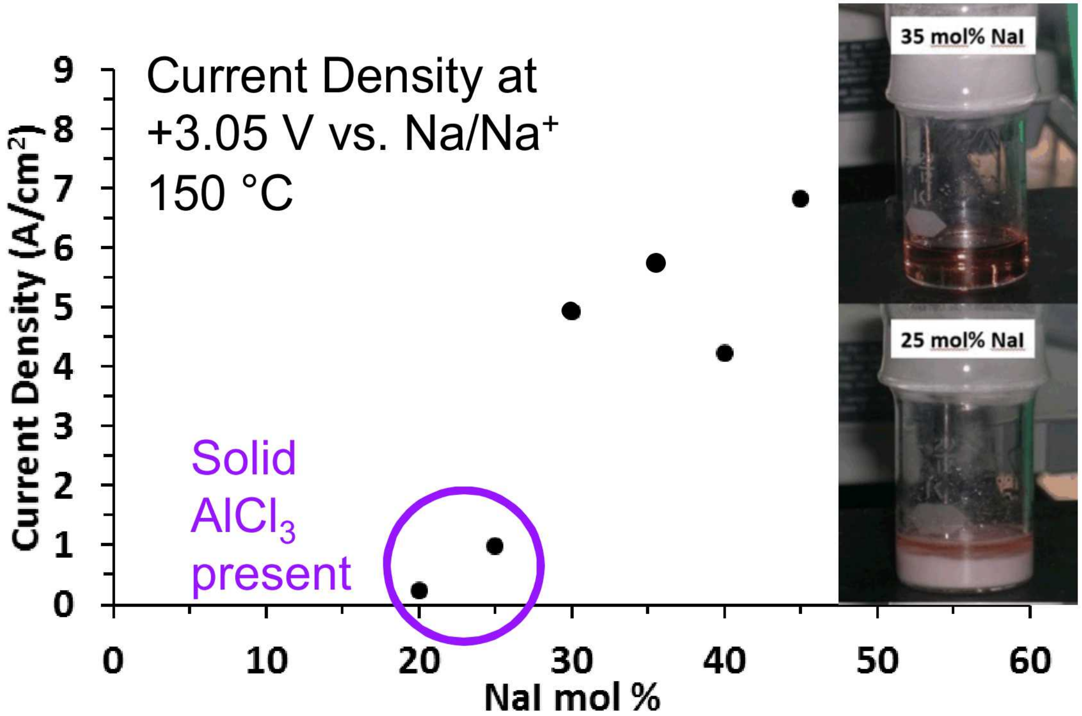




Current Density is significantly lower when solid secondary phases are present.

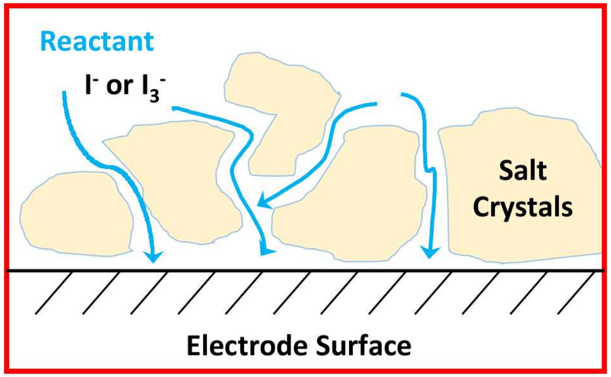
Percival, Small, and Spoerke. *J. Electrochem. Soc.*, **165** (14) A3531-A3536 (2018)

Catholyte Composition is Especially Important at Lower Temperatures

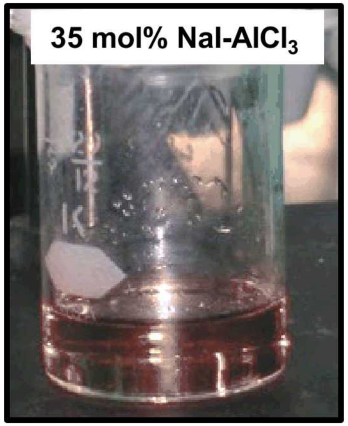
A fully molten catholyte avoids

a) Particle-hindered electrochemical processes

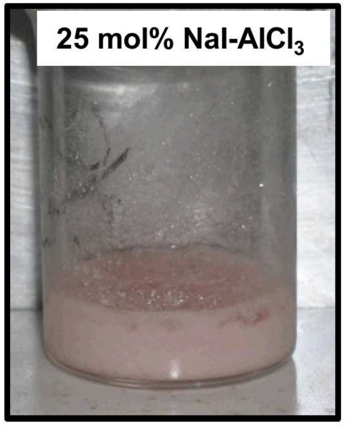
b) Particle-related loss of capacity



$NaI-AlCl_3$ at 150°C



$NaI-AlCl_3$ and $NaI-AlBr_3$ salts at 90°C



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

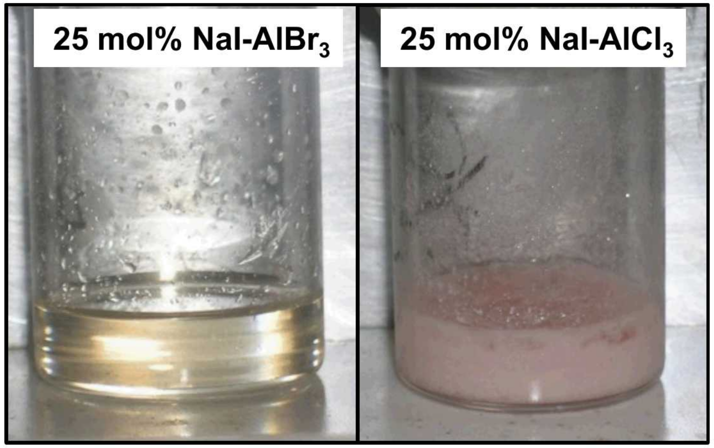
Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

NaI-AlBr$_3$: An Electrochemically Promising Low Temperature Molten Catholyte

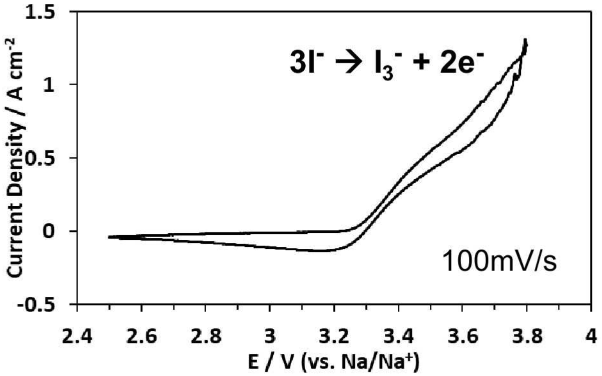
The NaI-AlBr$_3$ catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures.

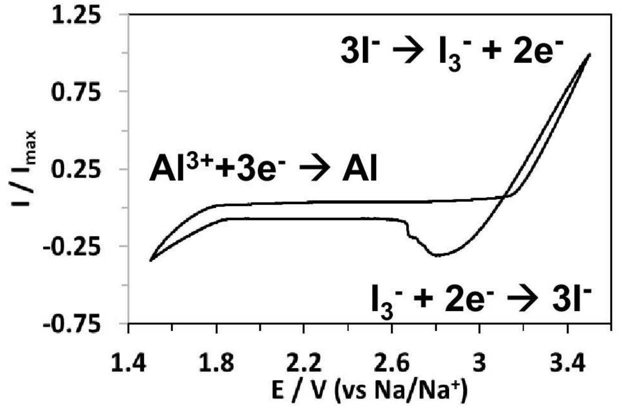
- 25:75 NaI-AlBr$_3$ salt completely molten at 90 °C
- Larger fully molten capacity range (~5-25 mol% NaI)

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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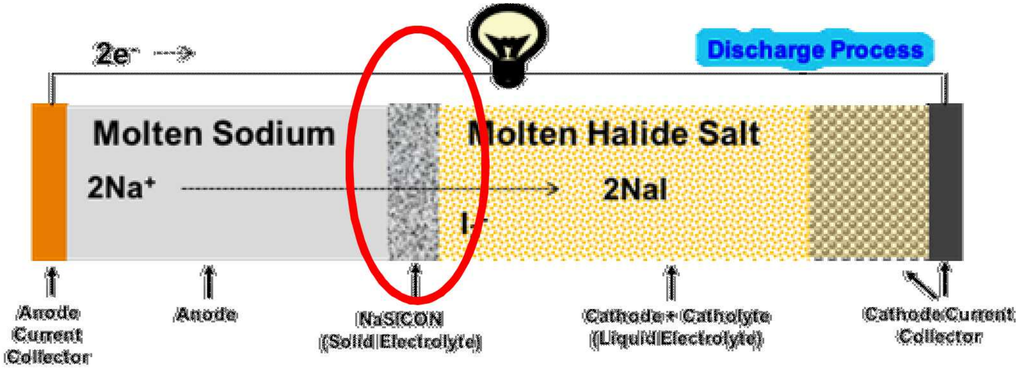

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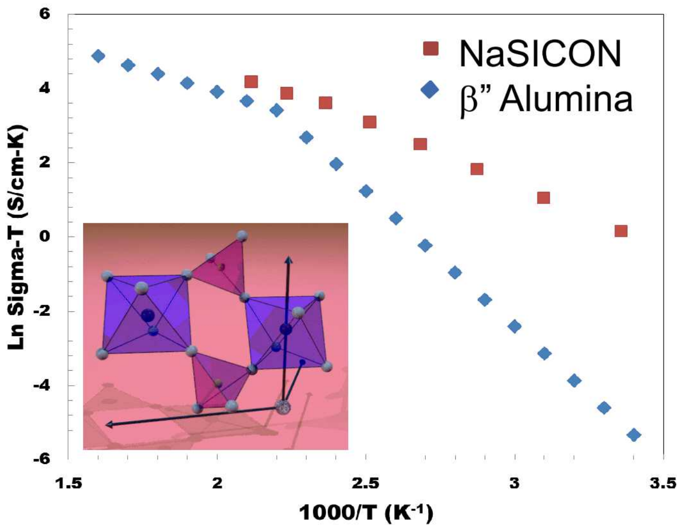
$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

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



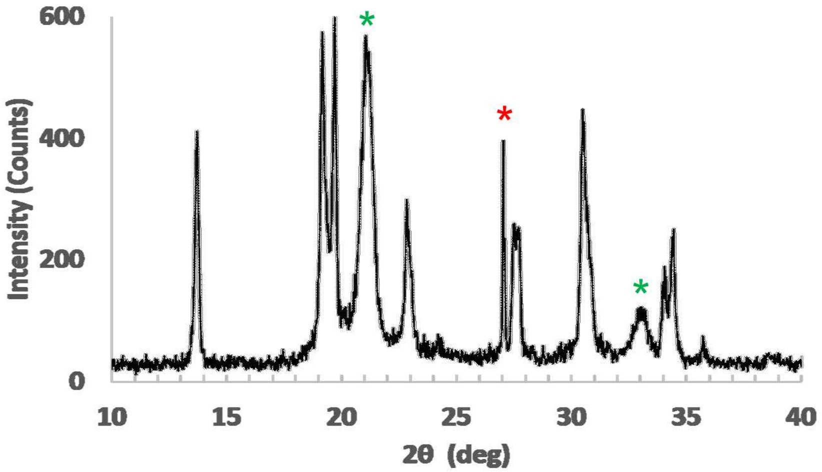
Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

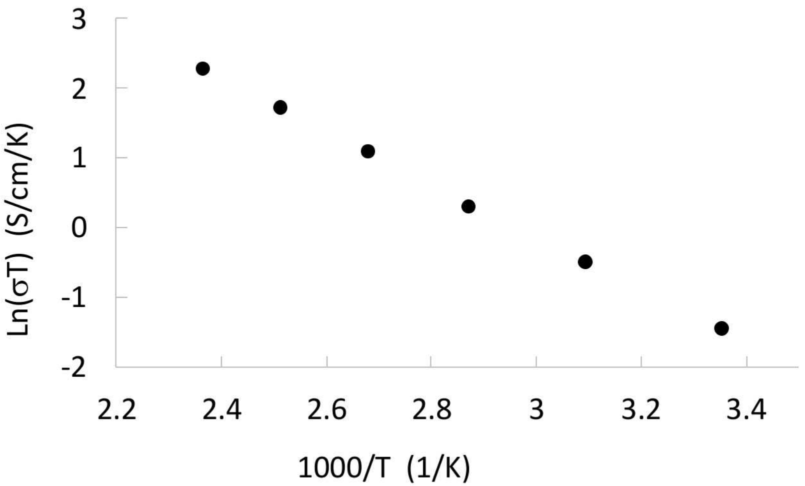
Conventional Synthesis

<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°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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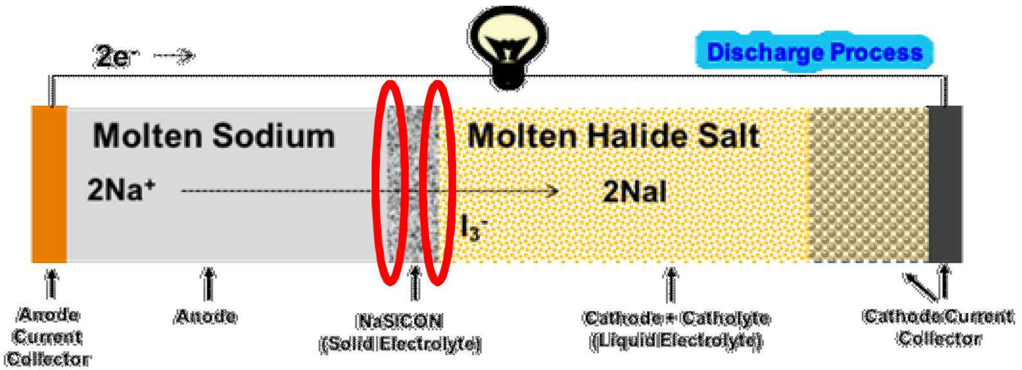

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Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

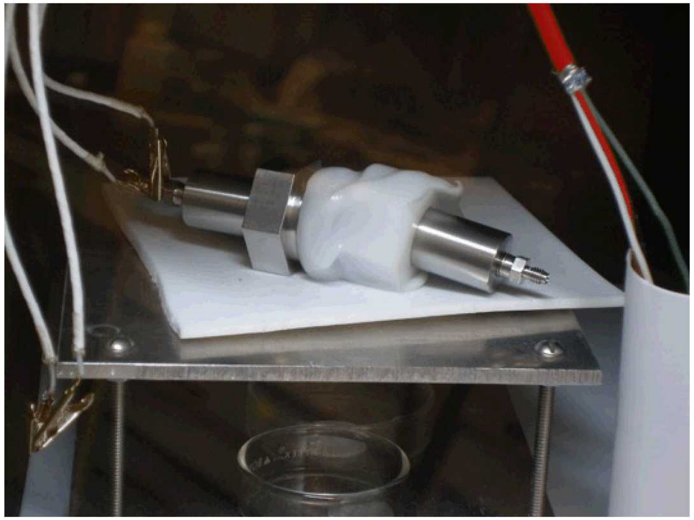
Compatibility must be considered for:

- 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.

