Na-Battery Development at PNNL

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Progression of Planar Sodium Battery Technology

**Gen 1:**
- High Temperature (250-300°C)
- High Volume manufacturing process
- Modular design, tunable power and energy, multi-market application.

**Gen 2:**
- Intermediate Temperature (110-250°C)
- Lower cost materials, additional sealing technologies available
- Ni free cathode.
- Requires electrolyte and catholyte development.

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

Dr. Yuyan Shao 9:00 am
Acknowledgements

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  - Dr. Mark Johnson, Dr. Dave Danielson

- DOE-OE Energy Storage Program,
  - Dr. Imre Gyuk

- PNNL internal LDRD Funding
EaglePicher Technologies- PNNL

Planar Na-Beta Batteries Development for Renewable Integration and Grid Applications
Eagle-Picher/PNNL Path to Planar Na Battery

3.0cm² Button Cell

Materials development and performance testing.

64cm² XL-Button Cell

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

➢ 3 year program to scale up and demonstrate planar Na-battery technology.

Multicell Planar Stack

Manufacturing friendly components and fabrication techniques.

200cm² Stack

➢ Tubular Na–Metal Halide chemistry demonstrated > 1000 cycles at high DOD.

➢ Decrease capital cost by moving to high volume planar manufacturing. Planar technology has higher volumetric power density than tubular architecture

➢ Increase cycle life by reduced temperature operation.
Basic Na-NiCl₂ Battery Chemistry

**Charging Reaction**

\[2e^- + Ni + 2NaCl \rightarrow 2Na + NiCl₂\]

**Discharging Reaction**

\[2Na + NiCl₂ \rightarrow 2e^- + Ni + 2NaCl\]

**Key elements**
- 2.58 V OVC
- ~3.0 V cutoff voltage for charging
  - Increase R from NiCl₂
  - Melt degradation.
- 1.8 V cutoff on discharging
  - Al plating from melt
- Typically 20 – 80% SOC swing.

**PNNL efforts focused on**
- Scale-up of BASE fabrication process.
- Development of durable glass seals capable of withstanding melt.
- Demonstrating larger scale 64 cm² cells.
- Cathode chemistry development to improve durability at higher specific energy density.
- Transition technology to EP.

**Cathode**
1. Ni
2. NaCl
3. NaAlCl₄
4. NiCl₂

**Anode Current Collector**

**BASE**

**Anode Compartment**

**Na**

**Cathode Current Collector**
BASE properties are function of fabrication, composition, and processing conditions.

64 cm² BASE sample glass sealed to an alumina ring prior to application of electrodes and resistivity test.

- Critical to understand impact of process conditions on flexural strength and conductivity.
- Goal: Maintain > 0.03 S/cm at 300 °C with RT flexural strength > 400 MPa flexural strength.
Progress of 64 cm² cell

- 64 cm² cell - 100 whr/kg at 1C - 91% efficiency - 280°C for over 700 cycles
- No capacity fade for first 800 cycles.

64 cm² cell, 100 Whr/kg at 1C - 280°C

64 cm² cell, 150 Whr/kg at C/4 - 280°C
EaglePicher – PNNL
Next Steps

- Assemble and test multicell 64 cm² stack – 150 Whr/kg of active cathode
- 1000 hrs durability of seal
- Larger scale cells running at 200 Whr/kg of active cathode.
- 5 kW module
Intermediate Temperature Sodium Battery Technology

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**Gen 3:**
- Low Temperature (RT -90°C)
- Approach to Na-ion (polymer membrane)
- Anode materials
- High energy capacity cathode.
Goal: To demonstrate Na-metal halide battery operated at ≤ 200°C

- 64 cm² cell with comparable performance compared to current cells operated at 280°C

Technical Challenges

- Catholyte and Cathode Chemistry
- Low-resistance BASE
- Na wetting at lower temperatures
- Seal and new cell design
Low Temperature Catholyte Development

Additions to NaAlCl₄

- Decrease $T_m$ of catholyte by 20 - 40°C
- High ionic conductivity < 200°C with ≥ 25% salt replacement.
- Does not impact electrochemical stability of catholyte.
Goal is to minimize electrolyte resistance while retaining sufficient strength for larger scale planar batteries.

