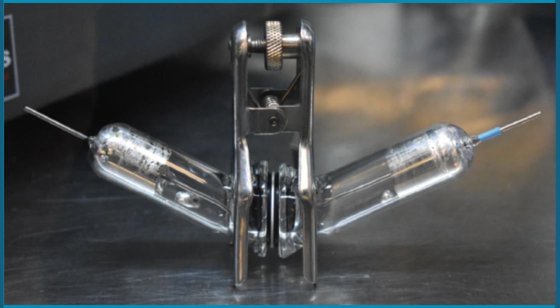
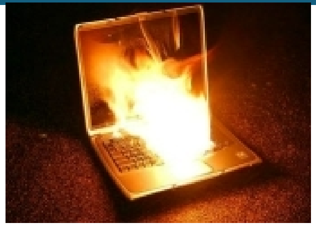
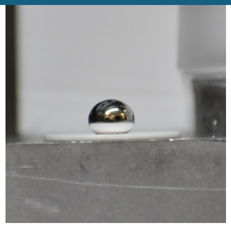
SAND2022-6145C

Sandia National Laboratories

Molten Salt-Based Batteries for Safe, Reliable, Long-Duration Energy Storage







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Josh Lamb
Leo J. Small

Materials Research Society Spring 2022 Meeting
EN05.07: Emerging Energy Storage Materials—Sodium Based Batteries

Honolulu, HI

May 10, 2022

edspoer@sandia.gov

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

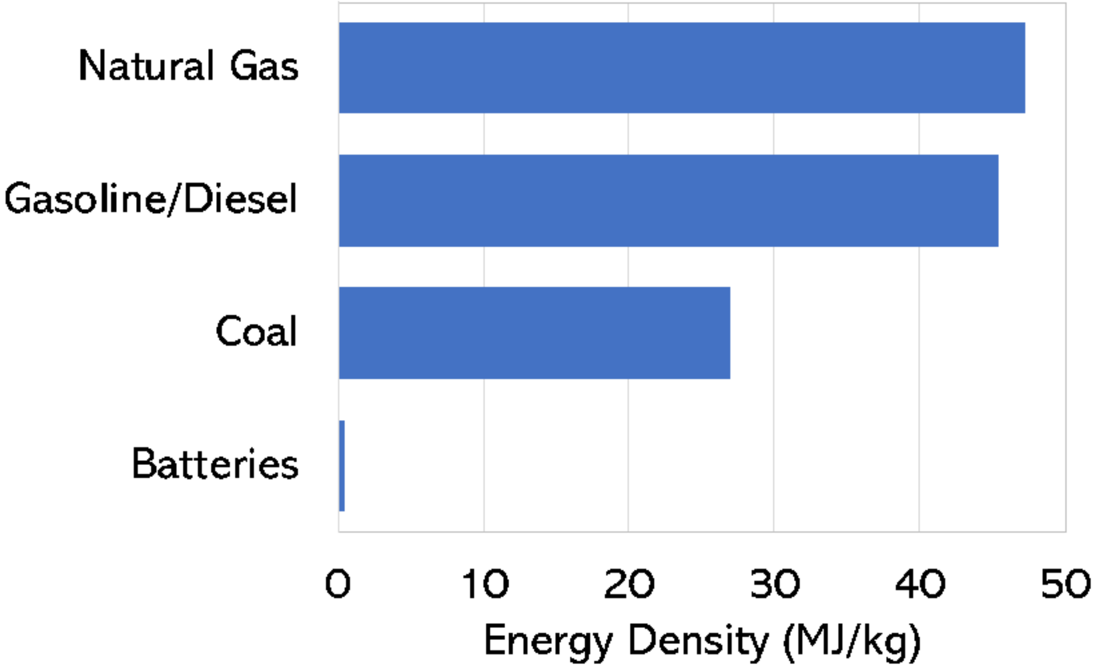
U.S. DEPARTMENT OF ENERGY   NNSA National Nuclear Security Administration

What is the Ultimate Challenge for LDES?

*How can we replace high energy density fossil fuels, not just for generation, but for **storage**?*

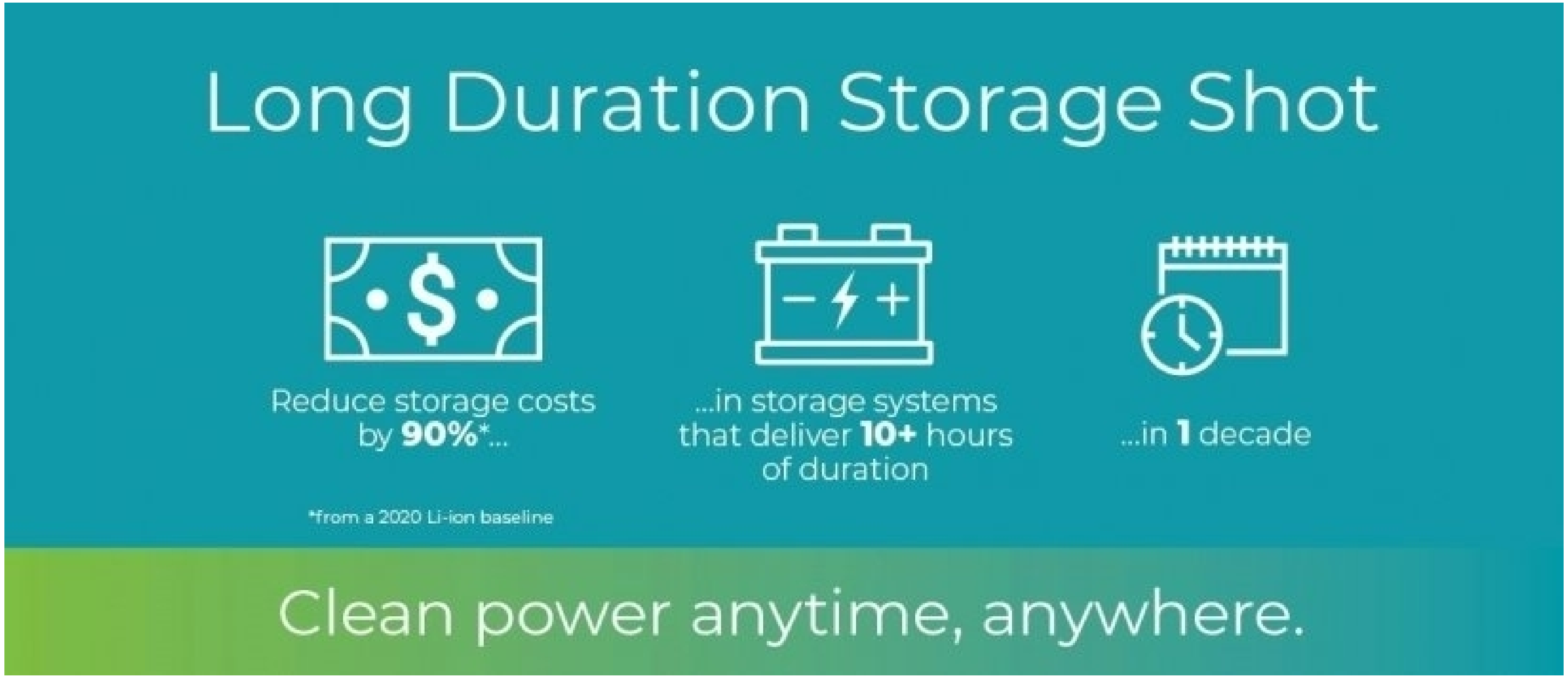
greengroundswell.com

Coal-based energy storage



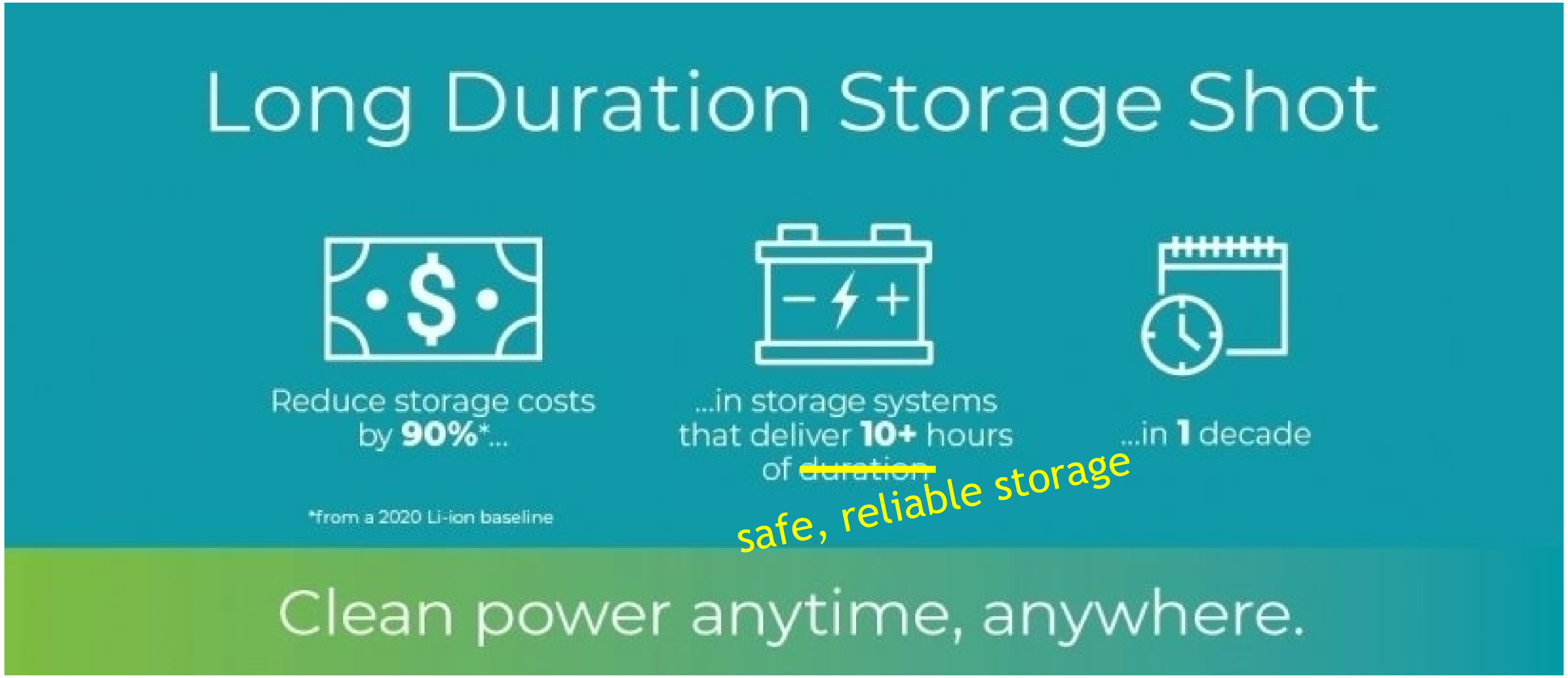
Long-Duration Energy Storage (LDES) Has Arrived at a National Scale

