Planar ZEBRA Battery for Renewable Integration and Grid Applications

Beyond Lithium Ion, PNNL Richland WA
June 7th- 9th 2011

Pacific Northwest
NATIONAL LABORATORY

Acknowledgements

- ARPA-E Storage Program

  PNNL directed R&D fund

- Staff at PNNL:

  Battery Team: Xiaochuan Lu, Guosheng Li, Vincent Sprenkle, Brent Kirby, Nathan Canfield, Jeff Bonnett, Richard Pearson, Eric Mast, Gary Yang, Kerry Meinhardt.

  NMR Team: Jianzhi Hu, Mary Wu, Ju Feng

  Project support: Jud Virden, Jun Lui, Gordon Graff

- EaglePicher: Bob Higgins, Jim Degruson, Dave Lucero

Pacific Northwest NATIONAL LABORATORY

Na-beta alumina membrane batteries (SBB)

SBB are electrochemical devices that store electrical energy via Na^+ transport through conductive solid oxide membrane (typically β''-Al_2O_3) at elevated temperatures.

Invented and first investigated by Ford for vehicle applications

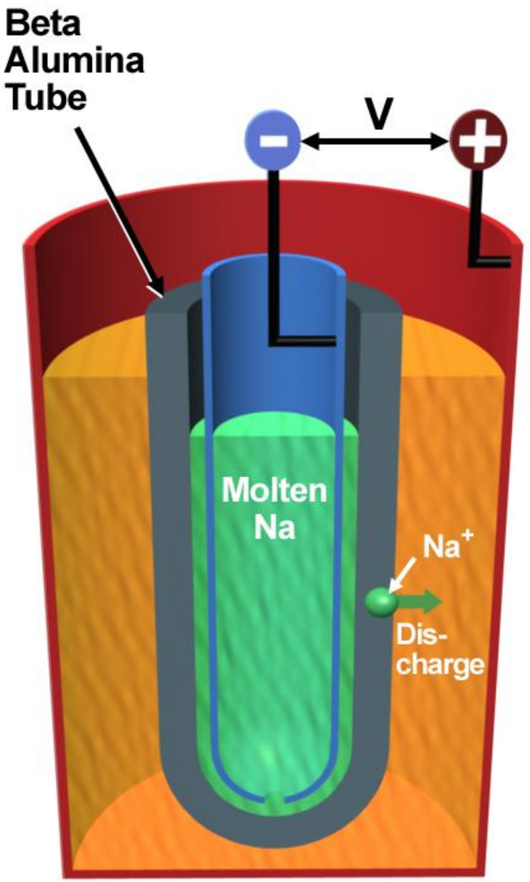
➢ Sodium-sulfur (SSB)

$$2Na + 4S \underset{d}{\overset{c}{\rightleftarrows}} Na_2S_4 \quad E = \sim 2.0\ V$$

➢ Sodium-metal chloride (ZEBRA)

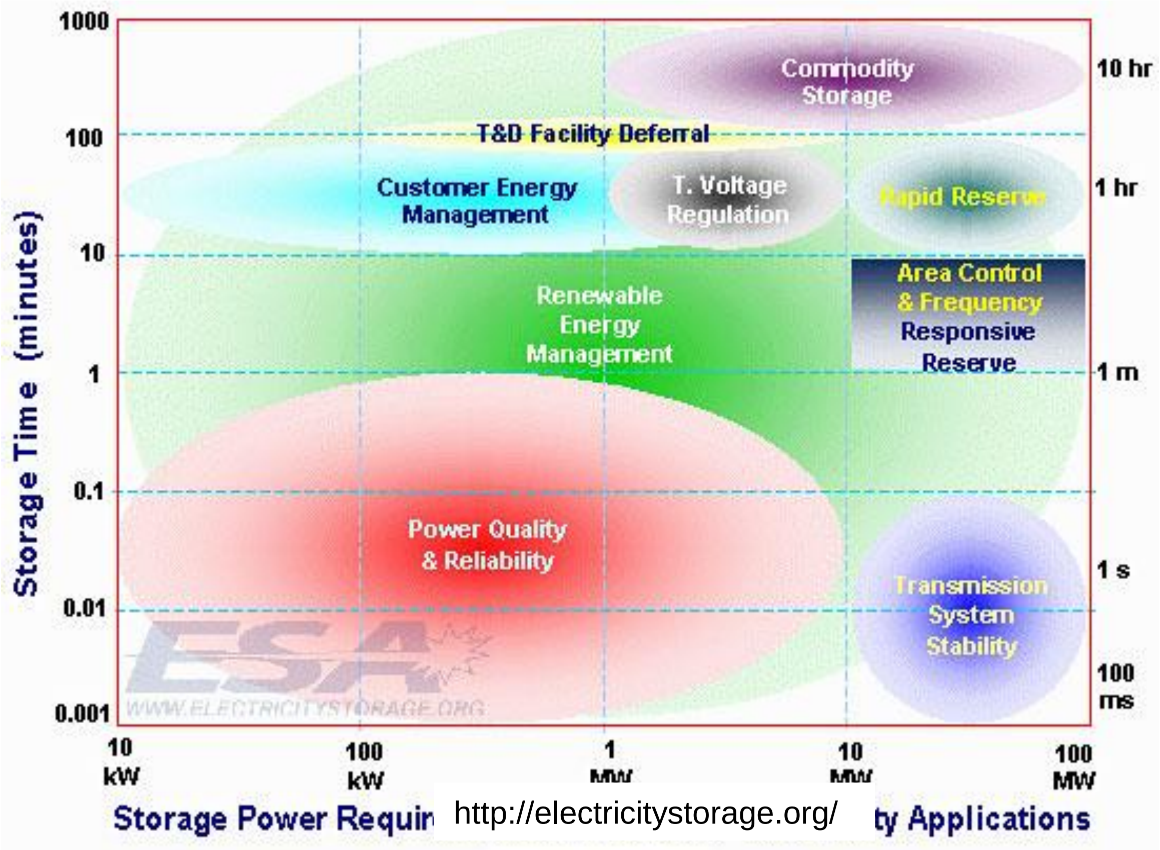
$$2NaCl + Ni \underset{d}{\overset{c}{\rightleftarrows}} NiCl_2 + 2Na \quad E = \sim 2.58\ V$$

- Operated at 300~350^oC
- High efficiency, up to >90%
- Capable of hours of discharge duration
- Quick response
- Up to 16MWhs demonstrated, for SSB



Technology requirements for GRID Storage

- **Energy/power**: depending on applications;
- **Quick response** preferable;
- **Discharge duration**: seconds ~ hours
- **Efficiency**: High, preferable;
- **Life**: >10~15yrs, >5,000 deep cycles, higher for shallow cycles, depending on applications;
- Safety



http://electricitystorage.org/

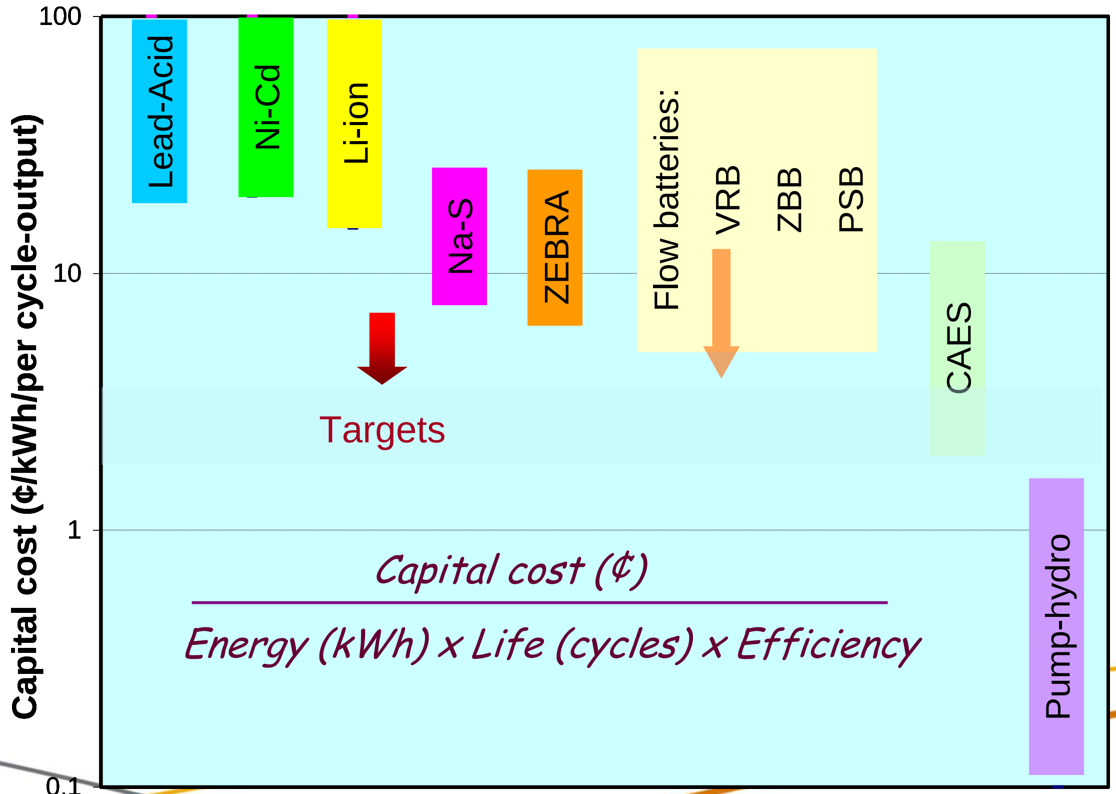
Data from Sandia Report 2002-1314

- **Costs**: low capital cost, life cycle cost, social cost (considering carbon effects)

Pacific Northwest NATIONAL LABORATORY

Economic and technical challenges

- Cost at least 2~3 x higher for broad market penetration
- Better economy reliant on improved reliability, durability, life and efficiency, along with manufacturing
- Require science and technology advancement



Life cycle cost: 4¢/kWh/cycle

Pacific Northwest
NATIONAL LABORATORY

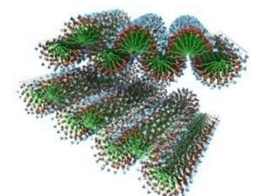
Electrochemical Energy Storage at PNNL

Transformational Materials Design and Synthesis

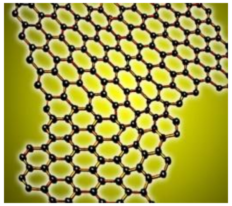
Key Focus:

- Synthesis and assembly of multifunctional nanomaterials
- Establish controlled defect chemistry and architectures
- Optimization of properties that effect transport and storage of charged species.

