EaglePicher™ Technologies, LLC
An OMG Company

Planar Na-Beta Batteries for Renewable Integration and Grid Applications

Award DE-AR0000045

Vincent Sprenkle

Pacific Northwest NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY

DOE Energy Storage Systems Program (ESS)

04 November 2010

Funded in part by the ARPA-e Program of the U.S. Department Of Energy

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"New Generation Na-Beta Batteries for Renewable Integration & Grid Applications"

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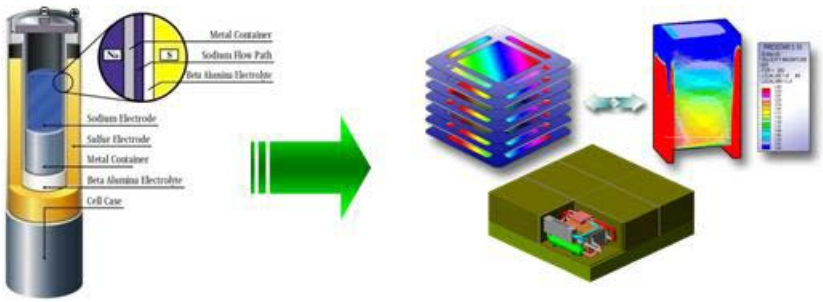
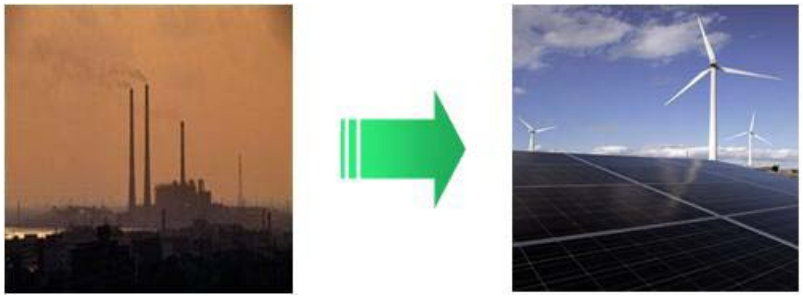
Proposed Technology vs. State of the Art



SOA Tubular Na-beta Design → **Leverage US National Lab Tech** → **Proposed Planar Na-beta Design**

- **Increased Energy Density**
- **Cost Reduction**
- **Temp Reduction**

ARPA-E Mission Area Impact



- **Renewable Energy Storage With Improved Na-beta battery reduces CO_2 emissions by 150 Million Tons/Year**
- **Improves/maintains US energy storage leadership**

Transition Strategy

Proof of Concept → Commercialization

PNNL Research and Development

Tech Transfer & IP

EaglePicher R&D

→ **1 Yr**

One Team: Concept Thru Production

No Tech Transfer Lag

No IP Transfer Lag

EaglePicher
Full Scale Development

→ **2 Yr**

EaglePicher
Establish Large Scale Production

→ **3Yr**

Program Summary

Period of performance:
36 months

ARPA-E funds:	**$7.2M**
Cost-share:	**$1.8M**
Total budget:	**$9.0M**

Annual Schedule Milestones

- Improved Na-beta cell demonstration & initial system model complete
- PNNL electrolyte & seal technology transfer complete & demonstration of multi-cell battery
- 5kW- battery model demonstration & system model complete

Meeting US Renewable Storage Needs at <3¢/kWh/cycle

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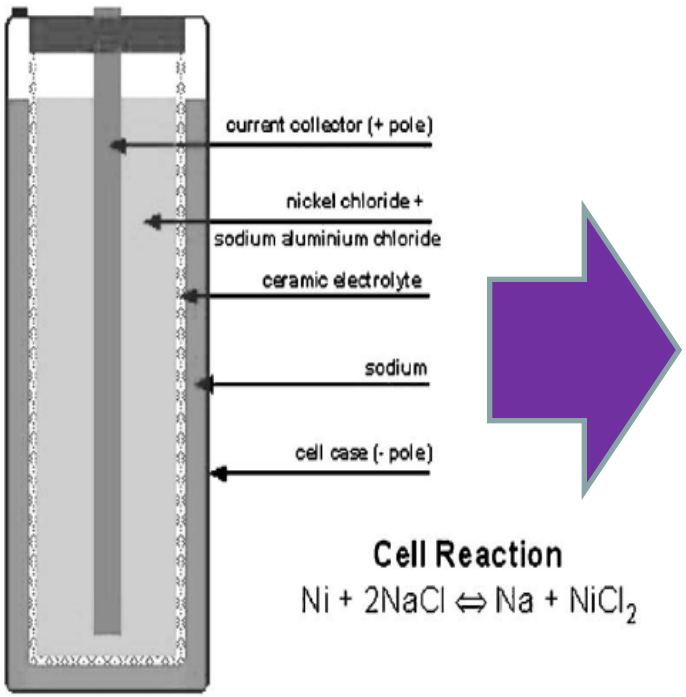
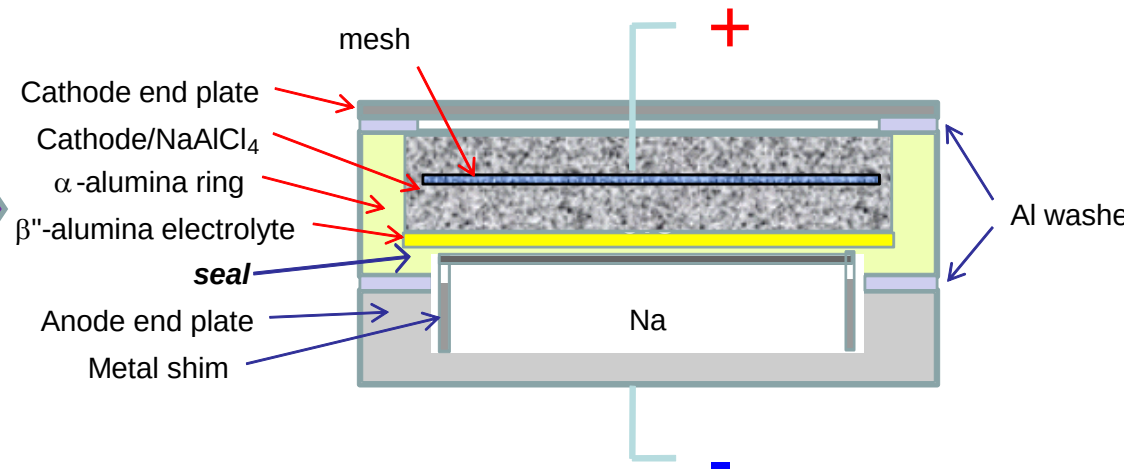
Tubular vs. Planar Design