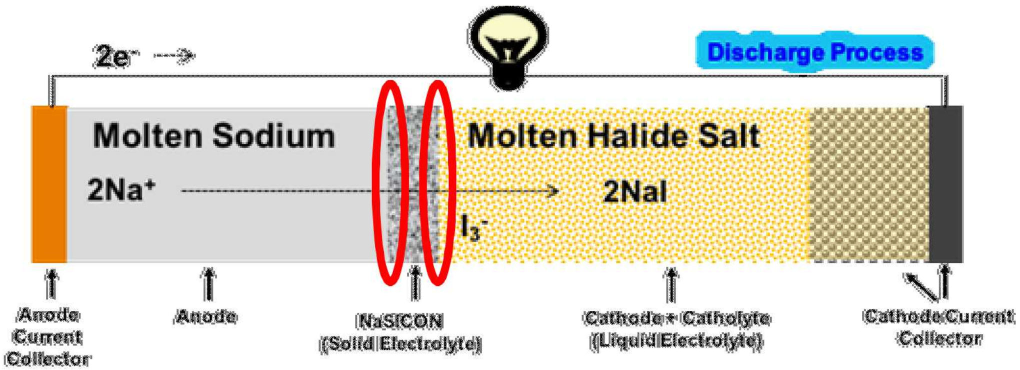
Thermal and mechanical stability



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.

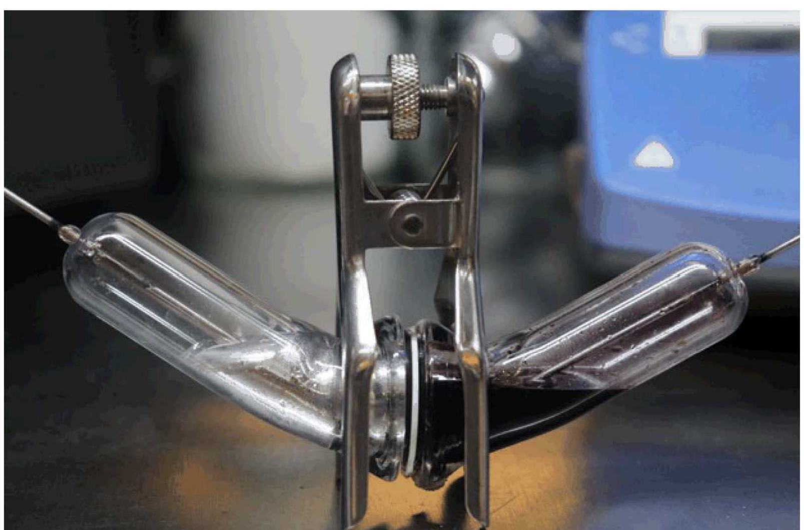


Na-NaI battery:

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

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

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



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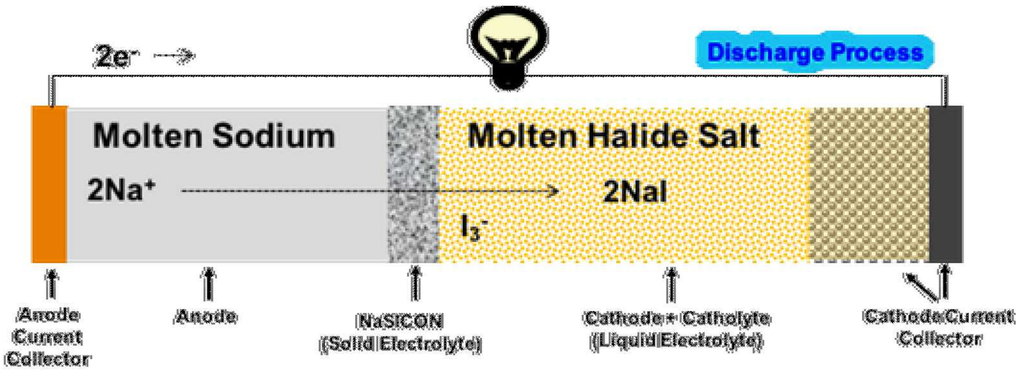

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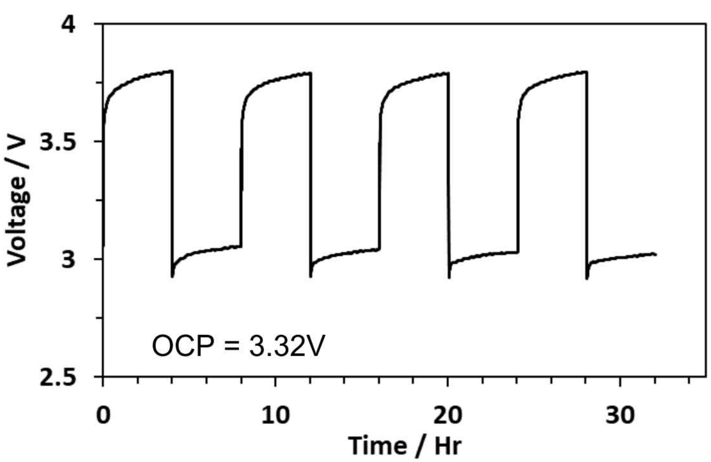
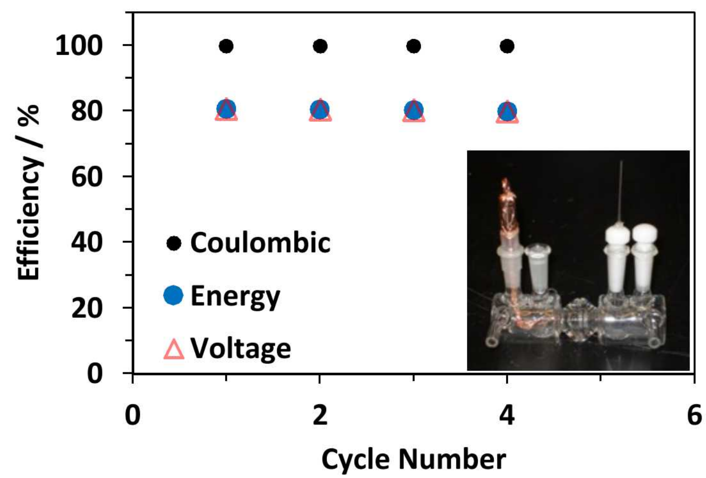
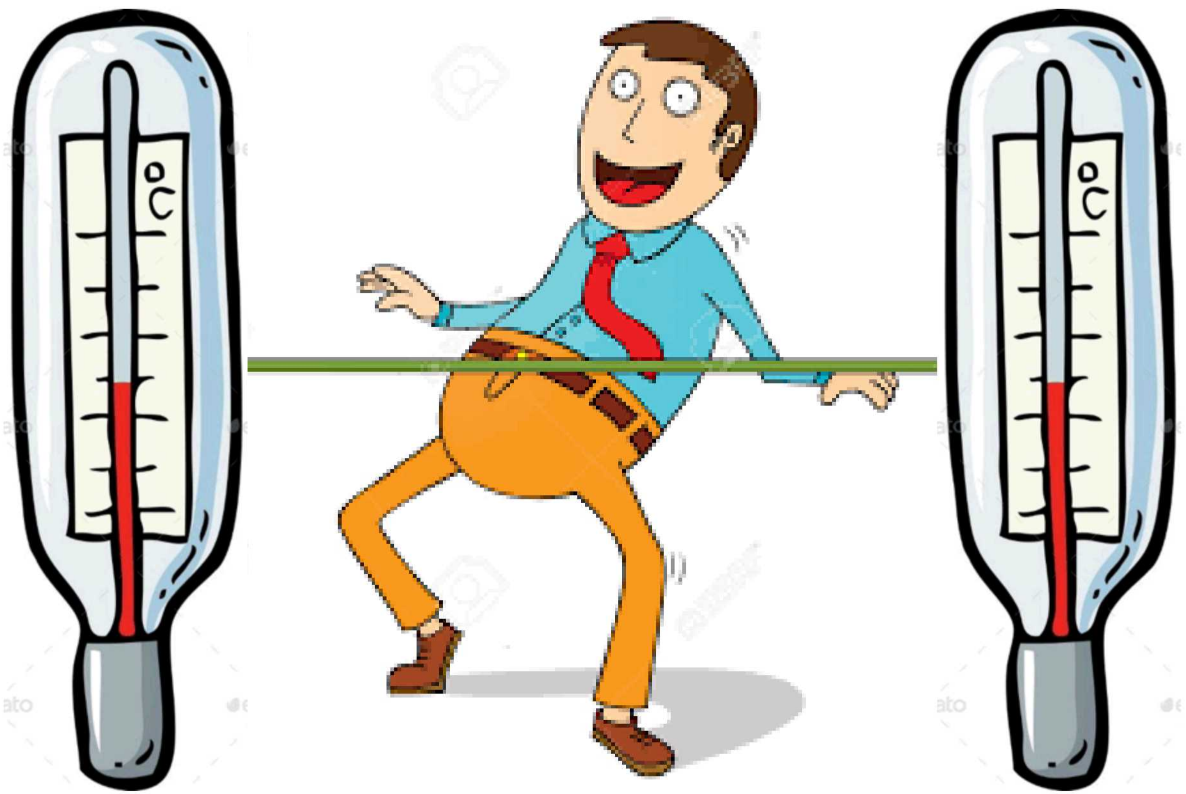


Battery cycling at 110°C!

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



How low can we go?



Low*est* Temperature Molten Na-NaI Batteries

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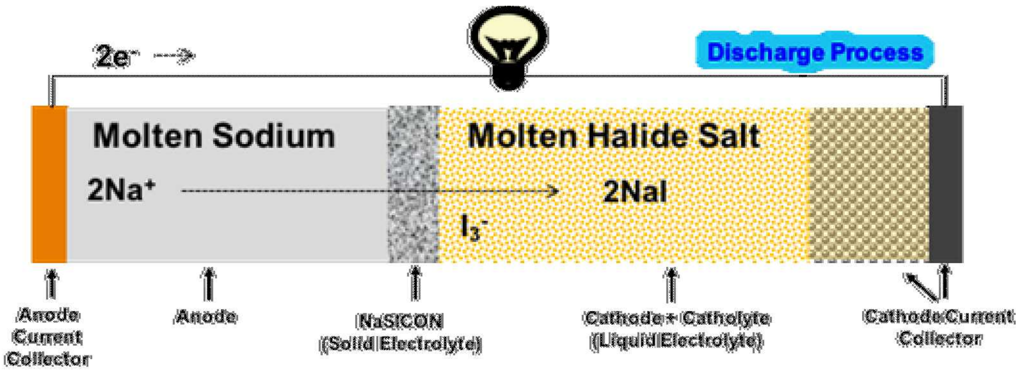

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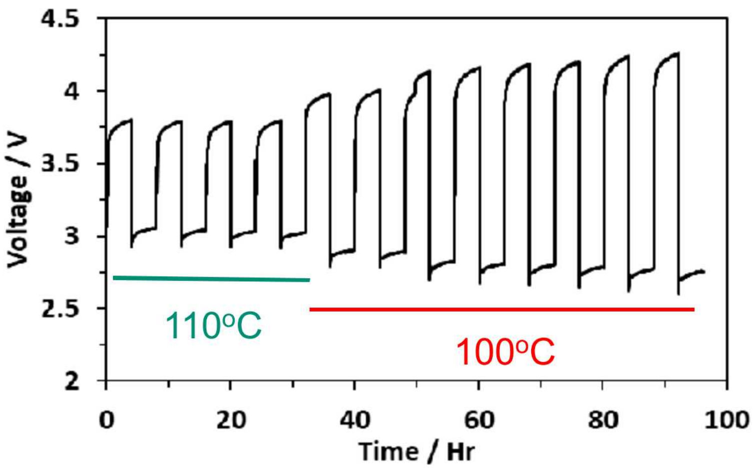
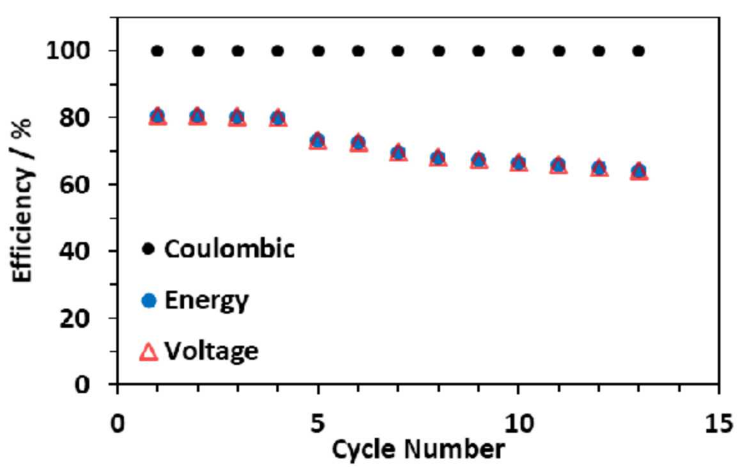


Battery cycling at **100°C**!