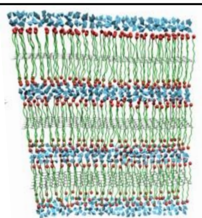
Molecular and Nano-scale Building Blocks



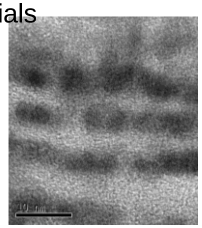
Polymers, metal oxides, surfactants, graphene sheets



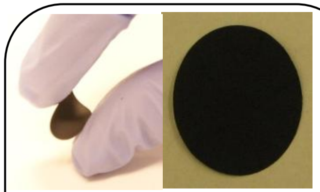
Self-Assembled Superstructures



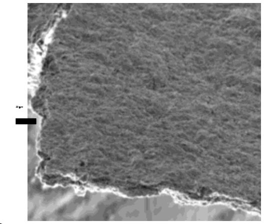
Multi-component nano-composites and nanoporous materials



High Performance Device Components

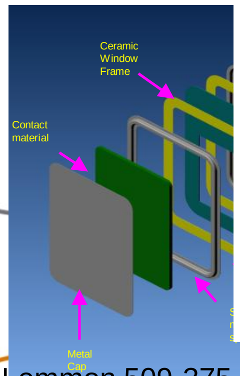


Electrodes for batteries, supercapacitors and sensors

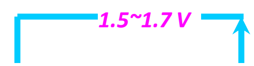


High Power Planar Sodium Metal Halide

Large area planar cell → battery stack



High Performance Lithium Ion



CHEMICAL REVIEWS

REVIEW

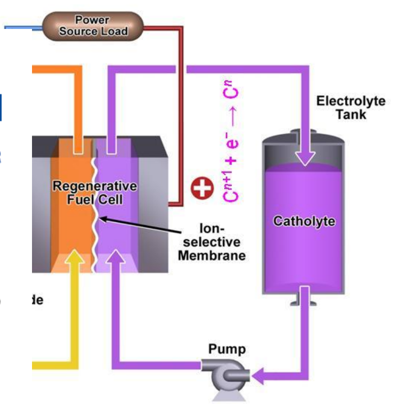
pubs.acs.org/CR

Electrochemical Energy Storage for Green Grid

Zhenguo Yang,* Jianlu Zhang, Michael C. W. Kintner-Meyer, Xiaochuan Lu, Daiwon Choi, John P. Lemmon, and Jun Liu

Pacific Northwest National Laboratory, Richland, Washington 99352, United States

Redox Flow Batteries V based and PV Charging



John P. Lemmon 509-375-6967

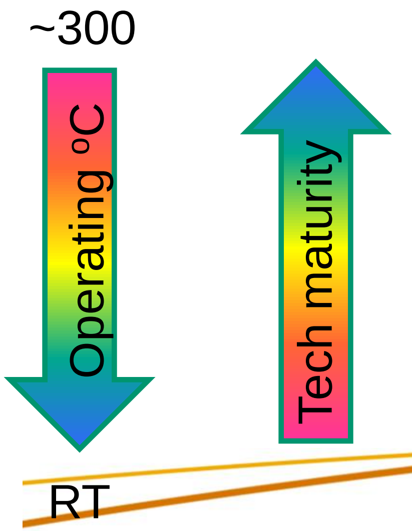
Na-Battery Focus Areas at PNNL

<u>Progression of sodium battery technology</u>

- Gen 1: High Temperature (250-300°C), BASE
    - Modular planar design (flat plate), tunable power and energy.
    - Multi-metal cathode, decrease Ni.
    - Need for better fundamental understanding – additives, mass transport.

- Gen 2: Reduced Temperature (110-250°C),
    - Approach to low cost and higher power density.
    - Na ion conducting membrane.
    - Stable catholyte

- Gen 3: Low Temperature (RT- 90°C),
    - Approach to Na-ion (polymer membrane)
    - Anode materials
    - High energy capacity cathode.



Pacific Northwest
NATIONAL LABORATORY

John P. Lemmon 509-375-6967

Sodium Ion Research Opportunities

	Generation 1 High Temp Planar 250 – 300C	**Generation 2 Medium Temp Planar 110-250C**	**Generation 3 Low Temp RT – 90C**
Application	Stationary	Stationary Light Truck Marine DOD	VT
Chemistry	• $Na\text{-}NiCl_2$ • $Na\text{-}NiFeCl_2$	• Na-Metal Halide • Na-Na organic • Na-Air	• Na-S • Na-Metal oxide • Na-Air
Anode	• Molten Na • BASE wetting agents.	• Molten Na • BASE wetting agents.	• Na Metal • Na Alloy • Na-MS • NaCxF • NaMxOy (Ti, Sn)
Cathode	• Ni-NiCl2(s)/NaAlCl4 • Ni Alloys-NiMClx • Additives	• Mx-MxCl2(sol), IL, Cx • Organic-Na organic	• NaMxOy (Ni,Mn, Co) • NaMPO4 • NaMxFy • Na-organic
Electrolyte	• BASE	• BASE • New SS inorganic • Org-Inorg Nanocomposite	Polymer Membrane-Liq SS inorganic glass

Down-select areas of high value with preliminary performance and cost modeling. Further down-select chance of success using thermodynamic and phase diagram based analysis.

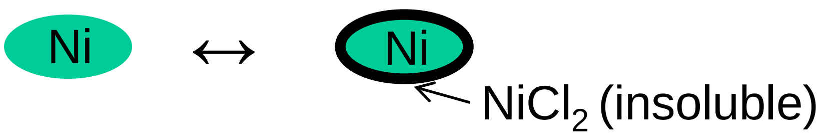
Medium Temperature Na-MH Concepts

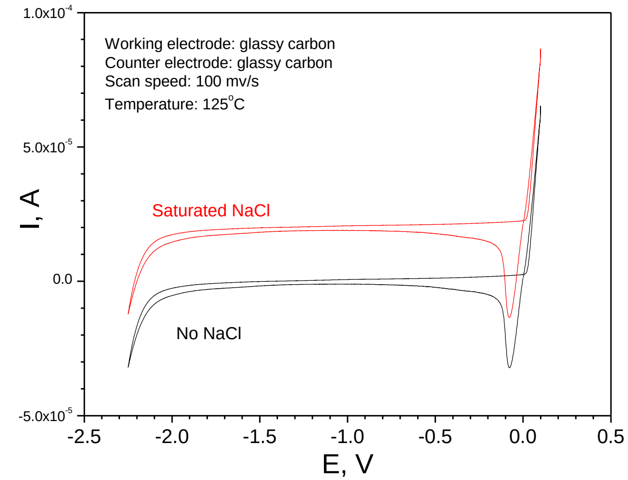
- Goal: Reduce temperature (100-250°C enables lower materials cost, (sealing, cell materials).
- Path: 1) Reduce BASE thickness, 2) Improve catholyte

ZEBRA type chemistry: insoluble MH

$Ni + 2NaCl \rightarrow 2Na + NiCl_2$ (charge)

$NiCl_2 + 2Na \rightarrow 2NaCl + Ni$ (discharge)

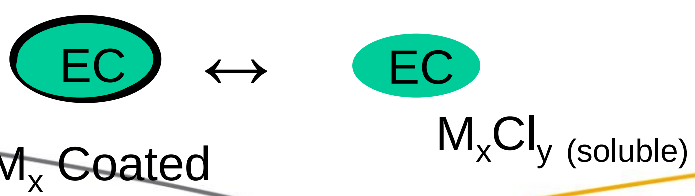


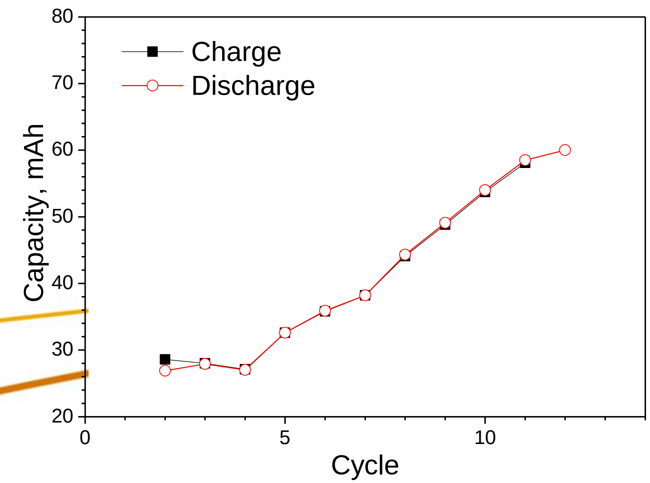


Metal coated chemistry: soluble MH

$EC/M_x + NaCl \rightarrow Na + M_xCl_y + EC$ (c)

$EC + M_xCl_y + Na \rightarrow NaCl + EC/Mx$ (d)



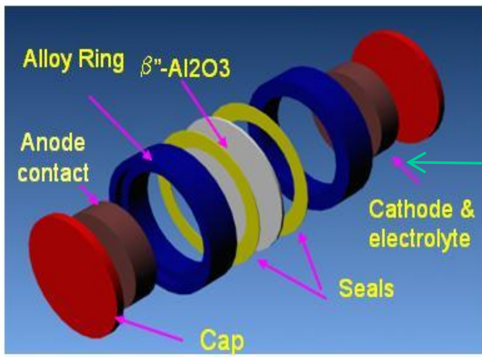


Internal DOE EED LDRD Funded FY2010, J. Lemmon, G. Li and X. Lu

Medium Temperature Na- Air with BASE

Goal: Improve performance, low cost alkali metal – air.
Path: Improve solubility of Na_xO_y products in cathode with higher temperature.

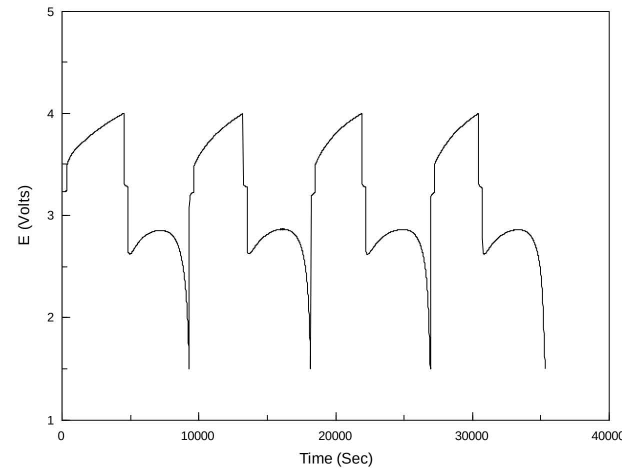
3.0cm^2 Button Cell

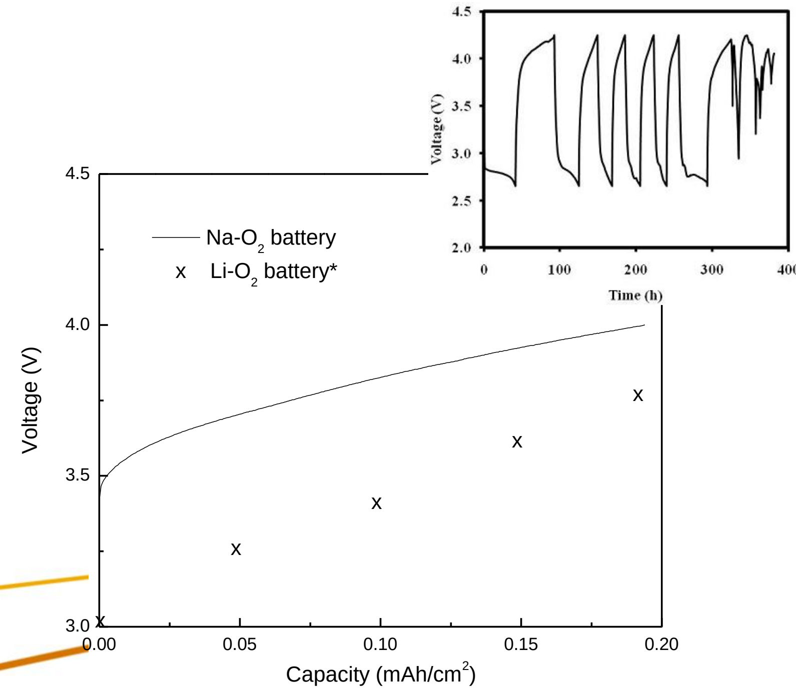


Replace metal cathode with temperature stable air cathode.

<u>Cell Characteristics:</u>
Temperature: 140°C
OCV: 3.2V vs Na
Current: 0.15mA/cm^2.

Na-Air Low rate cycling





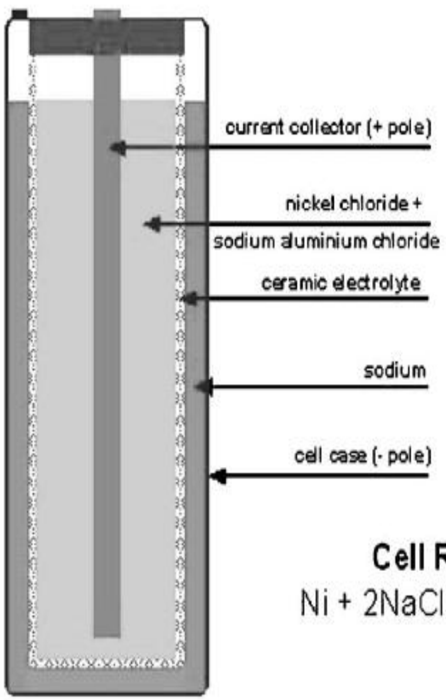
* J. Xiao, et al., J. Power Sources 196 (2011) 5674.

Summary:

- High IR from BASE electrolyte.
- Cycled in air, capacity decreases.
- Overpotential on charge higher than Li.
- Overpotential increase rate lower than Li.

