Advanced Development Concept

Nitrogen-Air Battery

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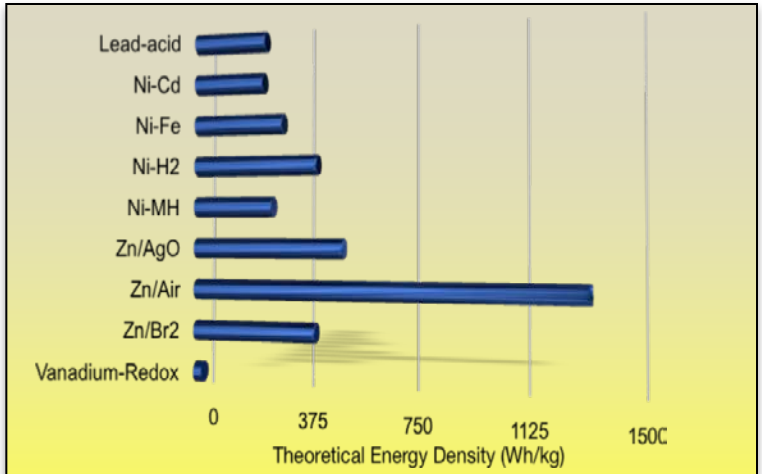
Full Air Breathing Battery Concept



Zn/Air has the highest energy density of aqueous battery chemistries because the weight of the cathode is not included in the calculation. The energy density would increase greatly beyond Zn/Air if the anode material were also derived from the air.

- Concept is to use O_2 and N_2 as the electrodes in a battery
- Novel because N_2 is considered inert
- Our group routinely reacts N_2 electrochemically
- Challenging but appears feasible based on preliminary experimental results
- Enormous potential impact on stationary and mobile energy storage in both energy storage density and in economic value

- Year 1 objectives
- Focus on nitrogen
  - establish electrochemical behavior of nitrogen species
  - measure gas solubility in electrolyte solutions

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Many Science and Engineering Challenges

- Nitrogen has a high energy density and low normalized cost
  - 6 electrons per molecule
    - 5743 mAh/g
  - low cost
  - benign (safe)
- N_2 reduction is highly complex
- Numerous other challenges
  - electrode structure
  - cell design
  - solubility
  - high reactivity of intermediates and products – e.g N^{3-}
  - electrolyte

- Half-reaction in aprotic media

  - $N_2 + 6e^- = 2N^{3-}$

Theoretical Calculations for the 6-e^- 6-H^+
Reduction of Nitrogen
Half-reaction $N_2 + 6e^- + 6H^+ = 2NH_3$

