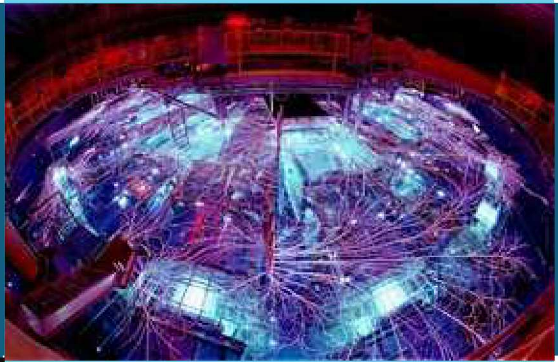
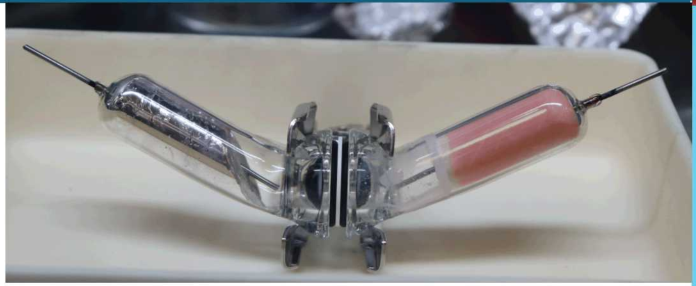
SAND2019-14004C

Advances in Low Temperature Molten Sodium Halide Catholytes for Sodium Batteries





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2019 ACS SWRM/RMRM
November 14, 2019
El Paso, TX USA

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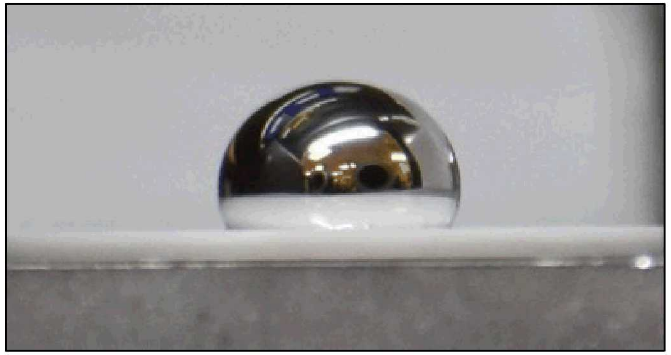
Todays Outline

Battery Background:

- Why is energy storage important?
- What are the current technologies?
- Why Na based batteries?



New Catholyte development:

- Electrochemical behavior of catholytes
- Importance of fully molten salt at low temperature

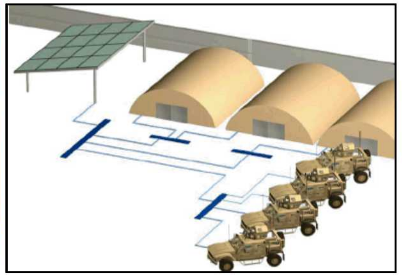
Battery cycling behavior at low temperatures using new catholytes – preliminary data

Key Design Criteria

There remains a need for grid-scale energy storage


Renewable/Remote Energy

Grid Reliability

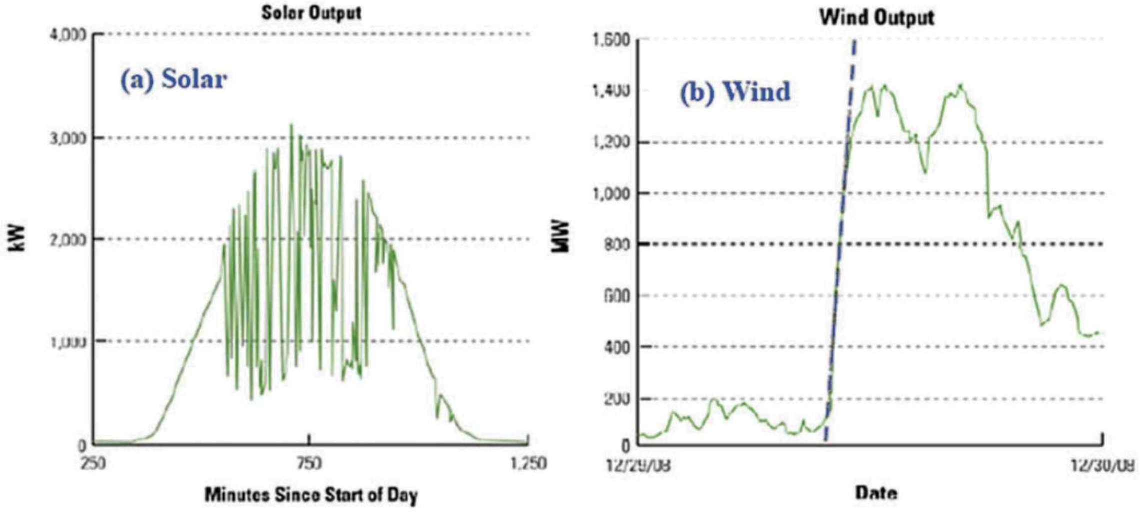


National Defense

Emergency Aid

Why is energy storage important? – To keep the lights on!

- Stores energy generated by renewables for use when the source (example: sun or wind) is not generating



Gür, T. M. *Energy Environ. Sci.* **2018**, *11*, 2696-2767.

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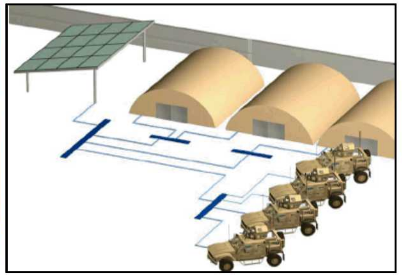


National Defense

Emergency Aid

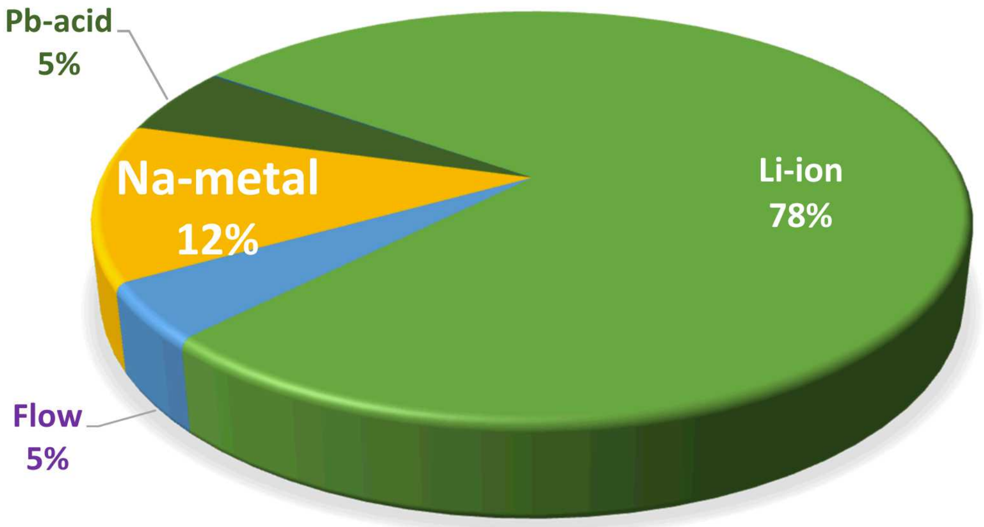
- Inherent Safety
- Low to Intermediate Temperature Operation
- Functional Energy Density (voltage, capacity)
- Low Cost and Scalable
- Long Cycle Life

Low to Intermediate Temperature Operation →

- Reduced operating costs
- Reduced materials costs
- Improved battery material lifetime
- Increases distribution availability
- Enables freeze-thaw cycles

Current Battery Energy Storage Deployments

- Many types of electrochemical energy storage:
  - Flow batteries, lithium ion, lead acid and **molten sodium**



*(Operational as of Nov. 2017)

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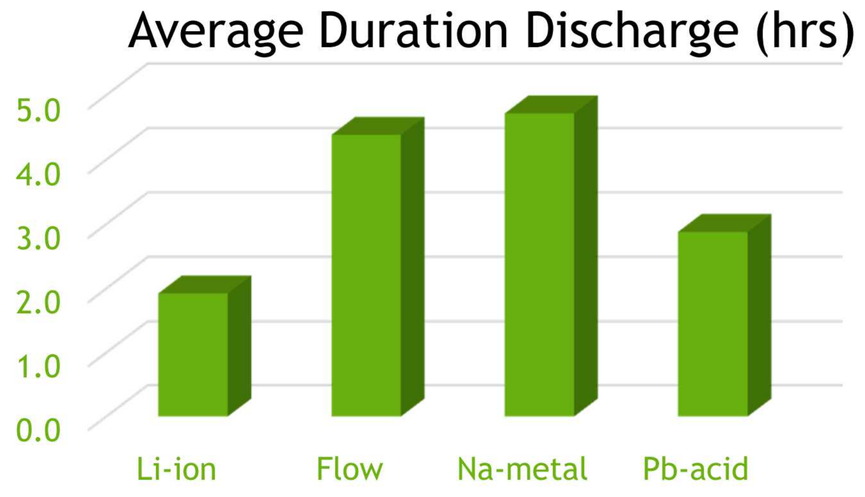
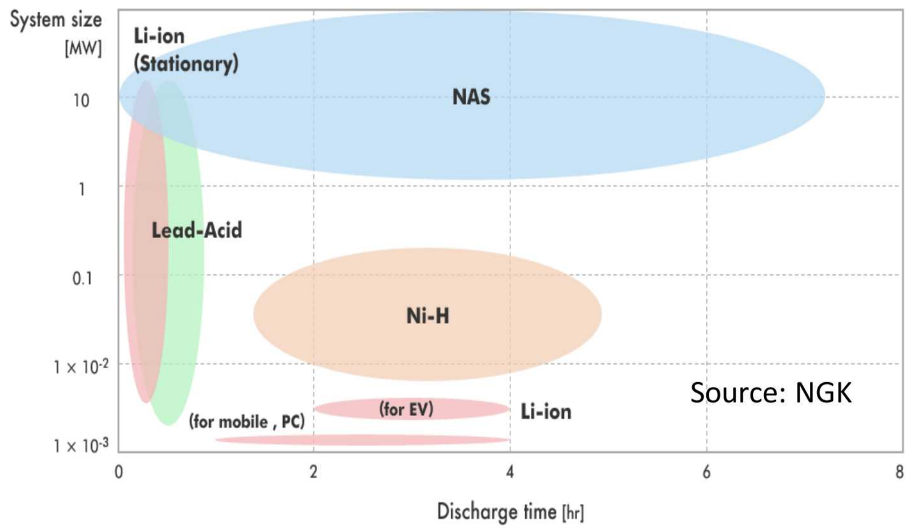


Source: *DOE Global Energy Storage Database*
http://www.energystorageexchange.org/ Nov. 2017



Source: NGK

Hazards of Li-Ion

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 home likely has 5 liters of liquid electrolyte.

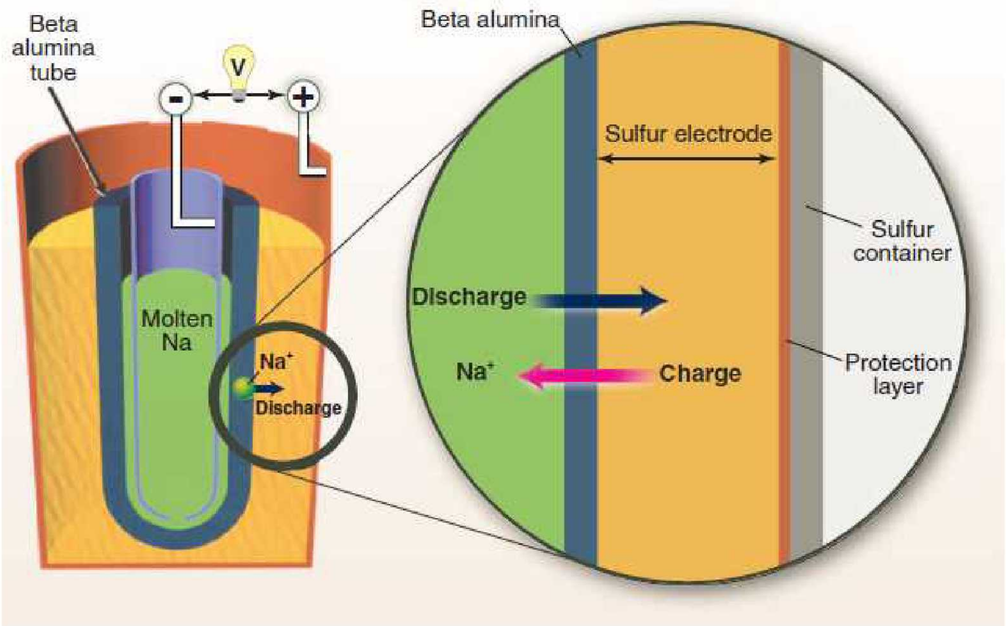
Thermal runaway and flammable organic electrolytes remain serious hazards for Li-ion batteries!

Li-ion batteries are inherently intolerant of harsh conditions.

Promise in Molten Sodium Based Electrochemical Battery Storage

Sodium-based batteries

- 6th most abundant element on earth.
- Proven technology base with Sodium/Sulfur (NaS) and ZEBRA (Na-$NiCl_2$) systems.
- Utilize zero-crossover solid state electrolytes.
- Yield favorable battery voltages (>2V).



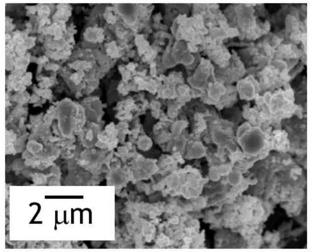
Traditional Na-Batteries operate at ~300^oC

- Improves separator ionic conductivity
- Increases Cost
- Limits Battery Lifetime

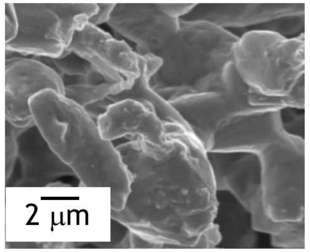
$$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$$

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

- Cycle lifetime (solid cathode phase)
- Cost (related to cycle lifetime and material costs)



Particle Coarsening →



$$2Na + 4S \leftrightarrow Na_2S_4$$

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

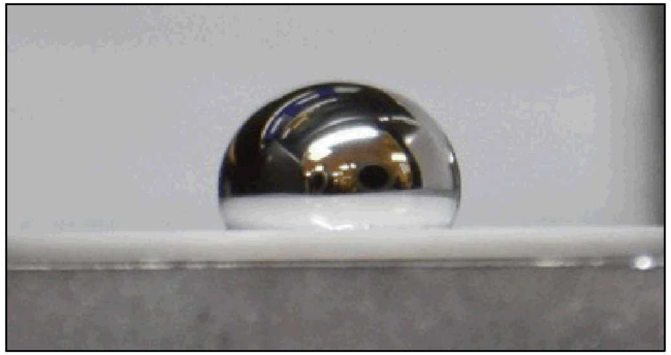
- Safety: Violent, toxic reactions between molten Na and molten S – cascading runaway!
- Corrosive, toxic chemistries

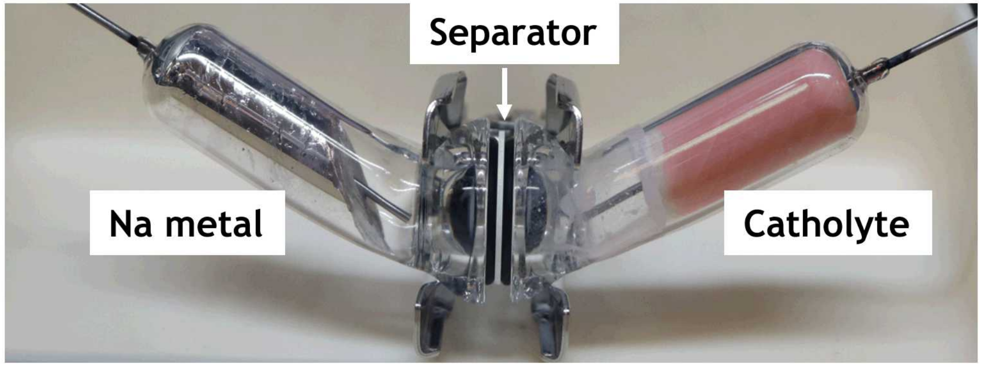
New Low Temperature Salt Composition

Challenge: How can the operating temperature be lowered towards the melting point of sodium metal (97.8 °C)?

Identifying and using new lower melting point catholytes.

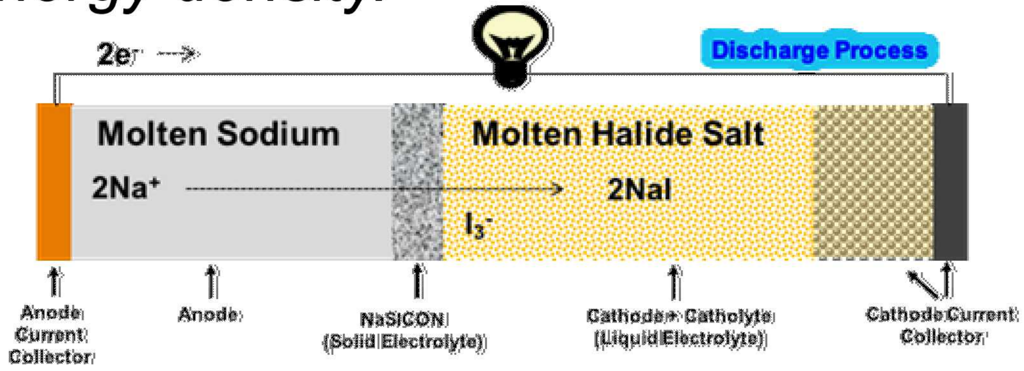
New catholyte consists of completely inorganic molten salt composed of NaI and AlX_3 (X = Cl or Br)





Low Temperature Molten Na-Halide Batteries

Na-NaI batteries show promise as safe, low-cost, highly cyclable battery with functional energy density.



- Newly developed salts utilize NaI as the reactant in the catholyte
  - Aluminum halides (AlX_3) are the secondary component

High operational voltage

Reversible battery reactions:

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

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

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

What is important for catholyte?