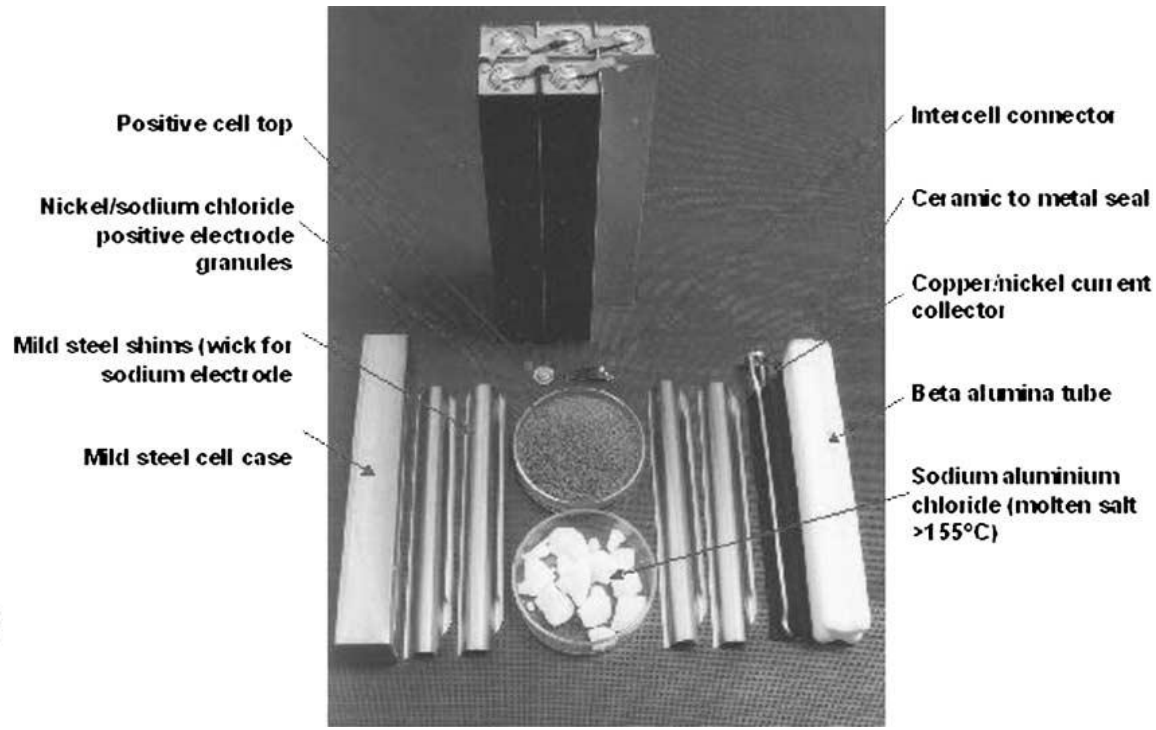
Na–Metal Halide - ZEBRA Battery

Beta Research and Development Ltd.



Cell Reaction

$$Ni + 2NaCl \Leftrightarrow Na + NiCl_2$$



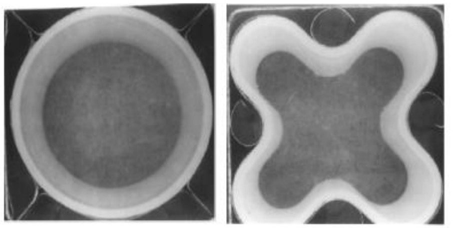
Advantages: High energy density, cycle life, short circuit failure mode, low cost materials, manufactured in discharged state.
Disadvantages: High IR, molten Na, high operating temperature.

Sudworth, J. L. *J. Power Sources,* **100**, 2001, 149-163

Na–Metal Halide - ZEBRA Battery

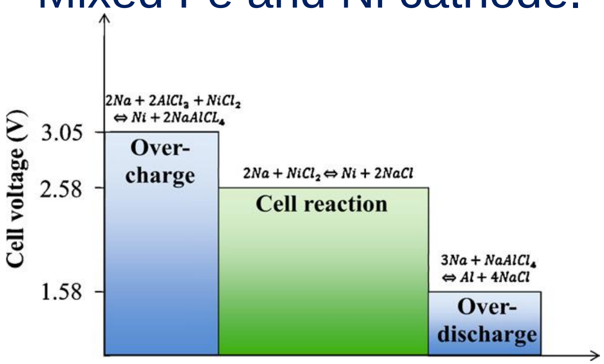
Beta Research and Development Ltd. high power cells.

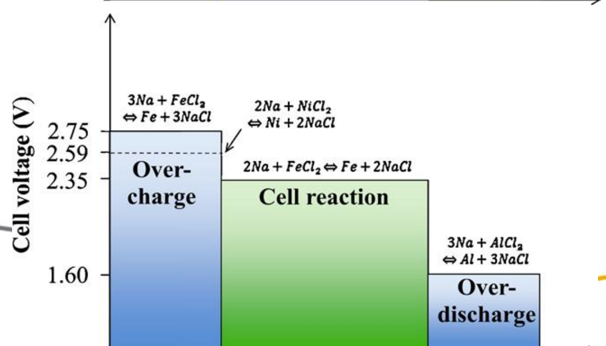
Decrease geometric factor.



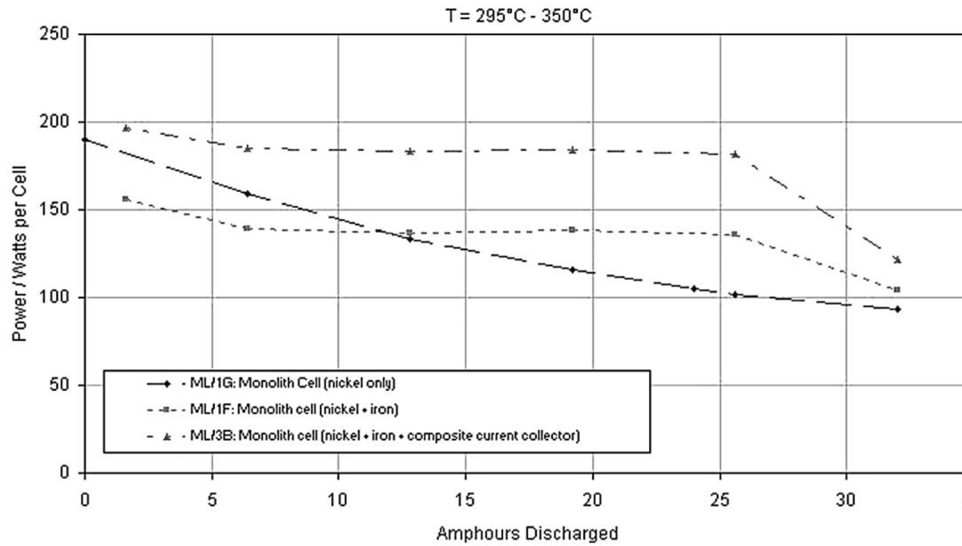
BASE Tubes, (1-2mm)

Mixed Fe and Ni cathode.

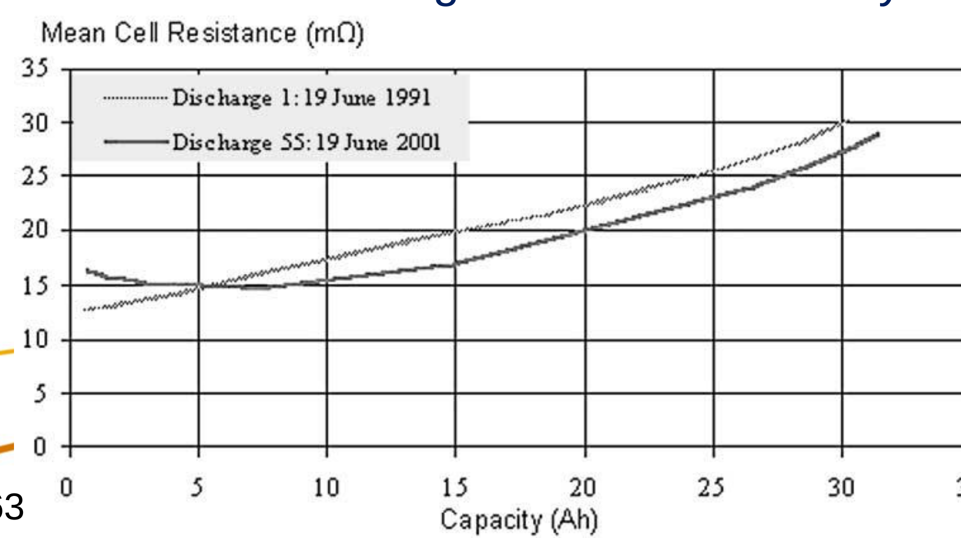




Pulsed power characteristics vs DoD

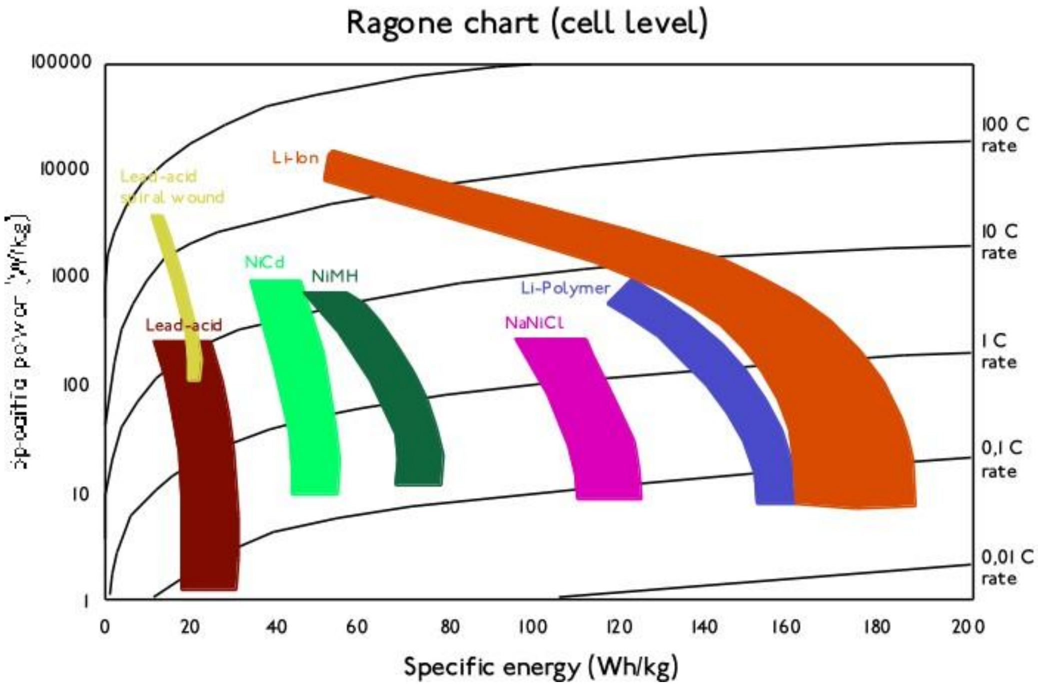


Effects of self discharge and freeze thaw cycles.



