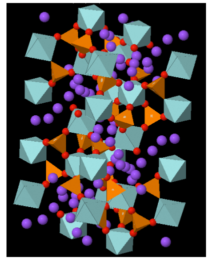

Sodium-Based Battery Development

SAND2013-8878C

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Sodium-based batteries

- Purpose
  - Demonstrate a family of sodium-based battery chemistries
    - sodium-iodine, sodium-bromine, sodium-air, sodium insertion, sodium-metal, etc
- Goals
  - reduce the cost of power and energy to values consistent with large-scale application needs, e.g. load leveling, frequency regulation, UPS, etc.
    - cost of energy goal: < 100 $/kWh
- Multi-organizational, multidisciplinary team encompassing both science and engineering
  - Sandia National Laboratories
  - Ceramatec
    - CoorsTek
  - Colorado School of Mines
  - University of Maryland
- Additional collaborations
  - Boulder Ionics
  - SK Innovation

Program is Predicated on the use of:

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NaSICON

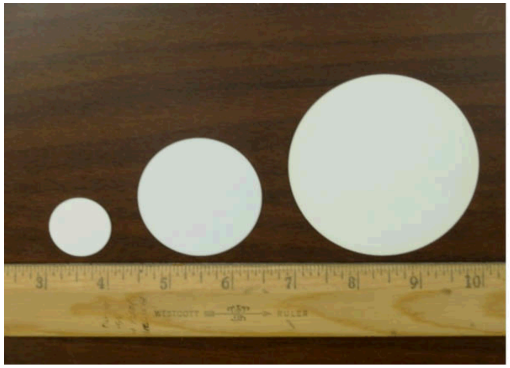
- Sodium Super-Ionic Conductor
  - Solid ceramic separator/electrolyte allows physical separation of anodic and cathodic compartments
    - eliminates cross-over, engenders use of wide range of cathodes
    - stable against molten sodium anode (sodium melts at 98 C)
    - high conductivity at low temperature
    - manufacturing demonstrated
      - variety of structures can/have been made, including plates, tubes, supported membranes, etc
- Near-Term Objectives
  - demonstrate behavior in laboratory prototypes
  - utilize advanced *materials* diagnostics & and development to understand behavior and improve performance using laboratory prototypes
  - develop large-scale conceptual design

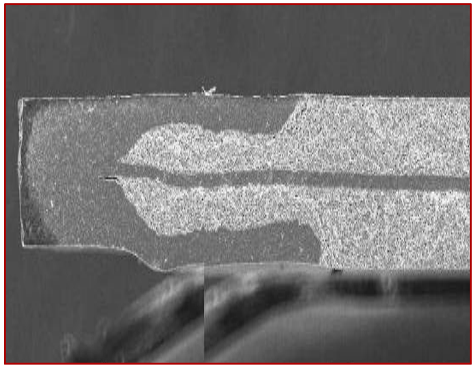
Sodium-Iodine Cell Chemistry

- Sodium metal anode
  - low cost ($2500/mt, 0.002 $/Ah)
  - high energy content (1.17 Ah/g & 1.14 Ah/cm^3)
  - highly reducing
- Iodine cathode (I_2)
  - low cost ($8000/mt, 0.038 $/Ah)
  - modest energy content (0.211 Ah/g & 1.04 Ah/cm^3)
  - > 3 V per cell when coupled with sodium
    - 1/3 fewer cells compared to NaS
- moderate temp – 120 C
  - faster kinetics – i.e. higher power

Cell Chemistry and Expected Voltages	
Anodic Reaction	Voltage vs NHE
$Na \Leftrightarrow Na^+ + e^-$	-2.71 V
Cathodic Reaction	
$I_2 + 2e^- \Leftrightarrow 2I^-$	0.54 V
Full Balanced Cell	Est. Cell Voltage
$2Na^+ + 2I^- \Leftrightarrow 2Na + I_2$	3.25 V

