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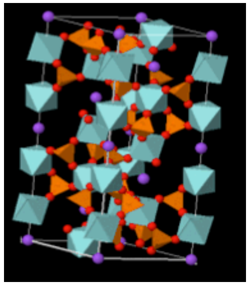

Advancing Sodium-Based Batteries for Grid-Scale Energy Storage

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Ceramatec, Inc. Salt Lake City, UT

232nd Electrochemical Society Meeting, National Harbor, MD October 1-5, 2017

Teaming

- Program Sponsor
  - Dr. Imre Gyuk – Program Manger, DOE-OE
  - DOE – Office of Electricity Delivery and Energy Reliability
- Team
  - **SNL**: Erik Spoerke, Leo Small, Jill Wheeler, Paul Clem, Josh Lamb, Eric Allcorn, Ganesan Nagasubramanian, John Hewson, and David Ingersoll*
  - **Ceramatec**: Sai Bhavaraju, Alexis Eccleston, Andrew Read, Matt Robins, Tom Meaders
  - **SK Innovation**: Jeongsoo Kim

This collaboration between National Laboratory and Industry aims to utilize state of the art expertise in materials chemistry, electrochemistry, and advanced characterization to drive the development of new sodium-based batteries.

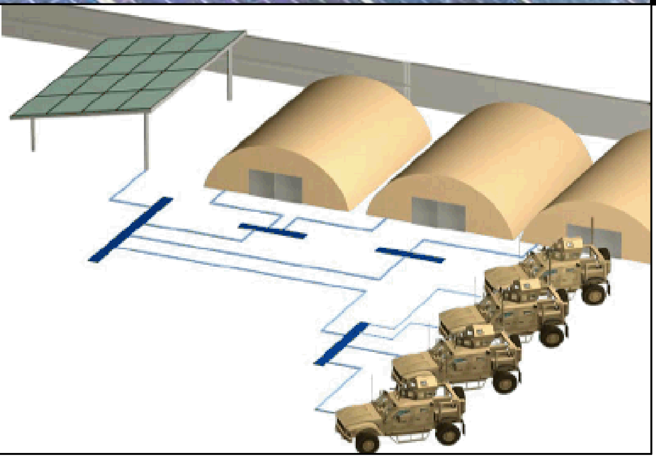
Sandia National Laboratories

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

SK

Critical need for Grid Scale Batteries



Safe, grid-scale electrical energy storage is critical!

- Renewable/Remote Energy
- Grid Reliability/Agility
- Humanitarian Efforts
- National Defense

Challenges with Current Battery Technologies

Pb-Acid: $Pb(s) + PbO_2\ (s) + 2H_2SO_4(aq) \leftrightarrow 2PbSO_4 + 2H_2O\ (l)$ $E_{cell} \sim 2.1V$

- Utilizes lead and sulfuric acid
- Overcharging (high charging voltages) produces potential explosion hazard from accumulation of hydrogen and oxygen.
- Capacity fades quickly from sulfation and grid corrosion (typically 200-300 cycles)

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Li-ion: $LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$ $E_{cell} \sim 3.6V$

- Cost (decreasing recently)
- Capacity fades relatively quickly (~500 cycles) from oxidation reactions, electrolyte degradation, cathode degradation, increased cell resistance, cell short circuits.
- Limited operational temperature range (near room temperature)
- Significant safety concerns associated with thermal runaway and flammable organic electrolytes

Safety Concerns with Li-Ion Batteries?

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Galaxy Note 7

<10Wh

Laptop Computer

<100Wh

Tesla EV Battery

kWh (~6895 18650 cells)

Battery Recycling Plant

MWh (?)

This 10 kWh battery pack depicted on the side of a building likely has 5 liters of liquid electrolyte.

Thermal runaway and flammable organic electrolytes remain serious hazards for Li-ion batteries!

Li-ion batteries are inherently intolerant of harsh conditions.

Challenges with Current Battery Technologies

Pb-Acid: $Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$ $E_{cell} \sim 2.1V$

- Utilizes lead and sulfuric acid (hazardous, heavy)
- Overcharging (high charging voltages) produces potential explosion hazard from accumulation of hydrogen and oxygen
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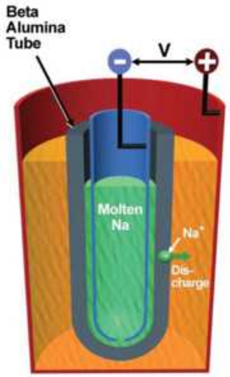
Na-S Batteries : $2Na + 4S \leftrightarrow Na_2S_4$ $E_{cell} \sim 2V$



- Cost (potentially feasible)
- Operates at elevated temperatures (270-350^{o}C – required for molten chemistry and solid state electrolyte operation). Cell freezing can cause mechanical failure.
- Corrosive, toxic chemistries
- Molten sodium and molten sulfur are highly reactive (cascading thermal runaway and fire hazard)

Notable Na-S Battery Fires

September, 2011: Fire from NGK-manufactured NAS (sodium-sulfur) batteries at the Tsukuba Plant (Joso City, Ibaraki Prefecture) of Mitsubishi Materials Corporation (Head office: Chiyoda-ku, Tokyo). Failure of single cell (out of 15,360 cells) led to short circuit and cascading thermal runaway.

February, 2010: Fire at the Oyama Plant (Oyama City) of Takaoka Electric Mfg. Co., Ltd. (Headquarters: Chuo-ku, Tokyo).

February, 2005: Fire at NGK's NAS battery plant in Komaki City. This fire broke out when a modular battery was undergoing high-voltage testing.

Na-S Batteries are still vulnerable to thermal runaway and cascading failure, particularly under non-ideal conditions.

Despite these challenges, Na-S battery deployment continues to expand:

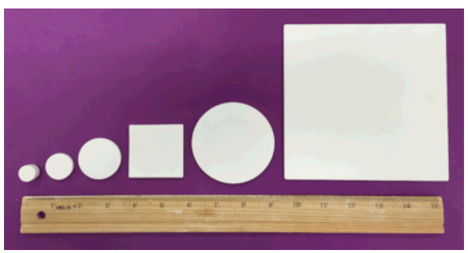
- 190 sites in Japan, more than 270MW installed
- More than 20MW installed in U.S.

There remains strong motivation to enable Na-based batteries!

Molten Salt Na-Based Batteries

<u>Our Goal</u>: to develop low cost (≤ $100/kWh), intermediate temperature (≤200°C), *long-lifetime, safe, nonflammable* Na-based alternatives to Na-S, Pb-acid, and Li-ion batteries.

- Na-chemistry utilizes abundant Na-supply
- Intermediate temperature enabled by highly conductive NaSICON (Sodium Super Ion CONductor) ceramic separator.
  - ✓ **High Na-conductivity (>10^{-3} S/cm at 25°C)**
  - ✓ **Scalable production (Ceramatec, Coorstek)**
  - ✓ **<u>Demonstrated up to 250Wh prototypes</u>**



250 Wh Nasicon tube

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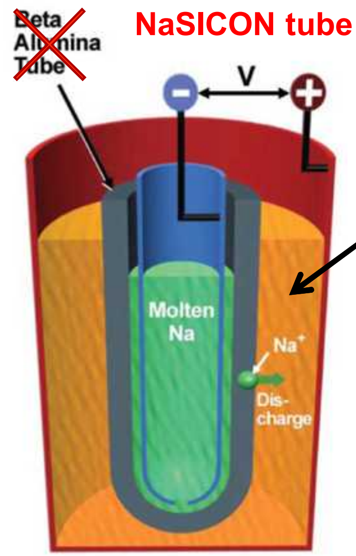
100 Wh, Na-battery prototype

NaSICON tube separator enables lower temperature operation



Molten salt catholyte

$Na-NiCl_2$ battery
- **Salt: $NiCl_2/AlCl_3$**

$Na-I_2$ battery
- **Salt: $NaI/AlCl_3$**

Sodium-nickel chloride (195°C, E_{cell}~2.6V):
$Na + ½\,NiCl_2 \leftrightarrow Na^+ + Cl^- + Ni(s$

Sodium-iodine (120-150°C, E_{cell}~ 3.25V):
$Na + ½\,I_2 \leftrightarrow Na^+ + I^-$

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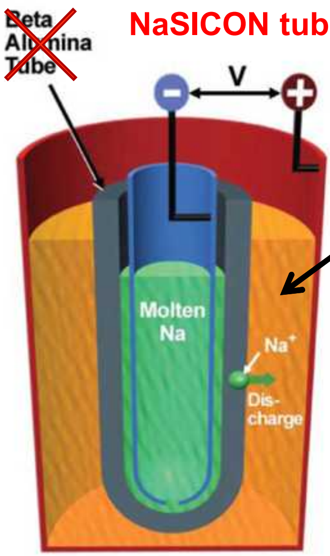
- Reduced temperature (relative to traditional Na-batteries) enables:
  - ✓ **Lower cost**
  - ✓ **Increased reliability and lifetime**
  - ✓ **Improved capacity retention (limitation of Li-ion and Pb-acid)**



NaSICON tube separator enables lower temperature operation

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SNL Principal Investigator: Dr. Erik Spoerke (edspoer@sandia.gov)

