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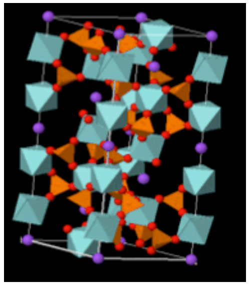

Sodium-Based Batteries: Toward Meeting Next Generation Challenges in Grid-Scale Energy Storage

Erik D. Spoerke

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Ceramatec, Inc. Salt Lake City, UT

Electrical Energy Storage Applications and Technologies 2017
San Diego, CA October 11-13, 2017

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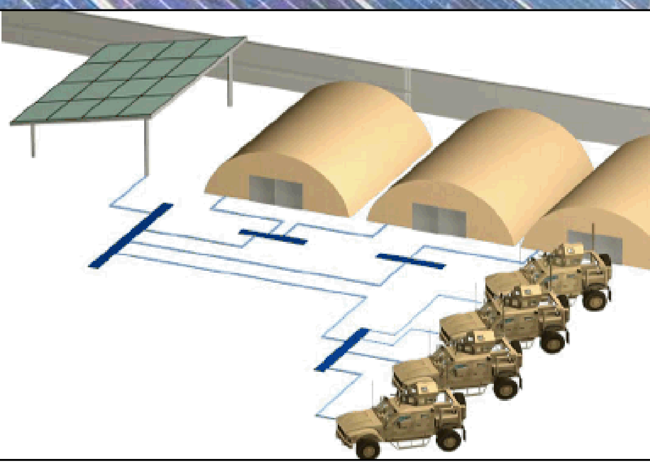
Critical need for Grid Scale Batteries



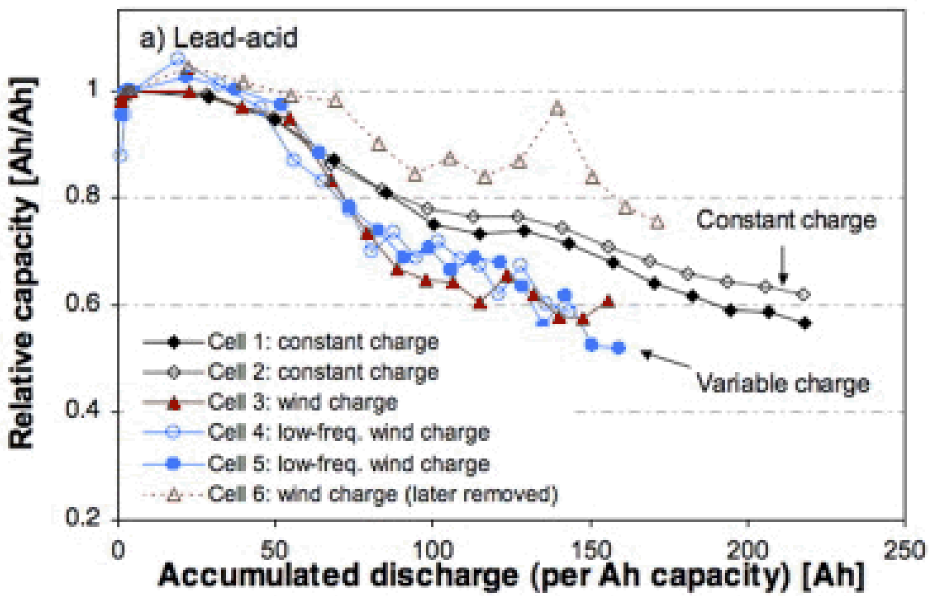
Safe, grid-scale electrical energy storage is critical!

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

Challenges with Current Battery Technologies

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

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

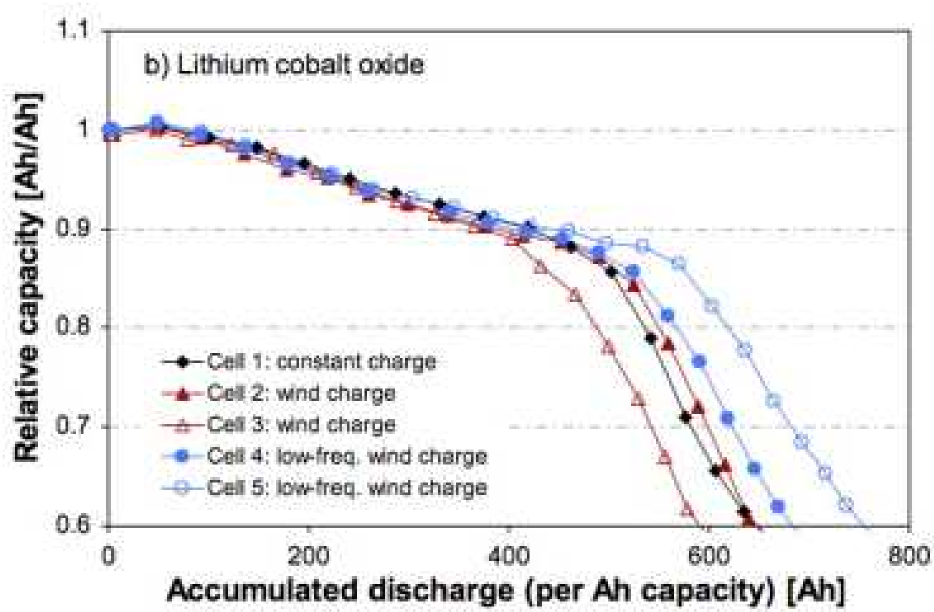


E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

Challenges with Current Battery Technologies

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

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



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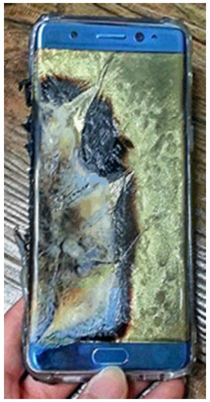
Cell Phone



<10Wh

Laptop Computer

<100Wh

Tesla EV Battery

kWh (~6895 18650 cells)

Battery Recycling Plant

MWh (?)

Challenges with Current Battery Technologies

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)

September, 2011: Fire at the Tsukuba Plant (Joso City, Ibaraki Prefecture). 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.

February, 2005: Fire at NGK's NAS battery plant in Komaki City. Fire broke from modular battery undergoing high-voltage testing.

Recurring themes…

In addition to useable energy density and power density, next generation grid scale battery requirements include:

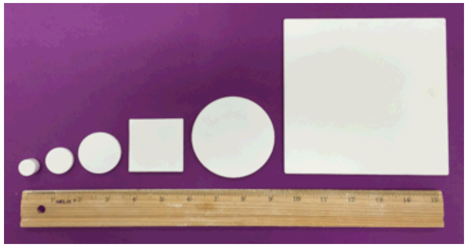
- Low cost
- Safety
- Long Cycle Life

Can we envision a low cost, long-lifetime, and inherently safer battery technology?

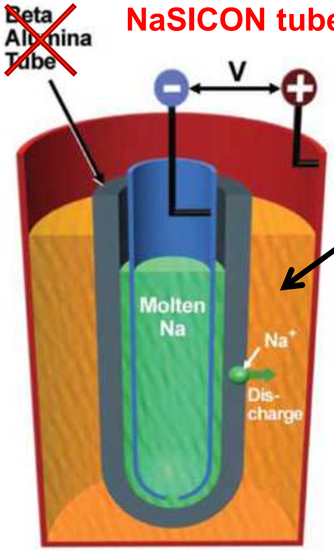
Intermediate Temperature Molten Salt Na-Based Batteries

<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**
  - ✓ **<u>Demonstrated up to 250Wh prototypes</u>**



100 Wh, Na-battery prototype



$Na\text{-}NiCl_2$ battery
- **Salt: $NiCl_2/AlCl_3$**

$Na\text{-}I_2$ 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):
$Na + ½ I_2 \leftrightarrow Na^+ + I^-$

CERAMATEC TOMORROW'S CERAMIC SYSTEMS SNL Principal Investigator: Dr. Erik Spoerke (edspoer@sandia.gov)

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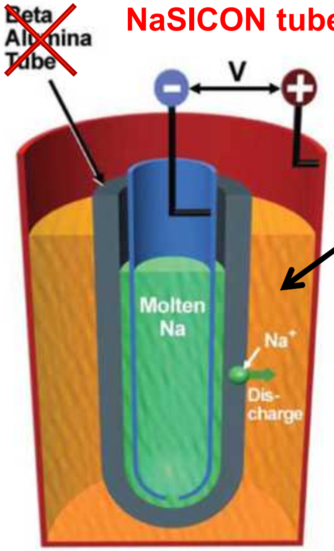
  - ✓ **Lower cost**
  - ✓ **Increased reliability and lifetime**
  - ✓ **Improved capacity retention (limitation of Li-ion and Pb-acid)**

NaSICON tube separator enables lower temperature operation



Molten salt catholyte

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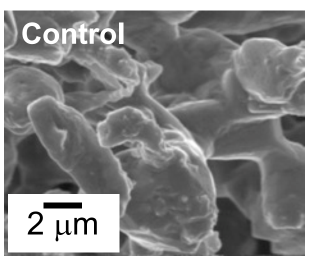
Stabilizing Na-$NiCl_2$ Cell Performance

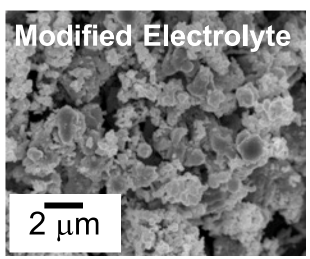
Nickel grain growth at high temperatures during cycling limits cycle life and charge-discharge kinetics for Na-$NiCl_2$ batteries.

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.

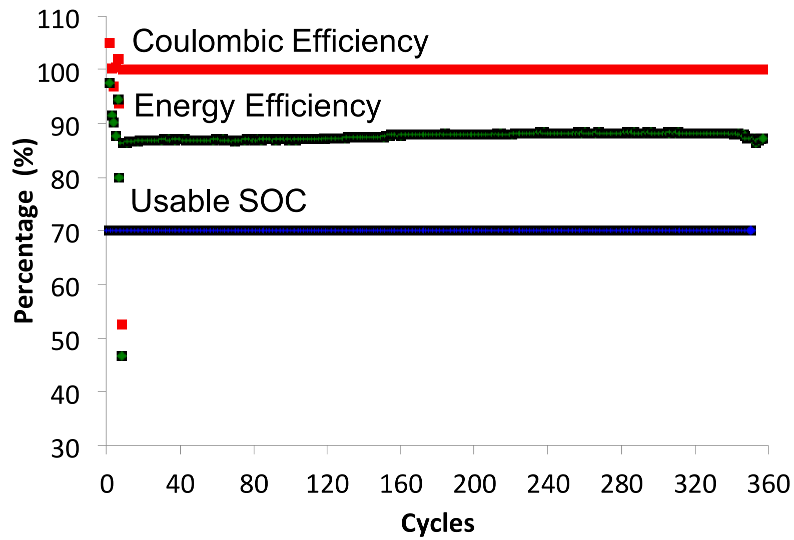
Together, these changes limit Ni metal particle growth and preserve stable battery performance over months (hundreds of cycles).





