Sodium-Based Battery Development

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Teaming

- **Program Sponsor**
  - Dr. Imre Gyuk – Program Manager, DOE-OE
  - DOE – Office of Electricity Delivery and Energy Reliability

- **Team**
  - **SNL**: Erik Spoerke, Leo Small, Jill Wheeler, Paul Clem, Josh Lamb, Eric Allcorn, Ganesan Nagasubramanian, John Hewson, and David Ingersoll*
  - **Ceramatec**: Sai Bhavaraju, Alexis Eccleston, Andrew Read, Matt Robins, Tom Meaders
  - **SK Innovation**: Jeongsoo Kim

*This collaboration between National Laboratory and Industry aims to utilize state of the art expertise in materials chemistry, electrochemistry, and advanced characterization to drive the development of new sodium-based batteries toward commercial application.*
Sodium-Based Batteries: A Path to Safe, Reliable, Cost-Competitive Energy Storage

Objective: We aim to develop low cost, low temperature, safe, nonflammable alternatives to Na-S and Li-ion batteries.

- Low cost (reduced material costs, low CAPEX, high cycle life)
  - Unit cost ~$146/kWh, module costs ~$175/kWh, Cycle life 5,000-10,000 cycles
  - LCOS $0.05-0.10/kWh-cycle
- Enabled by low to intermediate temperature (<200°C) ceramic Na-ion conductor (NaSICON)
  - Robust physical barrier - no electrode crossover!
  - Reduced operating costs
  - Lower cost materials/seals
  - Enables new cathode chemistries
- Engineered safe
  - Fully inorganic, no volatile organic electrolytes
  - Robust ceramic separator isolates anode and cathode
  - Cross-reaction generates benign byproducts

Our approach stands to enable numerous new Na-based battery technologies:

- Sodium-air
- Sodium-ion
- Aqueous Redox Flow
- Low temperature sodium-sulfur
- Sodium-bromine: Na + ½ Br₂ ⇌ Na⁺ + Br⁻
- Sodium-iodine: Na + ½ I₂ ⇌ Na⁺ + I⁻
- Sodium-nickel chloride: Na + ½ NiCl₂ ⇌ Na⁺ + Cl⁻ + Ni(s)
- Sodium-copper iodide: Na + CuI₂⁻ ⇌ Na⁺ +2I⁻ + Cu(s)
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NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

NaSICON (Na Super Ion CONductor): Na$_3$Zr$_2$PSi$_2$O$_{12}$

Engineered materials chemistry and advanced, scalable processing (Ceramatec, CoorsTek) make NaSICON a chemically/mechanically stable, low temperature, high conductivity (>10$^{-3}$ S/cm @RT) separator technology.

Poster: S. Bhavaraju
Features of Na-NiCl₂ Cell

- Open-circuit Voltage: 2.58 V
- Lower Operating Temperature: 195°C
- Less metal corrosion compared to NaS
- Safer reaction between Na and NaAlCl₄ in case of solid electrolyte fracture

\[ \text{NiCl}_2 + 2\text{Na}^+ + 2e^- \rightleftharpoons \text{Ni} + 2\text{NaCl} \]
**Stable Na-NiCl$_2$ Cell Performance**

*Nickel grain growth at high temperatures during cycling limits cycle life and charge-discharge kinetics for Na-NiCl$_2$ batteries.*

1 micrometer Ni Particle grows by more than 10X after multiple cycles

Using a NaSICON electrolyte allows us to lower temperature below 200°C and adding Ni metal growth inhibitors.

Together, these changes have allowed us to prevent Ni metal particle growth and preserve exceptional, stable battery performance over months (hundreds of cycles).

After electrochemical cycling, Ni-particle growth is suppressed using NaSICON and catholyte additives.

**Cycle test (Prototype cell)**

- Coulombic Efficiency
- Energy Efficiency
- Usable SOC

13 Wh Na-NiCl$_2$ (NaX) Cell operation for 9+ months. 70% Depth of Discharge, >85% energy efficiency at 65 mA/cm$^2$ Charge/Discharge NaSICON current density.
Scalable NaSICON Enables Scalable Cell Configurations

250Wh Commercial Cell Components & Design Concept

- Na-NiCl₂: 100-250 Wh commercial type unit cell testing/construction in progress
- NaI: 100 Wh pre-commercial prototype cell construction in progress

Assembled 250 Wh NaX Cell

- Metal Case
- Ceramic Subassembly
- Wicking Tube

Internal Structure
Consistent Performance Across Scales

100 Wh pre-commercial Na-NiCl$_2$ unit cell:
- operational for 4+ months.
- 500+ cycles (70% DOD)
- coulombic efficiency $\sim$100%
- energy efficiency 81.5 %
- 53 mA/cm$^2$ & C/7 rate