Ceramic is commercialized



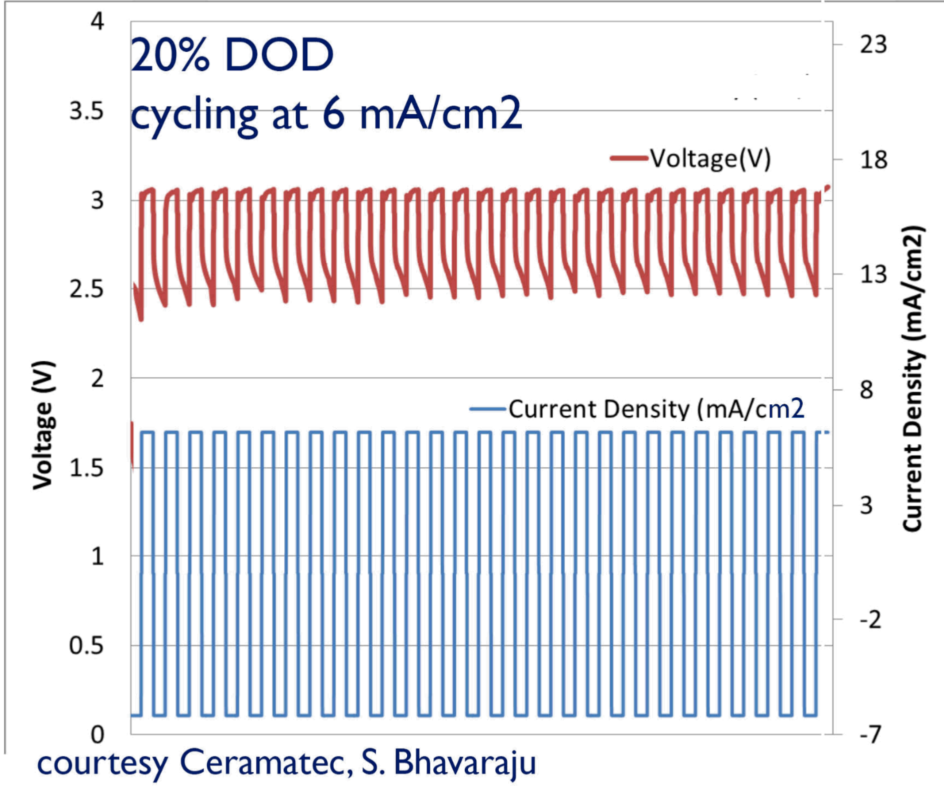


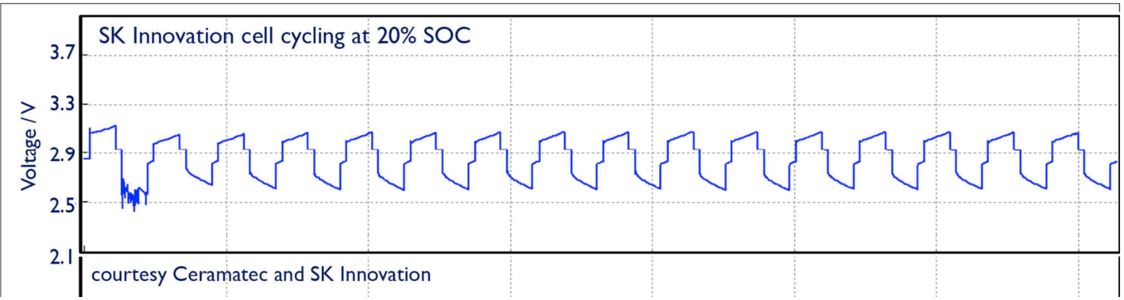
Cell Performance

- Cell Cycling by Ceramatec and SK Innovation
  - Temperature = 120 ˚C
  - Anode: molten Na
  - Cathode: 25 wt.% NaI in organic solvent + 0.5 moles of I_2 per mole NaI
  - Current densities: 6 mA/cm^2

- Notice that cell does not cycle at 3.25 V

- determined that other iodide species is the active cathode species and NOT iodine. This results in a lower cell voltage

