



# Materials Chemistry to Advance Na-Batteries

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Ceramatec, Inc. Salt Lake City, UT

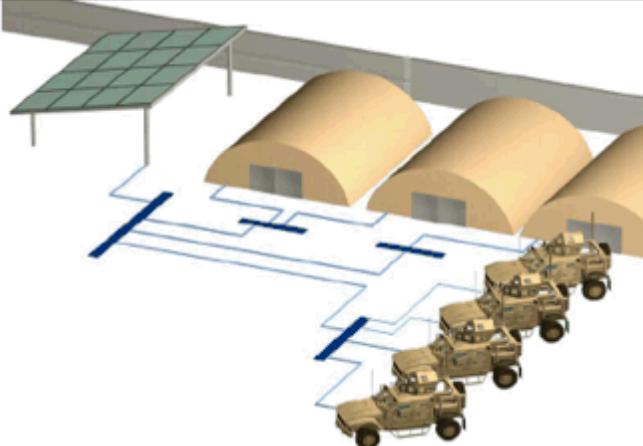
*DOE Office Electricity Delivery and Energy Reliability 2017 Peer Review  
San Diego, CA October 9-10, 2017*

# Teaming

- Program Sponsor
  - Dr. Imre Gyuk – Program Manager, 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/Field Upgrading:** Sai Bhavaraju, Alexis Eccleston, Andrew Read, Matt Robins
  - **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 enable development of new sodium-based batteries.*

# Critical need for Grid Scale Batteries



Safe, grid-scale electrical energy storage is critical!

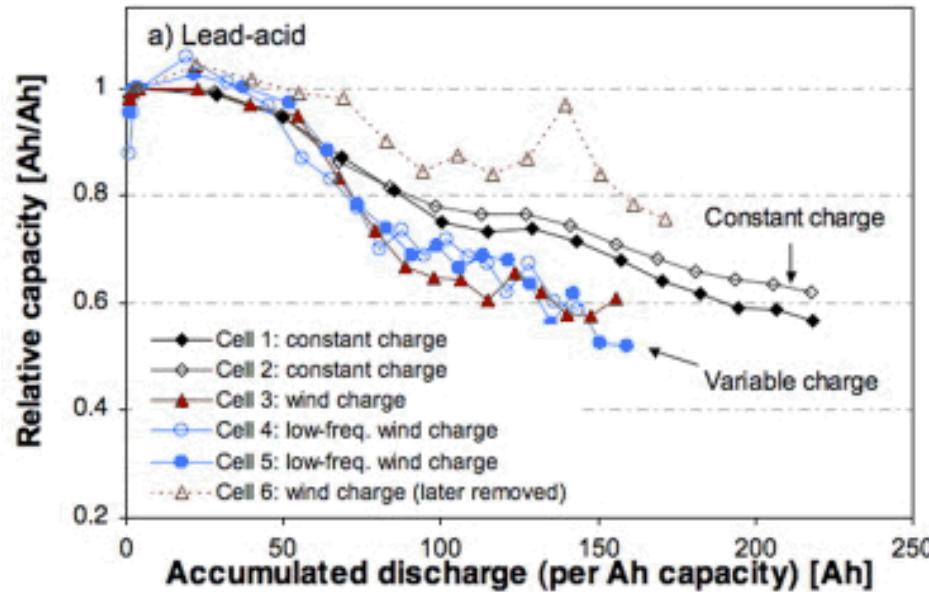
- Renewable/Remote Energy
- Grid Reliability/Agility
- Humanitarian Efforts
- National Defense



# Challenges with Current Battery Technologies

**Pb-Acid:**  $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \leftrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$   $E_{\text{cell}} \sim 2.1\text{V}$

- 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)

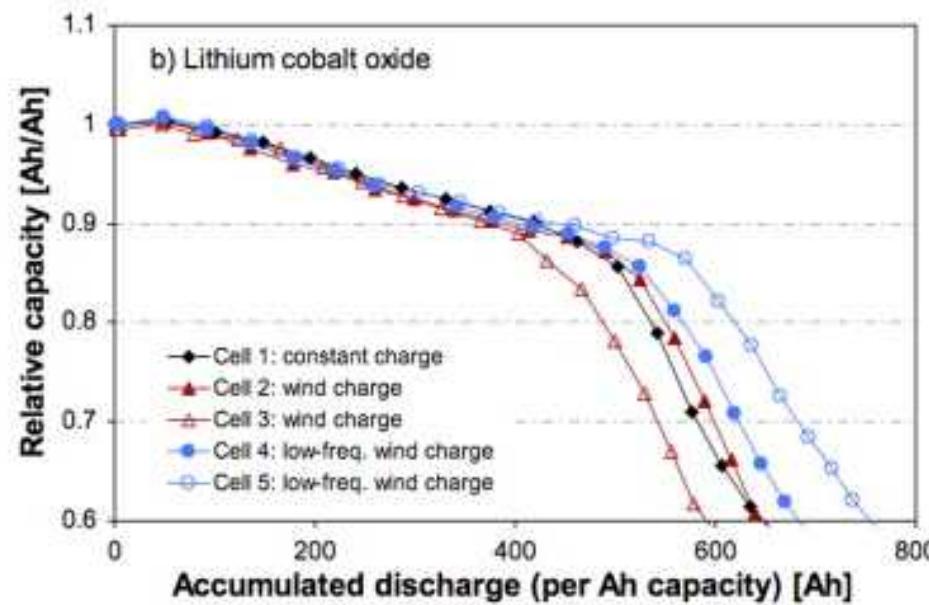


# Challenges with Current Battery Technologies

Li-ion:

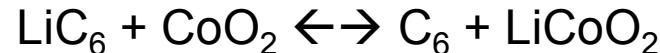


- Cost (decreasing recently)
- Limited operational temperature range (near room temperature)
- Capacity fades relatively quickly (~500 cycles) from oxidation reactions, electrolyte degradation, cathode degradation, increased cell resistance, cell short circuits
- Significant safety concerns associated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



# Challenges with Current Battery Technologies

**Li-ion:**



$$E_{\text{cell}} \sim 3.6\text{V}$$

- 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

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 :



- Cost (potentially feasible)
- Operates at elevated temperatures (270-350°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.

# Sodium-Based Batteries: A Path to Safe, Reliable, Cost-Competitive Energy Storage



Objective: We aim to *enable* development low cost, low temperature, safe, nonflammable alternatives to Na-S and Li-ion batteries.

- Low cost (reduced material costs, low CAPEX, high cycle life)
  - Target unit cost < \$100/kWh,
  - Cycle life 5,000-10,000 cycles
  - LCOS \$0.05-0.10/kWh-cycle
- Enabled by *low to intermediate temperature* (<200°C) ceramic Na-ion conductor (NaSICON)
  - Robust physical barrier - *no electrode crossover!*
  - Reduced operating costs
  - Lower cost materials/seals
- Engineered safe
  - Fully inorganic, no volatile organic electrolytes
  - Robust ceramic separator isolates anode and cathode
  - Cross-reaction generates benign byproducts

Our approach stands to enable numerous new Na-based battery technologies:

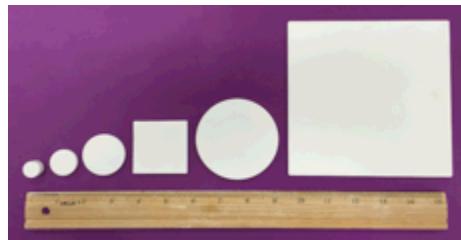
- Sodium-air
- Sodium-ion
- **Aqueous Redox Flow**
- Low temperature sodium-sulfur
- Sodium-bromine:  $\text{Na} + \frac{1}{2} \text{Br}_2 \rightleftharpoons \text{Na}^+ + \text{Br}^-$
- **Sodium-iodine:  $\text{Na} + \frac{1}{2} \text{I}_2 \rightleftharpoons \text{Na}^+ + \text{I}^-$**
- **Sodium-nickel chloride:  $\text{Na} + \frac{1}{2} \text{NiCl}_2 \rightleftharpoons \text{Na}^+ + \text{Cl}^- + \text{Ni(s)}$**
- Sodium-copper iodide:  $\text{Na} + \text{CuI}_2 \rightleftharpoons \text{Na}^+ + 2\text{I}^- + \text{Cu(s)}$

# Intermediate Temperature Molten Salt Na-Based Batteries

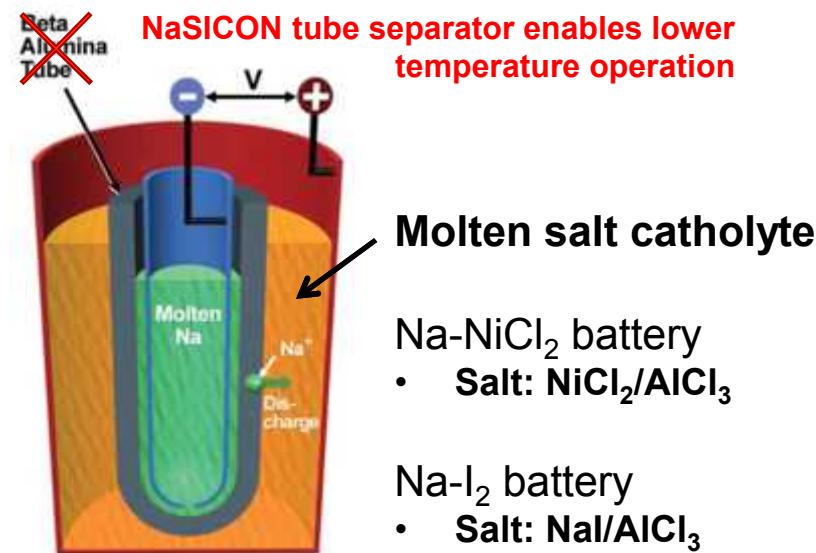


**Our Goal:** to develop low cost ( $\leq \$100/\text{kWh}$ ), intermediate temperature ( $\leq 200^\circ\text{C}$ ), *long-lifetime, safe, nonflammable* Na-based alternatives to Na-S, Pb-acid, and Li-ion batteries.

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



100 Wh,  
Na-battery  
prototype



Na-NiCl<sub>2</sub> battery

- Salt: NiCl<sub>2</sub>/AlCl<sub>3</sub>

Na-I<sub>2</sub> battery

- Salt: NaI/AlCl<sub>3</sub>

Sodium-nickel chloride ( $195^\circ\text{C}$ ,  $E_{\text{cell}} \sim 2.6\text{V}$ ):  
 $\text{Na} + \frac{1}{2} \text{NiCl}_2 \rightleftharpoons \text{Na}^+ + \text{Cl}^- + \text{Ni(s)}$

Sodium-iodine ( $120-150^\circ\text{C}$ ,  $E_{\text{cell}} \sim 3.25\text{V}$ ):  
 $\text{Na} + \frac{1}{2} \text{I}_2 \rightleftharpoons \text{Na}^+ + \text{I}^-$

# Pre-Commercial Demonstrations of Na-NiCl<sub>2</sub> Prototypes



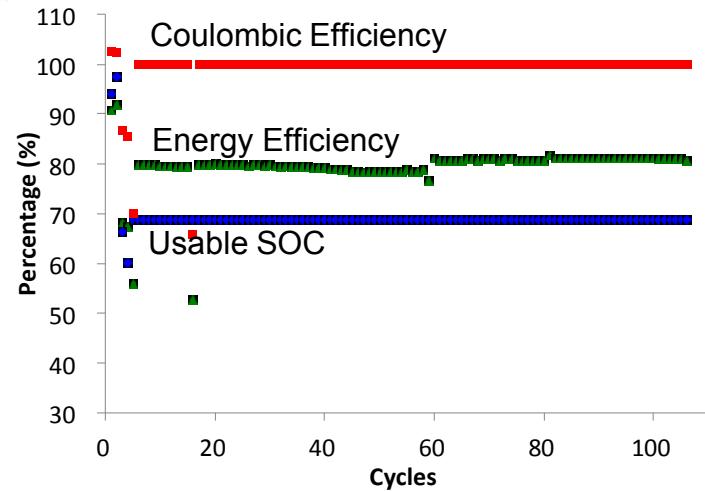
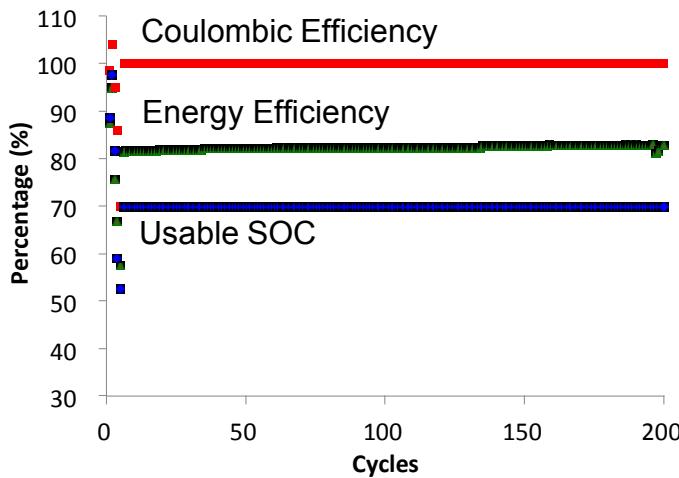
100 Wh pre-commercial Na-NiCl<sub>2</sub> unit cell:

- operational for 4+ months.
- 500+ cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 81.5 %
- 53 mA/cm<sup>2</sup> & C/7 rate

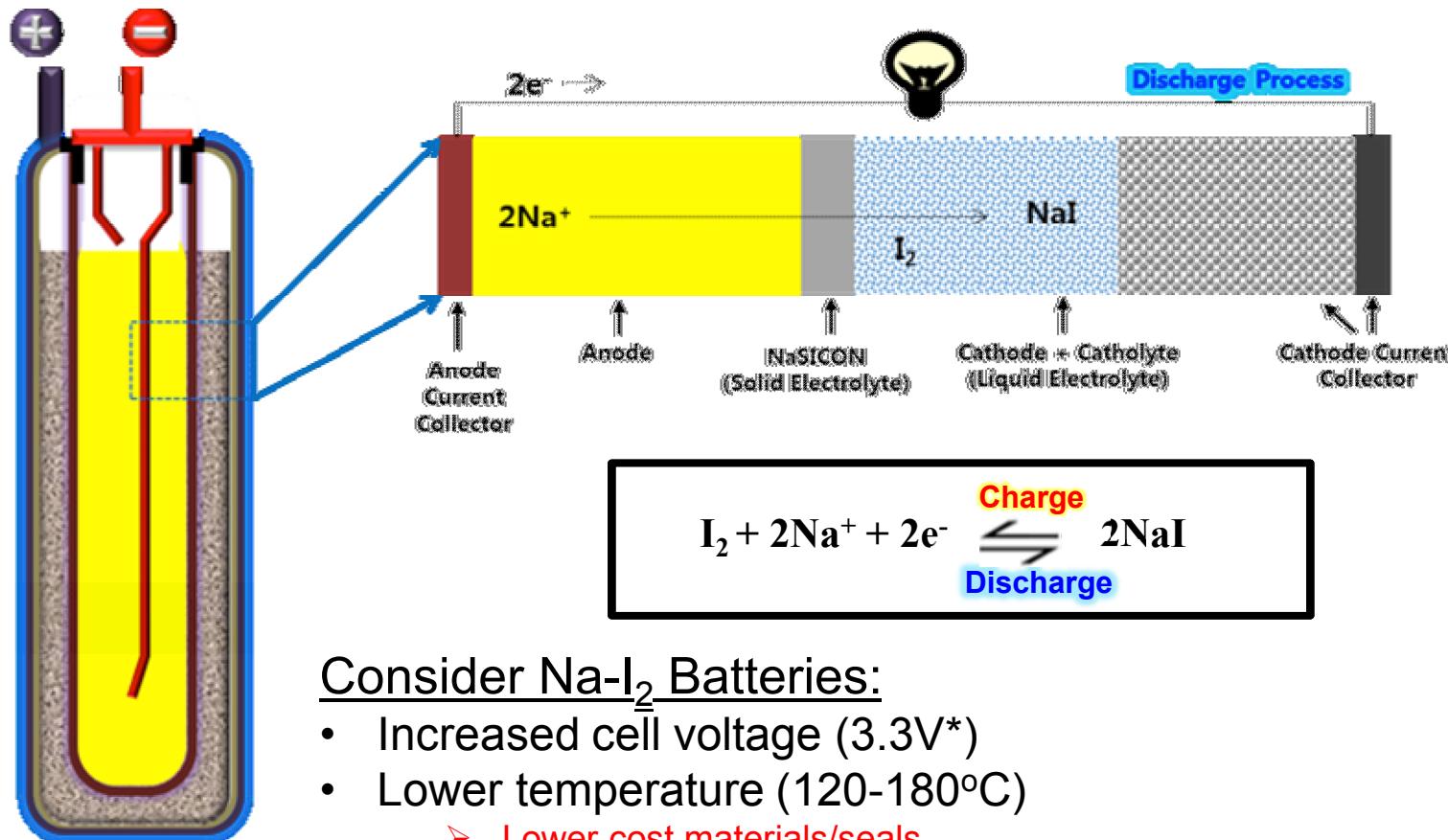


250 Wh pre-commercial Na-NiCl<sub>2</sub> unit cell:

- operational for 3+ months
- 110 cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 80 %
- 53 mA/cm<sup>2</sup> & C/7 rate