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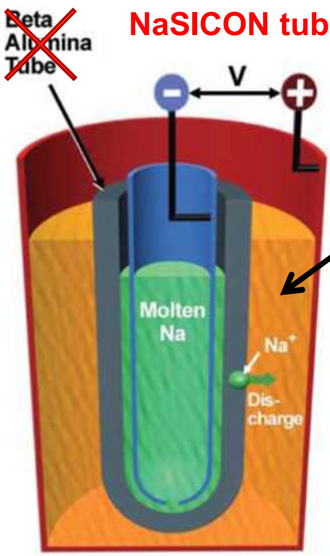
  - ✓ **<u>Demonstrated up to 250Wh prototypes</u>**
- Reduced temperature (relative to traditional Na-batteries) enables:
  - ✓ **Lower cost**
  - ✓ **Increased reliability and lifetime**
  - ✓ **Improved capacity retention (limitation of Li-ion and Pb-acid)**
- Safety-by-design in all-inorganic system
  - ✓ **No cascading thermal runaway**
  - ✓ **No flammable gas generation**
  - ✓ **Separator failure and electrode cross-over produces inert Al metal and NaCl.**



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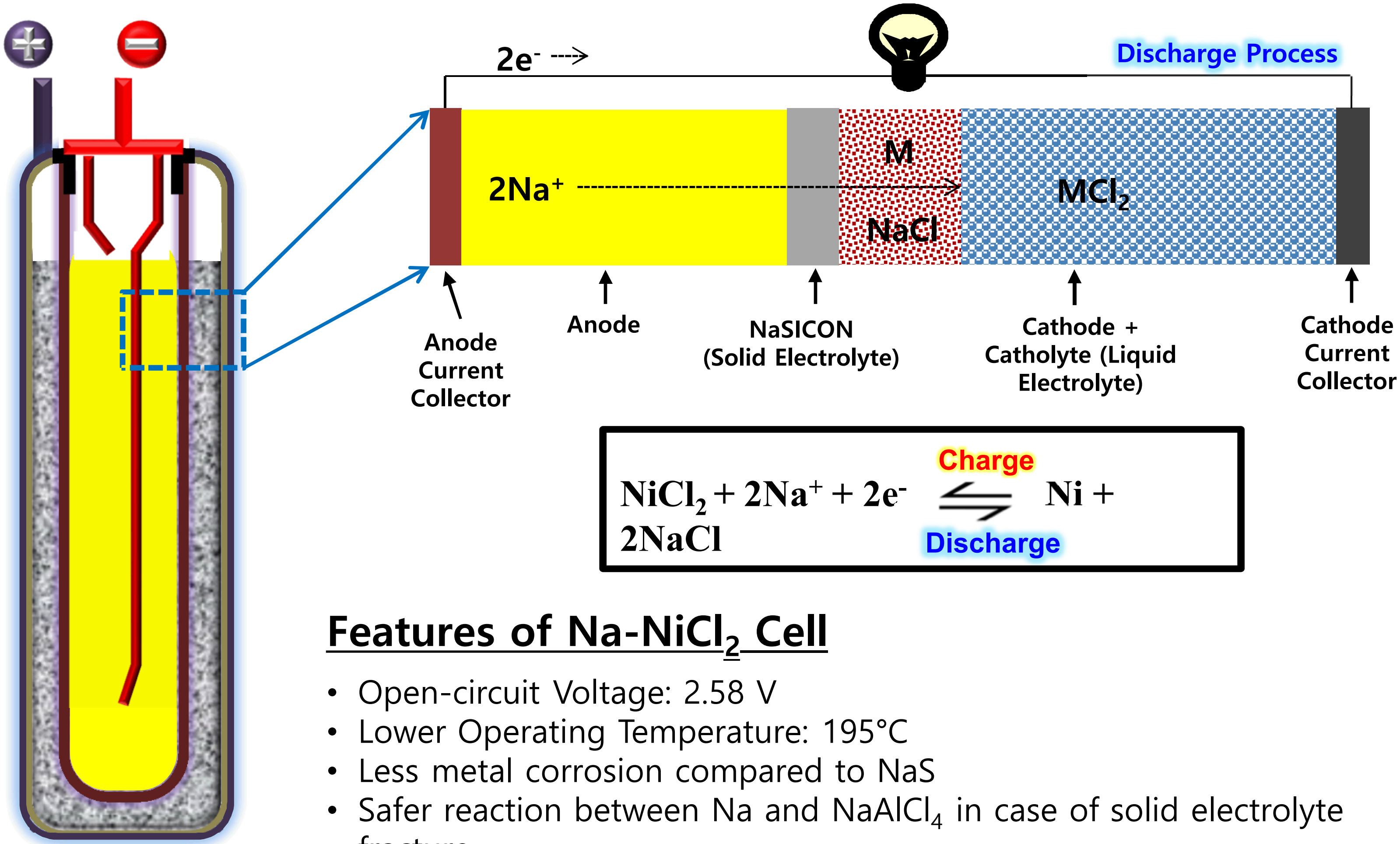
Na-NiCl$_2$ Battery Technology



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

Features of Na-NiCl$_2$ Cell

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

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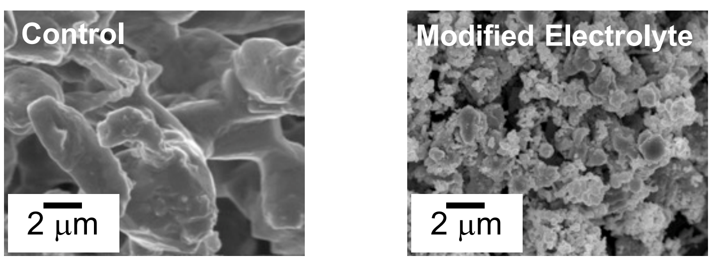
Stable $Na\text{-}NiCl_2$ Cell Performance

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

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

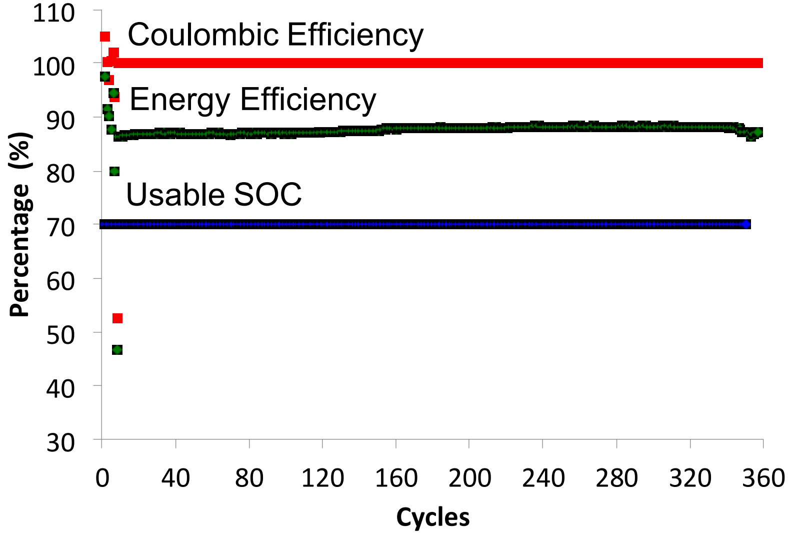
Using a NaSICON electrolyte allows us to lower temperature below 200°C and adding Ni metal growth inhibitors.

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



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

Cycle test (Prototype cell)



13 Wh $Na\text{-}NiCl_2$ (NaX) Cell operation for 9+ months. 70% Depth of Discharge, >85% energy efficiency at 65 mA /cm² Charge/Discharge NaSICON current density

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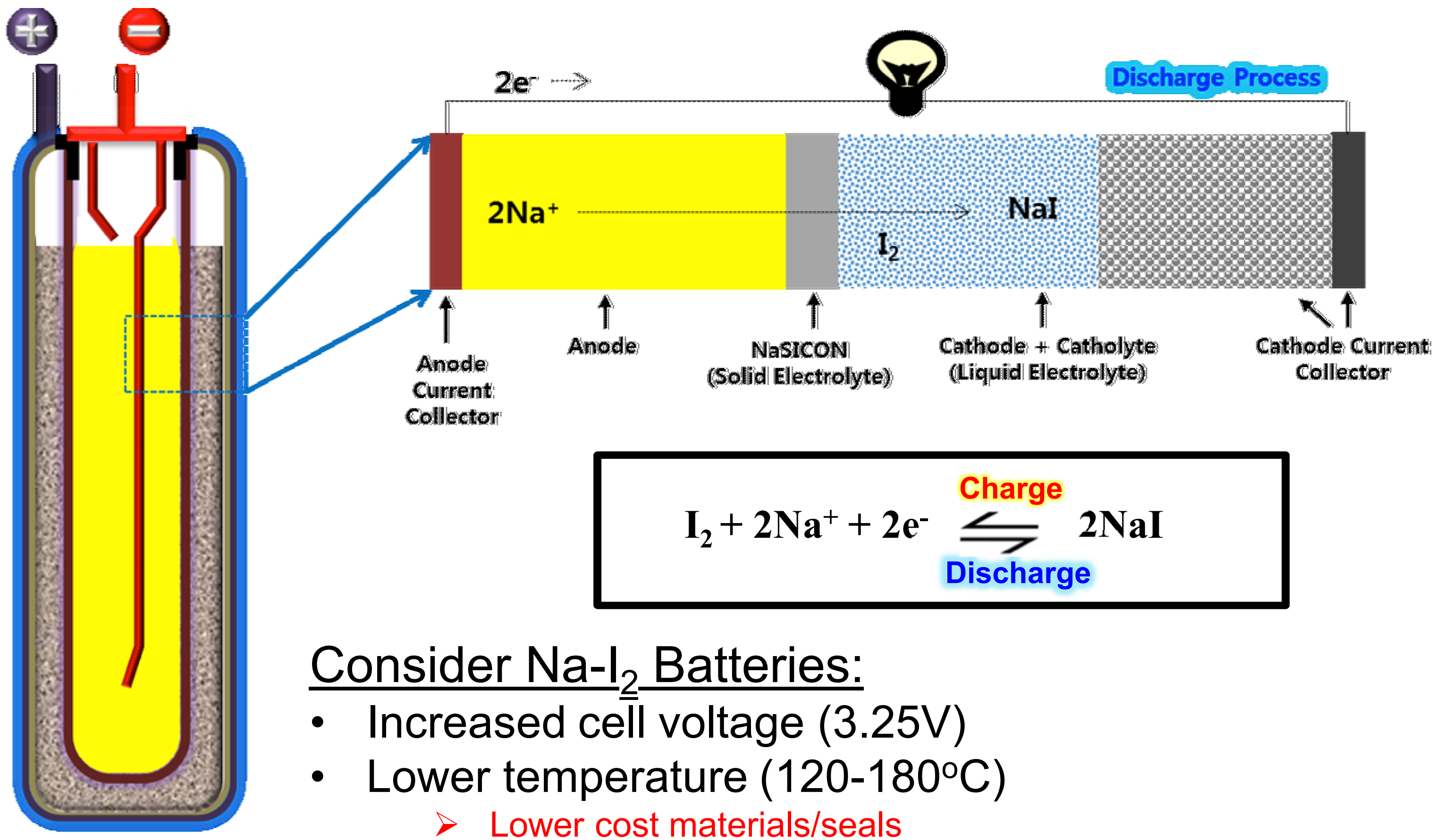
Na-I_2 Battery Technology