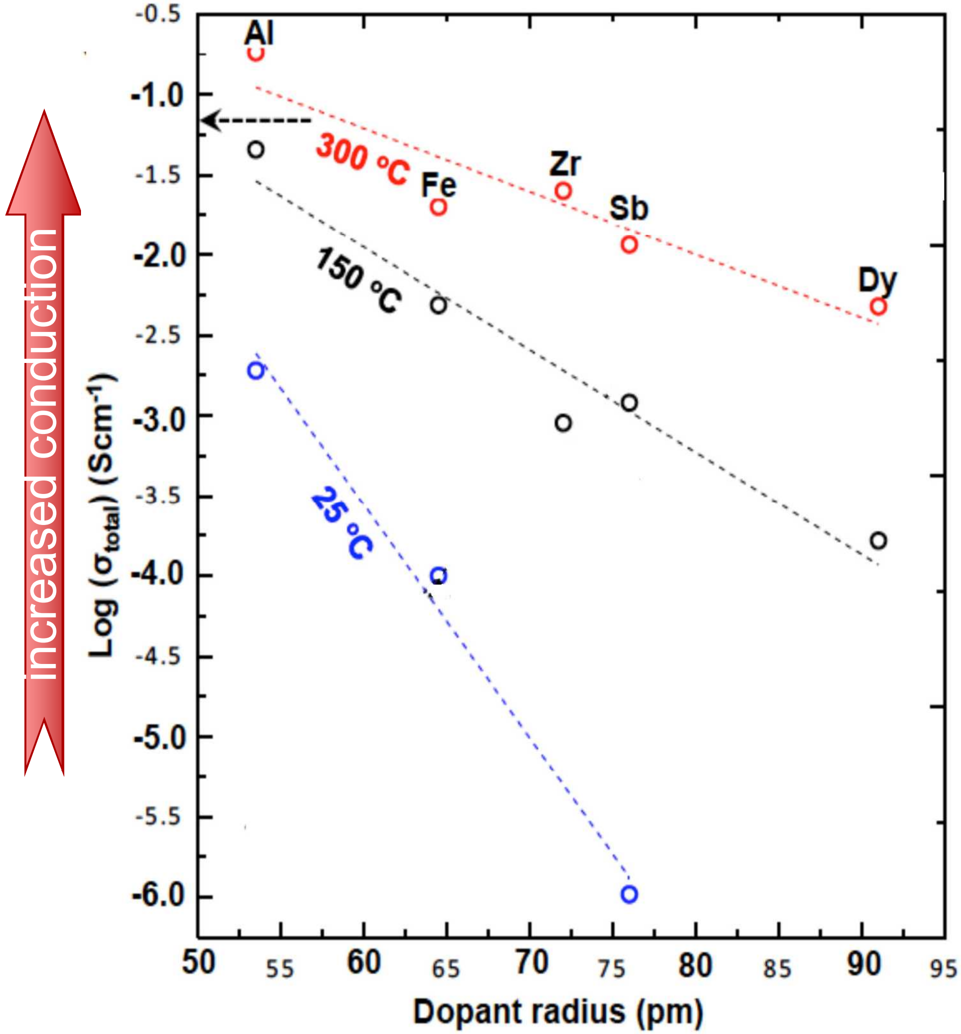




SK Innovation >250 20% SOC cycles and 80 % efficiencies

Improved NaSICON

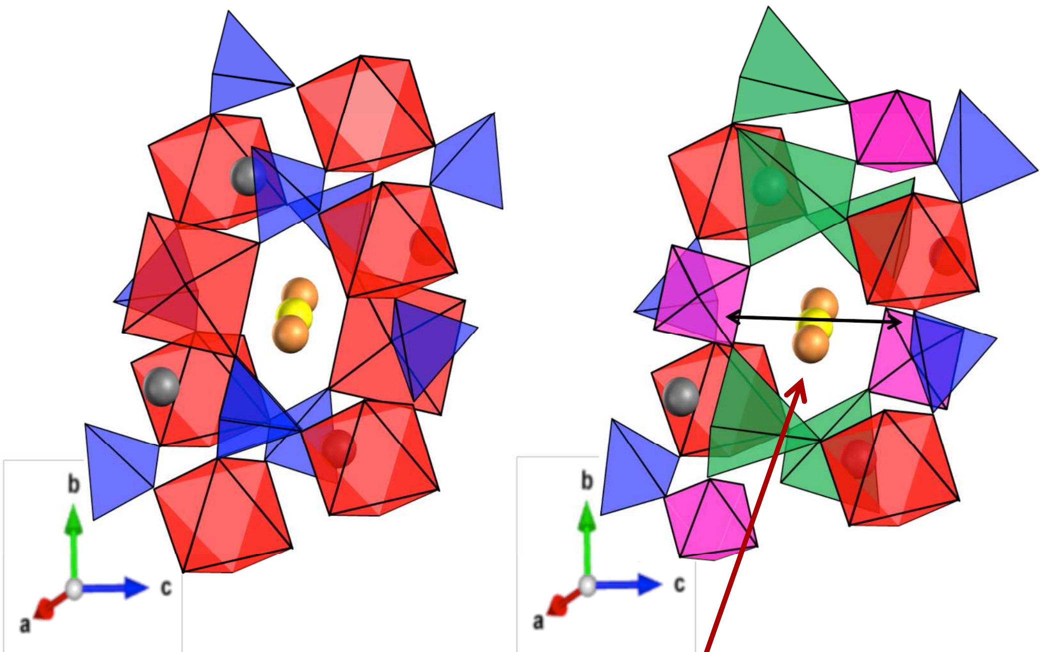
- Higher Conductivity NaSICON can to improved battery performance
- Toward this end, we have initiated work on improving NaSICON conductivity.
  - Have prepared a series of doped materials based on the belief that the conduction channels could be enlarged through selective doping of the lattice
- Notice that the conductivity is inversely proportional to the dopant radius, with smaller elements exhibiting superior behavior



We have developed a doped NaSICON whose conductivity rivals that of liquid organic electrolytes

Improved Nasicon

Smaller radii dopant, accommodates expansion of adjacent tetrahedral sites, by extended Si-O or P-O bond lengths, resulting in more open local structure for Na^+ conduction path.