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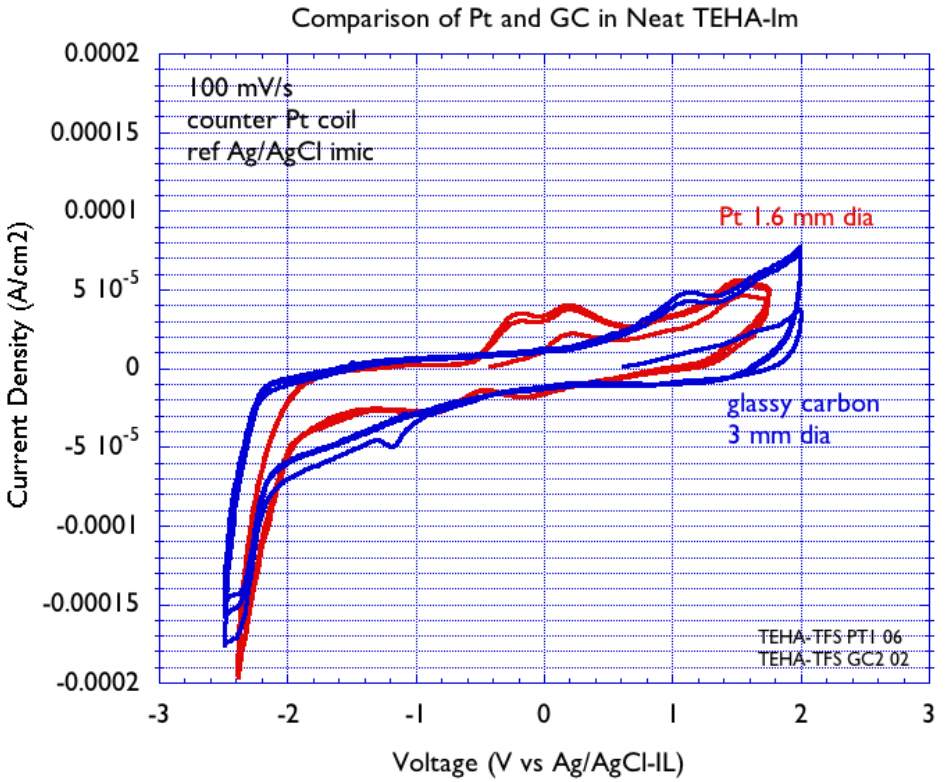
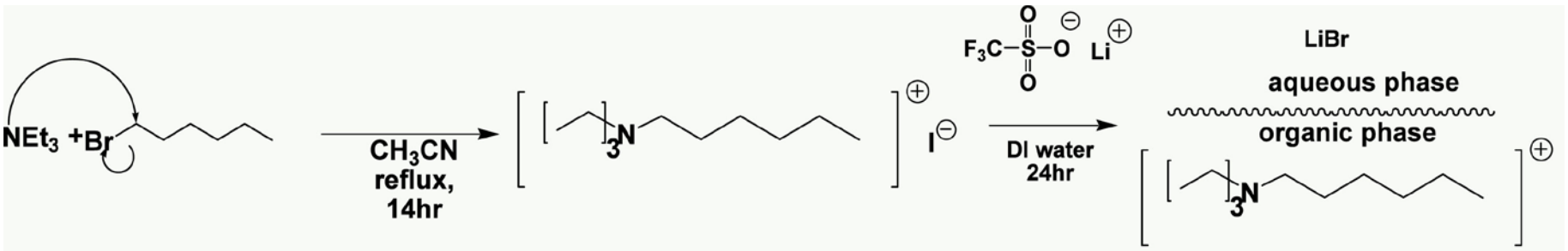
Electrolyte Working Range

- Molten salt as baseline electrolyte
  - high temperature
  - room temperature ionic liquid (IL)
- Numerous criteria
  - Electrochemically stable over the requisite working range
    - have synthesized and evaluated a number of ionic liquids
    - some are stable
  - reasonable solubility of gases