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

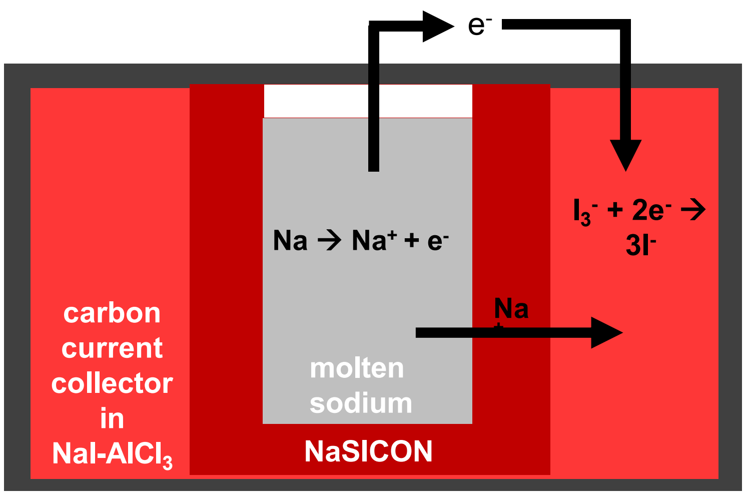
<u>Consider Na-I_2 Batteries:</u>

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

Na-I$_2$ Prototype Assembly

Lab Scale Test Conditions

- Up to 28Wh lab-scale cell
- Graphite felt + tungsten wire current collectors
- NaI-AlCl$_3$ based molten salt catholyte
- 1" NaSICON tube glass sealed to α-alumina
- T = 150-180˚C



Anode:
$Na \rightarrow Na^+ + e^-$ $E^0 = 0.00$ V vs. Na/Na$^+$

Cathode:
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$ V vs. Na/Na$^+$

Overall:
$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0 = 3.24$ V

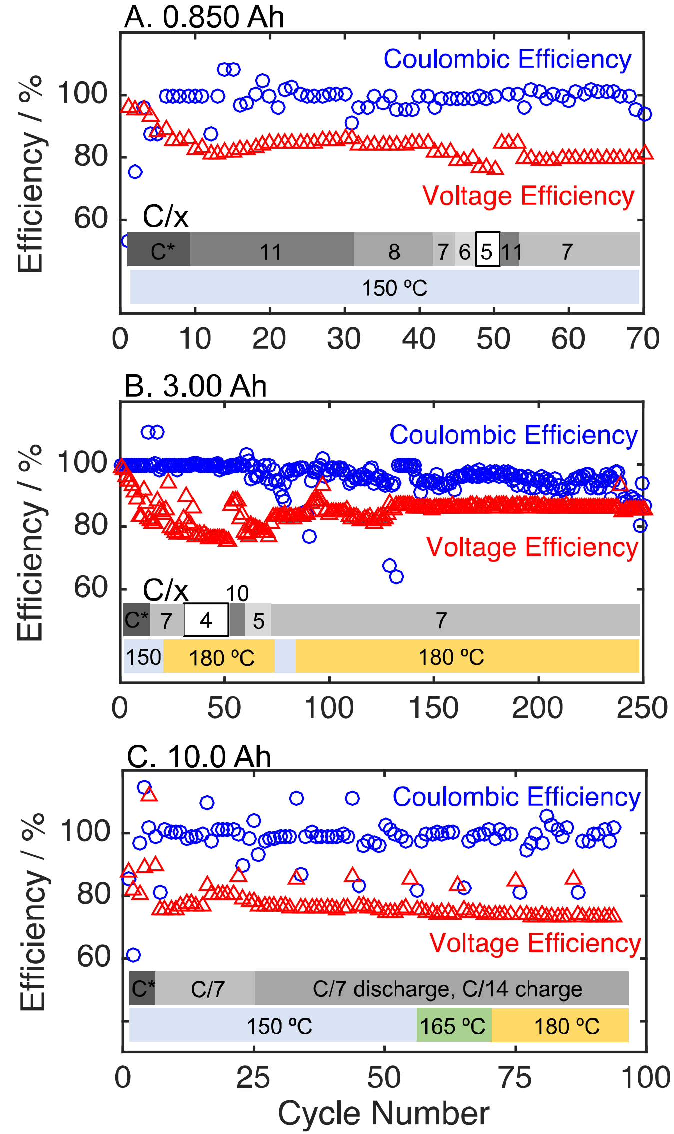
Promising in Na-I_2 Prototypes

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

- Promising cycle life across battery scales
- Functional C-rates
- 28.5 mA/cm^2 current density
- High energy efficiency of ~ 80%

Noted that for 28 Wh system, every 11th cycle benefited from a C/15 rate to “refresh” performance.

Could this be related to catholyte materials chemistry?