ENERGY earthshots U.S. DEPARTMENT OF ENERGY
Storage™



Long-Duration Energy Storage (LDES) Has Arrived at a National Scale

ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Storage™



What IS Safe, Reliable, Long-Duration Storage?

- Is it Long-Duration of Discharge?
  - DOE Energy Storage Workshop on LDES (BIG Energy Storage): >6 hours, 100MW_e
  - DOE Long Duration Storage Shot: 10 hours
  - ARPA-E DAYS (Duration Addition to electricitY Storage): 10-100 hours
  - Seasonal Storage (Weeks to Months?)

- Is it Long-Duration of Shelf-Life?
  - Emergency Response?
  - Seasonal Time Shifting?

- Is it Long-Duration of Lifetime?
  - 15-20 year lifetime
  - May be shorter duration discharge

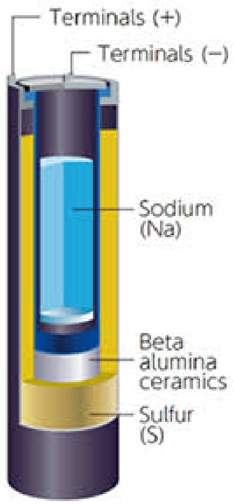
Are Safety and Reliability a Concern for Li-Ion on Large Scale and Long-Duration?

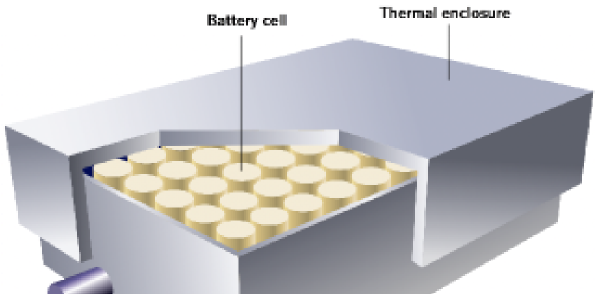
Despite a predominantly successful large-scale deployment to date, notable “mishaps” reveal a vulnerability of Li-ion.

- Moss Landing (300 MW, California) Shut down in Sept, 2021. No fire, but system offline.
- Victorian Big Battery (300MW, Australia) Fire, August 2021.
- McMicken (2 MW, Arizona) fire destroyed facility, hospitalized firefighters in April 2019.
- Carnegie Road (20MW, Liverpool, UK) fire in Sept, 2020.
- Approximately 30 large scale fires in South Korea from 2017-2019.

Aftermath of McMicken Li-ion Fire

High Temperature Molten Sodium Batteries





Molten Sodium Batteries

- Sodium is 6th most abundant element on earth.
- Sodium is 5X the annual production of aluminum.
- Favorable battery voltages (>2V).
- Very long lifetimes (15-20 years) with limited maintenance.
- Tolerate wide ambient temperature range (arctic to desert).
- Assembled/transported in discharged state (no metallic Na)

~300°C Operation!

2Cl$^-$ + Ni(s)

NGK, Insulators NaS Batteries

- 600 MW/4.2GWh of NaS storage in 200 locations

50MW Fukuoka Installation (Japan)

6-7 hour typical discharge duration

FZSoNick (Na-NiCl$_2$) Batteries)

- ~130MWh of Na-NiCl$_2$ in telecon, utilities, and grid services

Up to ~5 MWh systems

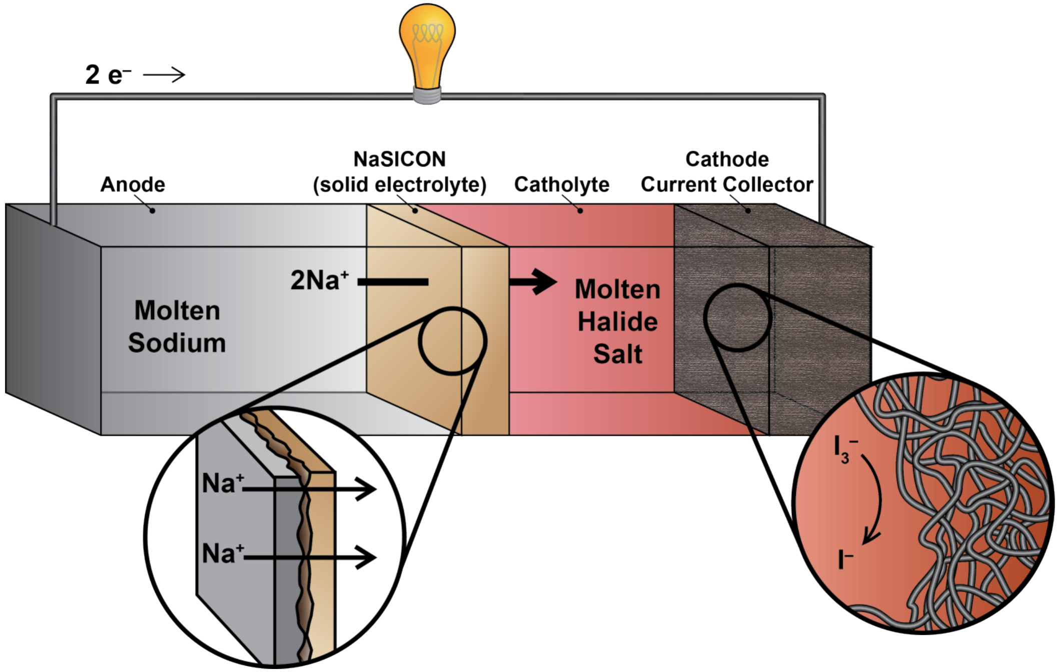
2-4 hour typical discharge duration

Low Temperature Molten Sodium (Na-NaI) Batteries: Not Your Grandmother's Sodium Battery!

Realizing a new, low temperature molten Na battery requires new battery materials and chemistries.

A Molten Sodium Battery at 110°C

- Molten Na anode (minimize dendrites?)
- Highly Na^+-conductive, physically robust separator (e.g., NaSICON)
- 25 mol% NaI in MX_3 catholyte – no organic electrolytes



Na-NaI battery:

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

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

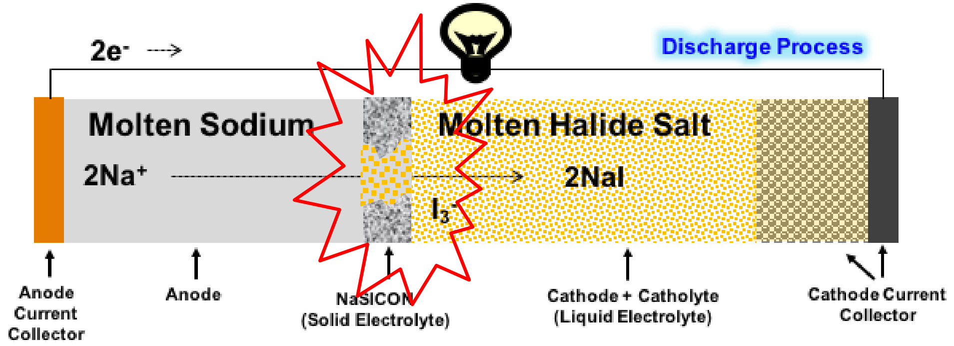
$2Na + I_3^- \rightarrow 2Na^+ + 3I^- \quad E^0_{cell} = 3.24V$

Virtues of a *low temperature* molten Na battery

- Improved material lifetimes
  - *Lower cost reliability constraints*
- Lower cost materials
- No complications from solid state electrodes
- Simplified heat management