# Na-I<sub>2</sub> Battery Technology: A Liquid Catholyte

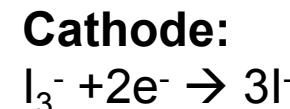
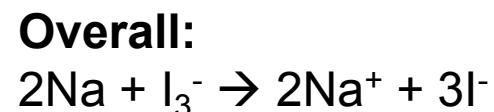
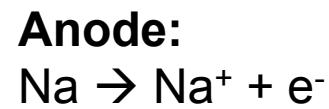
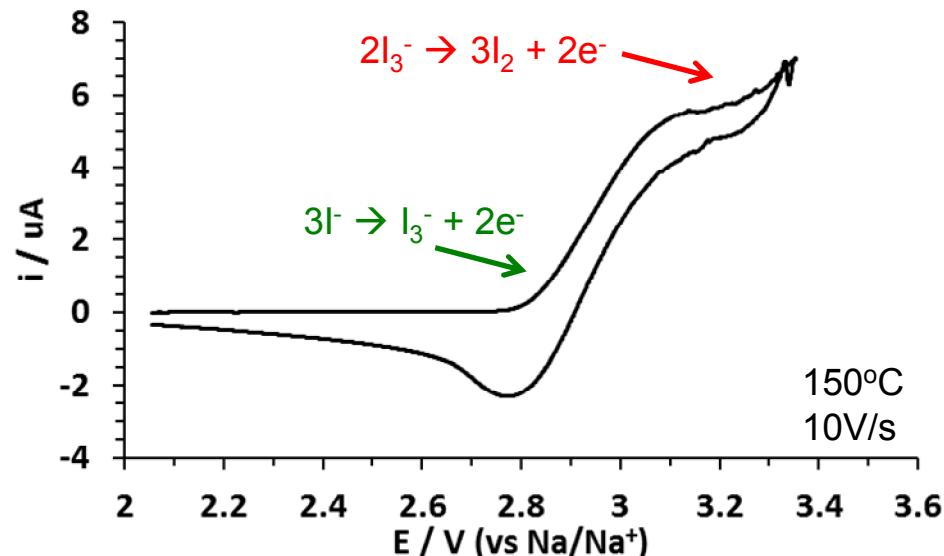
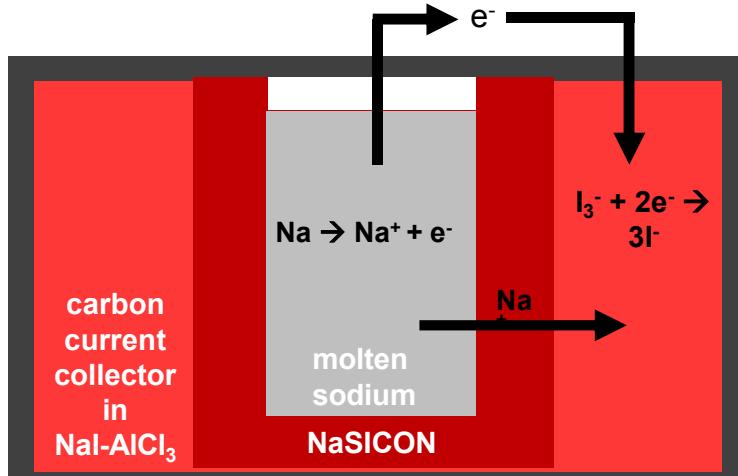
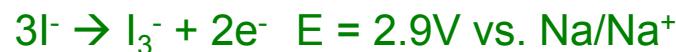


## Consider Na-I<sub>2</sub> Batteries:

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

# Na-I<sub>2</sub> Electrochemistry

The iodine generation step is a 2-stage reaction:

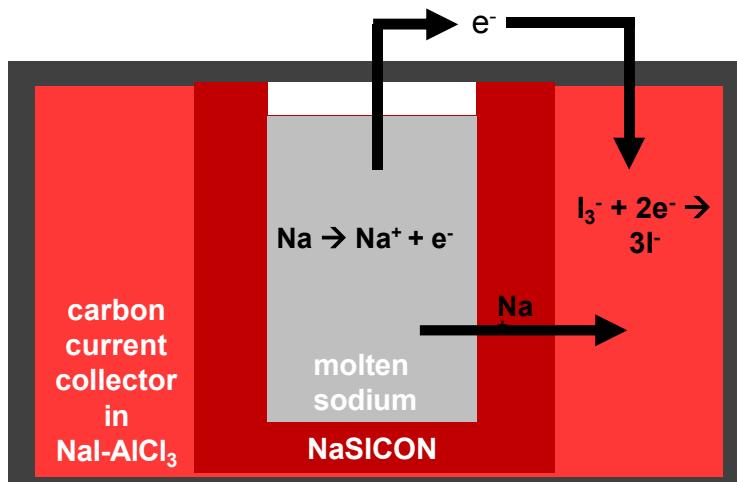


\*Practical OCV for tested batteries was 2.8-2.9V

# Na-I<sub>2</sub> Prototype Assembly

## Lab Scale Test Conditions

- Up to 28Wh lab-scale cell
- Graphite felt + tungsten wire current collectors
- NaI-AlCl<sub>3</sub> based molten salt catholyte
- 1" NaSICON tube glass sealed to  $\alpha$ -alumina
- T = 150-180°C



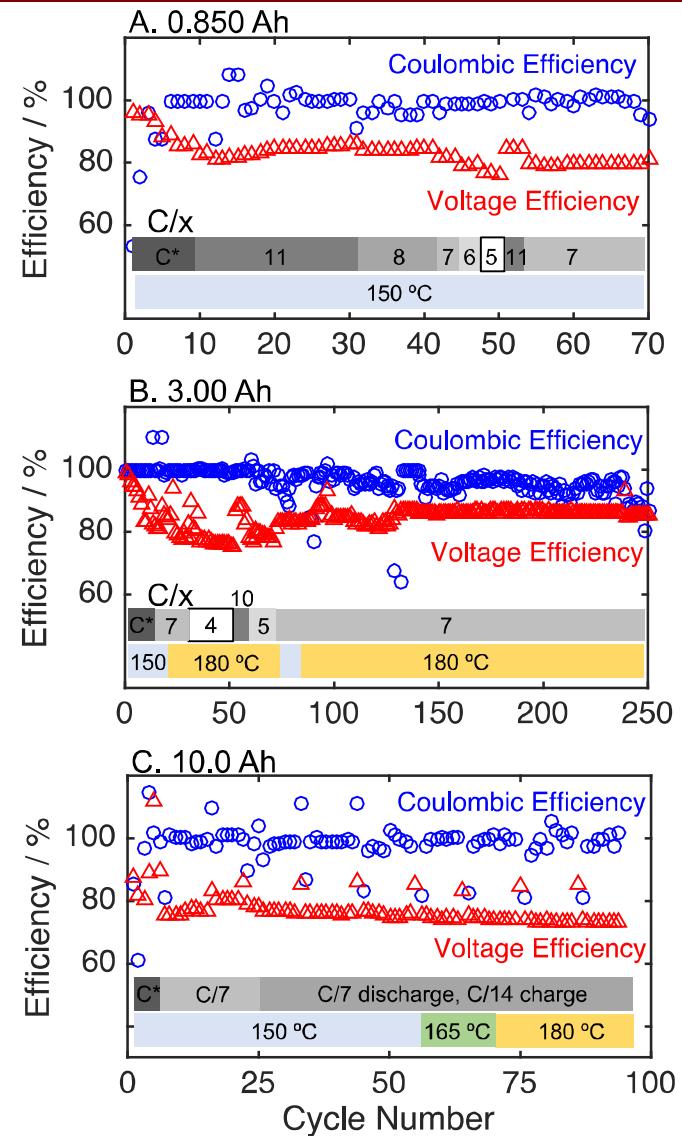
# Promise in Na-I<sub>2</sub> Prototypes!

✓ Demonstrated long term performance across multiple prototype scales

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

Data published as collaborative paper between SNL and Ceramatec in 2017:

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



# Defining a Path Forward



Having effectively established proof of principle for these Na-battery systems, our focus shifted in FY17 to emphasize:

1. Basic research and development of potential materials-based limitations to *long-term* success of Na-based batteries.
2. Inherent safety of all-inorganic molten salt system.
3. Identifying a pathway to large-scale NaSICON separator production.

# Reconfiguring Industrial Partnerships



In August, 2017, Ceramatec, Inc. sold its NaSICON technology to Field Upgrading, USA.

The core research team, including our lead collaborator (Dr. Sai Bhavaraju), will continue work developing and implementing NaSICON.

The primary NaSICON application emphasis will be on the large scale extraction of sulfur from marine fuels.

To meet these new application demands, Field Upgrading is planning a \$100M demonstration plant capable of dramatically increasing the rate of NaSICON production: “commoditizing” NaSICON.

*This scale-up of NaSICON production by Field Upgrading is expected to substantially enable the application of NaSICON for large scale battery production.*

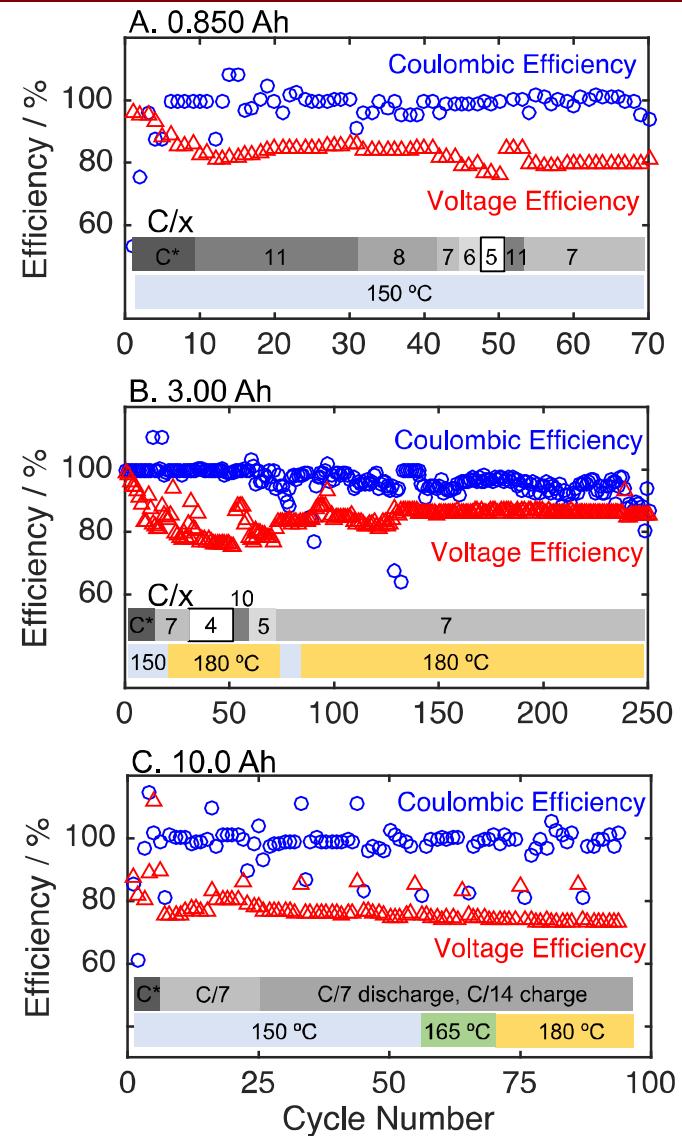
# Promise in Na-I<sub>2</sub> Prototypes!

✓ Demonstrated long term performance across multiple prototype scales

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

\*Note that for 28 Wh (10 Ah) system, every 11<sup>th</sup> cycle benefited from a C/15 rate to “refresh” performance.

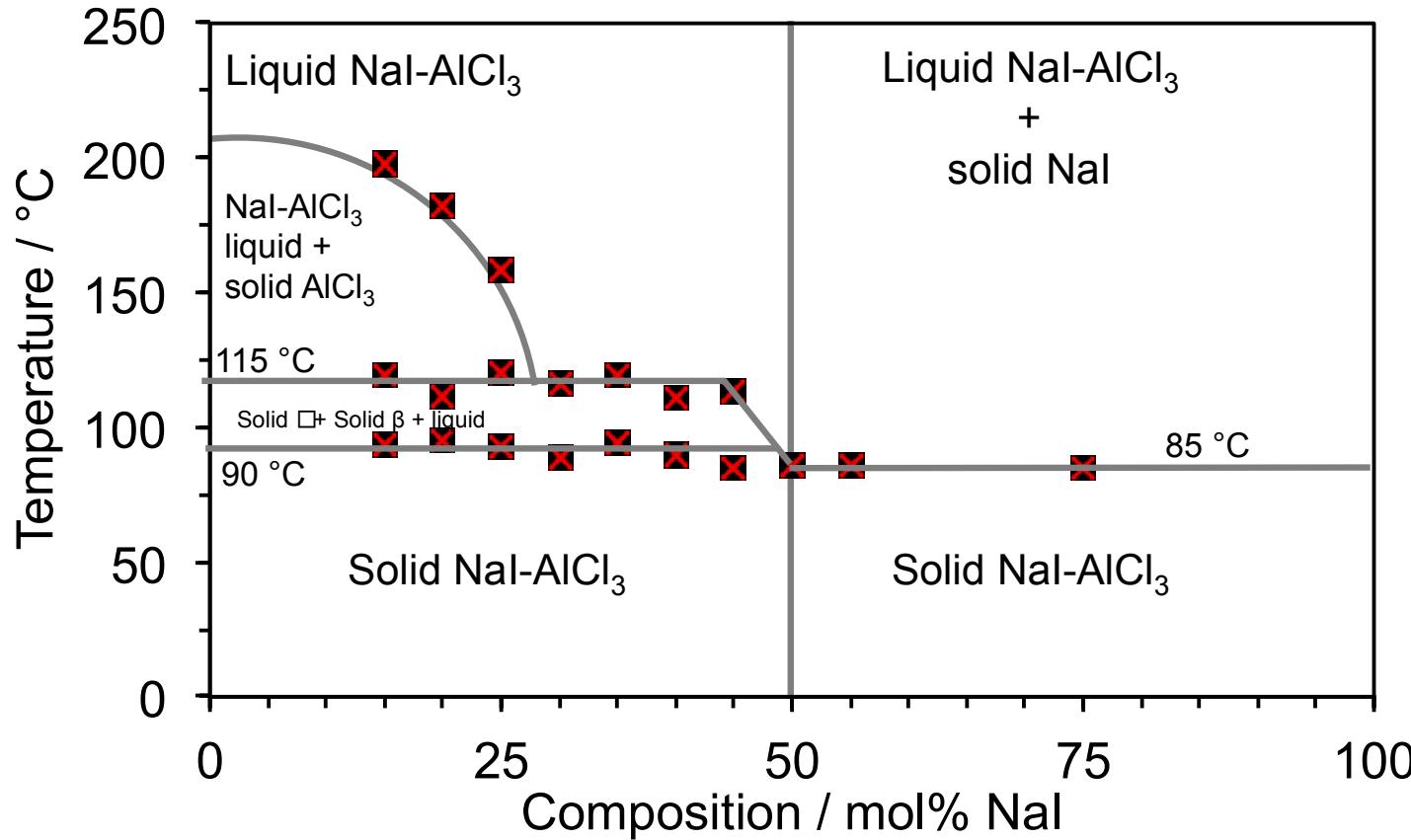
*Could this issue be related to catholyte materials chemistry?*



Can we eliminate particle phase  
in catholyte?