Understanding Basic Cathode Materials Chemistry

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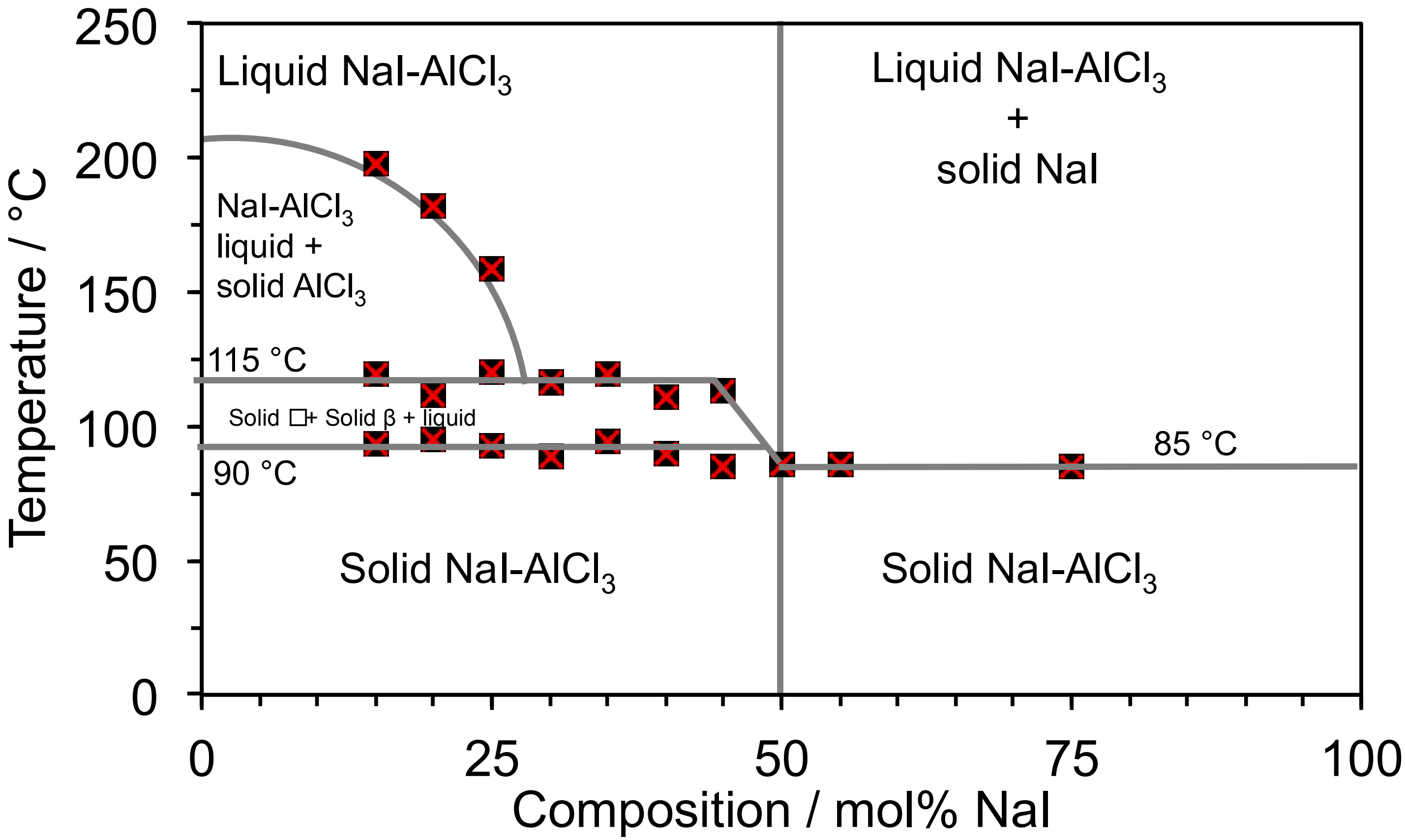
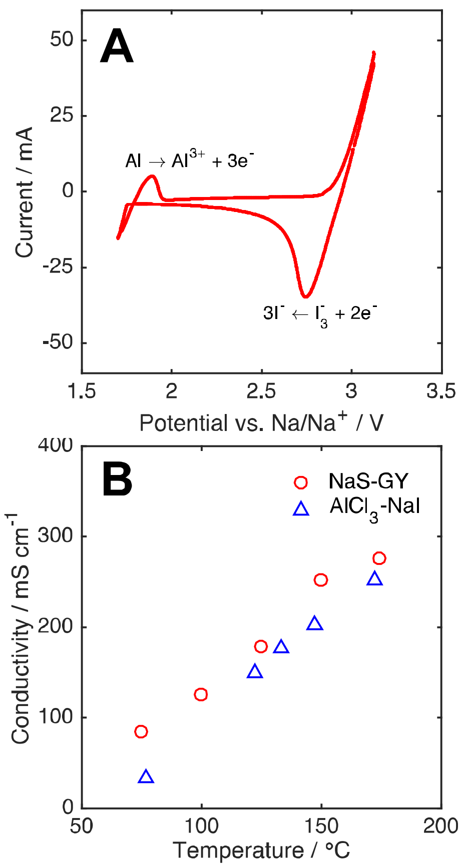
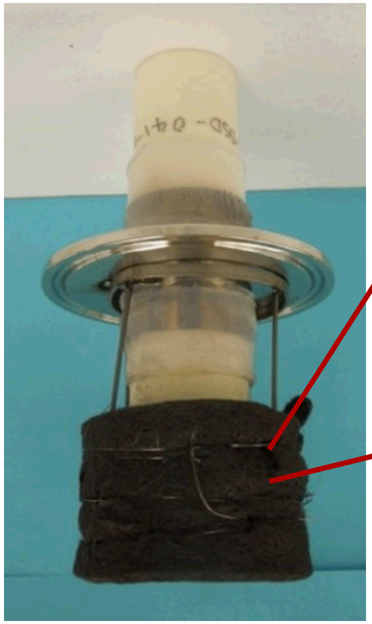
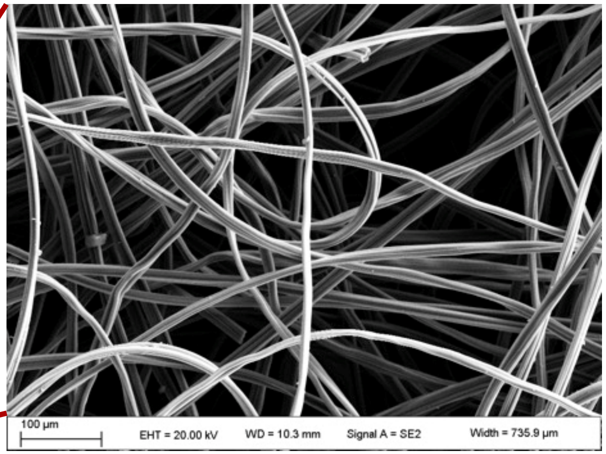
Preliminary Phase Diagram of NaI-$AlCl_3$ Catholyte



Molten Catholyte Current Collector





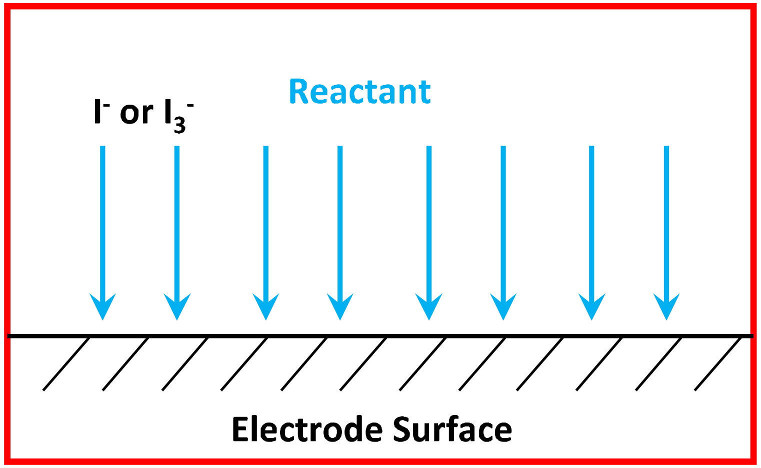


Motivated by the microscale fibers of the carbon felt current collector, we used a carbon microelectrode to probe the electrochemical properties of the catholyte salt.

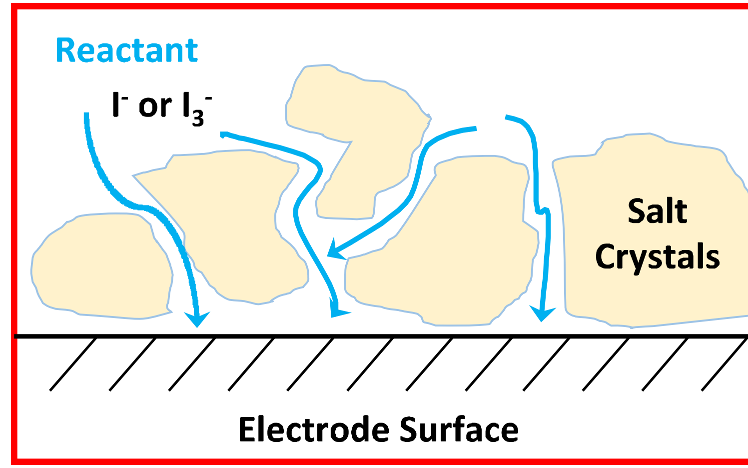
(A) CV of a carbon felt electrode in the 40$AlCl_3$:60NaI catholyte at 125 °C and 100 mV s^{-1}. (B) Ionic conductivity of the 40$AlCl_3$:60NaI catholyte and NaSICON NaS-GY as a function of temperature.

