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

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ASU IOWA STATE

Purpose

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

•Strategies:

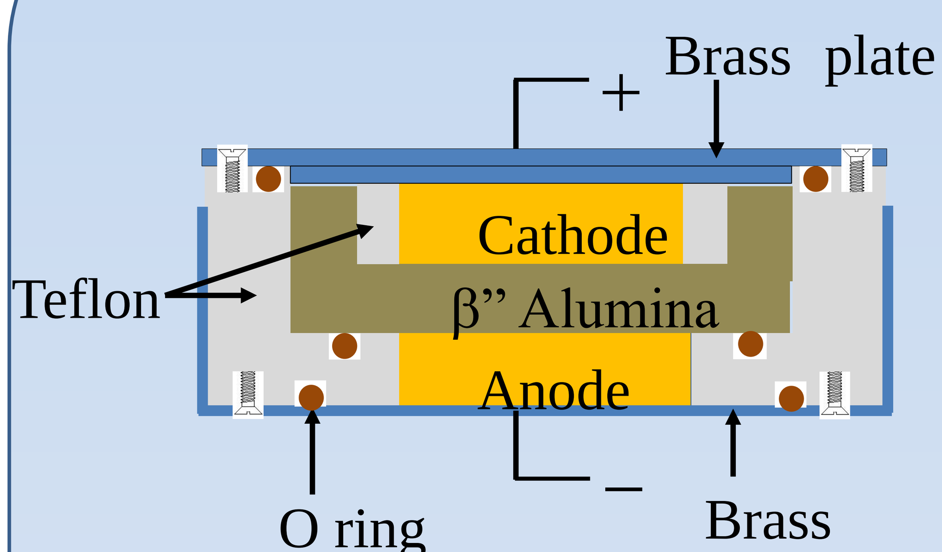
- **Anode**: Use Na-K alloy anode,
- **Separator**: Na-K alloy anode demands use of joint Na+/K+ conducting separator: **use β"-Al_2O_3.**
- **Cathode contact electrolyte**: $NaAlCl_4$ freezes at 185ºC. Need low-melting non-volatile additives to produce ***"ionic oils"*** e.g. the chlorosulfonylfluorosulfonyl imides of Li+
- **Cathode: $NiCl_2$ solid (**or possibly 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"

Preliminary Results



At ISU, we have:

- Designed new versatile cell to cycle different combinations of the battery components, anode, cathode, and electrolyte, over a temperature range of -20 to 100ºC.
- **Liquid anode** contained inside β"-alumina/composite cup.

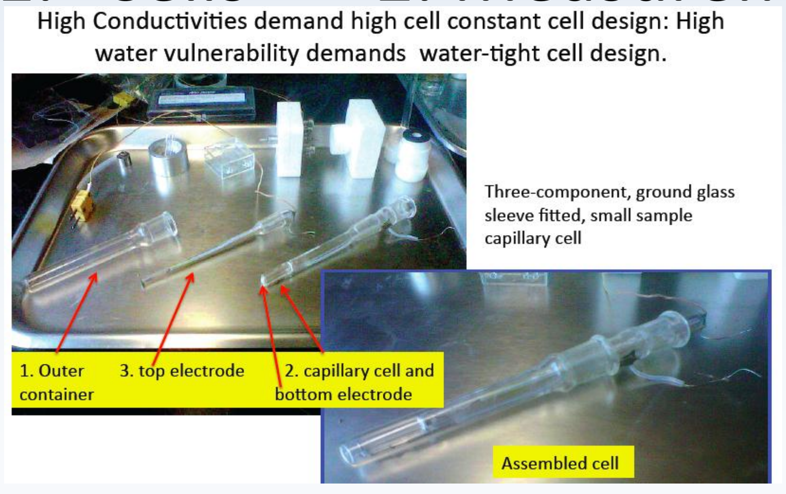
•Liquid cathode is contained in the bottom cup formed by the seal teflon container. Liquid (sulfur complex or bromine red oil) cathode or $NiCl_2$ (Zebra version)