- Inherent Safety
- Low to Intermediate Temperature Operation
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Failure event results in reactants mixing to produce aluminum metal and table salt!

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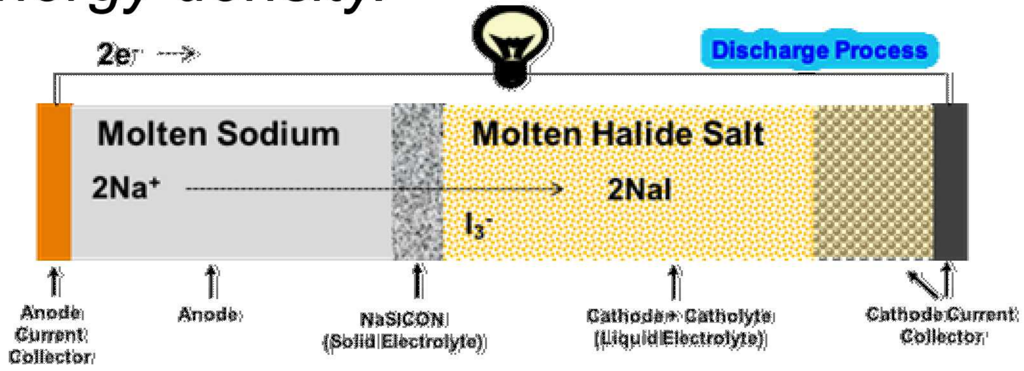

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High predicted voltage window of >3 V

High energy density with I^- solubility ~11 M

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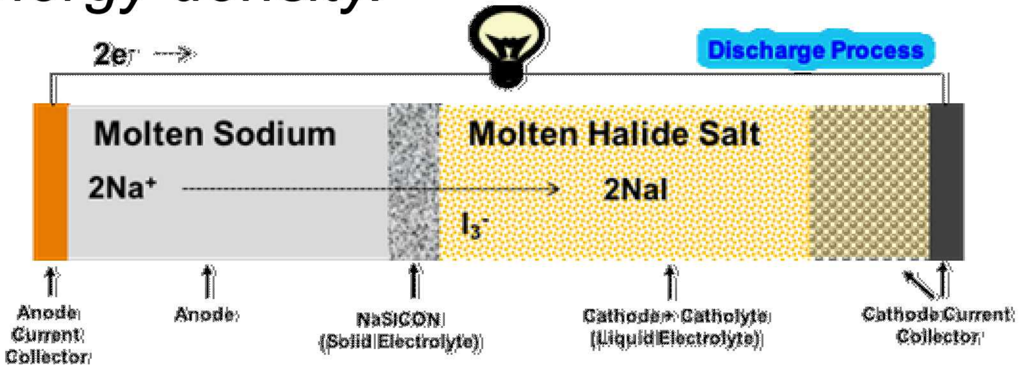

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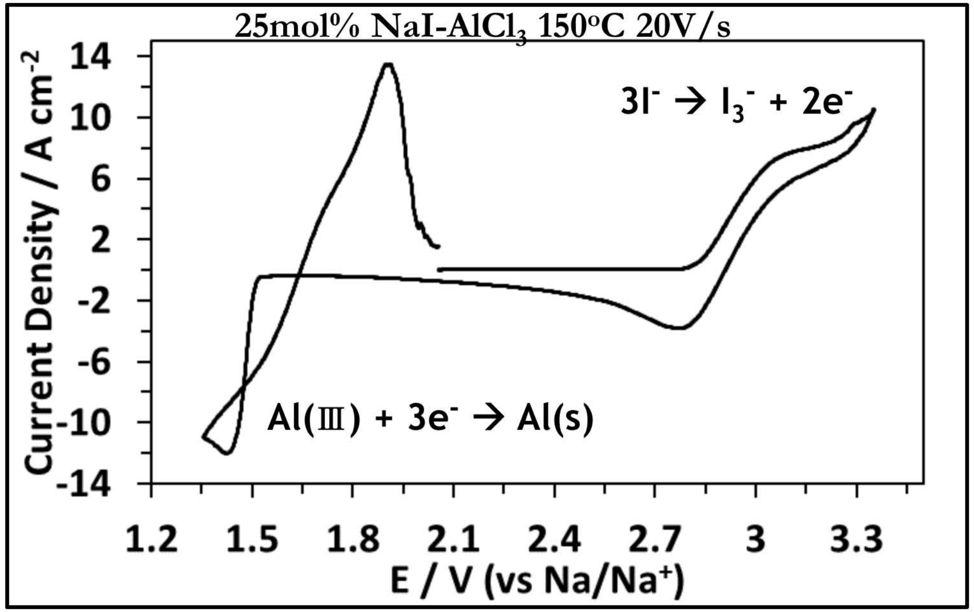


Scaled Performance of a Functional Na-Halide Battery

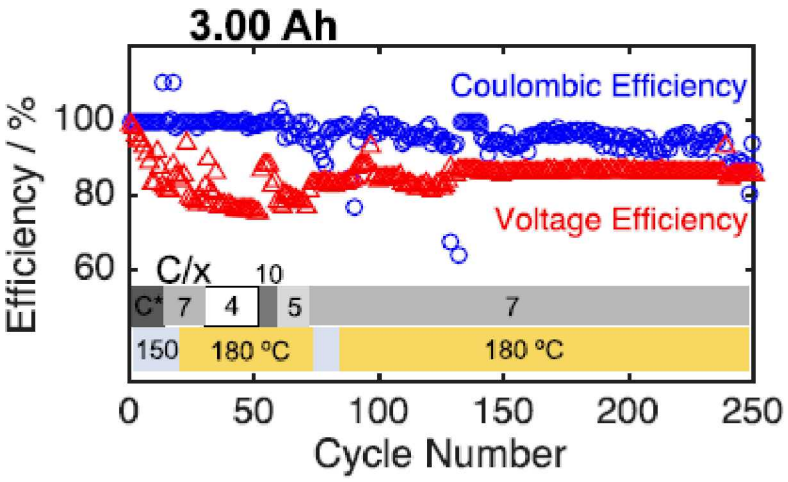
- First batteries utilizing the NaI-$AlCl_3$ catholyte were **loaded with excess NaI** in an effort to maximize capacity
  - Done by a collaborating company – Ceramatec Inc.

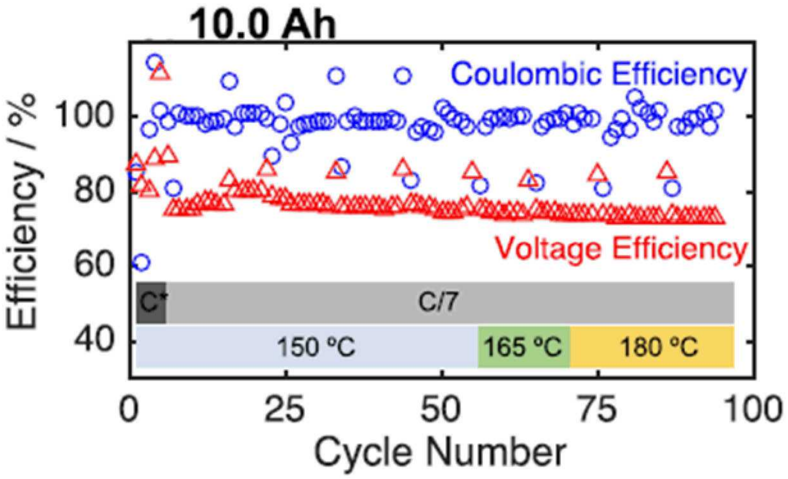
- Electrochemical behavior of catholyte not thoroughly investigated and understood

- Larger batteries needed a “reconditioning” step every 11 cycles (at a very slow rate!)

- Could the materials chemistry of the catholyte be affecting the performance?

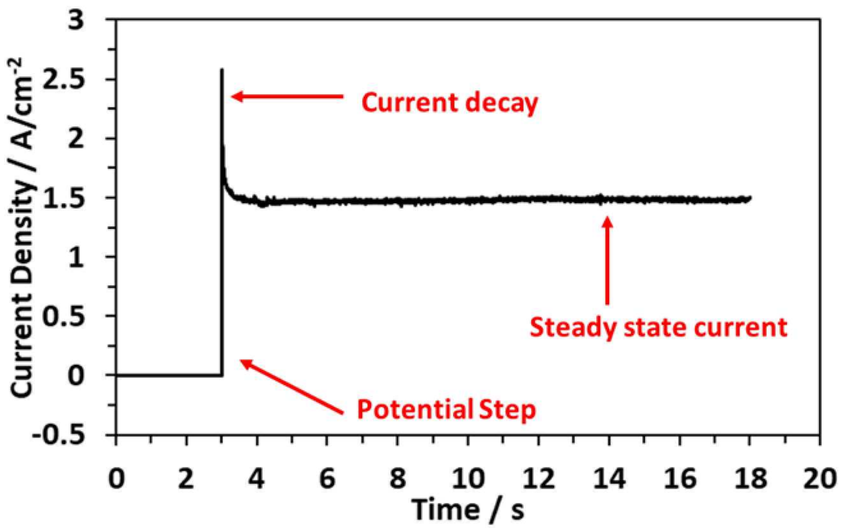
Utilized macro and ultra micro electrodes (UMEs) to investigate electrochemical behaviors and key aspects of molten salt catholytes

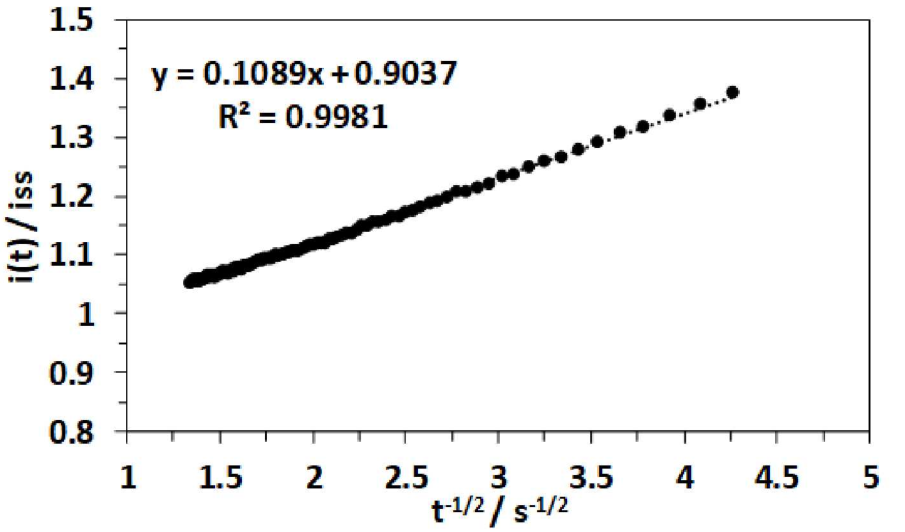




Small, L. J.; et al. *J. Power Sources* **2017,** *360* (31), 6.

Chronoamperometric Analysis





- Determined operationally important parameters of diffusion coefficients and current densities of reactant (I^-) in different molten salt compositions
- Dramatic change in diffusion coefficients can identify if there is a substantial change in viscosity with changing composition
- Chronoamperometric analysis of salts according to previously published procedure by Allen Bard
    - Rate of decay of the transient current trace plotted vs $t^{-1/2}$

$$D = \frac{\pi a^2}{16 S^2}$$

D = diffusion coefficient
a = radius of the electrode
S = slope of the line

Denuault, G.; Mirkin, M. V.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *308*, 27-38

Percival, S. J.; Small, L. J.; Spoerke, E. D. *J. Electrochem. Soc.* **2018**, *165*, A3531-A3536

NaI-$AlCl_3$ Current Densities and Diffusion Coefficients

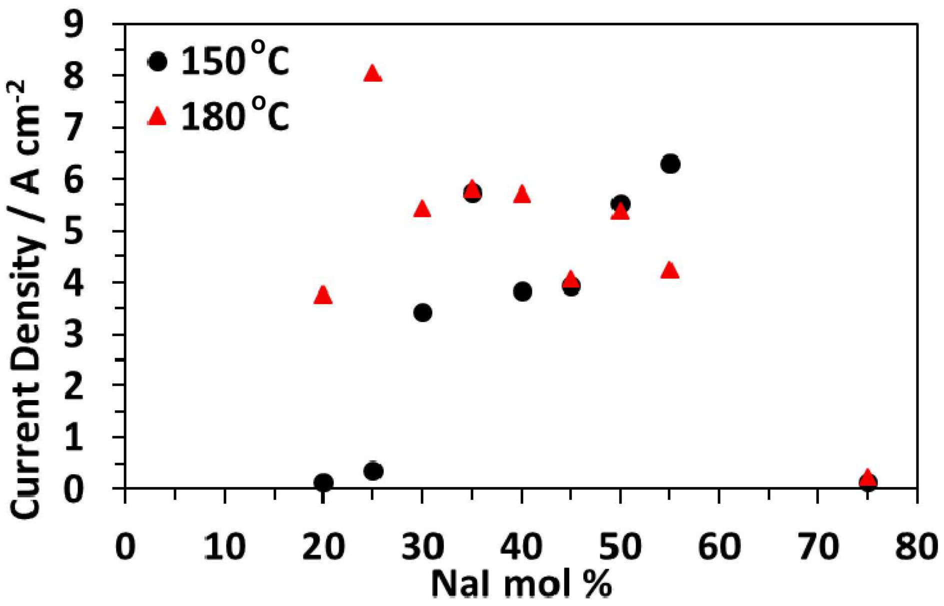
- Diffusion coefficients determined from CA traces.
- Diffusion coefficient shows a peak at 35 mol% NaI and is generally high where the fully molten range lies.
- Diffusion coefficients inform relative charge/discharge rates as composition changes – necessary to avoid unwanted secondary reactions from occurring

Composition / mol% NaI	Diff. Coef. @ 150 °C / 10^{-6} $cm^2\,s^{-1}$	Diff. Coef. @ 180 °C / 10^{-6} $cm^2\,s^{-1}$
20	N/A	2.2
25	1.4	5.1
30	3.2	3.8
35	5.2	7.2
40	5.7	6.2
45	3.5	5.2
50	1.9	2.9
55	1.6	2.1
75	2.9	5.3

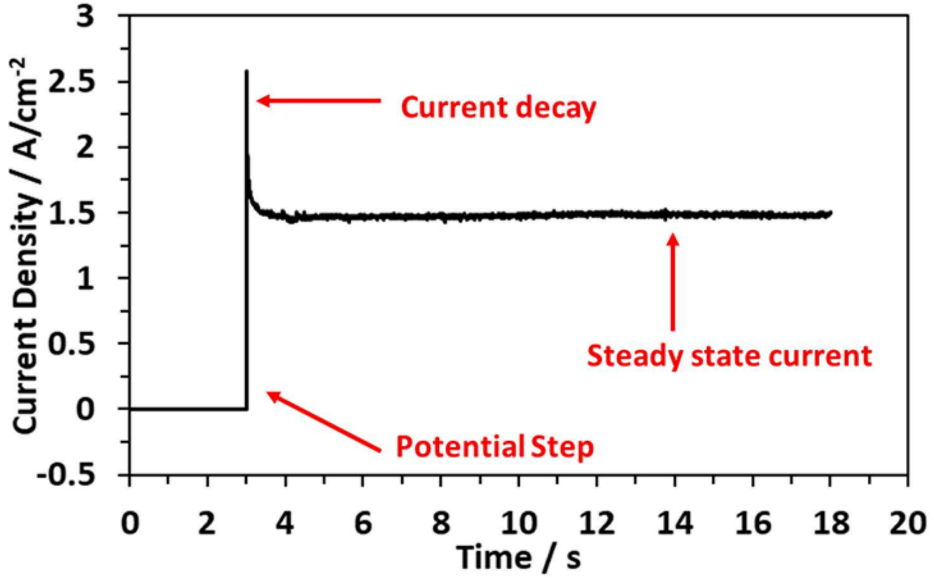
Current Densities

Essential for battery operation that achieves high energy efficiency.

Current density much higher than needed for battery operation at most compositions.