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

Cycle test (Prototype cell)



13 Wh Na-$NiCl_2$ (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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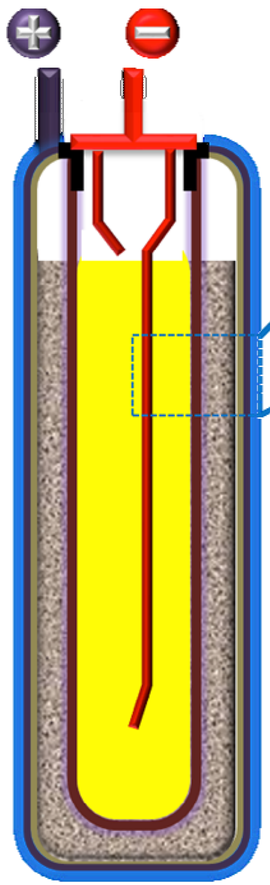
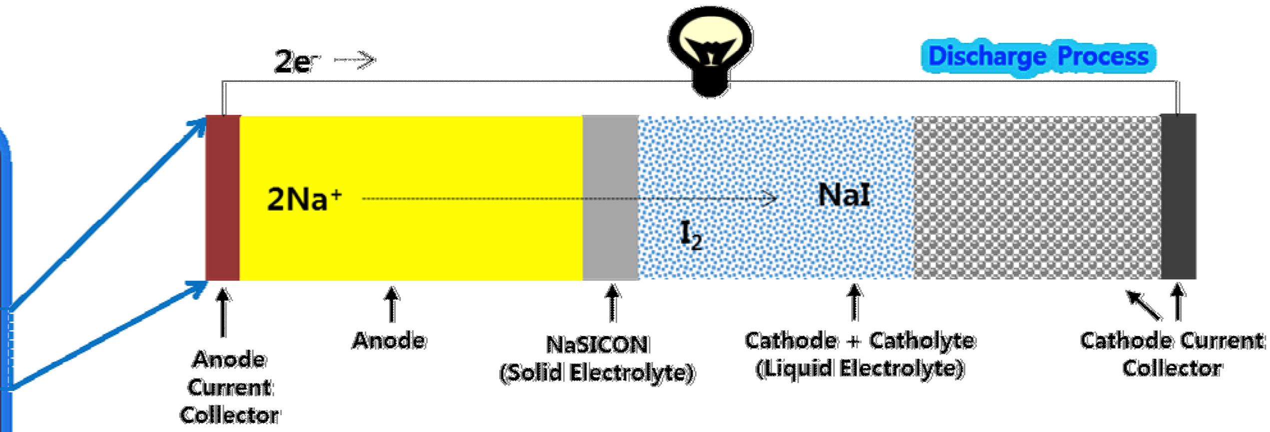
SK

Toward Improved Battery Lifetime

Can we eliminate particle phases in molten catholytes?

Na-I_2 Battery Technology: A Liquid Catholyte





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

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

- Increased cell voltage (3.3V*)
- Lower temperature (120-180^{o}C)
    - Lower cost materials/seals
    - Lower operational costs
    - New cathode chemistries
- *Liquid cathode increases feasible cycle life*

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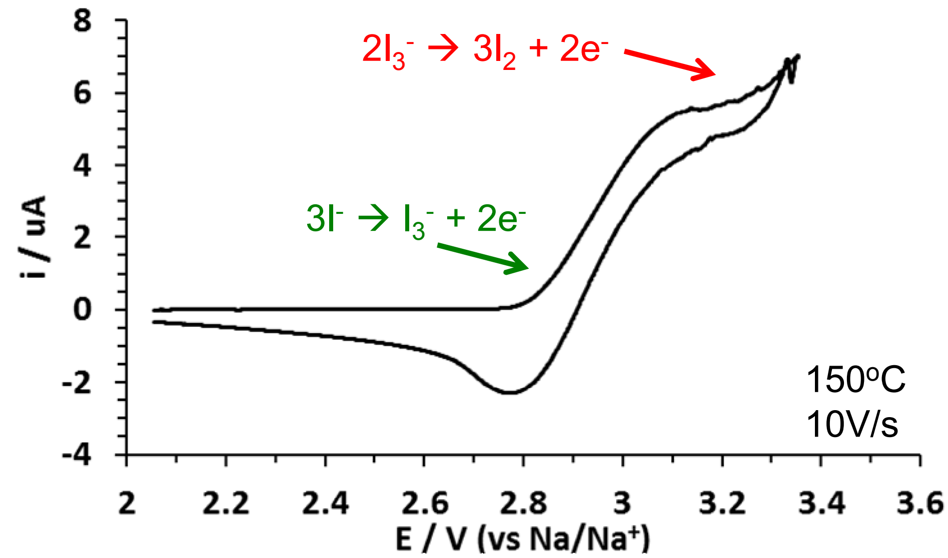
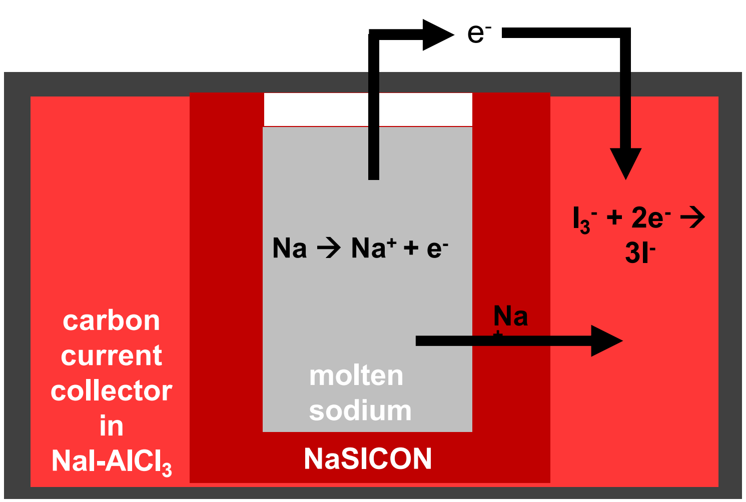
Na-I_2 Electrochemistry

The iodine generation step is a 2-stage reaction:

$3I^- \rightarrow I_3^- + 2e^-$ E = 2.9V vs. Na/Na^+

$2I_3^- \rightarrow 3I_2 + 2e^-$ E = 3.3V vs. Na/Na^+





Anode:
Na → $Na^+ + e^-$

Cathode:
$I_3^- + 2e^- \rightarrow 3I^-$

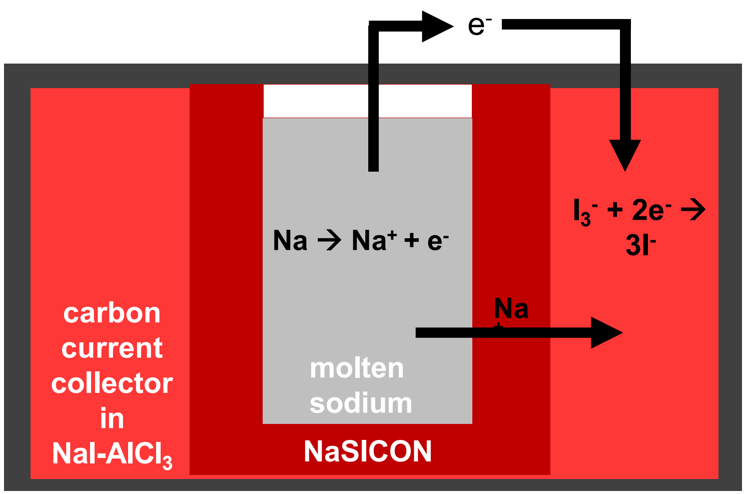
Overall:
$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$

*Practical OCV for tested batteries was 2.8-2.9V

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



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

Promise in Na-I_2 Prototypes!

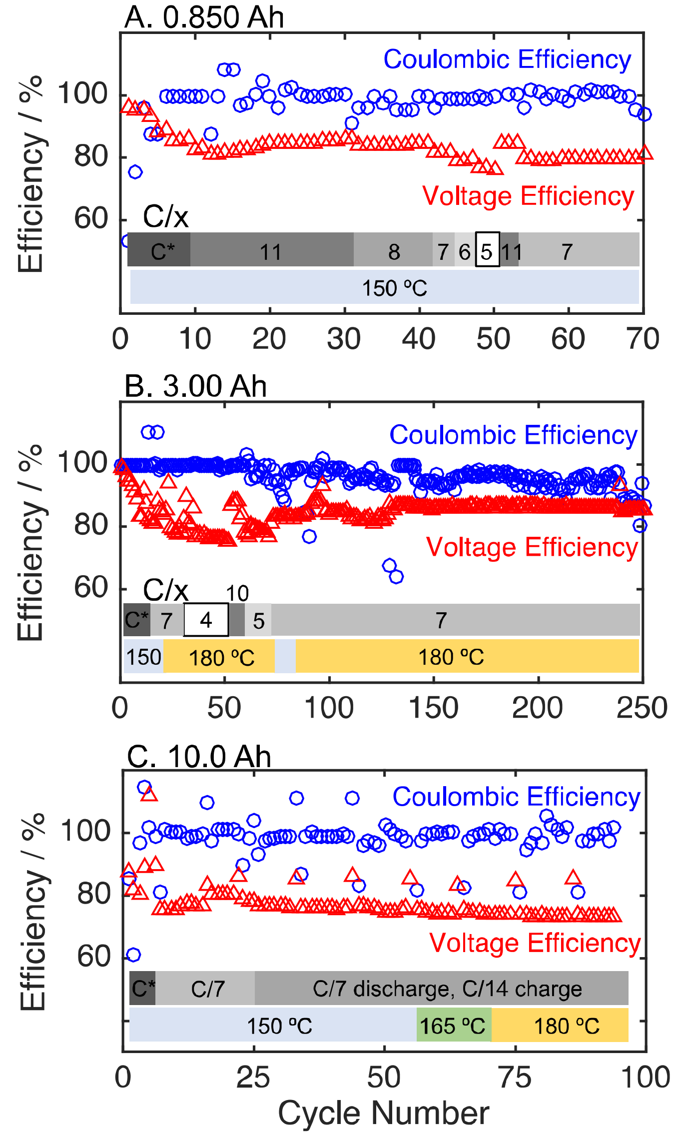
Sandia National Laboratories

✓ **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%

*Note that for 28 Wh (10 Ah) system, every 11th cycle benefited from a C/15 rate to "refresh" performance.

Could this issue be related to catholyte materials chemistry?