- 50 µm β” electrolyte on porous support
- Currently focused on determining strength – porosity relationship.
Low Temperature Na wetting

- As-prepared BASE shows extensive hydration after exposure to air. Wetting angle > 90° for all temperatures studied and poor adherence.
- Vacuum treated BASE shows improved wetting and adherence.
- Wetting angle > 130° at 250°C - significant issues for low temperature operation?

Na drop showed no adherence to β” surface
→ Na rolled off surface
θ ~ 180°

T = 250°C

T = 300°C

θ ~ 130°

Treated BASE
425°C – 60 hr vacuum

θ ~ 100°

Na drop showed no adherence to β” surface
→ Na rolled off surface
θ ~ 180°

T = 325°C

θ ~ 90°

Untreated BASE

Na drop showed no adherence to β” surface
→ Na rolled off surface
θ ~ 180°

T = 350°C

θ ~ 75°
# Intermediate Temperature Na-S

**Goal:** Develop 150 – 200°C temperature Na – S battery which can:
- Less corrosive environment
- Built in discharge state and charged on site
- Can withstand multiple freeze/thaw cycles.

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### Sulfur Solubility in Various Organic Solvents (wt.%)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point (°C)</th>
<th>25°C</th>
<th>50°C</th>
<th>100°C</th>
<th>150°C</th>
<th>200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>tri(ethylene glycol) dimethyl ether</td>
<td>216</td>
<td>------</td>
<td>0.5</td>
<td>2.5</td>
<td>7.0</td>
<td>------</td>
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<tr>
<td>tetra(ethylene glycol) dimethyl ether</td>
<td>275</td>
<td>0.16</td>
<td>1.01</td>
<td>3.0</td>
<td>7.0</td>
<td>------</td>
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<tr>
<td>di(ethylene glycol) dibutyl ether</td>
<td>256</td>
<td>------</td>
<td>------</td>
<td>0.5</td>
<td>1.5</td>
<td>------</td>
</tr>
<tr>
<td>Dimethylaniline</td>
<td>194</td>
<td>3.37</td>
<td>6.92</td>
<td>38.4</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>propylene carbonate</td>
<td>242</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>ethylene carbonate</td>
<td>244</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
</tbody>
</table>
Na-Metal Halide Concepts (non-Ni)

- Goal: Replace highest cost material component (Ni) with lower cost metals with improved performance.

ZEBRA type chemistry: insoluble MH

\[ \text{Ni} + 2\text{NaCl} \rightarrow 2\text{Na} + \text{NiCl}_2 \text{ (charge)} \]
\[ \text{NiCl}_2 + 2\text{Na} \rightarrow 2\text{NaCl} + \text{Ni} \text{ (discharge)} \]

![Ni ↔ NiCl₂ (insoluble)](image)

Metal coated chemistry: soluble MH

\[ \text{EC/M}_x + \text{NaCl} \rightarrow \text{Na} + \text{M}_x\text{Cl}_y + \text{EC} \text{ (c)} \]
\[ \text{EC} + \text{M}_x\text{Cl}_y + \text{Na} \rightarrow \text{NaCl} + \text{EC/M}_x \text{ (d)} \]

![EC ↔ EC/Mₓ Coated] Mₓ Coated → MₓClₙ (soluble)

![Graph showing I, A vs E, V](image)

Working electrode: glassy carbon
Counter electrode: glassy carbon
Scan speed: 100 mV/s
Temperature: 125°C

![Graph showing Capacity vs Cycle](image)

No NaCl → Saturated NaCl

ZEBRA type chemistry: insoluble MH

Metal coated chemistry: soluble MH

Internal DOE EED LDRD Funded FY2010, J. Lemmon, G. Li and X. Lu
**Intermediate Temperature Na-Air with BASE**

**Goal:** Improve performance, low cost alkali metal – air.
Path: Improve solubility of Na$_x$O$_y$ products in cathode with higher temperature.

**3.0cm$^2$ Button Cell**

Replace metal cathode with temperature stable air cathode.

**Cell Characteristics:**
- Temperature: 140°C
- OCV: 3.2V vs Na
- Current: 0.15mA/cm$^2$.

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

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