Molten Catholyte Development

Regular Diffusion

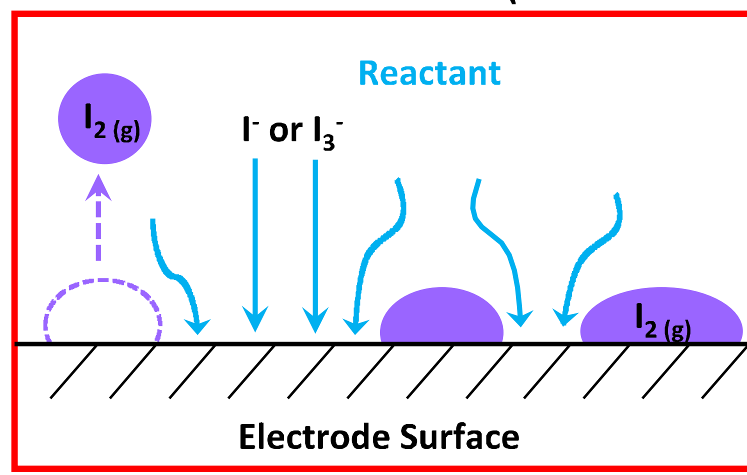


Hindered Diffusion – Solid Phase



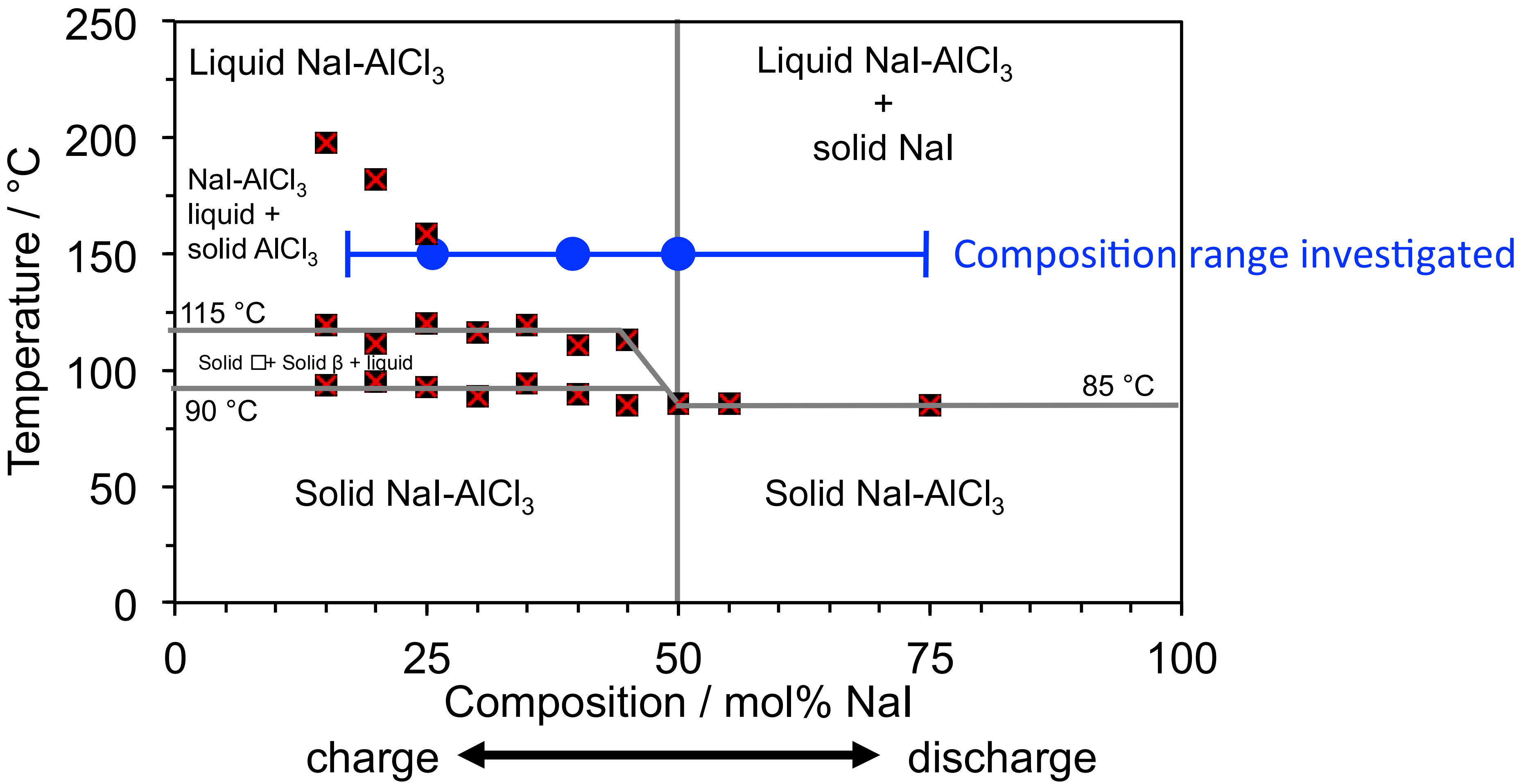
- Regular Diffusion vs Hindered diffusion
  - Fast mass transport
  - Slow mass transport due to reactant blocking
- Presence of solid salt crystals (or bubbles) can slow mass transport down near the electrode surface
  - Significantly affects the "C rate"
- Reactant that is not in molten salt will slow charge/discharge rates
  - Solid crystal phase – such as un-molten NaI
  - Gas phase – such as vaporized I_2

Hindered Diffusion – Gas Phases (Bubble Formation)