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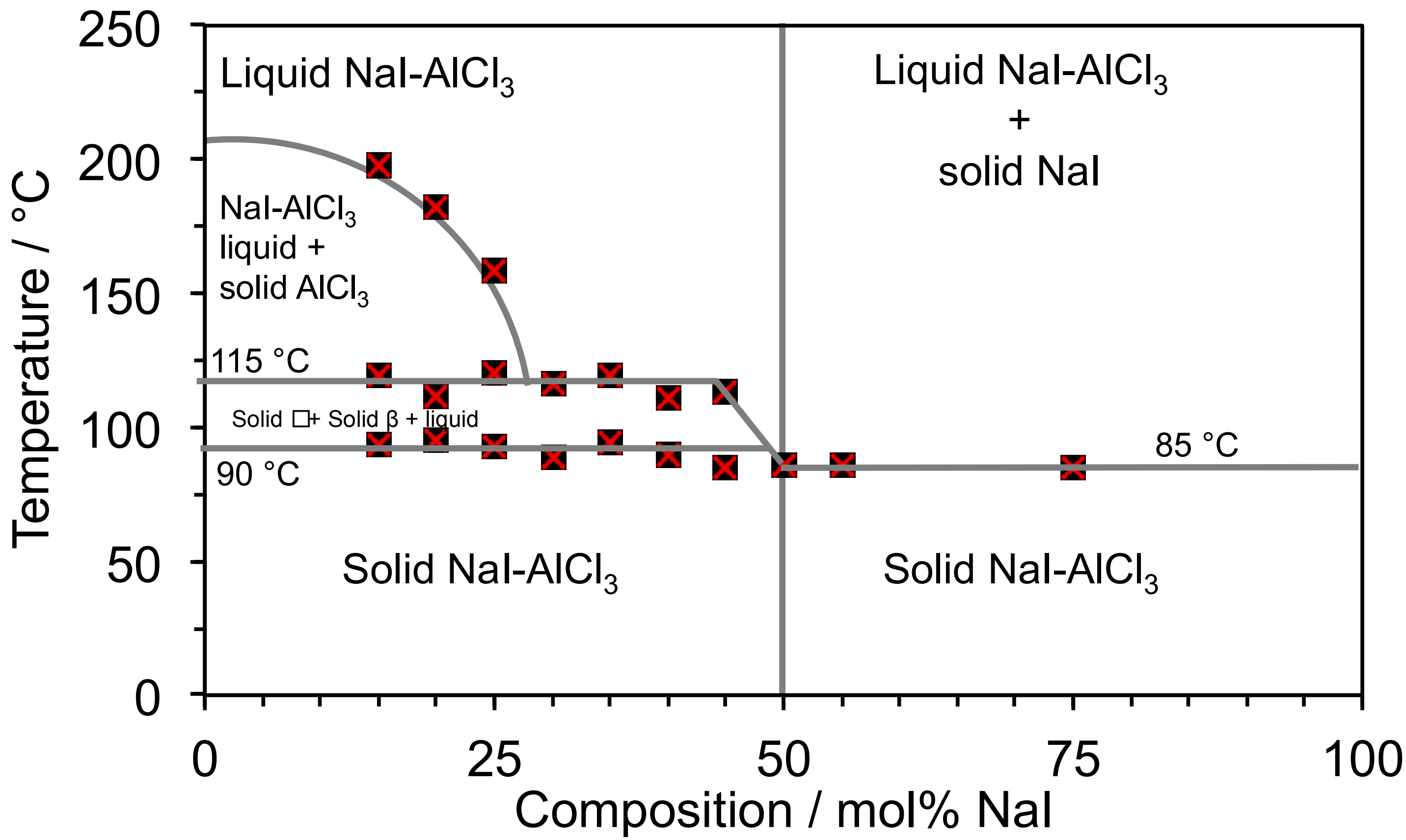
Understanding Basic Cathode Materials Chemistry

Preliminary Phase Diagram of $NaI-AlCl_3$ Catholyte



Phase diagram created from differential scanning calorimetry data.

Molten Salt Conductivity Compares with NaSICON Conductivity

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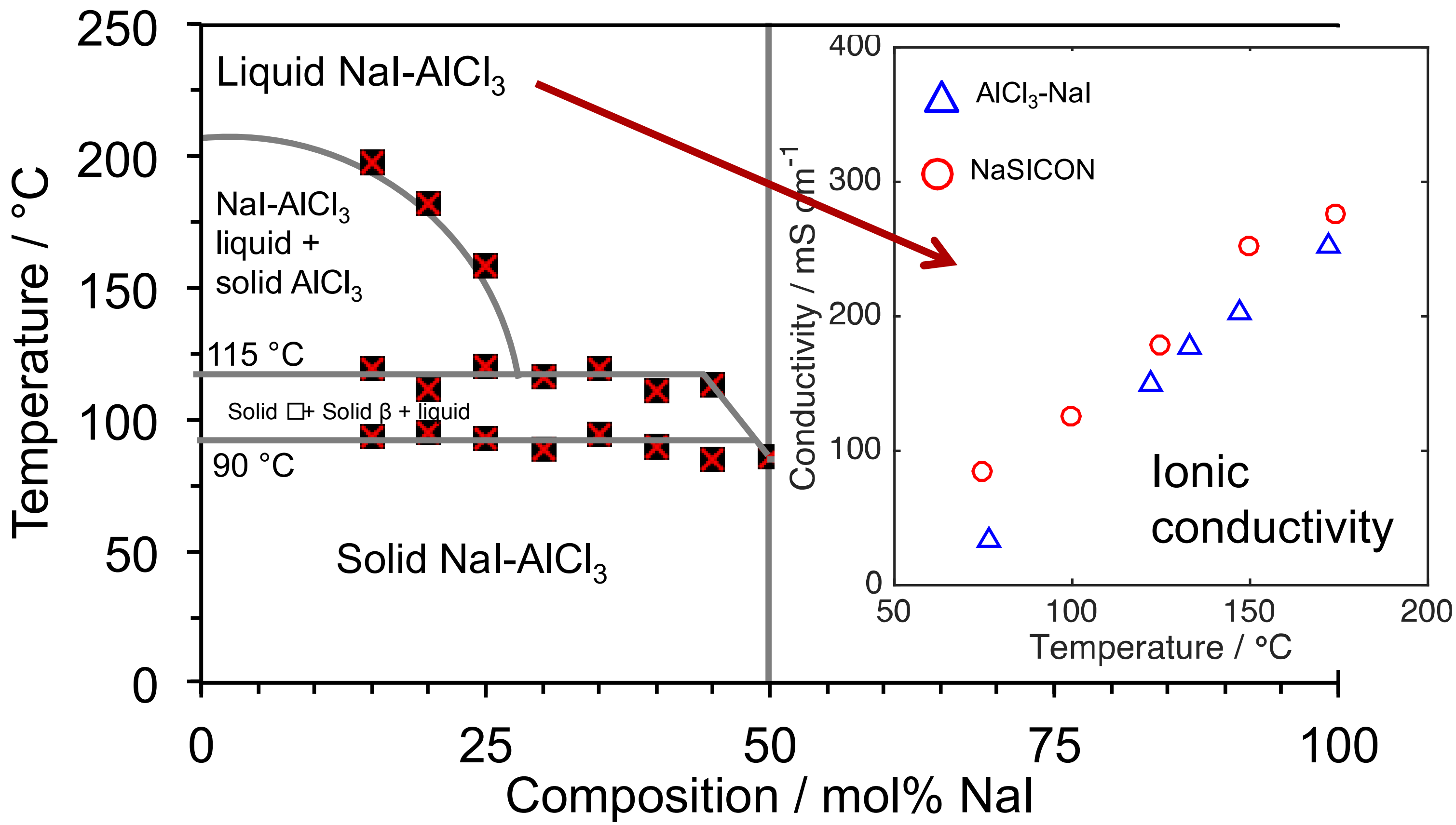
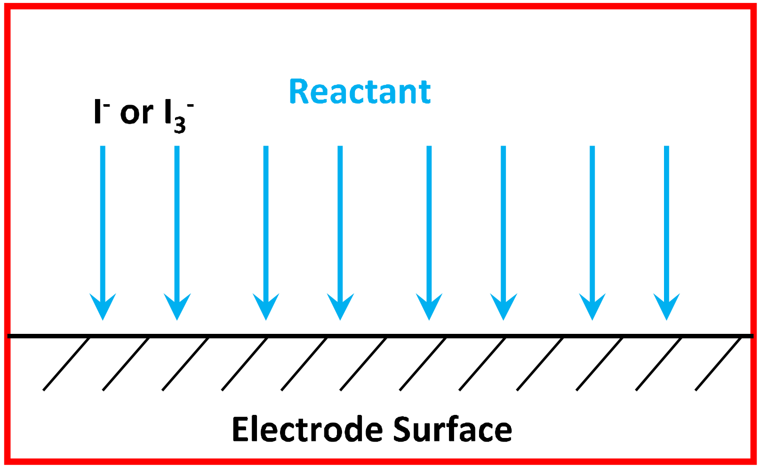


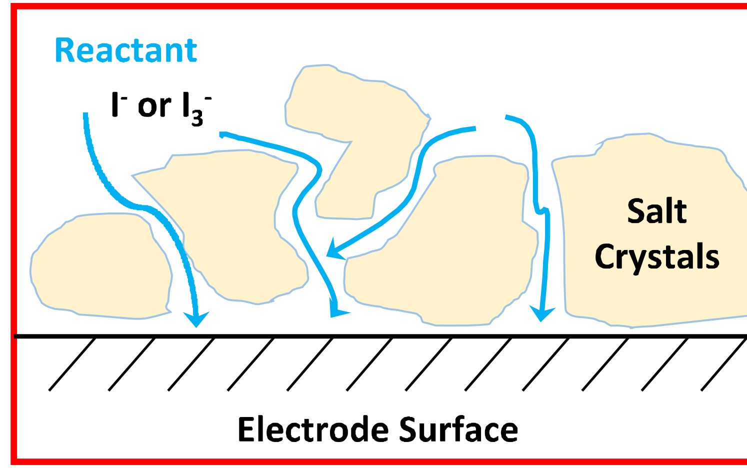
Ionic conductivity of molten salt phase should not limit battery performance.

Molten Catholyte Development

Regular Diffusion

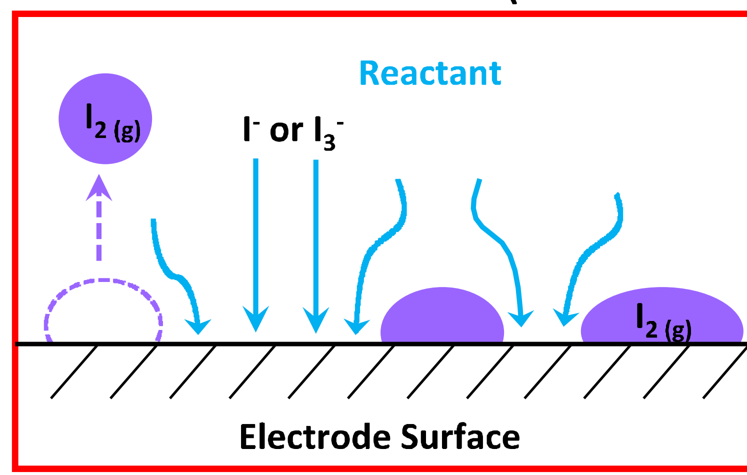


Hindered Diffusion – Solid Phase



- 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)