Determined from steady state current from amperometric trace



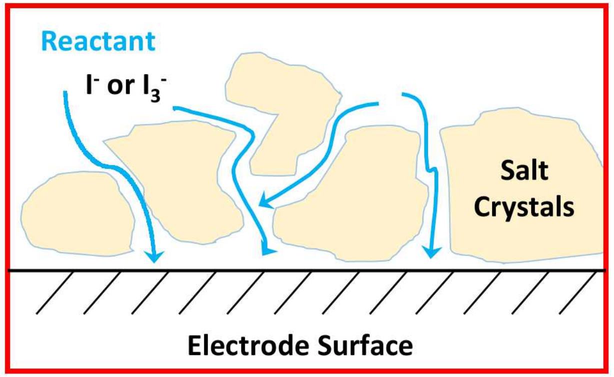
Small current densities observed for some compositions

Catholytes are Key to Low Temperature Operation

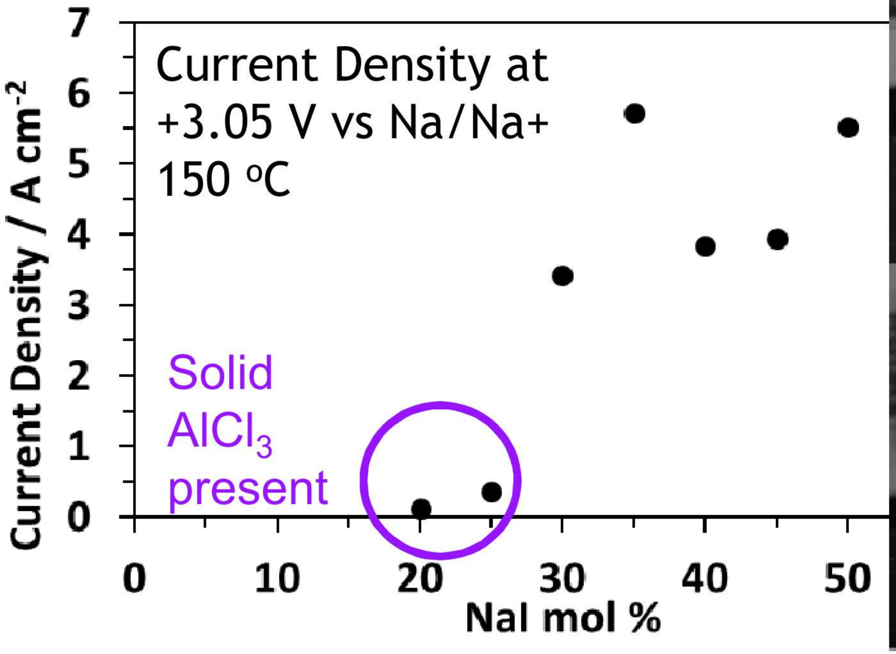
A fully molten catholyte avoids

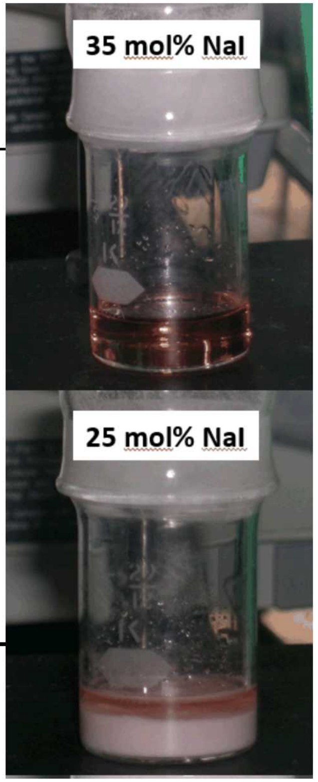
a) Particle-hindered electrochemical processes

b) Particle-related loss of capacity



Particle precipitation at the electrode can easily block the surface

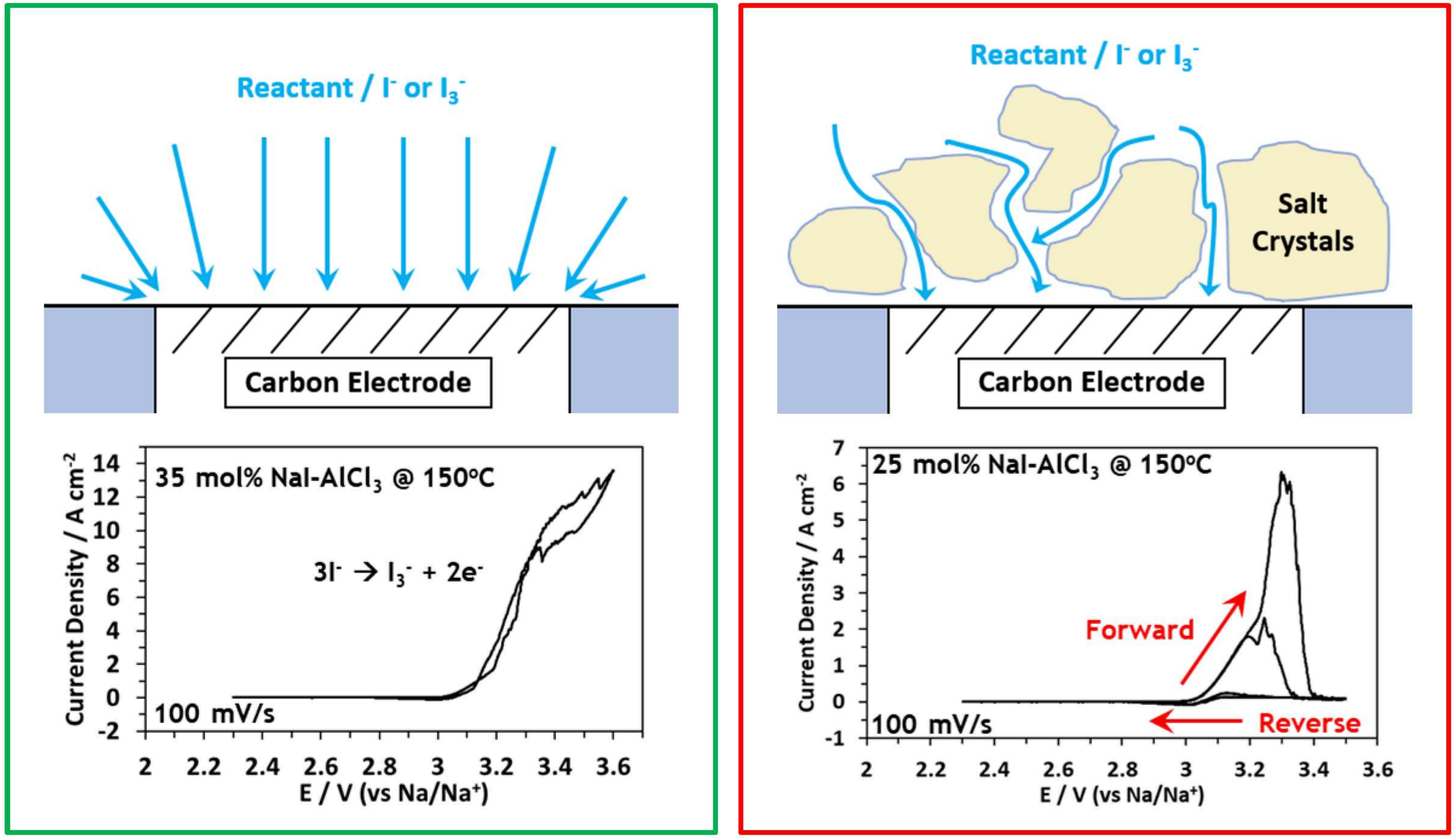




Current Density is significantly lower when solid secondary phases are present.

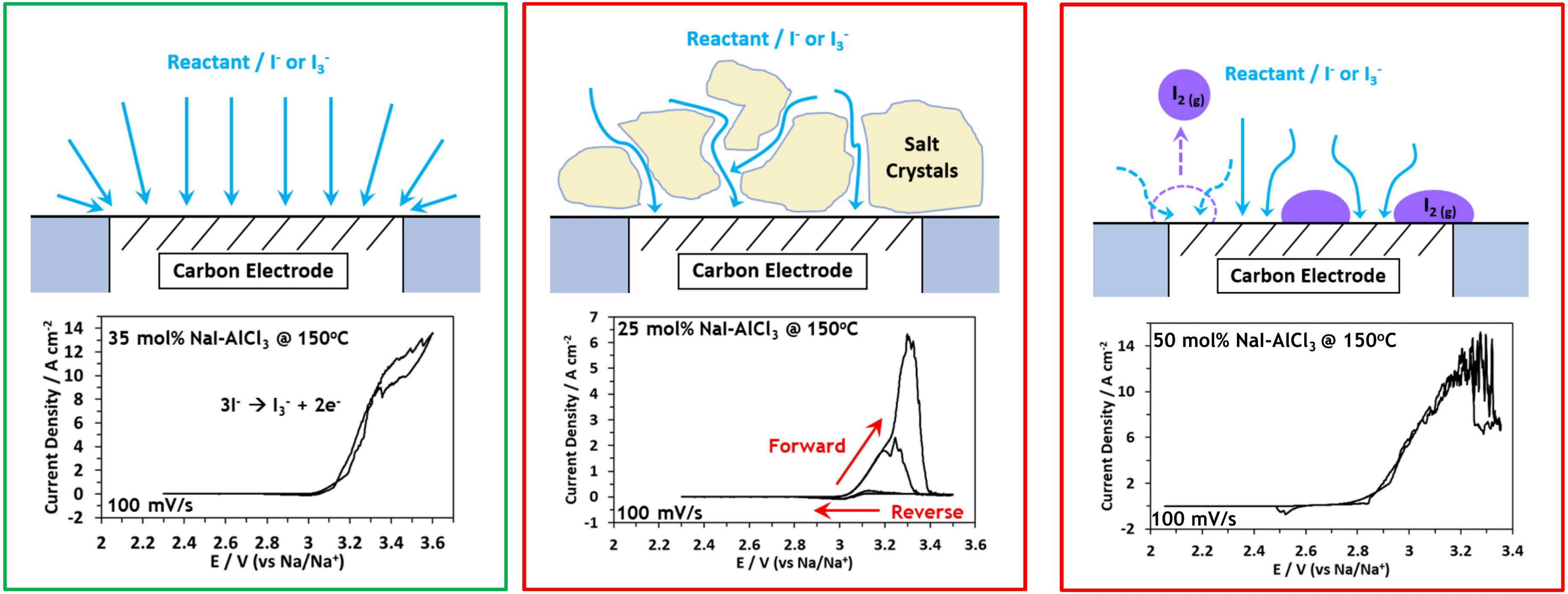
Percival, Small, and Spoerke. *J. Electrochem. Soc.*, **165** (14) A3531-A3536 (2018)

Understanding Catholyte Behavior is Essential



- **Ideal Case:** Electrode surface is free from any impeding solid phases and displays expected electrochemical behavior
- **Hindered by Other Phases:** Presence of solid of gas phases in the melt can hinder free diffusion. This will affect battery performance and efficiencies

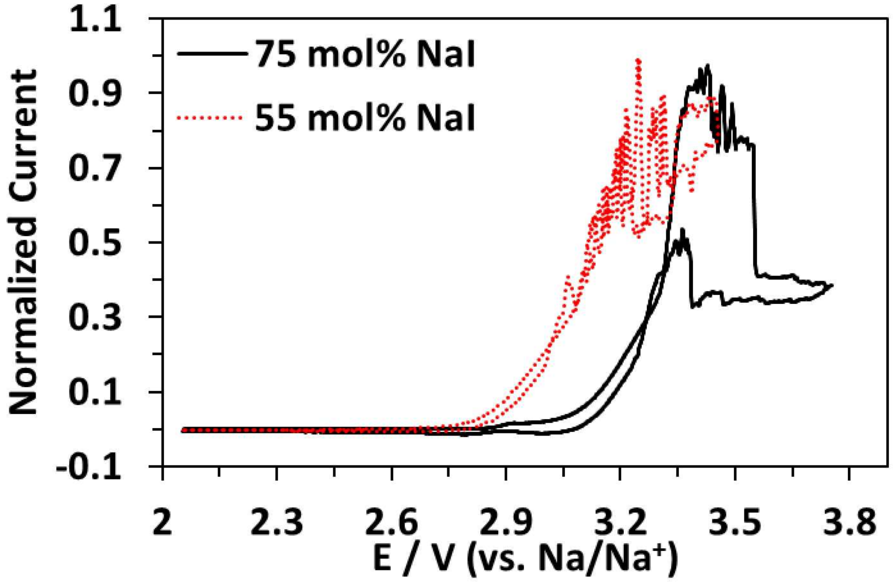
Gas Generation



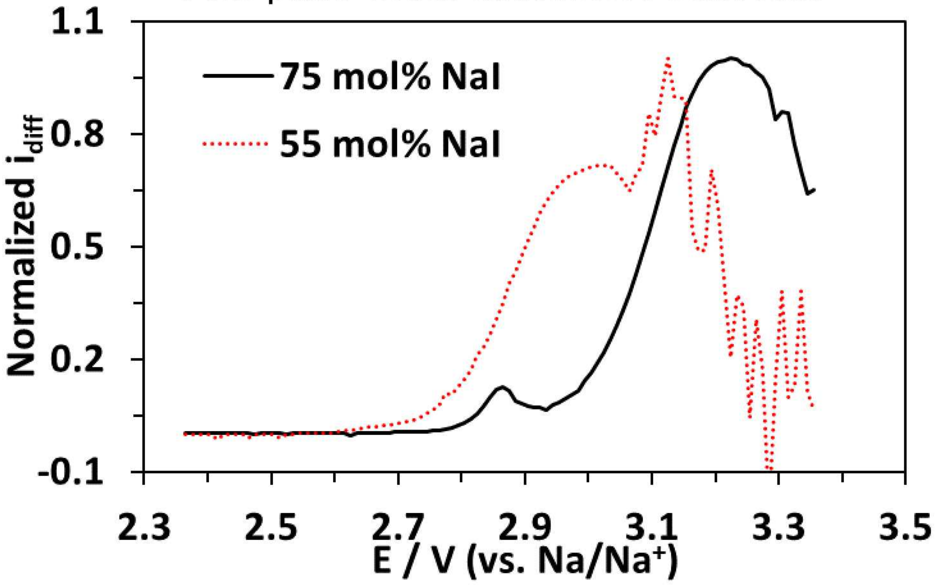
- **Gas (or immiscible liquid) Phases:** Presence of other phases in the melt can also hinder free diffusion.
- High current densities will drive unwanted battery behavior creating unstable battery performance and reducing energy efficiency

Very High NaI Compositions

180 °C 100 mV/s



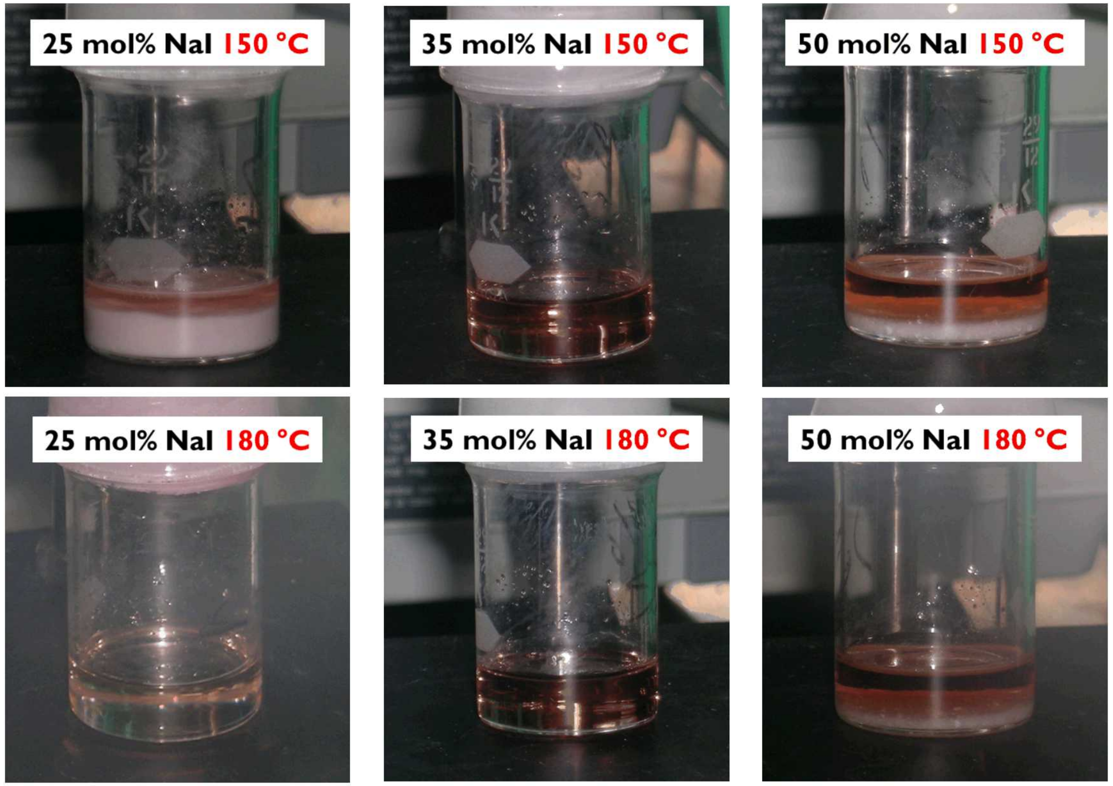
180 °C pulse amplitude 50mV with
5 ms pulse width and10mV/s scan rate



Differential Pulse voltammetry used to determine reaction potentials

- At high very NaI compositions there is an unexpected shift in the I-V curve
- Small oxidation wave seen at 75 mol% NaI where the expected I- oxidation should be
- Much larger wave seen at higher potentials – possibly due to formation of polyiodides

Fully Molten Compositions Identified



- Compositions identified (around 35 mol% NaI-$AlCl_3$) that are fully molten at the lower 150 °C temperature.
- Multiple phases observed in some compositions (25 mol% NaI-$AlCl_3$) which can fully melt with increased temperature.
- **Problem: upon cycling, precipitates would still form at 150 °C.**

New Low Temperature Salt Composition

- How can the operating temperature be lowered towards the melting point of sodium metal (97.8 °C) while avoiding phase separations?

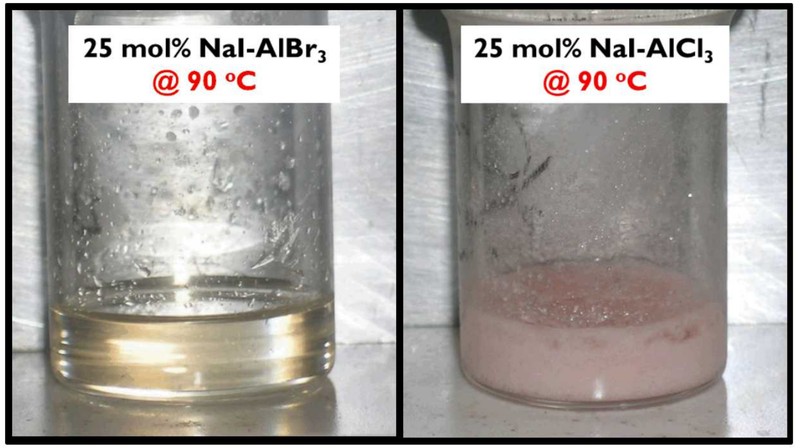
- **$NaI\text{-}AlBr_3$ compositions identified that are fully molten at 90 °C (below the melting point of sodium)!**

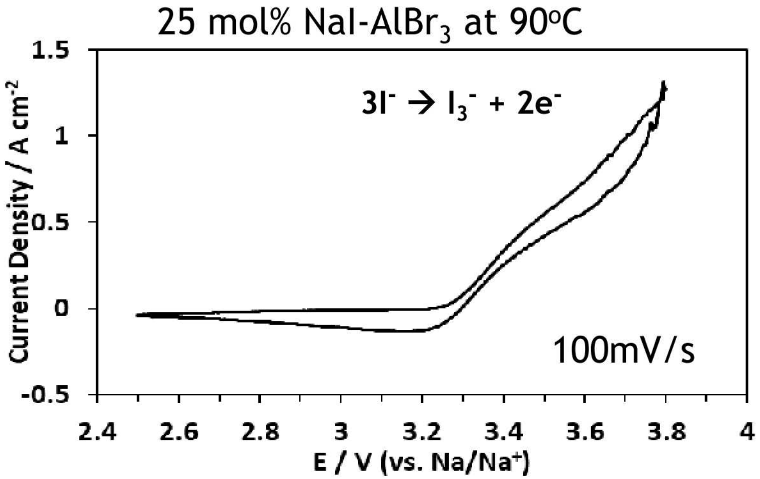
- New $NaI\text{-}AlBr_3$ chemistry allows a fully inorganic molten salt catholyte at much lower temperatures than previously demonstrated

- $AlCl_3$ compositions still frozen or have large amounts of solids at 90 °C

NaI-AlBr$_3$ Electrochemical Behavior

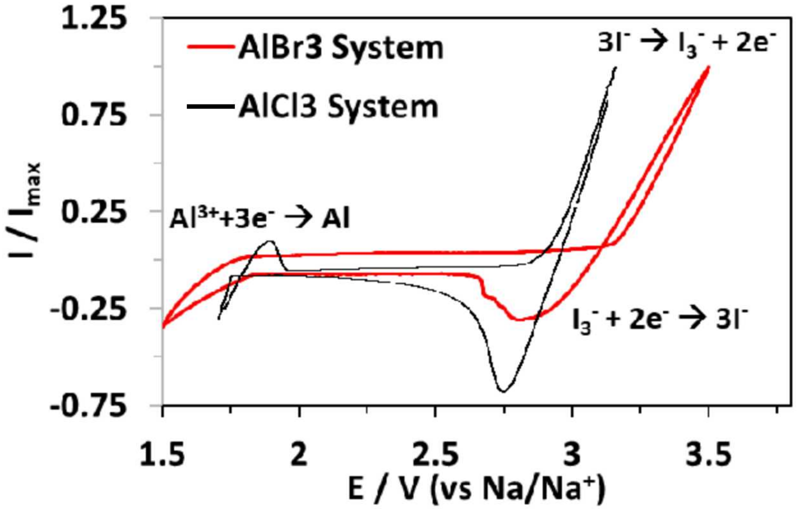
- 25:75 NaI-AlBr$_3$ salt completely molten at 90 °C
- Larger fully molten capacity range (~5-25 mol% NaI)





The NaI-AlBr$_3$ catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures (90°C).