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

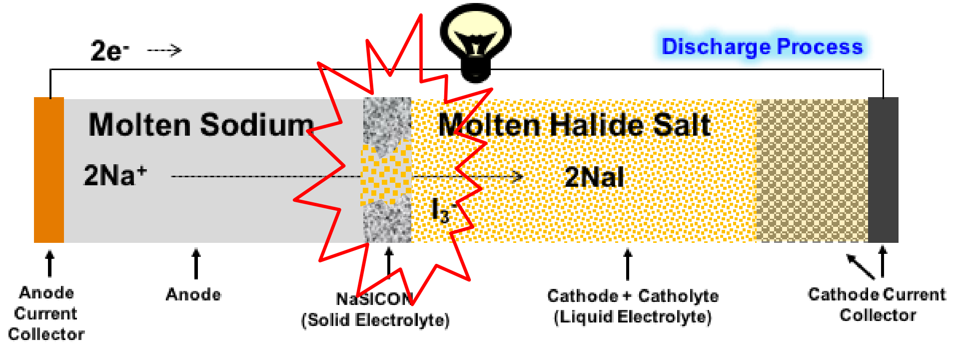
Battery Safety: Evaluating Potential Hazards of "Failed" Na-NaI Batteries



High temperature molten sodium mixing with molten sulfur (e.g., sodium-sulfur battery) can yield, violent, toxic, reaction and thermal runaway…

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

Battery Safety: Evaluating Potential Hazards of "Failed" Na-NaI Batteries

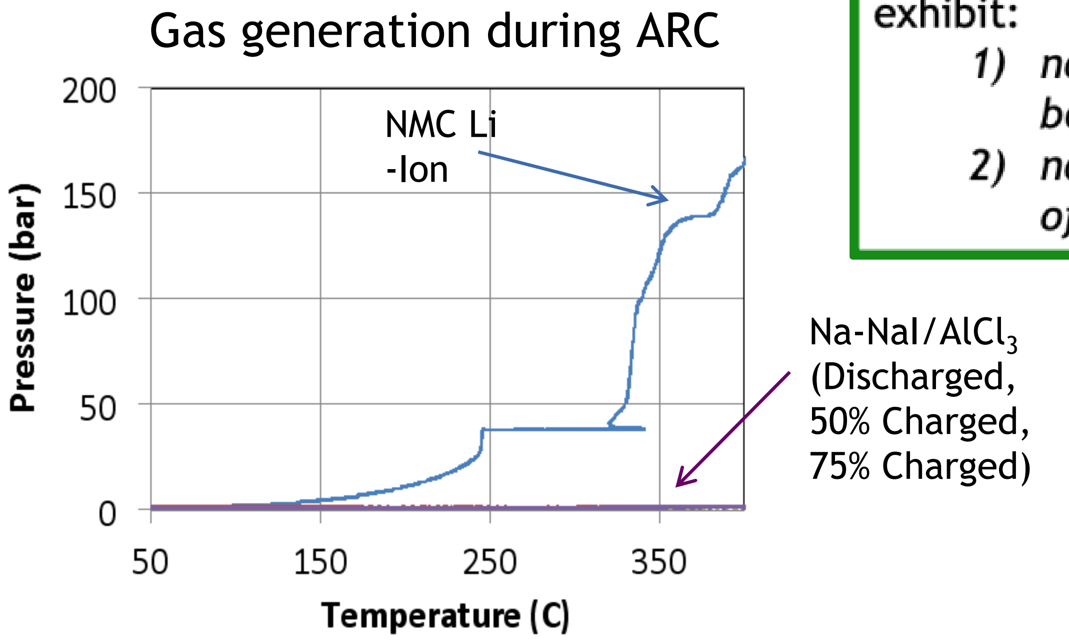


Simulating separator failure, metallic Na and NaI/AlX_3 were combined and heated.

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

Accelerating Rate Calorimetry (ARC) reveals that Na-NaI/AlX_3 mixtures exhibit:

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



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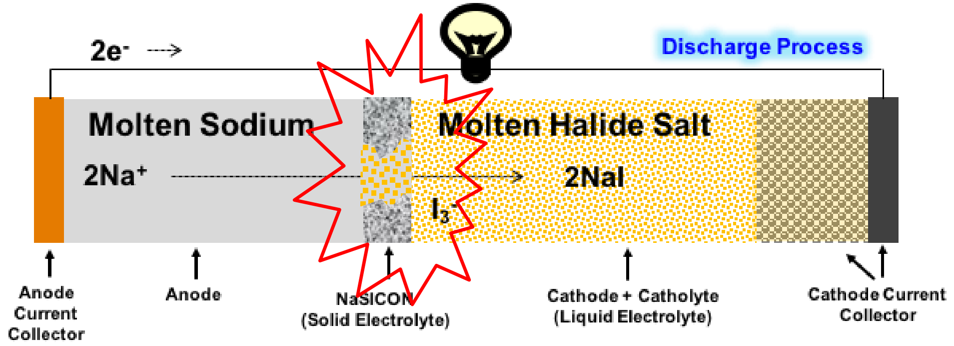

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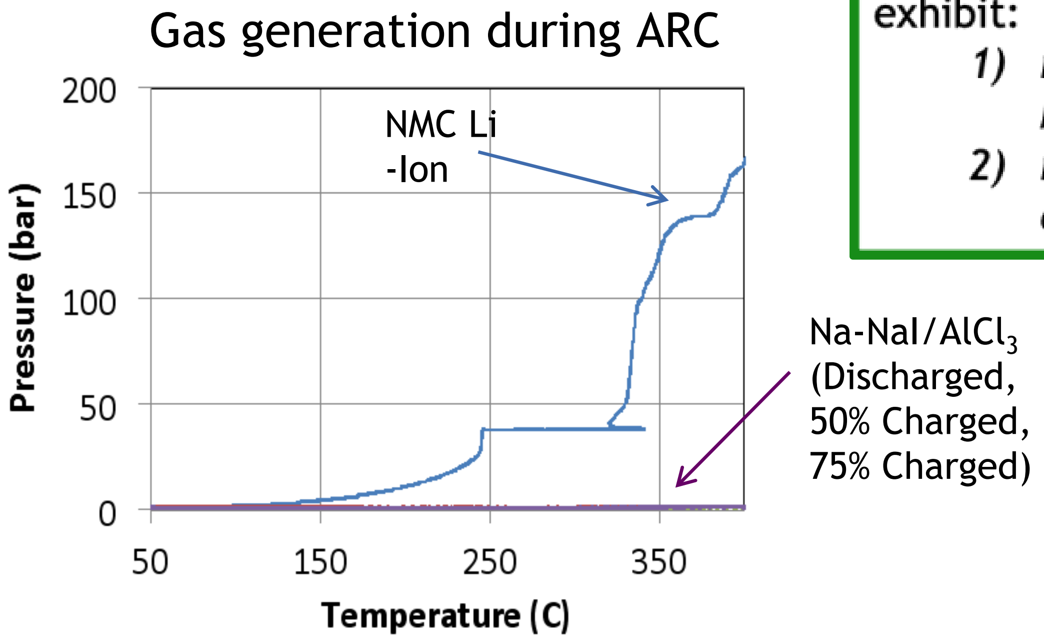
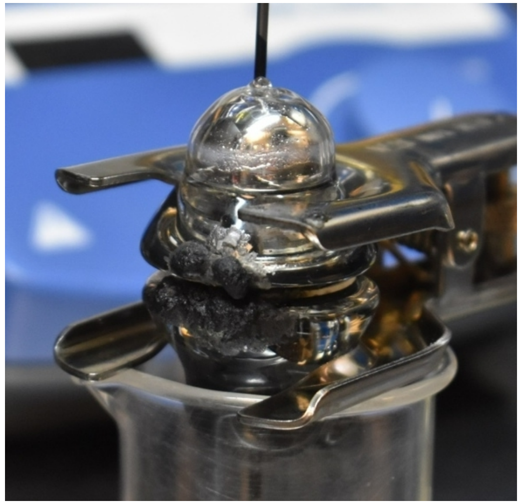




Failed separator led to termination of battery, but no significant hazardous conditions.

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

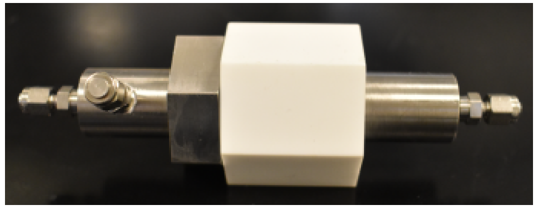
Material Selection for Battery Safety

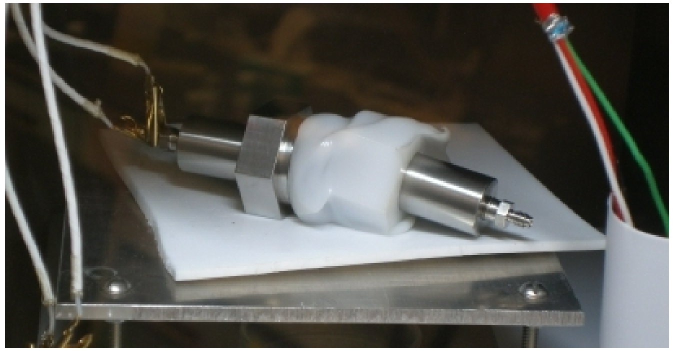
Polymer incorporation highlights the importance of careful material selection and *validation*!