# Understanding Basic Cathode Materials Chemistry

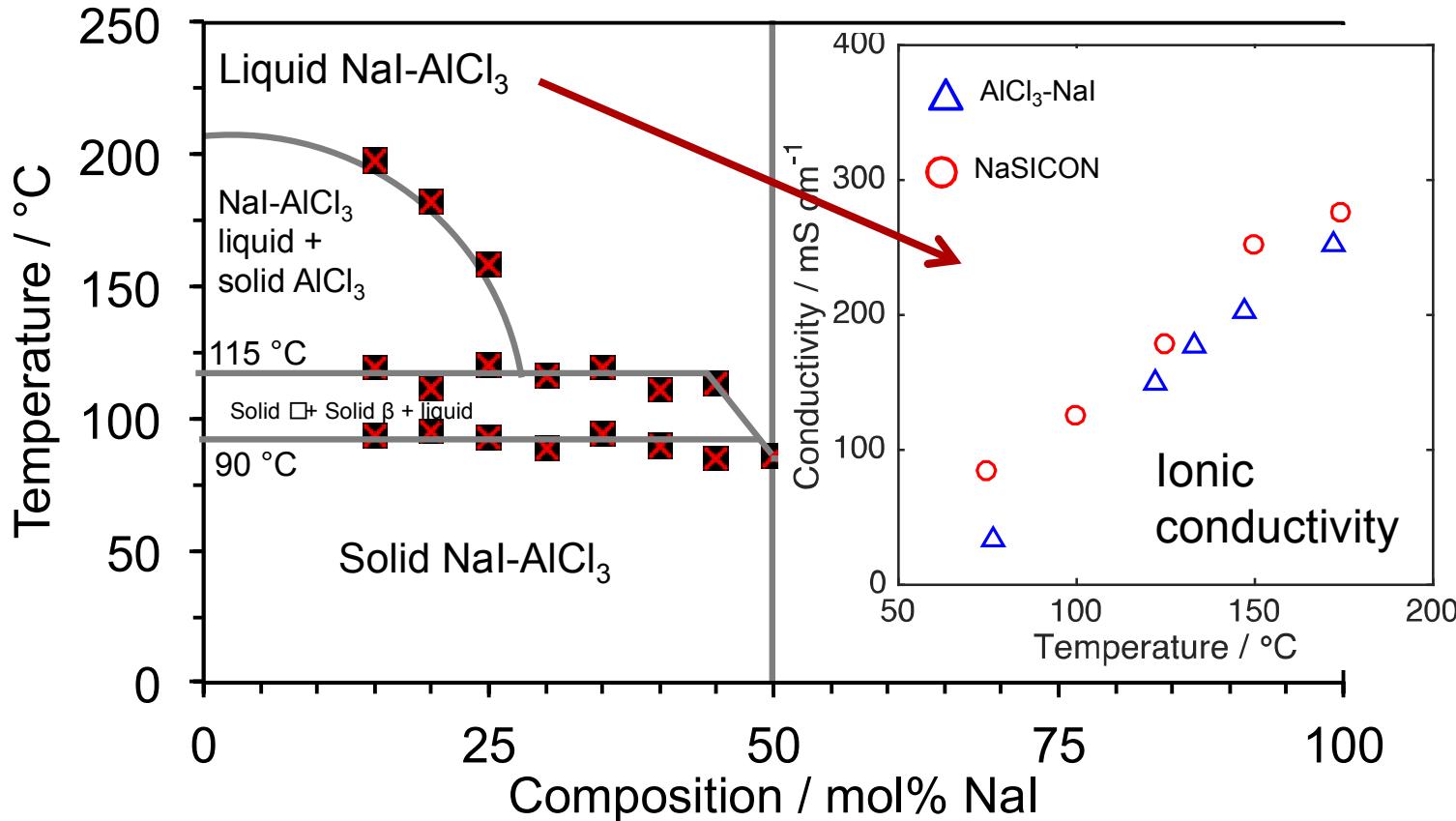
Preliminary Phase Diagram of  $\text{NaI-AlCl}_3$  Catholyte



Phase diagram created from differential scanning calorimetry data.

# Molten Salt Conductivity Compares with NaSICON Conductivity

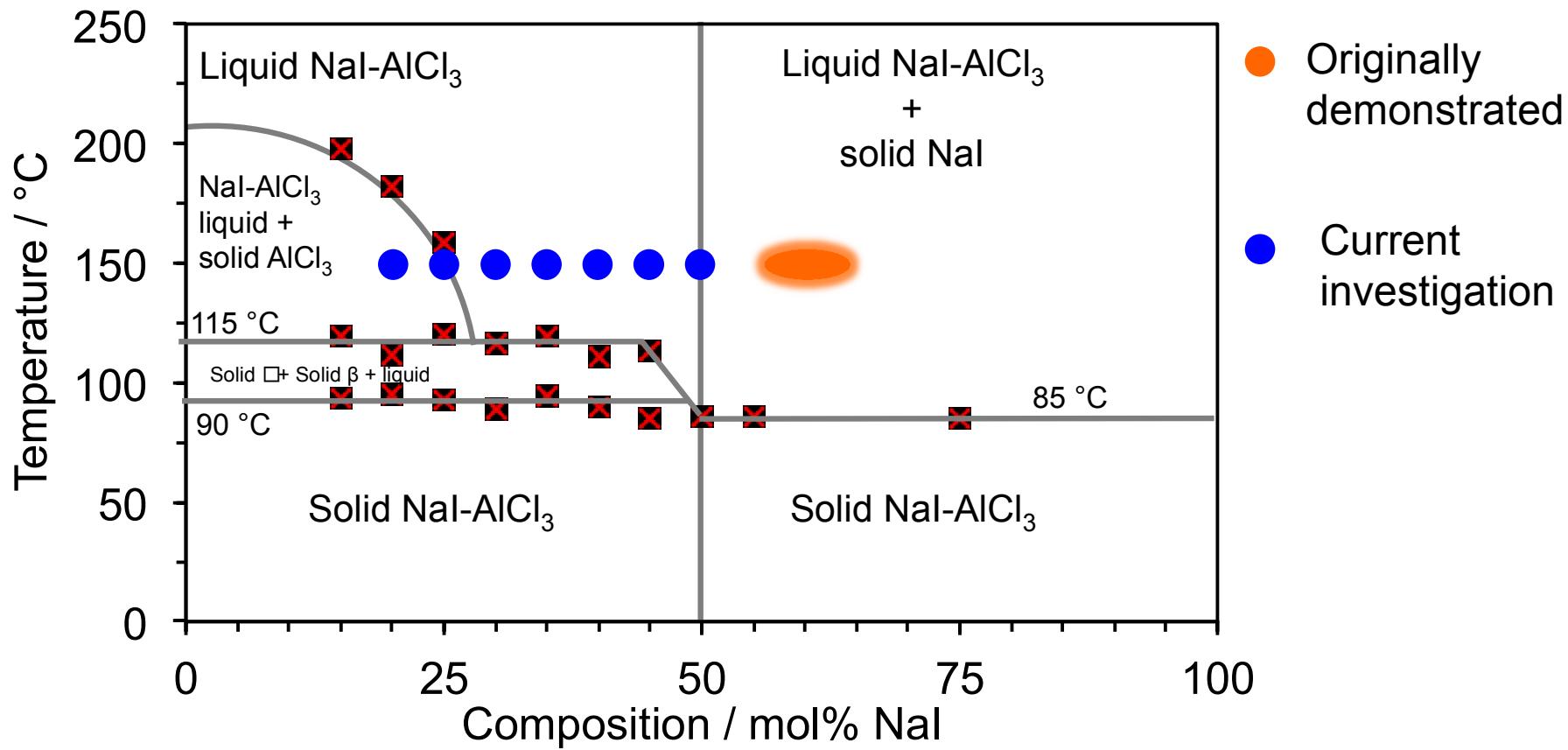
Preliminary Phase Diagram of  $\text{NaI}-\text{AlCl}_3$  Catholyte



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

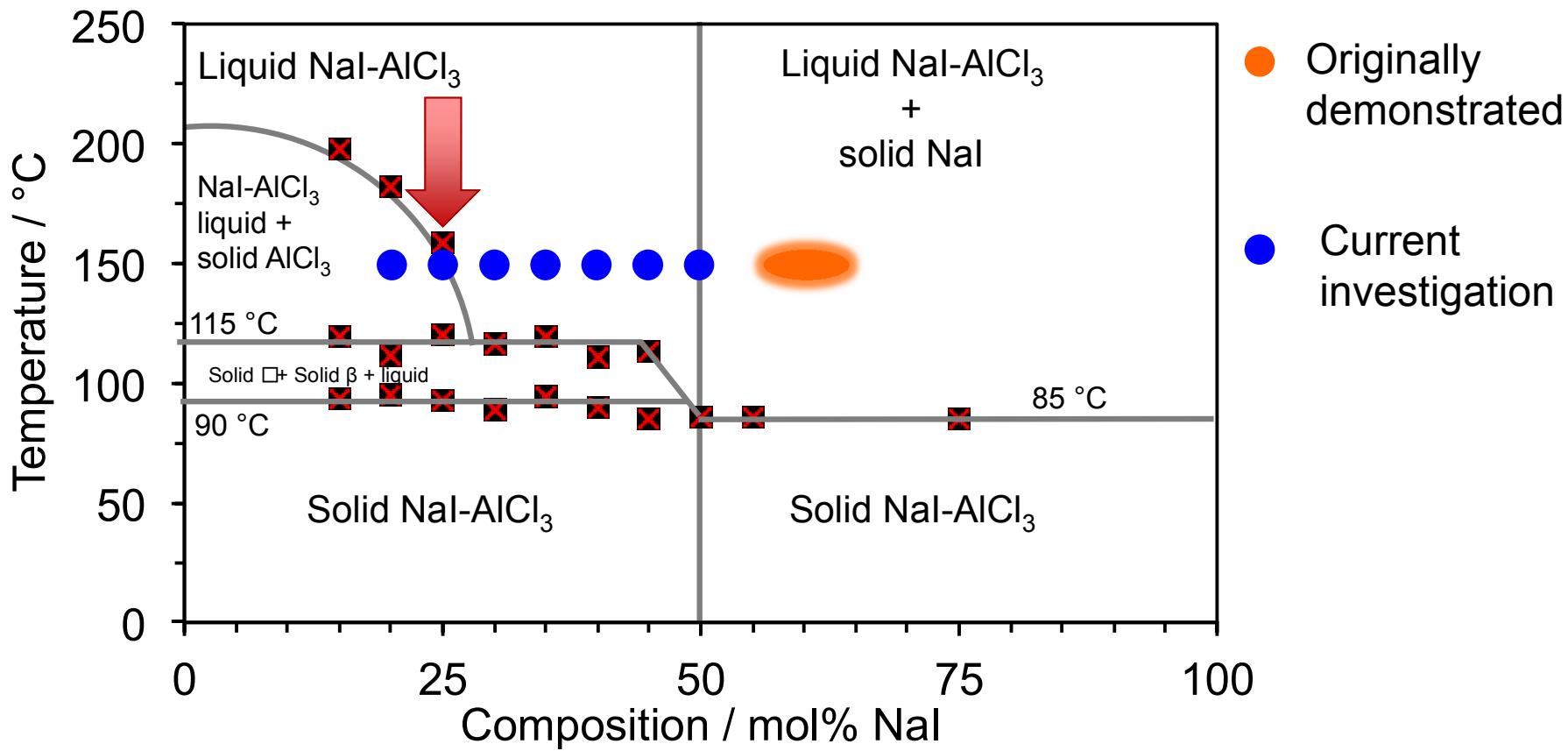
# Catholyte Compositions Tested

Preliminary Phase Diagram of  $\text{NaI-AlCl}_3$  Catholyte



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Preliminary Phase Diagram of  $\text{NaI-AlCl}_3$  Catholyte

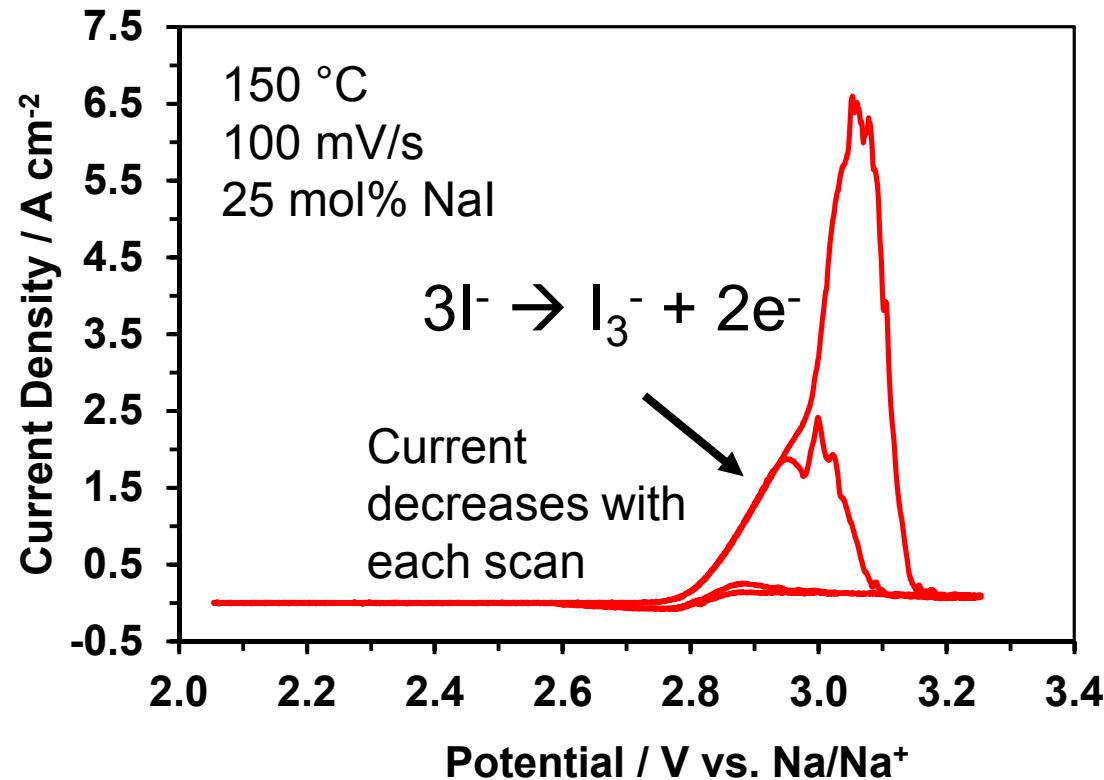
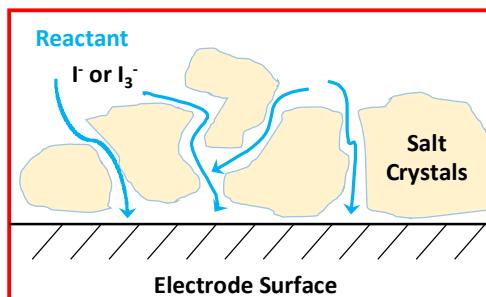


# Hindered Diffusion: Solid State

Possible solid precipitation observed at electrode surface

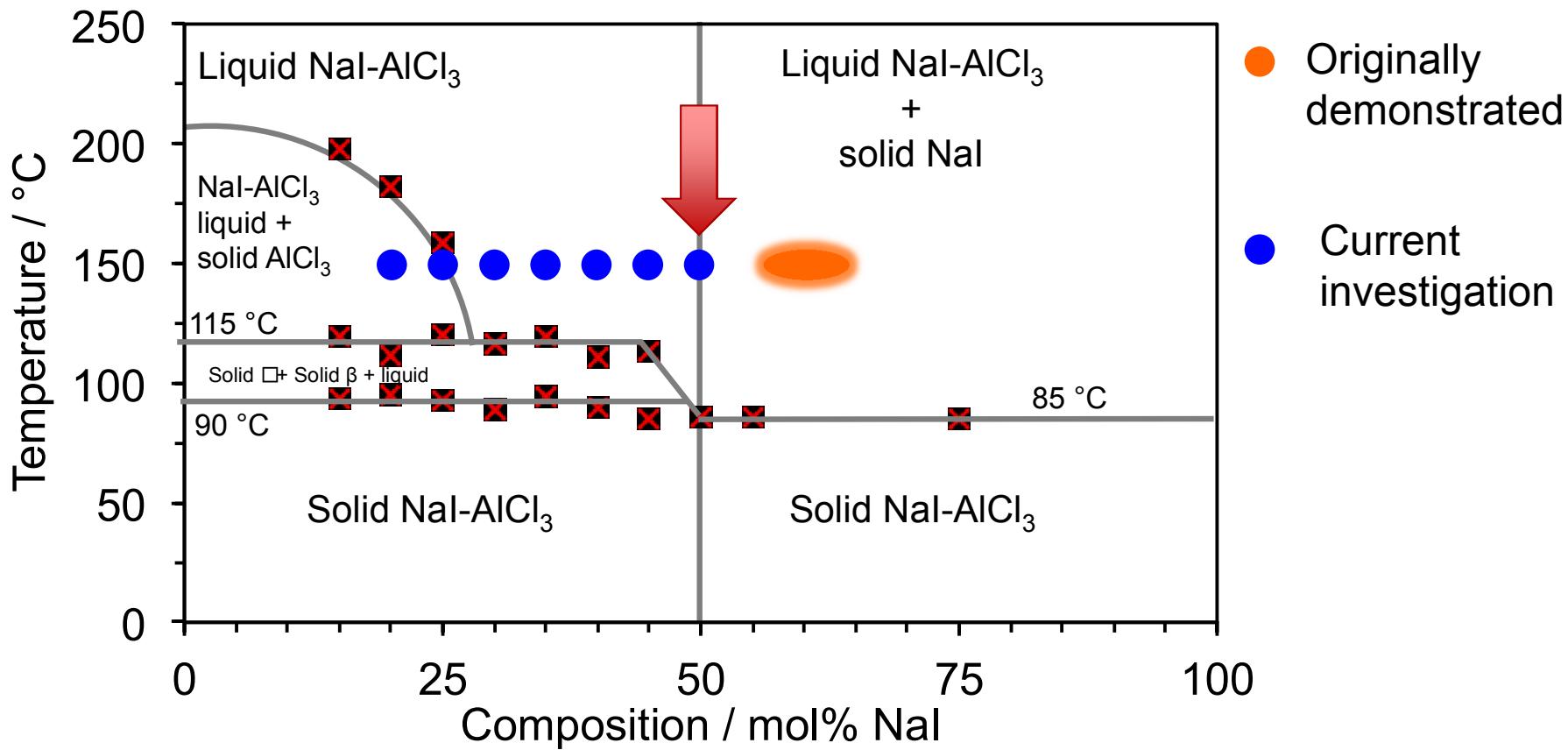
- Hindered diffusion from presence of solids near electrode