Cell Reaction

$Ni + 2NaCl \Leftrightarrow Na + NiCl_2$



General Properties

- Thick electrodes: high capacity- limited power
- Single cells: – complicated interconnects
- BASE: high cost-low yield
- Robust design: long life at low power

General Properties

- Electrodes: adjustable power and energy ratio,
- Modular: – simplified interconnects
- BASE: low cost, higher conversion increased yield
- Robust design: long life at high power

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Path to Planar Na Battery

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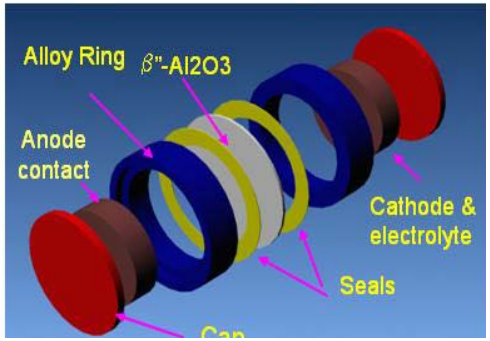
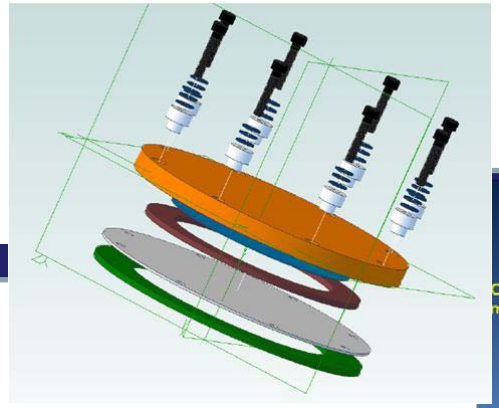
3.0cm^2 Button Cell



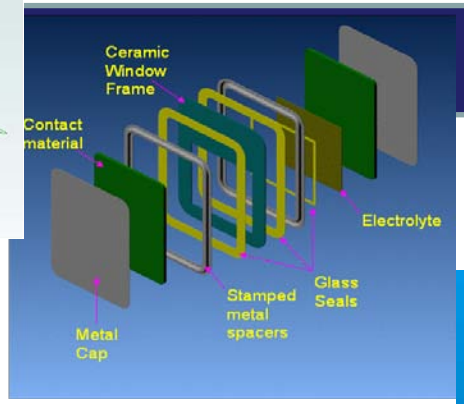
Materials development and performance testing.

64cm^2 XL-Button Cell



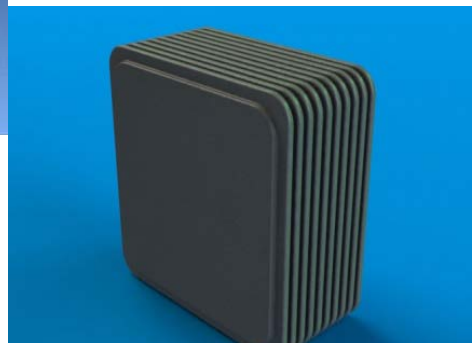
Materials scale-up with large-scale performance and life testing.

100cm^2 Planar Cell



Manufacturing friendly components and fabrication techniques.

200cm^2 Stack



Modular stack design with performance and life testing.

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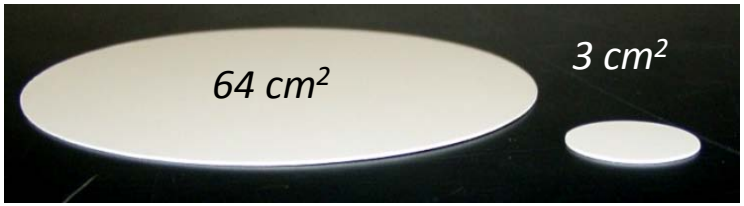
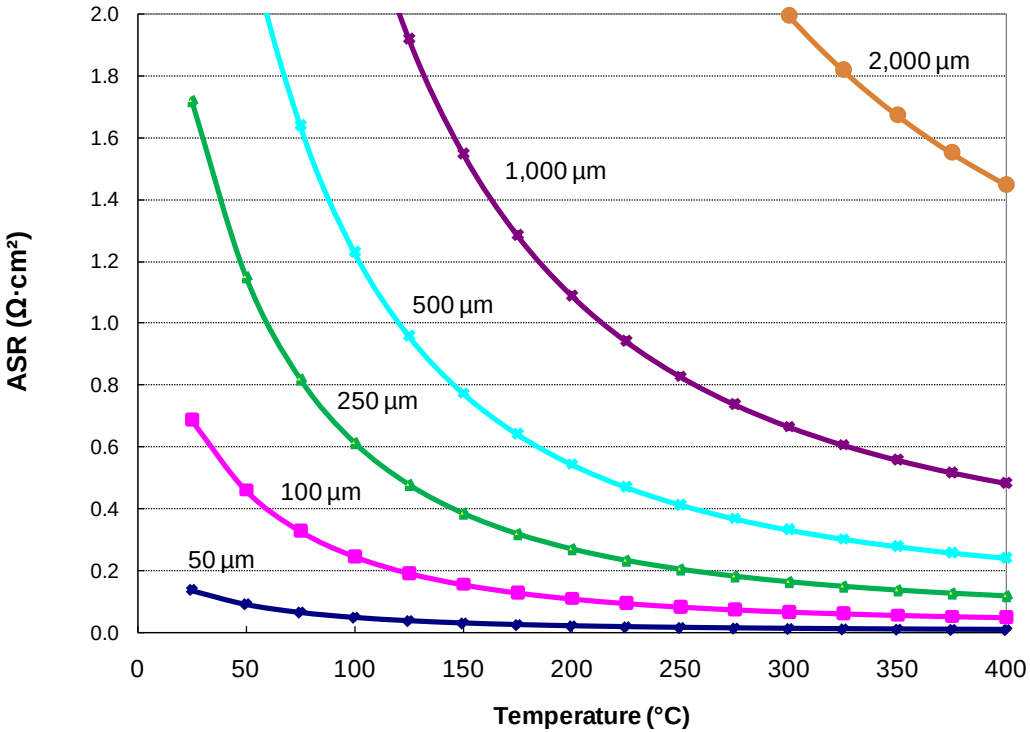
BASE Ohmic Properties