Molten Salt Compositions Tested

Preliminary Phase Diagram of NaI-$AlCl_3$ Catholyte

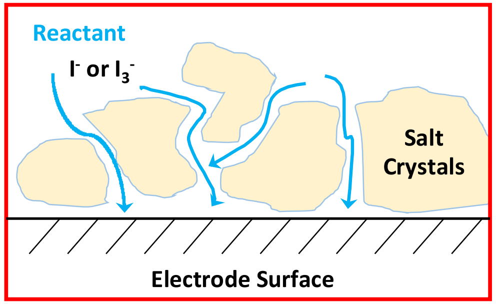


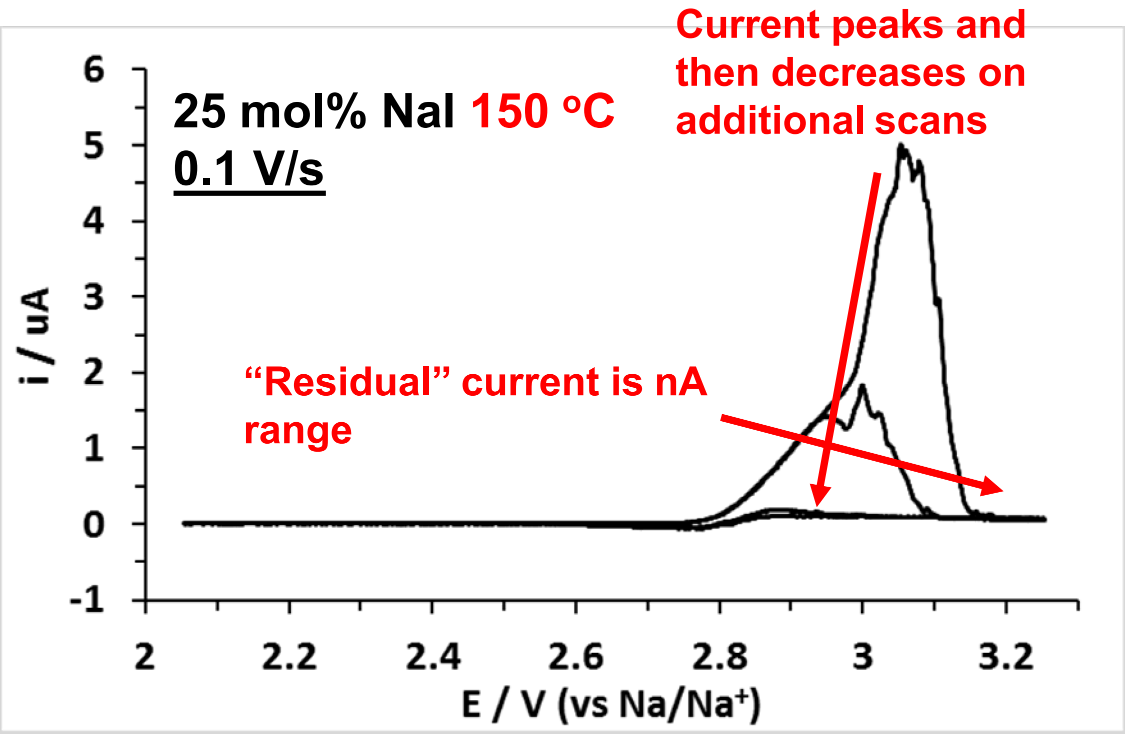
Hindered Diffusion: Solid State

Possible solid precipitation observed at electrode surface

- Hindered diffusion from presence of solids near electrode

Current Peaks then settles to a lower “residual” current

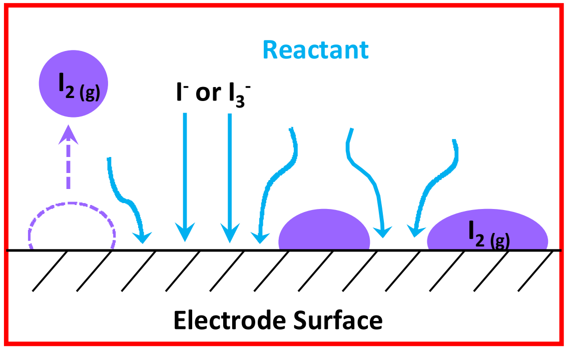


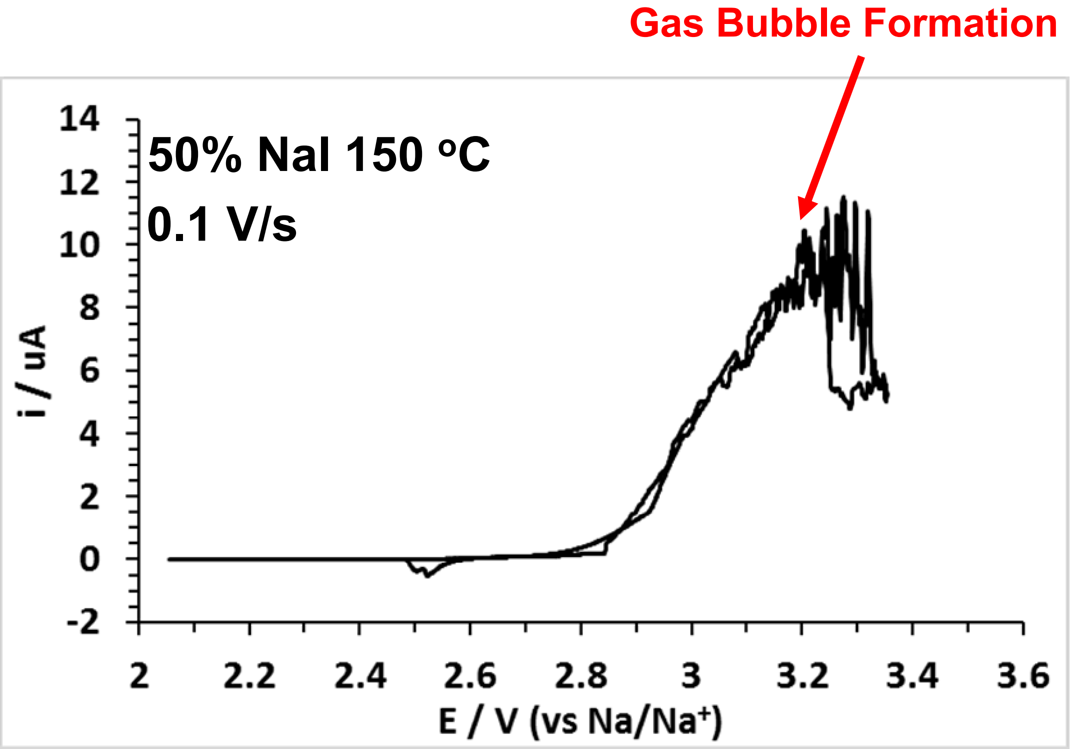


Hindered Diffusion: Gas State

Stable bubble formation observed for very high NaI mol% compositions

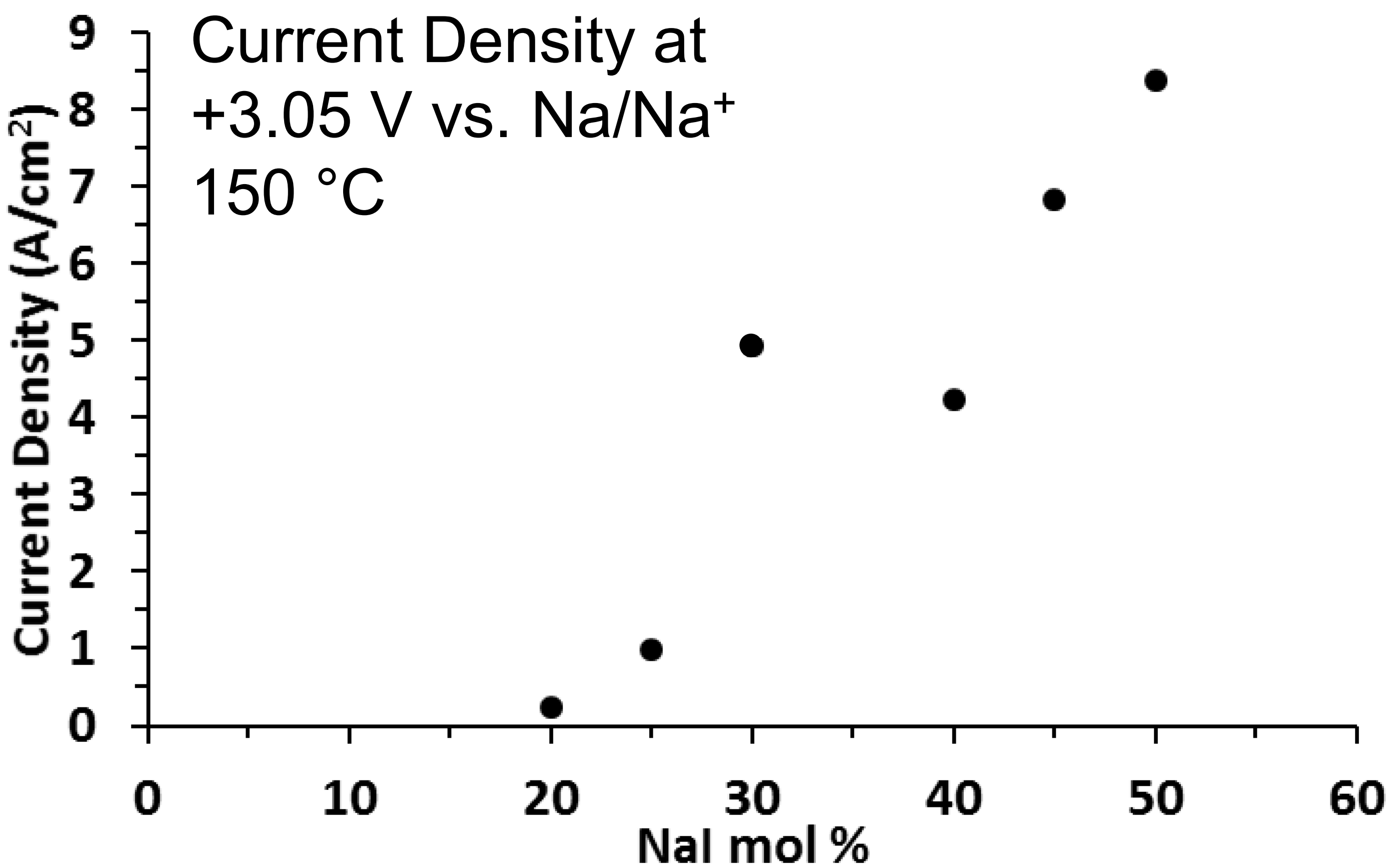
- I_2 being generated at a very fast rate stabilizes the bubbles
- Dissolution/diffusion of I_2 is in equilibrium with generation rate





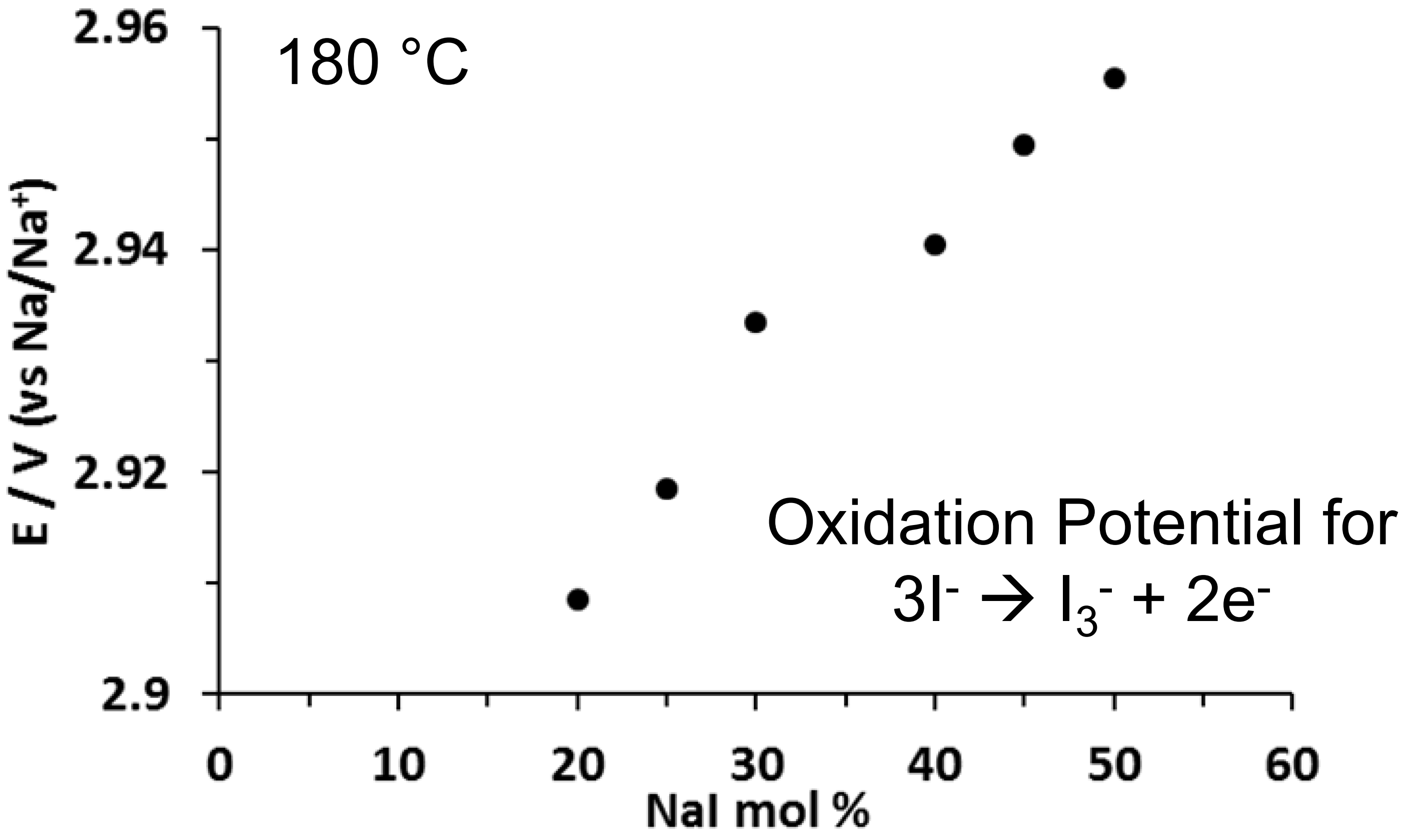
Electrochemical Performance of Catholyte

Highest current densities are observed at highest NaI concentrations. There is a significant drop in current density when solid $AlCl_3$ is formed.