Catholyte Compositions Tested

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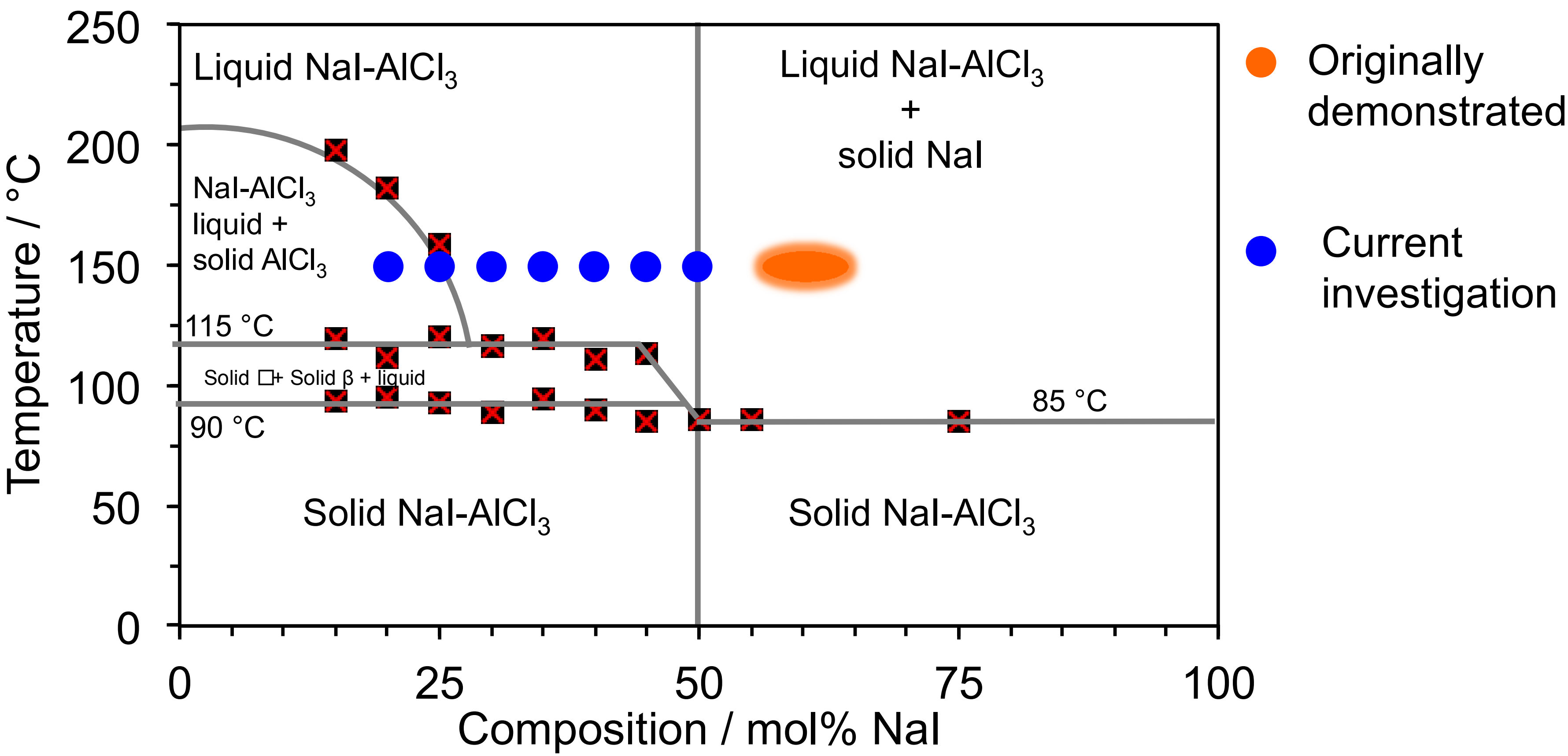

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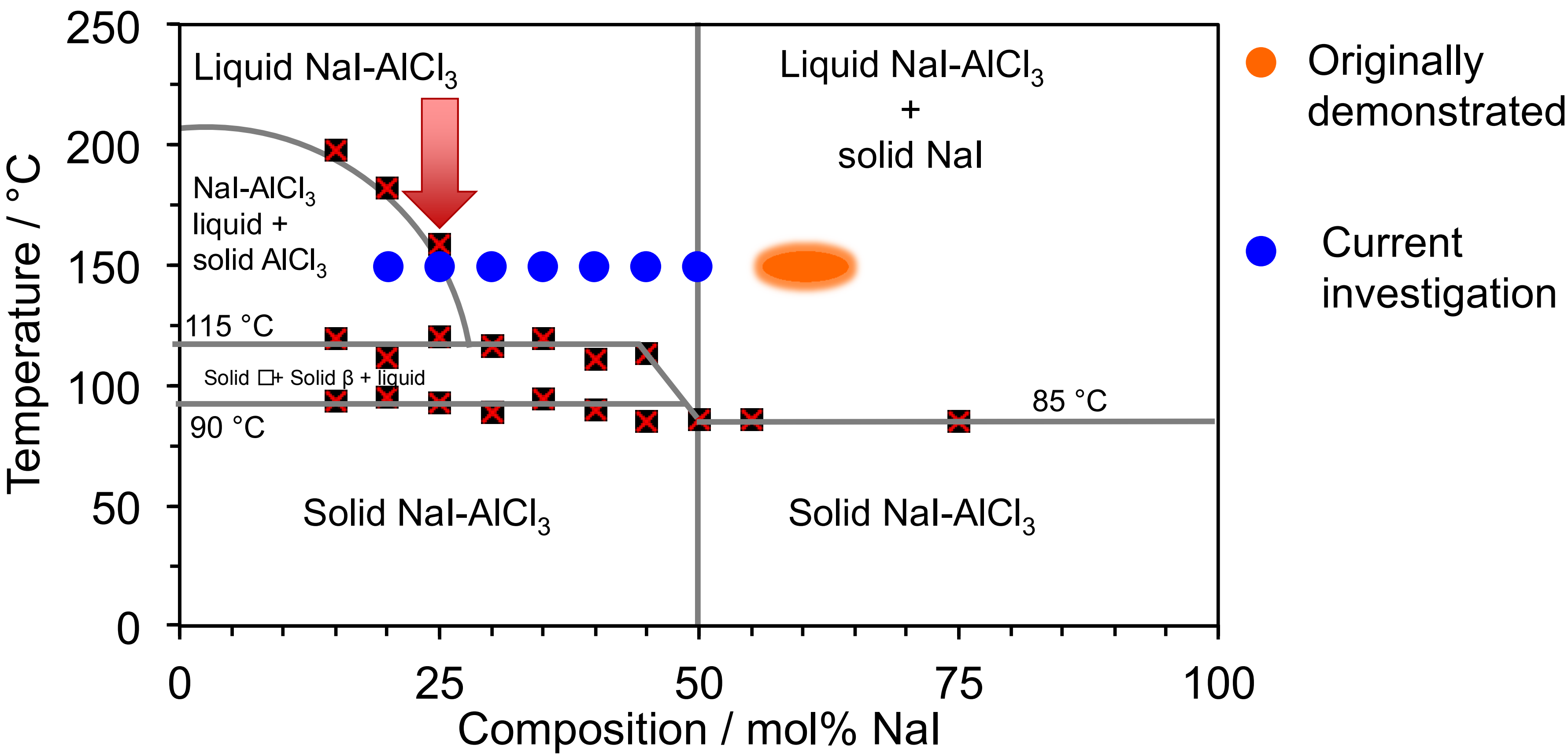
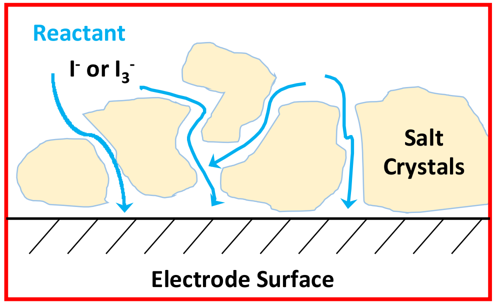