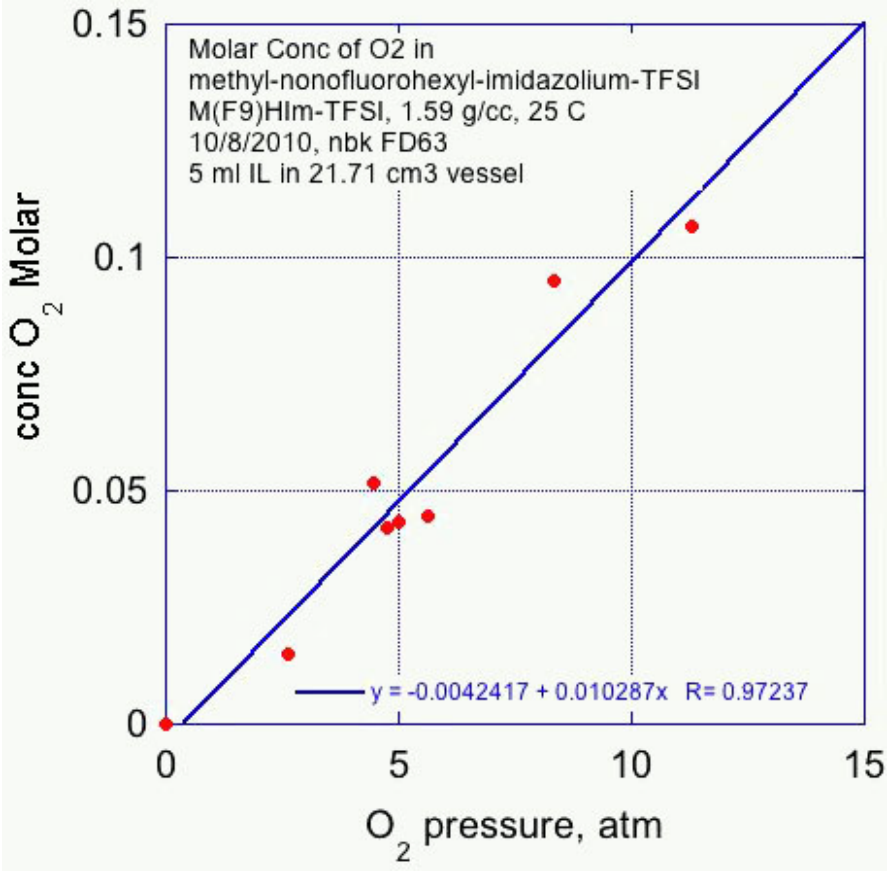


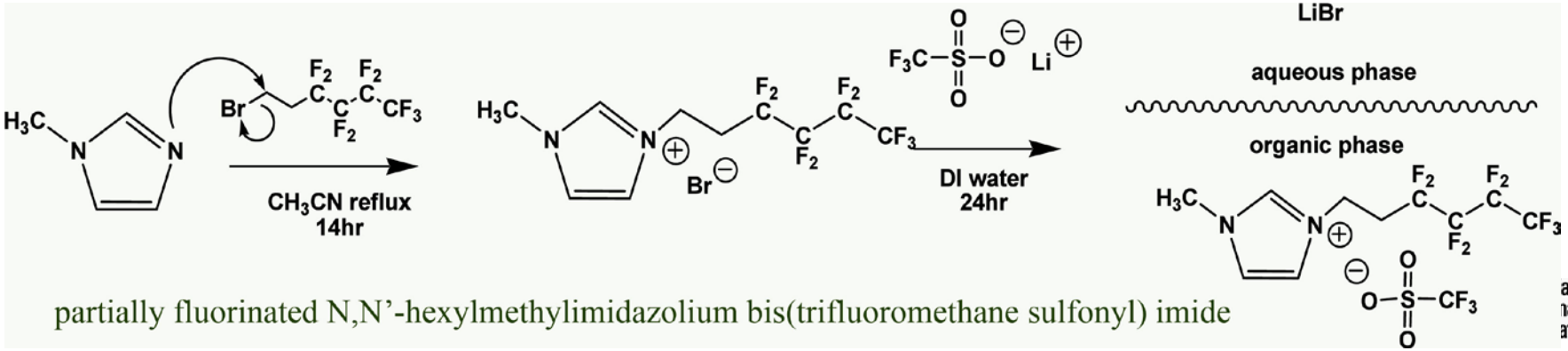


Synthesis of triethylhexylammonium bis(trifluoromethane sulfonyl) imide (TEHA-Im)