High Power Requirements

- *Thinner electrolyte → decrease R*
- *Lower BASE R → higher current densities*
- *Minimize defects in BASE → increased cycle life.*
- *Effective electron percolation in cathode → decrease R*

500 μm BASE





Planar design key to limiting R by decreasing electrolyte thickness and enable lower temperature operation.

β" alumina (BASE) Crystal structure

β" - phase
$Na_2O \cdot 5.33Al_2O_3$

β - phase
$Na_2O \cdot 11Al_2O_3$

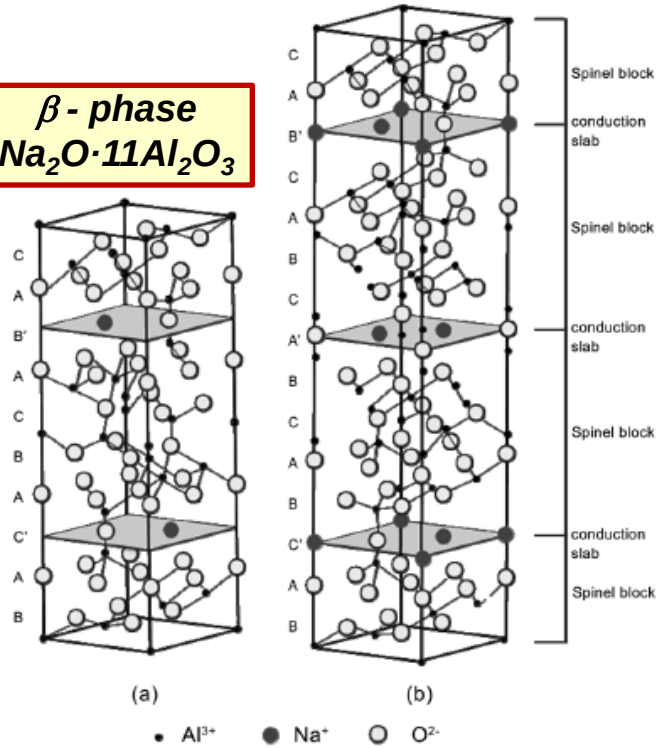


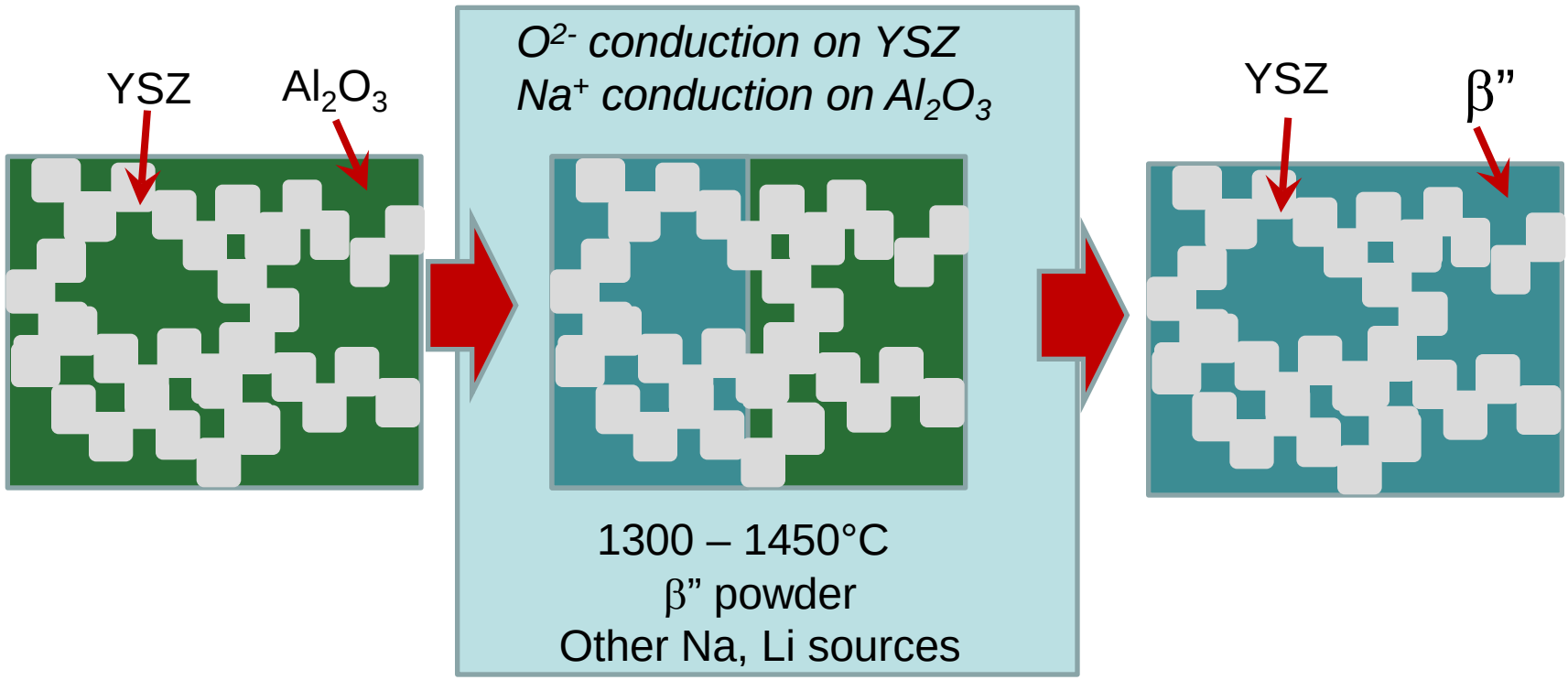
Fig. 2. Perspective drawings of the idealized structures of (a) β-alumina (b) β"-alumina [8, 9].