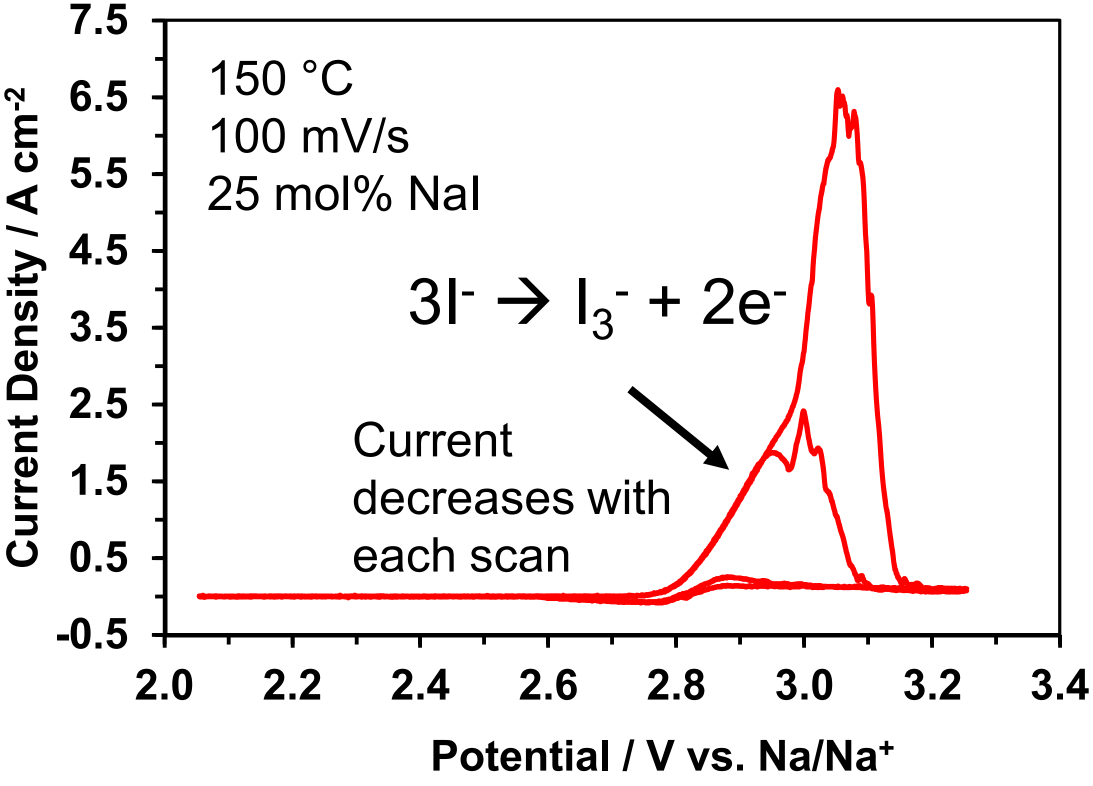
Hindered Diffusion: Solid State

Possible solid precipitation observed at electrode surface

- Hindered diffusion from presence of solids near electrode

Current Peaks then settles to a lower “residual” current





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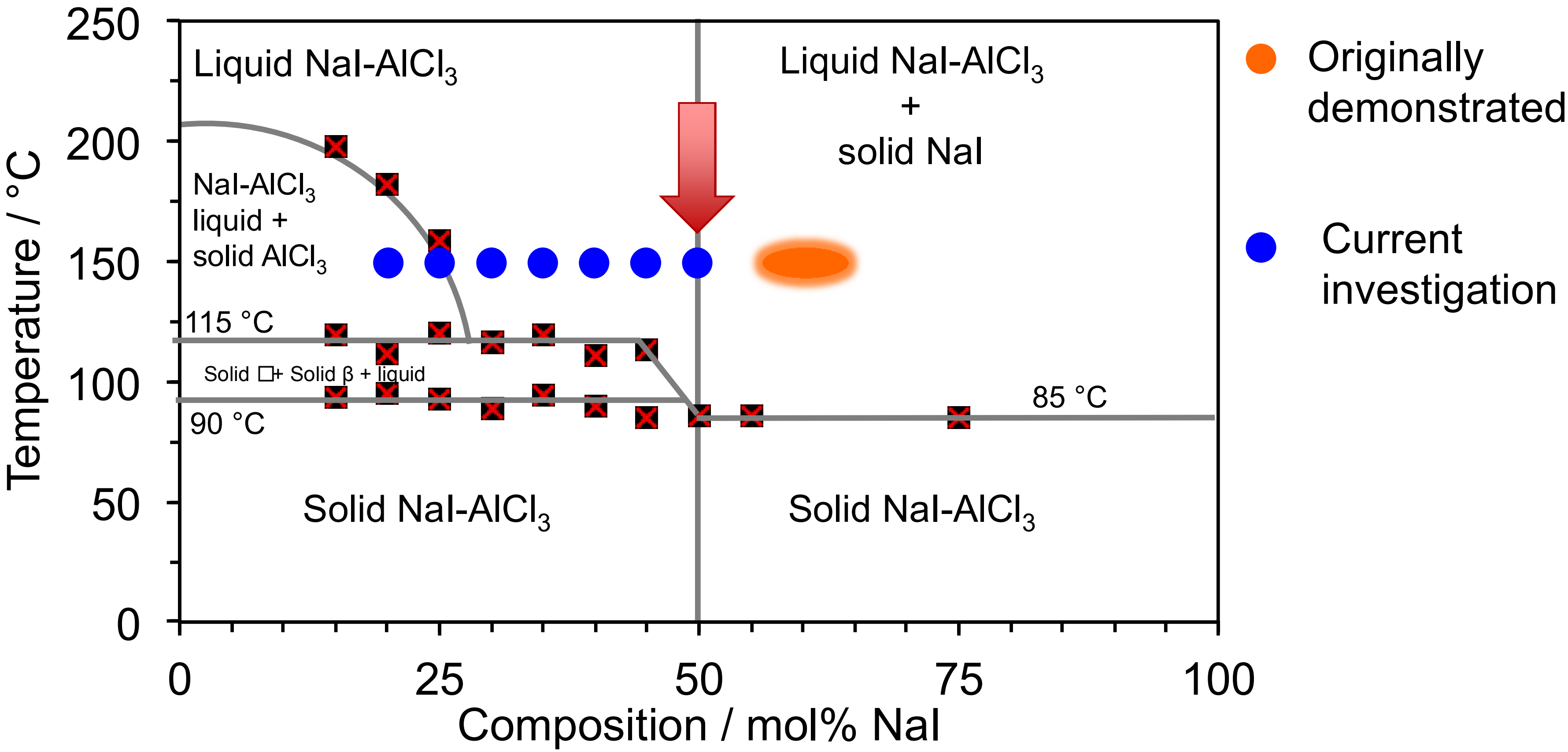
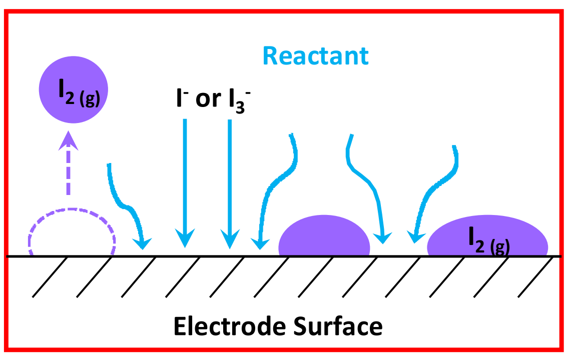
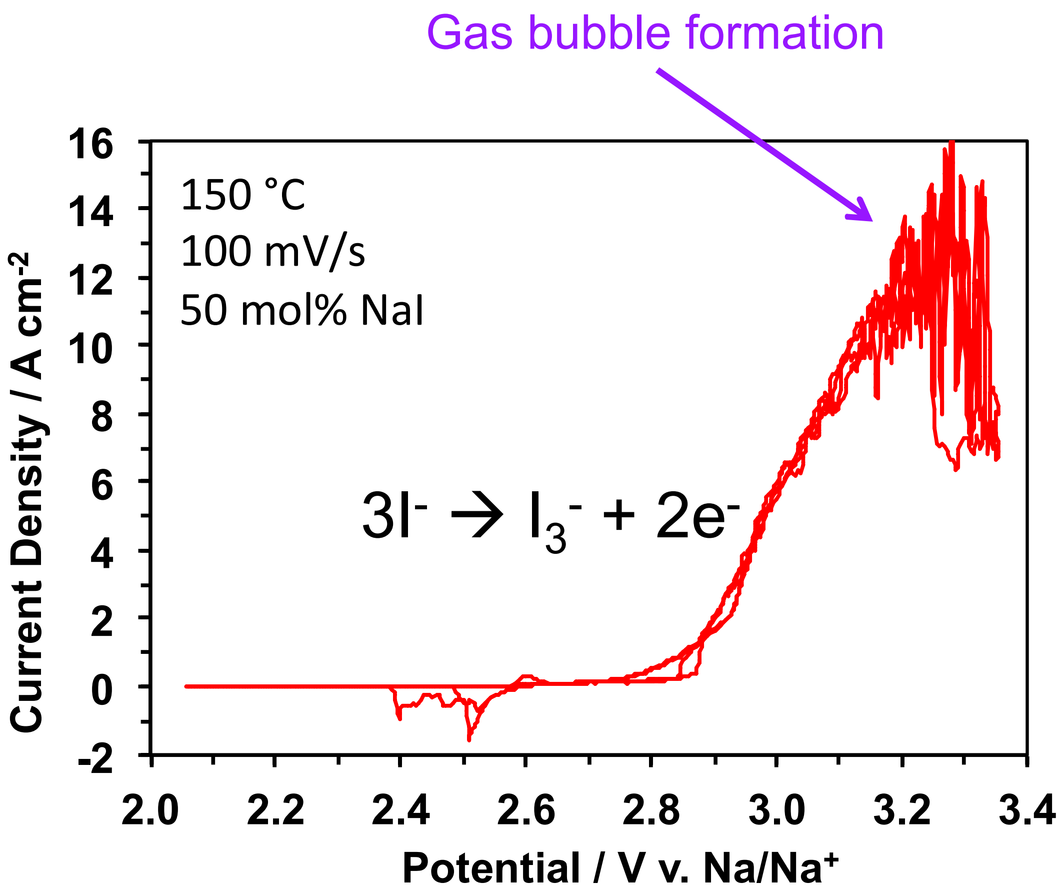


Hindered Diffusion: Gas State

Stable bubble formation observed for very high NaI-content salt compositions

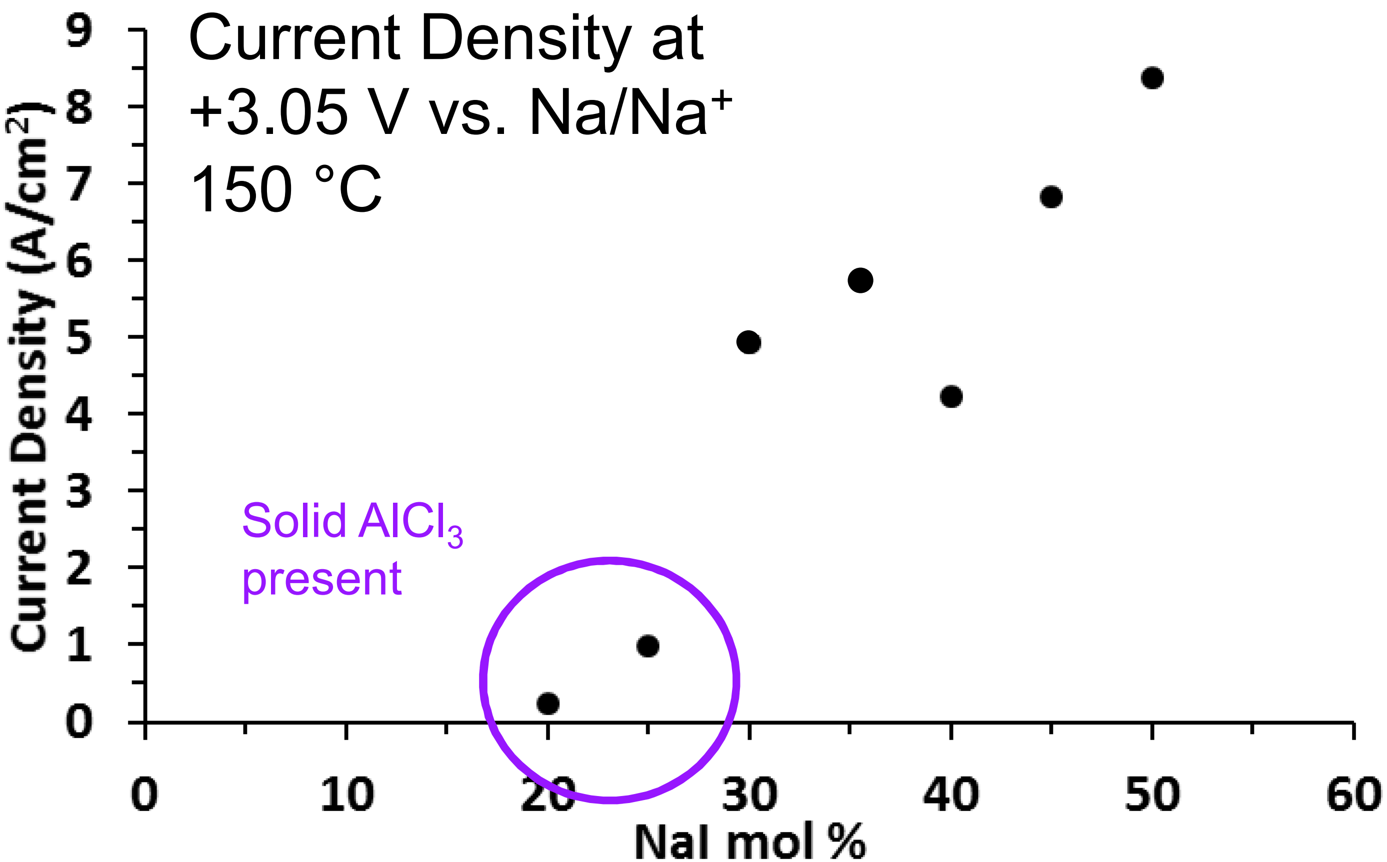
- Rapid I_2 generation stabilizes bubbles
- Dissolution/diffusion of I_2 is in equilibrium with generation rate





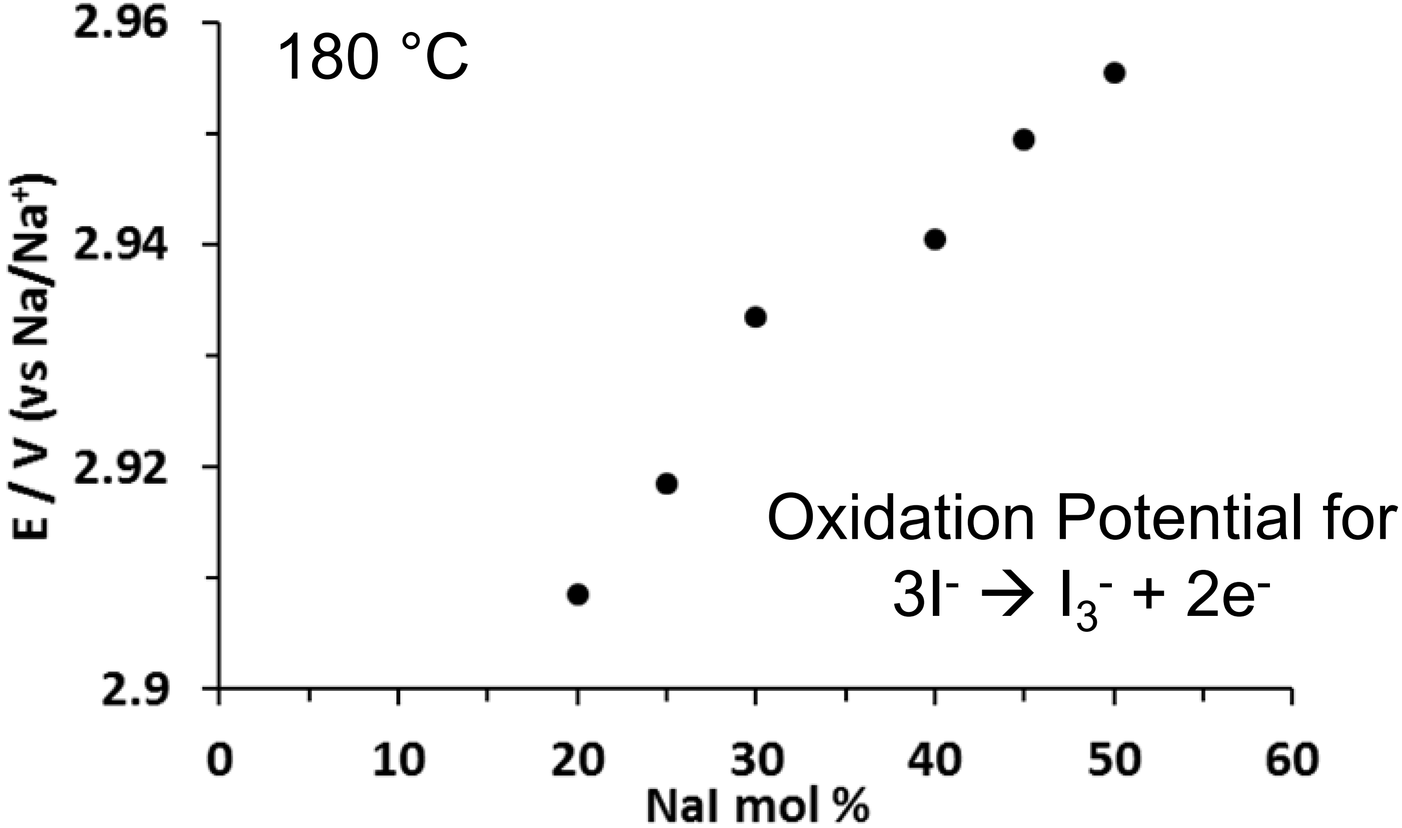
Electrochemical Performance of Catholyte