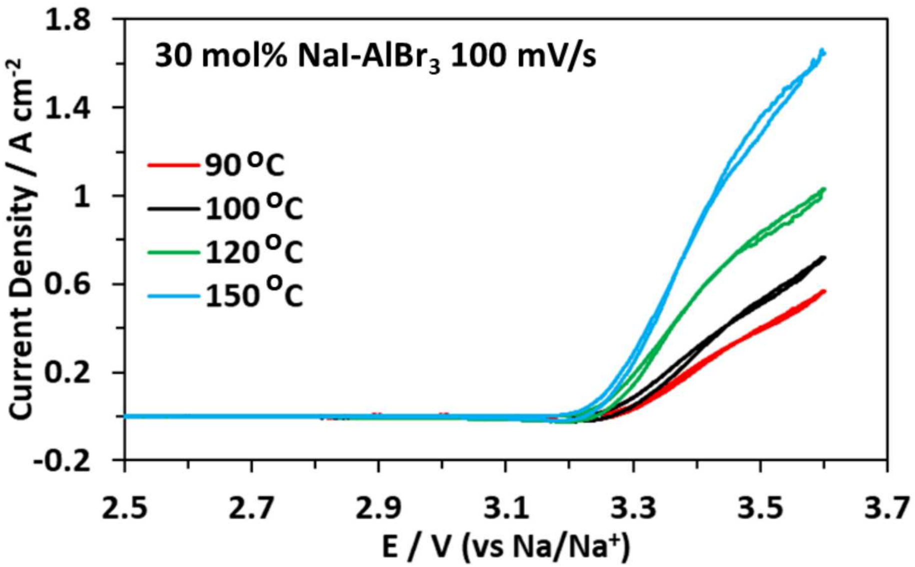
- Evaluation of new AlBr$_3$ catholyte at higher temperatures show similar electrochemical behavior compared to AlCl$_3$ catholyte
  - Voltage window >1V
  - Electrochemically reversible – necessary for battery operation
  - Increased oxidation potential for the AlBr$_3$ system compared to AlCl$_3$ may deliver higher energy density

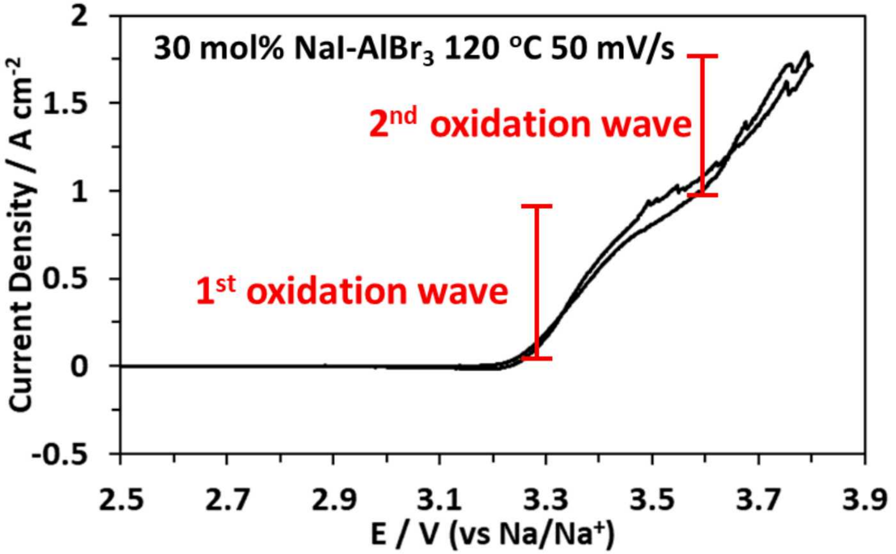


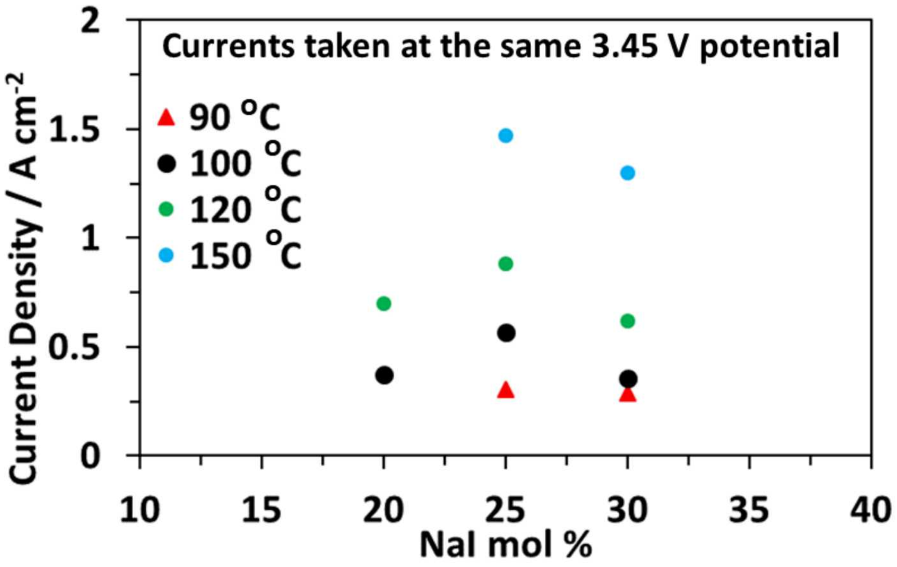
AlCl$_3$ (40mol%NaI) system at 125 °C and 100 mV/s
AlBr$_3$ (20mol% NaI) system at 120 °C and 1V/s

NaI-AlBr$_3$ Current Densities and Diffusion Coefficients

- NaI-AlBr$_3$ current response shows the standard 2:1 ratio for the I^- and I_3^- oxidation waves
- Current density of AlBr$_3$ salt increases with increasing temperature
- Even at 90 °C the current density is still higher than would be required to cycle a battery

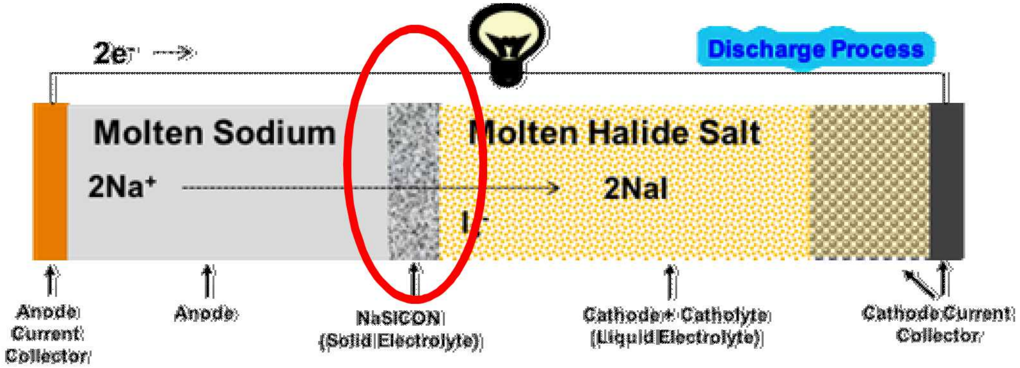






Low Temperature Molten Na-NaI Batteries

Fully Assembled Molten Sodium-based Battery Comprises: A robust, **highly Na^+-conductive, zero-crossover separator** and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.



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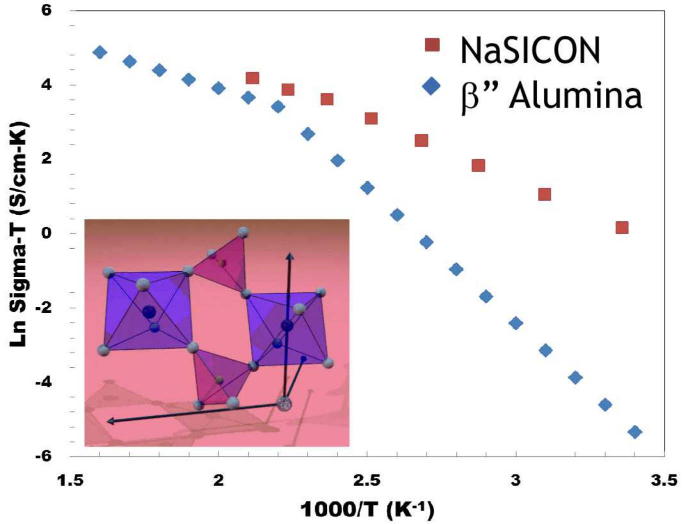
Cell: $2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^o_{cell} = 3.24V$

Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ – we synthesize $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity (>10^{-3} S/cm at 25^oC)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover

- **Invented by John Goodenough (2019 NOBEL prize in Chemistry winner)**



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

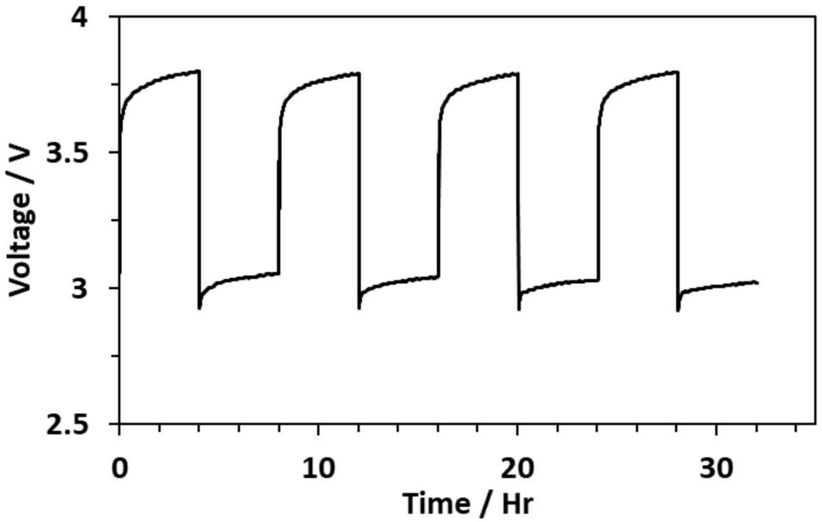
Low Temperature Molten Na-NaI Batteries

- Lab scale battery made using NaI-$AlBr_3$ catholyte successfully cycled at 100 °C
  - Used 25 mol% NaI-AlBr3
  - Open Circuit Potential = 3.29 V

- High Coulombic efficiencies

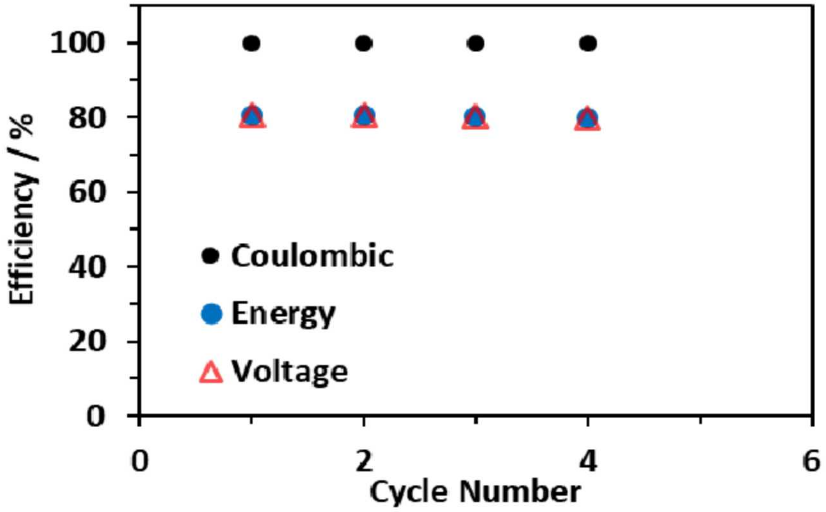
- Promising voltage and energy efficiencies at 110 °C

Glass cell used loaded with 25 mol% NaI-$AlBr_3$ catholyte

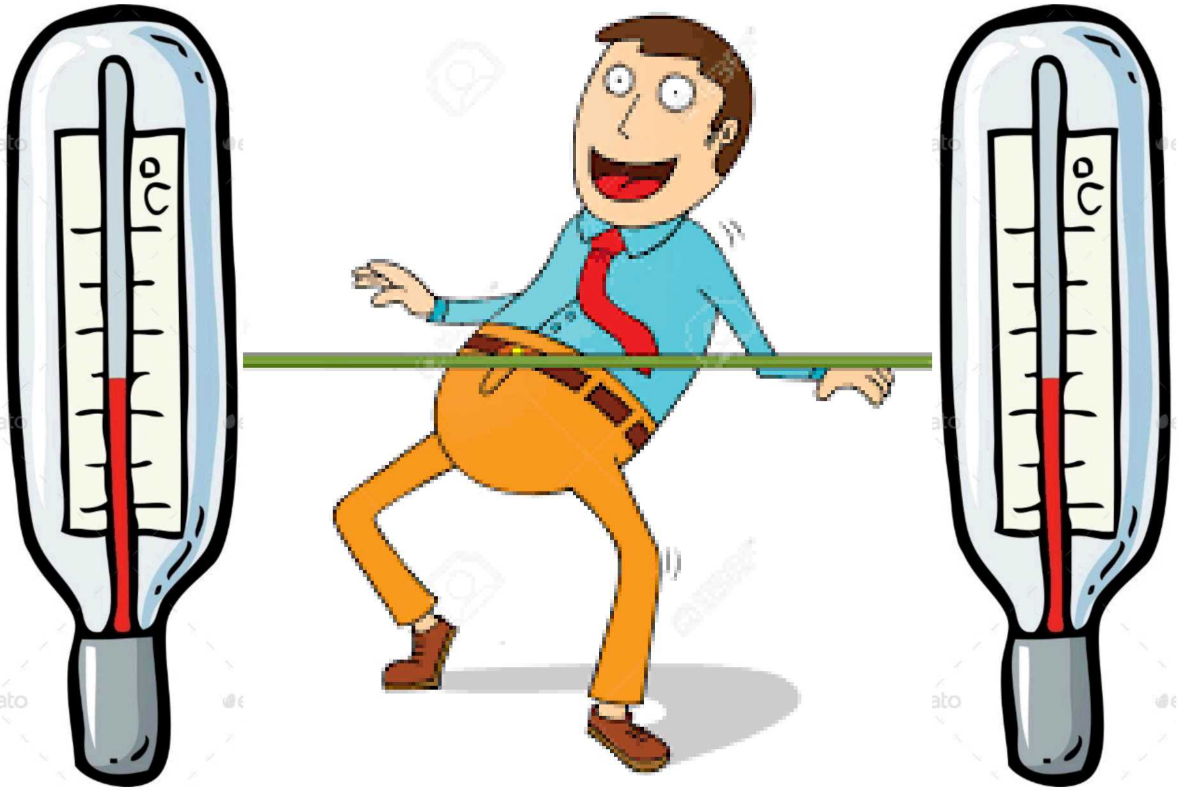


Battery cycling at 110°C!

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



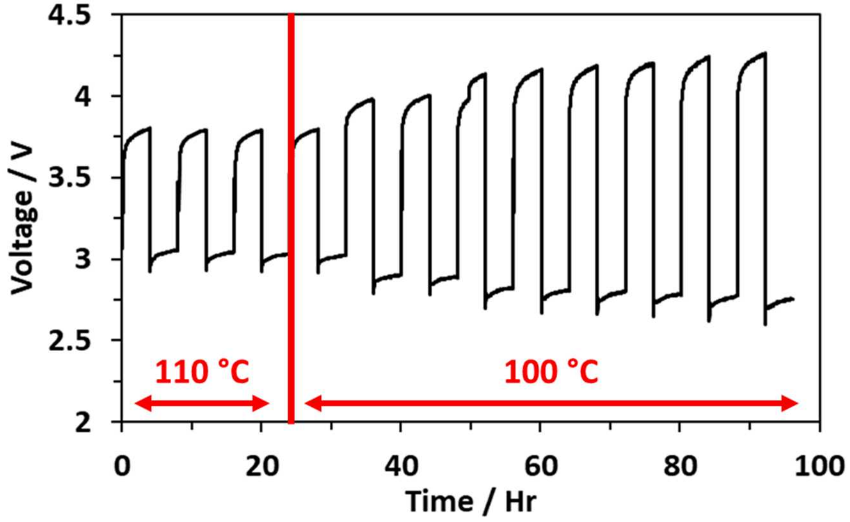
How low can we go?