Compatibility must be considered for:

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

Thermal and mechanical stability



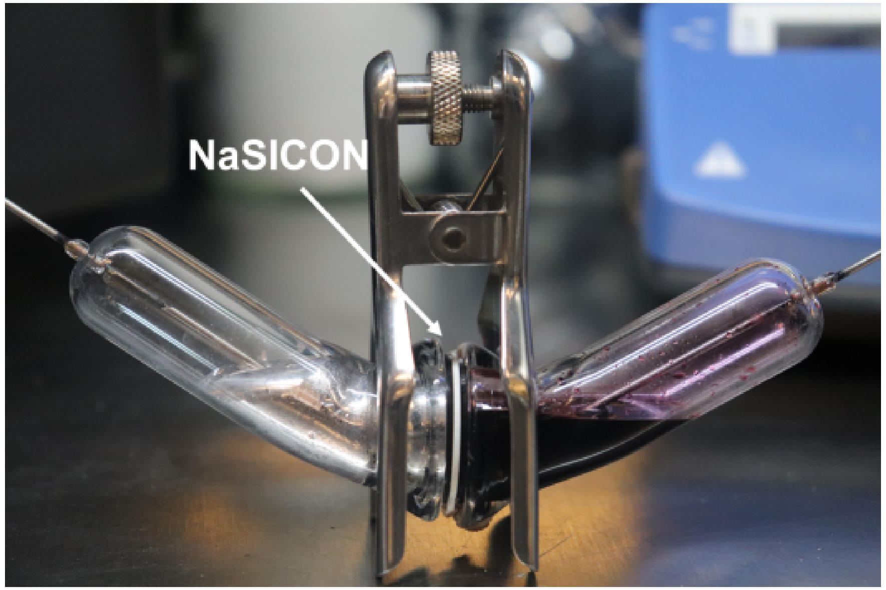


Chemical compatibility

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.

Inorganic, Molten-Salt Design is Robust!



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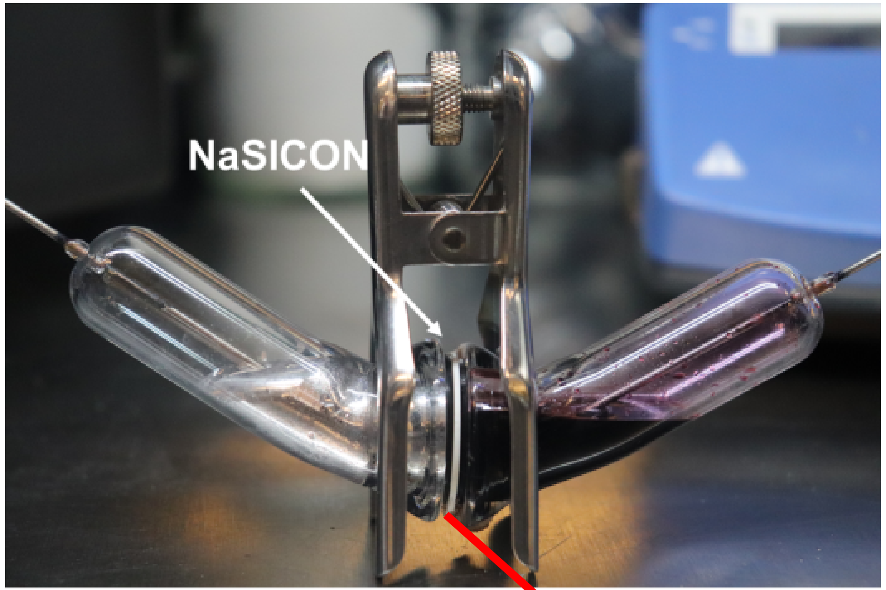
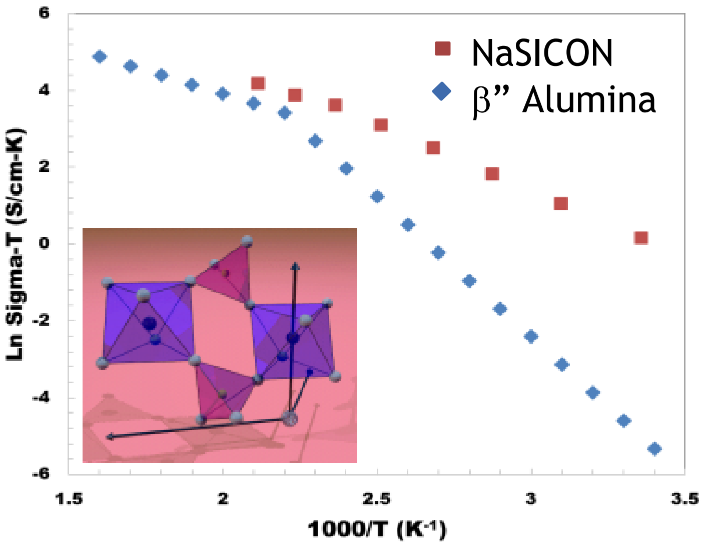


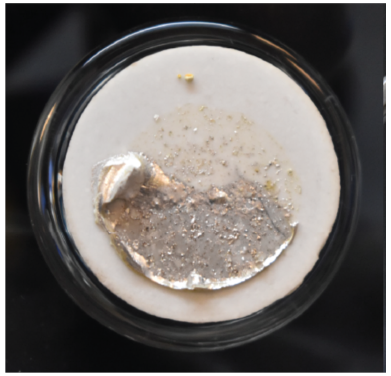
Stable, Highly Conductive NaSICON Separator
(Anodic Gasket: inert rubber
Cathodic Gasket: Commercial Fluoropolymer)

Na

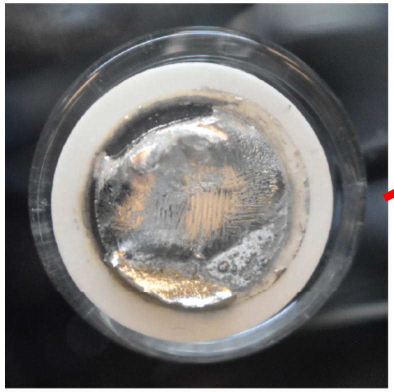


Inorganic, Molten-Salt Design is Robust!

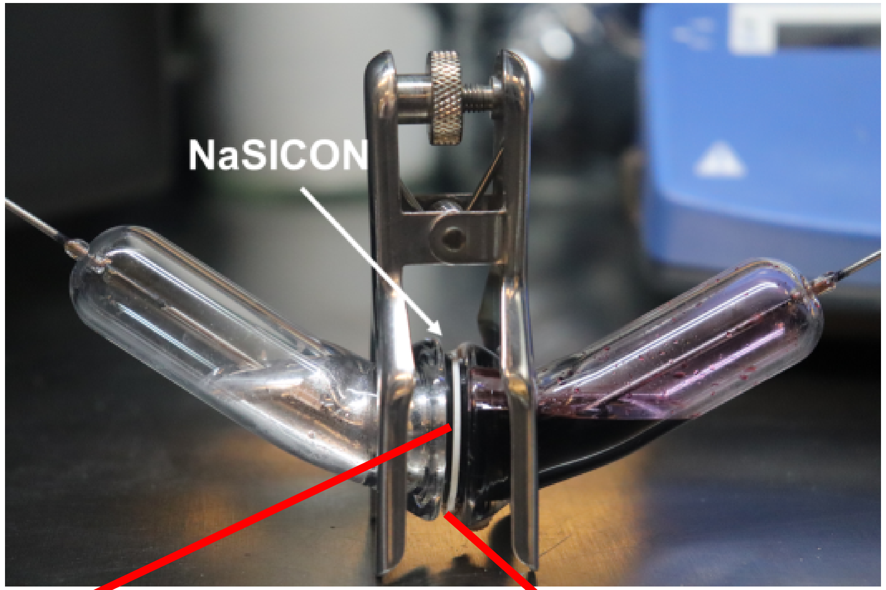
Strong Anodic Interfaces



Na poorly wets bare NaSICON



Na strongly wets Sn-coated NaSICON

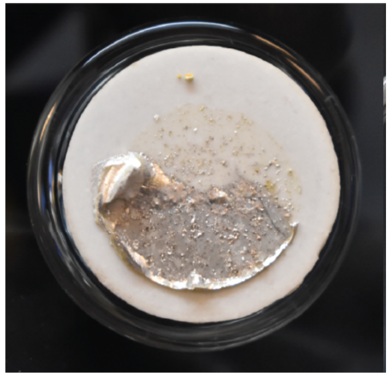


Stable, Highly Conductive NaSICON Separator

M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M.A. Rodriguez, E.D. Spoerke, *J. Mater. Chem. A* (2020) 8, 17012

Inorganic, Molten-Salt Design is Robust!

