# STRATEGIES FOR LIQUID ANODE ALKALI BATTERIES OF HIGH ENERGY DENSITY OPERATING AT 0 to 100ºC.

OFFICE OF
ELECTRICITY DELIVERY &
ENERGY RELIABILITY

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## Purpose

- To develop a lower temperature, thermally cycle-able, Zebra cell (chosen by big corporations like GE, etc) for stationary large energy storage installations

**•Strategies**:

- **Anode**: Use Na-K alloy anode,
- **Separator**: Na-K alloy anode demands use of joint Na+/K+ conducting separator: **use β"-$Al_2O_3$**.

**•Cathode contact electrolyte**: $NaAlCl_4$ freezes at 185ºC. Need low-melting non-volatile additives to produce ***"ionic oils"***. Best choices are ionic liquids like EMIM-$AlCl_4$.

**•Cathode: $NiCl_2$ on Ni foam** (or a "red oil" $Br_2$, or sulfur)

## Impact on DOE OE Energy Storage Mission

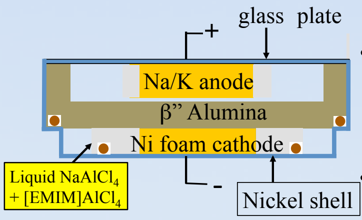
**• Enhanced operating flexibility enabled by non-solidifying cell chemistry, allowing battery shutdown**

- Zebra cell (Na/$NiCl_2$) and Na/S cells with planar technology are robust.
- but.. Zebra cell and Na/S cell both are constrained to run at T>250ºC.
- Shut-down in each case is tedious, and dangerous to cell integrity.

**• Lower temp operation improves system efficiency**

- Systems running at low temperatures, such as the Zebra cell and Na/S cells we proposed, will have higher voltages and may include alkali halide types not yet evaluated,
- e.g. **Na-K**/$NaAlCl_4$-Na,K(XYZ)/**$Br_2$**"red oil"

## Recent Results



**At ISU**, we are commissioning a

- **New density-stable flat panel cell** with exchangeable electrolyte and solid state separator parts for testing the battery components,
- **Liquid alkali anode** contained inside β"-alumina/composite cup.

**•Ionic liquid electrolyte** is contained in the bottom immersing nickel (uncharged state) cathode, liquid (sulfur complex or bromine red oil) cathode or $NiCl_2$ (Zebra version).

**•Single ion conducting separator** β" $Al_2O_3$ (or novel Na boro-epoxide glasses or complex inorganic $Na^+$-conducting plastic crystal)

•Powdered β" $Al_2O_3$, as base conductor, incorporated in $Na^+$ conducting $Na_2S + P_2S_5$ glasses at ISU, then heat treated at 380 ºC and 480 ºC

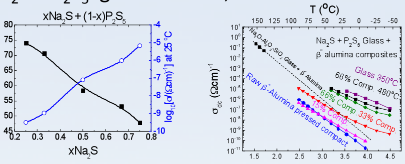
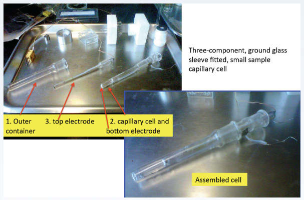
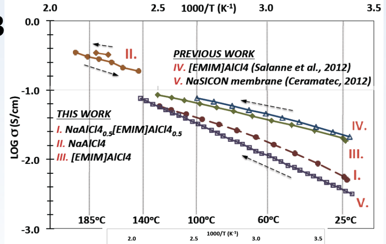


**Figure 2. $Na^+$ ion conductivities of pure $Na_2S + P_2S_5$ glasses (left) and composites with Na β" $Al_2O_3$ consolidated at the indicated T (right) and compared to oxide glass - Na β" $Al_2O_3$ composites of much lower conductivity**

### Cathode electrolyte: Low-melting eutectics (at ASU)

1. Cells
2. Data **Fig. 3**





3. **Syntheses** **(i) of new low-melting *inorganic* salts: unsuccessful**
**(ii) of novel inorganic $Na^+$-conducting plastic crystals,** *successful*

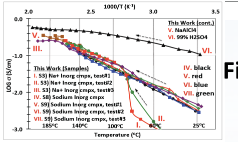


**Figure 4**

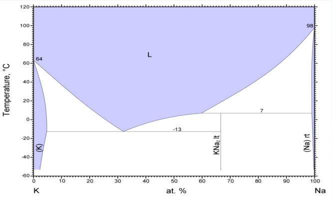
## Research Plan

### At ASU:

1. **Determine liquidus surfaces for systems of ionic liquids with (Na,K)$AlCl_4$** using DTA system for (preliminary studies) **(b)** and DSC for key cases.
2. **Determine viscosities** to compare with measured conductivities, and then use Walden plots to evaluate conductivity losses by alkali cation self-trapping suggested by results Figure 3.
3. **Develop all-inorganic plastic crystal alkali ion conductors** of Figure 4 as alternative (higher-conducting) electrolytes for **sodium-potassium-ambient-air storage** systems.

### At ISU:

1. **Using commercial β" $Al_2O_3$ separators, homemade composite, and plastic crystal separators,** test the adjacent cell design with ambient liquid Na-K anode (see phase diagram), and liquid cathode (bromine for alkali-halide cell), or gas cathode (for Na/air cell).
2. **Develop liquid halogen and liquid sulfur**-type formulations for cathodes.
3. **Produce prototype energy storage cell,** using best combination of above cell components.



**Na-K phase diagram** showing ambient liquids, 13 to 72at.% sodium, (from ASM 90146).

Sandia National Laboratories

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