Low*est* Temperature Molten Na-NaI Batteries

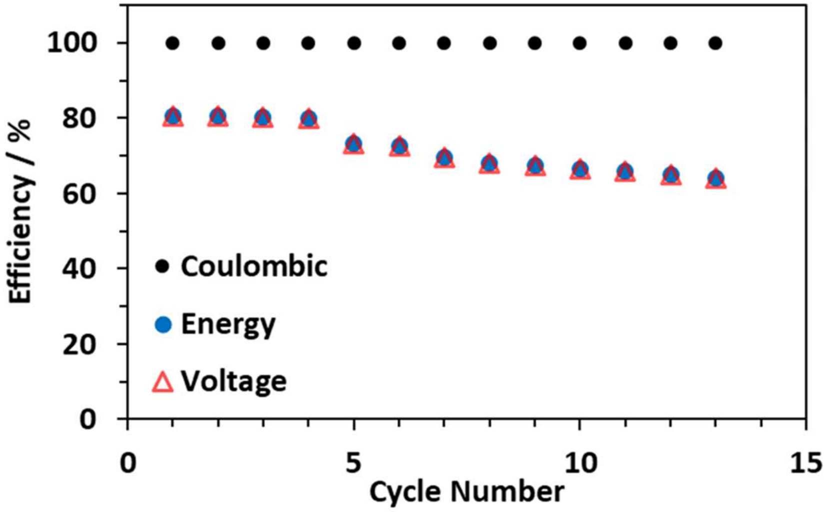
- Lab scale battery made using NaI-$AlBr_3$ catholyte successfully cycled at 100 °C
  - Used 25 mol% NaI-AlBr3
  - Open Circuit Potential = 3.29 V
- High Coulombic efficiencies for all temperature ranges
- Promising voltage and energy efficiencies at 110 °C, began decreasing near the melting point of sodium
  - Internal resistance increased upon lowering the temperature to 100 °C

Glass cell used loaded with 25 mol% NaI-$AlBr_3$ catholyte



Battery cycling at **100°C**!

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

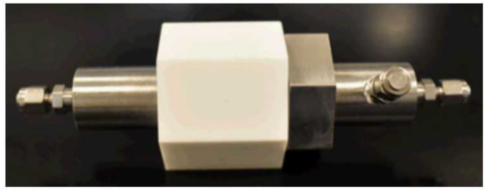


Cell Re-Engineering for Ideal Na-Battery Test Platform

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.

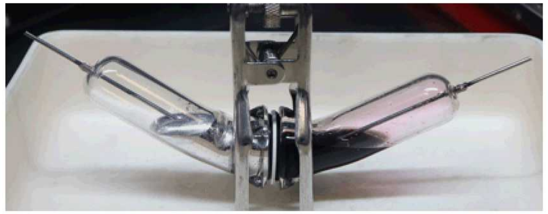


Many new cell designs and geometries built and tested (7 different types!)

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

New Cell Designs

Enable easy assembly, high throughput and functional geometry



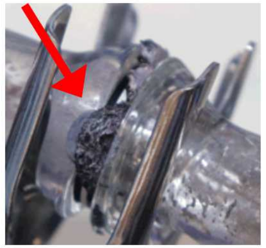
Includes 3 designs that are fully interchangeable and reusable

Importance of Seals

Testing failures in many prototypes was due to compromised seals.

Sodium Compatible Seal Material

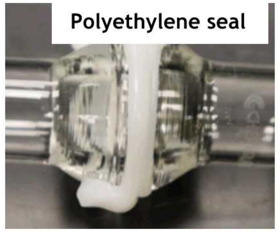
Sodium reacting with the Kalrez o-ring



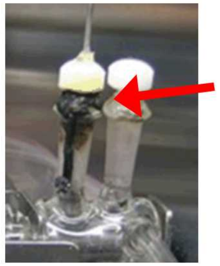
Polyethylene seals from molten polyethylene to seal the sodium side

Not re-useable and hard to apply properly

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

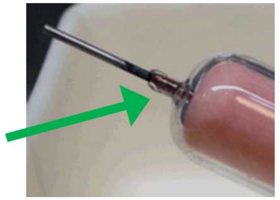


Molten Salt Compatible Seal Material



Vapors from molten salt aggressively attacking the epoxy seals

Glass to metal seals eliminate unwanted side reactions from salt vapors



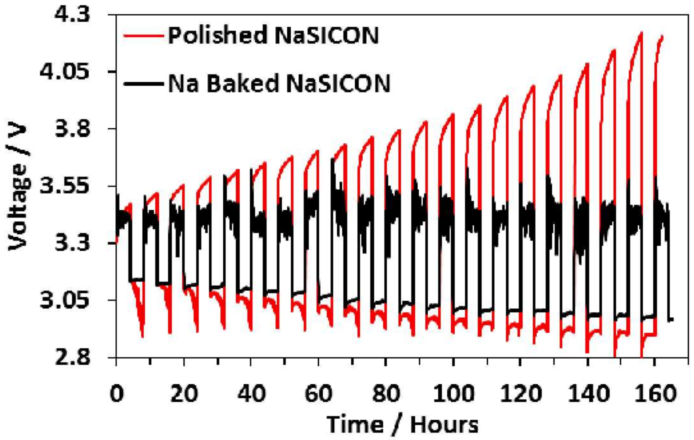
Separator Treatment Affects Cell Performance

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

Heated below 200°C for 30 minutes

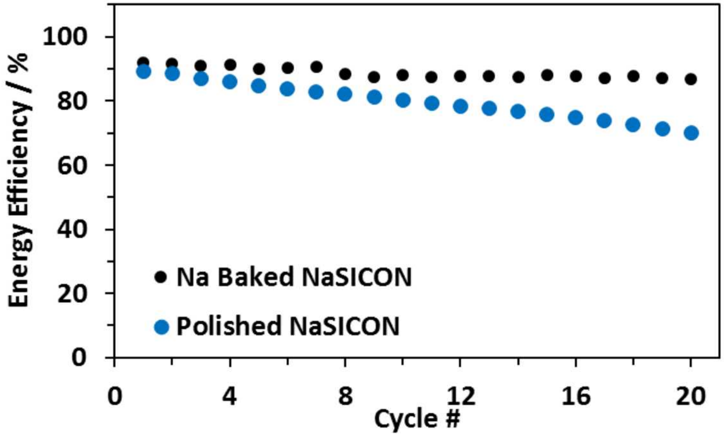
Heated above 380°C for 30 minutes

Na-treated NaSICON shows lower overpotentials on battery cycling.



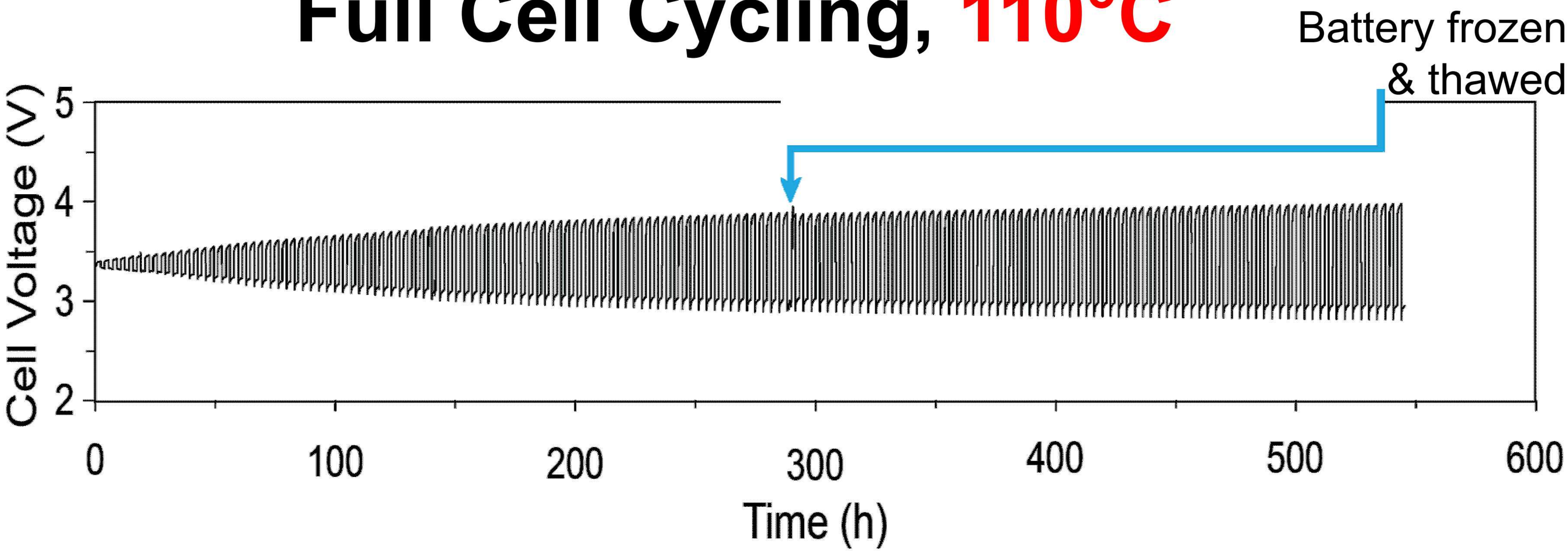
Battery cycling at 110°C!

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



- Polished NaSICON battery operated at ±0.897 mA C/4 1% DOD
- Na Baked NaSICON battery operated at ±0.894 mA C/4 1% DOD

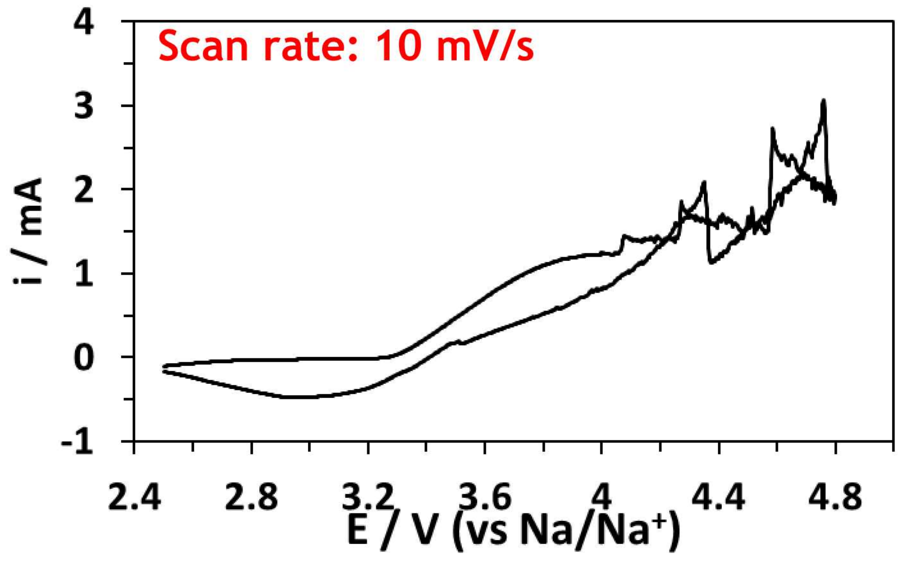
Full Cell Cycling, 110°C



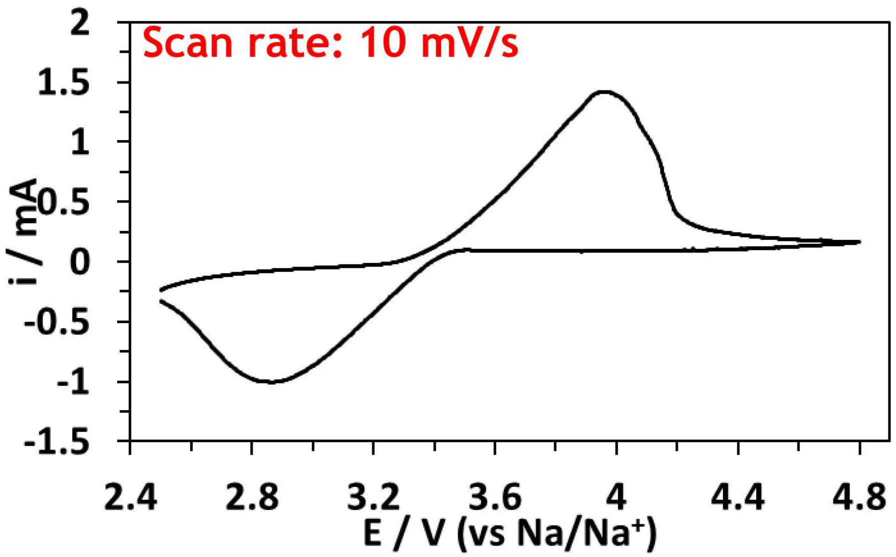
- Integration of **NEW CATHOLYTE** and optimized NaSICON interface enables long-term battery cycling at low temperatures: **Battery achieved 200 cycles!**
- Even after freeze/thaw, interfaces remain intact with uninterrupted cycling!

Electrode Material Affects Electrochemistry

1.5mm tungsten 110 °C 25mol% NaI-AlBr3



3mm graphite 110 °C 25mol% NaI-AlBr3



- Carbon seems to display slower kinetics for a secondary reaction compared to tungsten (such as AlBr3 oxidation or I_3^- oxidation forming I_2 that is strongly adsorbed)
- **Slows I^- oxidation and lowers current drastically**
- **Points to reason batteries suffer from high overpotentials which eventually make them fail**

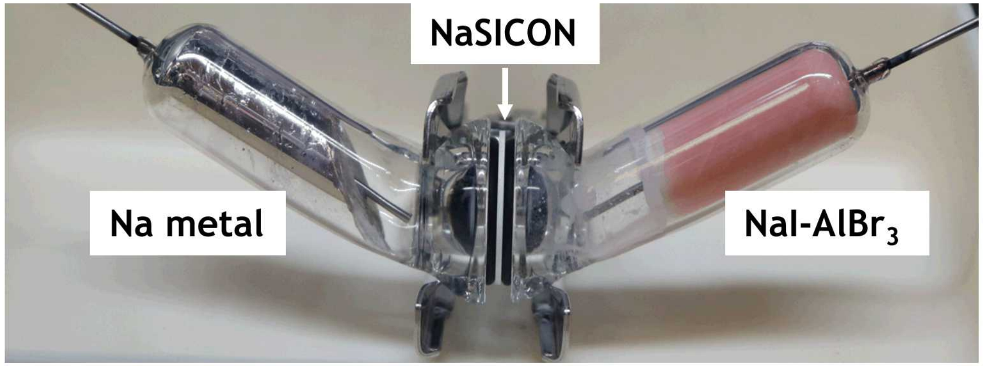
Take Away Messages

- Na Batteries are significantly under-represented in grid-scale electrical energy storage.
- Low temperature molten sodium batteries offer promise for safe, cost effective, long-life grid scale energy storage.
- Molten salt catholyte evaluated for electrochemical behavior due to presence of different phases.
- Compositions at very high or low NaI concentrations shown to be detrimental to ideal electrochemistry and battery cycling.
- Developed new low temperature fully molten NaI-$AlBr_3$ salt catholyte which shows promising physical and electrochemical behavior.
- **First ever demonstration of completely inorganic molten Na-Halide battery operating near melting point of sodium!**

Continued Catholyte development and electrochemical evaluation will be key to developing a new generation of molten-sodium batteries* offering efficient, long lifetimes for grid scale energy storage*!

Acknowledgements

- Collaborators:
  - Dr. Erik Spoerke
  - Dr. Leo Small
  - Dr. Martha Gross
  - Amanda Peretti



- Funding:
  - Work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity Delivery and Energy Reliability (DOE-OE).

Sandia National Laboratories

OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

Acknowledgements

Thank you for your attention!