Strong Anodic Interfaces



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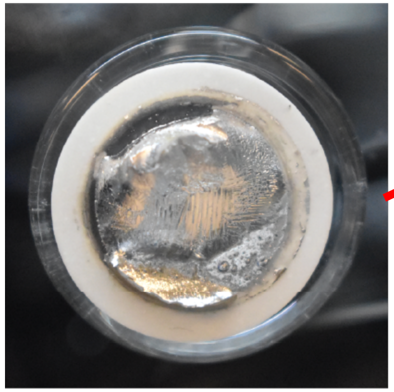

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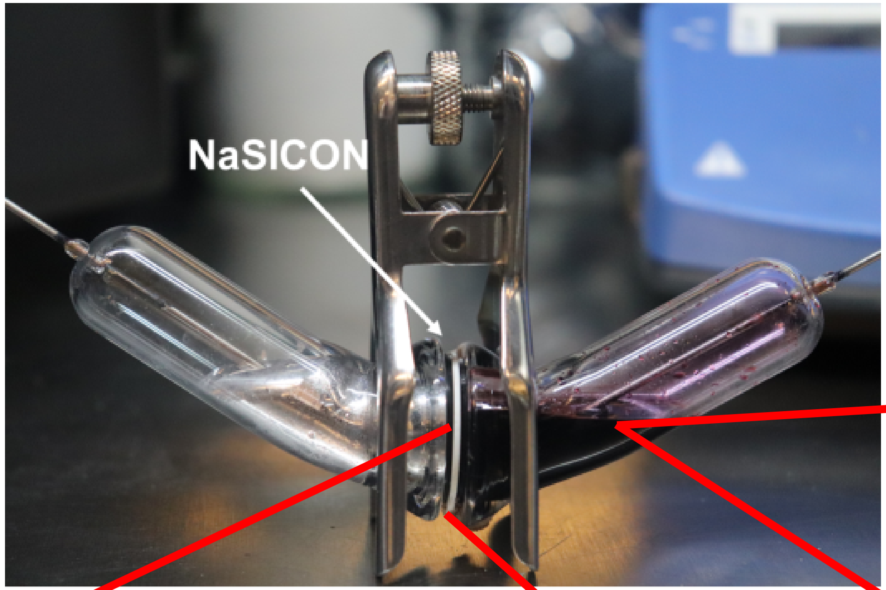


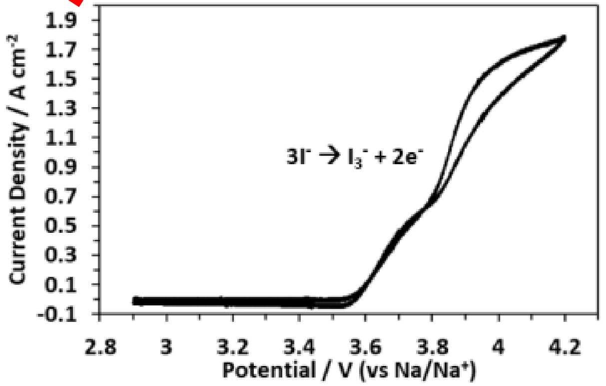
Stable, Highly Conductive NaSICON Separator

Electroactive, Low Melting Temperature Molten Salt

NaI-GaCl$_3$ "Phase Diagram"

Temperature (°C)	10	20	25	30	40
130	L	L	L	L	L+S
120	L	L	L	L	L+S
110	L	L	L	L	L+S
100	L	L	L	L+S	L+S
90	L	L	L	L+S	L+S
80	L	L	L	L+S	L+S
70	S+L	L	L+S	L+S	S
60	S+L	L	L+S	S+L	S
50	S+L	L	S+L	S+L	S
40	S	S+L	S	S	S
30	S	S	S	S	S

Composition (mol% NaI)

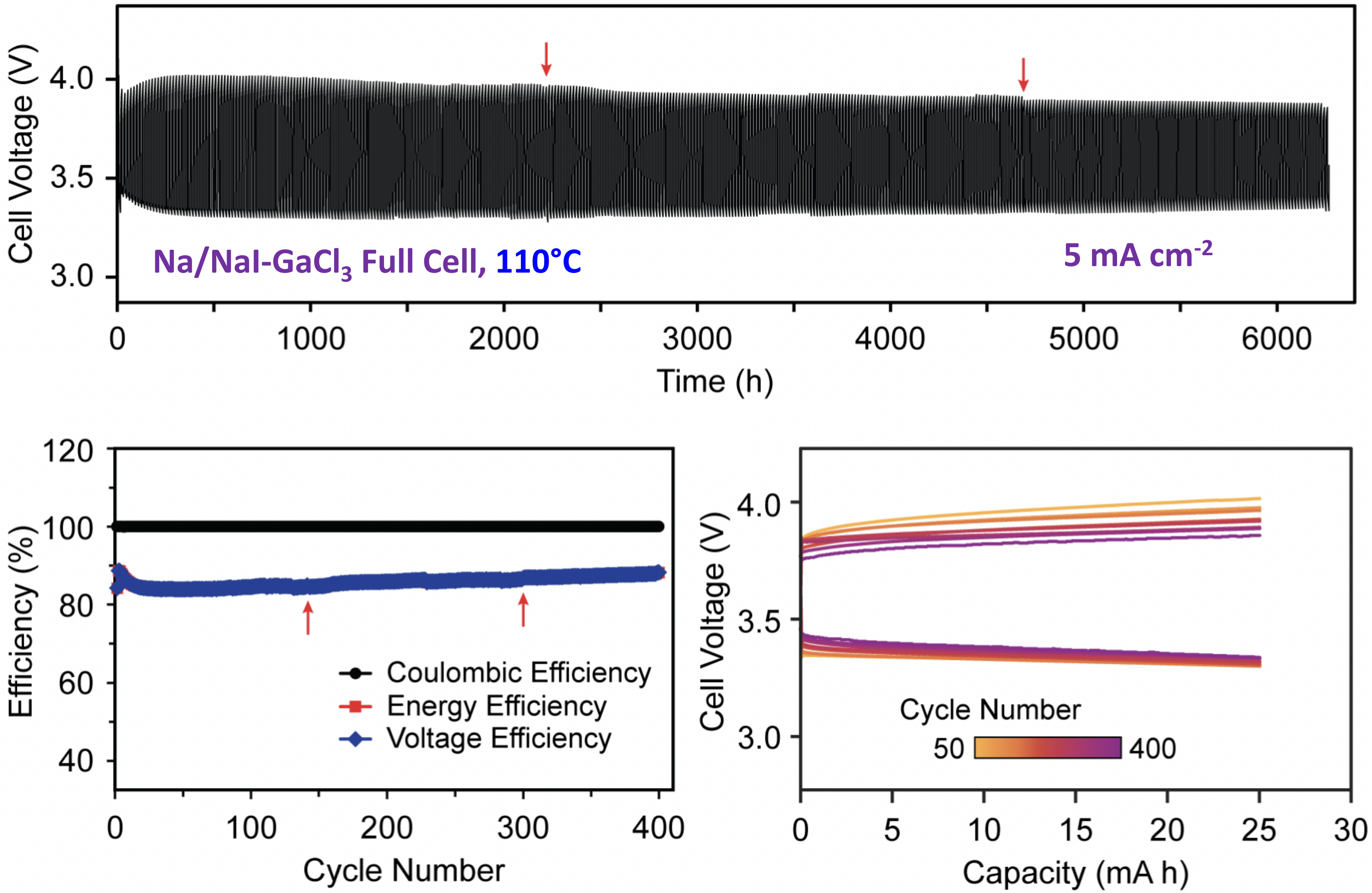


M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, L.J. Small, *Cell Rep. Phys. Sci.,* 2 (2021) 100489
M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M.A. Rodriguez, E.D. Spoerke, *J. Mater. Chem. A* (2020) 8, 17012

Robust Design Enables Robust Performance

Full Cells Demonstrated Unprecedented Performance at 110^{o}C:

- Excellent, stable cycling for over 8 months!
- High voltage (3.6V)!



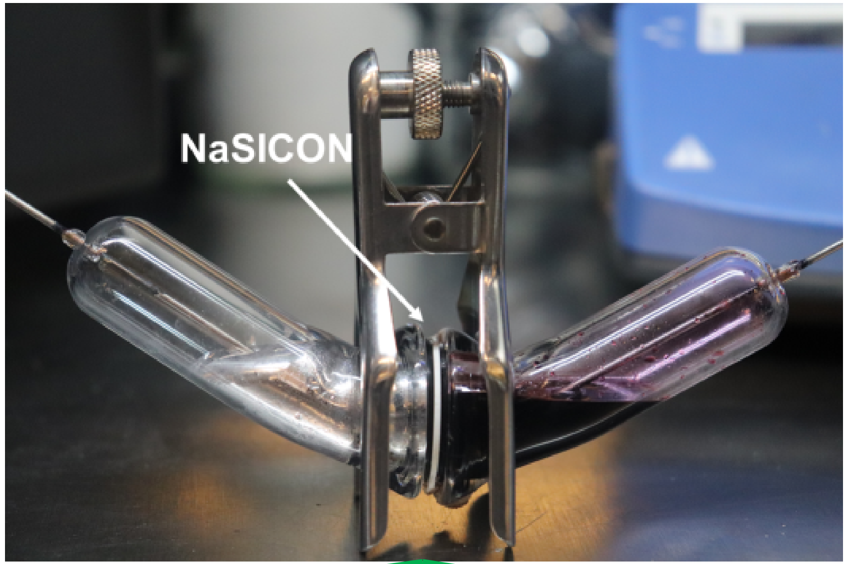
A Fortunate Inconvenience…

- The red arrows indicate where the batteries froze and were restarted.
- Battery performance was not substantially impacted!

M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, L.J. Small, *Cell Rep. Phys. Sci.,* 2 (2021) 100489

Exploring Long Shelf-Life Storage: Seasonal Storage with a Lower-Cost Catholyte

- In a “frozen” state, the batteries should maintain stable charge for extended durations.
- The lower temperature of the Na-NaI batteries dramatically reduces restart energy losses.