Current Peaks then settles to a lower “residual” current



# Catholyte Compositions Tested

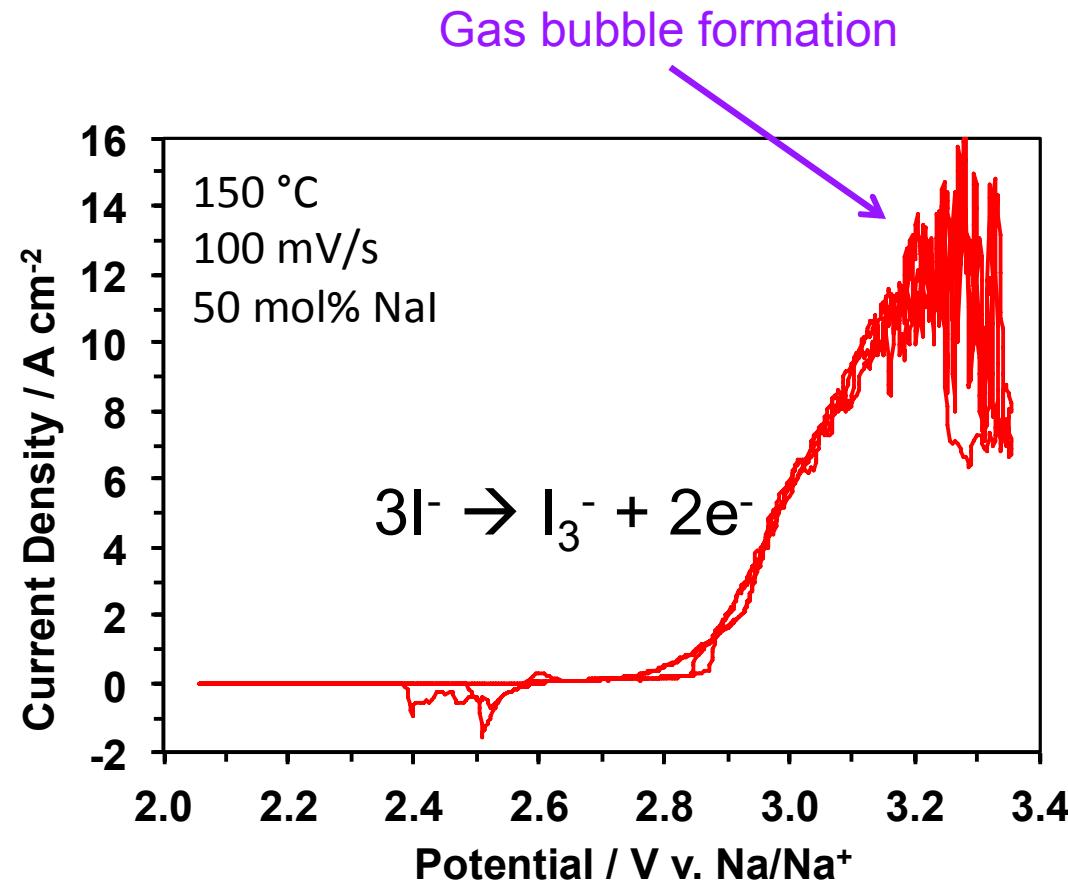
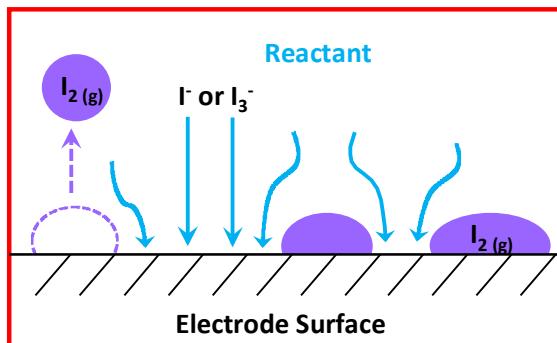
Preliminary Phase Diagram of  $\text{NaI-AlCl}_3$  Catholyte



# Hindered Diffusion: Gas State

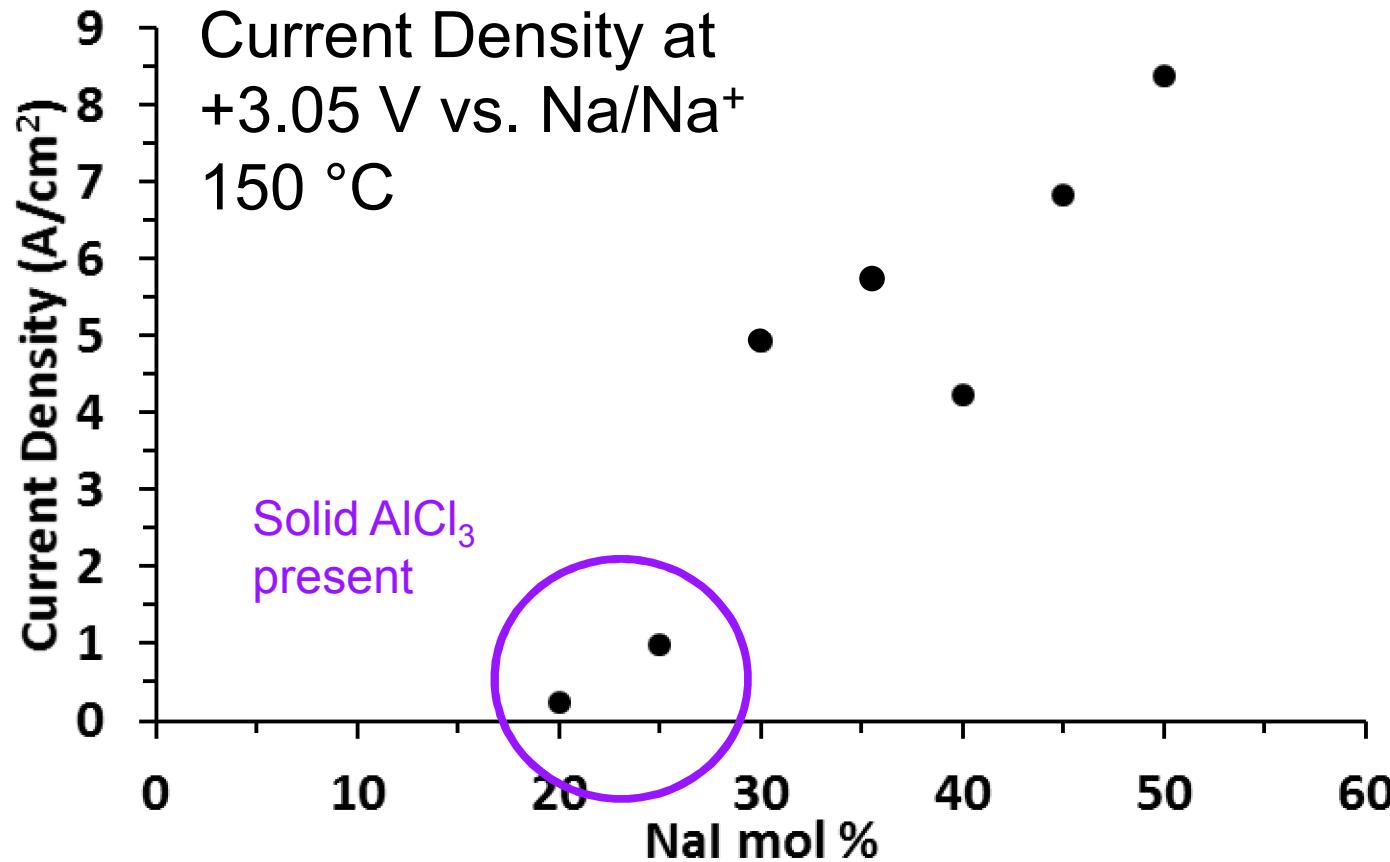
Stable bubble formation  
observed for very high NaI-  
content salt compositions

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



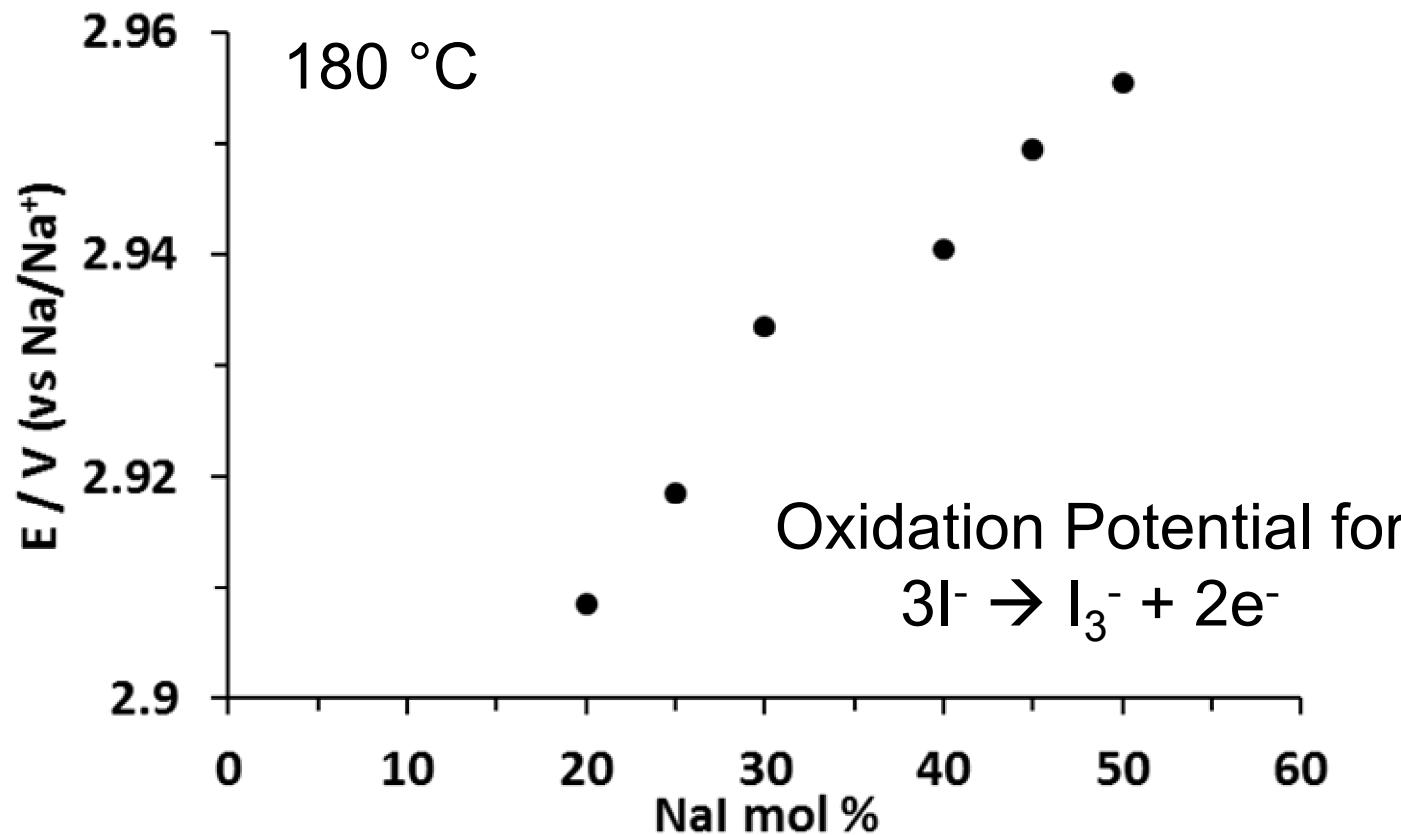
# Electrochemical Performance of Catholyte

Highest current densities are observed at highest NaI concentrations. There is a significant drop in current density when solid  $\text{AlCl}_3$  is formed.



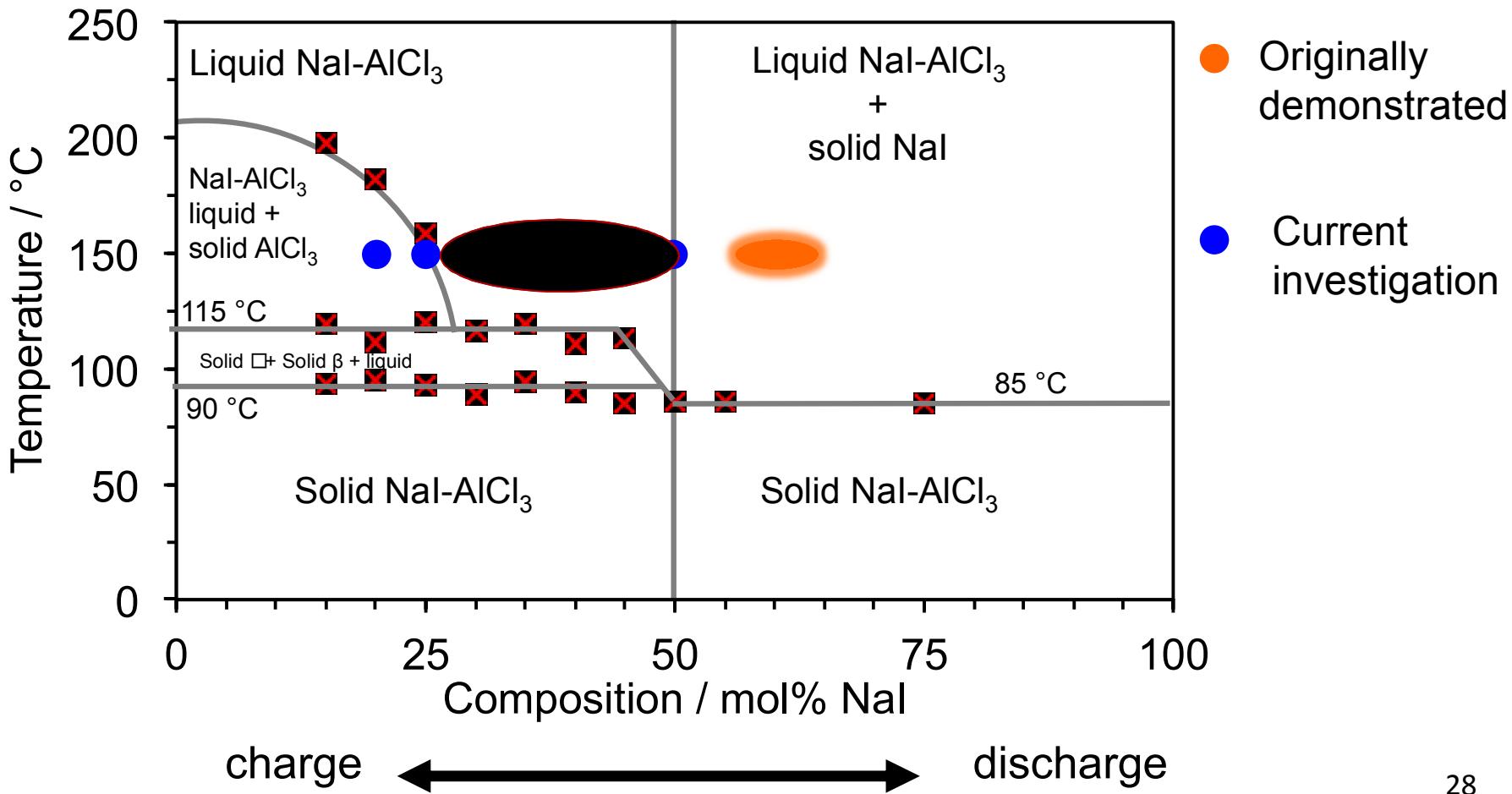
# Battery Potential is Modestly Affected by Catholyte Composition

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



# Molten Catholyte Desired

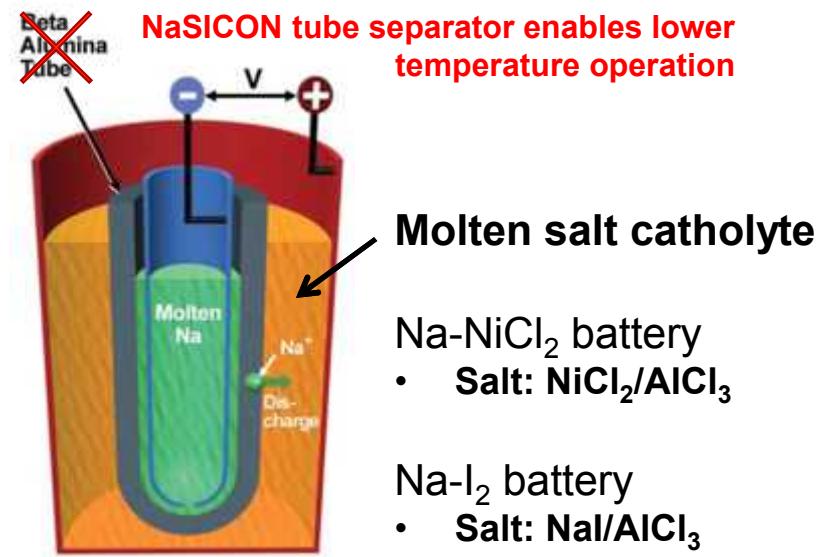
Preliminary Phase Diagram of  $\text{NaI-AlCl}_3$  Catholyte



