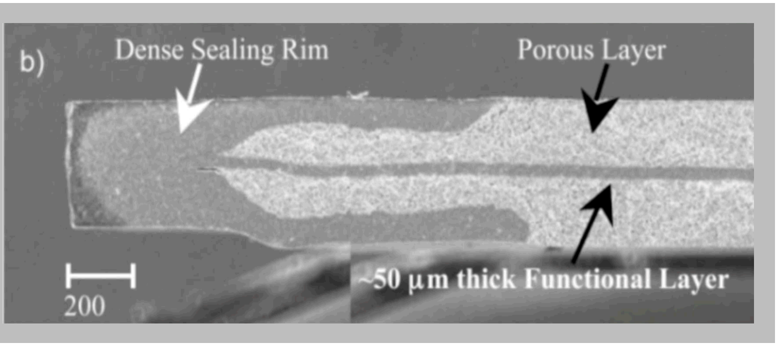
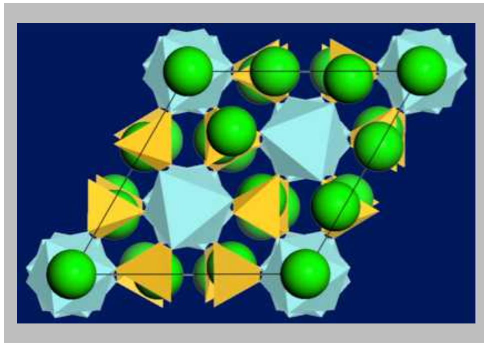
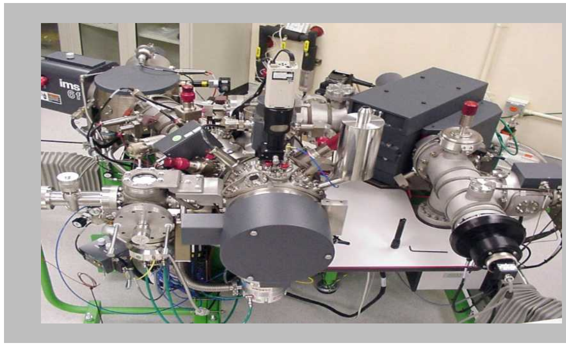
SAND2012-3035C

Exceptional service in the national interest







Sodium-based Battery Development

Programmatic Overview

D. Ingersoll et.al.

Sandia National Laboratories

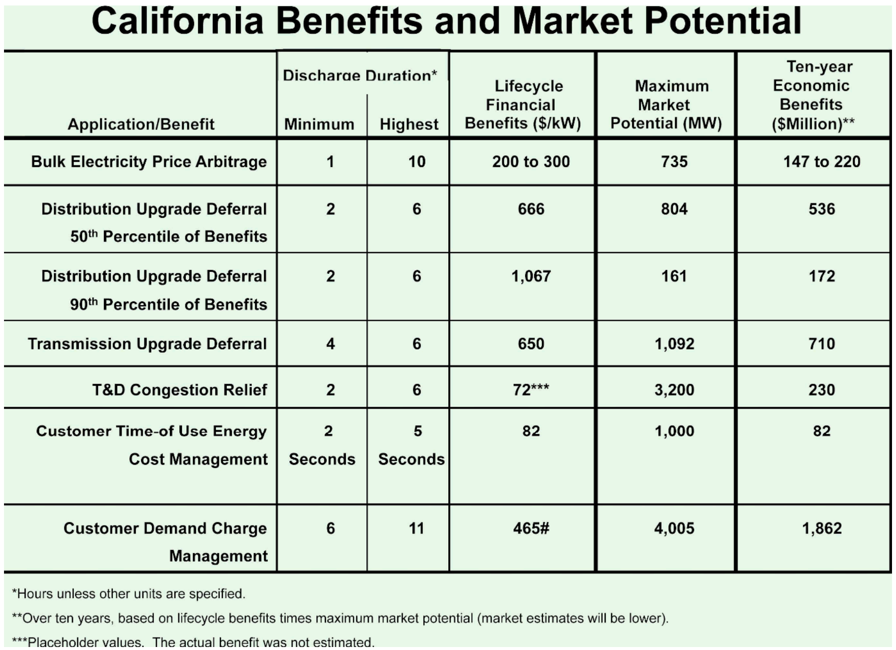
Sandia-RASEI-CU/CEAS Workshop on Advances in Battery Technology