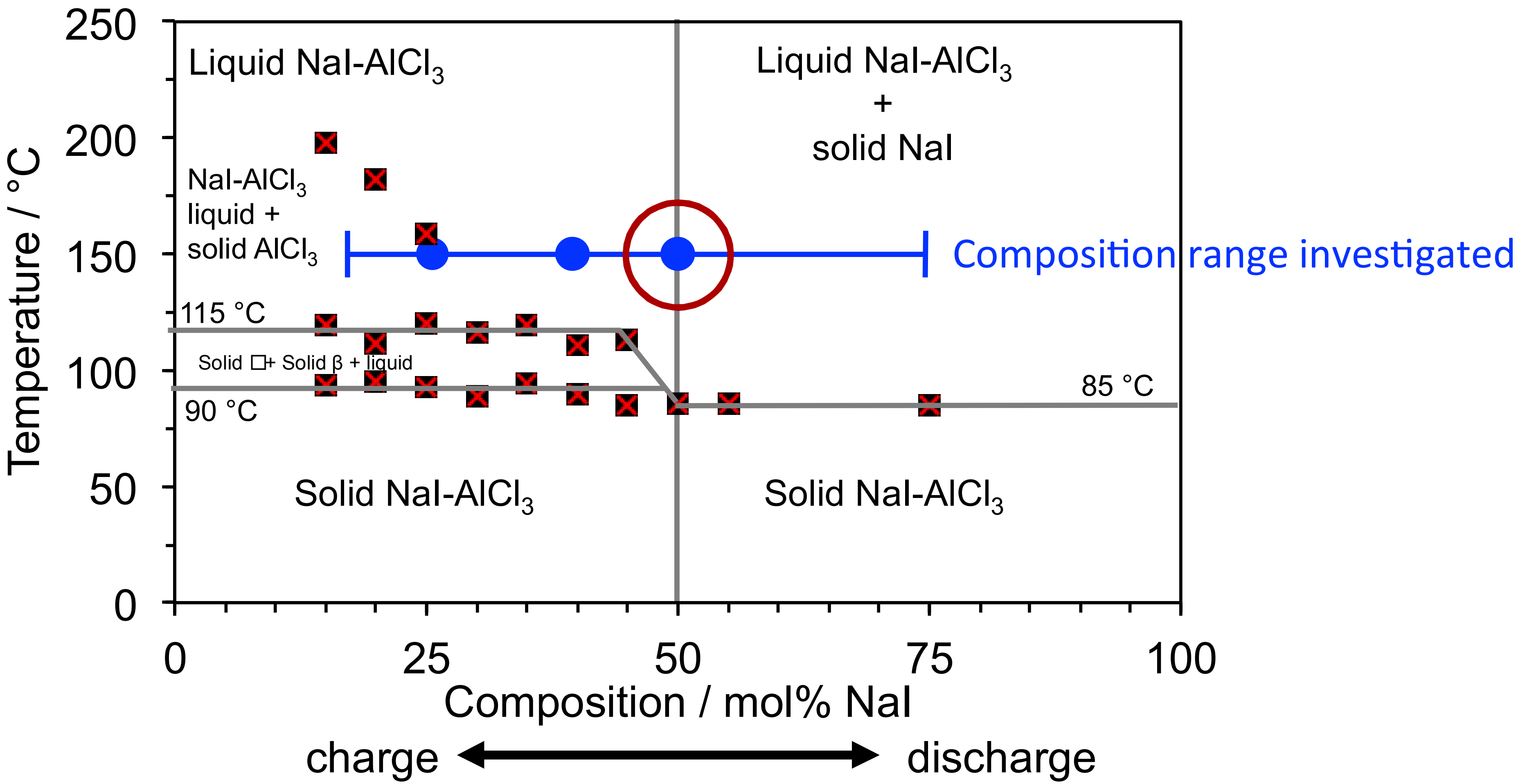
Battery Potential is Modestly Affected by Catholyte Composition

Higher battery operating potentials seen at higher NaI concentrations.



Molten Salt Compositions Tested

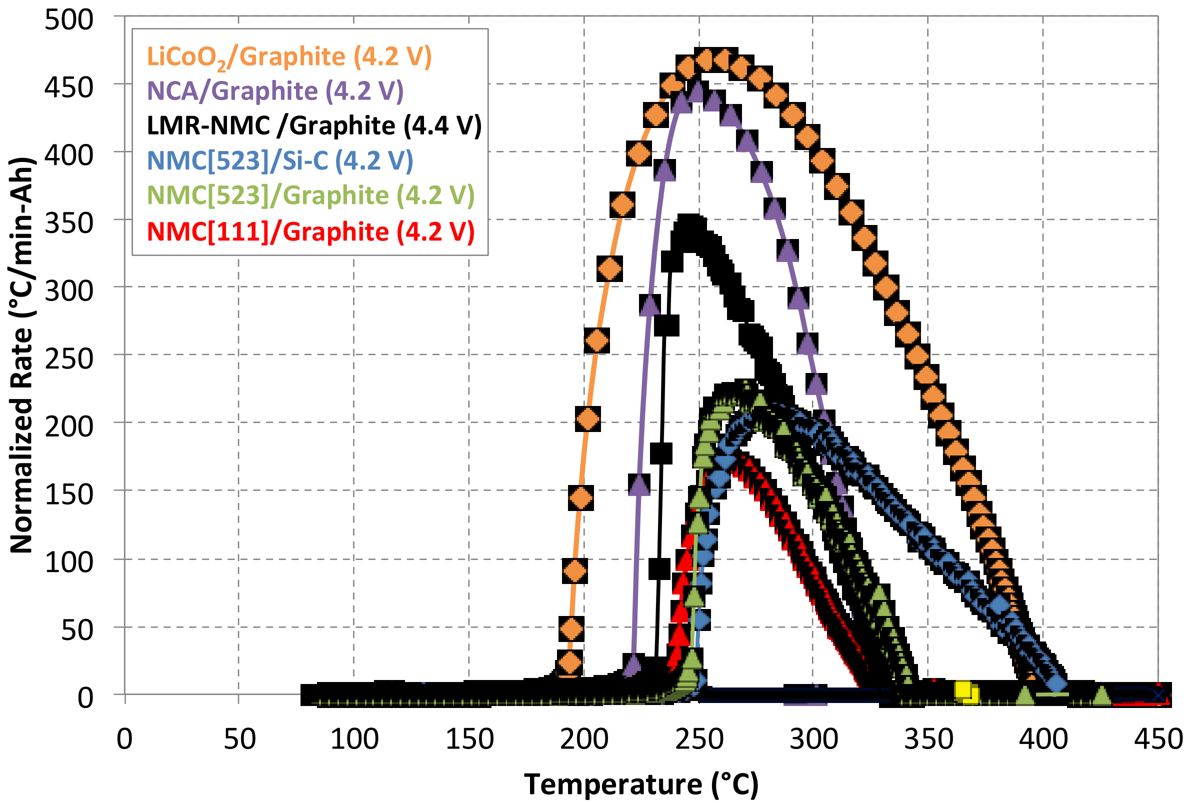
Preliminary Phase Diagram of $NaI-AlCl_3$ Catholyte



Safety Performance of Catholyte Salt

Accelerating Rate Calorimetry (ARC) Shows No Significant Exotherms

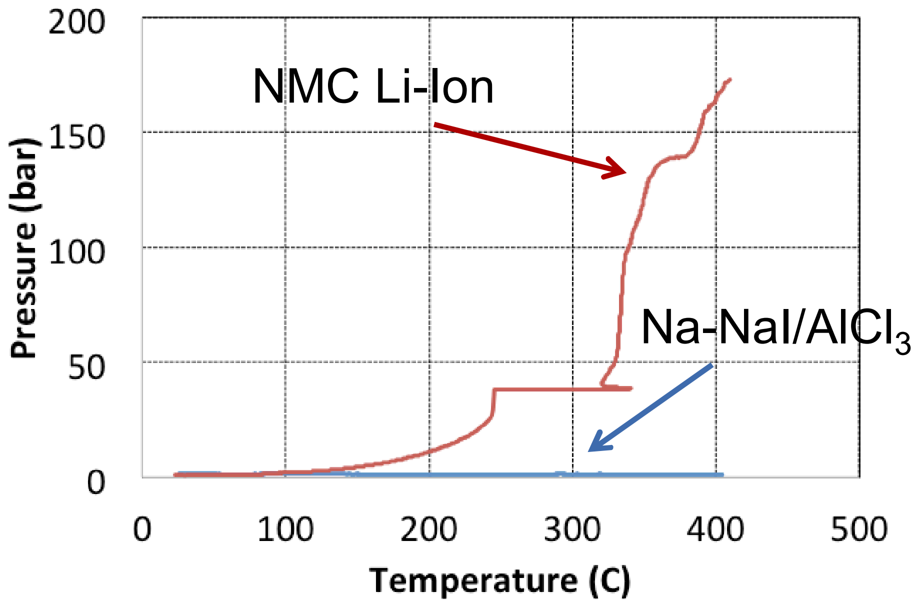
When complete separator failure is simulated by mixing Na metal and NaI/$AlCl_3$ catholyte, ARC testing reveals no hazardous runaway exothermic behavior!



Na-System Shows Minimal System Pressurization

Measuring pressure generated during ARC testing shows no significant gas generation/pressurization from the Na-NaI/$AlCl_3$ mixture. Even in up to 75% charge state, no significant gas pressurization (e.g., I_2 evolution) was observed.

In contrast volatile components of an NMC Li-Ion produce a dramatic pressure spike at elevated temperatures.



This minimal pressurization represents a dramatic safety benefit of Na-batteries.

Take Home Messages

- ✓ There is a critical needs for *safe, low-cost,* grid scale energy storage technologies with *reliable, long-term* performance.
  - ✓ Na-batteries offer the potential to meet this demand!
  - ✓ Na-I_2 batteries offer potential as a new, long-lived stationary energy storage technology.
- ✓ Not all battery chemistries are the same! Identifying specific materials chemistry benefits and drawbacks for a specific application is important.
- ✓ Understanding the materials chemistry of a molten catholyte can inform potential improvements in battery reliability, safety, and functional lifetime.

- ✓ Continued collaborations between National Laboratories, academia, and industry will prove powerful in enabling next generation grid-scale energy storage solutions.

Thank you!

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

Work on Na-$NiCl_2$ batteries was performed through collaboration between Ceramatec and SK Innovation.