We developed a new Na^+ solid electrolyte: $Na_4ZrAlSi_2PO_{12}$

- Increased room temperature conductivity 3 orders of magnitude relative to our baseline NaSICON
- High Na^+ conductivity: $1.9x10^{-3}$ S-cm^{-1} @ room temperature
- Matching that of liquid organic electrolytes

larger opening in doped material

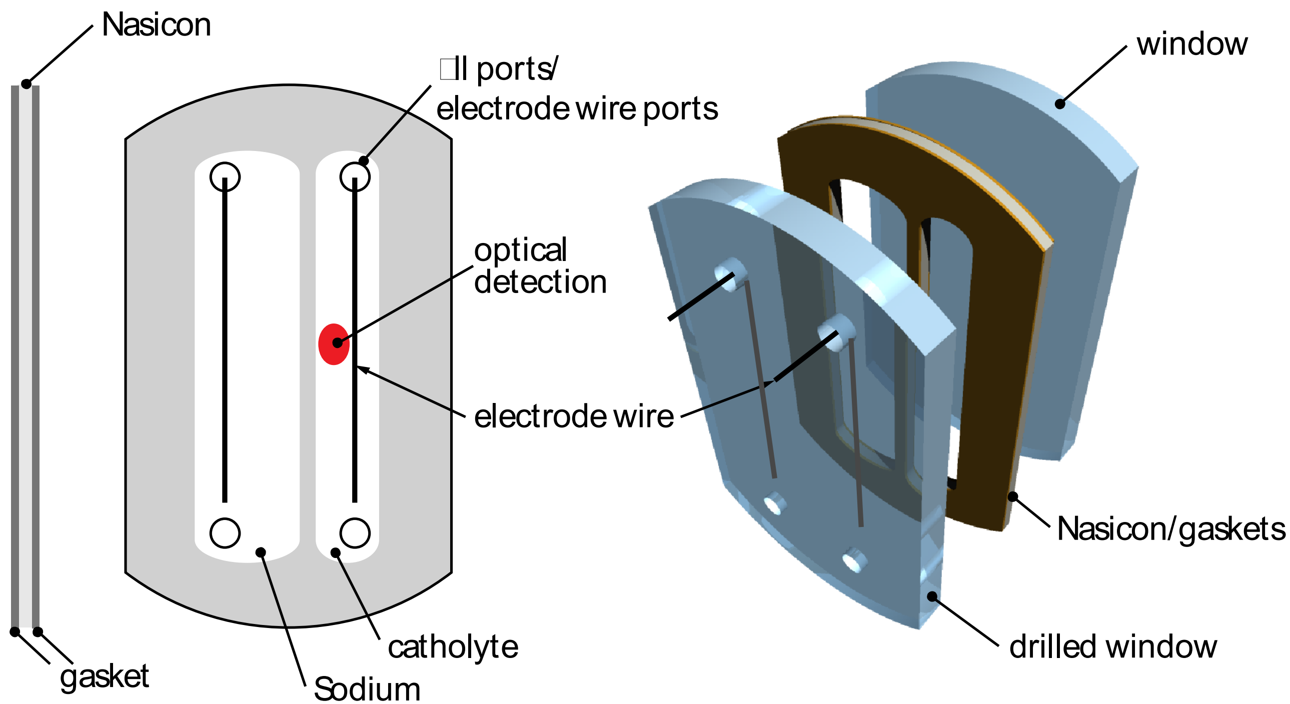
In-situ Spectroscopic Diagnostics

- We have developed an in-situ NaSICON cell and a suite of spectroscopic diagnostics that will allow us to:
  - determine iodine speciation and predict cell voltages
  - determined speciation as a function of SOC
  - better understand cell chemistry
  - identify impurities
  - identify decomposition products
  - Validate CSM battery models