April 16-17, 2012

Objective

Develop a family of batteries suited to stationary storage needs

- A suite of solutions for the multiple application needs of large-scale storage
  - both the utility and customer side of the grid
- Reduce the cost of large-scale storage
  - *System* level *life-cyle* cost, and not just the cost of the cells themselves
  - Projected cost goals < 100 $/kWh
- Eliminate/reduce geopolitical constraints sometimes associated with battery chemistries, specifically lithium-ion



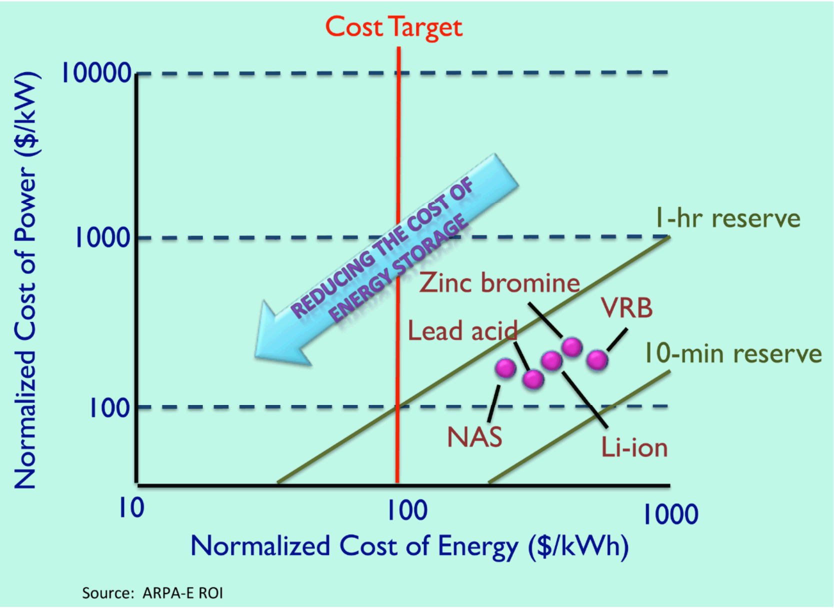
California Benefits and Market Potential

Application/Benefit	Discharge Duration* Minimum	Discharge Duration* Highest	Lifecycle Financial Benefits ($/kW)	Maximum Market Potential (MW)	Ten-year Economic Benefits ($Million)**
Bulk Electricity Price Arbitrage	1	10	200 to 300	735	147 to 220
Distribution Upgrade Deferral 50th Percentile of Benefits	2	6	666	804	536
Distribution Upgrade Deferral 90th Percentile of Benefits	2	6	1,067	161	172
Transmission Upgrade Deferral	4	6	650	1,092	710
T&D Congestion Relief	2	6	72***	3,200	230
Customer Time-of Use Energy Cost Management	2 Seconds	5 Seconds	82	1,000	82
Customer Demand Charge Management	6	11	465#	4,005	1,862

*Hours unless other units are specified.