Batteries Assembled at 110°C

(45 mol% NaI, 55 mol% $AlCl_3$, 5% SOC)

Preconditioned (0.75 mA/cm^2 to 1% DOD)

Cycled and then charged at 2.5 mA/cm^2

Frozen Rest

- Cooled to 25°C (Froze)
- Rested for 1 Month
- Reheated to 110°C (hrs)
- Cycled through 30% total iodide content

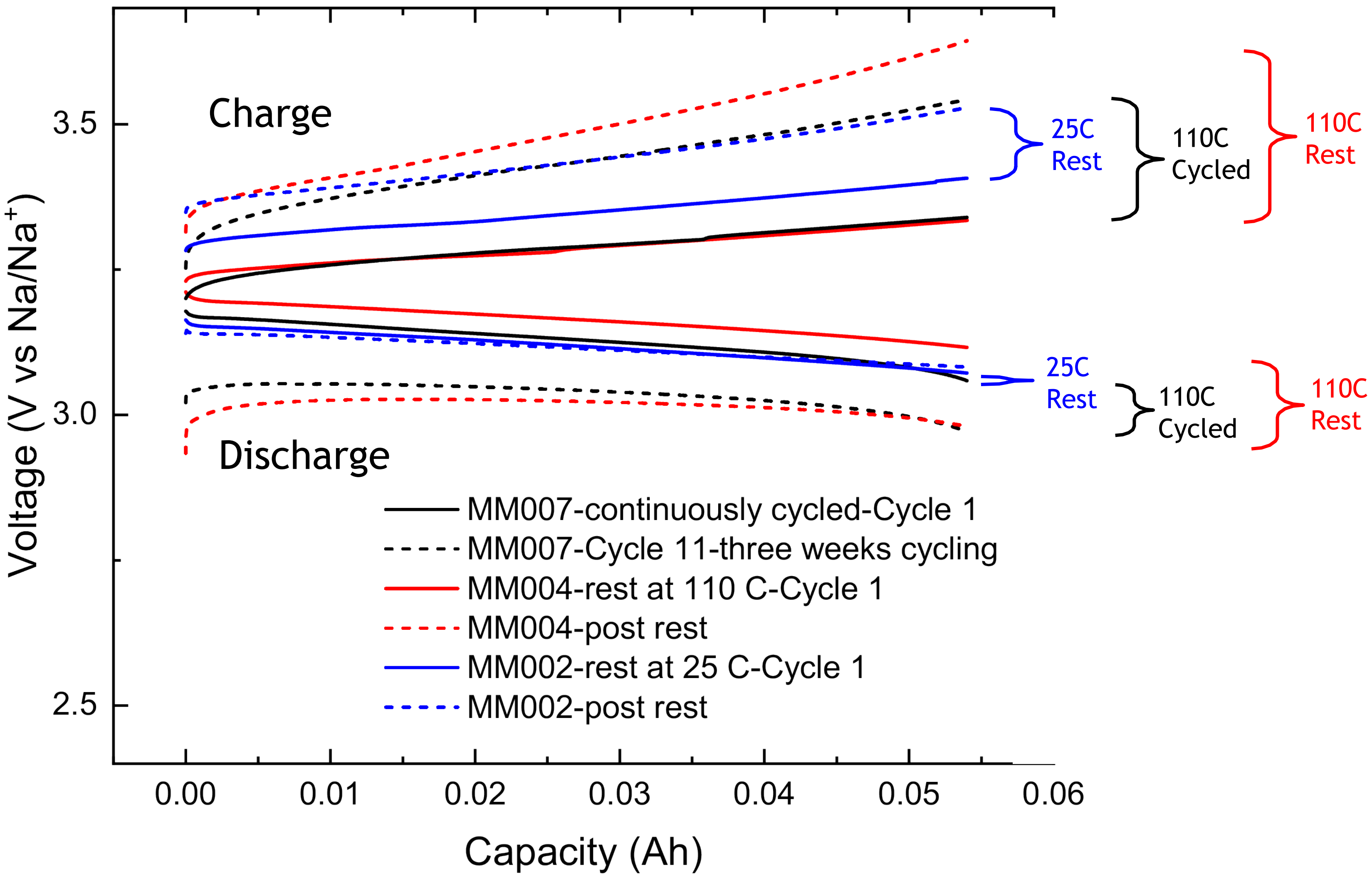
Heated Rest

- Maintained at 110°C
- Rested for 1 Month
- Restarted
- Cycled through 30% total iodide content

Heated Cycle

- Maintained at 110°C
- Cycled Continuously for 1 Month
- Cycled through 30% total iodide content

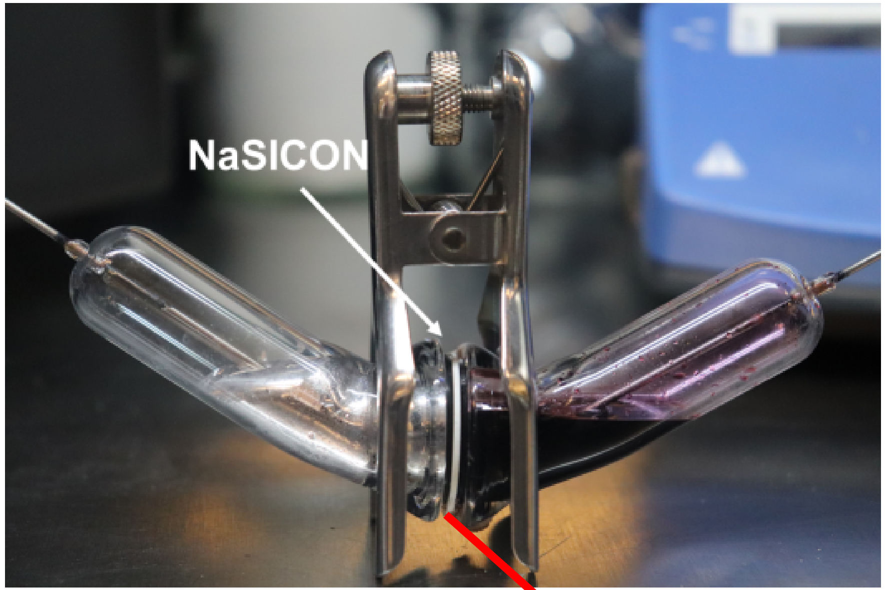
Evaluating Initial Long Shelf-Life Performance



Preliminary Observations

- Increases in overpotential are higher on charge than discharge for all samples.
- Samples held at 110°C for ~1 month show similar increases in overpotential whether cycled or resting.
- Frozen samples show smallest increases in overpotential with little or no changes on discharge.

Inorganic, Molten-Salt Design is Robust!

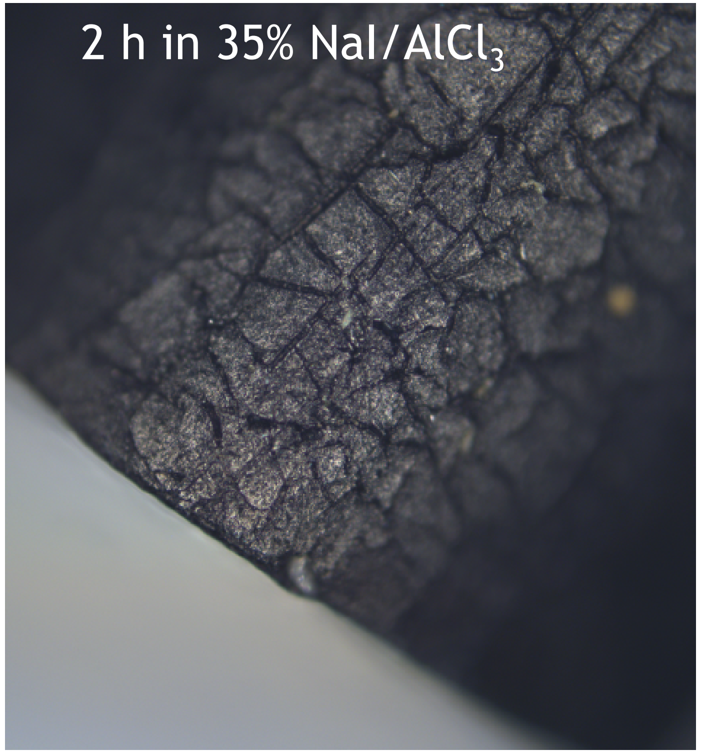


Stable, Highly Conductive Ceramic Separator
(Anodic Gasket: inert rubber
Cathodic Gasket: Commercial Fluoropolymer)

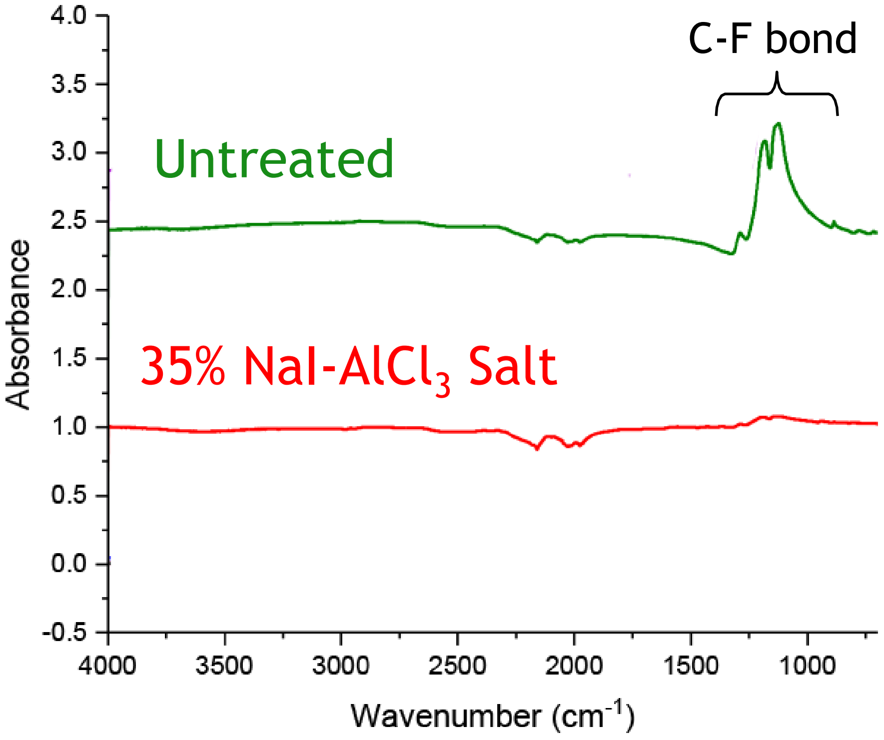
Post-Mortem Analyses Reveal a Surprising Problem

The $AlCl_3$-based salt attacks the typically inert fluorinated gasket!