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



Low*est* Temperature Molten Na-NaI Batteries

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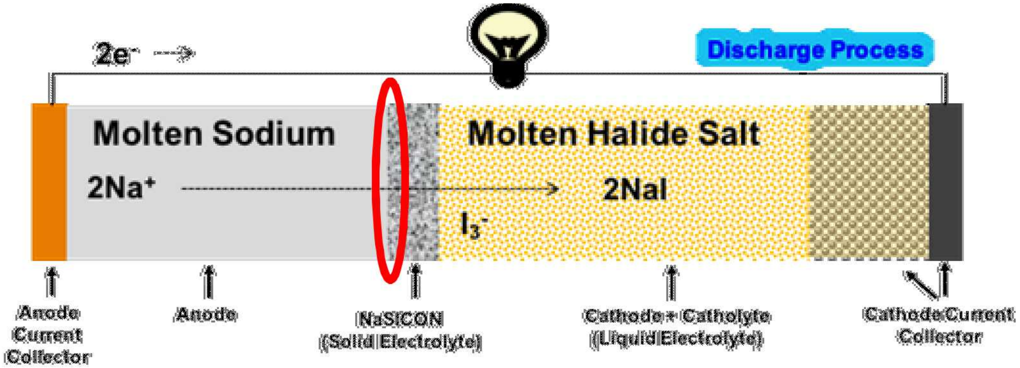

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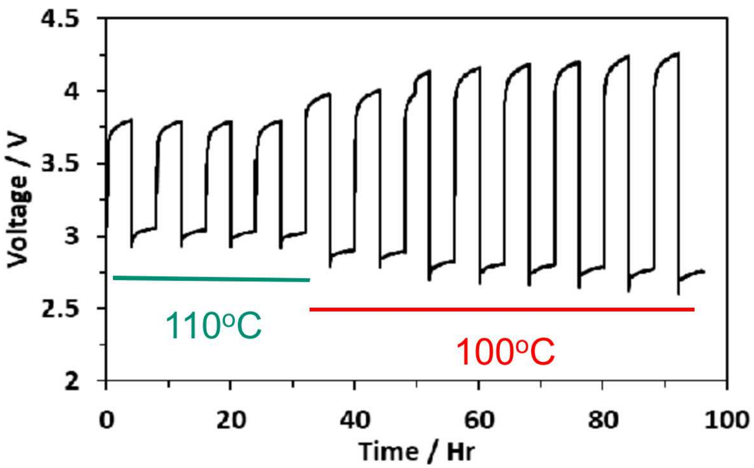

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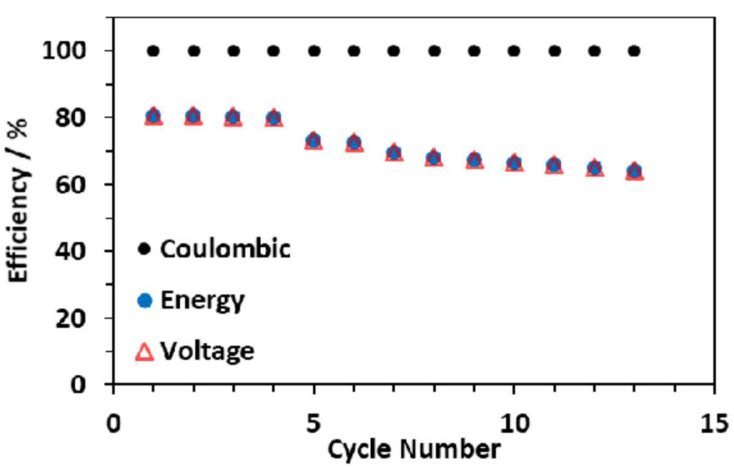
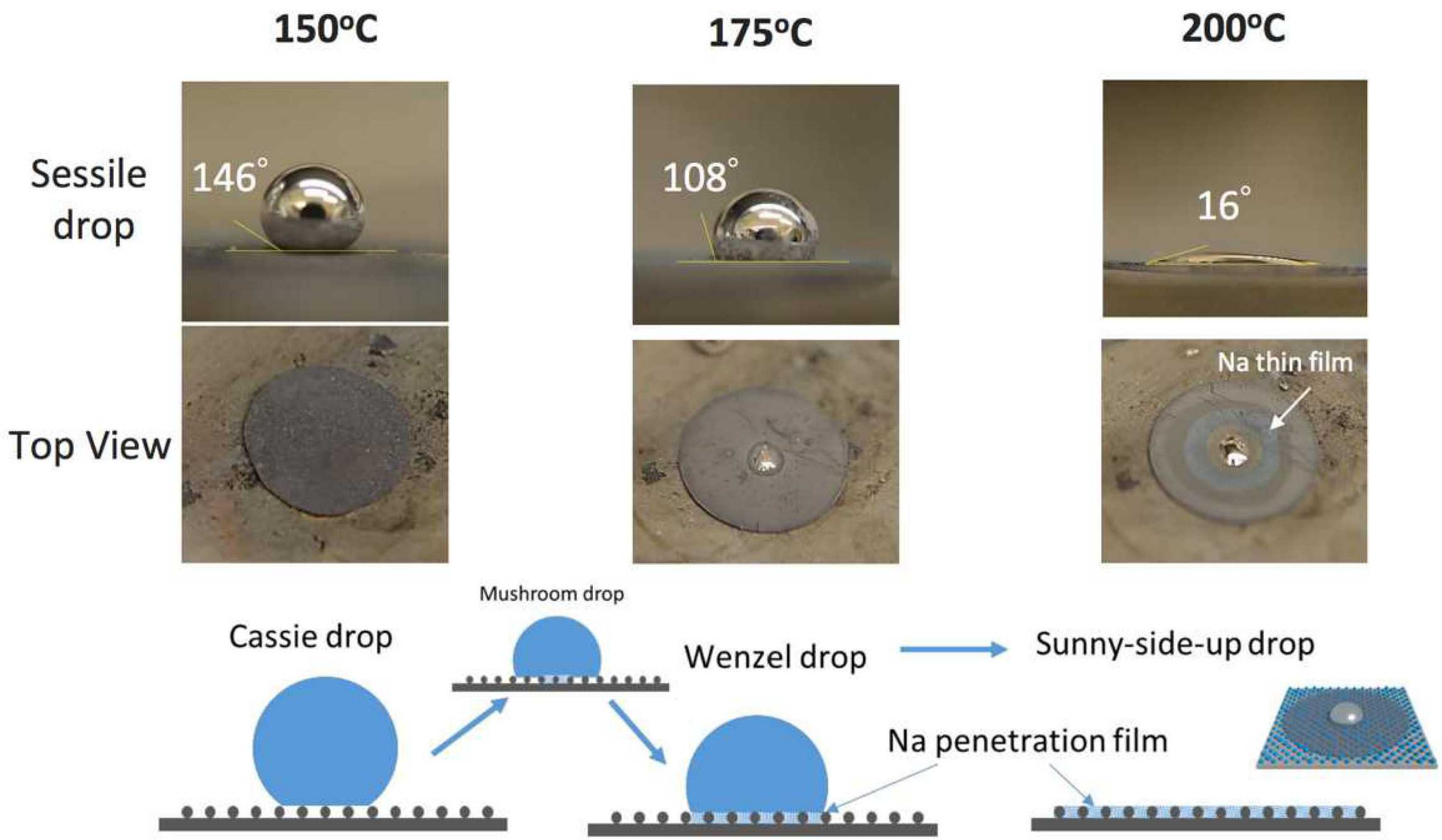


Follow the Bouncing…Sodium!

110^{o}C

Molten Na-Wetting is Temperature Dependent



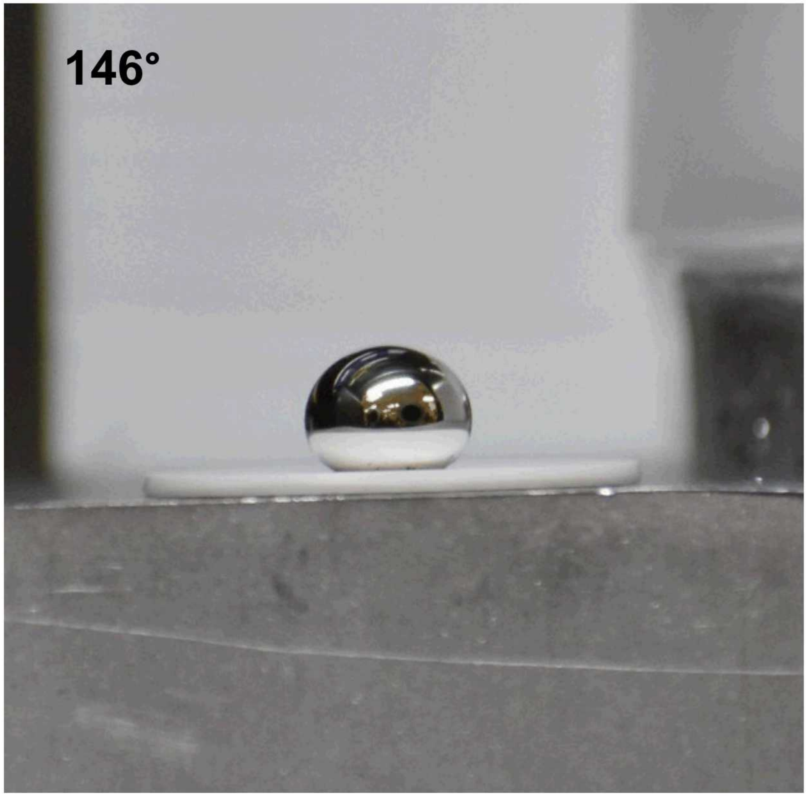
- ❑ Na wetting in "sunny-side-up" shape is responsible for high battery performances

G. Li, 2018 DOE OE Peer Review

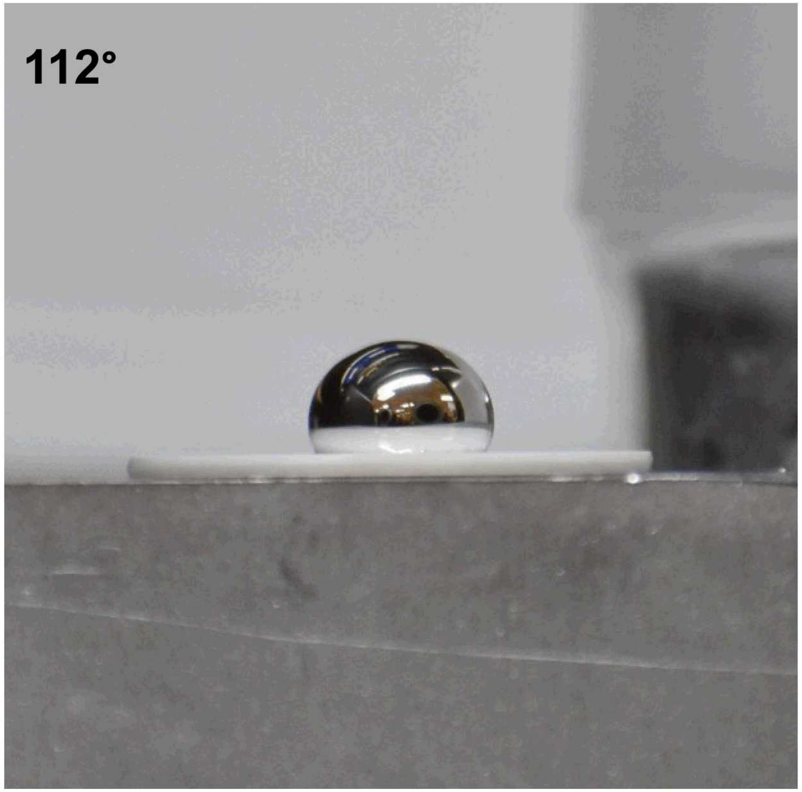
NaSICON Surface Treatment Affects Na-Wetting

Polishing NaSICON surface significantly improves Na-wetting at 110^{o}C.