250 Wh pre-commercial Na-NiCl$_2$ unit cell:
- operational for 3+ months
- 110 cycles (70% DOD)
- coulombic efficiency $\sim$100%
- energy efficiency 80 %
- 53 mA/cm$^2$ & C/7 rate
Consider Na-I\textsubscript{2} Batteries:

- Increased cell voltage (3.25V)
- Lower temperature (120-180°C)
  - Lower cost materials/seals
  - Lower operational costs
  - New cathode chemistries
- Liquid cathode increases feasible cycle life
Na-I$_2$ Prototype Performance

**Lab Scale Test Conditions**

- 8.7 Wh lab-scale cell
- Graphite felt + tungsten wire current collectors
- NaI-AlCl$_3$ based molten salt catholyte
- 1" NaSICON tube (15 cm$^2$) glass sealed to $\alpha$-alumina
- T = 150-180°C

✓ **Demonstrated long term performance**

- More than 269 cycles @ 60% DOD
- Discharged 483Ah
- C/7 rate
- High energy efficiency of ~ 80%
- 28.5 mA/cm$^2$ current density
The 100 Wh cell was built using Carbon felt/Tungsten mesh, infiltrated with NaI. The majority of the cycling was done at 150 °C, until the last 9 cycles where the temperature was raised to 165 °C. The cell operated 360 hours (29 cycles) before failure.

Promising Progress!
Improving Cathode Structure

**Electrolessly Coated Tungsten/Carbon Electrodes**

Carbon electrode (graphite, powder, foam) → Intermediate coating → Convert to W-precursor → Reductive anneal creates **Crystalline, metallic tungsten.**

- **X-ray diffraction**
  - Log (Intensity / A.U.)
  - Graphite, inter 1, inter 2, tungsten
  - 2θ / degrees (Cu Kα)
  - Graphite, W metal

- **Cyclic Voltammetry**
  - Current / mA
  - Potential vs. Ag/AgCl / V
  - 28 Ω (tungsten coated)
  - 55 Ω (as-received)
  - Carbon foam 10 mM K₃Fe(CN)₆, 500 mM NaCl, 100 mV/s

*2X Reduction in electrode resistance will reduce ASR and enable superior electrochemical performance.*
Na-Batteries: Engineering Safety

In contrast, Na-batteries are engineered safe:

- All inorganic construction eliminates explosive organic solvents
- Robust ceramic separator isolates anolyte and catholyte
- Cross-reaction generates benign byproducts (Al metal and NaCl)

\[
3\text{Na} + \text{AlCl}_3 \rightarrow 3\text{NaCl} + \text{Al(s)}
\]

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

Li-Ion batteries are inherently intolerant of harsh conditions…
Accelerating Rate Calorimetry (ARC)

- ARC testing is used to determine the time, temperature, and pressure relationships for exothermic reactions.
When complete separator failure is simulated by mixing Na metal and NaI/AlCl$_3$ salt, ARC testing reveals essentially no self-heating.
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Measuring pressure generated during ARC testing shows no significant gas generation/pressurization from the Na-Nal/AlCl₃ mixture.

In contrast volatile components of an NMC Li-Ion produce a dramatic pressure spike at elevated temperatures.

This minimal pressurization represents a dramatic safety benefit of Na-batteries.
Alternative Na-based Battery Chemistries

NaSICON separators offer the high conductivity, chemical and mechanical stability, and ion-selectivity needed to enable Na-based, aqueous redox flow batteries.

Fe(bpy)$^{2+/3+}$ (0.9V) \hspace{2cm} \text{Fe(EDTA)$^{2-/3-}$ (0V)}

Full Cell CV @ 5 mV/sec
Fe$^{3+}$(EDTA) // NaSICON // Fe$^{2+}$(BPY)
0.4M Na$_2$SO$_4$

Cell charges at ~1.0 V

Cell discharges at ~0.8 V

Poster: E. Allcorn
FY16 Programmatic Accomplishments

- **Papers**

- **Intellectual Property**
Path Forward (FY17-18)

NaSICON-enabled batteries offer a promising pathway to cost-effective, commercially scalable, safe energy storage.

- Target 10 kWh sodium demonstration
  - 40 250Wh Cells
- Improve performance (cycle life, energy efficiency) of larger-scale (100Wh and 250Wh) cells for Na-I$_2$ chemistry
  - Improved cathode structure/chemistry
  - Optimized cell design
Thanks

This work was generously supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity Delivery and Energy Reliability.

Work on Na-NiCl$_2$ batteries was performed through collaboration between Ceramatec and SK Innovation.

Follow on posters:

- Dr. Sai Bhavaraju: “Low-cost Sodium Battery for Grid Scale Energy Storage”
- Dr. Leo Small: “Electroless Process for Depositing Tungsten Metal for Sodium Battery Electrodes”
- Dr. Eric Allcorn: “Aqueous Na-ion Redox Flow Battery with Ceramic NaSICON Membrane”