Journal of Ceramic Processing Research. Vol. 11, No. 1, pp. 86~91 (2010)

- *2-D conduction plane*
- *Stabilizing agents such as Mg or Li added to spinel block to enable higher Na content.*
- *Processing by traditional ceramics fabrication routes leads to:*
  - *Na depletion*
  - *H_2O sensitivity*
  - *Larger grain size*

α → β" Conversion Process

Al_2O_3 → Na_2O~5.33Al_2O_3 (β")



Developed by A. Virkar
Allows ceramic processing standard Al_2O_3 and YSZ materials

- *Minimal H_2O sensitivity , smaller grain size*

Significant difference in solid state and vapor diffusion rates.
~3% volume expansion during α to β" conversion

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Mechanical testing to evaluate robustness of BASE structure

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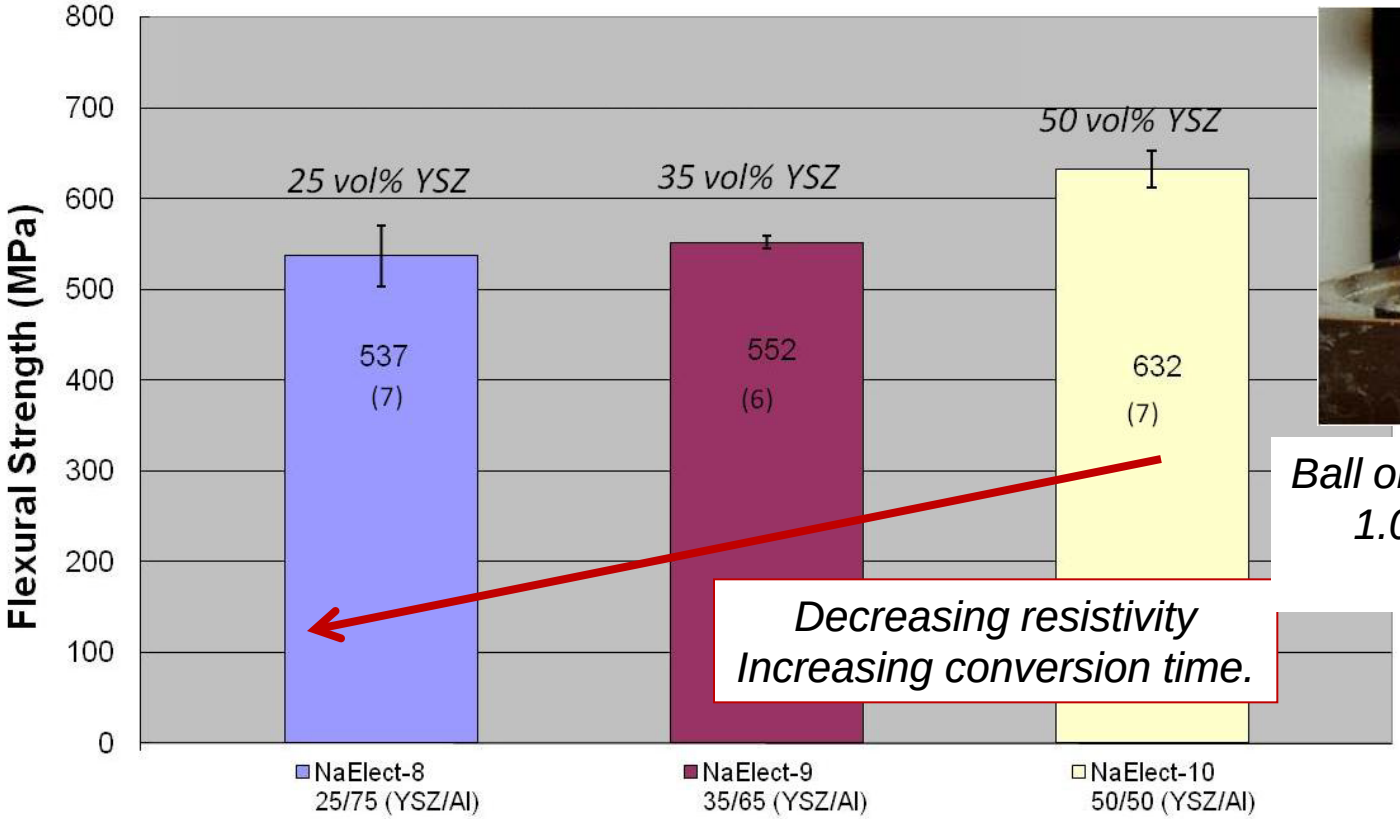
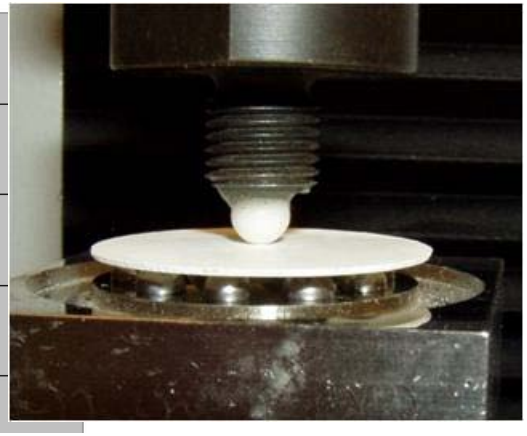