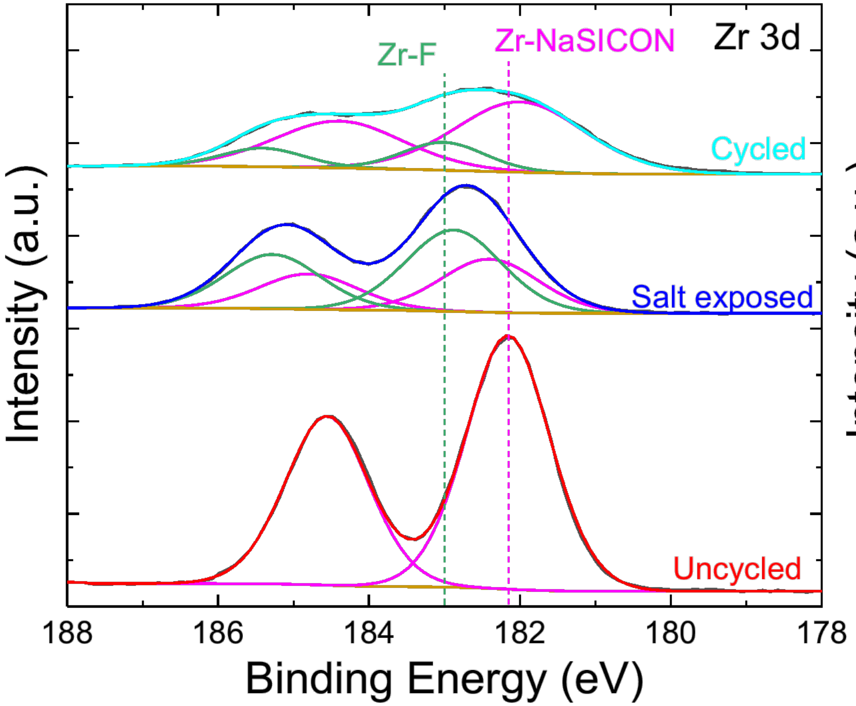
Gasket cracking

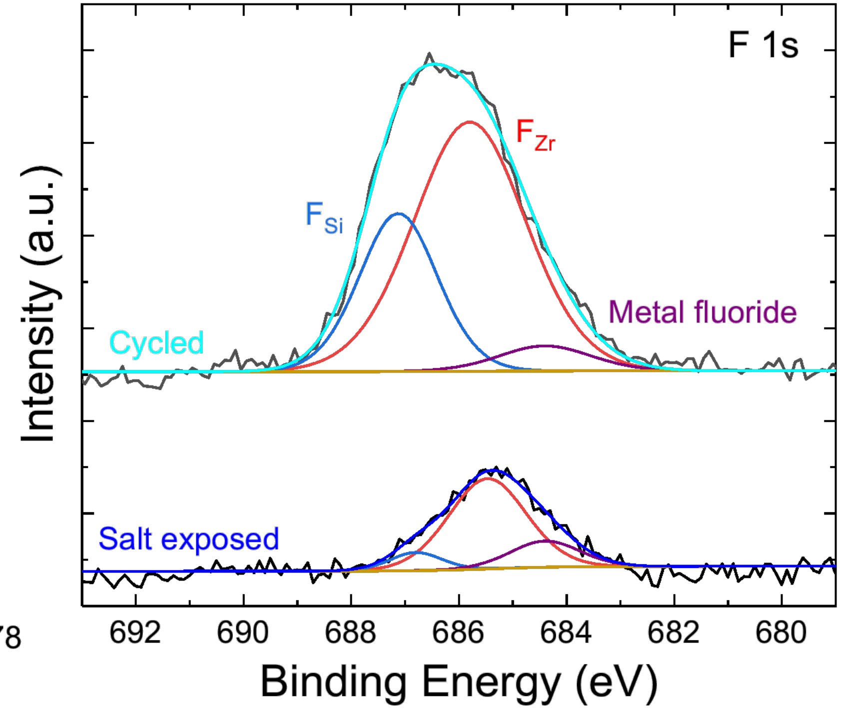


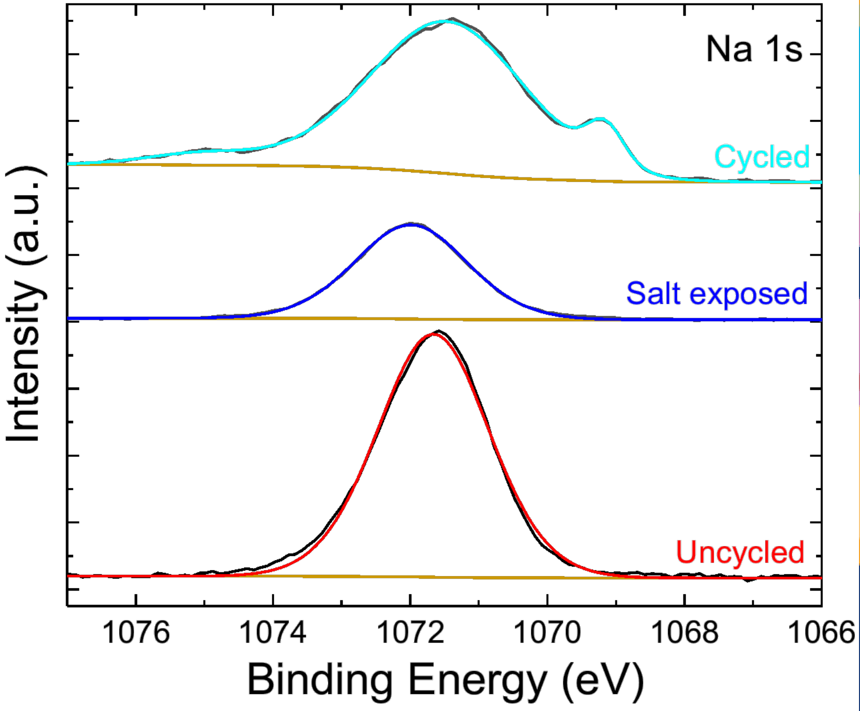
FTIR reveals degradation of C-F bonds



XPS Analysis Reveals Unexpected Reaction with NaSICON







- Shift of Zr peaks to higher BE consistent with formation of F -bonds.
- Broadening of peaks after cycling is indicative of changes to chemical environment.

- Largest F peaks match BEs of F-Si-Zr-O compounds[1] with additional small metal fluoride peak.
- Quantification shows increase in F concentration at the NaSICON surface after cycling (1 at % to 7 at %).

- Na region develops additional very oxidized and very reduced peaks after cycling.

1. Bosman, H. J. M.; Pijpers, A. P.; Jaspers, A. W. M. A., *Journal of Catalysis* ***1996, 161 (2), 551-559.***

Summary and Opportunities

- Molten Na-Batteries have great potential for safe, reliable, long-duration storage
  - Long discharge
  - Long shelf-life
  - Long lifetime
- Low temperature Na-NaI molten salt batteries offer advantages in cost, safety, and potential long-term reliability…
  - *No thermal runaway*
  - *Lower basic materials reliability costs*
  - *Reduced operational complexity and cost*
  - *No solid state electrode evolution/degradation*
- *…but* materials challenges unique to low-temperature, low-cost chemistries remain.
  - Seals
  - Chemical compatibilities
  - Facile ionic and electronic interactions

Thank you!

This work at Sandia National Laboratories is supported through the Energy Storage Program, managed by Dr. Imre Gyuk in the U.S. Department of Energy's Office of Electricity.

Contact: Erik Spoerke (edspoer@sandia.gov)

Additional talk by Ryan Hill:

- "Characterization of NaSICON Solid Electrolytes Exposed to Thermal and Electrochemical Cycling in Molten Sodium Environment."

Thursday, 10:30 a.m./ HCC, L3, 323A

Thanks to those who actually did this work!