**Over ten years, based on lifecycle benefits times maximum market potential (market estimates will be lower).

***Placeholder values. The actual benefit was not estimated.

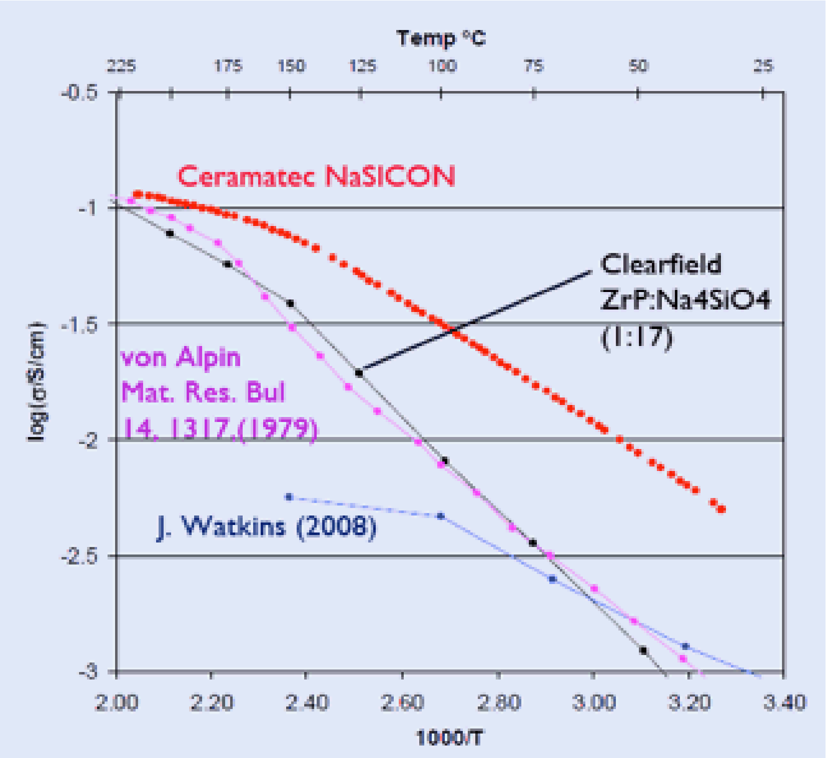


Source: ARPA-E ROI

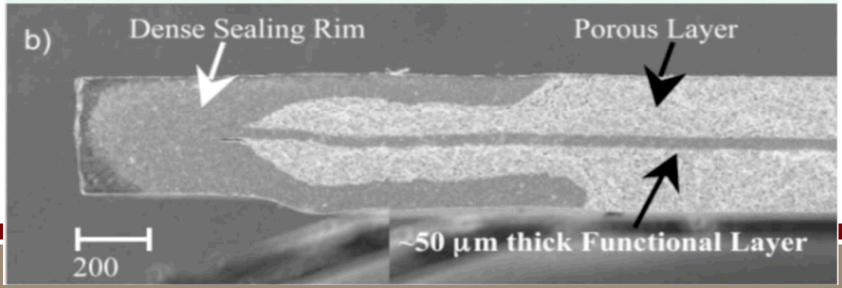
Approach

In a transformational move away from lithium-based battery chemistries, we are developing a family of sodium-based battery chemistries.

- Why Sodium-based systems
  - high energy content & very low cost of metallic anodes
  - U.S. has large reserves of sodium commodities
  - can be coupled with a variety of cathodes
  - a solid-state perm-selective sodium-ion conductor is available
- NaSICON – Sodium Super Ionic Conductor
  - solid ceramic developed decades ago having high room temperature conductivity
    - these early materials were not stable against molten sodium
  - Current materials are stable
  - exhibit room temperature conductivities on the order of 10^{-2} S/cm
  - Discrete NaSICON ceramic structures can be fabricated