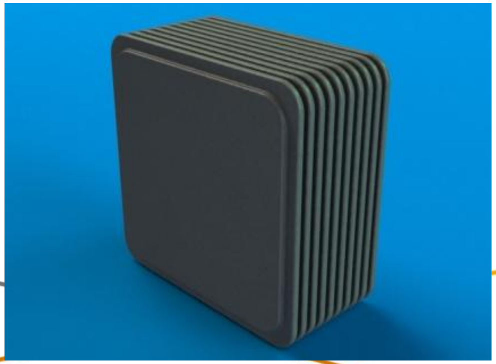
Sudworth, J. L. *J. Power Sources*, **100**, 2001, 149-163

Na-metal halide battery development

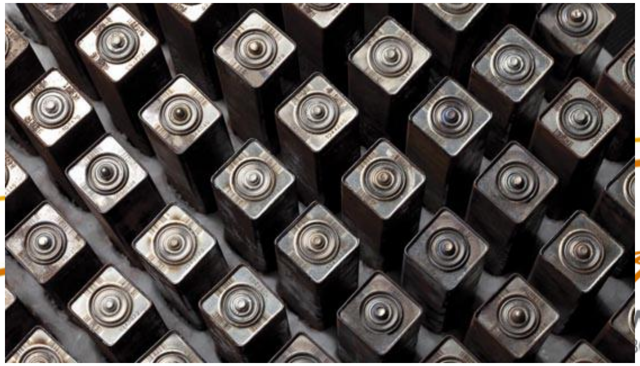


- MESDEA and FZ Sonick (joint venture b/w FIAMM MESDEA) for both mobile and stationary applications

- Eagle Picher developing planar designs

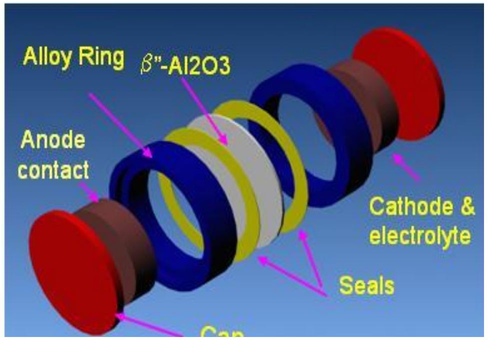


- General electric for locomotive and backup power applications



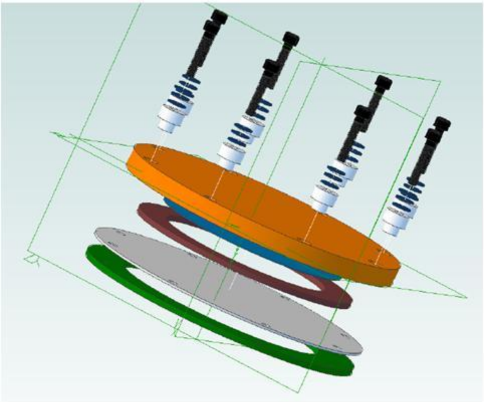
Path to Planar Na Battery

3.0cm^2 Button Cell



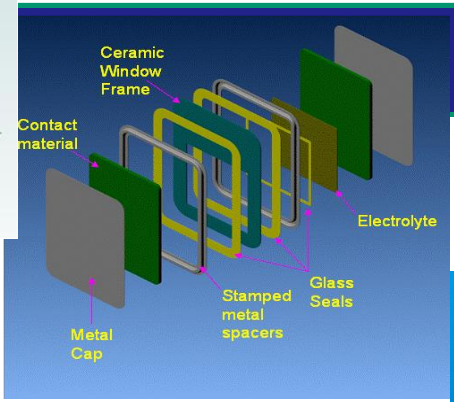
Materials development and performance testing.

64cm^2 XL-Button Cell



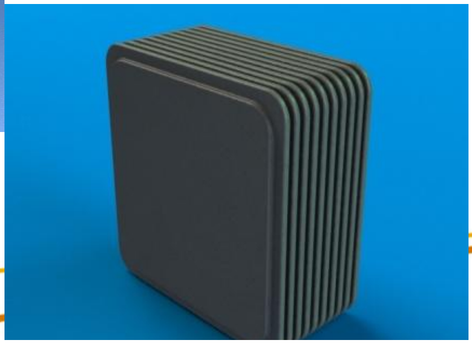
Materials scale-up with large-scale performance and life testing.

100cm^2 Planar Cell



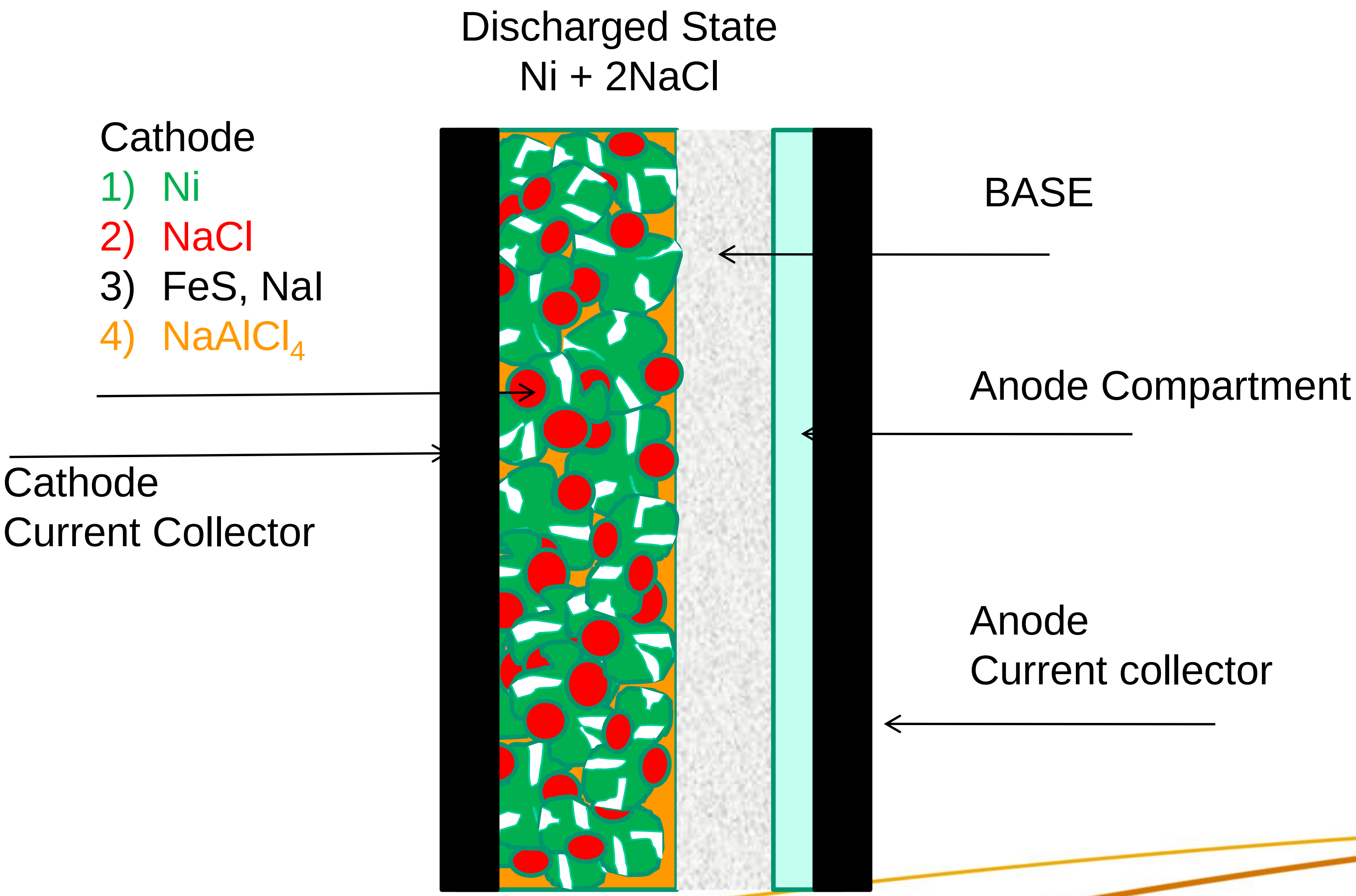
Manufacturing friendly components and fabrication techniques.

200cm^2 Stack



Modular stack design with performance and life testing.

Na-$NiCl_2$ Battery Description



BASE Conversion Process

Mixed region of β and β”
$Na_2O \cdot nAl_2O_3$ (5.33 ≤ n ≤ 8.5).

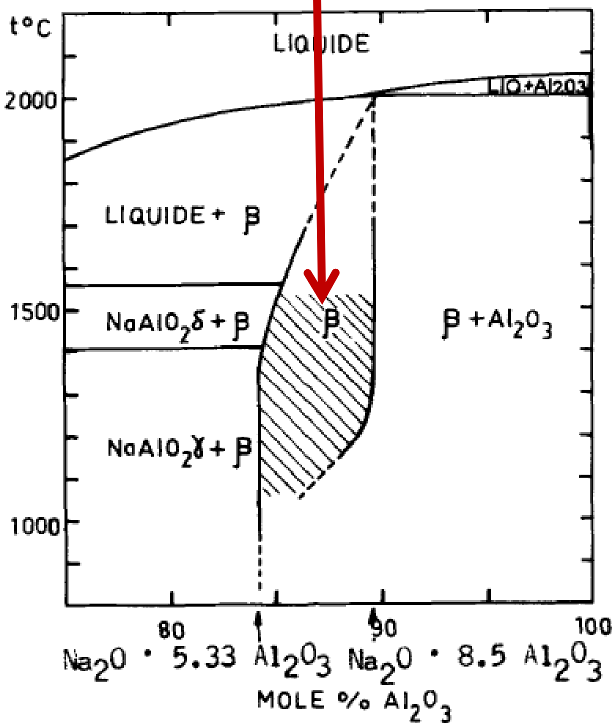
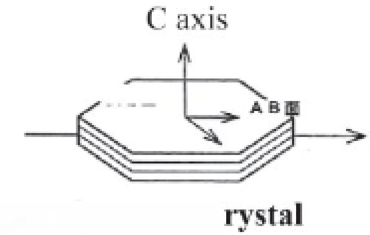
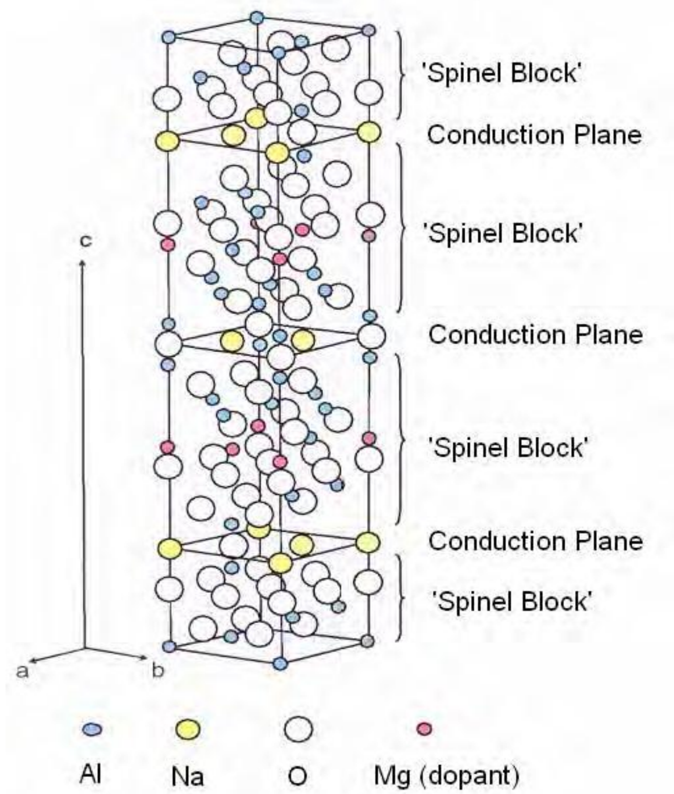


Fig. 1. Existence range of β-alumina. β + β″ coexist in the cross hatched region of the diagram.