Have demonstrated Infrared and UV detection

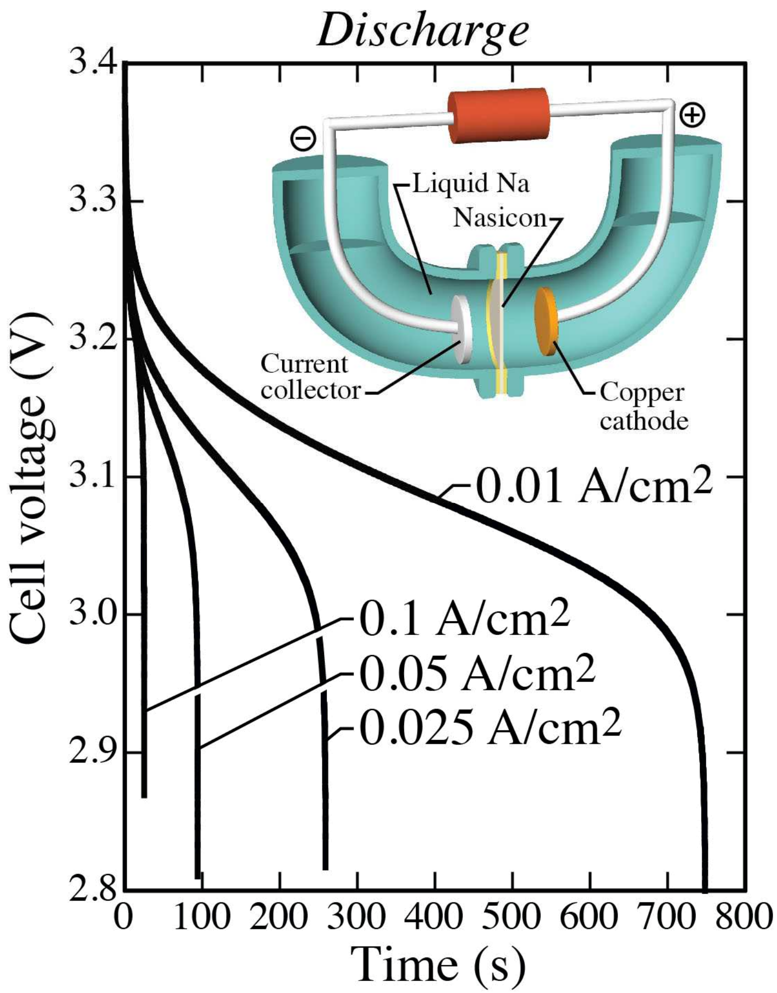
Have demonstrated sensitivity to 0.1 mol% for select analytes

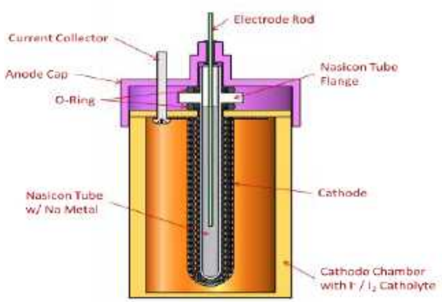
Rapid & low cost diagnostic



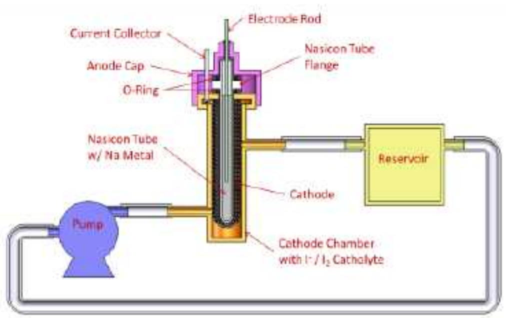
Mod-Sim as an Aid to Cell Design

- Derive and implement physically based *predictive* models
- Apply models to aid in cell design and system development
  - Models to predict charge & discharge behavior as functions of:
    - geometry – cell design
    - operating conditions – temperature, cell operation, cell chemistry, etc
- Model for Sodium-metal (Zebra-analog) system developed
  - Ion transport limitations limit charge and discharge capacity at high rate
- Have begun to use the model for cell design for the sodium-iodine system