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



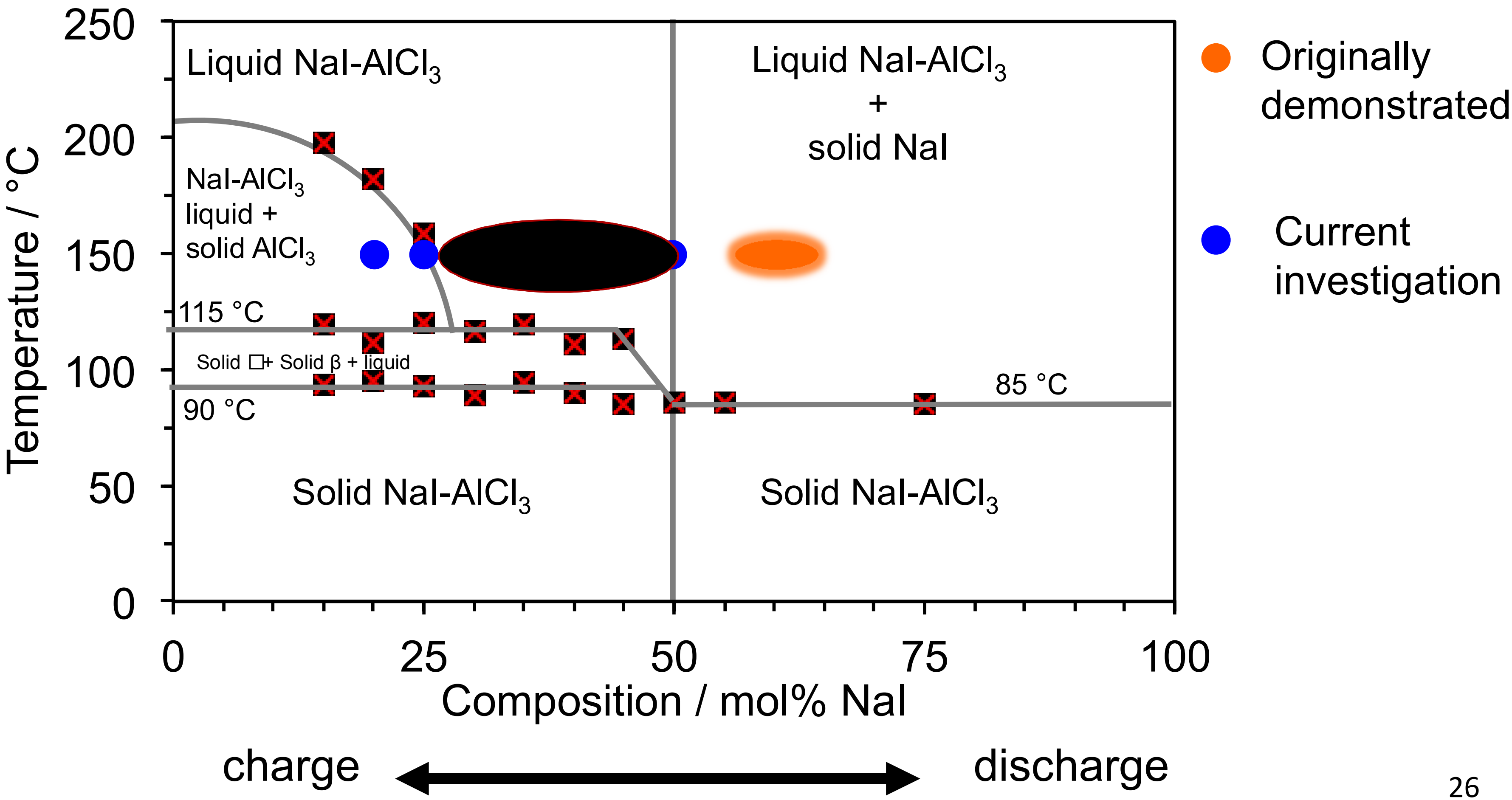
Battery Potential is Modestly Affected by Catholyte Composition

As expected, slightly higher battery operating potentials seen at higher NaI concentrations.



Molten Catholyte Desired

Preliminary Phase Diagram of $NaI-AlCl_3$ Catholyte



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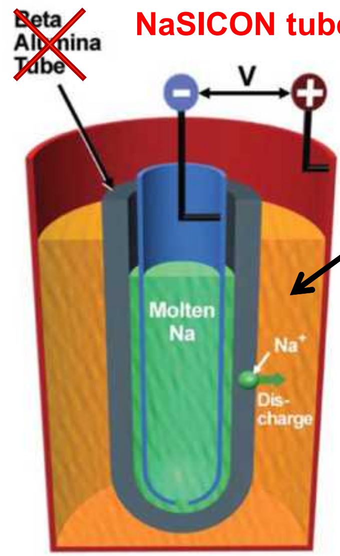
  - ✓ **Increased reliability and lifetime**
  - ✓ **Improved capacity retention (limitation of Li-ion and Pb-acid)**
- [illegible]

NaSICON tube separator enables lower temperature operation



Molten salt catholyte

Na-$NiCl_2$ battery
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Na-I_2 battery
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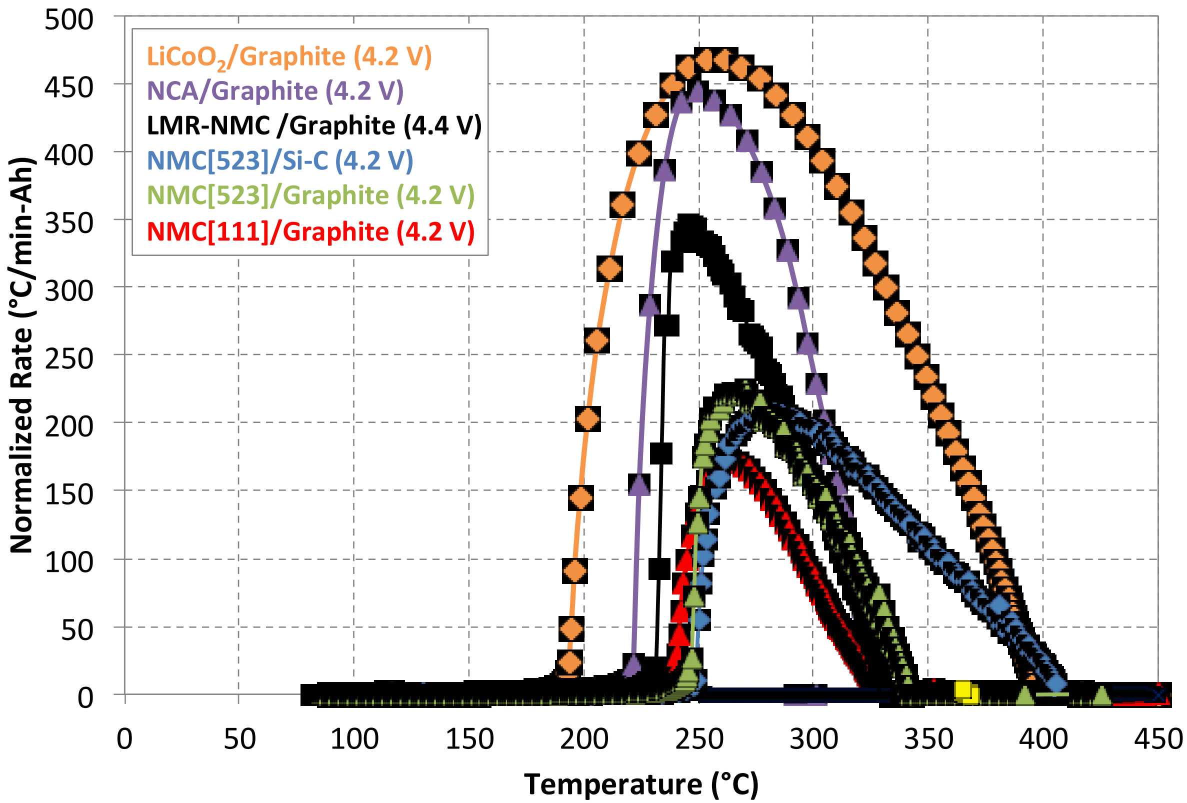
Safety Performance of Catholyte Salt

Accelerating Rate Calorimetry (ARC) Shows No Significant Exotherms

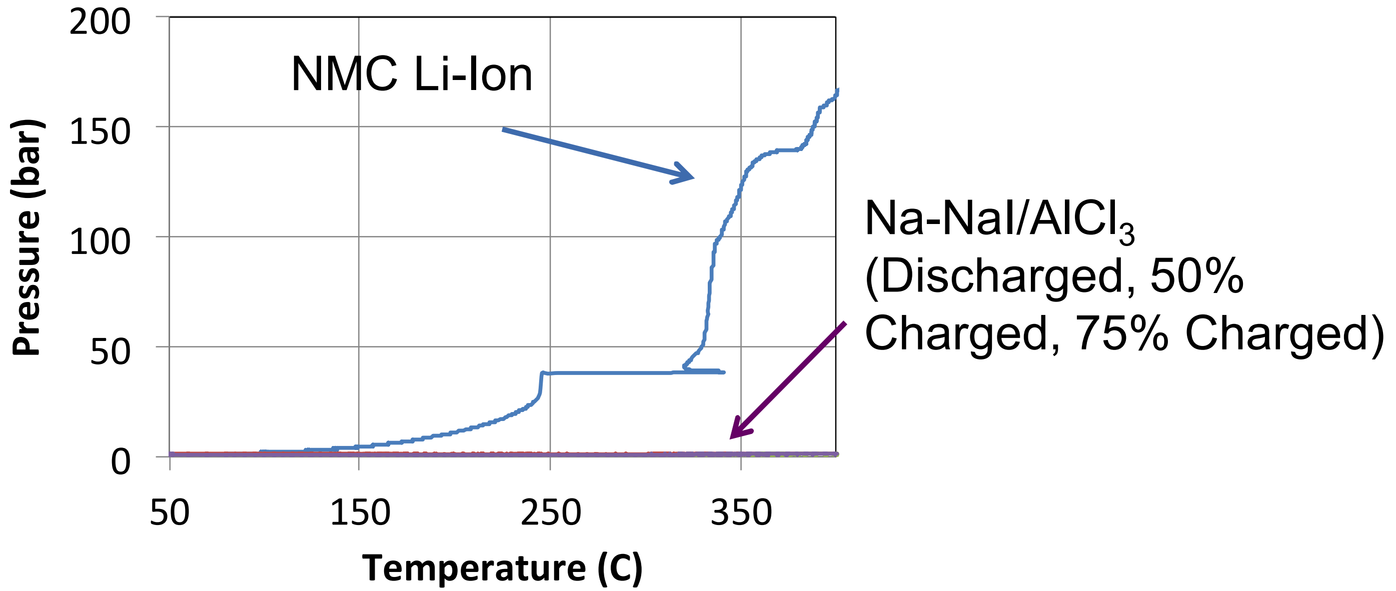
When complete separator failure is simulated by mixing Na metal and NaI/$AlCl_3$ catholyte, ARC testing reveals no hazardous runaway exothermic behavior!