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

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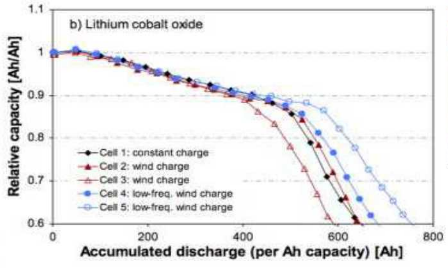
Supporting Information

Challenges with Some Existing Batteries

Li-ion (E_{cell} ~ 3.6V)

$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$

- Safety (flammable organic electrolytes
- Cycle lifetime limited
- Cost

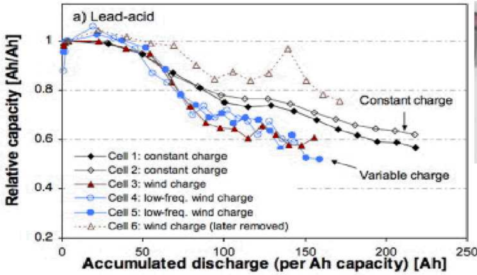


E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

Pb-Acid (E_{cell} ~ 2.1V)

$Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$

- Capacity fades quickly (typically 200-300 cycles)
- Temperature-sensitive



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

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

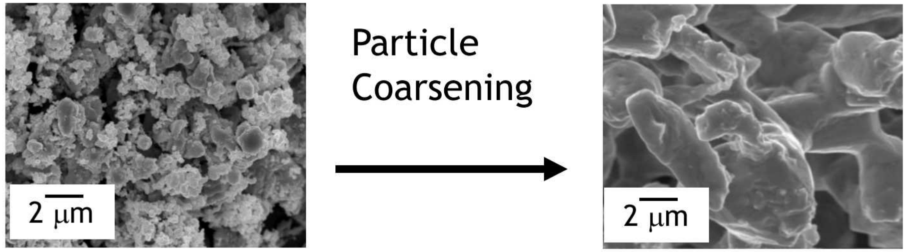
$2Na + 4S \leftrightarrow Na_2S_4$

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

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

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

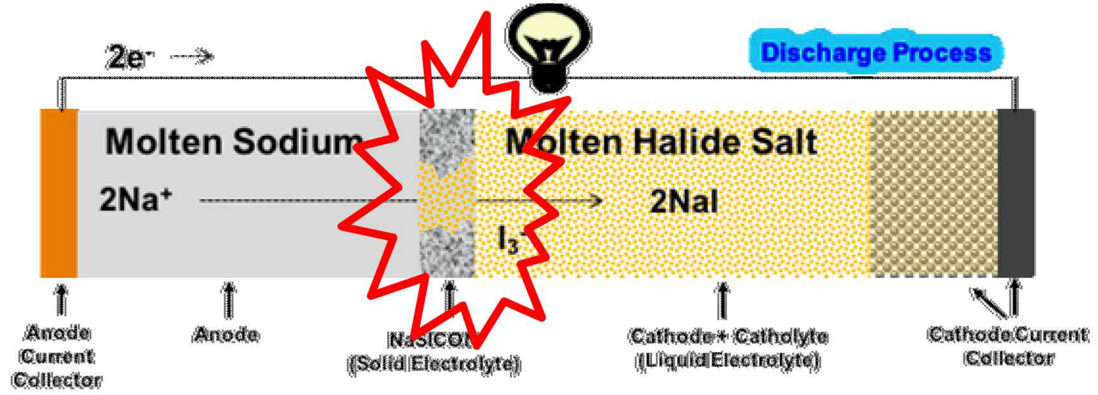
- Cycle lifetime (solid cathode phase)
- Cost (related to cycle lifetime and material costs)
- High temperature operation (typically > 200^{o}C)

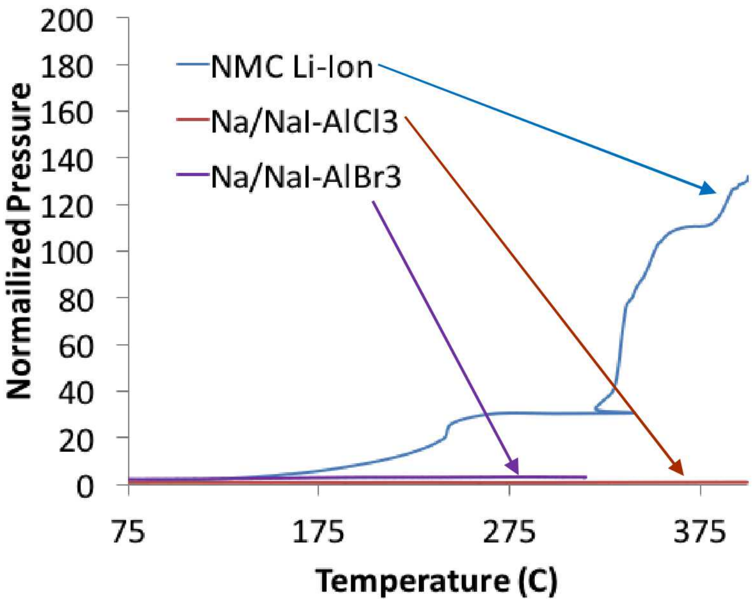


Na-NaI Exhibits Inherent Improved Safety

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

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





Dr. Joshua Lamb (SNL) – Gas evolution tests

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

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

Li ion (NMC) undergoes a very exothermic decomposition generating copious amounts of gas, heat and pressure

Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

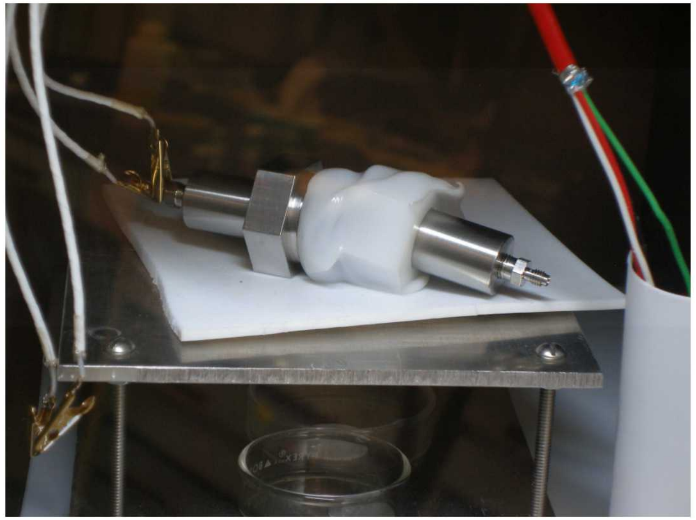
Compatibility must be considered for:

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

Magnesium metal and Teflon (PTFE) are elements of decoy flares…Sodium has a similar reactivity.

Molten sodium and fluoropolymers should not be considered stable, especially for long-term use.

Thermal and mechanical stability



Chemical compatibility

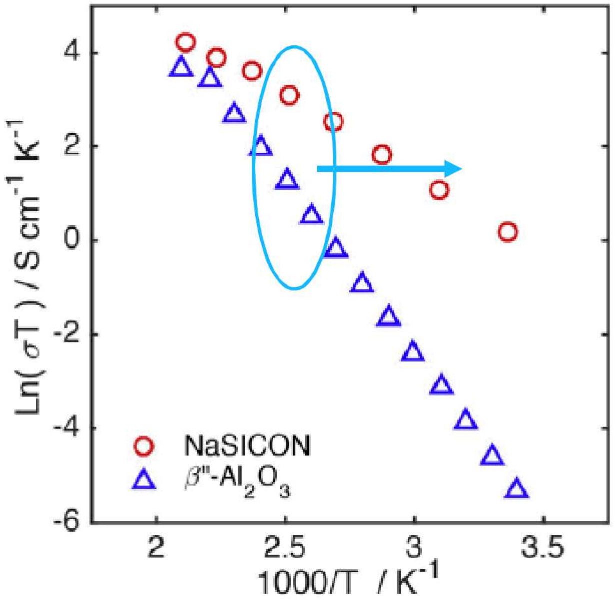
NaSICON Solid State Electrolyte

NaSICON (Na Super Ion CONductor): $Na_3Zr_2PSi_2O_{12}$ ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$)

Key Separator Properties:

- Selective, high ionic conductivity at reduced temperature (<150^oC)
  - (>10^{-3} S/cm at 25^oC)
- Chemical compatibility (molten Na, molten halide salts, strong base)
- Mechanical robustness
- Low cost, scalable production

- **Sodium ion conductor needs to have zero crossover and <u>high conductivity</u>**
  - 2 main types: Beta Alumina (β"- Al_2O_3) or NaSICON
- Conductivity of NaSICON much higher
  - NaSICON conductivity > 10^{-3} S/cm at 25^oC



Small, L. J.; et al. *J. Power Sources* **2017,** *360* (31), 6.

Based on its high Na-ionic conductivity and established chemical compatibility, NaSICON ceramics are good candidates for low temperature battery development.

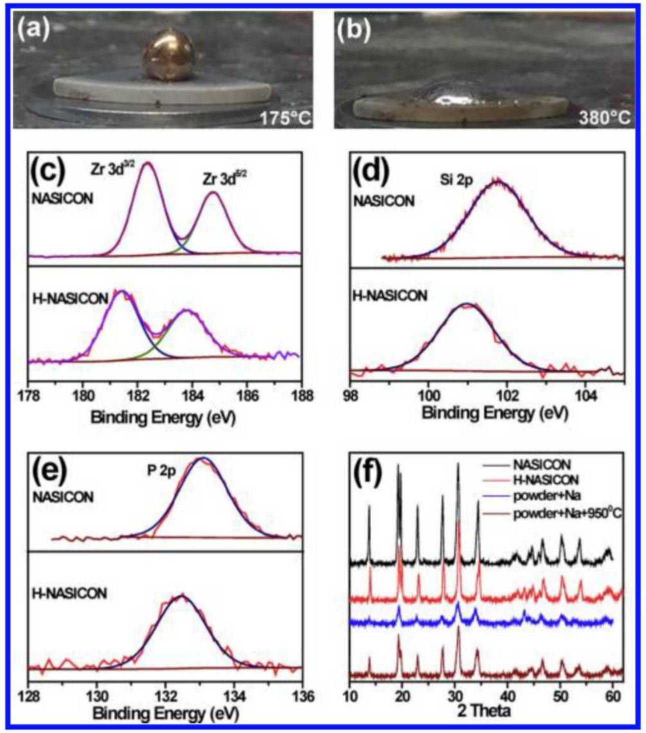
Separator Treatment Affects Cell Performance

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

Heated below 200°C for 30 minutes

Heated above 380°C for 30 minutes

Based on treatments applied to NaSICON in a solid-state system, the change in pellet surface is believed due to formation of an amorphous, reduced NaSICON surface.

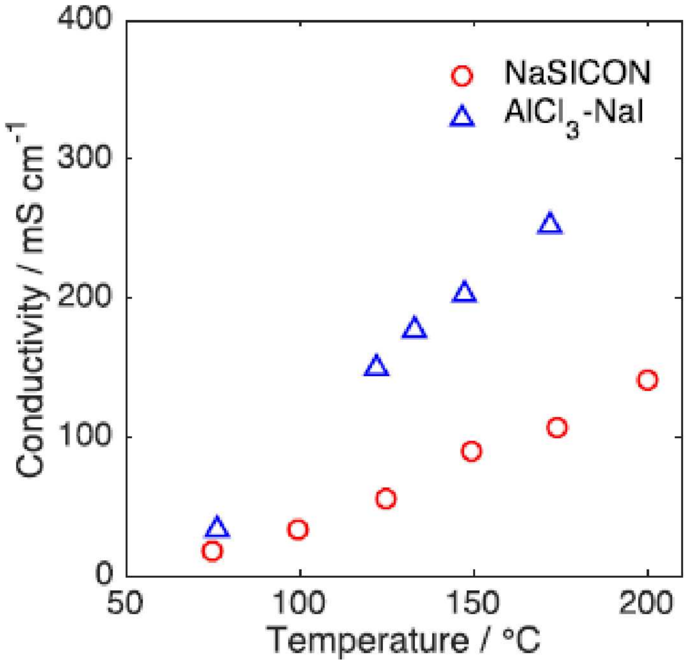


W. Zhou, *et al*. *ACS Cent. Sci*. (2017) **3**, 52-57.

Molten Salt Conductivity

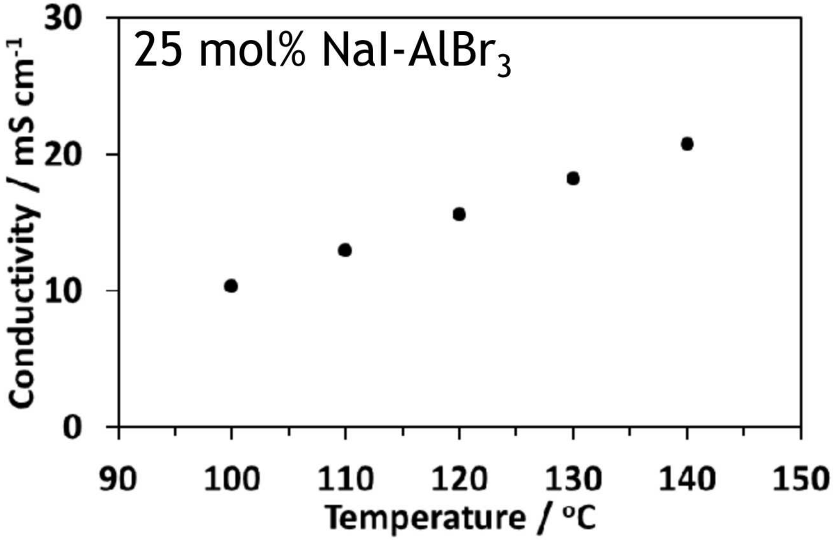
- Molten salt conductivity much higher than that of NaSICON at elevated temperatures
  - Salt composition was 60 mol% NaI-$AlCl_3$

- Molten salt catholytes will not be the limiting factor in cycling rate



50 mol% NaI-$AlCl_3$

Small, L. J.; et al. *J. Power Sources* **2017,** *360* (31), 6.



- Conductivity of 25 mol% NaI-AlBr3 still above NaSICON conductivity at the same temperature

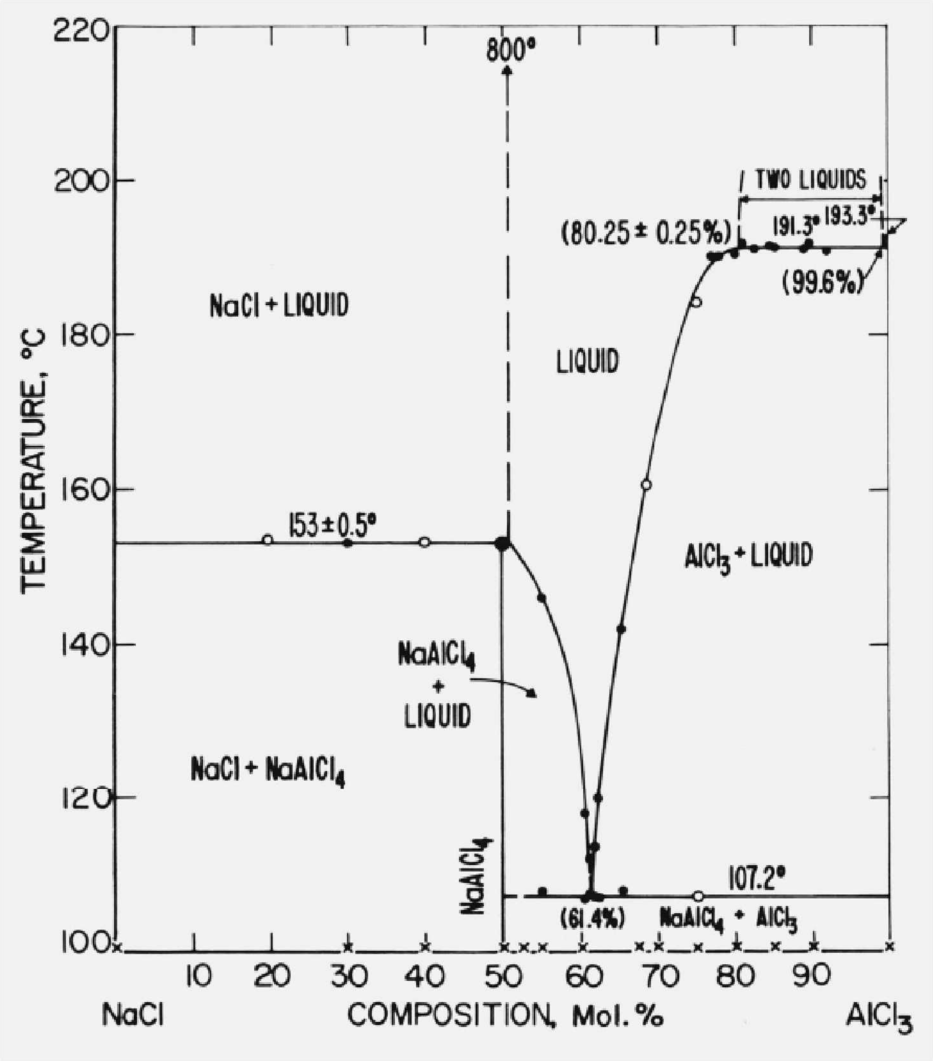
*Measured using a 4 point probe (potentiostatic EIS)

NaCl-AlCl$_3$ Phase Diagram

Phase diagram for NaCl-AlCl$_3$ system shows eutectic region near 40 mol% NaCl

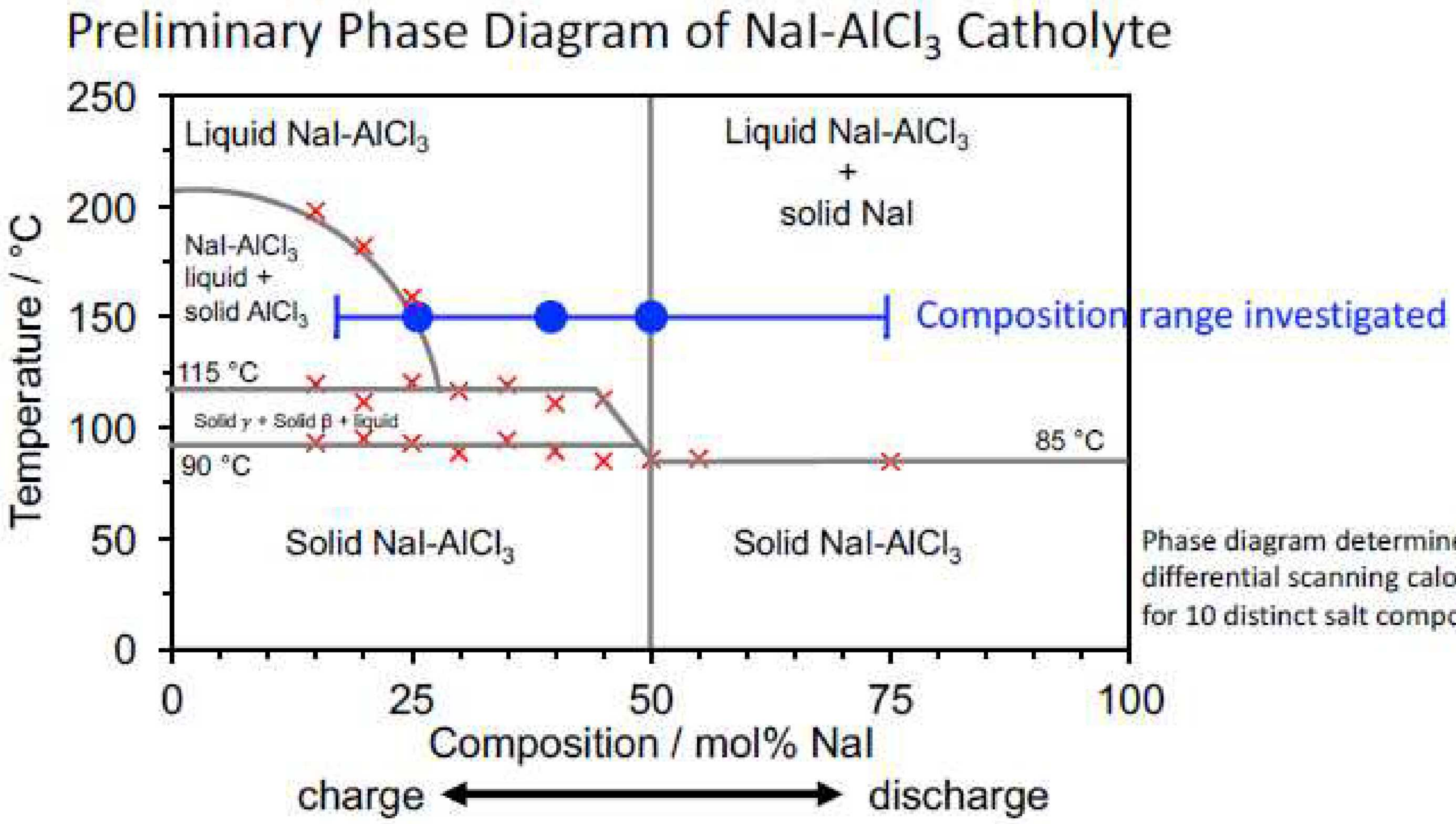
Not easily applicable to NaI-AlCl$_3$ system

Confirms our findings that there are solids present at too high or low NaI composition at 150 °C



Levin, E. M.; Kinney, J. F.; Wells, R. D.; Benedict, J. T.; *J. Res. Natl. Bur. Stand. Sec. A*, **78A**, 505 (1974).