Decreasing resistivity
Increasing conversion time.



Ball on Ring flexural testing on 1.0" diameter converted BASE.

- *Flexural Strength (MPa) vs. vol% YSZ in BASE.*
- *25.4 mm diameter samples*
- *Converted 1450°C – 10 hrs*
- *(x) = number of samples tested.*
- *Assumed Poisson's ratio of 0.25 – actual 0.29-0.33 so flexural strength in graph is underestimated ~ 50 MPa.*

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Seal Design Development

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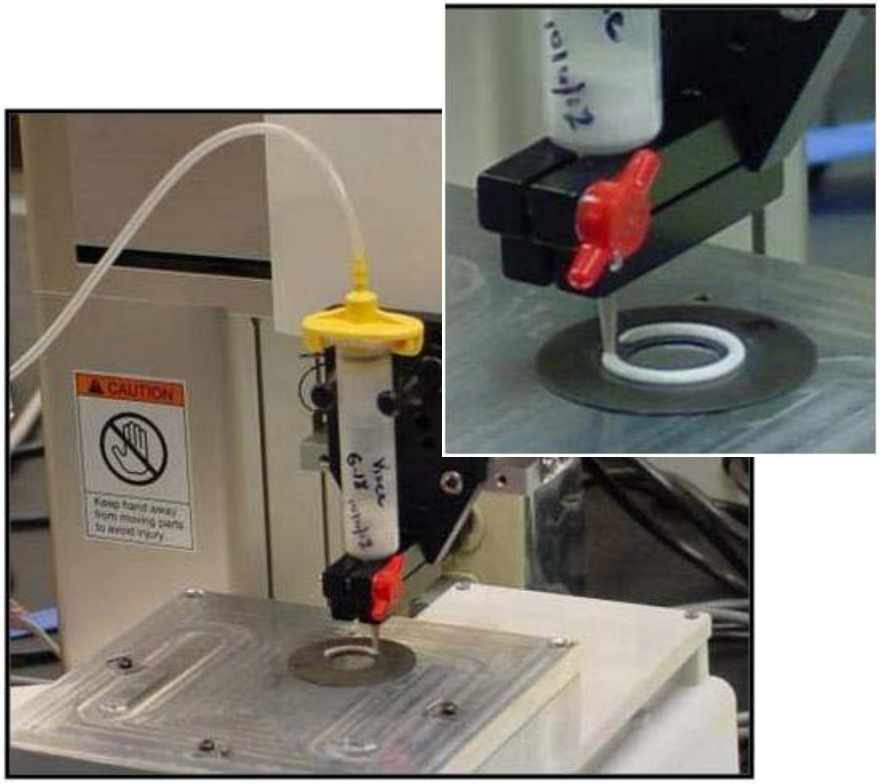
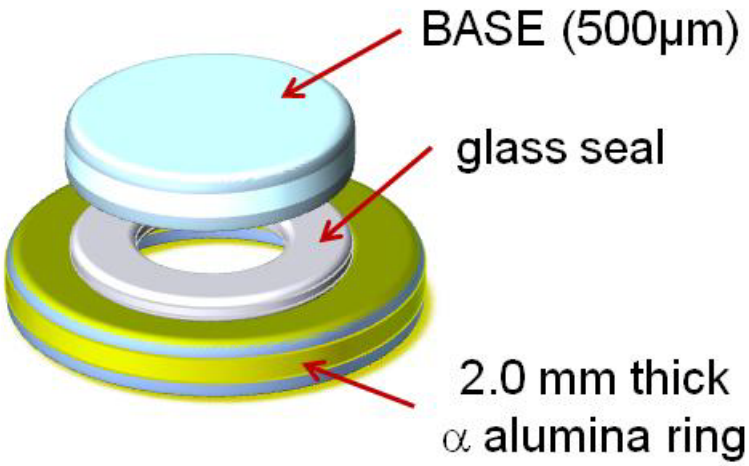


Schematic of popgun sample assembly



- **Prepared by dispensing glass or apply tape gasket between the BASE and frame.**
- **Enable representative seals and interfaces to be tested under differential pressure conditions.**