Fally, et al JECS 120[10] 1973

β” - phase
$Na_2O \cdot 5.33Al_2O_3$

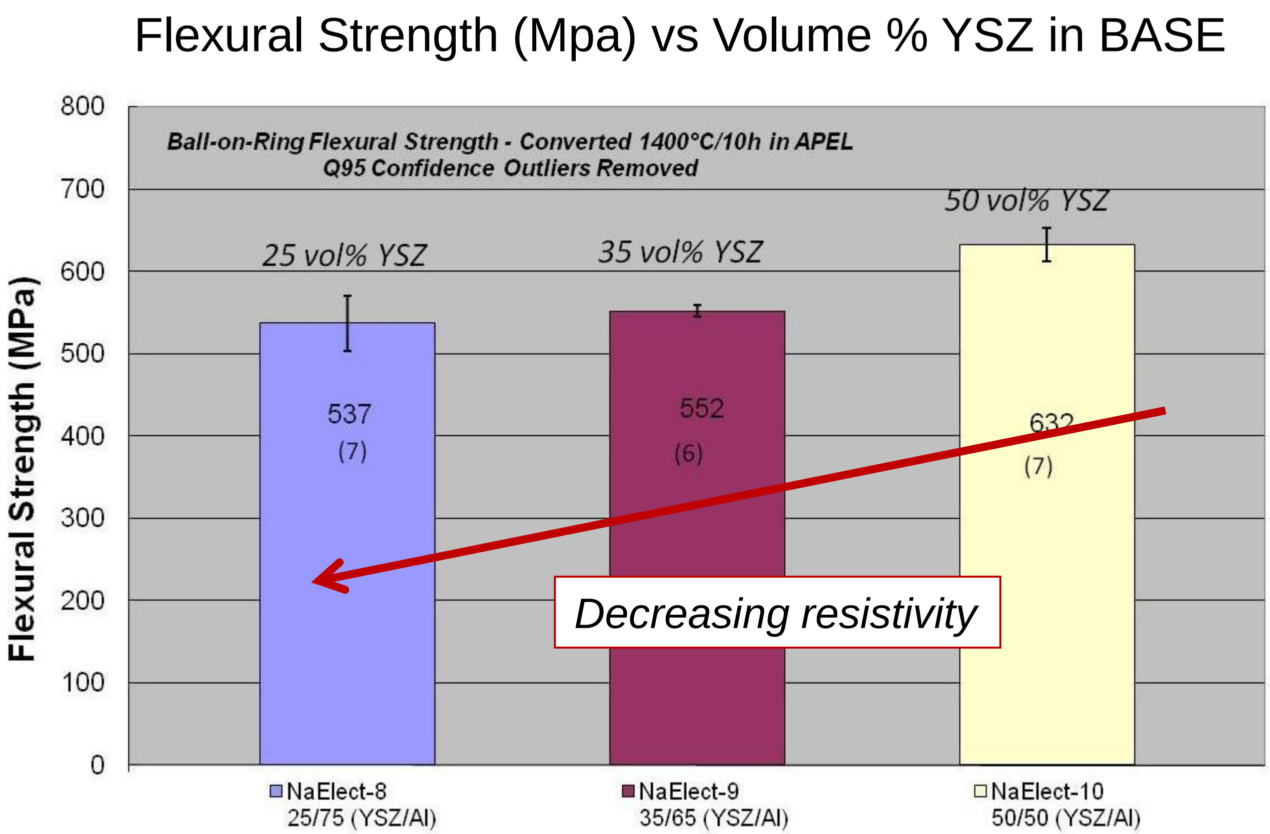


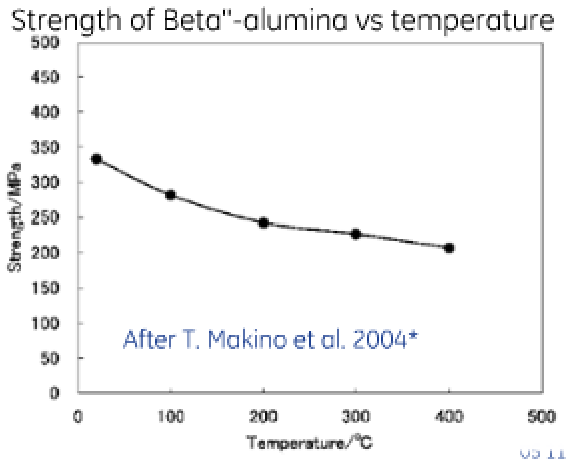


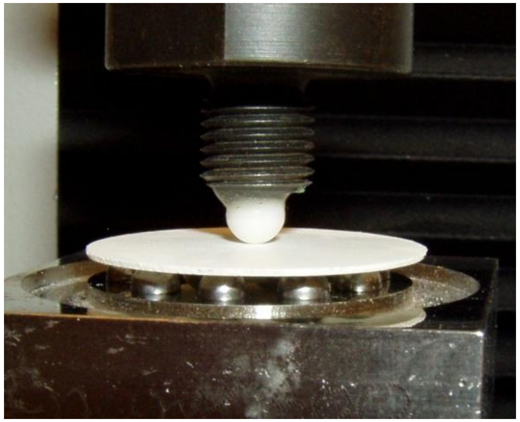
Journal of Ceramic Processing Research. Vol. 11, No. 1, pp. 86~91 (2010)

Complete conversion of $Al_2 0_3$ to BASE is critical to consistent performance. Other factors influencing performance include, grain size, orientation, and density to avoid failure modes.

BASE Strength Properties





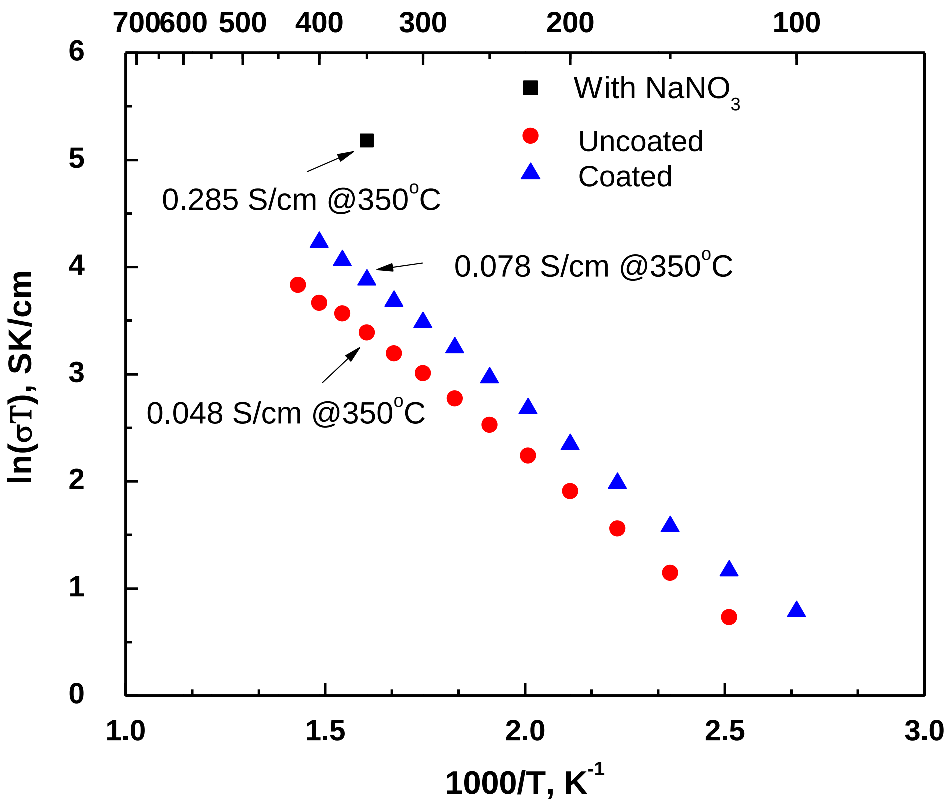


Optimize BASE formulation for strength and conductivity.

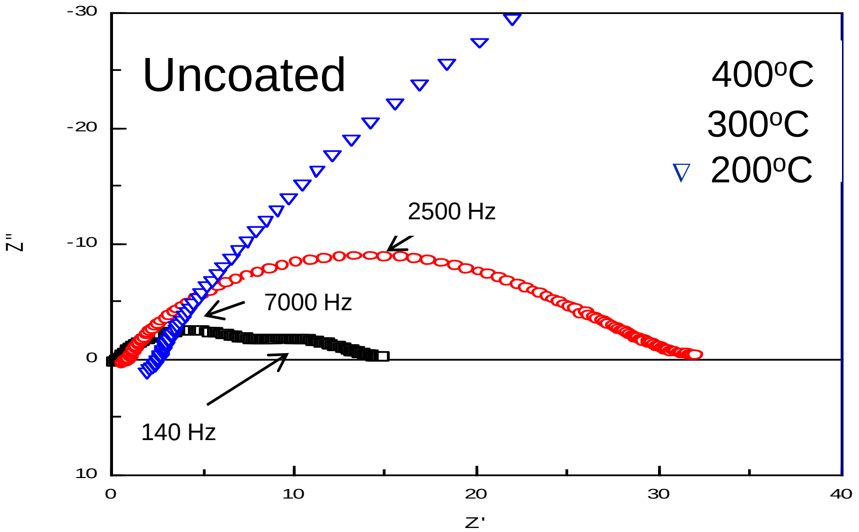
- *Ball on Ring flexural testing on 1.0" diameter converted BASE. 25 to 50% YSZ content.*

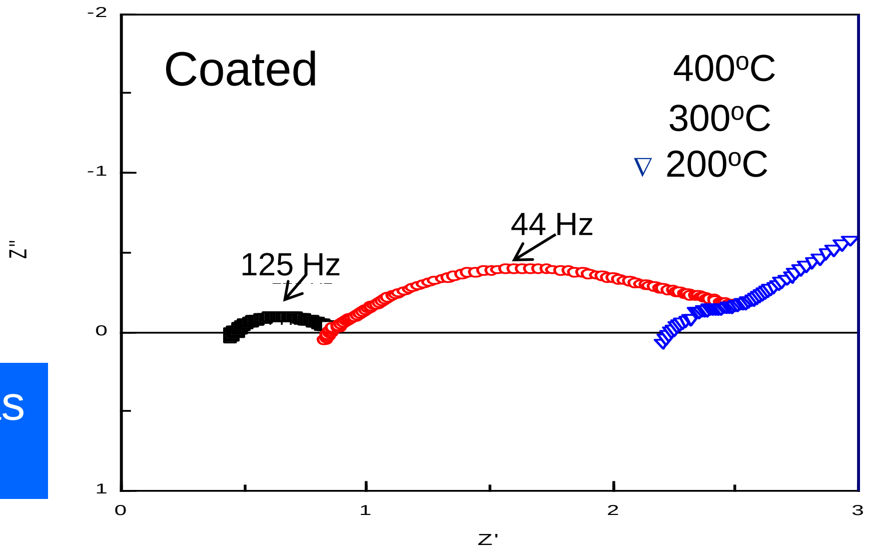
BASE Surface Properties(1mm)

Effect of BASE coating on β"-Al_2O_3 (Ionotec) conductivity at 200mA/cm² in Na/BASE/Na cell.



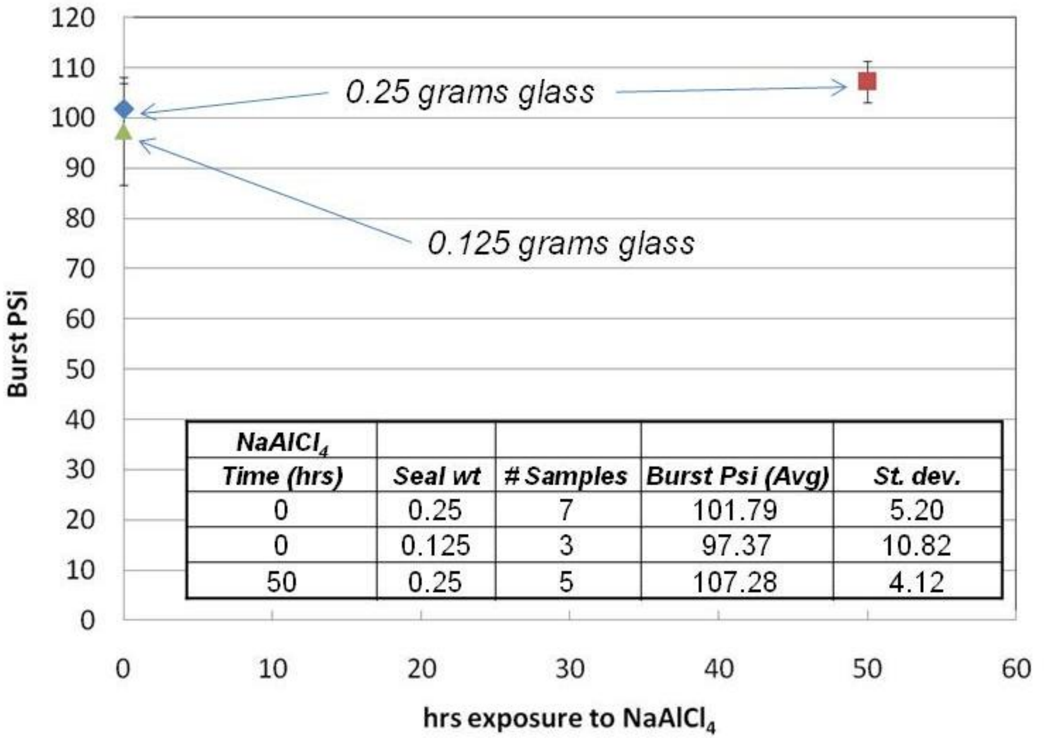
Comparison of interfacial resistance using EIS of Ionotec BASE in Na/BASE/Na Cell





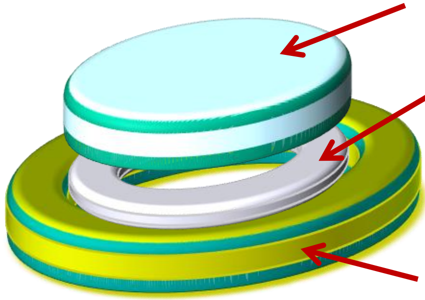
Large decrease in interfacial resistance as a function of surface and coating agents.