NaI-$AlCl_3$ Phase Diagram



Phase diagram determined by differential scanning calorimetry for 10 distinct salt compositions.

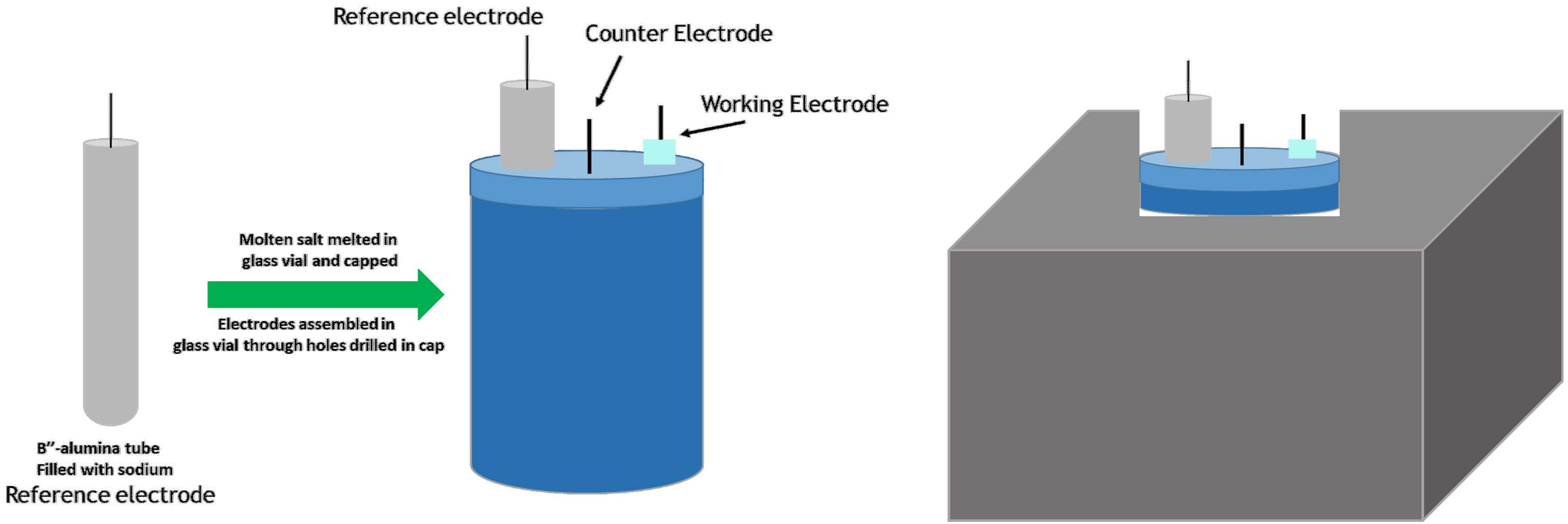
Electrochemical Cell

Experimental cell:

Working electrode = carbon fiber UME, tungsten or graphite macro electrode

Reference electrode = sodium metal in Na+ conducting ceramic (b''- alumina)

Temperature control provided by heated aluminum block where cell was contained and monitored using a type J thermocouple



Aluminum block for temperature regulation

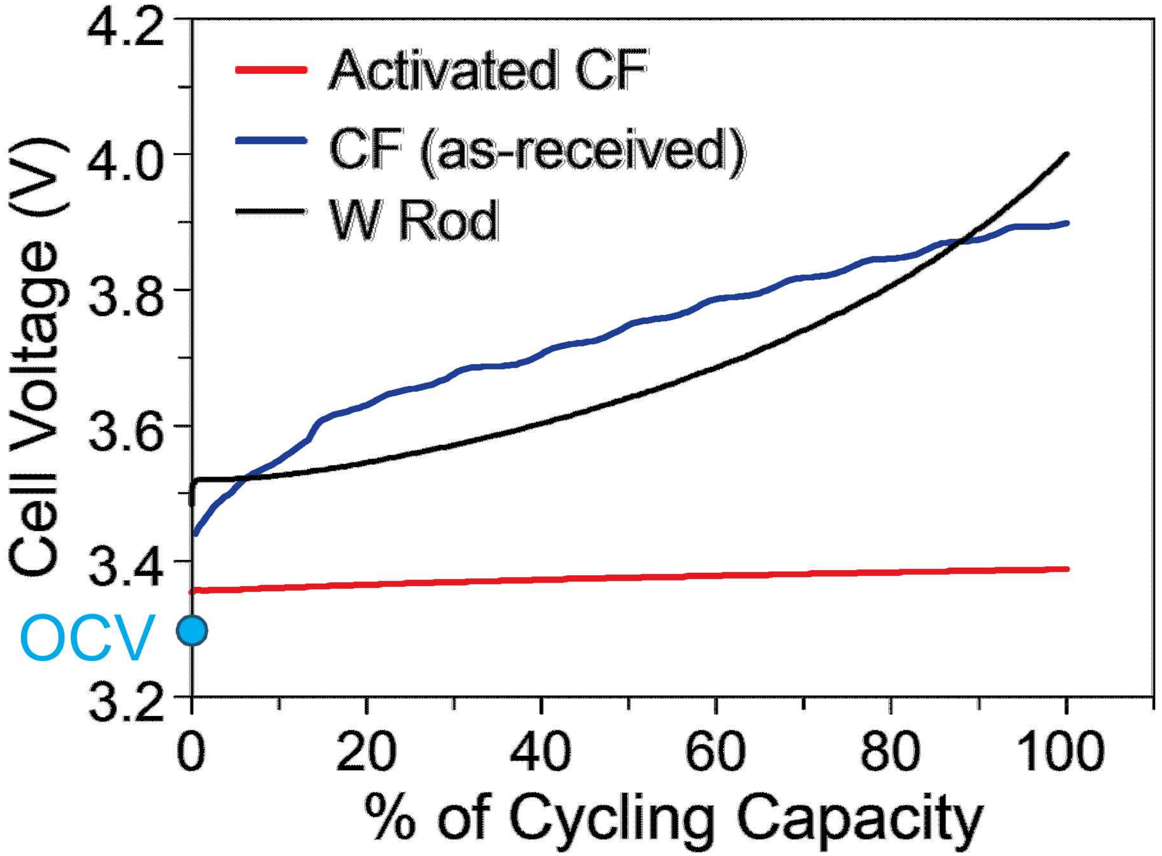
Improving Cathodic Current Collector

Important Properties of the Current Collector

- Fast Charge Transfer
- High Surface Area
- Chemically & Electrochemically Inert

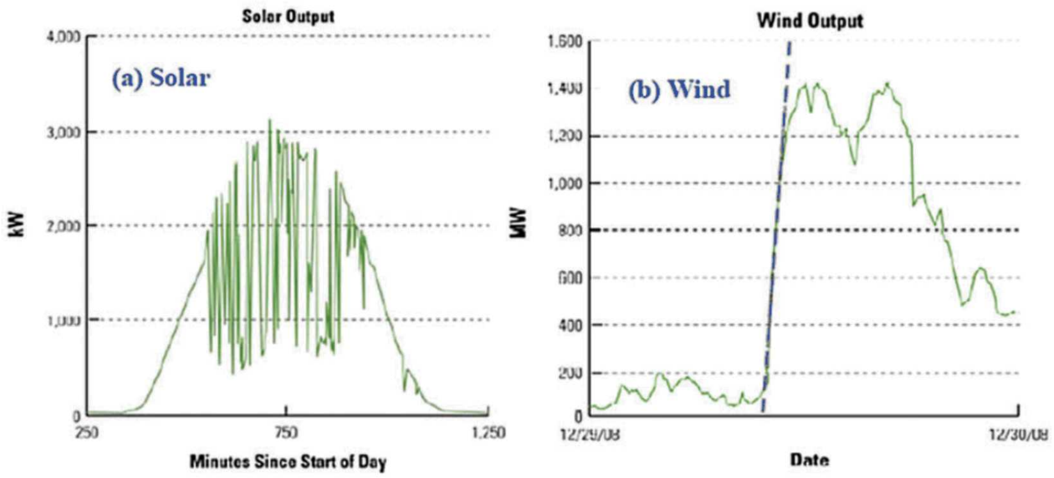
- Tungsten (W) rod: high stability, low surface area
- Carbon Felt (CF) – 1000x surface area of W rod, but no improvement in overpotential
  - – poor charge transfer
- Activation of CF: thermal treatment by heating 400°C in air, or acid treatment by cleaning with 0.1M HCl
- **Activated CF dramatically lowers overpotential**

Full Cell, Single Charge: 110°C



Energy Storage

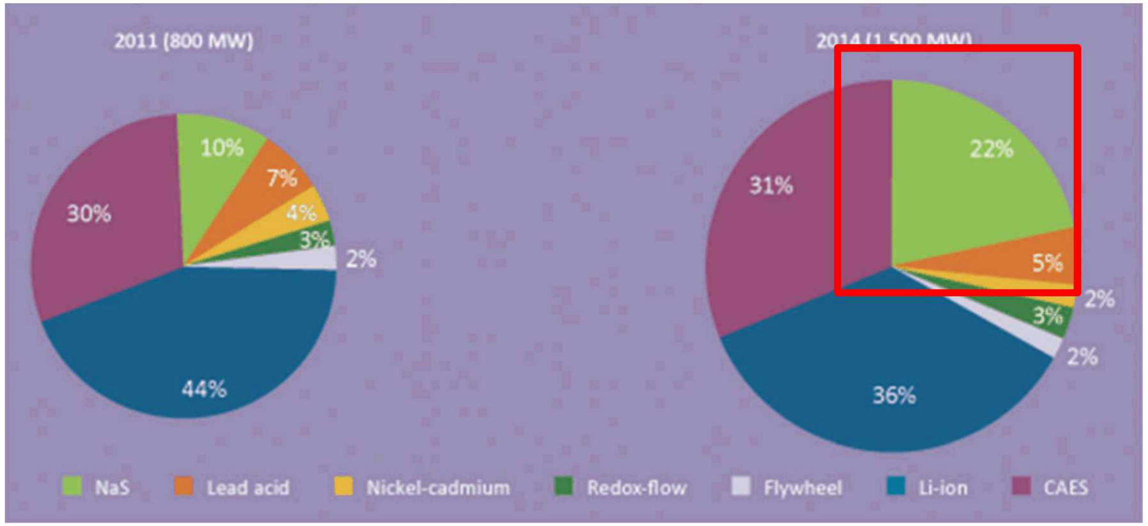
- Why is energy storage important? – To keep the lights on!
  - Stores energy generated by renewables for use when the source (example: sun or wind) is not generating



Gür, T. M. *Energy Environ. Sci.* **2018**, *11*, 2696-2767.

- Many types of energy storage:
  - Pumped hydro
  - Flywheels
  - Compressed air
  - Electrochemical – including flow batteries, lithium ion, lead acid and **molten sodium**

- In 2014 molten Na-S batteries made up ~22% of all global energy storage
- Other Na batteries include:
  - $Na\text{-}NiCl_2$ (ZEBRA battery)
  - Na-S (with organic solvent)



Gür, T. M. *Energy Environ. Sci.* **2018**, *11*, 2696-2767.

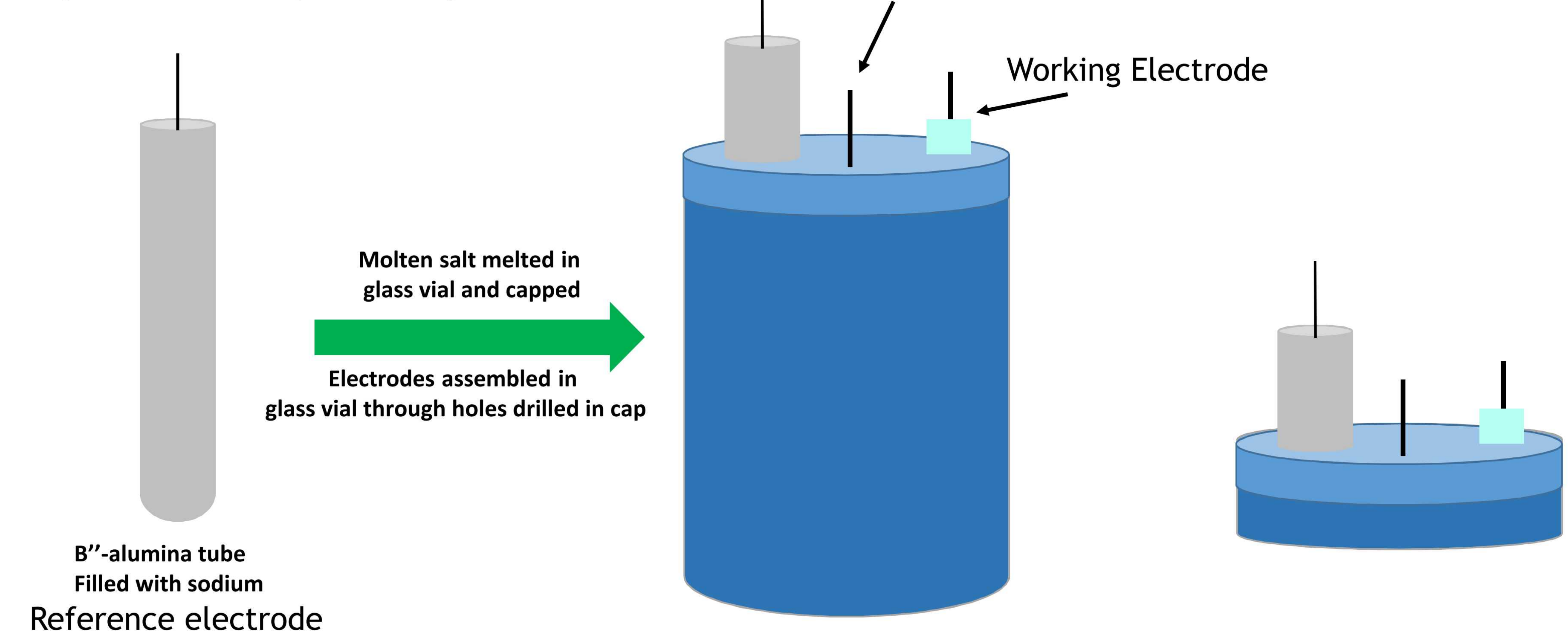
Electrochemical Cell

Experimental cell:

Working electrode = carbon fiber UME, tungsten or graphite macro electrode

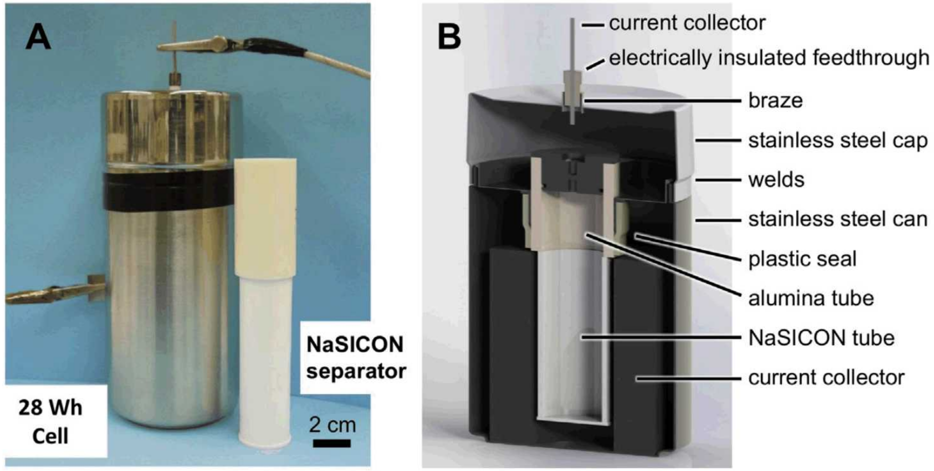
Reference electrode = sodium metal in Na+ conducting ceramic

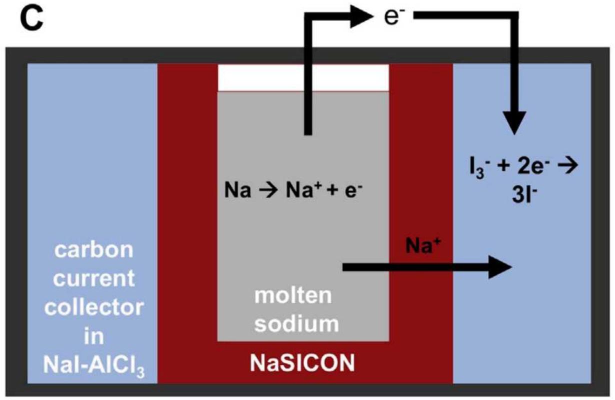
Temperature control provided by heated aluminum block where cell was contained