Cross Sectional View of NaSICON Structure



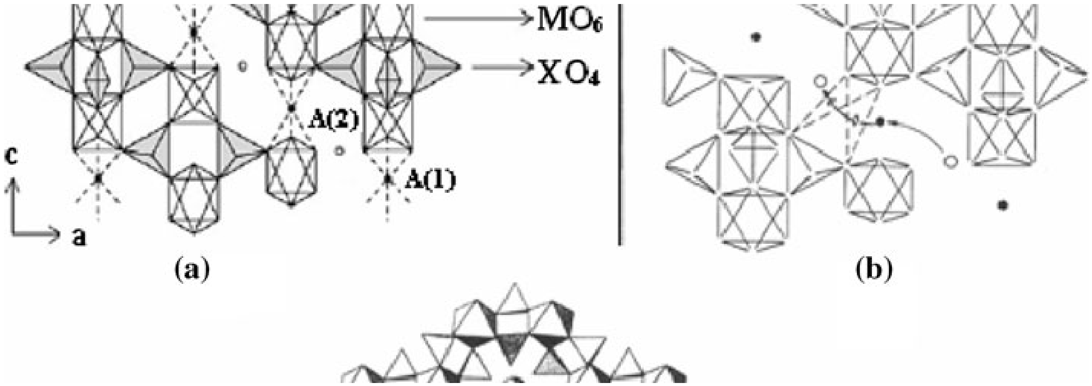
Multi-disciplinary Partnership

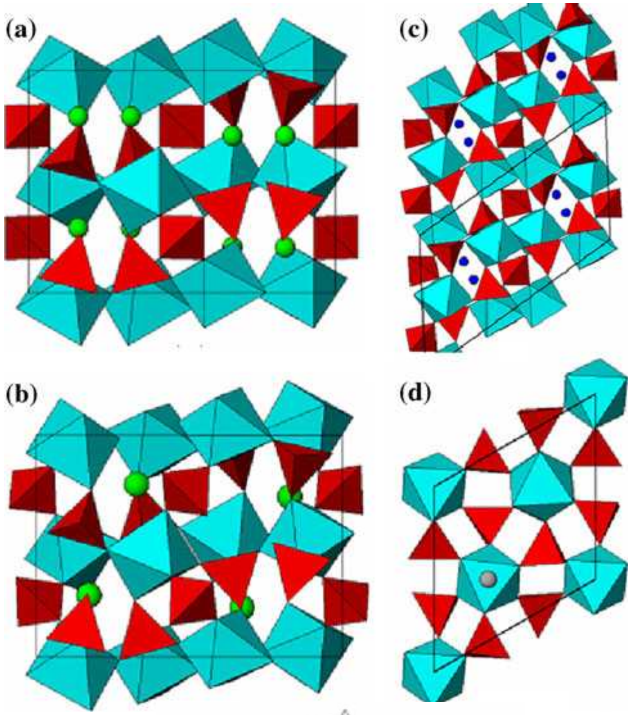
Industry, Universities, and Government

- D. Ingersoll – PI
- SNL Personnel
  - R. Cygan: transport mechanisms
  - C. Apblett: sodium-air battery
  - F. Delnick: sodium-ion battery
  - E. Spoerke & N. Bell: NaSICON material and stability
  - T. Anderson: cathode development
  - J. Ihlfeld
- Ceramatec Inc & Coorstek
  - C. Boxley
  - S. Bhavaraju
  - A. Elangovan
  - D. Beeaff
- University of Maryland
  - Prof. E. Wachsman
- Colorado School of Mines
  - Prof. R. Kee
  - Prof. J. Porter
- Boulder Ionics (indirect partner)
  - J. Martin: Ionic liquids
- DOE – Office of Electricity
  - Dr. I. Gyuk

NaSICON: *structure, activity, charge distribution stability*

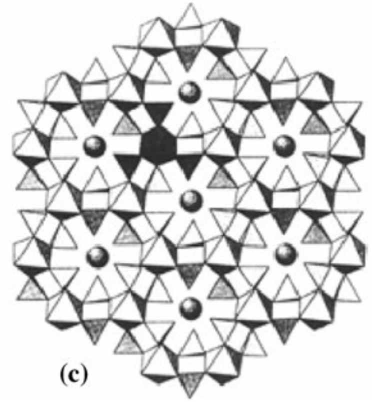
Baseline Compositions: $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (NZP = $NaZr_2P_3O_{12}$, NZS = $Na_4Zr_2Si_3O_{12}$)





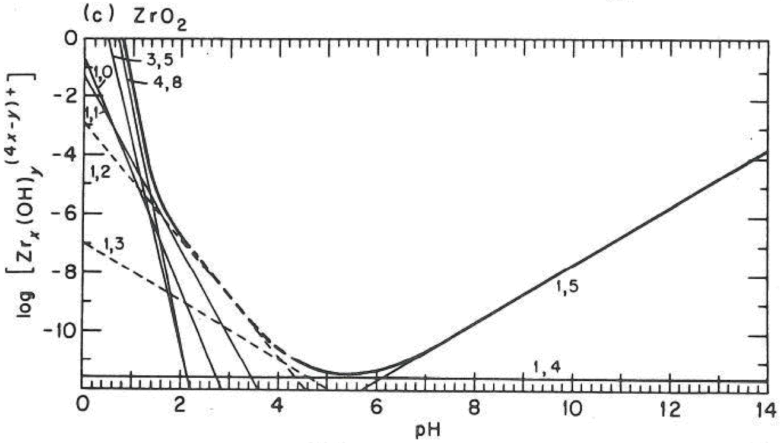
Zr sites: all octahedral
P, Si sites: all tetrahedral
O sites: all bridging (octahedra to tetrahedra)