# Intermediate Temperature Molten Salt Na-Based Batteries

**Our Goal:** to develop low cost ( $\leq \$100/\text{kWh}$ ), intermediate temperature ( $\leq 200^\circ\text{C}$ ), *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 ( $>10^{-3} \text{ S/cm}$  at  $25^\circ\text{C}$ )
  - ✓ Scalable production
  - ✓ Demonstrated up to 250Wh prototypes
- Reduced temperature (relative to traditional Na-batteries) enables:
  - ✓ Lower cost
  - ✓ Increased reliability and lifetime
  - ✓ Improved capacity retention (limitation of Li-ion and Pb-acid)
- 



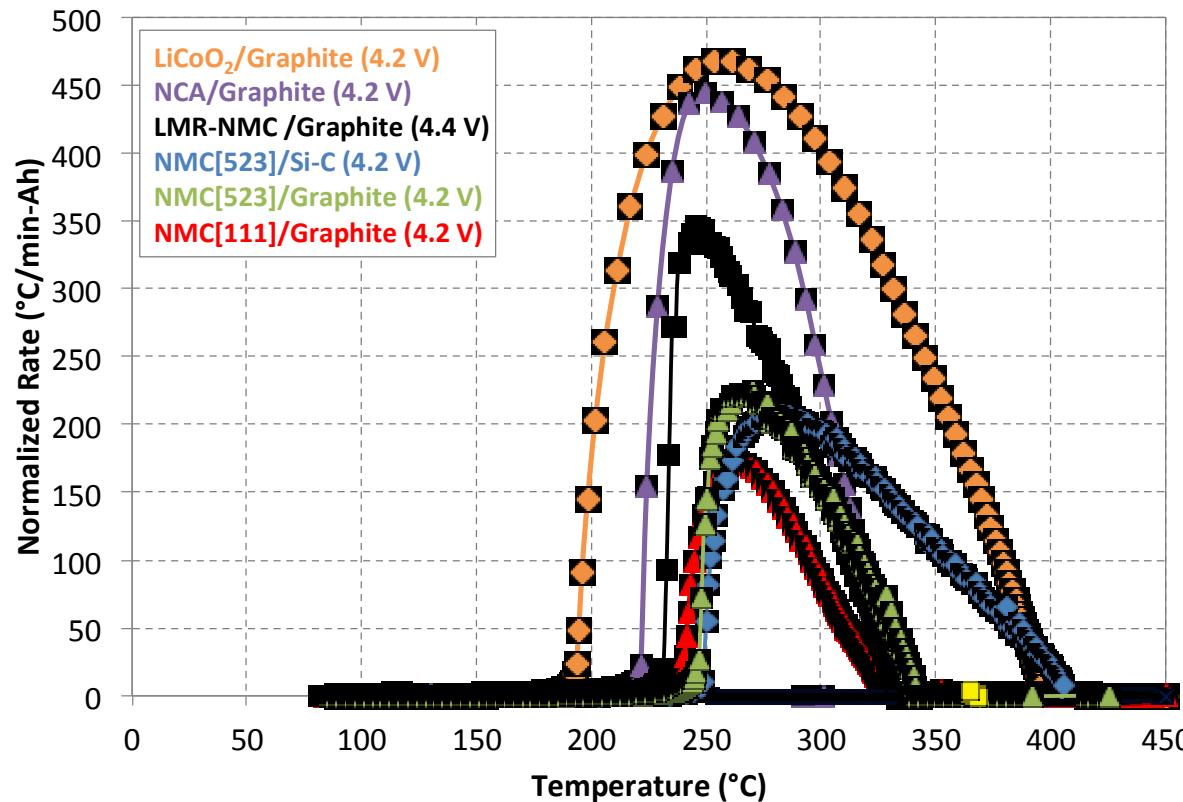
Sodium-nickel chloride ( $195^\circ\text{C}$ ,  $E_{\text{cell}} \sim 2.6\text{V}$ ):  
 $\text{Na} + \frac{1}{2} \text{NiCl}_2 \rightleftharpoons \text{Na}^+ + \text{Cl}^- + \text{Ni(s)}$

Sodium-iodine ( $120-150^\circ\text{C}$ ,  $E_{\text{cell}} \sim 3.25\text{V}$ ):  
 $\text{Na} + \frac{1}{2} \text{I}_2 \rightleftharpoons \text{Na}^+ + \text{I}^-$

# Safety Performance of Catholyte Salt

# Accelerating Rate Calorimetry (ARC) Shows No Significant Exotherms

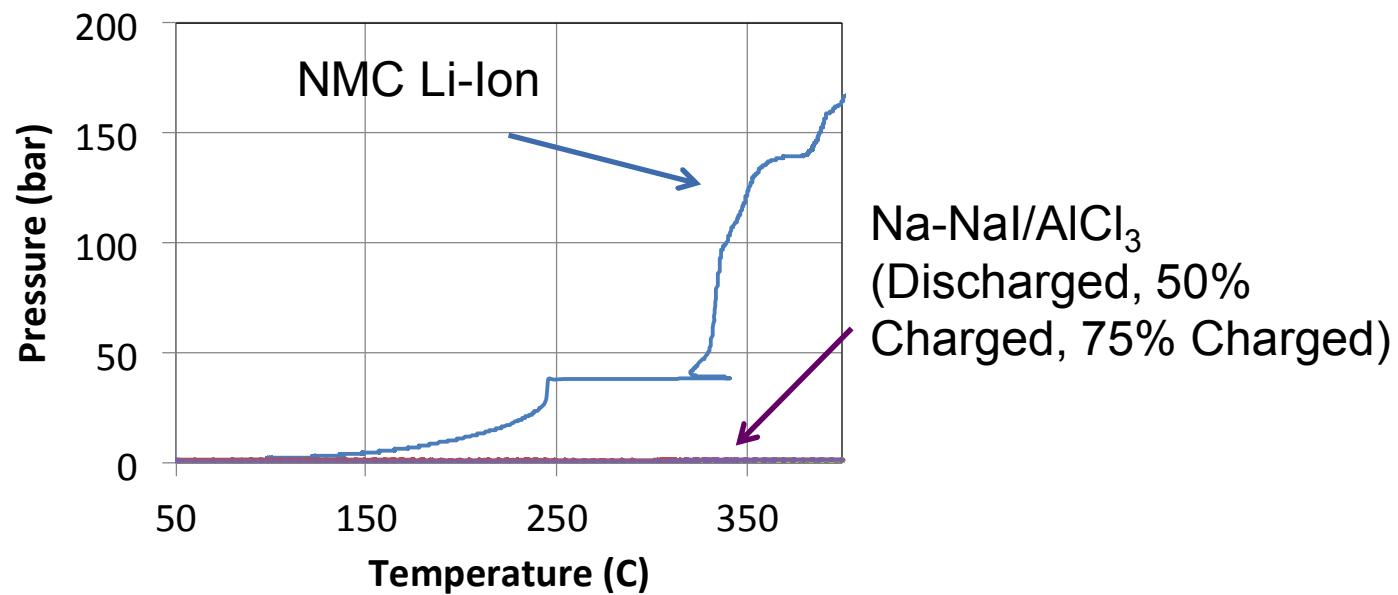
*When complete separator failure is simulated by mixing Na metal and NaI/AlCl<sub>3</sub> catholyte, ARC testing reveals no hazardous runaway exothermic behavior!*



# Na-System Shows Minimal System Pressurization

Measuring pressure generated during ARC testing shows no significant gas generation/pressurization from the Na-NaI/AlCl<sub>3</sub> mixture. Even in up to 75% charge state, no significant gas pressurization (e.g., I<sub>2</sub> evolution) was observed.

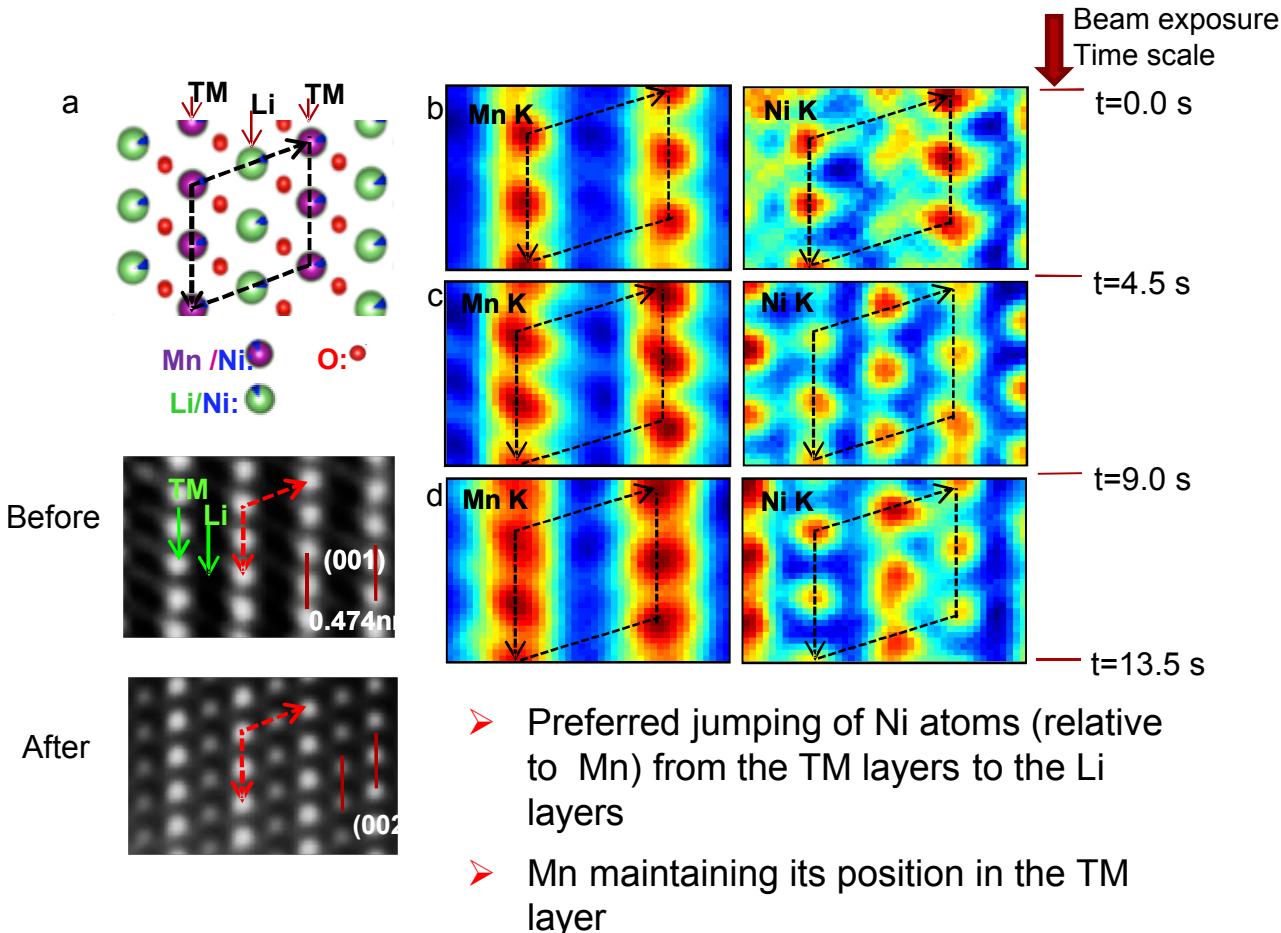
In contrast volatile components of an NMC Li-Ion produce a dramatic pressure spike at elevated temperatures.



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

# Ultrafast Imaging with AC-STEM

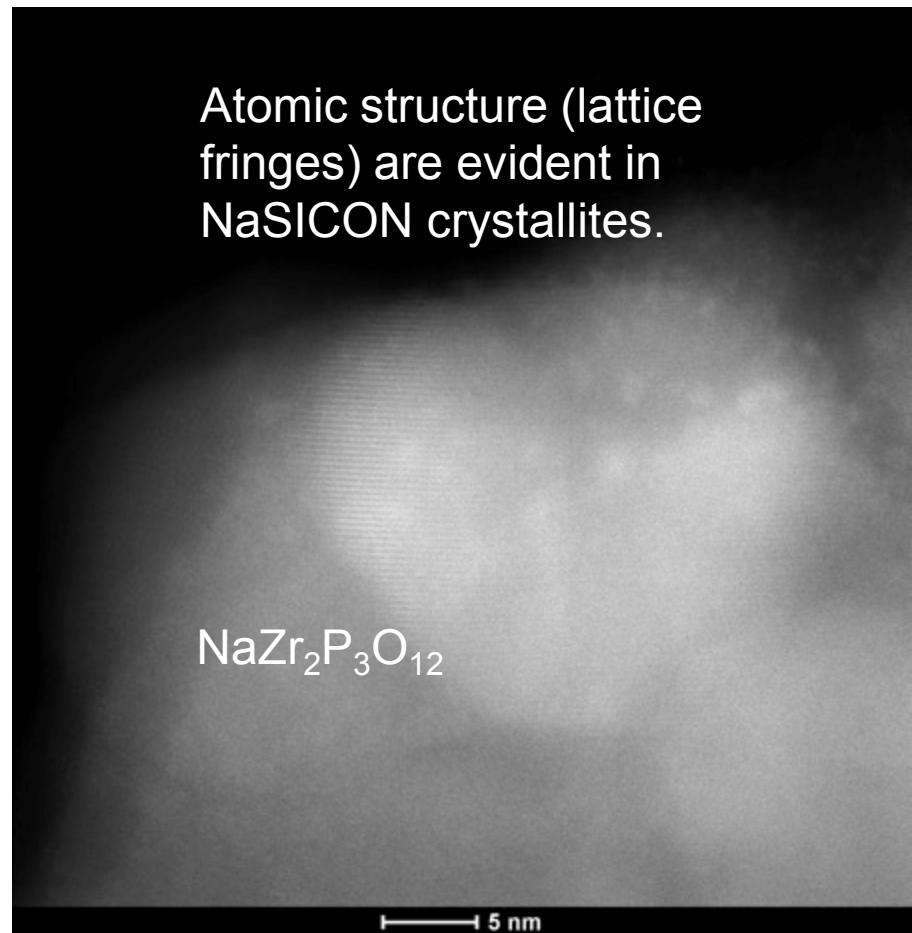
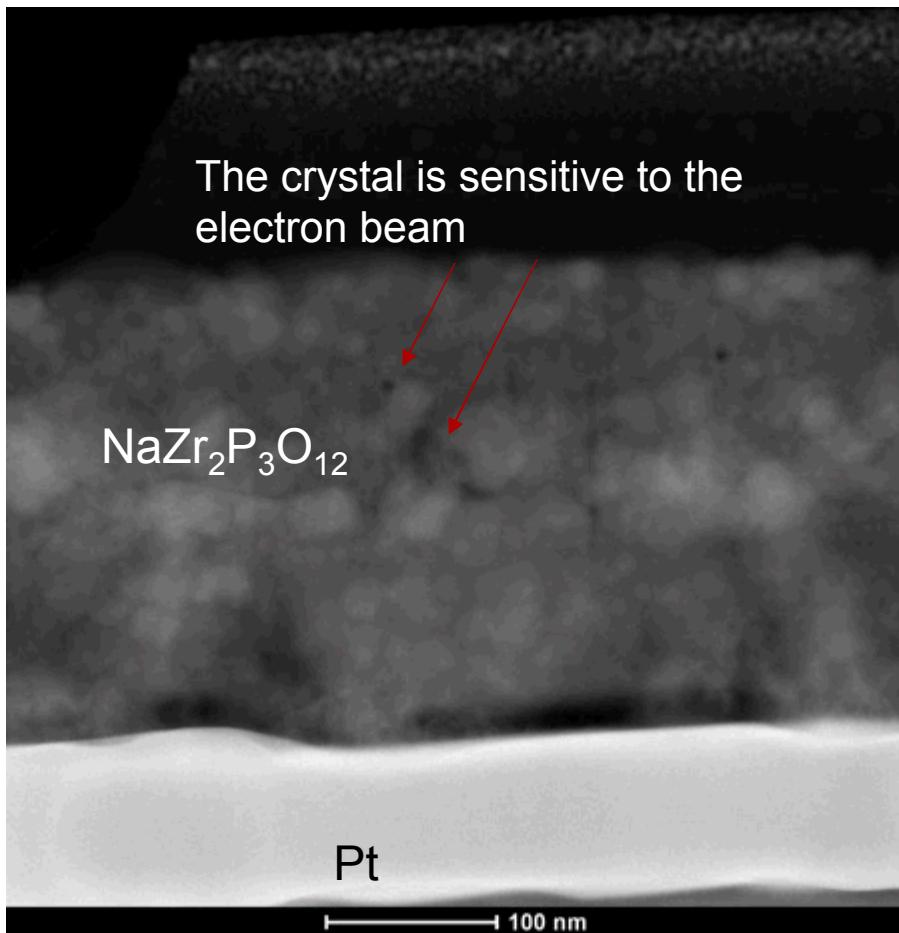
## Time-resolved atomic-scale chemical imaging



Using an SNL-developed technique for ultrafast imaging and chemical mapping allows for visualization of atomic movement in ion-conductive materials.