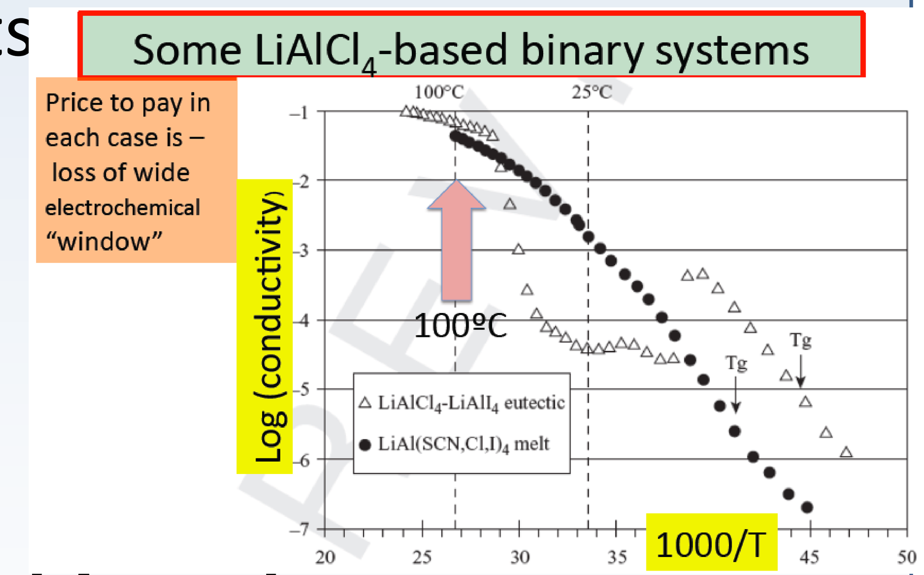
Separator: Composite β" Al_2O_3 trials.

- Powdered β" Al_2O_3, as base conductor, is being incorporated in sparse (sinter-type) matrices of high individual conductivities
  - (a) at ISU, in Na+ conducting glasses. (Trials begun)
  - (b) at ASU, in nanporous Ti epoxide nets filled with Na+ "ionic oil"

Cathode contact electrolyte: Low-melting eutectic

1. Cells 2. Measurements





3. **Syntheses of new low-melting salts.**

We have sought to create new sodium salts by combination of sodium (basic anion)-ide and $AlCl_3$, using phenoxide and perfluoroalkylxide, so far without success. More stable anions like triflate, and BETI, are OK. We now work on chloroimides.

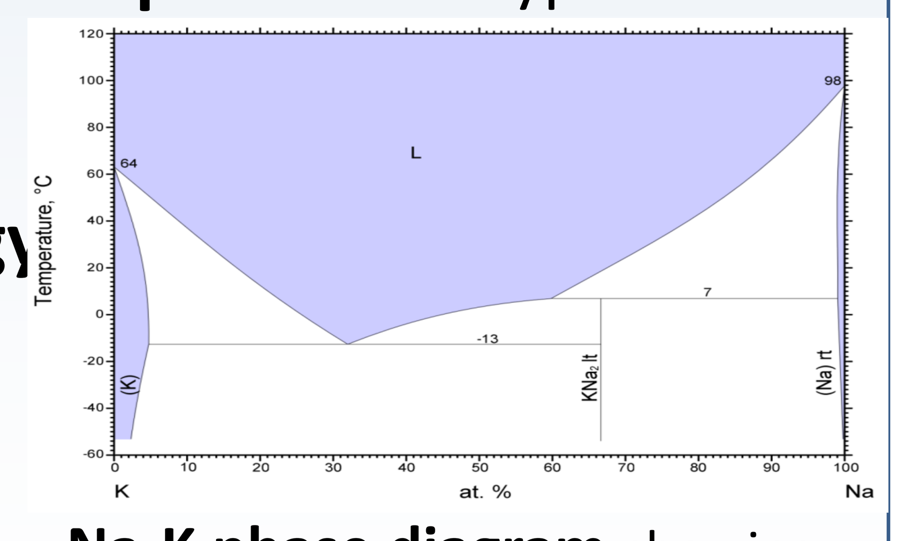
Research Plan

At ASU:

1. **Synthesize new sodium salts and evaluate their eutectics with (Na,K)$AlCl_4$. (a)** use homemade DTA system for preliminary studies **(b)** use DSC for best cases to determine phase diagram (using carefully tested samples since leaks of ionic liquids kill DSCs)
2. **Determine conductivities** and viscosities, and then form Walden plots to seeking "superionic oils", highly conducting but stable at ambient temperature.
3. **Form nanoporous nets** to decorate with anionic sites so Na+ ions, but nothing else, can migrate through. Use as glue for β" Al_2O_3

At ISU:

1. **Using commercial, and homemade glass-treated β" Al_2O_3 separators,** test the adjacent cell design with ambient liquid Na-K anode (see phase diagram), and liquid cathode (bromine for alkali-halide cell) or proprietary chain polysulfides (for Na/S 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).

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