Formal Oxygen Charges:
Zr-O-Si = -1/3
Zr-O-P = -1/12



The anionic charge in NASICON is very diffuse.
Channel dimensions for Na^+ vary with structure.
H_2O, H_3O^+ are marginal fits.
Hydrated cations should be excluded.

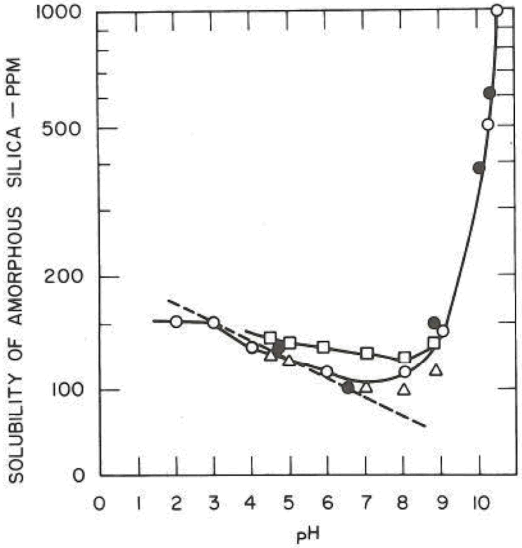
Stability in solution – predictive



Acidic Degradation:
Zr is the weak link.
Proton attack on bridging oxygens should occur below pH 3.

Basic Degradation:
Si should be the weak link (Zr is point of attack for Si-free NASICON).
Hydroxide attack on Si, Zr should increase 10x for each ∆pH of 1.

Stability Window: 4 < pH < 11 (NZS)
3 < pH < 14 (NZP)



Ion Exchange Degradation:
Cation exchange to form hydronium should only occur below pH 3-4.
In open channel structures, ion selectivity should follow: $K^+ > Na^+ > Li^+$.

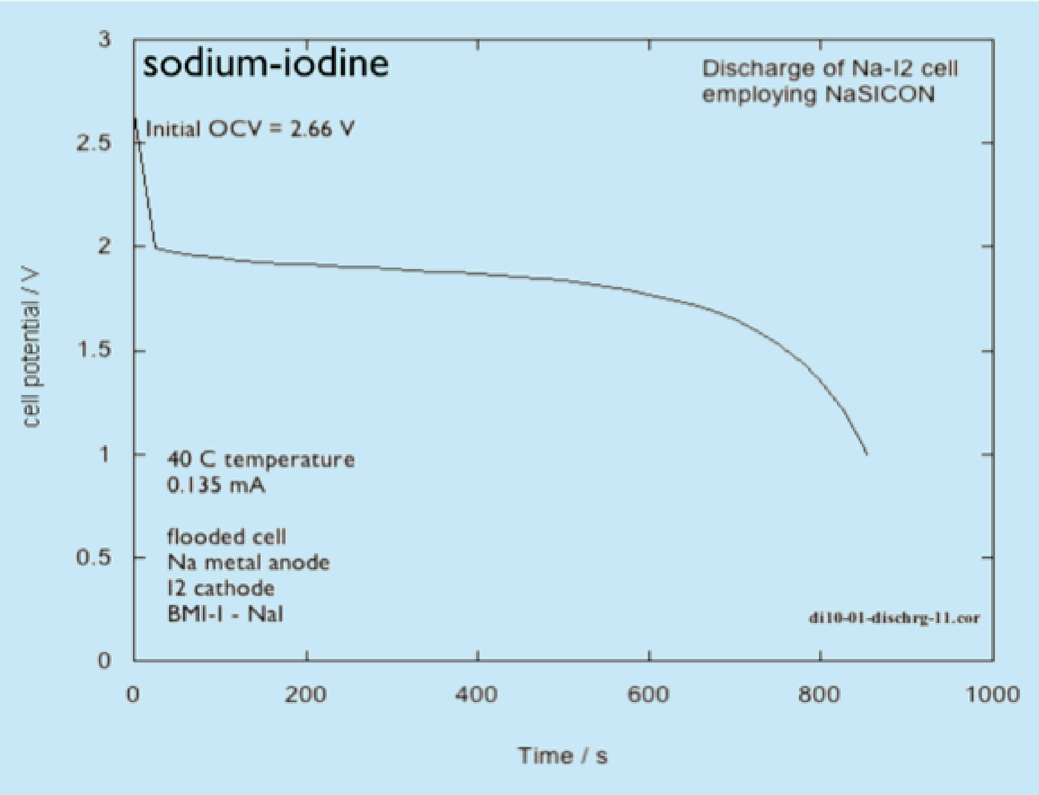
Predictive statements being validated/measured in the lab