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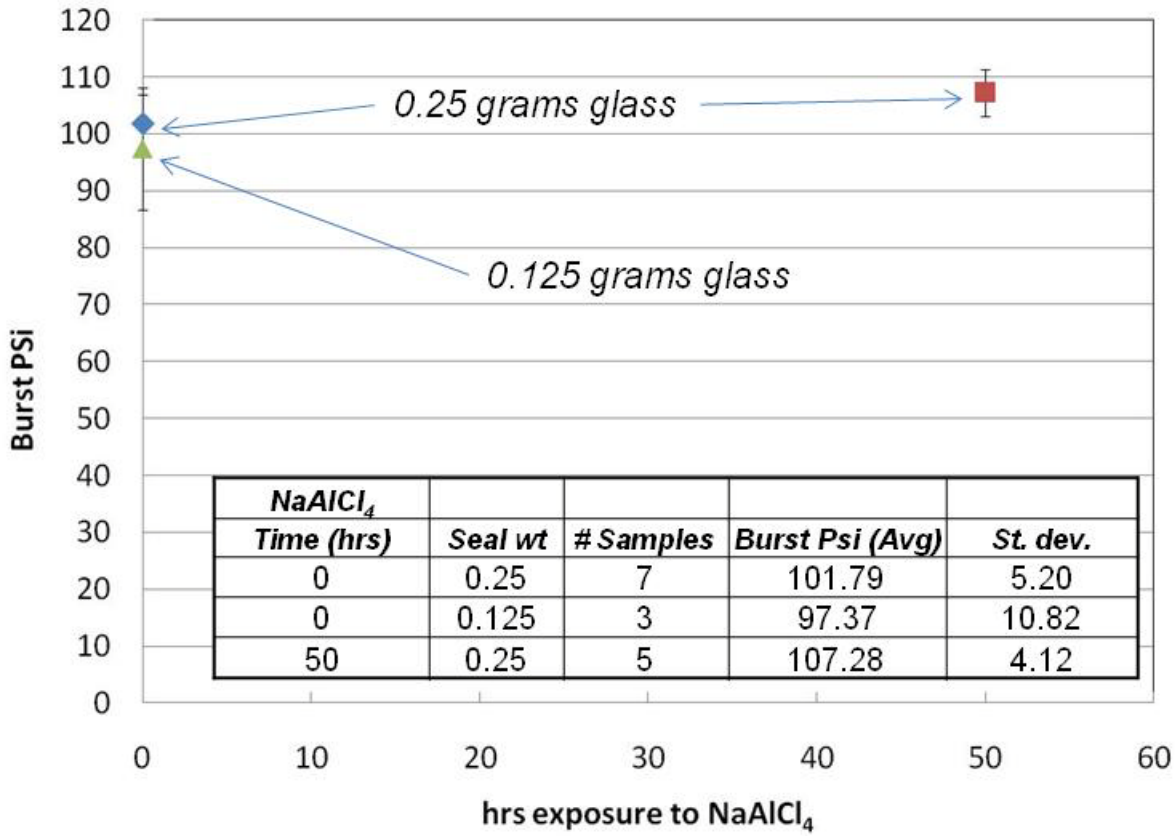
Seal Pressure Testing



$NaAlCl_4$ Time (hrs)	Seal wt	# Samples	Burst Psi (Avg)	St. dev.
0	0.25	7	101.79	5.20
0	0.125	3	97.37	10.82
50	0.25	5	107.28	4.12

Pop-gun results for 0.5 mm thick BASE joined to α-alumina ring with glass seal. 0.125 grams of glass same as 3 cm^2 cell test.

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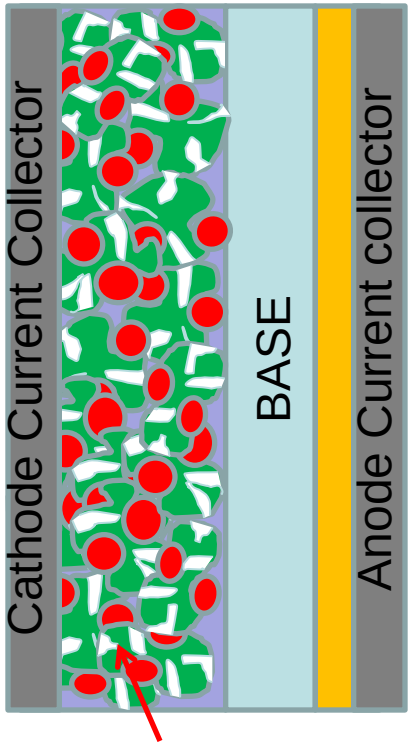
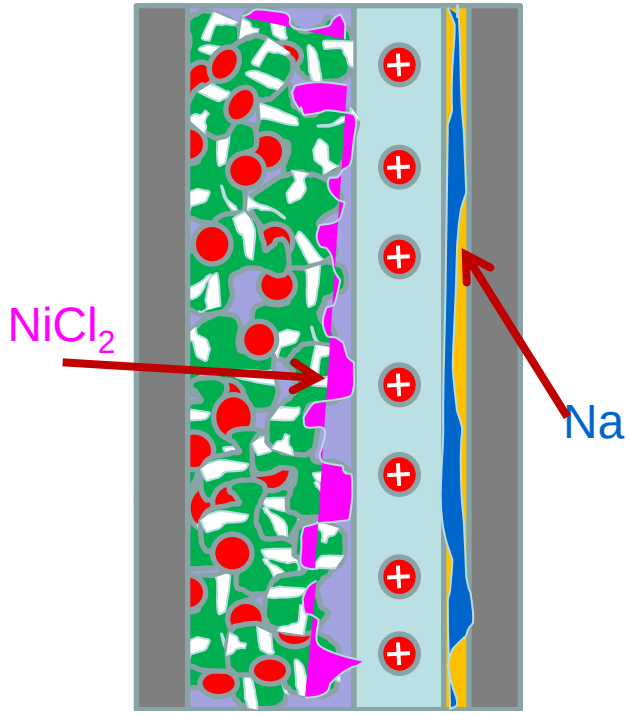
Na-$NiCl_2$ Battery