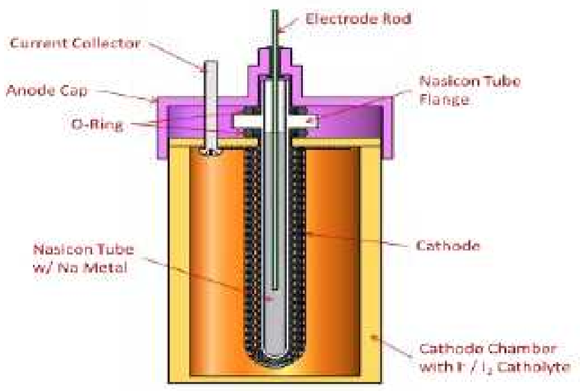
Non-flow design



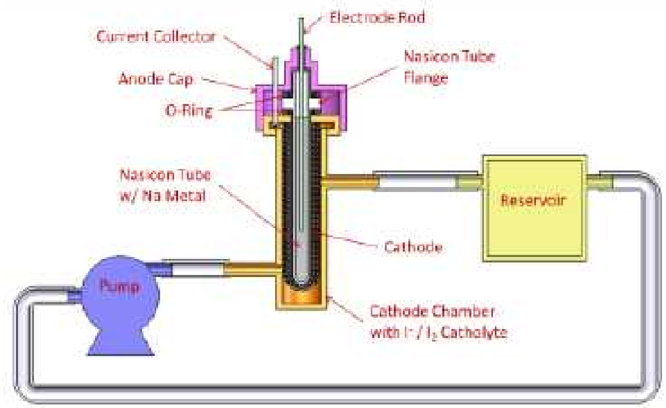
Hybrid design

Alternative Cell Designs Being Considered

Models will be used to aid in design evaluation

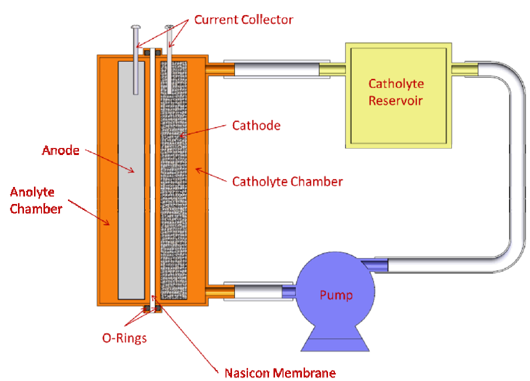


Non-flow design

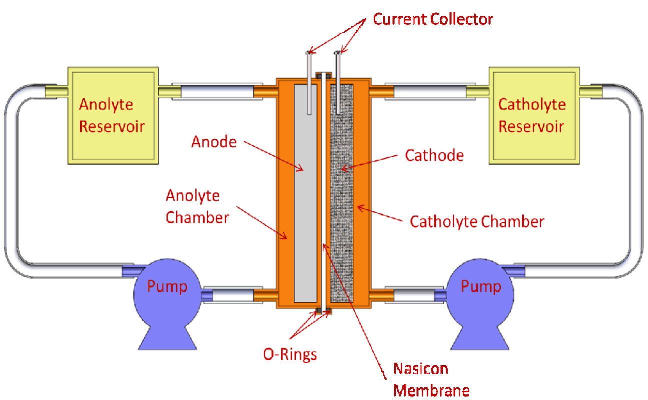


Hybrid design

Cylindrical Cell Configuration



Hybrid



Full Flow

Planar Cell Configuration

Understanding NaSICON Ceramic as a Solid State Electrolyte

- We are developing an understanding of the materials chemistry of the solid-state ion-conductor NaSICON