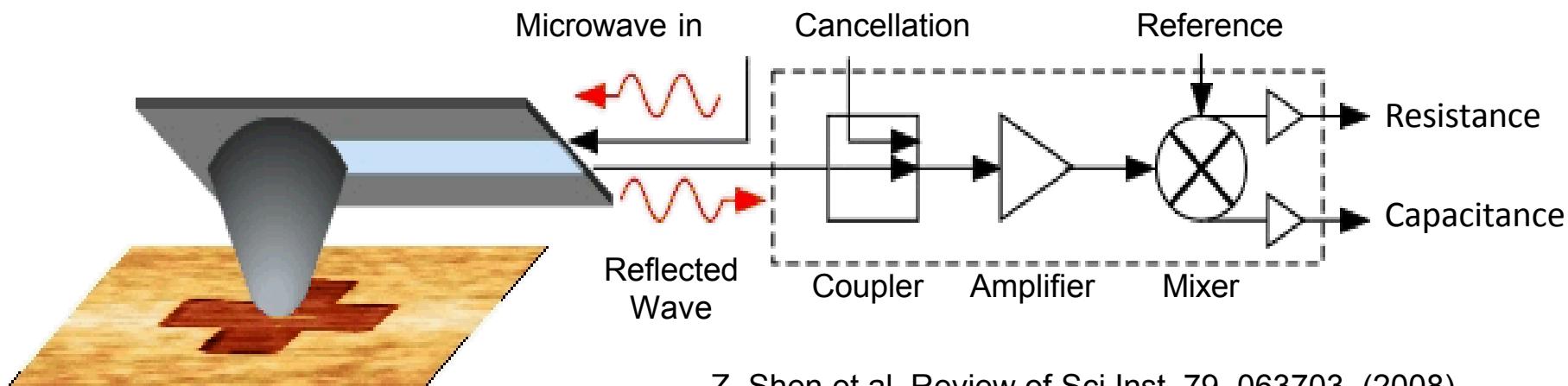
- Preferred jumping of Ni atoms (relative to Mn) from the TM layers to the Li layers
- Mn maintaining its position in the TM layer

# Ultrafast Imaging with AC-STEM



Initial AC-STEM imaging of local crystal planes in beam-sensitive NaSICON highlights feasibility of ultrafast imaging of Na-movement in NaSICON.

# Scanning Microwave Impedance Microscopy (SMIM)

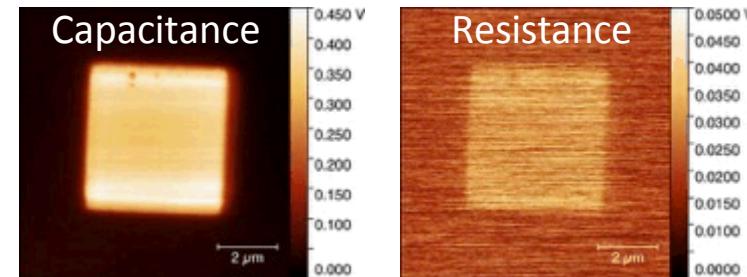


Z. Shen et al, Review of Sci Inst, 79, 063703, (2008)

- Shielded tip for higher SNR
- Look at variation of local impedance (electrical properties – C & R,  $\epsilon$  &  $\sigma$ )
- Monotonic in signal response

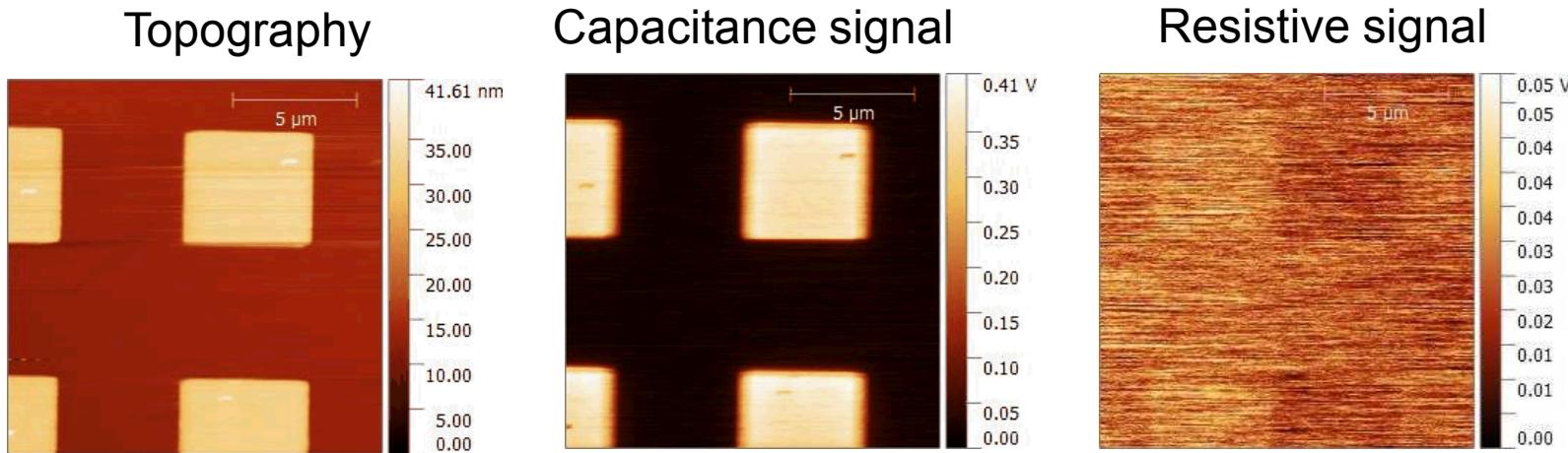


Demodulation on Al dots on  $\text{SiO}_2$

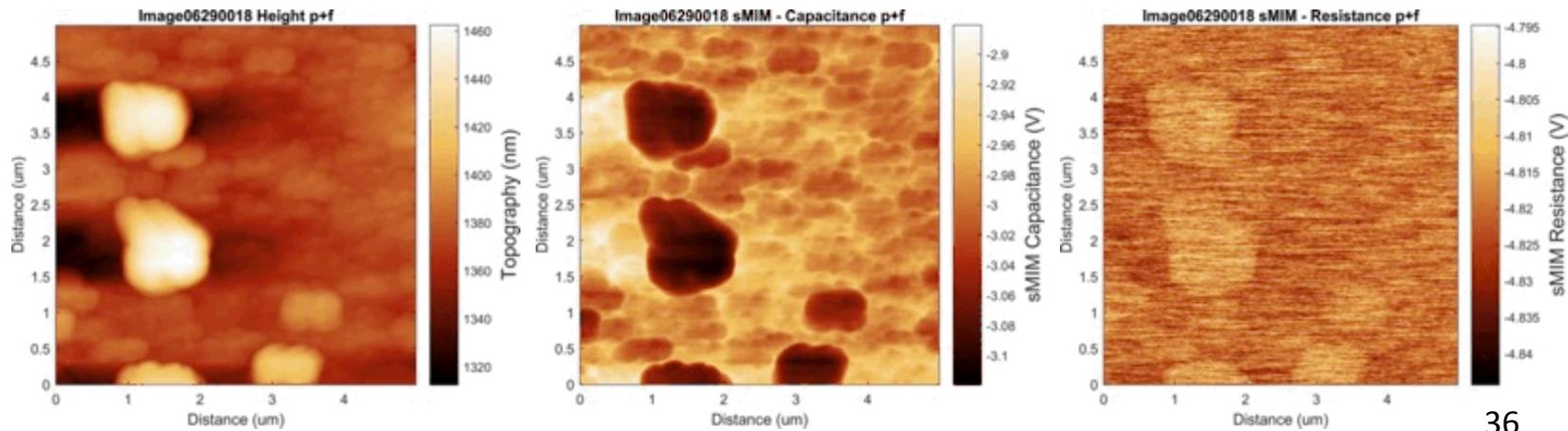


# MIMS Reveals Functional Differences in Phase Chemistry of NaSICON

$\text{Al}_2\text{O}_3$   
on Si



NaSICON  
thin film



# EESAT Presentations



Oral Presentation by Erik Spoerke

“Sodium-Based Batteries: Toward Meeting Next Generation Challenges in Grid-Scale Energy Storage”  
(Wednesday 10:00-12:00)

Poster Presentation by Leo Small:

Molten NaI-AlCl<sub>3</sub> Catholytes for use in a Sodium Battery  
(Wednesday Evening 17:30-19:00)

# Programmatic Accomplishments



## **Presentations:**

E.D. Spoerke, L.J. Small, et al. "Emerging Stationary Battery Technologies." (Invited) 2017 DLA Worldwide Energy Conference (04/2017) (Invited)

E. D. Spoerke, L.J. Small, et al. "Enabling Next Generation Sodium-Based Batteries with Engineered NaSICON Ion Conductors." Electronic Materials and Applications 2017 (EMA 2017) (01/2017)

E.D. Spoerke, L.J. Small, et al. "Safety-by-Design in All-Inorganic Sodium Batteries." 2017 ESS Safety Forum, (02/2017)

E.D. Spoerke, L.J. Small, et al. "Sodium-Based Batteries: Engineering Interfaces for Optimized Performance." 2017 Spring Materials Research Society Meeting (04/2017)

## **Conference Organization:**

E.D. Spoerke - Co-organizer of Ion Conducting Ceramics symposium at Electronic Materials and Applications 2017 (an American Ceramics Society meeting). January, 2017, Orlando, FL.

E.D. Spoerke and S. Bhavaraju – Organizers for 2018 Spring Materials Research Society Meeting: "Next Generation Solid State Super Ion Conductors."

# Programmatic Accomplishments



## Journal Publications:

L.J. Small, E.D. Spoerke, et al. "Next generation molten NaI batteries for grid scale energy storage." (2017) *J. Power Sources*. **360**. 569-574.

L.J. Small, E.D. Spoerke, et al. "Deposition of tungsten metal by an immersion process." (2017) *J. Electrochem. Soc.* **164** (6) D269-D274.

E. Allcorn, et al. "Elimination of Active Species Crossover in a Room Temperature, Neutral pH, Aqueous Flow Battery using Ceramic NaSICON Membrane." (2017) *J. Power Sources*, in revision.

L.J. Small, et al. "Enhanced Alkaline Stability in a Hafnium-Substituted NaSICON Ion Conductor." (2017) *J. Mater. Chem. A*, in review.

## Patents:

E.D. Spoerke, L.J. Small, et al. "Cation-Enhanced Chemical Stability of Ion-Conducting Zirconium-Based Ceramics." 3/16/2017 U.S Patent Appl. 15/460,570.

L.J. Small, E.D. Spoerke, et al. "Electroless Process for Depositing Refractory Metals." 12/9/2016 U.S. Patent Appl. 15/374,775.

D. Ingersoll, E. Allcorn, G. Nagasubramanian. "Aqueous Na-ion Redox Flow Battery with Ceramic NaSICON Membrane" Prov. Pat. 62397664 (Sept, 2016).

# FY18 Path Forward



- Develop high surface area, chemically compatible current collector configuration for high efficiency molten salt battery performance.
- Characterize relationships between microstructure, material phase, and ion conduction in solid-state ion conducting materials (e.g. NaSICON and related materials).
- Apply aqueous-stabilized NaSICON chemistry (SNL-developed) for novel asymmetric aqueous battery systems.
- Optimize composition and properties of molten salt catholytes for high efficiency charge transfer processes at reduced temperatures.
- Adapt current concentric tubular battery configuration for more versatile ceramic separator integration (e.g., ceramic plates).
- Continue to engage industrial partners to enable ultimate commercialization of Na-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-NiCl<sub>2</sub> batteries was performed through collaboration between Ceramatec and SK Innovation.



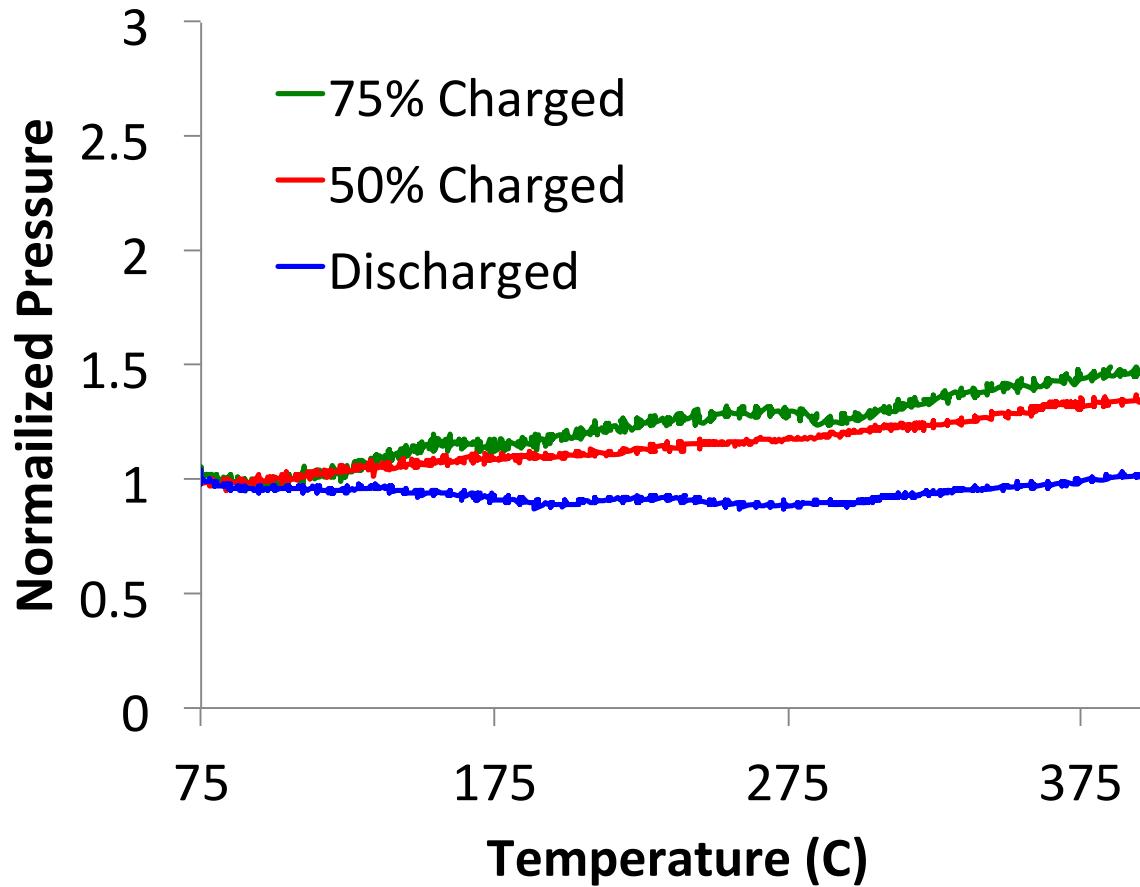
Related presentations at EESAT:

Spoerke, Small.

