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

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Purpose
• To develop a lower temperature, thermally cycleable, 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“-Al₂O₃.
  • Cathode contact electrolyte: NaAlCl₄ freezes at 185ºC. Need low-melting non-volatile additives to produce “ionic oils”. Best choices are ionic liquids like EMIM-ACl₂.
  • Cathode: NiCl₂ on Ni foam (or a “red oil” Br₂, or sulfur)

Impact on DOE OE Energy Storage Mission
• Enhanced operating flexibility enabled by non-solidifying cell chemistry, allowing battery shutdown
  • Zebra cell (Na/NaCl₂) 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/NaAlCl₂-Na,K(XYZ)/Br₂ “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 NiCl₂ (Zebra version).

• Single ion conducting separator β“ Al₂O₃ (or novel Na boro-epoxide glasses or complex inorganic Na⁺-conductive plastic crystal)

• Powdered β” Al₂O₃, as base conductor, incorporated in Na⁺ conducting Na₂S + P₂S₅ glasses at ISU, then heat treated at 380 ºC and 480 ºC

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

Research Plan
At ASU:
1. Determine liquidus surfaces for systems of ionic liquids with (Na,K)AlCl₄ 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” Al₂O₃ 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.

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