- Dr. Adam Maraschky
  - (Poster: Experimental and Modeling Studies of Metal Halide Catholyte and Cathode Materials to Enable Low-temperature Molten Sodium Batteries.")
- Dr. Melissa Meyerson
- Dr. Martha Gross
- Dr. Leo Small
- Amanda Peretti
- Dr. Stephen Percival
- Dr. Joshua Lamb
- Sara Dickens
- Rose Lee
- Dr. Babu Chalamala

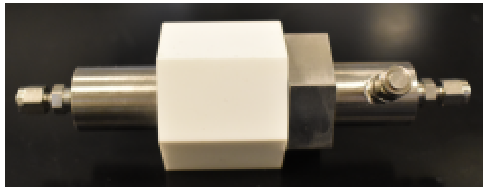
Backup Slides

Identifying a Viable Na-Battery Test Platform

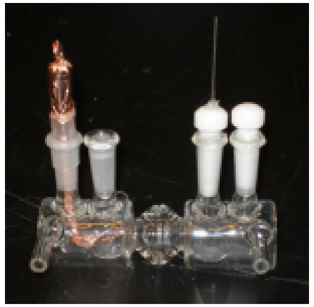
Cell geometry, interfacial interactions, and materials compatibility were identified as key design elements.

Re-Engineered Cell Variants

A functional cell design is critical to prototype development and testing.



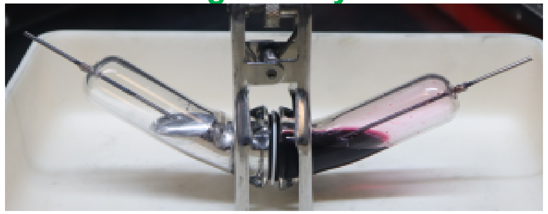
Many new cell designs and geometries built and tested (7 different types!)

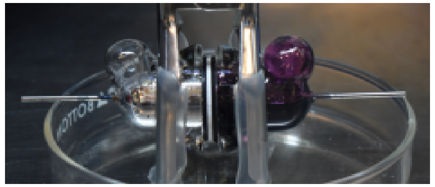


Some designs were time consuming, laborious and could be **used only once!**

New Cell Designs

Enable easy assembly, high throughput and functional geometry





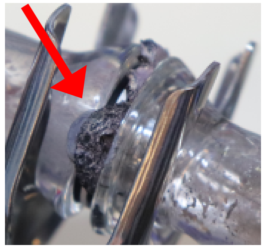
Includes 3 designs that are fully interchangeable and reusable

Importance of Seals

Testing failures in many prototypes was due to compromised seals.

Sodium Compatible Seal Material

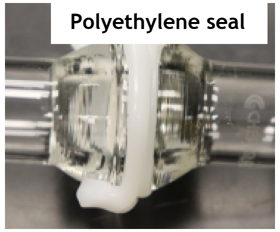
Sodium reacting with the Kalrez o-ring



Polyethylene seals from molten polyethylene to seal the sodium side

Not re-useable and hard to apply properly

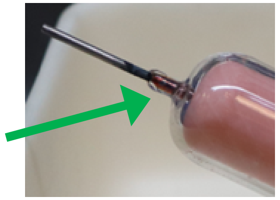
Identified new EPDM o-rings that do not react with molten Na



Molten Salt Compatible Seal Material

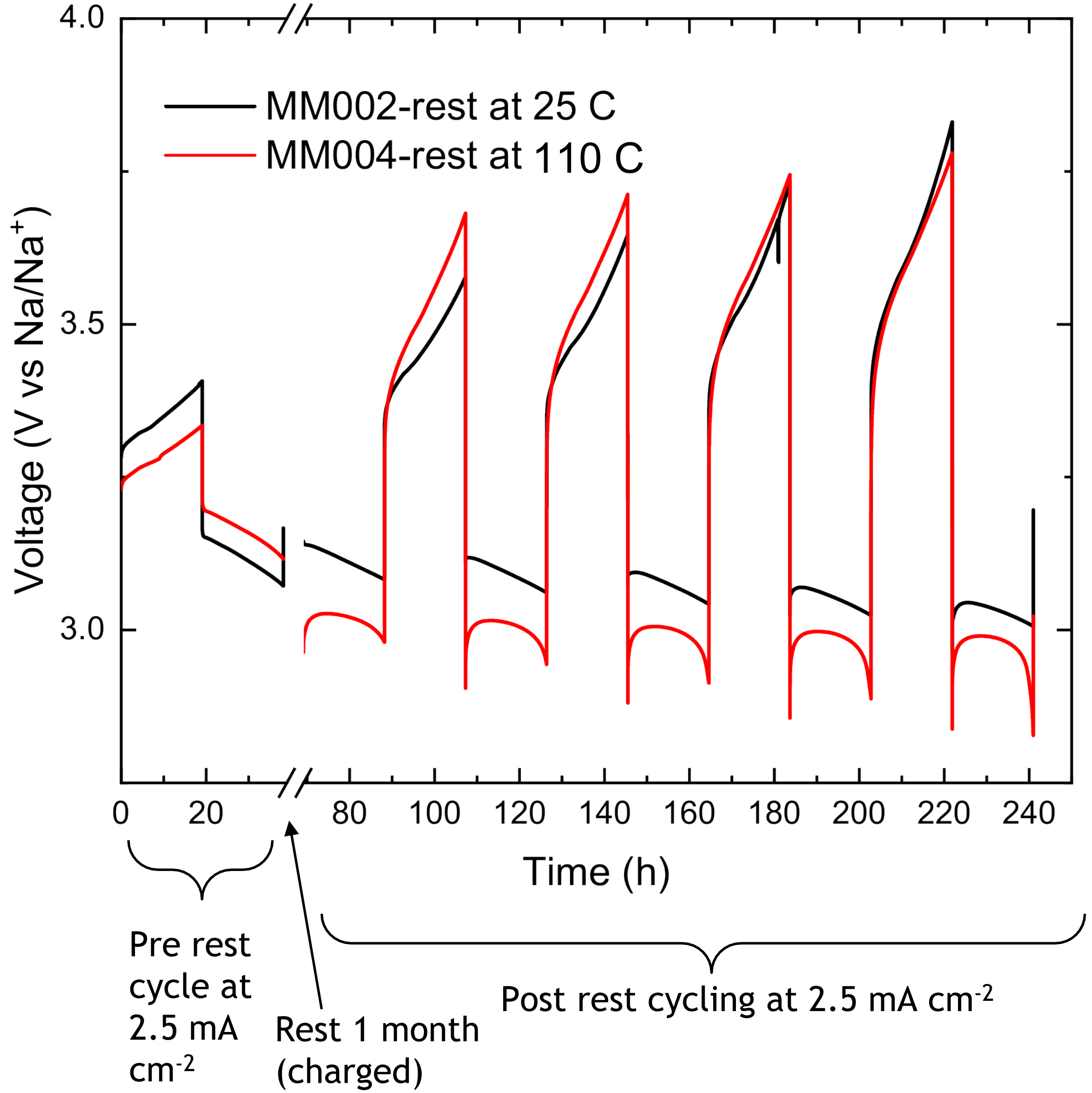
Vapors from molten salt aggressively attacking the epoxy seals

Glass to metal seals eliminate unwanted side reactions from salt vapors



Stephen Percival

Cells Benefit from Frozen Resting State



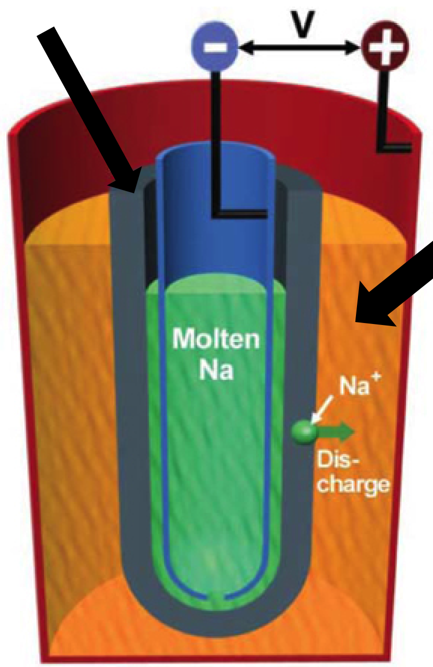
"Rested" Battery Characteristics

		Before rest	After 1 month rest
110°C	Impedance at 100 mHz	16 Ω	108 Ω
	VE	97.03%	86.39%
25°C	Impedance at 100 mHz	35 Ω	40 Ω
	VE	93.08%	90.55 %

Samples frozen and rested at 25°C show the best retention of performance after reactivation.

Molten Sodium Batteries: Where Does the Industry Stand?

Molten Sodium Battery Basics



Na-S

NGK INSULATORS

$xS + 2Na \leftrightarrow Na_2Sx$ $(3 \le x \le 5)$ E_{cell} ~2.08 V at 350ºC

✓ 600 MW/4.2 GWh of deployed storage in over 200 cites globally

Na-$NiCl_2$

FZSoNick

$NiCl_2$ (s) + 2Na (l) $\leftrightarrow$ 2NaCl + Ni (s) E_{cell} ~2.58 V at 300ºC

✓ Approximately 130MWh deployed storage globally

	Practical Energy Density (Wh/L)	Expected Cycle Life (cycles at 80% DOD)	Expected Lifetime (years)	Operating Temperature (°C)	Suitable Ambient Temperature (°C)	Discharge Duration (at rated power)	Round Trip Efficiency
NaS	300-400	4,000-4,500	15	300-350	-20 to + 40	6-7 hours	80%
Na-$NiCl_2$	150-190	3,500-4,500	20	270-300	-20 to +60	2-4 hours	80-85%

- Na-S takes advantage of low cost materials, but introduces some safety concerns.
- Na-$NiCl_2$ is a safer, greener chemistry, but high cost of Ni is a challenge.

NaS and Na-$NiCl_2$ batteries are used today for Renewables Integration, Grid Services, Consumer Applications, and Microgrids