Select Battery Chemistries

Metallic anode in combination with different cathodes

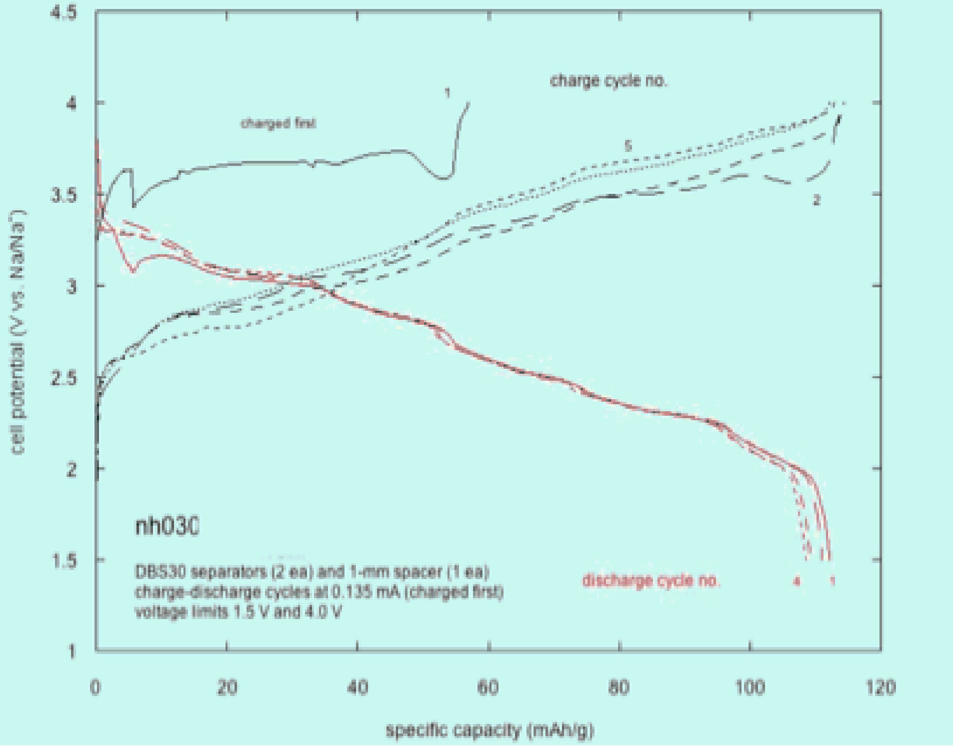
Battery chemistries under development

1. sodium-bromine Na + ½ Br_2 ←→ Na+ + Br- 3.79 V 987 Wh/kg
2. sodium-iodine Na + ½ I_2 ←→ Na+ + Br- 3.25 V 581 Wh/kg
3. Low temperature sodium-sulfur
4. Sodium-ion
5. Sodium-air



Sodium-ion

- developing new cathodes
    - have developed a new manganese oxide phase having higher specific capacities than traditional material ($Na_{0.44}Mn$)
- currently evaluating performance



Sodium-ion Cell. Initial cycling with non-aqueous electrolyte. Sodium metal anode - manganese oxide insertion cathode. NaSICON not yet in place

Acknowledgements

- Dr. I. Gyuk
    - DOE Office of Electricity