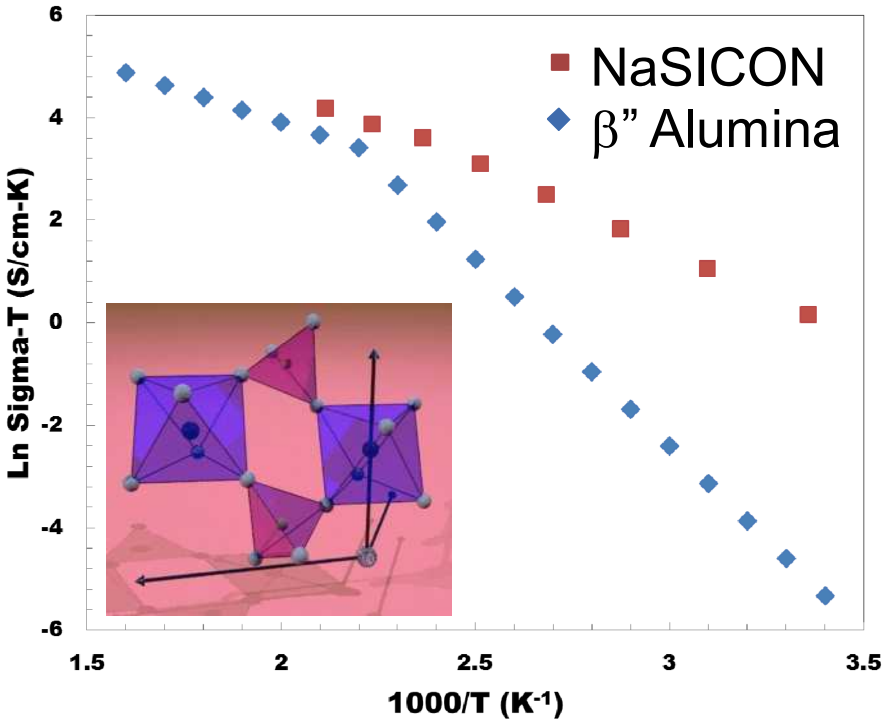
Post-doctoral positions at SNL will be available in FY18 for qualified candidates.

Contact: Erik D. Spoerke, Ph.D.
edspoer@sandia.gov

Backup Slides

NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

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



Engineered materials chemistry and advanced, scalable processing (Ceramatec, CoorsTek) make NaSICON a *chemically/mechanically stable, low temperature, high conductivity (>10^{-3} S/cm @RT)* separator technology.

Poster: S. Bhavaraju

Considerations for Battery Selection

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

Pre-Commercial Na-$NiCl_2$ systems

Recently demonstrated high performance cycling in precommercial prototypes at 195°C at 53mA/cm^2 and C/7 rate (w/ Ceramatec, Inc. and SK Innovation):

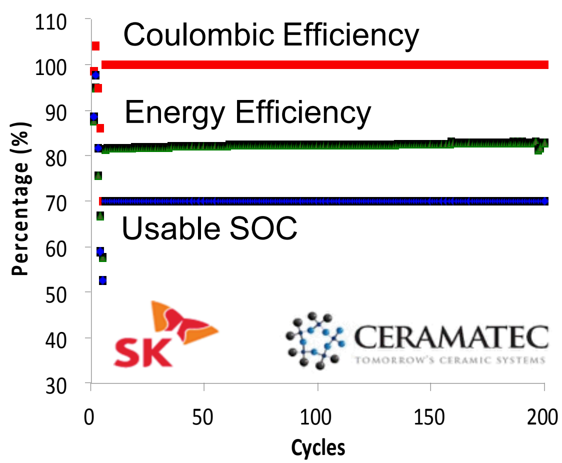
100 Wh Na-$NiCl_2$ unit cell:

- operational for 4+ months.
- 500+ cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 81.5 %

250 Wh Na-$NiCl_2$ unit cell:

- operational for 3+ months
- 110 cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 80 %

100Wh Cycling Data



100 Wh, Na-battery prototype →

Proposed 10 kWh Na module:
40x250Wh Ceramatec cells

Ongoing efforts targeting for large scale (10kWh), intermediate temperature demonstrations (w/ Ceramatec: 180 Wh/l, \$150/kWh, 2.6V, 40 cells).

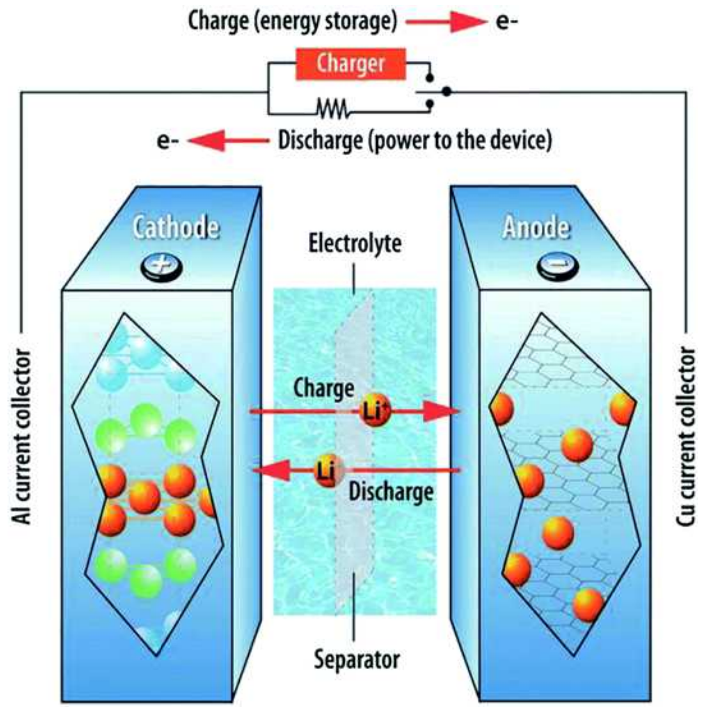
We are currently seeking industry partners to advance large-scale demonstrations and drive commercialization of these batteries.

SNL Principal Investigator: Dr. Erik Spoerke (edspoer@sandia.gov)

Interfacial Considerations in Basic Battery Design

Although most batteries are similar in concept
not all batteries are equivalent!

Different battery chemistries introduce unique interfacial challenges.



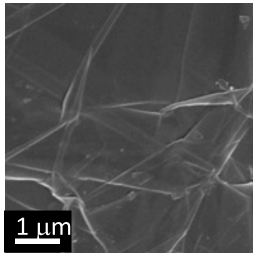
<u>Basic elements of all (most) batteries:</u>

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

M. Osiak, *et al*. *J. Mater. Chem. A*, (2014), **2**, 9433-9460.

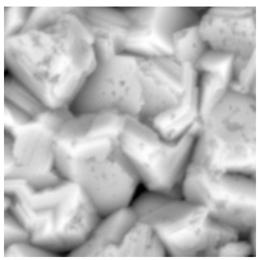
Improving Cathode Structure

Electrolessly Coated Tungsten/Carbon Electrodes



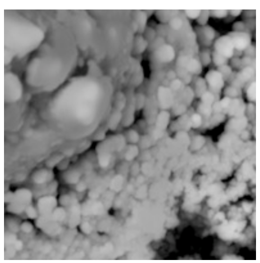
Carbon electrode
(graphite, powder, foam)

↓



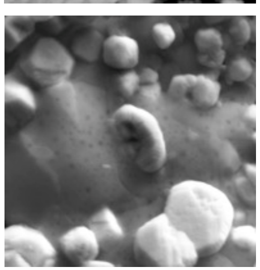
Intermediate coating

↓

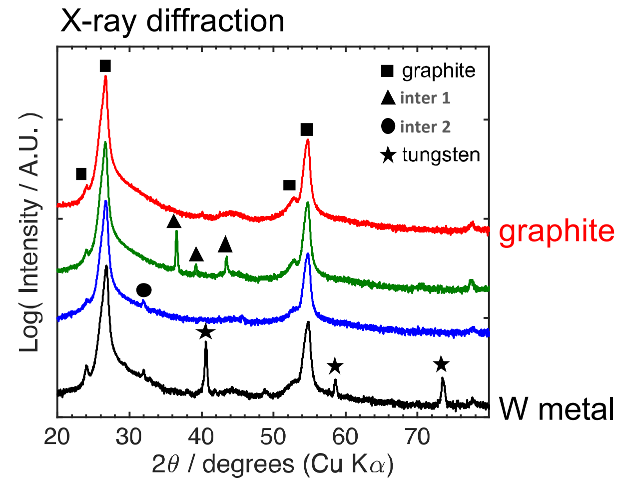


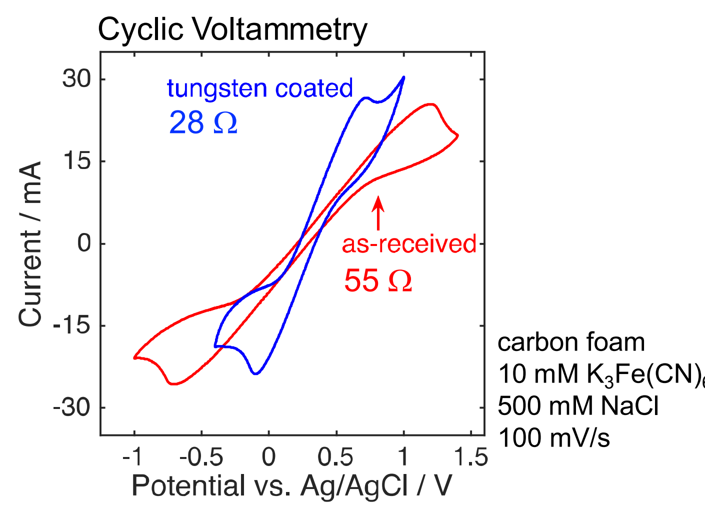
Convert to W-precursor

↓



Reductive anneal creates
Crystalline, metallic tungsten.





2X Reduction in electrode resistance will reduce ASR and enable superior electrochemical performance.