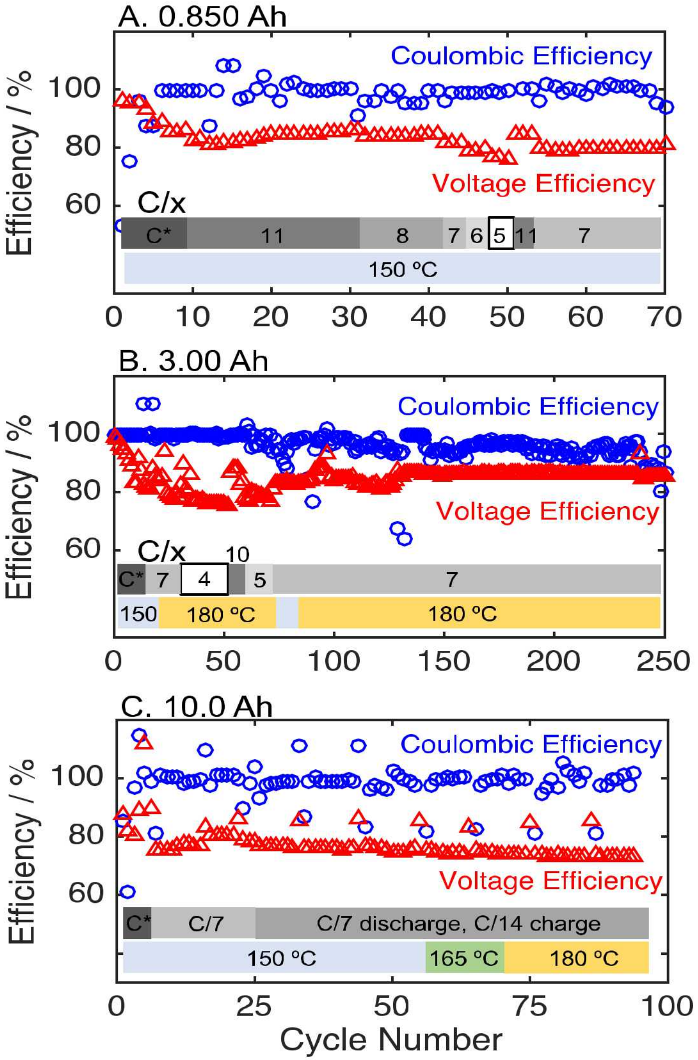


An Intermediate Temperature Na-NaI Battery

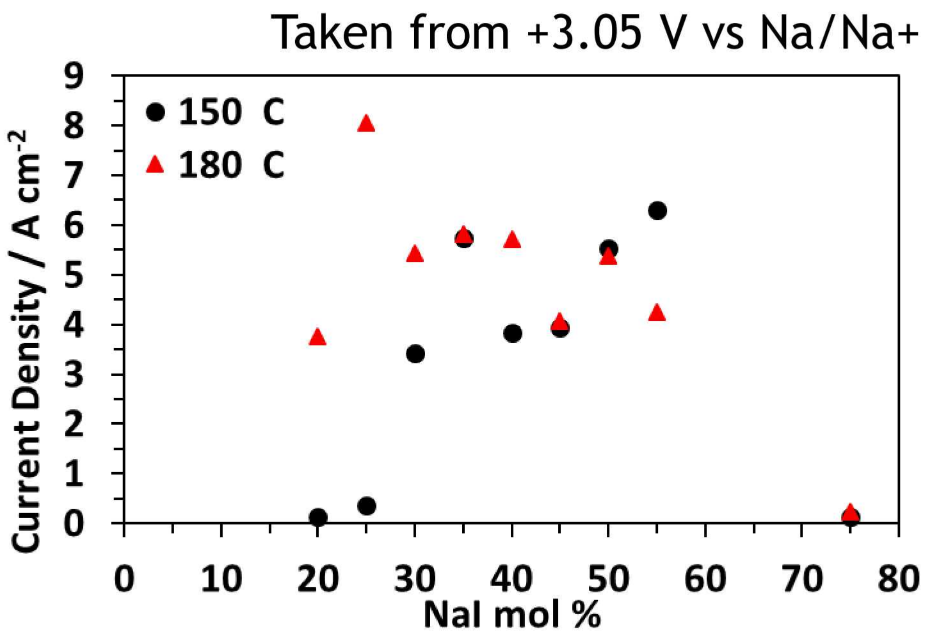
Na-NaI battery was demonstrated across several scales at 150-180^{o}C.

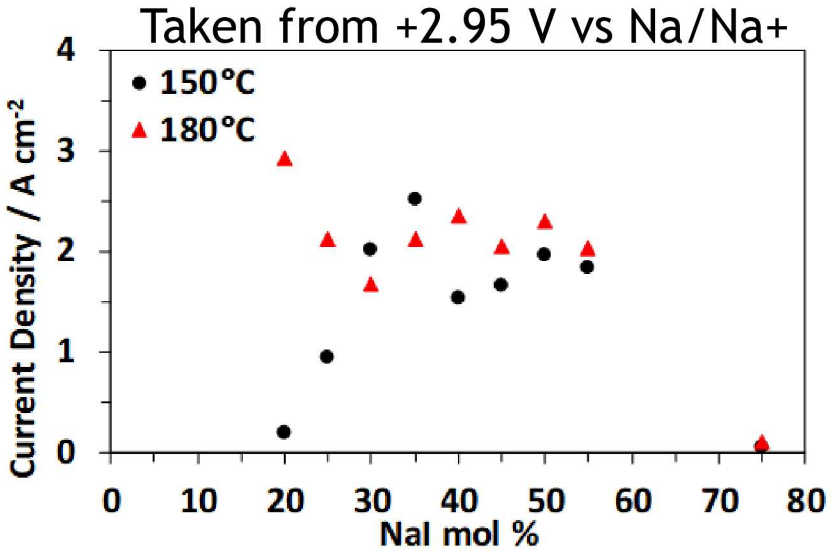


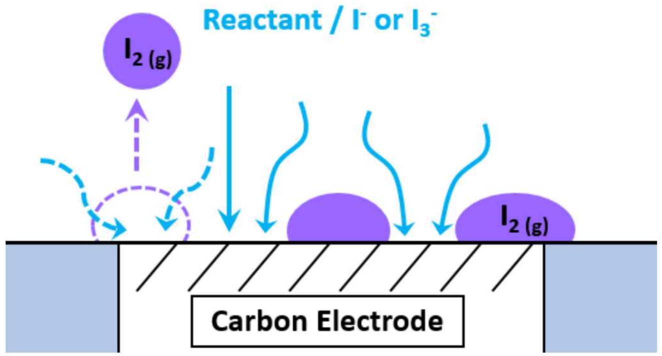


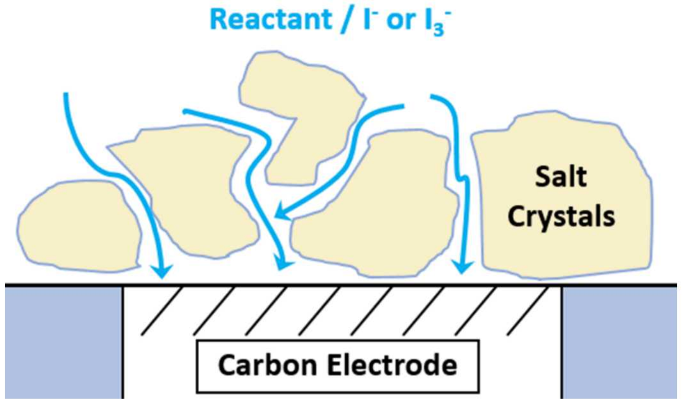


L.J. Small, E.D. Spoerke, *et al*. *J. Power Sources* (2017) **360** 569-574.


Taken from +3.05 V vs Na/Na+
150 C
180 C
Current Density / A cm-2
NaI mol %

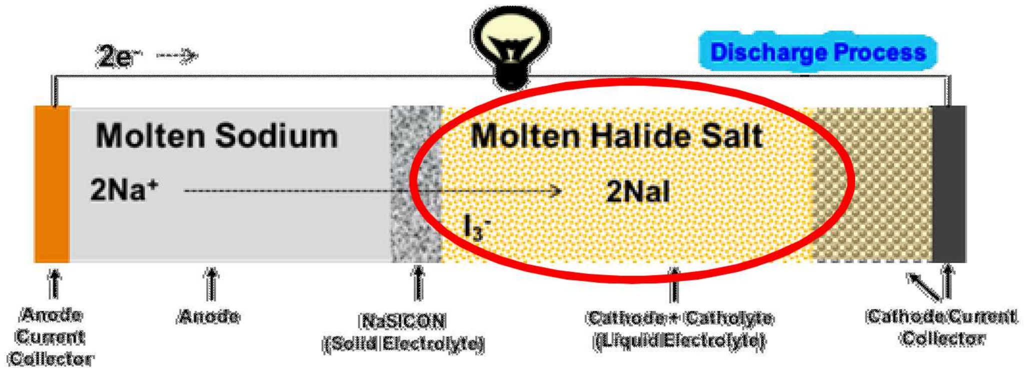

Taken from +2.95 V vs Na/Na+
150°C
180°C
Current Density / A cm-2
NaI mol %


Reactant / I- or I3-
I2 (g)
I2 (g)
Carbon Electrode


Reactant / I- or I3-
Salt
Crystals
Carbon Electrode

Low Temperature Molten Na-Halide Batteries

Our Vision: A molten sodium-based battery that comprises a robust, highly Na^+-conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.



Used macro and ultra micro electrodes (UME) to investigate electrochemical behaviors and key aspects of molten salt catholytes

- Newly developed salts utilize NaI as the reactant in the catholyte
  - Aluminum halides (AlX_3) are the secondary component

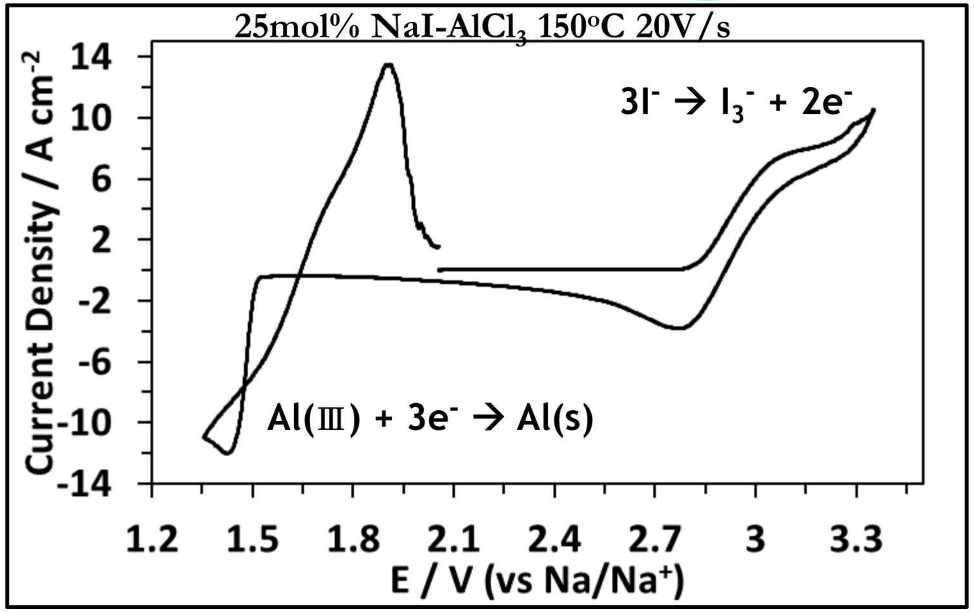
High operational voltage

Reversible battery reactions:

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

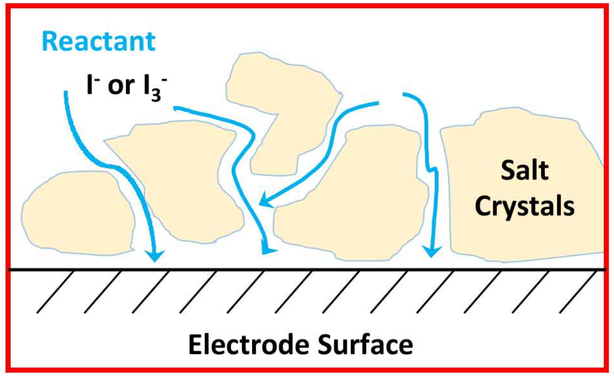
Cathode: $3I^- \rightarrow I_3^- + 2e^-$ E° = 3.24 V vs Na/Na⁺

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



Catholytes are Key to Low Temperature Operation

A fully molten catholyte avoids
- a) Particle-hindered electrochemical processes
- b) Particle-related loss of capacity



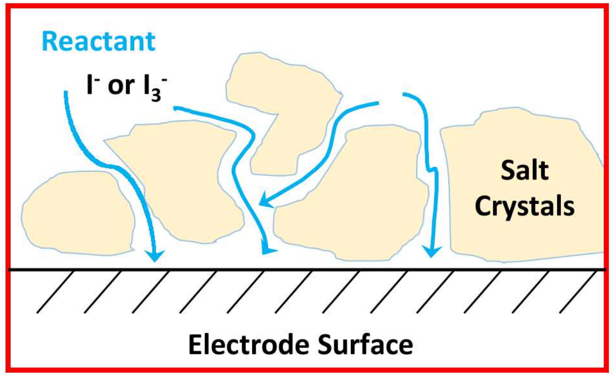
$NaI\text{-}AlCl_3$ at 150°C

$NaI\text{-}AlCl_3$ and $NaI\text{-}AlBr_3$ salts at 90°C

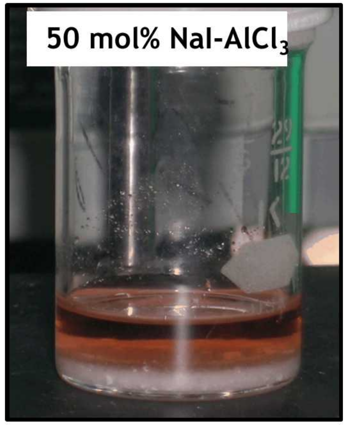
Molten $NaI\text{-}AlBr_3$ composition range spans 5-25% NaI and cell voltage is near or above 3V.

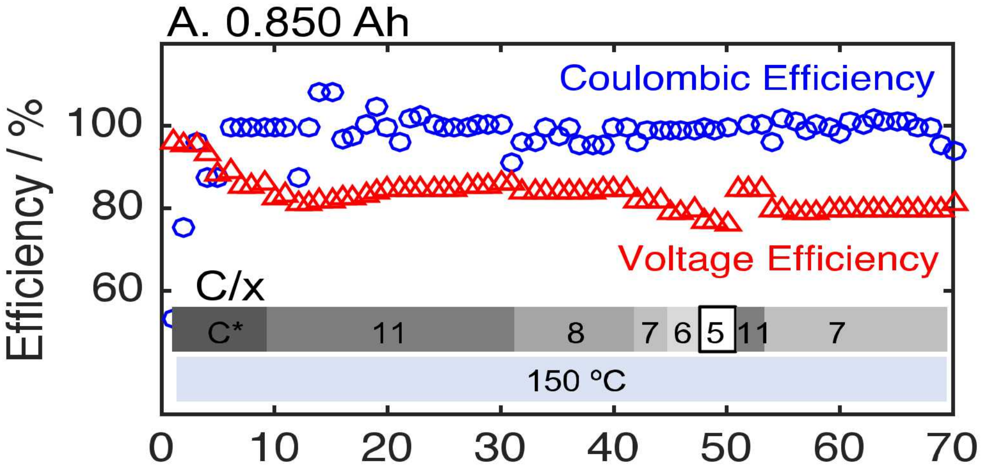
Catholytes are Key to Low Temperature Operation

A fully molten catholyte avoids
- a) Particle-hindered electrochemical processes
- b) Particle-related loss of capacity



NaI-$AlCl_3$ at 150°C





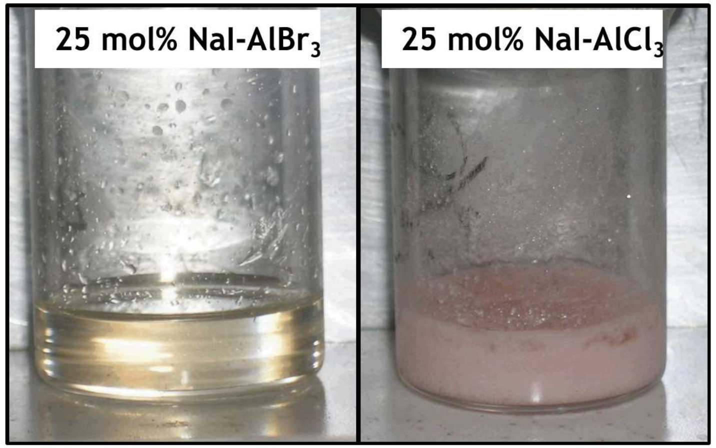
Small, L. J; et al. *J. Power Sources*. **360**. 569-574.

NaI-$AlBr_3$: A Low Temperature Molten Catholyte

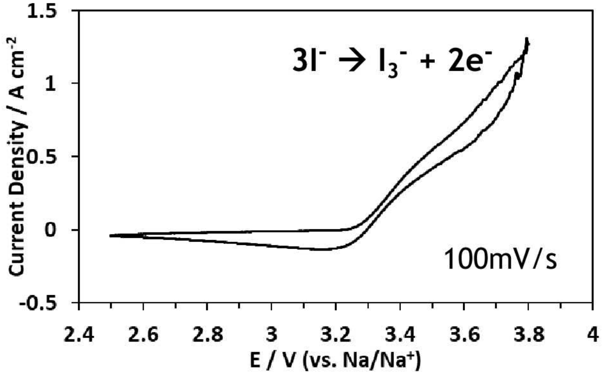
The NaI-$AlBr_3$ catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures.

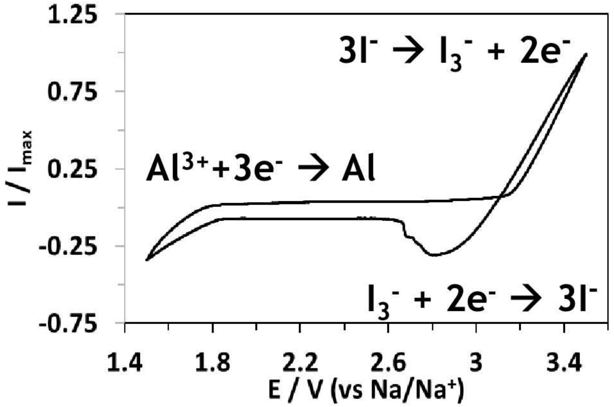
- 25:75 NaI-$AlBr_3$ salt <u>completely molten</u> at 90 °C
- Larger fully molten capacity range (~5-25 mol% NaI)

Samples at 90°C



- Carbon Fiber microelectrode shows excellent electrochemical behavior of 25 mol% NaI-$AlBr_3$ at 90°C





- NaI-$AlBr_3$ system shows good iodide electrochemical reversibility.
  - $AlBr_3$ (20mol% NaI) system at 120 °C and 1V/s

- Diffusion coefficients calculated at different temperatures
  - Valuable information for cathode current collector design