Unpolished

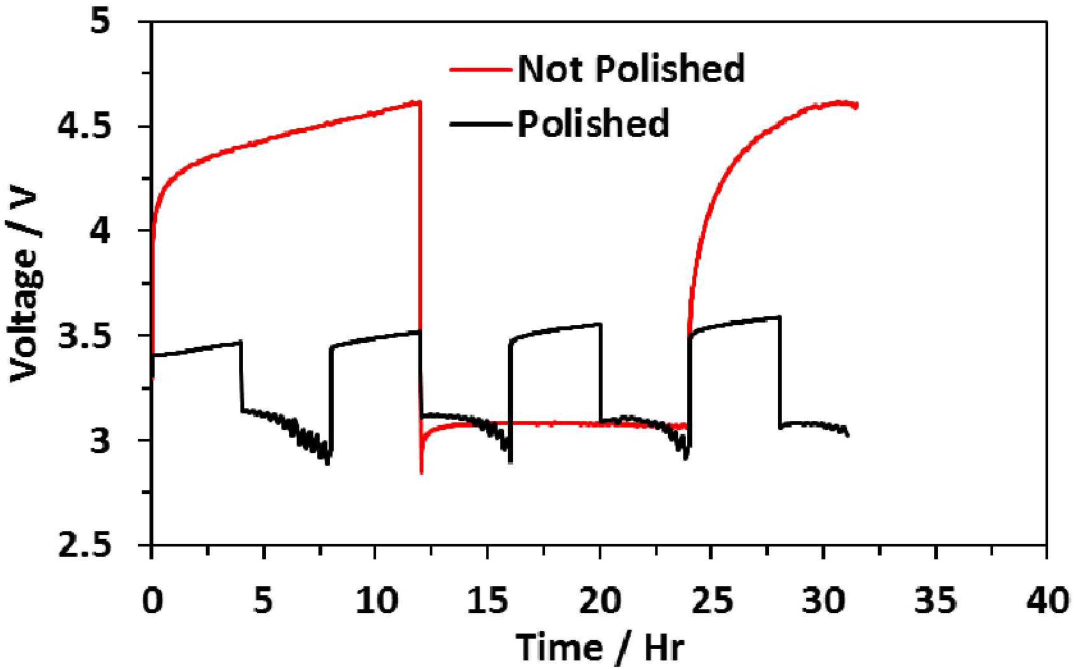


Polished



Separator Treatment Affects Cell Performance

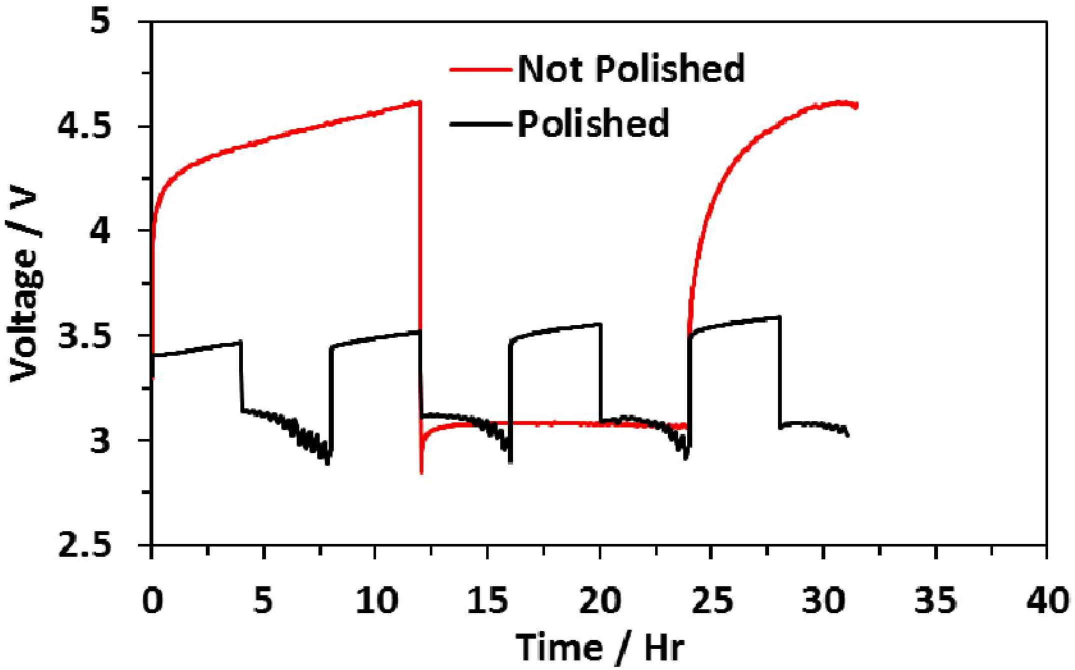
First, clearing roughening the NaSICON surface with a surface polish allowed higher operating current density and lower overpotentials.

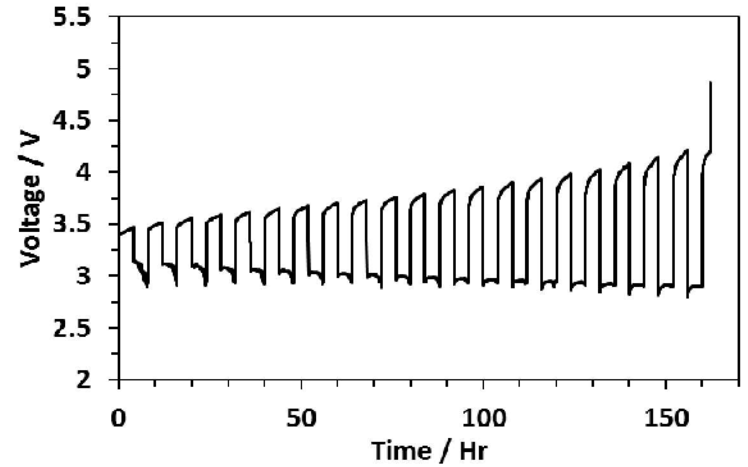


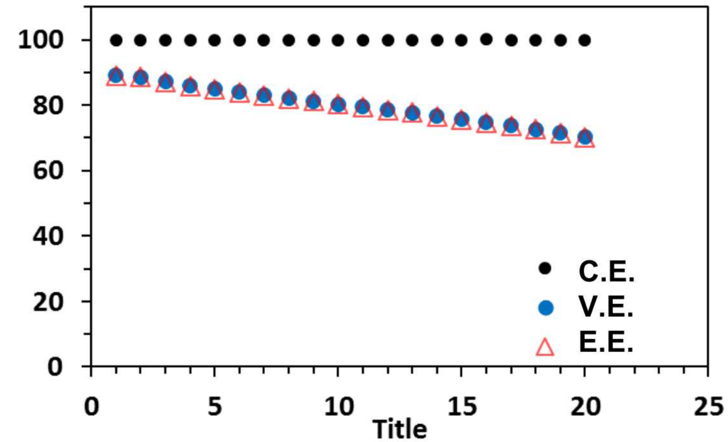
- **Un**polished NaSICON battery operated at ± 0.299 mA current C/12 1% DOD
- Polished NaSICON battery operated at ±0.897mA C/4 1% DOD

Separator Treatment Affects Cell Performance

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

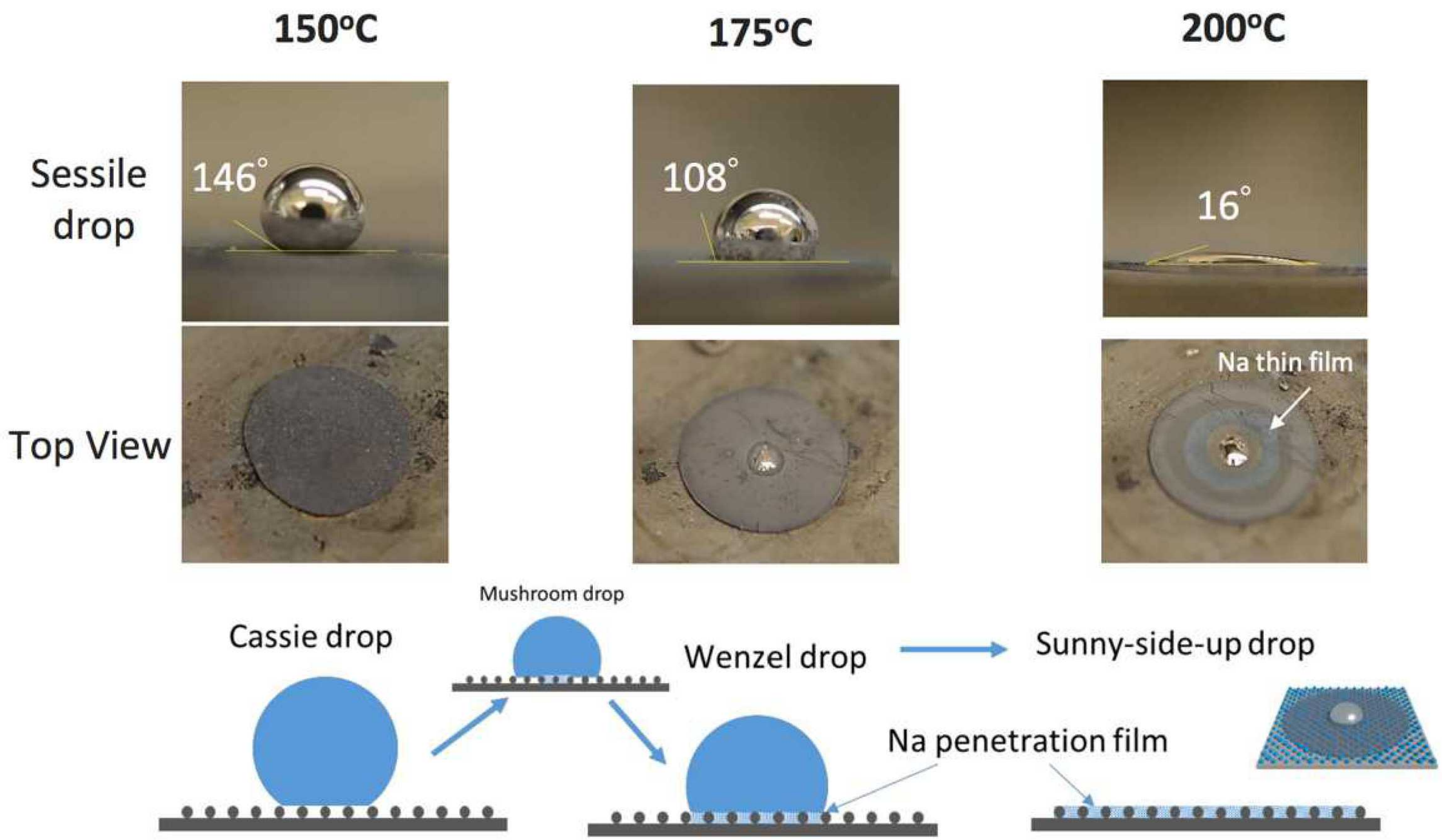






Polished NaSICON alone still shows relatively rapid performance fade.

What about PbO?



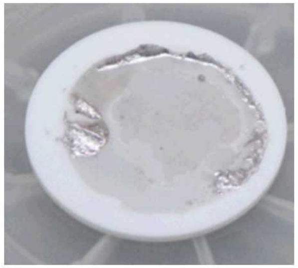
- ❑ Na wetting in "sunny-side-up" shape is responsible for high battery performances

Pacific Northwest NATIONAL LABORATORY

G. Li, 2018 DOE OE Peer Review

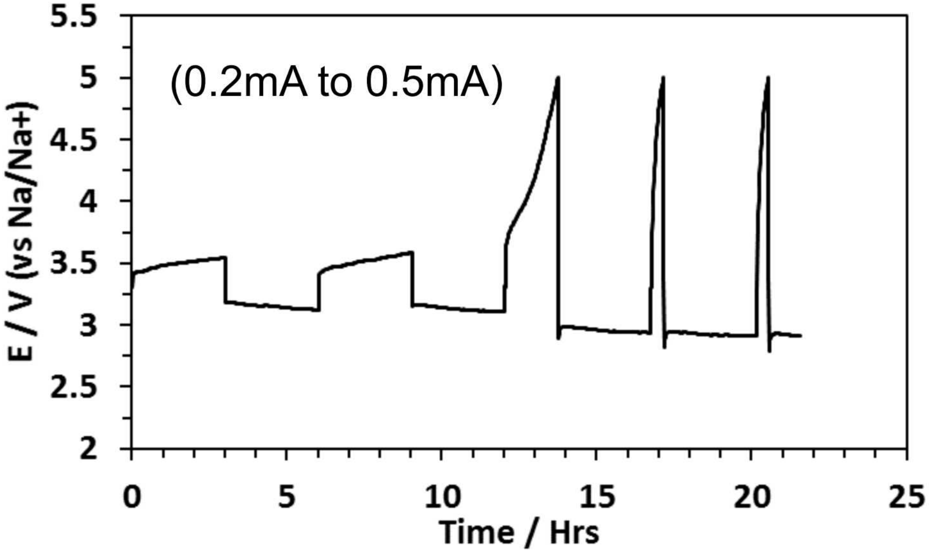
Carbon Coating NaSICON

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



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

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



Separator Treatment Affects Cell Performance

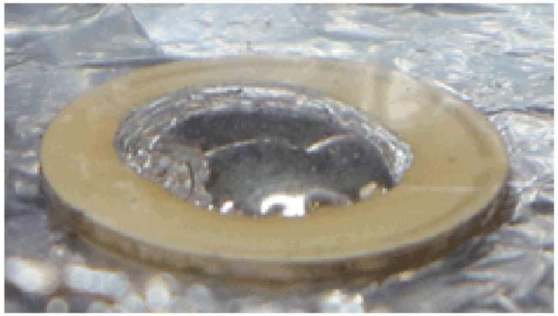
At reduced temperatures, sodium wetting on NaSICON is not adequate.

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

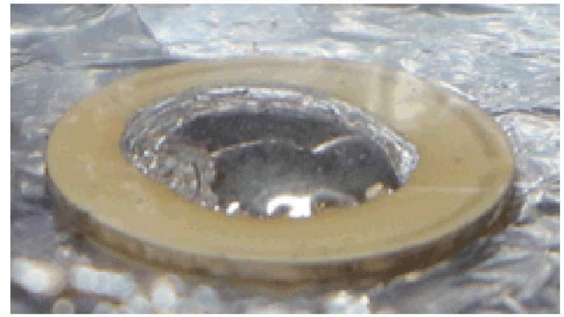


Heated above 380°C for 30 minutes

Separator Treatment Affects Cell Performance

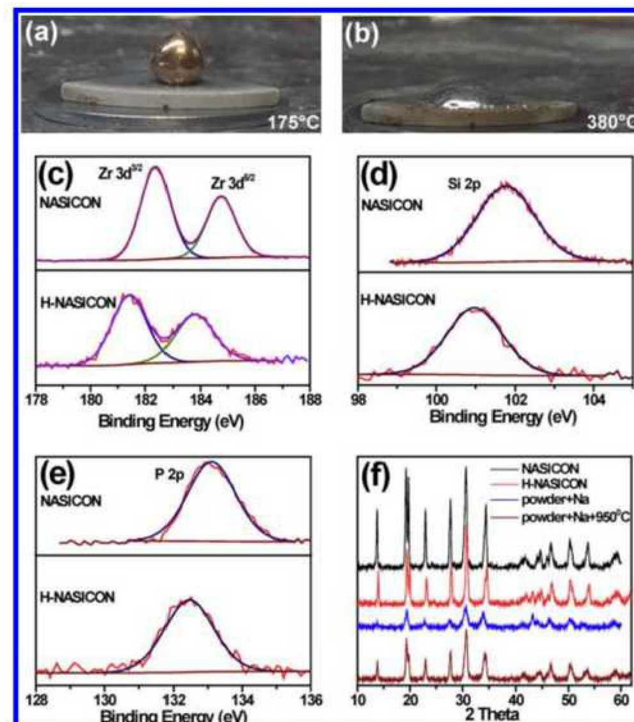
A high temperature soak of Na metal on the NaSICON modifies interfacial wetting.

Heated at 100-200°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.