*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



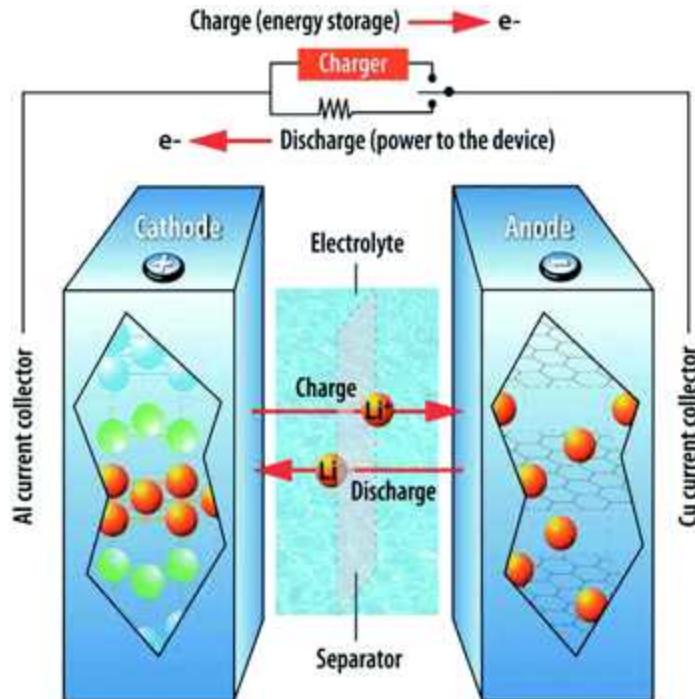
*This minimal pressurization represents a dramatic safety benefit of Na-batteries.*

# 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?

# Advancing Basic Materials Chemistry Across the Cell

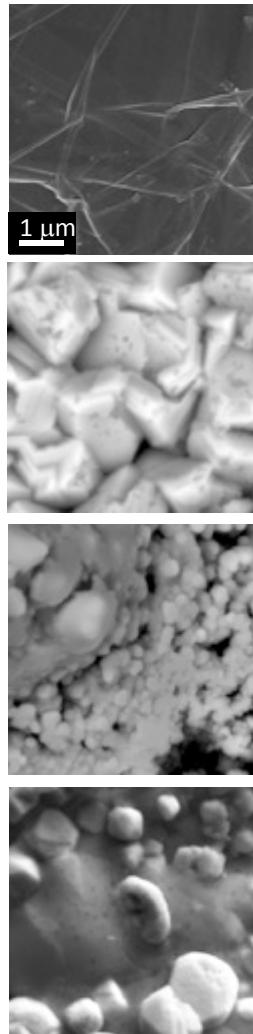


## Basic elements of Na-Batteries:

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

# Improving Cathode Structure

## Electrolessly Coated Tungsten/Carbon Electrodes



Carbon electrode  
(graphite, powder, foam)



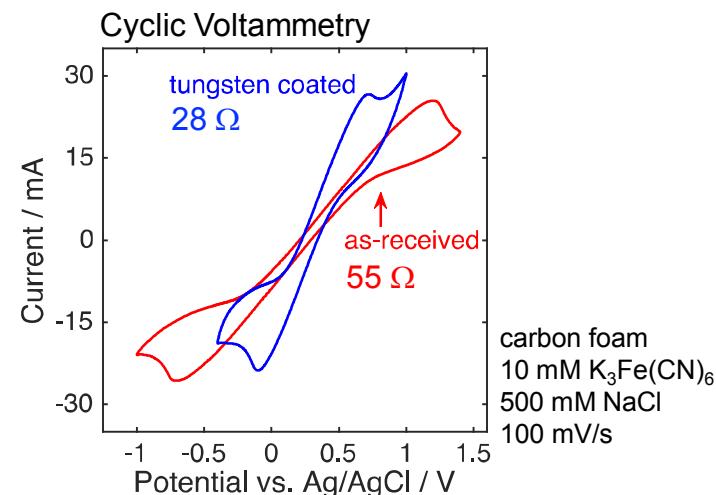
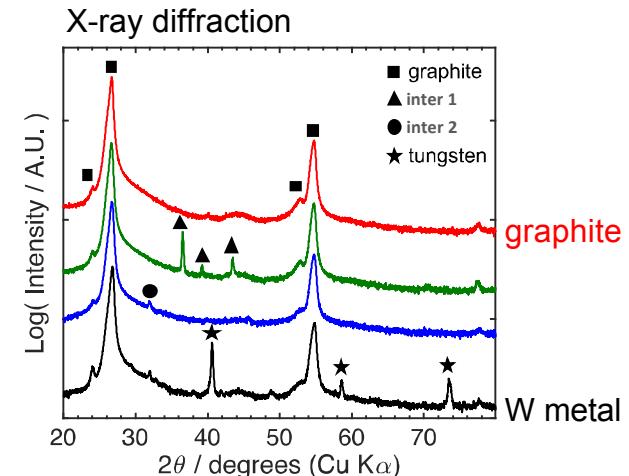
Intermediate coating



Convert to W-precursor

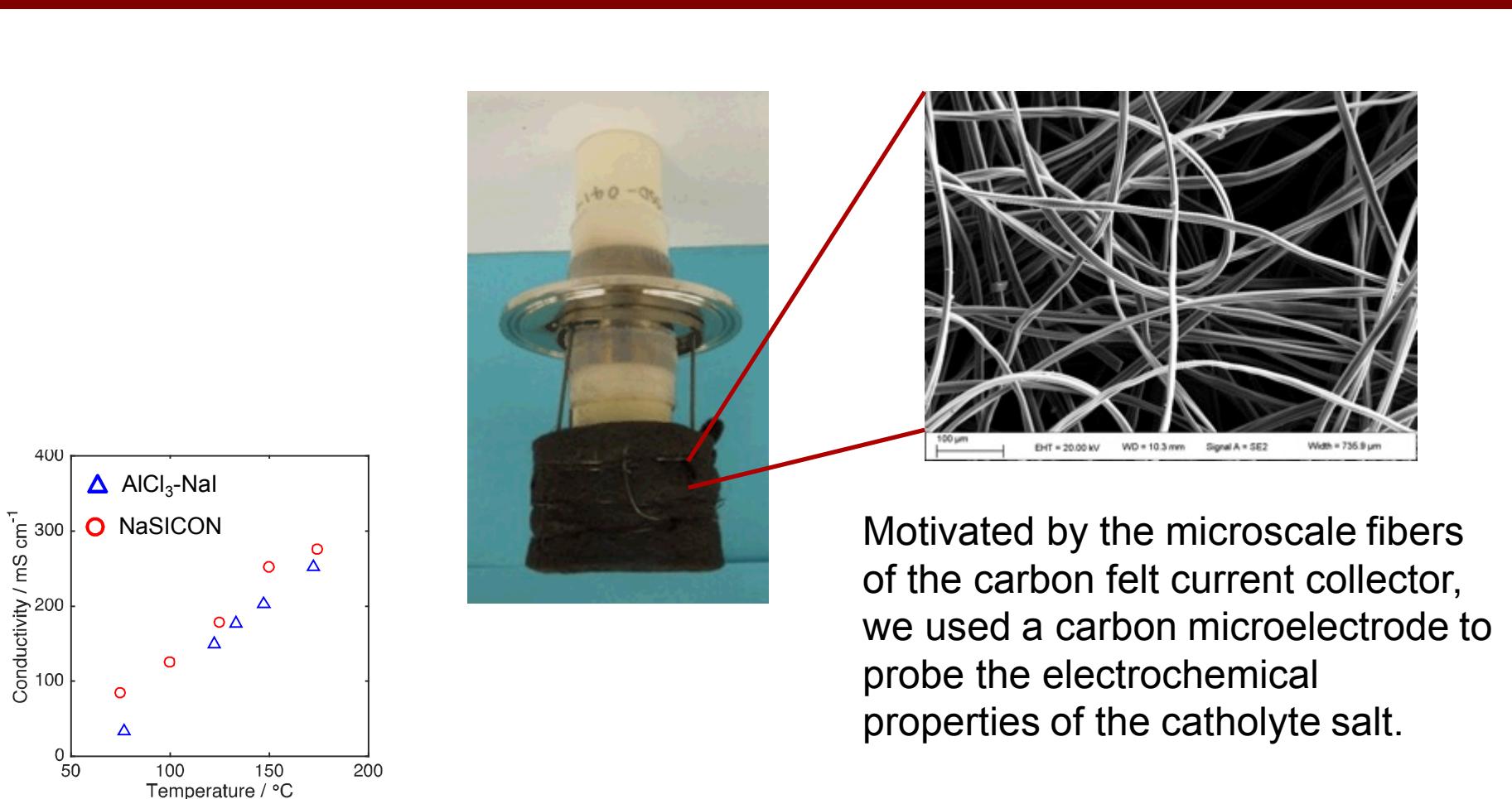


Reductive anneal creates  
***Crystalline, metallic tungsten.***



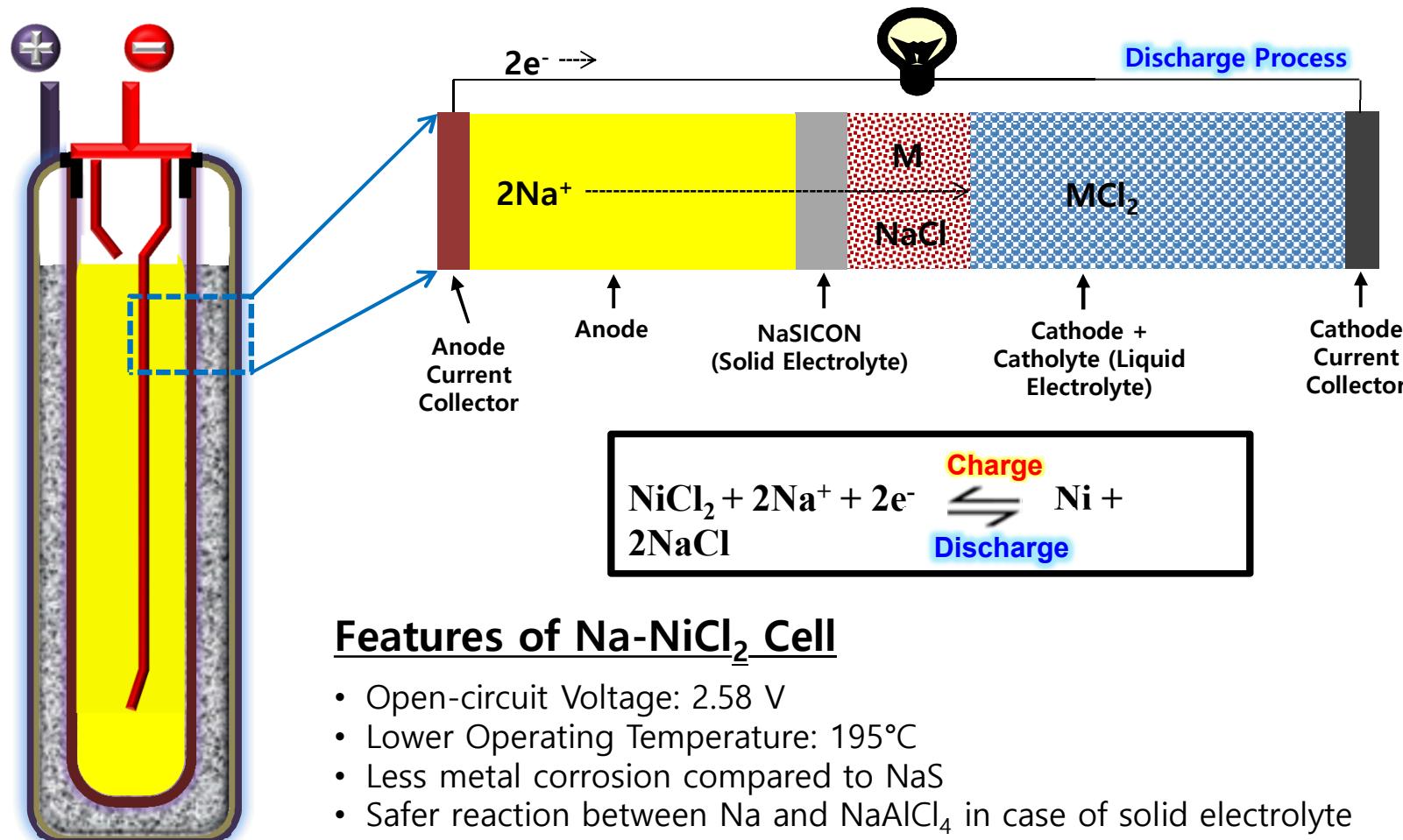
***2X Reduction in electrode resistance will reduce ASR and enable superior electrochemical performance.***

# Molten Catholyte and Carbon Felt Current Collector



(A) CV of a carbon felt electrode in the 40AlCl<sub>3</sub>:60NaI catholyte at 125 °C and 100 mV s<sup>-1</sup>. (B) Ionic conductivity of the 40AlCl<sub>3</sub>:60NaI catholyte and NaSICON NaS-GY as a function of temperature.

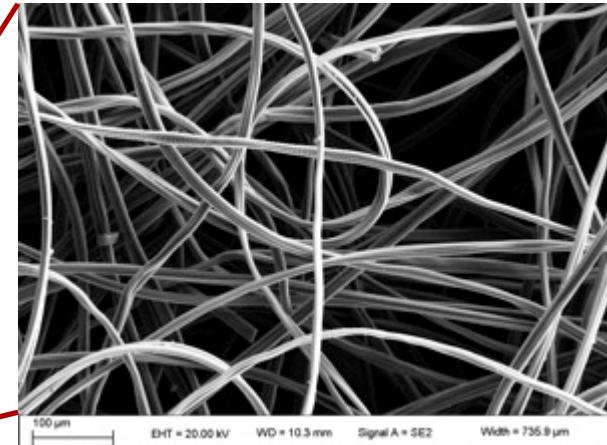
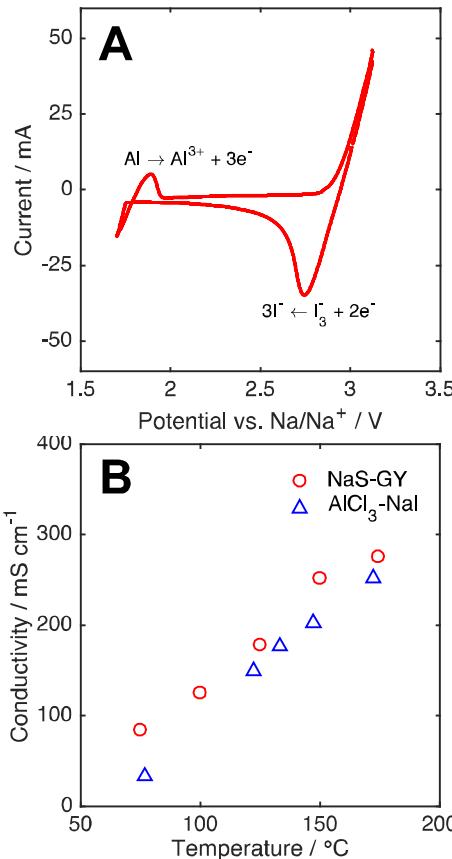
# Na-NiCl<sub>2</sub> Battery Technology



## Features of Na-NiCl<sub>2</sub> Cell

- Open-circuit Voltage: 2.58 V
- Lower Operating Temperature: 195°C
- Less metal corrosion compared to NaS
- Safer reaction between Na and NaAlCl<sub>4</sub> in case of solid electrolyte fracture

# 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 40AlCl<sub>3</sub>:60NaI catholyte at 125 °C and 100 mV s<sup>-1</sup>. (B) Ionic conductivity of the 40AlCl<sub>3</sub>:60NaI catholyte and NaSICON NaS-GY as a function of temperature.

# 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 (?)



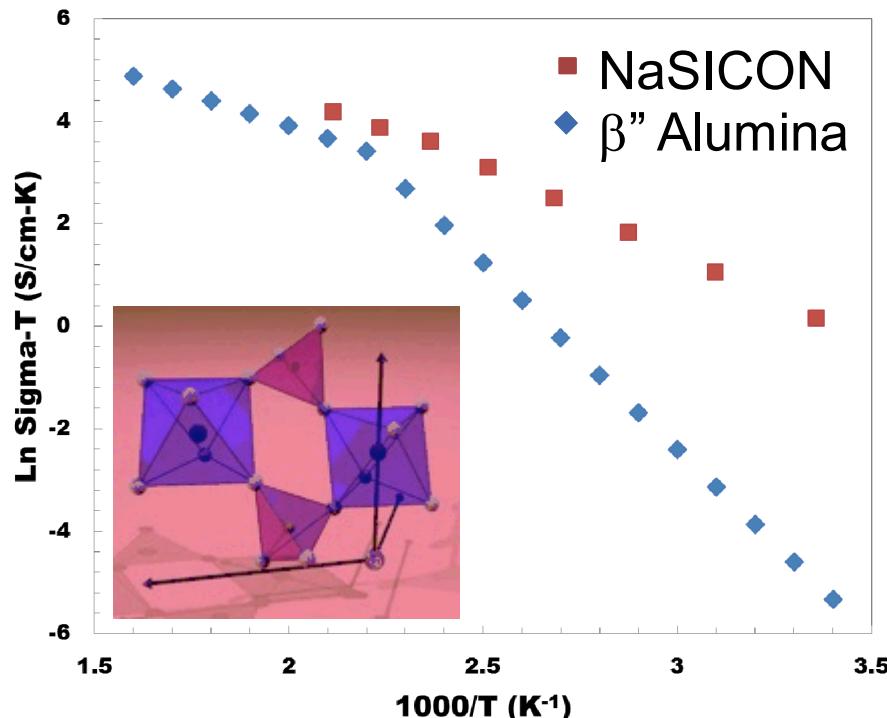
This 10 kWh battery pack depicted on the side of a building likely has 5 liters of liquid electrolyte.