Discharged State
Ni + 2NaCl



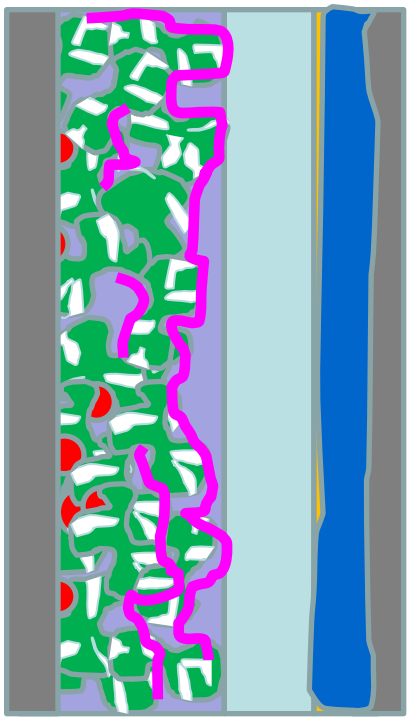
Cathode
1) Ni
2) NaCl
3) $NaAlCl_4$

Charging Rxn
2e- + Ni + 2NaCl
→ 2Na + $NiCl_2$



- *Na ions close to the BASE migrate to anode.*
- *$NiCl_2$ coats Ni particle.*
- *High R of $NiCl_2$ requires excess Ni loading to collect current.*

Charged State
$NiCl_2$ → Na



- *R increase as SOC*
- *Accessing NaCl deep in the cell becomes more difficult.*
- *Avoid over charging, melt turns acidic and $NiCl_2$ will dissolve.*

Battery Metrics: Factors in Power and Energy

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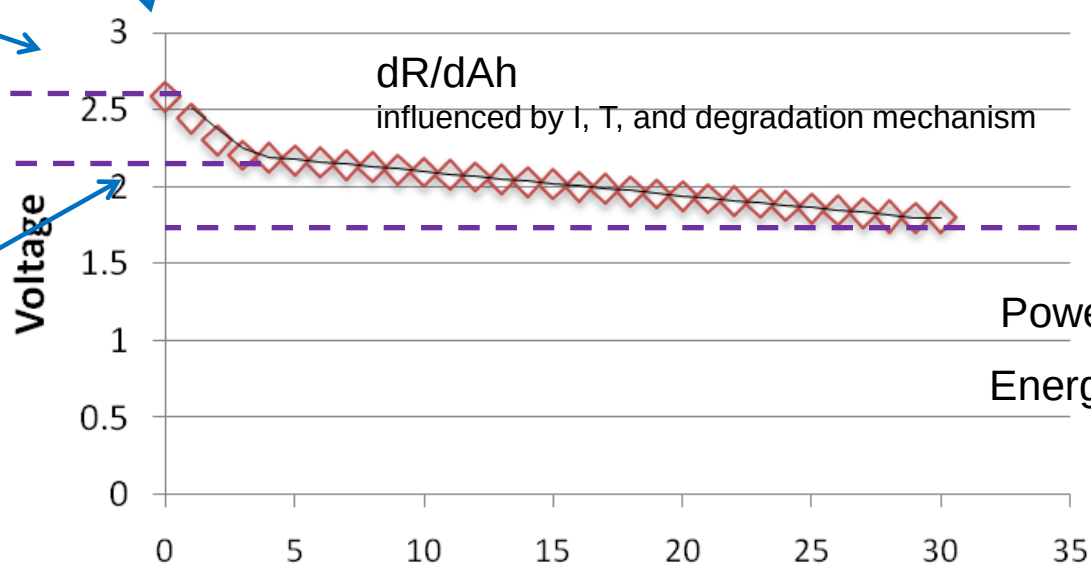
- Increased R from NiCl2
- V cutoff below 3.0V
- Melt degradation
- Acidic melt

Open Circuit Voltage (OCV)
Determined by chemistry

Discharge curve for Na-$NiCl_2$ Battery (ZEBRA) in constant current mode

- Al plating
- Lower IR

Overvoltage (OV) OCV-V
mass transfer , R , kinetics



dR/dAh
influenced by I, T, and degradation mechanism

Cutoff Voltage
Determined by chemistry
NaAlCl4→ Al

Operating Voltage (V)

Power= V* I ($R*I^2$ (W)

Energy = V* Ah (Wh)

Capacity = amount of electro-active materials
Determined by chemistry, electrons/molecule

Specific Power = W/kg (mass)
Volumetric Power = W/L (vol)

Specific Energy = Wh/kg (mass)
Volumetric Energy = Wh/L (vol)

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New Cell Performance

100 Whr/kg at 1C at 280°C

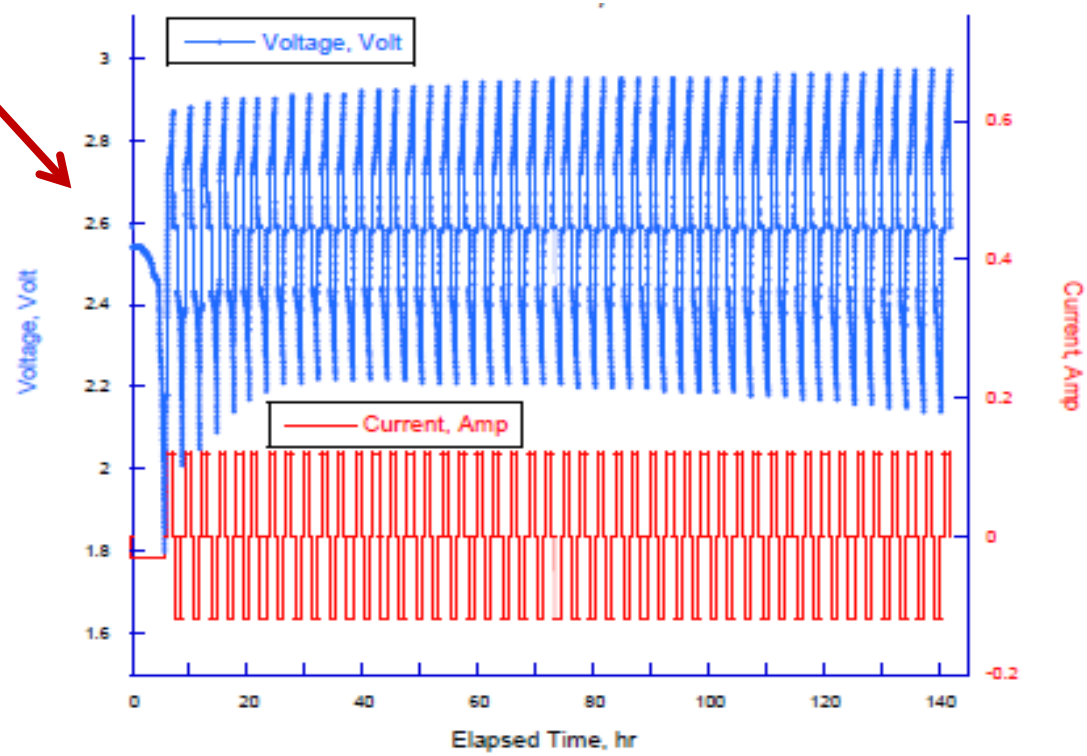
- Equivalent to 46 cycles
- New anode coating and shim design
- Online cell and temperature monitoring.