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.

Teaming

- 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
- Program Sponsor
  - Dr. Imre Gyuk – Program Manger, DOE-OE
  - DOE – Office of Electricity Delivery and Energy Reliability

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.

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.

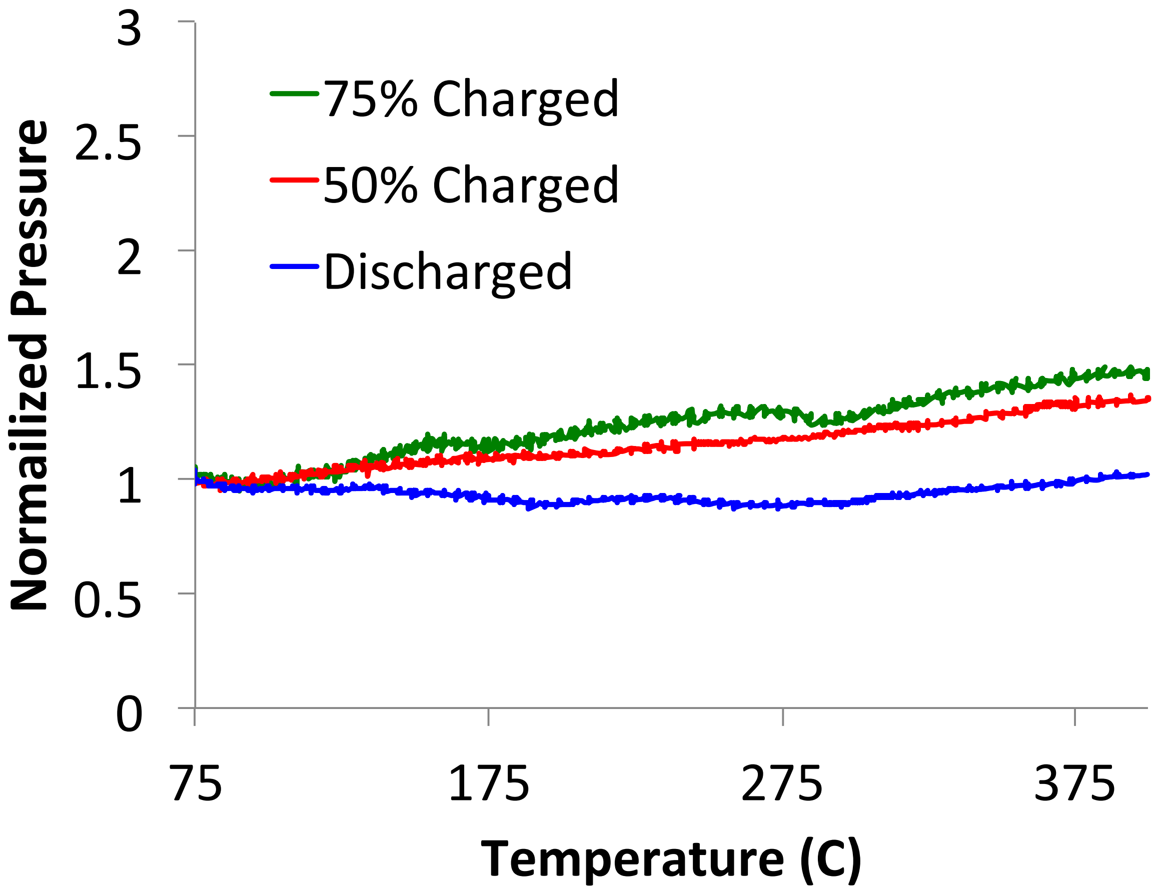
Work on $Na\text{-}NiCl_2$ batteries was performed through collaboration between Ceramatec and SK Innovation.

Post-doctoral positions at SNL expected in FY18 for qualified candidates.

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

Backup Slides

Na-System Shows Minimal System Pressurization



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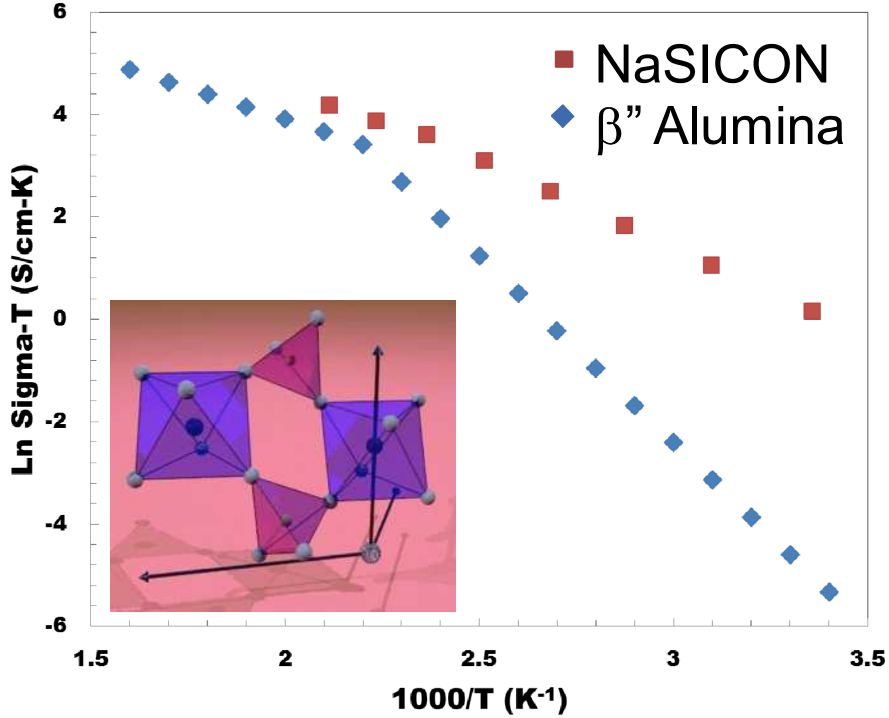
NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

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.

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

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?

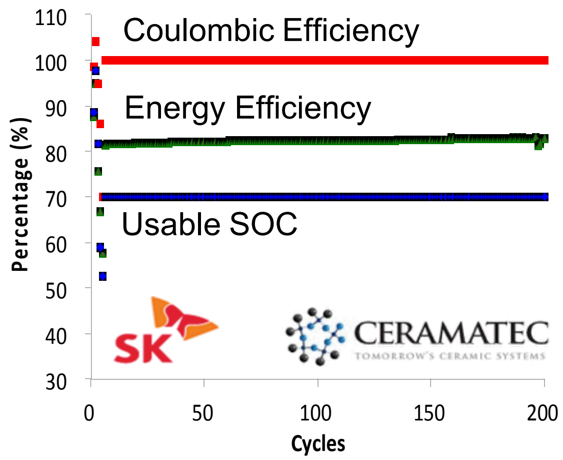
Pre-Commercial Na-$NiCl_2$ systems

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

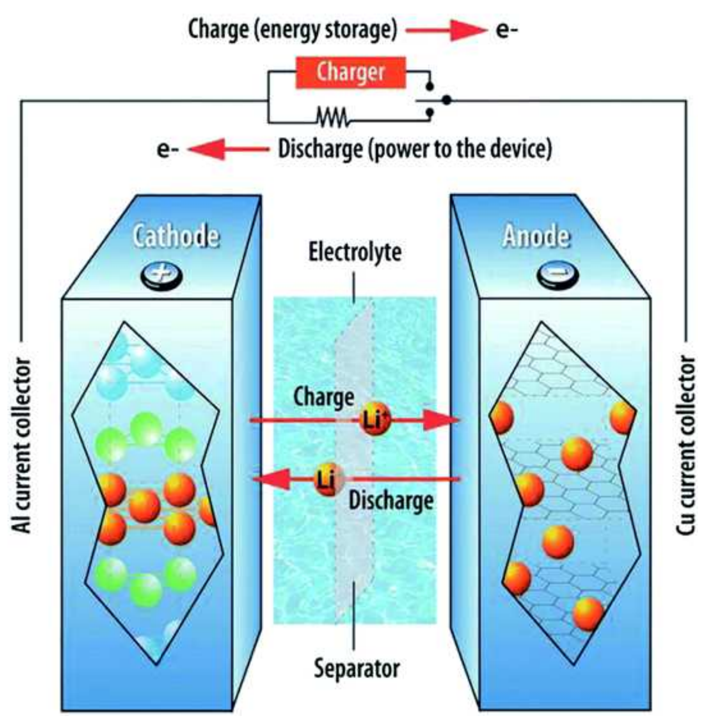
Ongoing efforts targeting for large scale (10kWh), intermediate temperature demonstrations (w/ Ceramatec: 180 Wh/l, $150/kWh, 2.6V, 40 cells).

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

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.



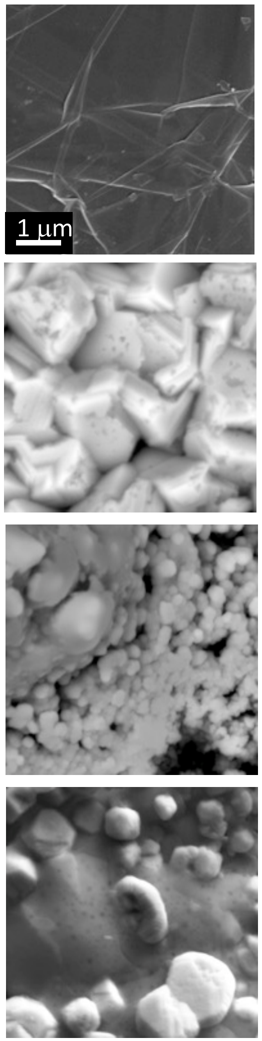
<u>Basic elements of all (most) batteries:</u>

- 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)

↓

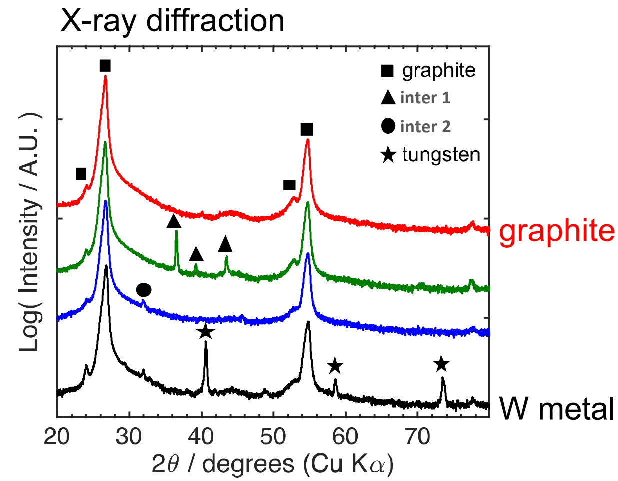
Intermediate coating

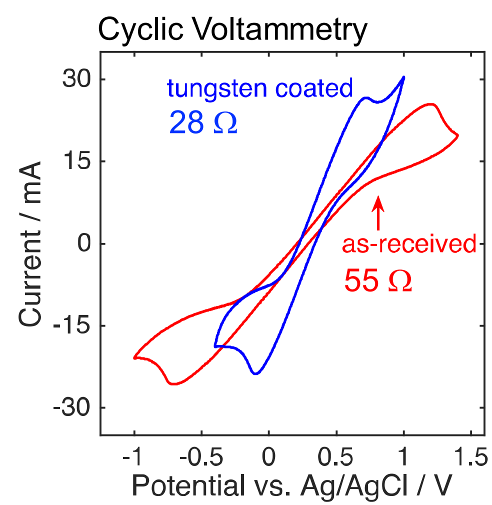
↓

Convert to W-precursor

↓

Reductive anneal creates
Crystalline, metallic tungsten.