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

*Li-ion batteries are inherently intolerant of harsh conditions.*

# NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

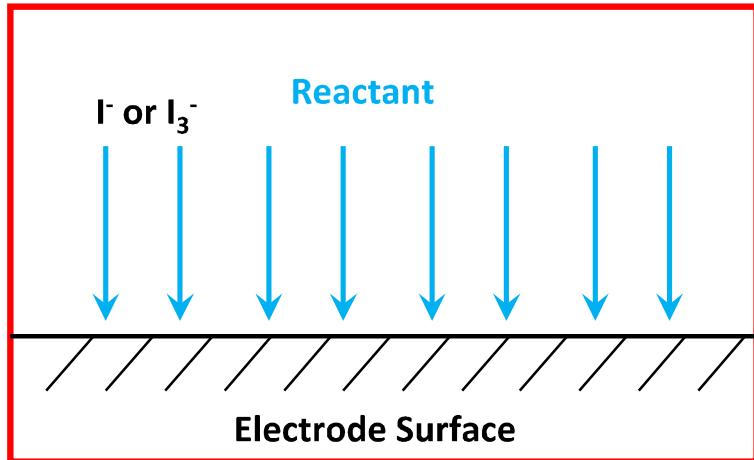
NaSICON (Na Super Ion CONductor):  $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$



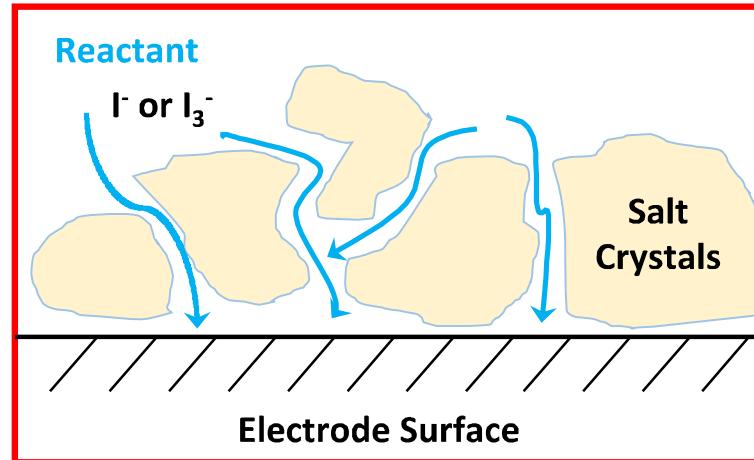
Engineered materials chemistry and advanced, scalable processing (Ceramatec, CoorsTek) make NaSICON a *chemically/mechanically stable, low temperature, high conductivity (>10<sup>-3</sup> S/cm @RT) separator technology.*

# Molten Catholyte Development

Regular Diffusion

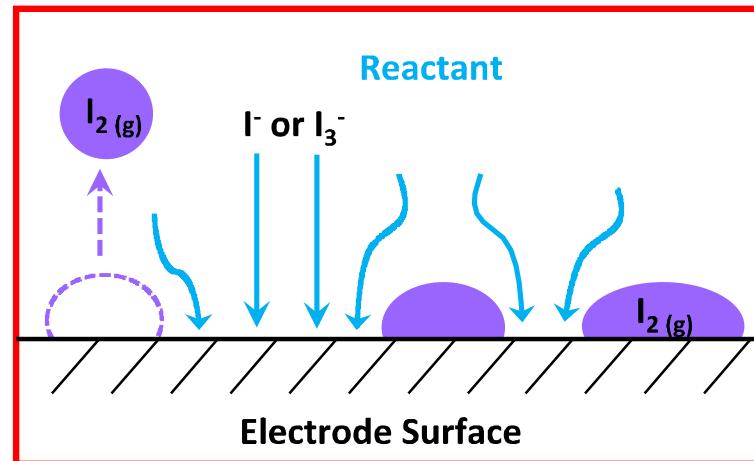


Hindered Diffusion – Solid Phase



- 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<sub>2</sub>

Hindered Diffusion – Gas Phases (Bubble Formation)



# Pre-Commercial Na-NiCl<sub>2</sub> systems



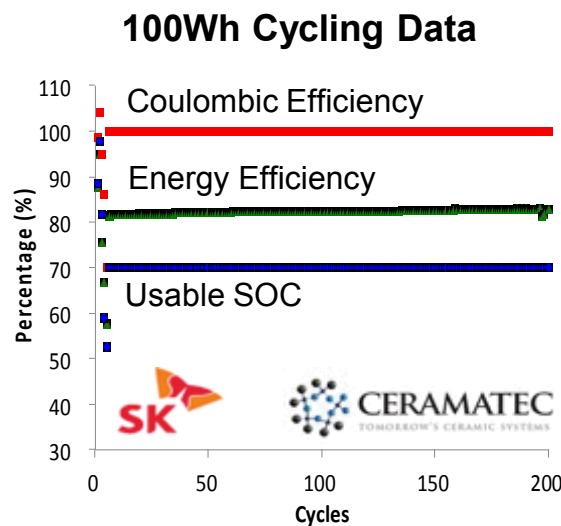
Recently demonstrated high performance cycling in precommercial prototypes at 195°C at 53mA/cm<sup>2</sup> and C/7 rate (w/ Ceramatec, Inc. and SK Innovation):

## 100 Wh Na-NiCl<sub>2</sub> unit cell:

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

## 250 Wh Na-NiCl<sub>2</sub> unit cell:

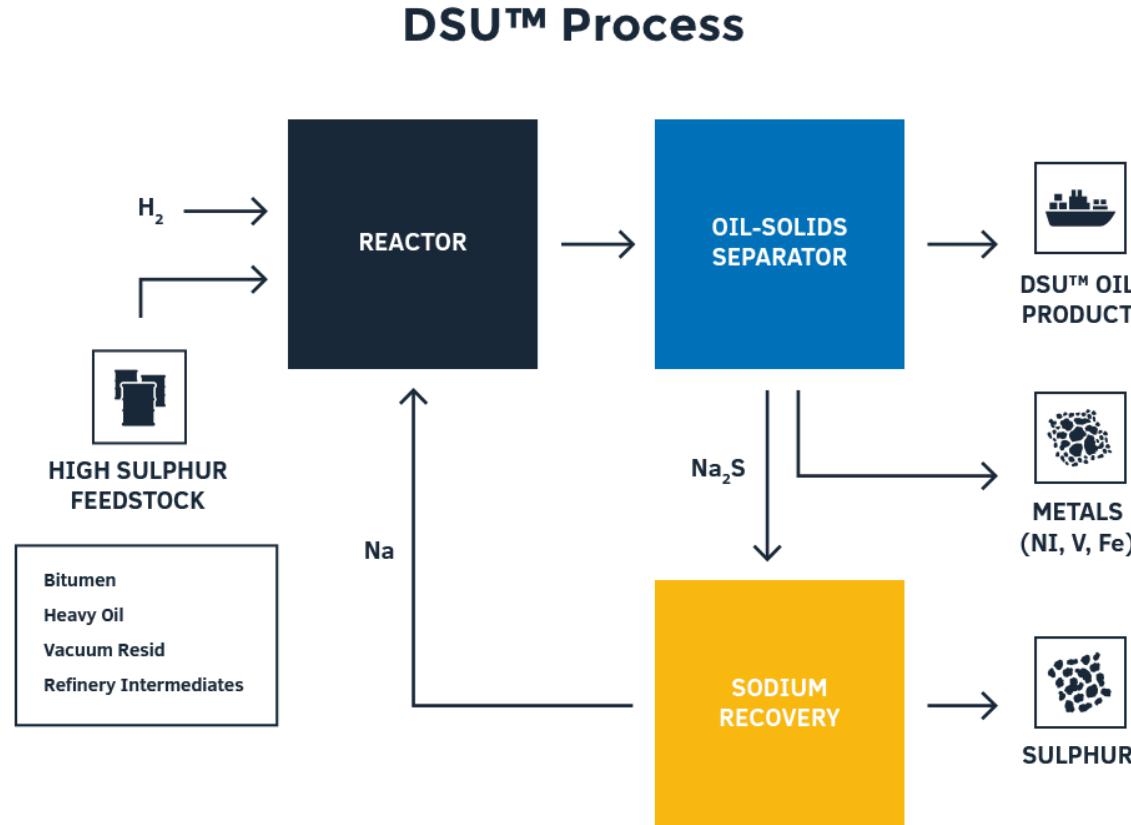
- operational for 3+ months
- 110 cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 80 %



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

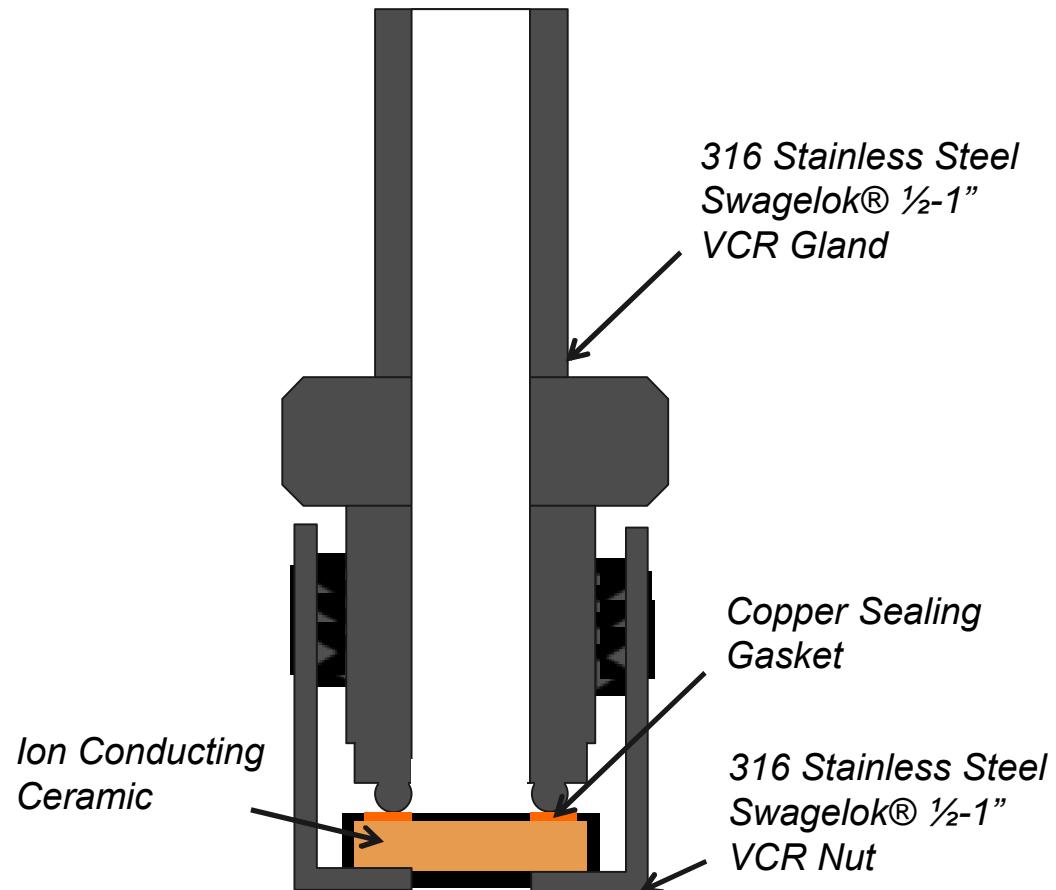
*We are currently seeking industry partners to advance large-scale demonstrations and drive commercialization of these batteries.*

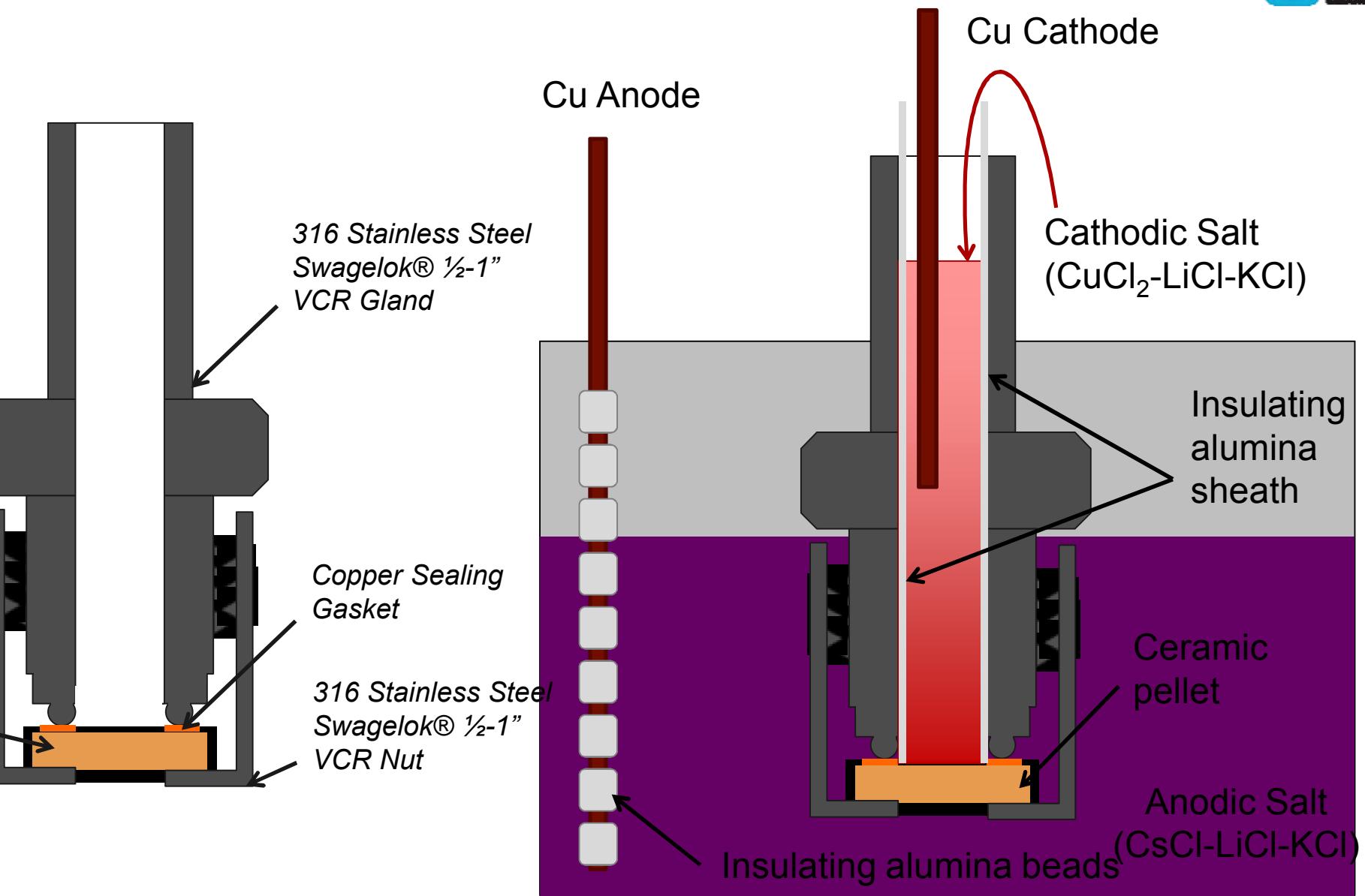
# NaSICON Utilization for DSU Purification Process by Field Upgrading



As a short-term alternative to using ceramic tubes, a secondary, pellet-based scheme will be employed to demonstrate volumetric salt purification.

This approach will use a VCR fitting with a copper gasket to seal polished ceramic pellets into a steel tube.





# Take Home Messages

- ✓ There is a critical need 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<sub>2</sub> 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.

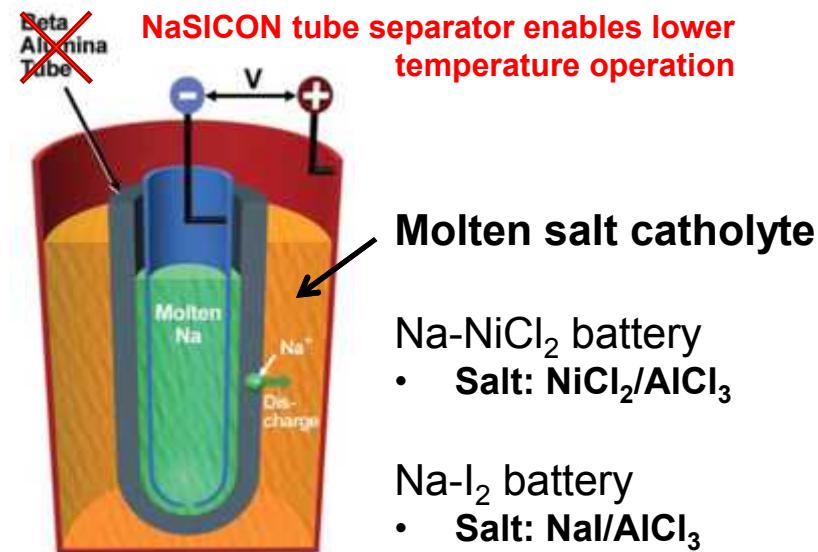


- ✓ Continued collaborations between National Laboratories, academia, and industry will prove powerful in enabling next generation grid-scale energy storage solutions.

# Intermediate Temperature Molten Salt Na-Based Batteries

**Our Goal:** to develop low cost ( $\leq \$100/\text{kWh}$ ), intermediate temperature ( $\leq 200^\circ\text{C}$ ), *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 ( $>10^{-3} \text{ S/cm}$  at  $25^\circ\text{C}$ )
  - ✓ Scalable production
  - ✓ Demonstrated up to 250Wh prototypes
- Reduced temperature (relative to traditional Na-batteries) enables:
  - ✓ Lower cost
  - ✓ Increased reliability and lifetime
  - ✓ Improved capacity retention (limitation of Li-ion and Pb-acid)



**Molten salt catholyte**

Na-NiCl<sub>2</sub> battery

- Salt: NiCl<sub>2</sub>/AlCl<sub>3</sub>

Na-I<sub>2</sub> battery

- Salt: NaI/AlCl<sub>3</sub>

Sodium-nickel chloride ( $195^\circ\text{C}$ ,  $E_{\text{cell}} \sim 2.6\text{V}$ ):



Sodium-iodine ( $120\text{-}150^\circ\text{C}$ ,  $E_{\text{cell}} \sim 3.25\text{V}$ ):