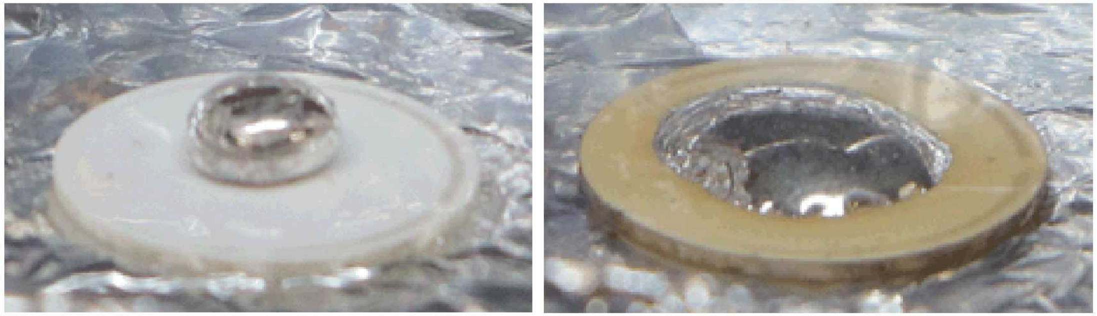


W. Zhou, *et al. ACS Cent. Sci.* (2017) **3**, 52-57.

Separator Treatment Affects Cell Performance

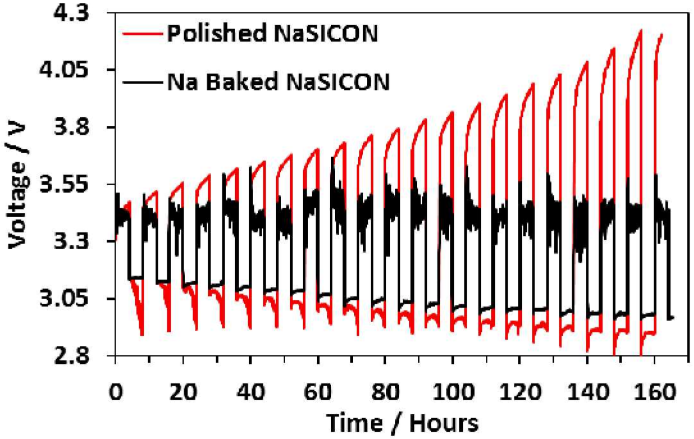
A high temperature soak of Na metal on the NaSICON modifies interfacial wetting.

Heated below 200°C for 30 minutes



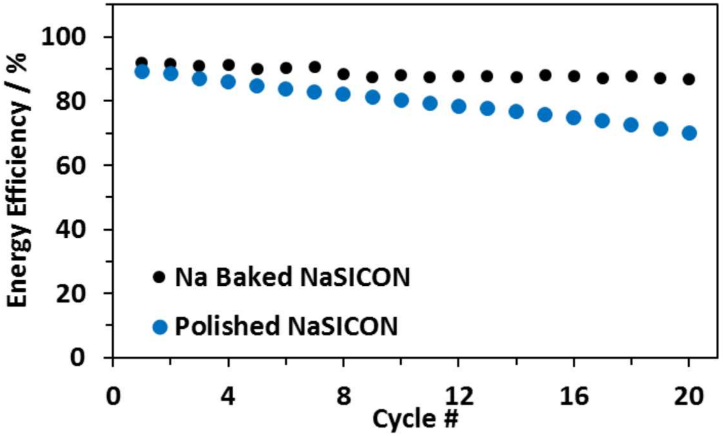
Heated above 380°C for 30 minutes

Na-treated NaSICON shows lower overpotentials on battery cycling.



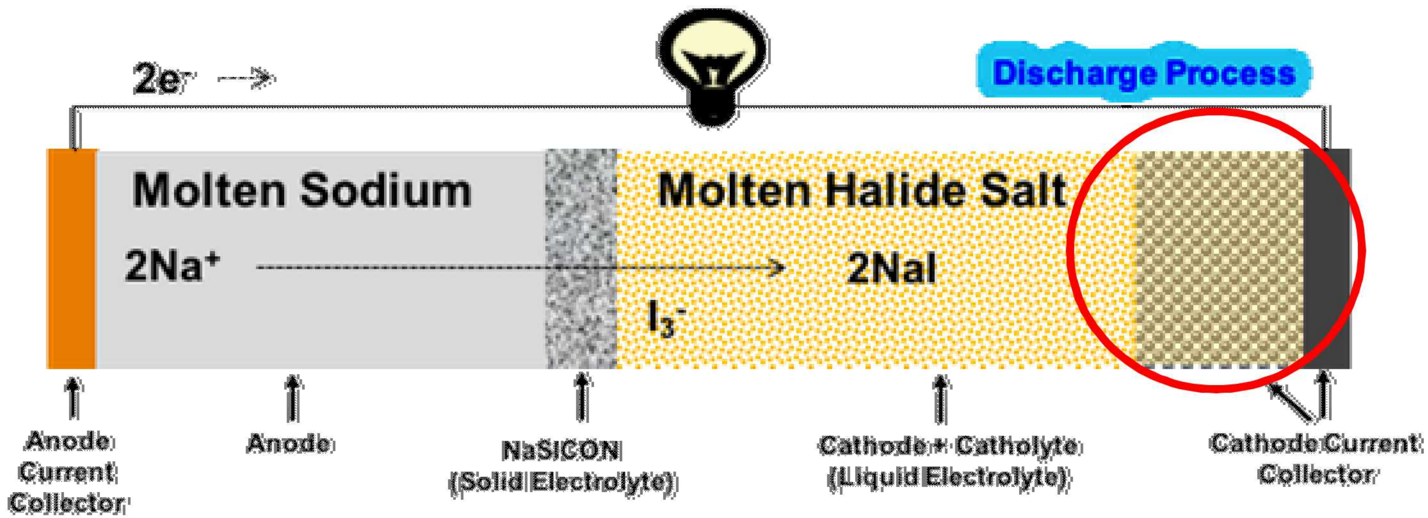
Battery cycling at 110°C!

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

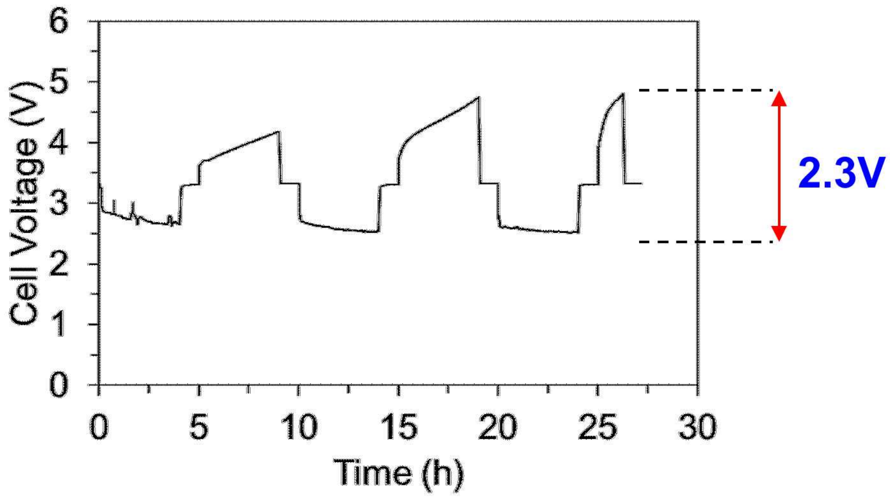
Is this “Good Enough?”


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

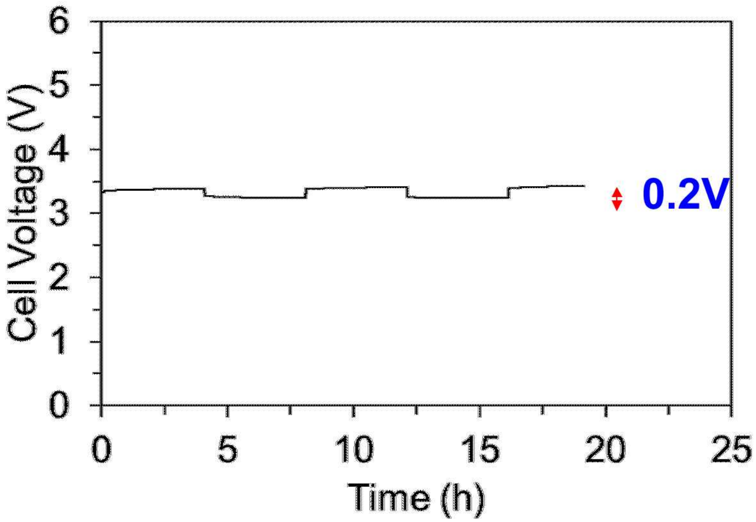
Cathode Current Collector

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

Without carbon felt current collector



With carbon felt, treated with 0.1M HCl overnight

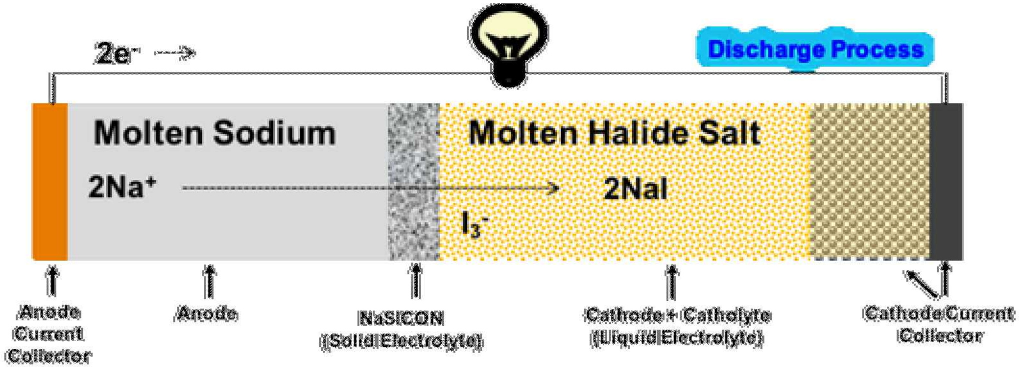


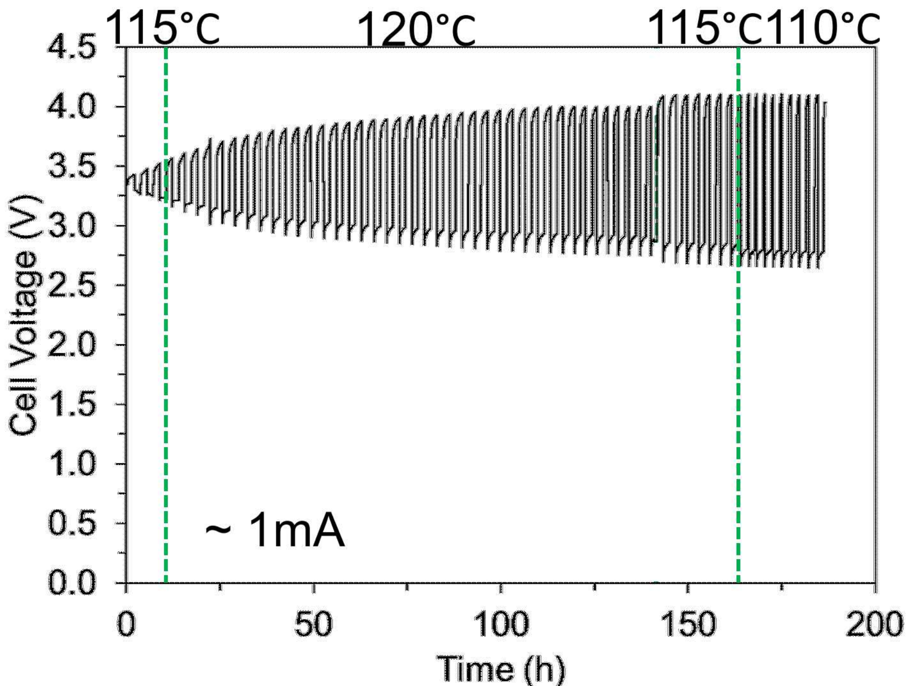
- 0.5mA current, 4h charge & discharge
- 1 hour rest between charge and discharge

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

Putting it all together

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

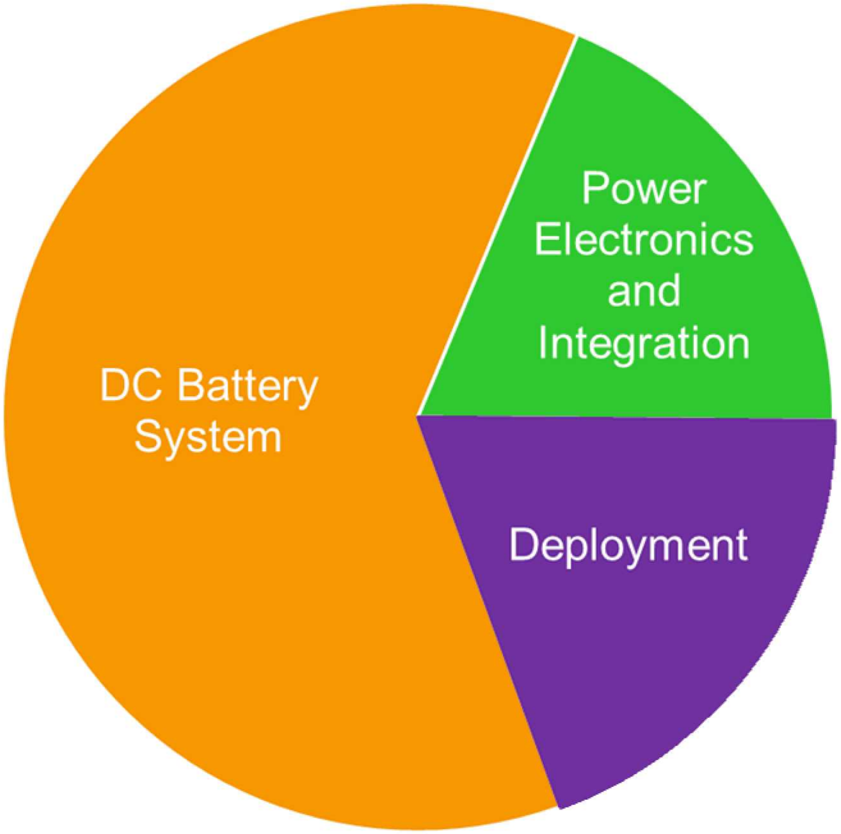




The right materials allow for high cyclability at low temperatures!