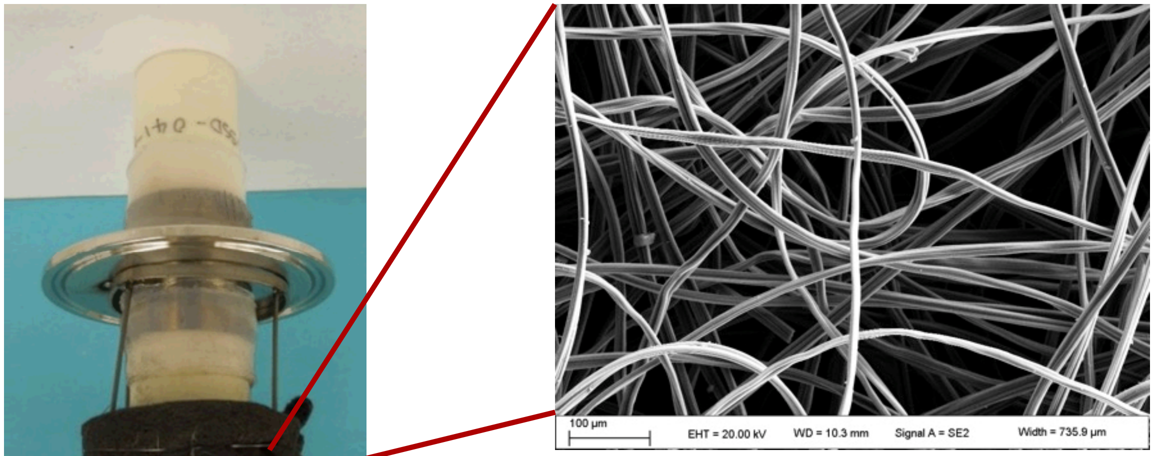




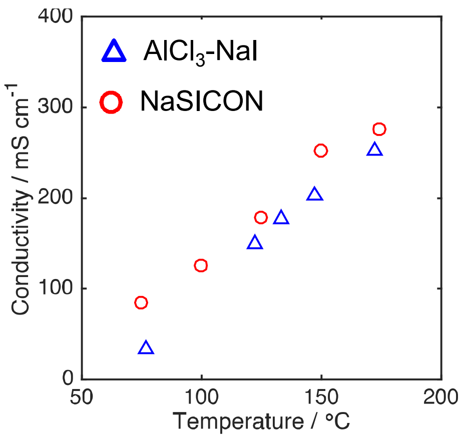
carbon foam
10 mM $K_3Fe(CN)_6$
500 mM NaCl
100 mV/s

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

Molten Catholyte and Carbon Felt Current Collector

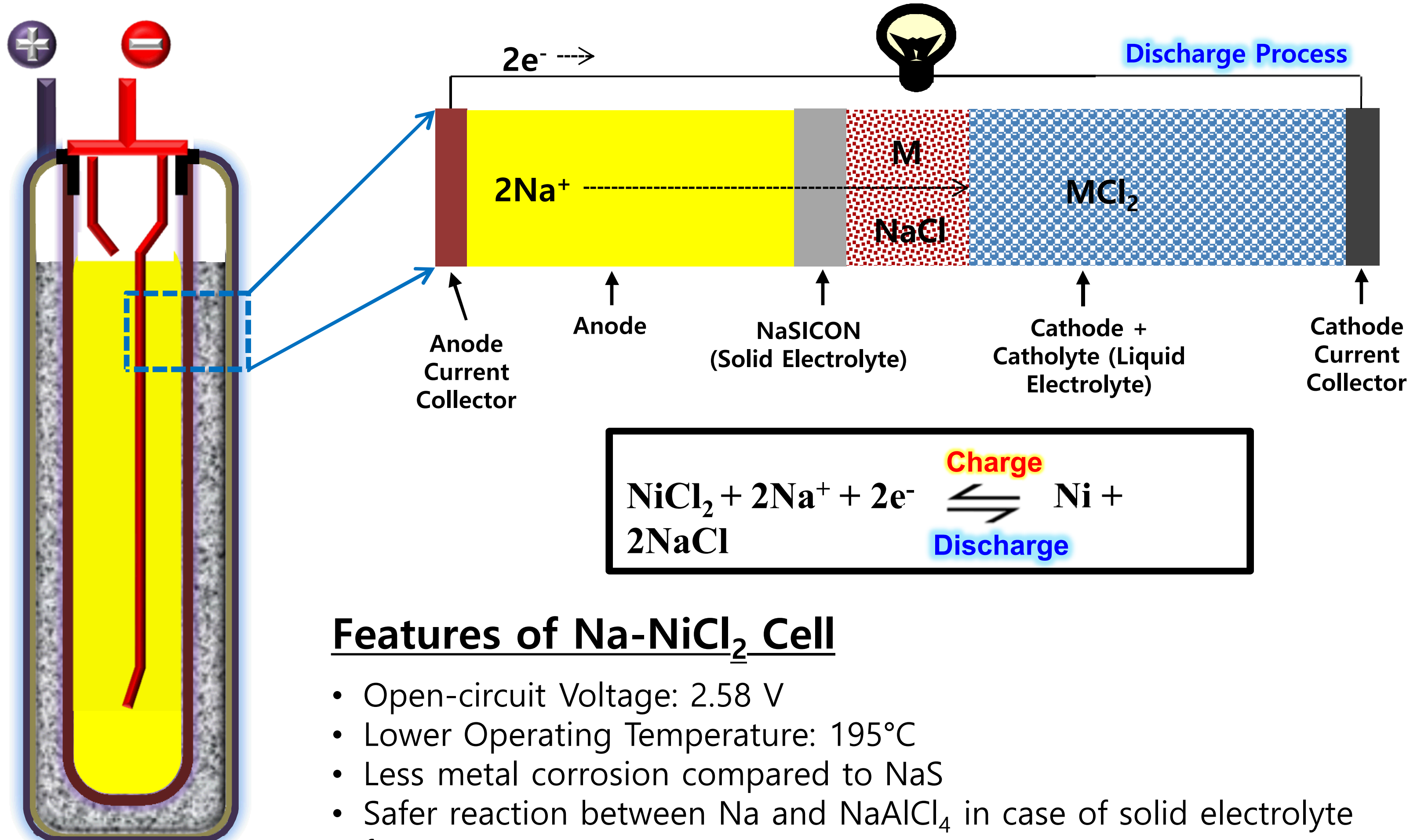


Motivated by the microscale fibers of the carbon felt current collector, we used a carbon microelectrode to probe the electrochemical properties of the catholyte salt.



(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.

Na-NiCl$_2$ Battery Technology



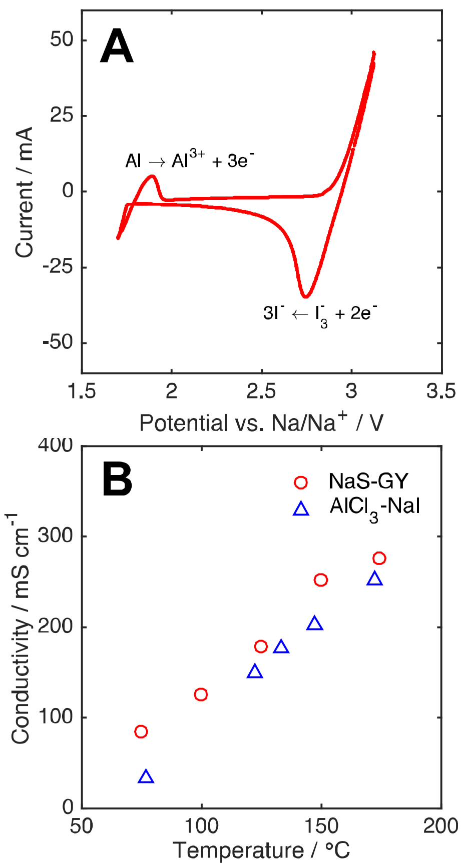
$$NiCl_2 + 2Na^+ + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Ni + 2NaCl$$

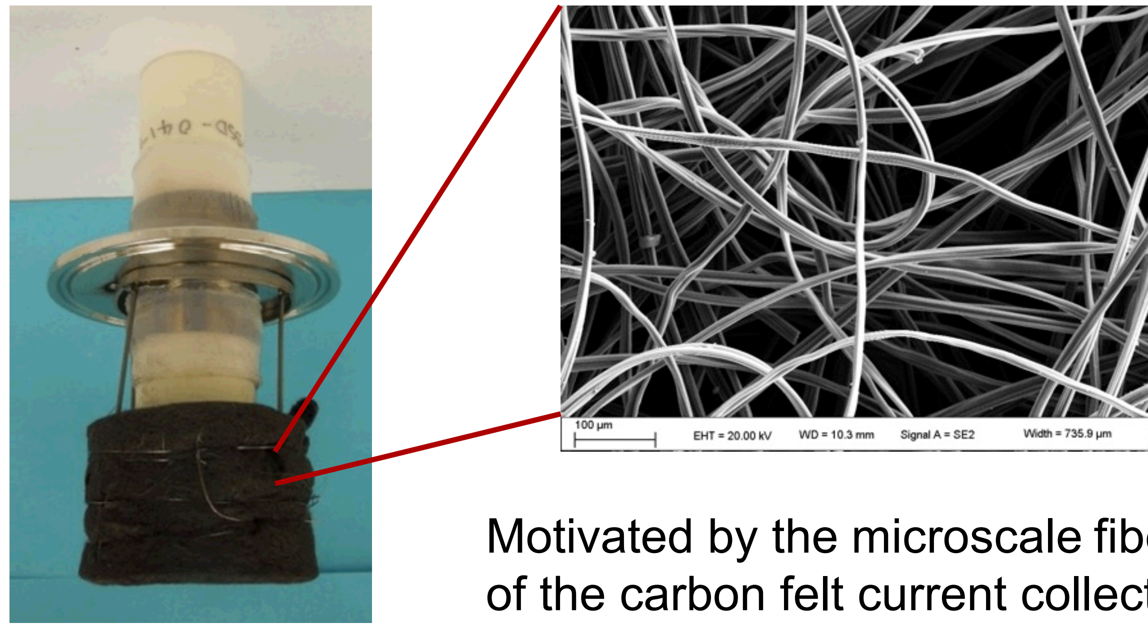
Features of Na-NiCl$_2$ Cell

- 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

Molten Catholyte and Carbon Felt Current Collector

Sandia National Laboratories





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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!

Safety Concerns with Li-Ion Batteries?

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.