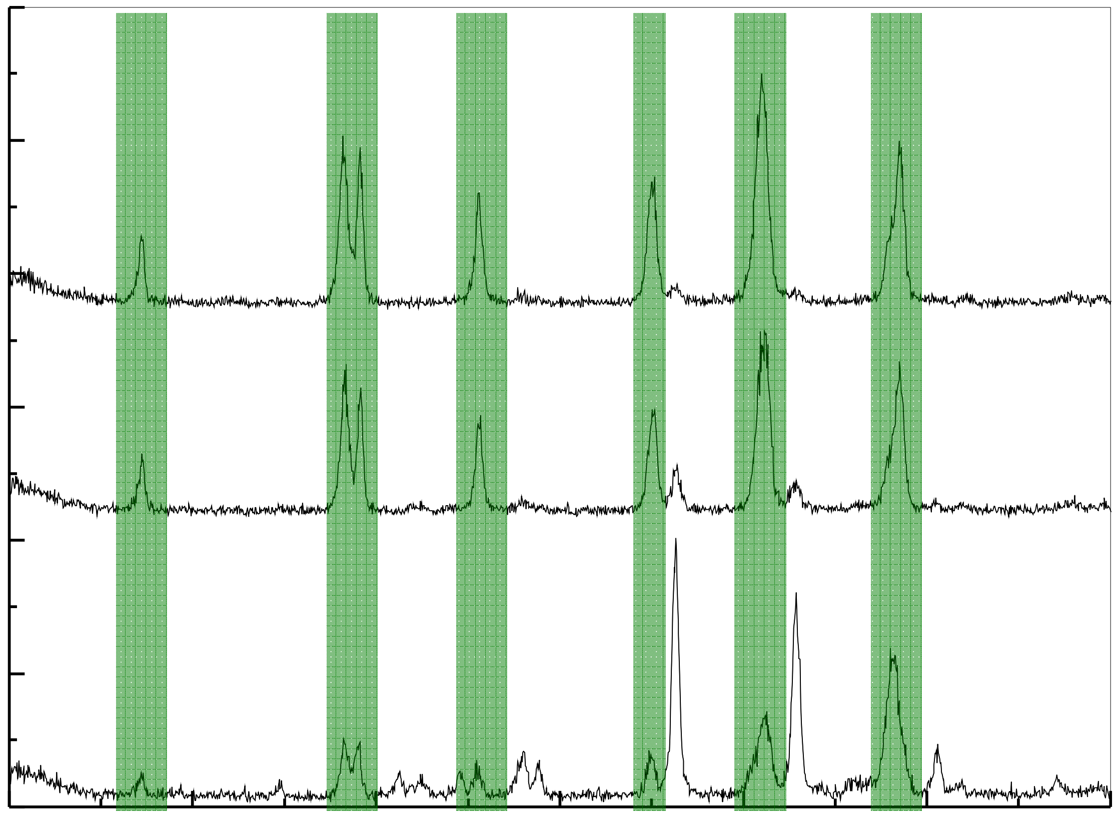
- We are correlating the material chemistry to materials properties (e.g., chemical stability, ionic conductivity, ceramic integrity)

- Based on this understanding, we hope to improve to NaSICON through implementation of process controls and composition

  - We have determined that the addition of small amounts of excess sodium dramatically reduces secondary phase formation at lower temperatures. and also allows us to process the materials at lower temperatures, which could impact materials cost