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 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-Na blocking NaSICON wetting treatments (Sb?, Sn?)
- Chemical compatibility of 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

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Amanda Peretti
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Dr. Eric Allcorn
Sara Dickens
Dr. Babu Chalamala

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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

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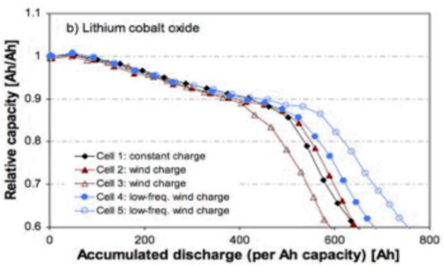
Backup Slides

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

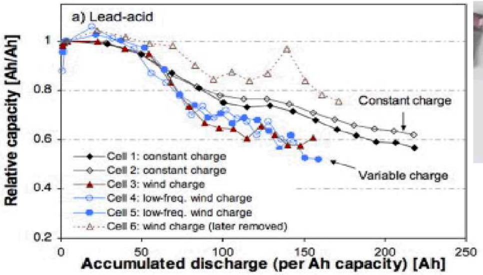


E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

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



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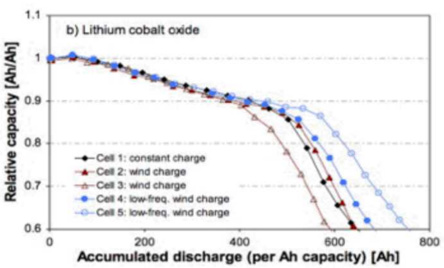

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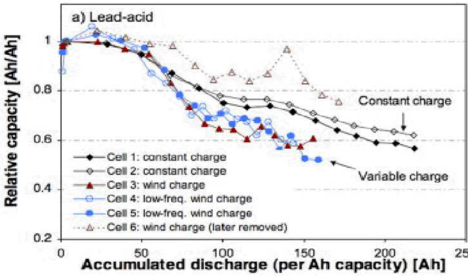


E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

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

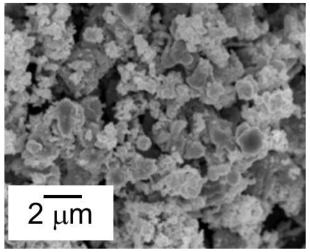
$2Na + 4S \leftrightarrow Na_2S_4$

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

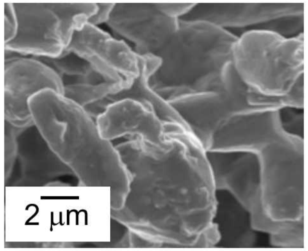
Na-NiCl$_2$ (E_{cell} ~ 2.6V)

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

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



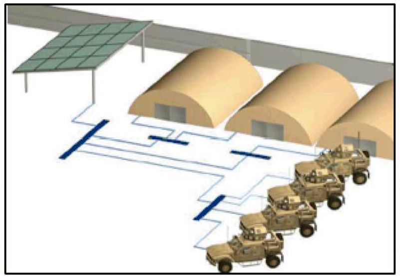
Particle Coarsening →



A Need for Grid-Scale Energy Storage Research


Renewable/Remote Energy

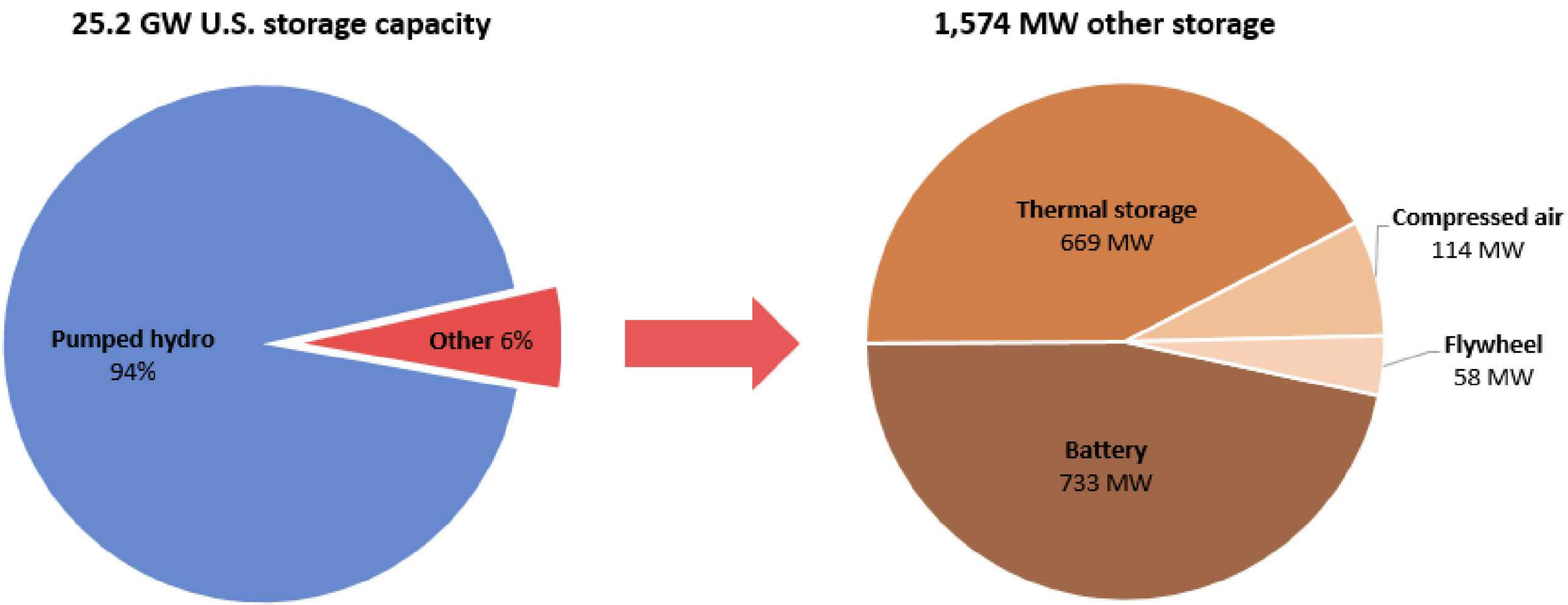
Grid Reliability



National Defense

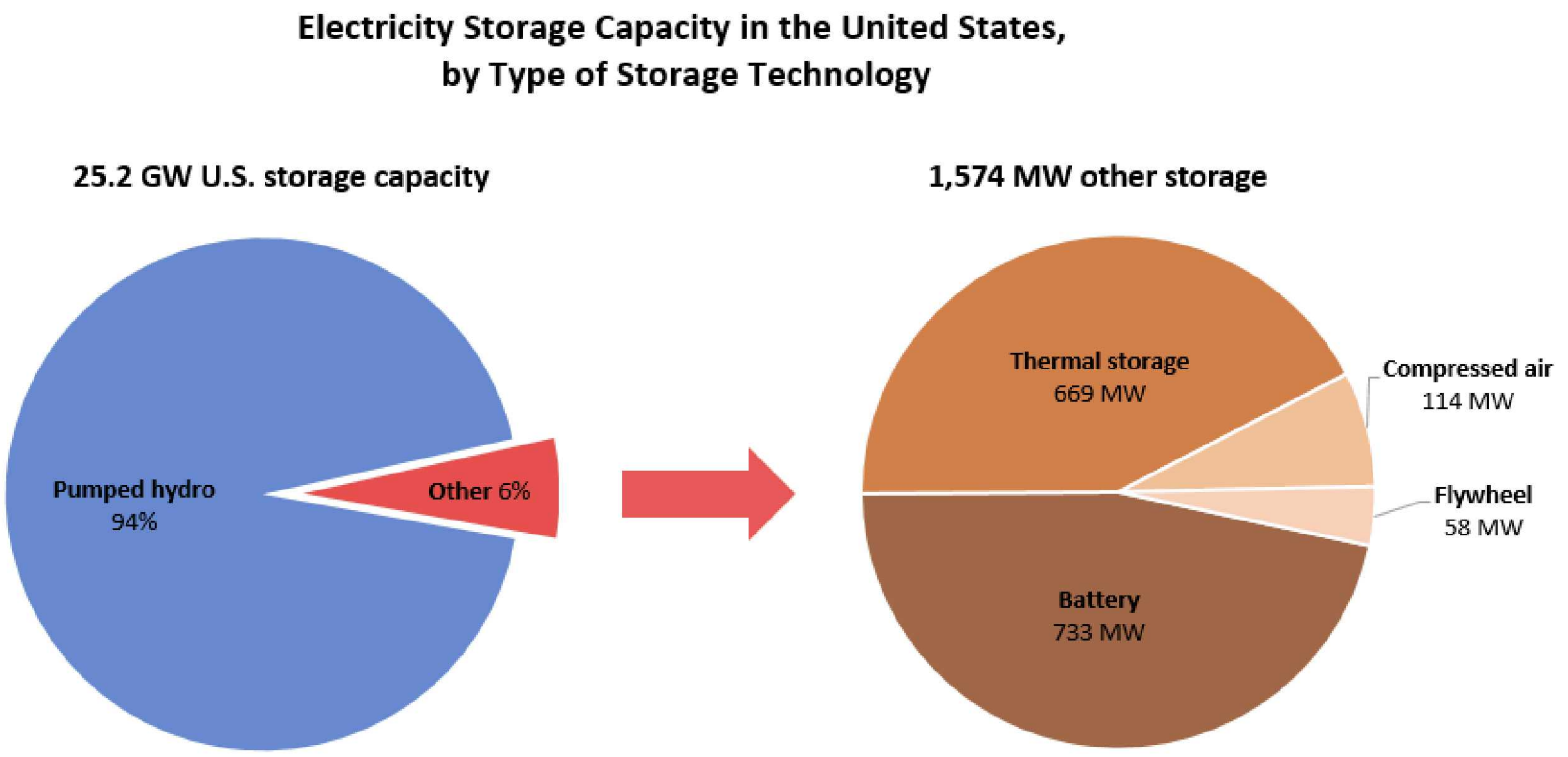
Emergency Aid

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

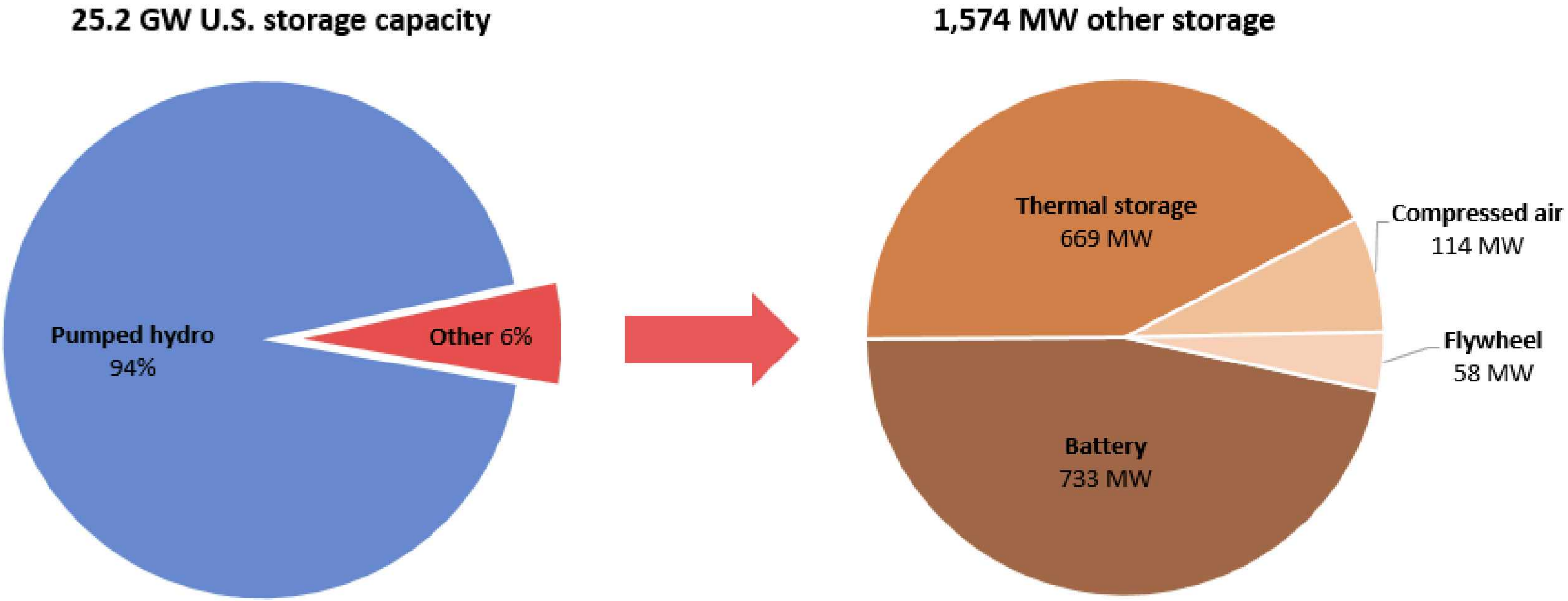
2.2% Battery Energy Storage and Pumped Hydro Storage

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

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!

Image from Can Stock Photo

Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

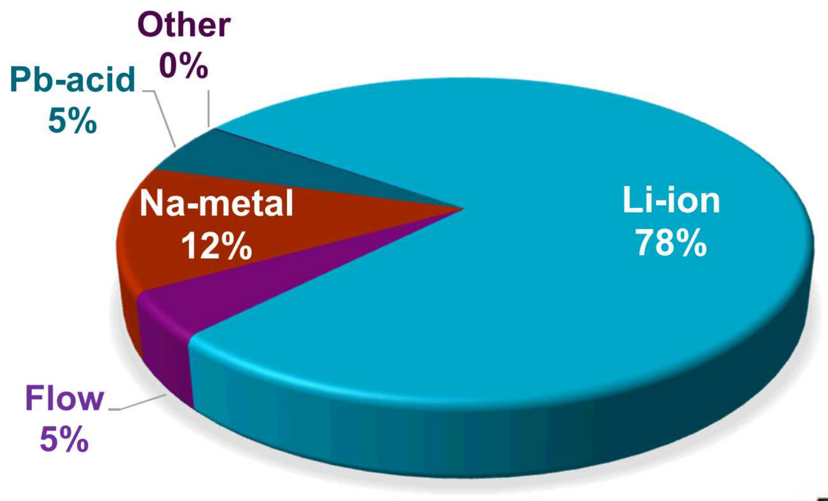
Alternative Summary

- 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!