BASE/Seal Differential Pressure Test and Chemical Stability

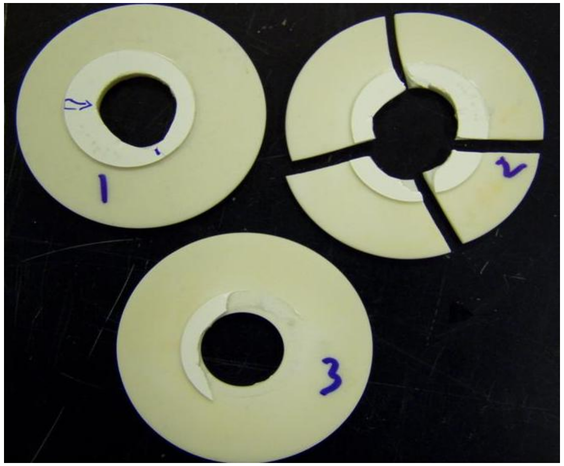


$NaAlCl_4$ Time (hrs)	Seal wt	# Samples	Burst Psi (Avg)	St. dev.
0	0.25	7	101.79	5.20
0	0.125	3	97.37	10.82
50	0.25	5	107.28	4.12

Schematic of pressure sample assembly

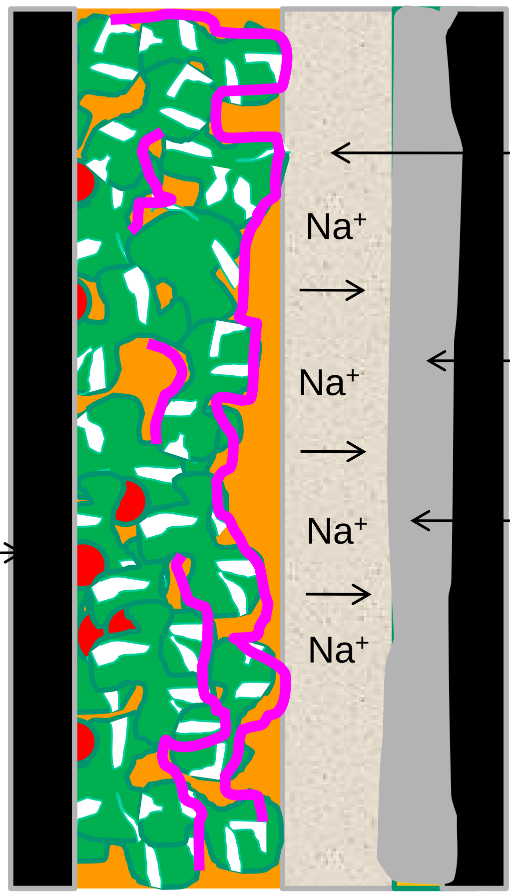


Failure Modes



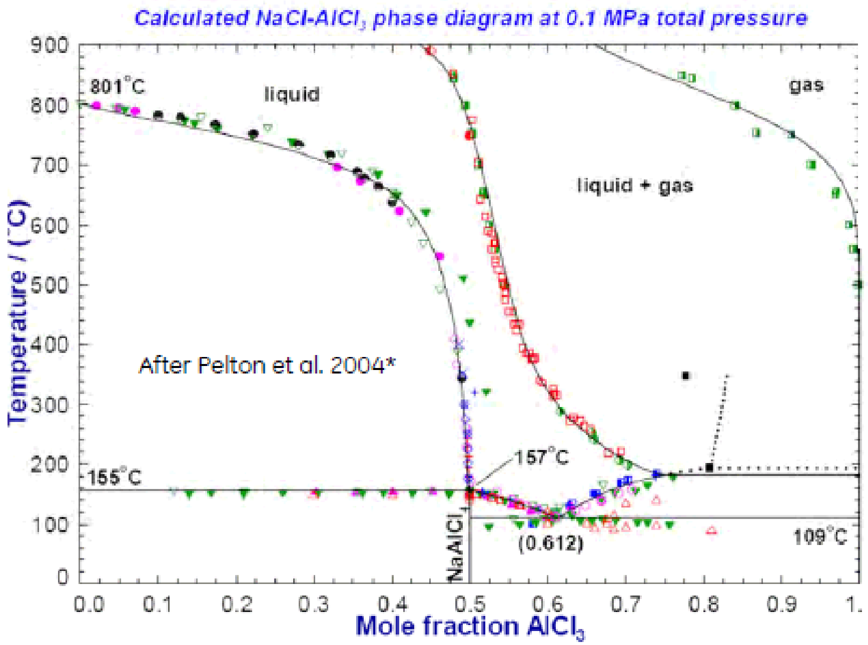
Differential pressure in cell can reach 2 atm on cycling. Current seal holds 6atm DP, with only one failure at the seal. Larger cells use current collector as support structure.

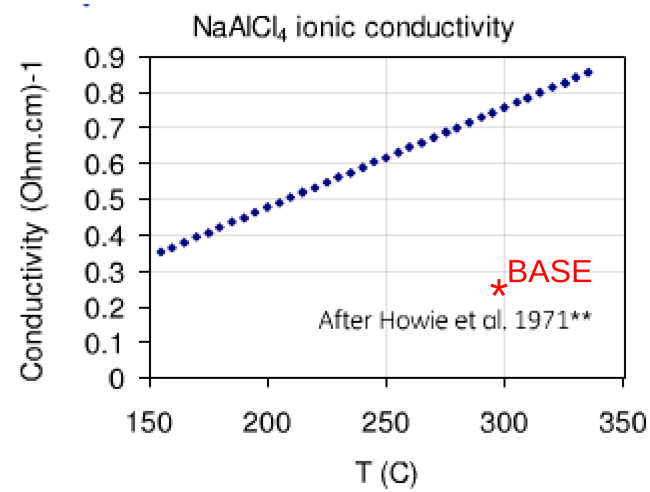
$Na\text{-}NiCl_2$ Battery Description

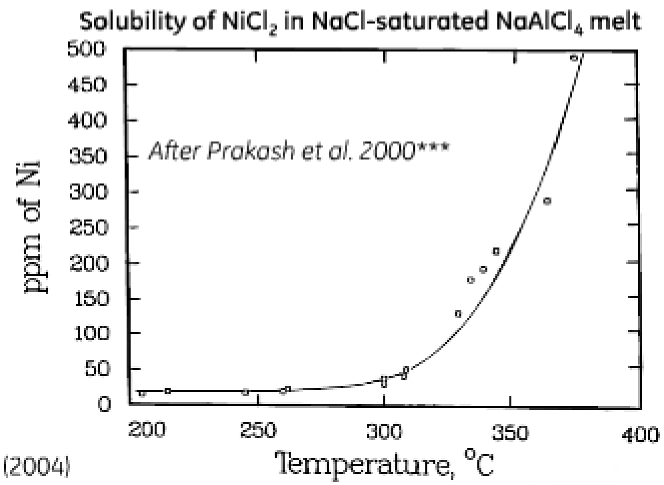


- R increase as SOC as $NiCl_2$ deposits.
- Accessing NaCl deep in the cell becomes more difficult.
- Avoid over charging, melt turns acidic and $NiCl_2$ will dissolve.

Secondary Electrolyte ($NaAlCl_4$) Properties







Basic

- ($NiCl_4^{2-}$) formation.

Solubility increases w/ temperature swings > 320°C, renders Ni electrochemically inaccessible.

Acidic

- Ni^{2+} increased solubility
- Localized acidic areas

during high pulse power, Ni^{2+} detrimental to BASE

(2004)
86 (1971)

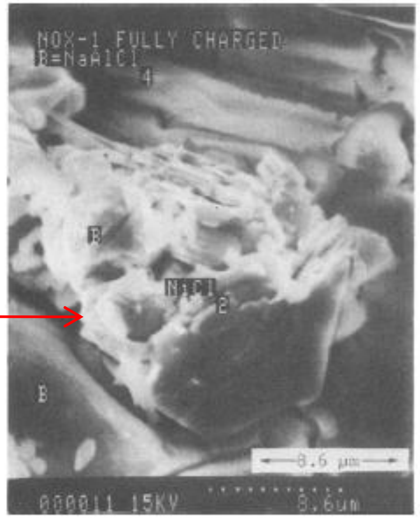
* C. Robelin et al. J. Chem. Therm. 36, 683 (2004)
** Howie et al J. Inorg. Nucl. Chem., 33, 3686 (1971)
*** J.Prakash et al., J. Electrochem. Soc., 147502 (2000)

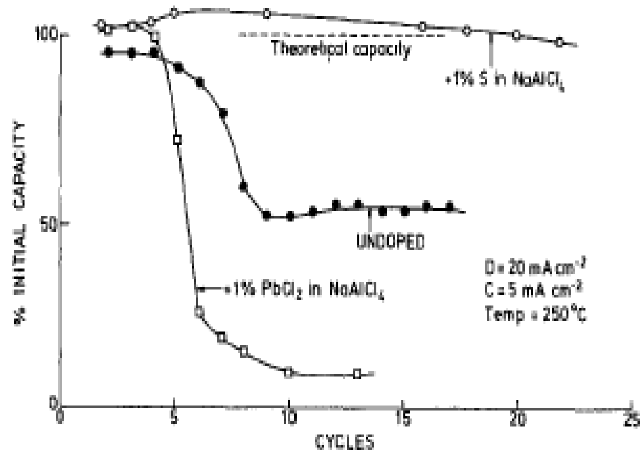
Non equilibrium conditions in melt affects performance and cycle life.

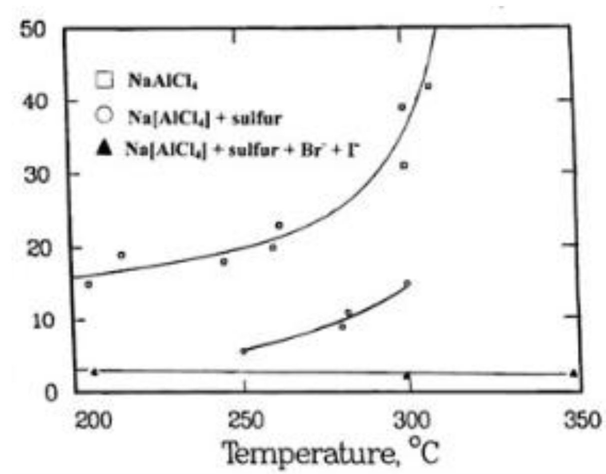
Cathode and SE ($NaAlCl_4$) Sulfur Additives

Role of S additives in charged state:

$NiCl_2$/Ni





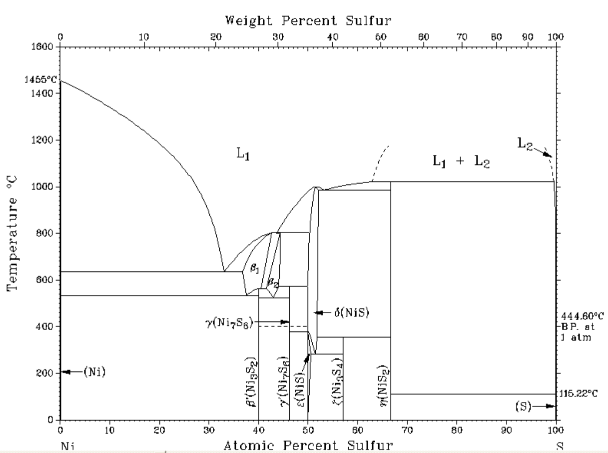


J. Electrochem. Soc., Vol. 136, No. 5, May 1989

Effect of S additive on cell capacity and $NiCl_2$ solubility in basic SE

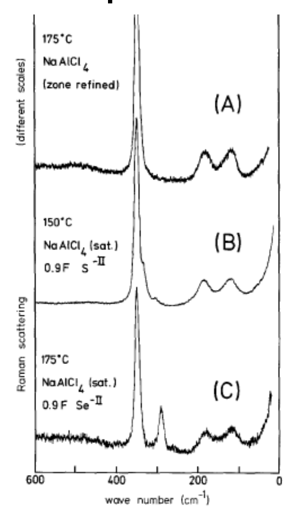
Sulfur distribution in cathode:

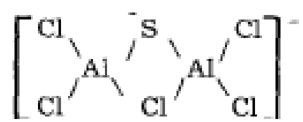
A) Reaction with Ni



J. Electrochem. Soc., Vol. 140, No. 12, December 1993

B) Complex formation





C) Electrochemical

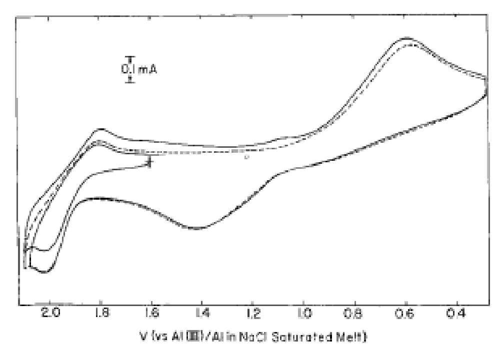
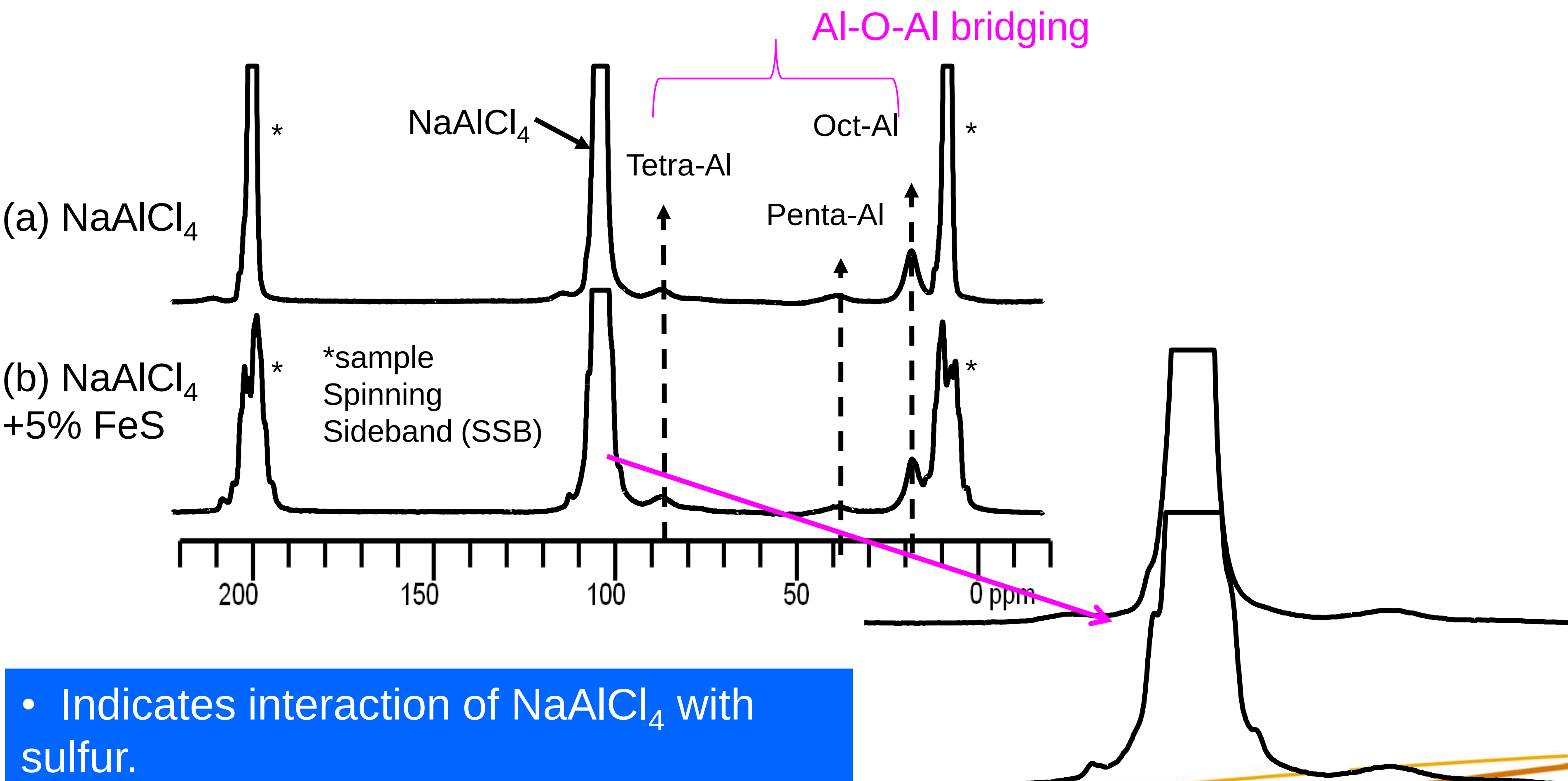


Fig. 2. Cyclic voltammogram at a glassy carbon electrode (area 0.07 cm^2) in a 1.8×10^{-2} molal sulfur solution in NaCl-saturated melt at 175°C. Scan rate 0.1 V-sec^{-1}. Potentials vs. Al(III)/Al reference electrode in NaCl-saturated melt.

Cathode and SE ($NaAlCl_4$) Sulfur Additives

Preliminary Results: Ultra-high field ^{27}Al MAS NMR at PNNL

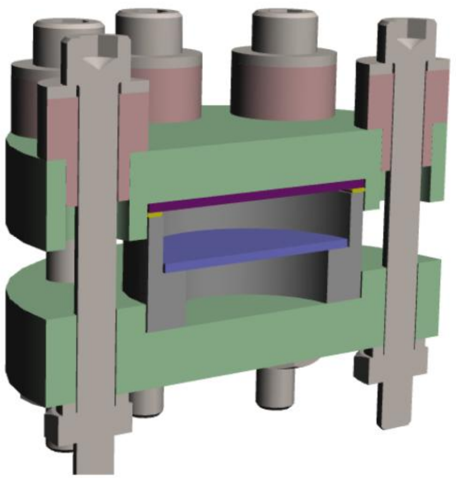


- Indicates interaction of $NaAlCl_4$ with sulfur.
- Building high temperature cell with cycling capability.

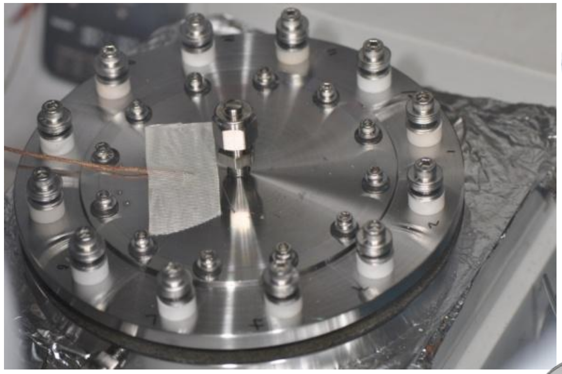
Cell Work Flow and Testing

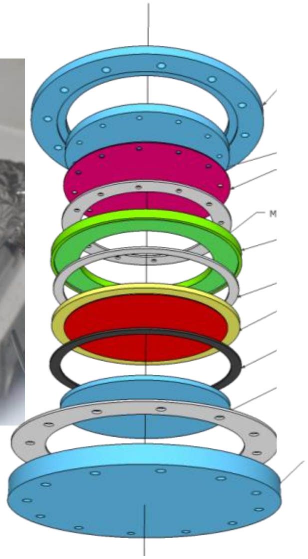
Granule formulation → Ni, NaCl, Additives → Infiltrate

3cm^2 Research Cell (16 test stands)



64cm^2 Scale-up Cell 4 Test stands





High power charging remains challenging due to small voltage window and increased resistance as function of SOC.

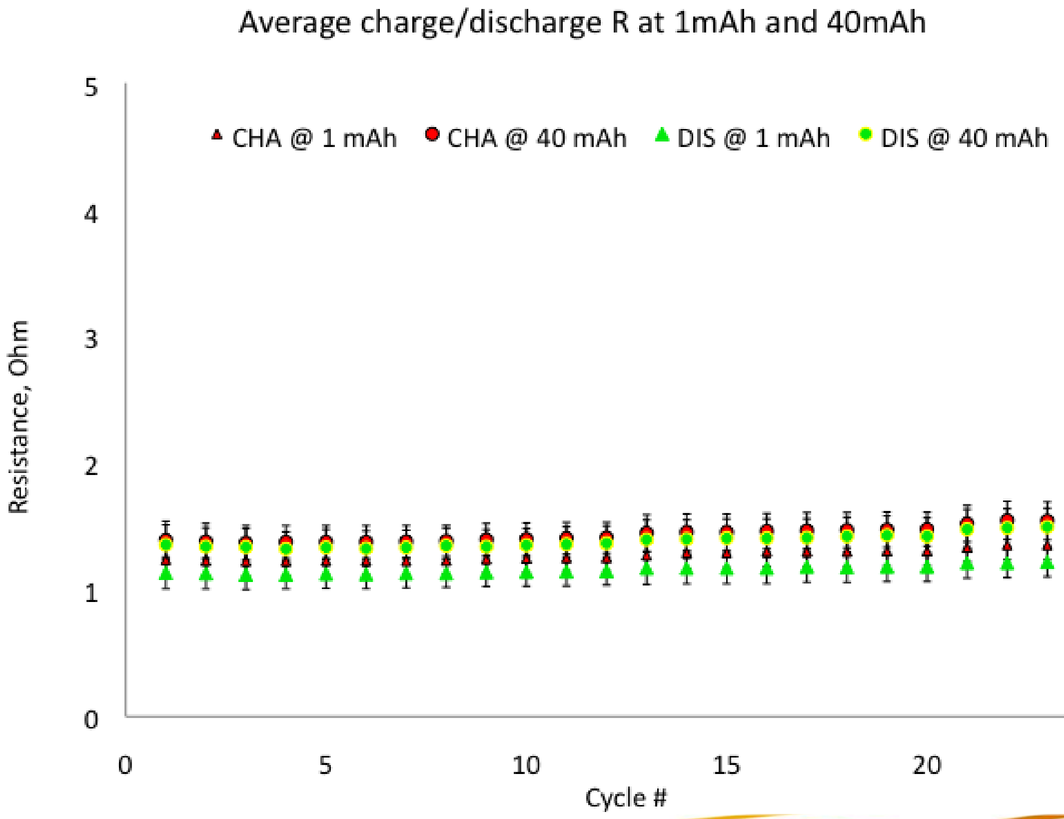
Na-Ni/$NiCl_2$ 3cm^2 Cell Reproducibility

<u>150 Whr at 1C at 280°C</u>

• Calculated from 3 replicate cells.

• Minimum resistance is 1 Ohm due to BASE only.

• Maximum resistance before 3.0V cutoff is 4.5 Ohm.