Cycle Life Issues

- Slight R rise → NaCl ripen SOC reset
- $NaAlCl_4$ wick
- Light sinter of Ni network

Next Steps:

- Baseline variability
- DoE cell cathode
- Improve to 150 Whr/kg at 1C



New Cell Design and Fabrication

- *No molten Na in cell during build.*
- *Maiden charge at 320°C*
- *BASE coated with selected wetting agents*
- *New anode shim*
- *New break-in protocol*

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Summary

- Planar configuration offers versatile power and energy cell design.
- BASE conversion process
  - lowers conversion temperature/time, improves strength,
  - decreases Na conductivity, volume expansion can lead to warpage.
- Glass seal pressure tested to withstand differential pressure of up to 6 atm. Robust chemical resistance to $NaAlCl_4$
- Developed new anode side BASE coating with improved wetting.
- Over 100 cycles at 100Wh/kg at 1C rate, for baseline chemistry in $3cm^2$ cells.
- Developing scaled-up cell ($64cm^2$ - between 6-8Ahr) and test-stands

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Acknowledgements

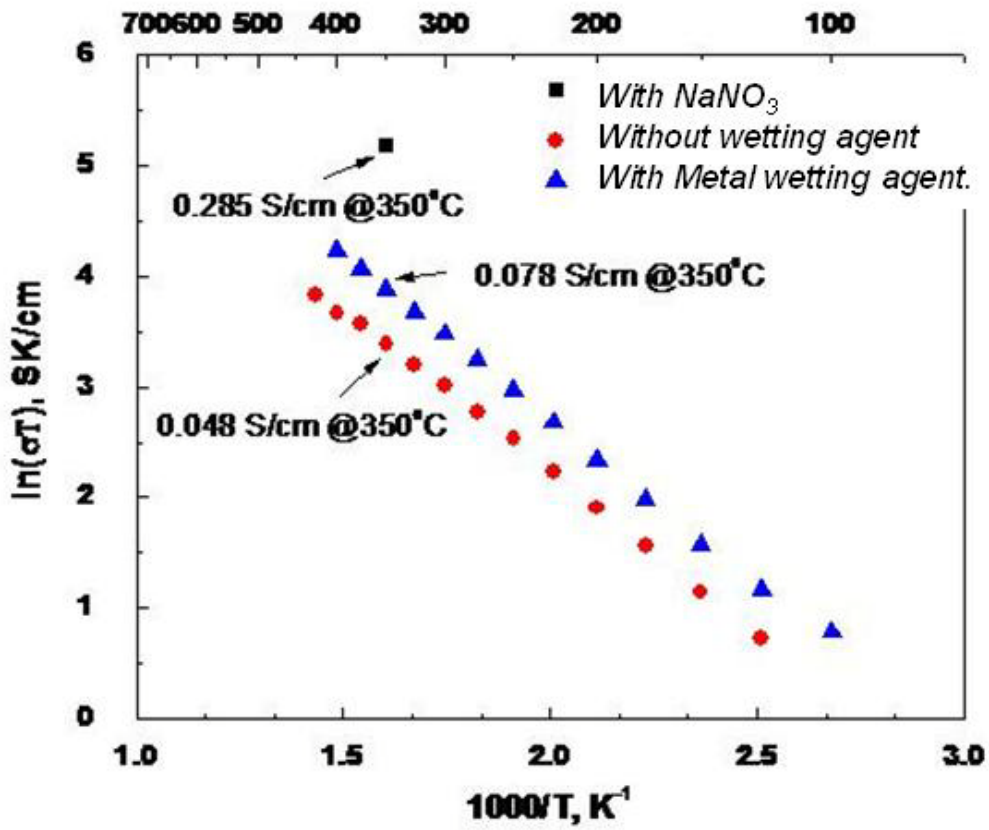
Planar Na-Beta Batteries for Renewable Integration and Grid Applications *Award DE-AR0000045*

Dr. Dave Danielson – ARPA-E Program Director

EaglePicher *– Dave Lucero, Bob Higgins, Jim Degruson, Rebecca Cragun, Geoffrey Swift, Joe Edington, Elvin Listerud, Julie Baumann, Uma Viswanathan, Charlie Lamb, R. Thillaiyan, Glen Sutherland, Darrell Ideker.*

PNNL *- John Lemmon, Vincent Sprenkle, Xiaochuan Lu, Guosheng Li, Greg Coffey, Kerry Meinhardt, Nathan Canfield, Jeff Bonnett, Eric Mast, Richard Pearson, Brent Kirby, Gary Yang*

Back-up slides

Resistivity Testing

ionotec Measurements at PNNL