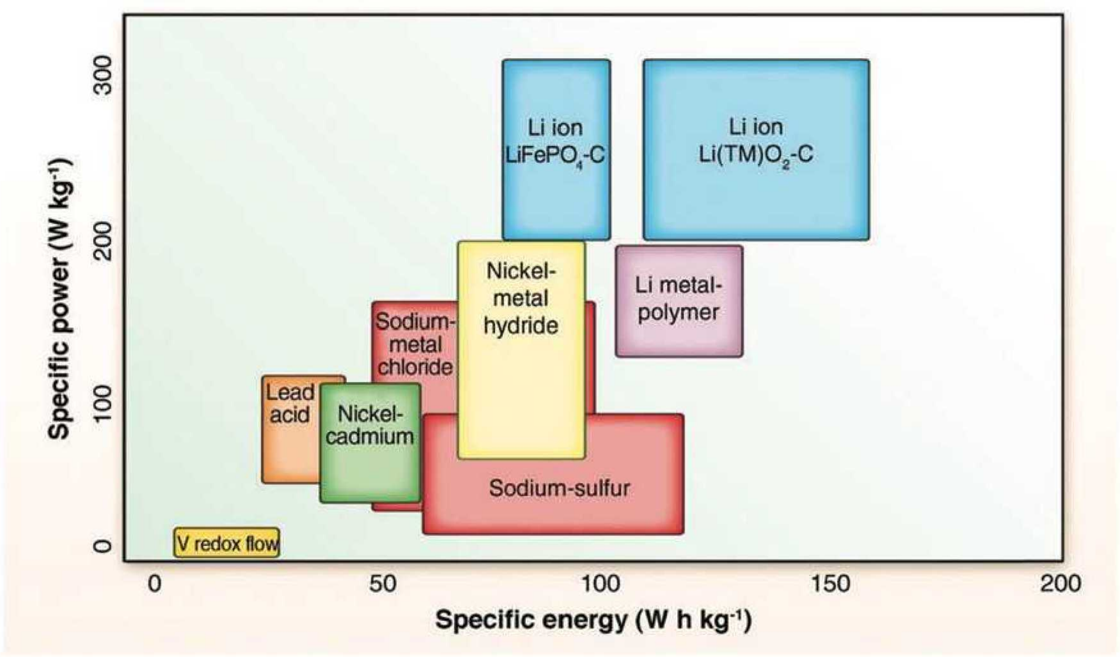
Current Battery Storage Deployments



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

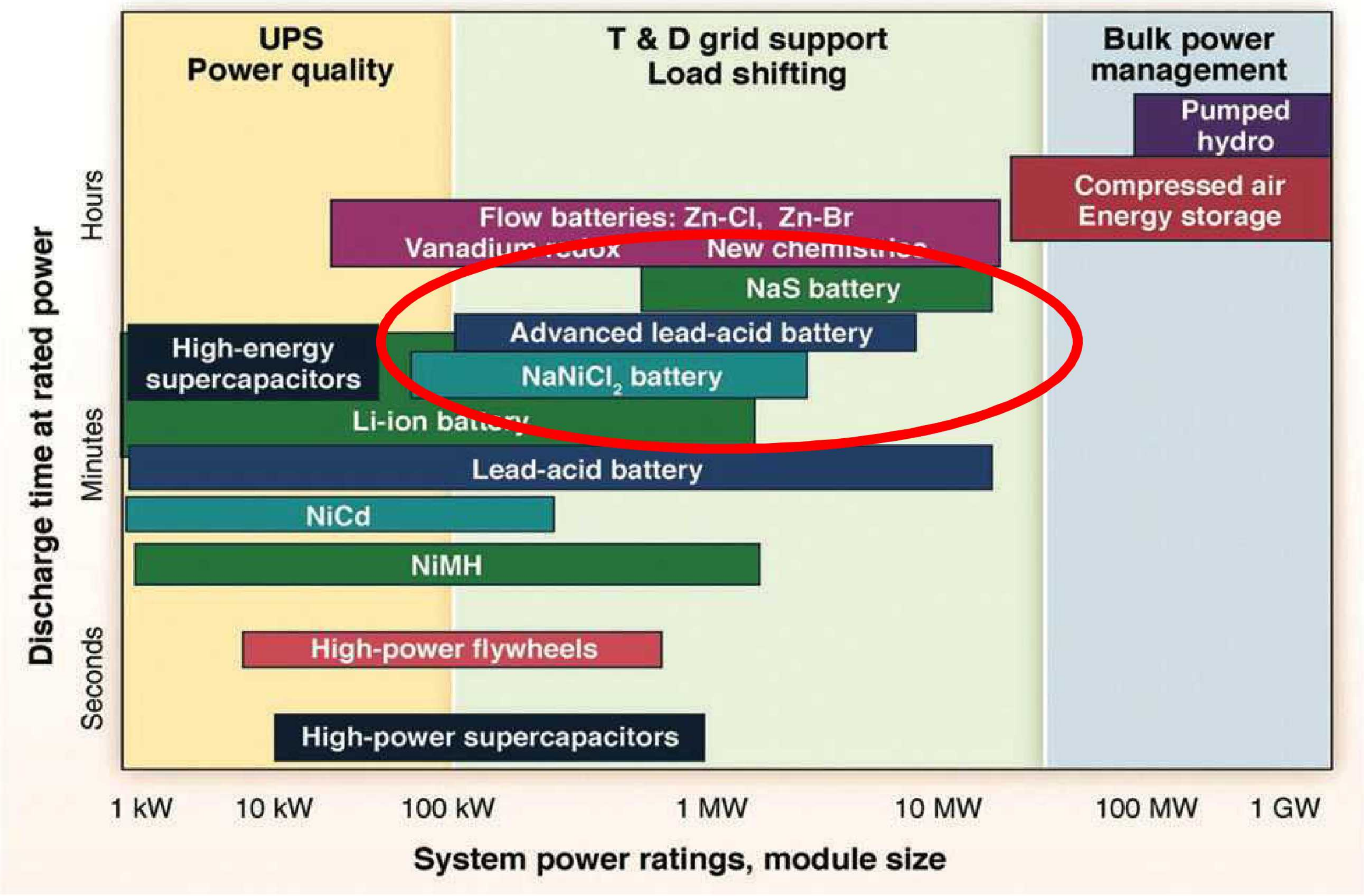
Li-ion batteries can not and should not become our singular grid-scale storage solution.

Different batteries have variable energy densities and power densities….

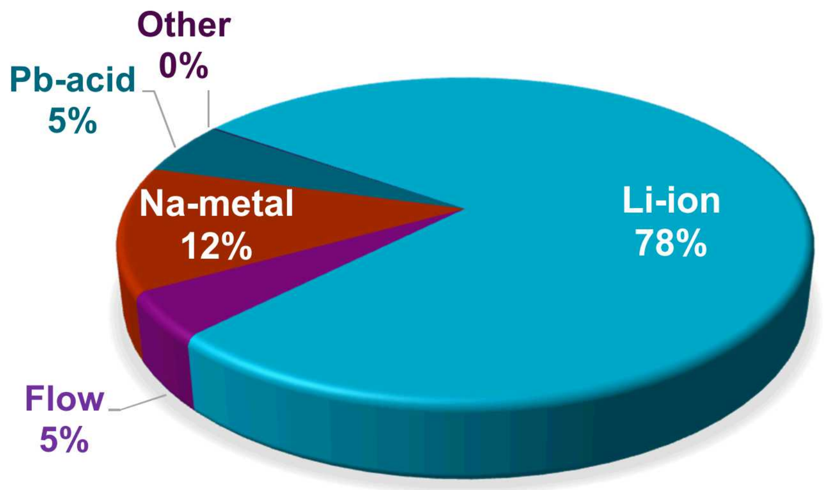


From: B. Dunn, *et al.*, *Science*, 2011, 334, 928–935.

Variable Battery Utility Matches Variable Battery Capability



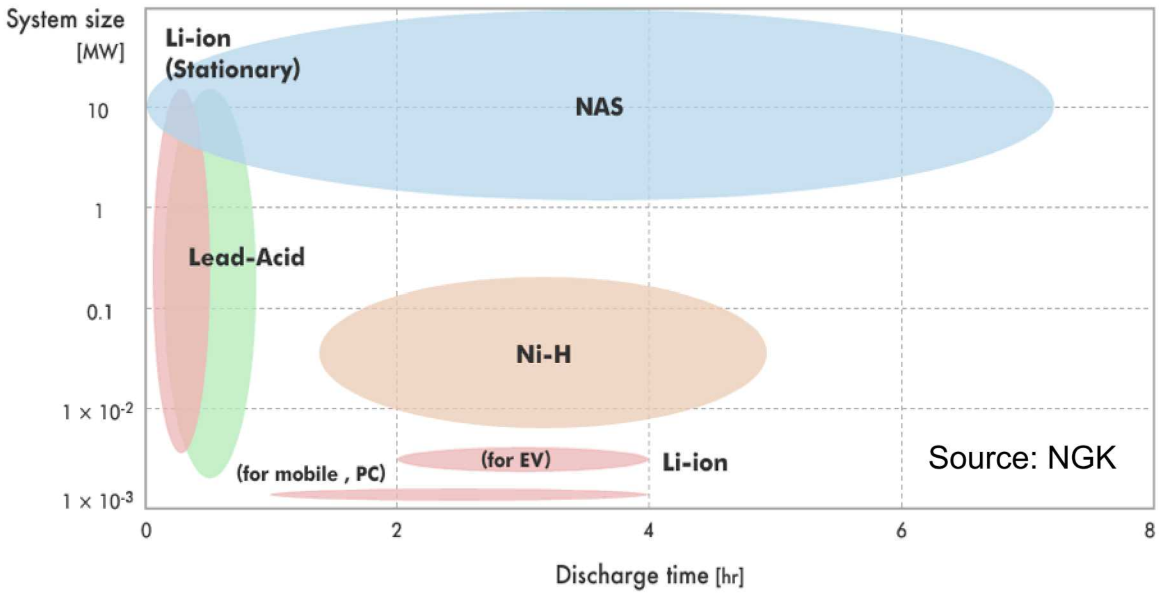
Current Battery Storage Deployments



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.

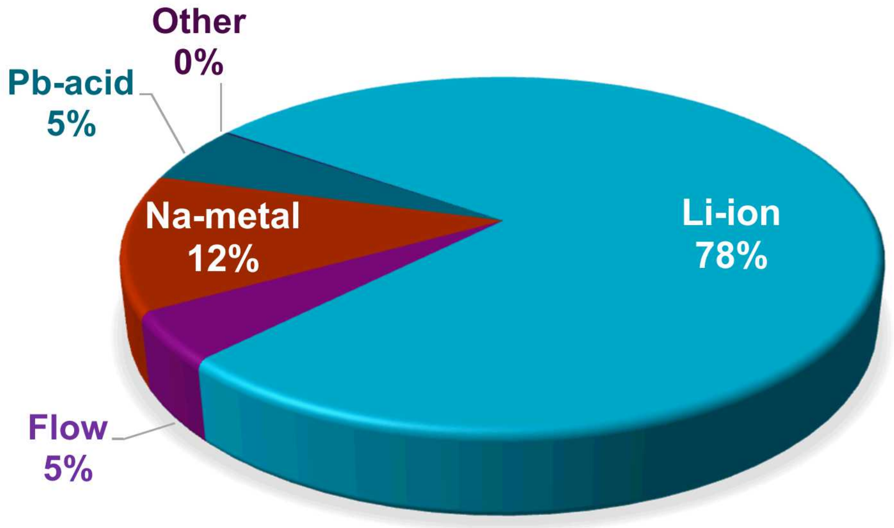
Different batteries have variable discharge durations…

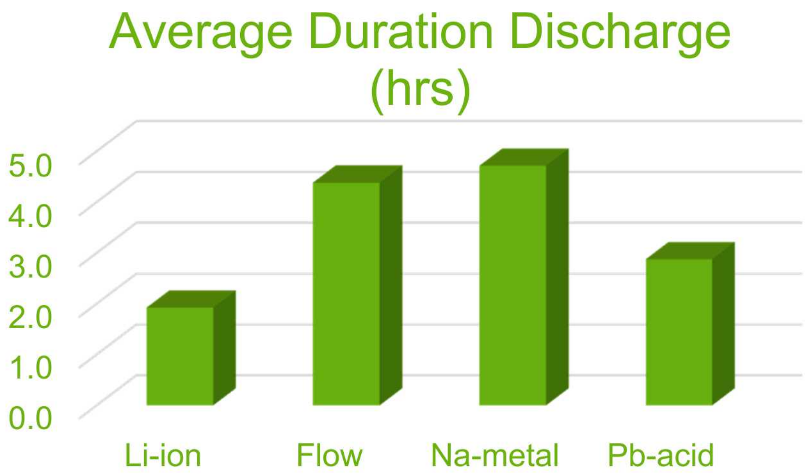


Source: NGK

Current Battery Energy Storage Deployments

*(Operational as of Nov. 2017)



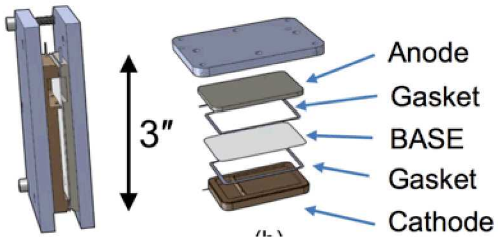


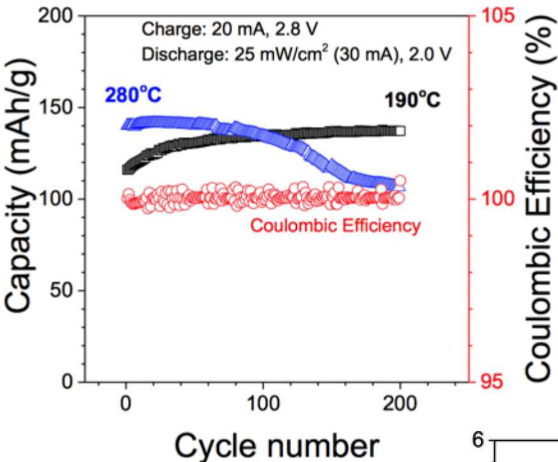
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

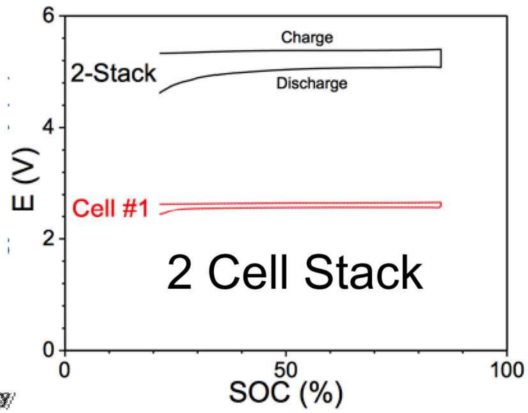
Source: *DOE Global Energy Storage Database*
http://www.energystorageexchange.org/ Nov. 2017

Intermediate Temperature "ZEBRA" Batteries

Planar Stack Configuration







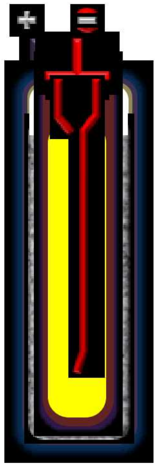
Pacific Northwest NATIONAL LABORATORY

RIST Research Institute of Industrial Science & Technology

Tubular Configuration

100Wh

250Wh



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.