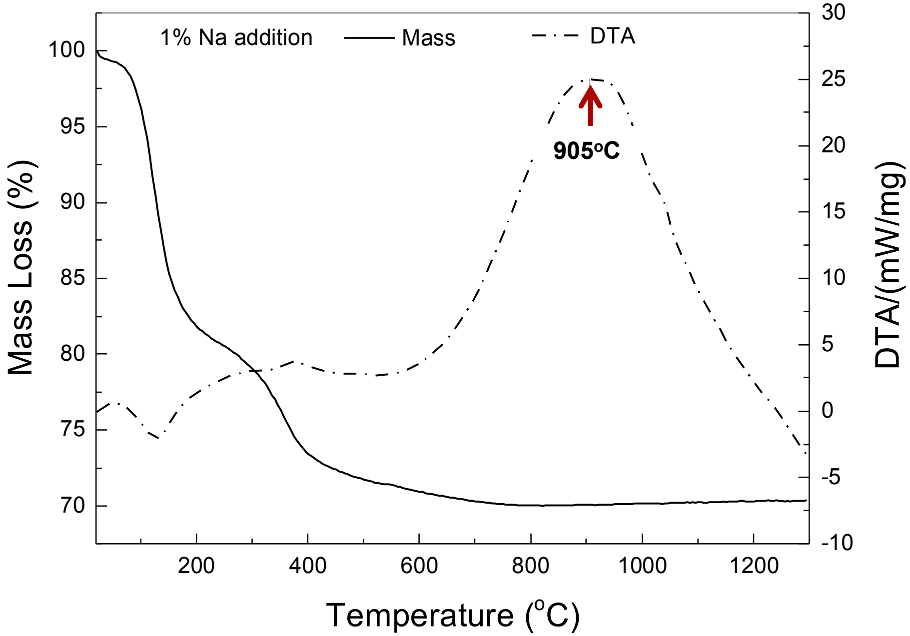
Excess Sodium Addition

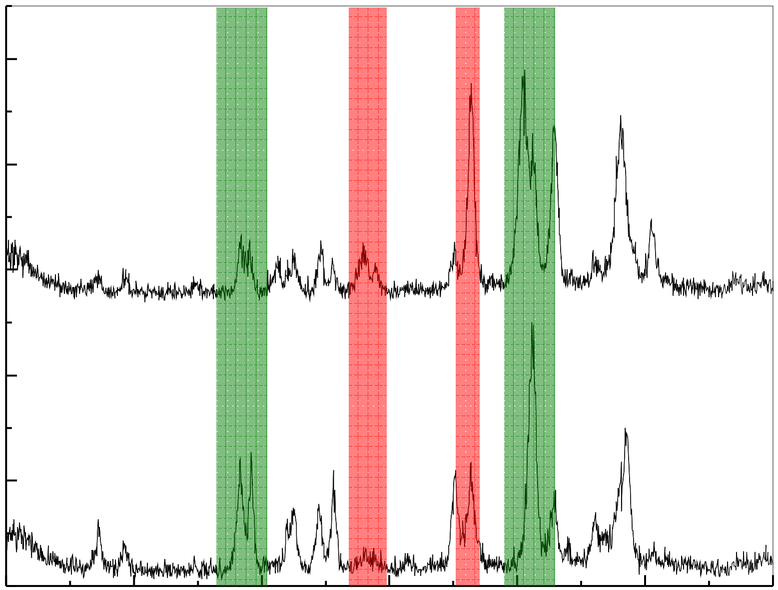
NaSICON with excess sodium fired at 1000^{o}C shows dramatically cleaner phase chemistry!



Excess Sodium Reduces Effective Processing Temperature

Thermal Analysis and XRD show NaSICON formation at lower temperatures with excess Na! (900 C vs >1200 C)





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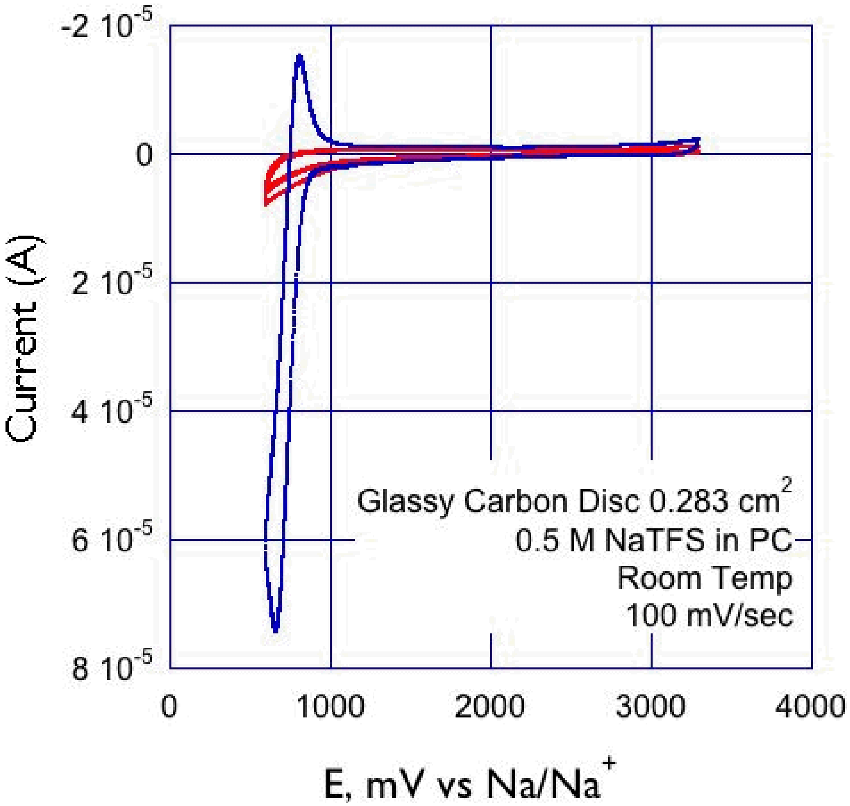
Excess sodium changes the energetics of NaSICON conversion, likely by affecting mass transport in liquid phase elements of sintering.

Alternative Anodes

- Baseline anode – sodium metal
  - high energy density
  - low cost
  - molten above 100 C
    - no dendrites
  - below 100 C, solid
    - employing secondary electrolyte
    - dendrites
- Other anodes being developed
- that allow:
  1. flow configuration
  2. eliminate/mitigate dendrite issues at temperatures below 100 C

- lower energy density, but:
  - can be more easily pumped than sodium metal
  - simplifies means for eliminating shunt current associated with molten sodium (metallic conductor)
  - engenders lower cost plumbing than sodium metal



Cyclic Voltammogram showing redox behavior of possible alternative anode.

FY14 Future Work

- Demonstrate long-term cycling of sodium-iodine cell
- Develop large-scale conceptual design
- Develop cost basis

Acknowledgements & References

Thanks for generous support from Dr. Imre Gyuk.

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Publications & Patents

Sandia National Laboratories

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