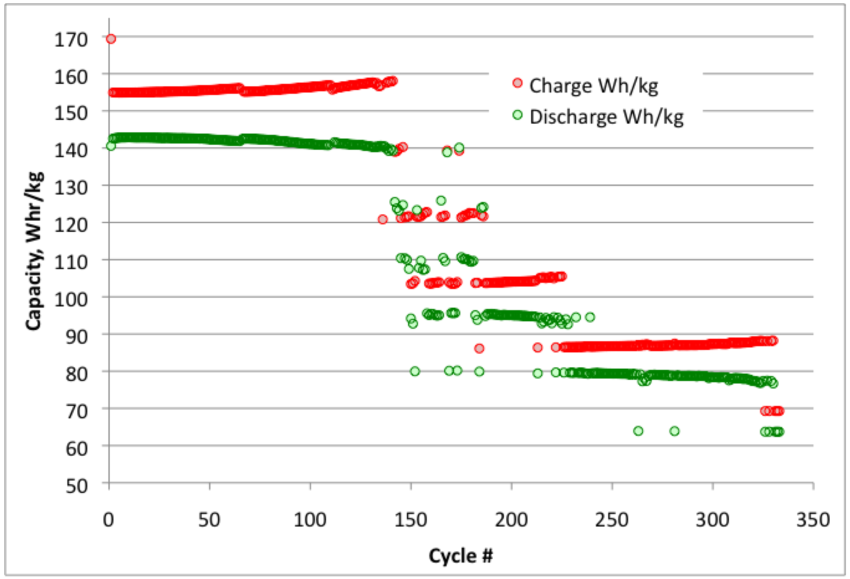


Pacific Northwest NATIONAL LABORATORY

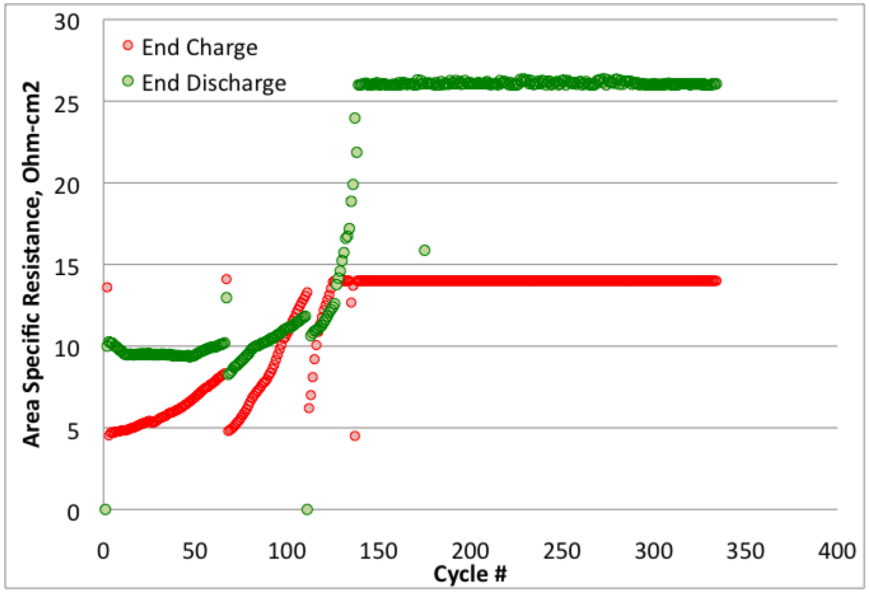
Na-Ni/$NiCl_2$ $3cm^2$ Cell Performance

Cycle Conditions: 150Whr/kg (active cathode material) at 1C rate at 280°C

Whr/kg vs Cycles, (170mAhr cell)



ASR vs Cycles, (170mAhr cell)



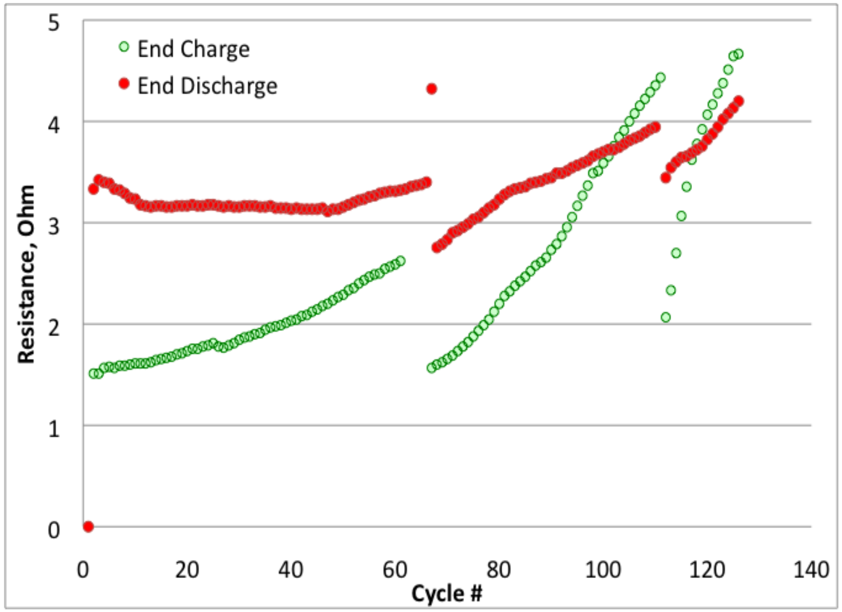
Resistance rise at end of charge dominates overall resistance rise.

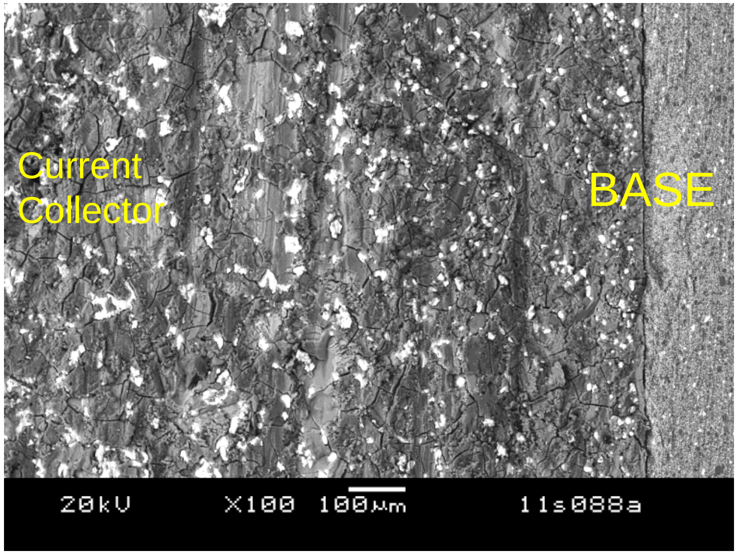
- End of charge → $NiCl_2$
- Rising resistance →Loss of electron percolation path.
- End of discharge resistance increases later cycles.

Na-Ni/$NiCl_2$ 3cm^2 Cell Tear Down

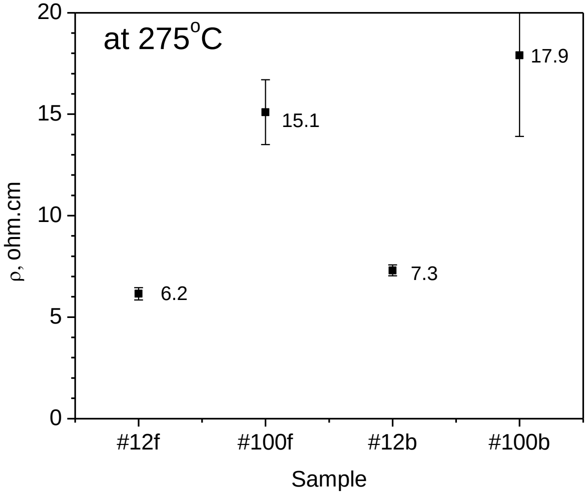
Cycle Conditions: 150Whr/kg (active cathode material) at 1C rate at 280°C

Resistance vs Cycles, (170mAhr cell)





Resistance vs Ni size

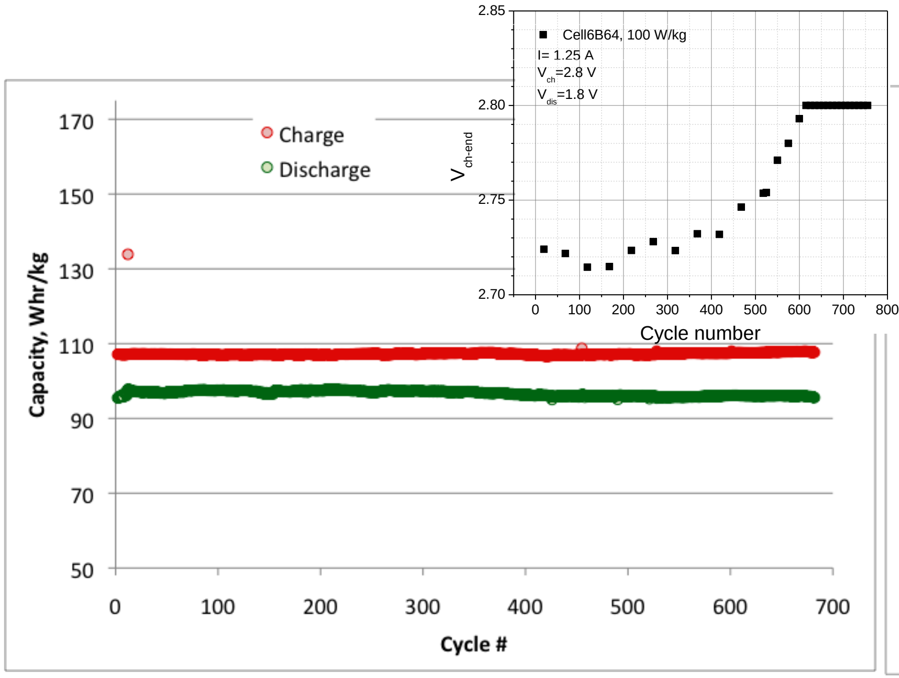


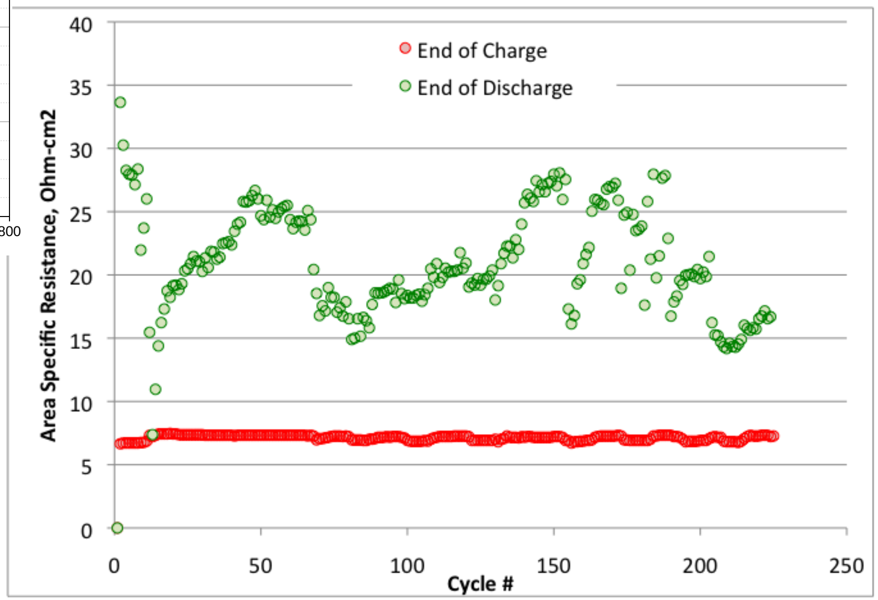
Probable cause for R increase

- Poor distribution of S additive.
- Decreased Ni granule size.
- Ni migration from BASE

Na-Ni/$NiCl_2$ 64cm^2 Cell Performance

Cycle Conditions: 100Whr/kg (active cathode material) at 1C rate at 280°C

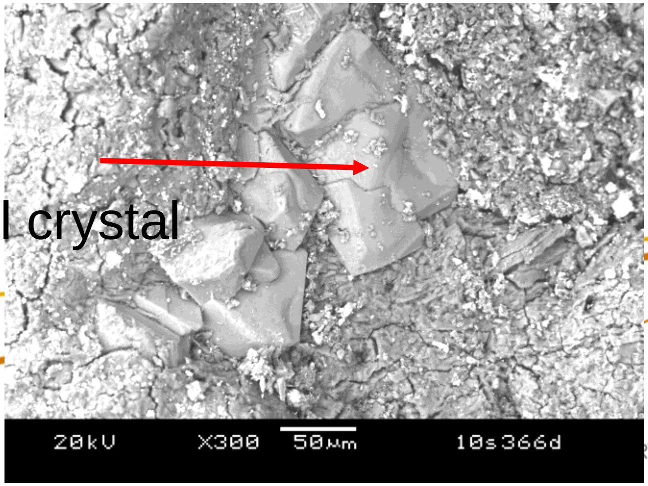




Performance analysis:

- For charging, larger amount of material, distribution of S additive.
- Decreased current density.
- NaCl grain grow effects discharge R.

NaCl crystal



Summary

- Planar configuration offers versatile power and energy cell design.
- ZrO_2 doped BASE lowers conversion temperature, improves strength.
- Reproducible BASE conductivity, however decrease by 3x compared to undoped BASE.
- 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 150Wh/kg at 1C rate, for baseline chemistry in 3cm^2 cells. Developing new chemistry and additive approach to increase cycle life.
- Over 600 cycles at 100Wh/kg at 1C rate at 280C$^\circ$ for 64cm^2 cells.
- Developing 200cm^2 cell, with 20-30Ahr capacity.
- Developing integrated triple cell mini-stack.

Pacific Northwest NATIONAL LABORATORY