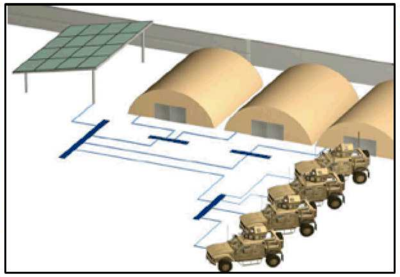
SK

CERAMATEC TOMORROW'S CERAMIC SYSTEMS

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*
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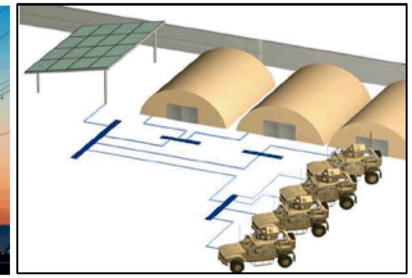

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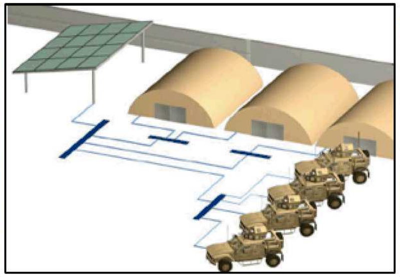

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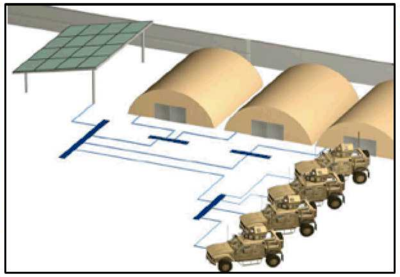

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We will need much, much more storage on our grid to accommodate increasing renewable penetration and the transition to a clean energy economy.

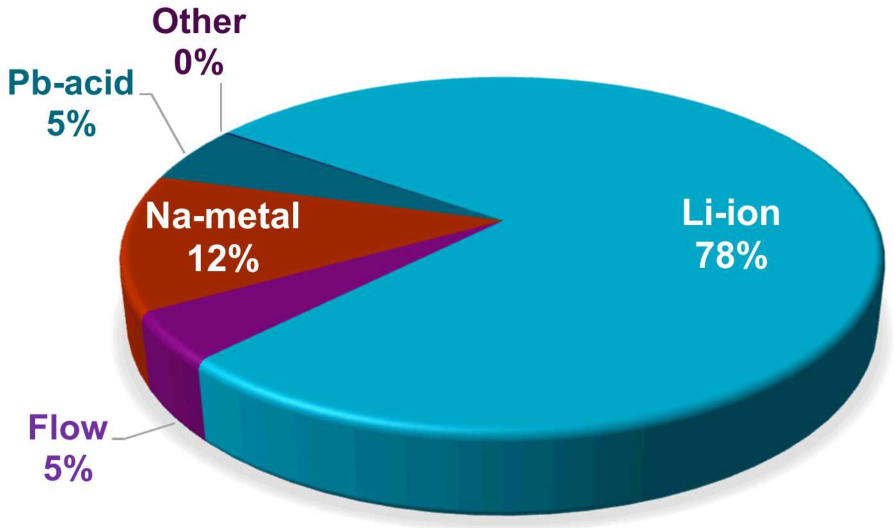
- "Energy" applications – slower times scale, large amounts of energy
- "Power" applications – faster time scale, real-time control of the electric grid

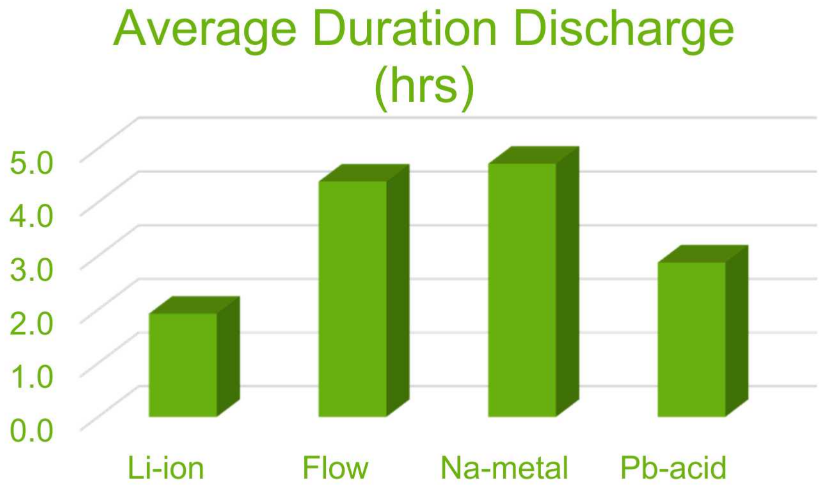
Current Barriers:

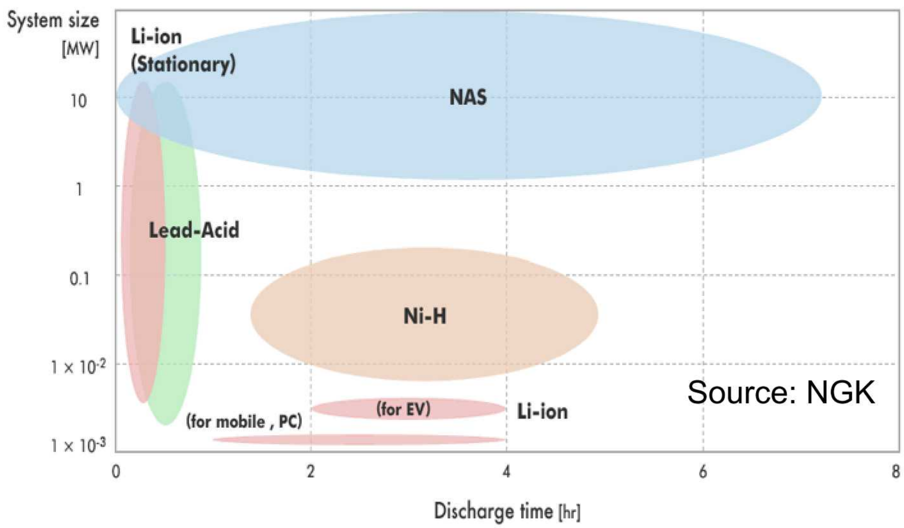
- Expensive, especially in energy markets (need for continued R&D)
- Electricity markets do not have market mechanisms for services ES can provide (need to reduce regulatory and policy hurdles)

Current Battery Energy Storage Deployments

*(Operational as of Nov. 2017)







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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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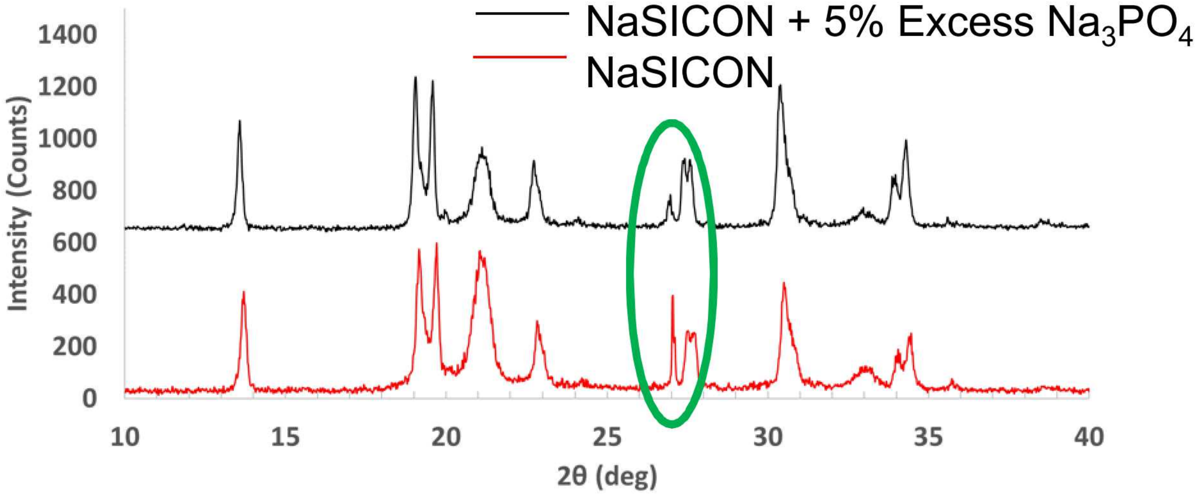
Secondary Phase Formation

- 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!

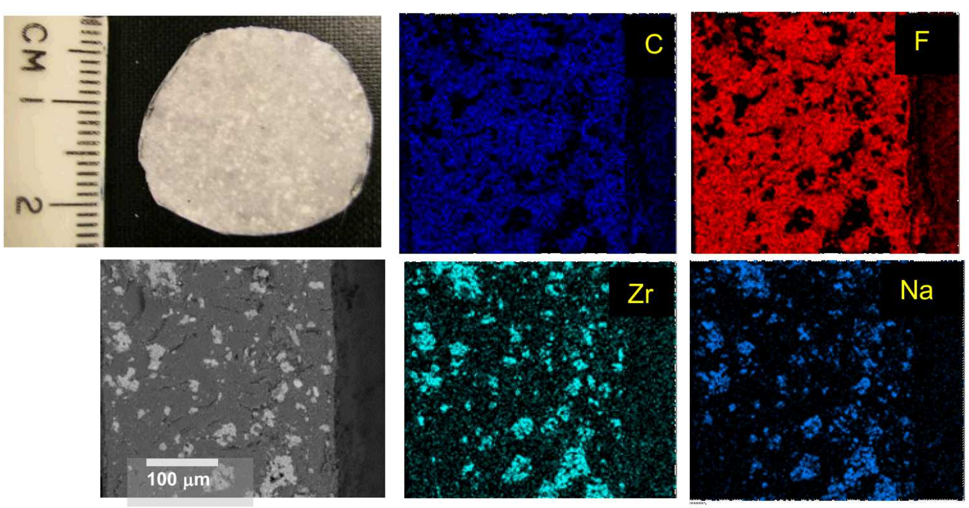
Composite Separator Innovation

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



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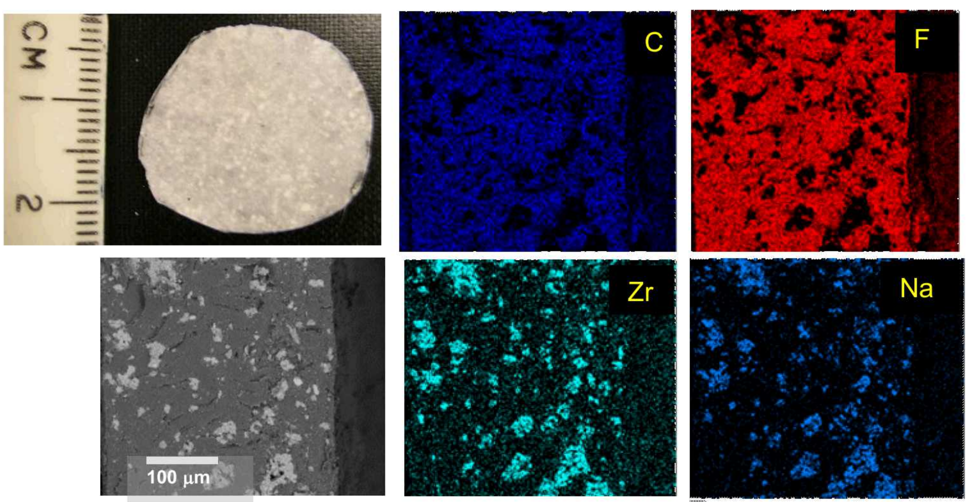
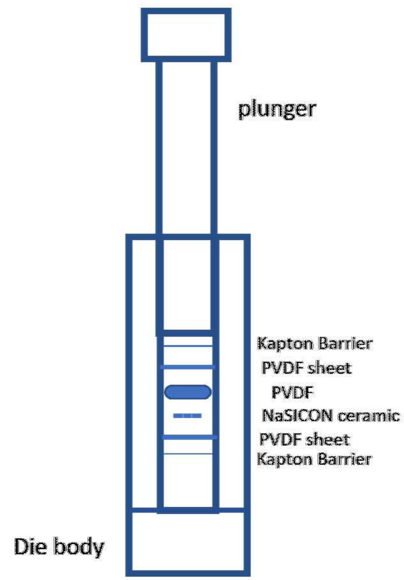
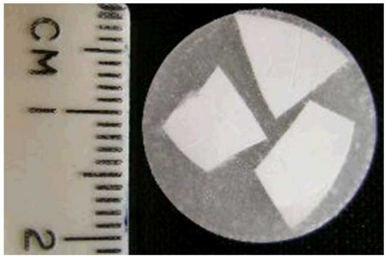


An alternative approach

- 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.

σ_{RT} ~0.5 mS/cm for composite!