Gas Solubility in the Electrolyte

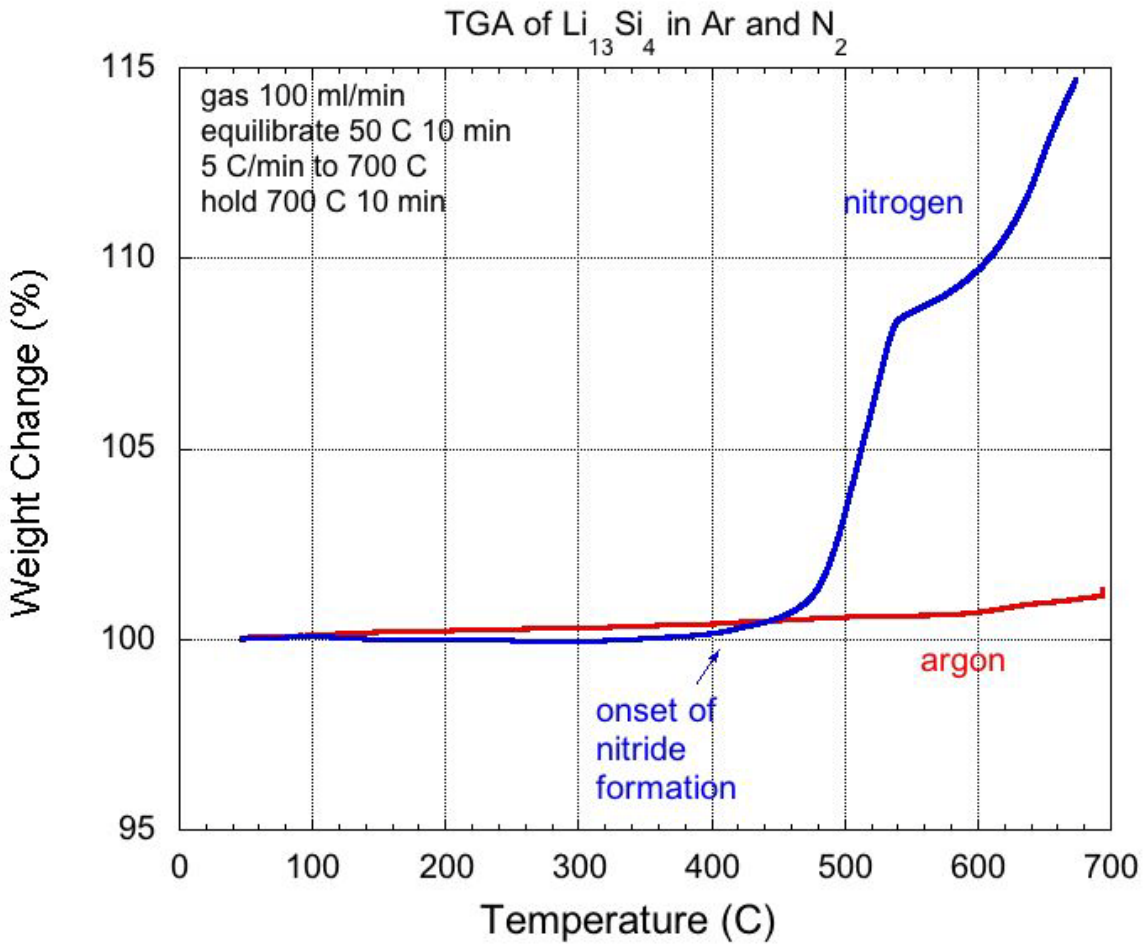
- Have determined the solubility of gases in a variety of ionic liquids
  - O_2, N_2, CO_2
  - CO_2 very soluble
  - O_2 and N_2 - vanishingly small
- Increasing the solubility of species in the electrolyte to optimize rate
- Tailoring the solution to increase gas solubility
    - gas diffusion electrode
    - engineer the properties of the ionic liquid
      - fluorinated IL increases O_2 solubility
      - N_2 not yet measured





Chemistry of Nitrogen and Reaction Products

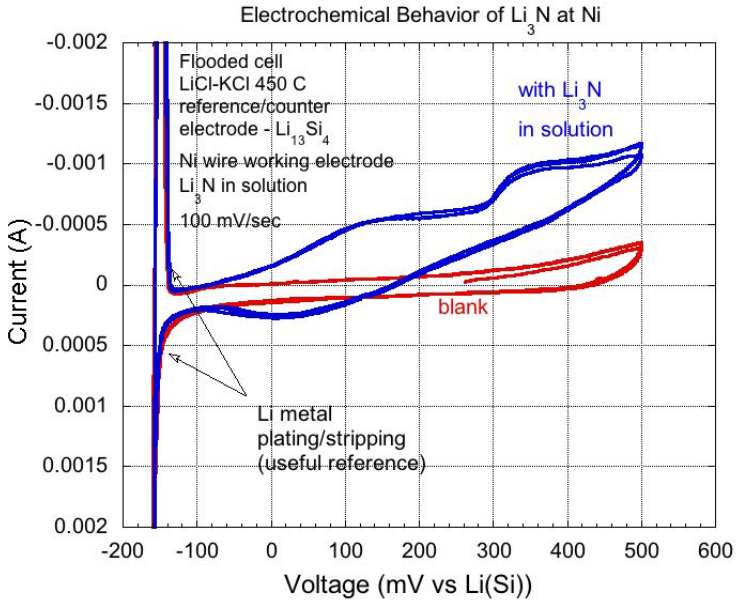
- Understanding the chemistry of N_2 and the species involved in its reduction is critical
- We have used a variety of techniques to characterize these species
  - spectroscopy of N^{3-} in ILs
    - IR
    - Raman
    - UV-Vis
    - NMR
  - Thermal
    - TGA
    - DTA
    - DSC
  - others

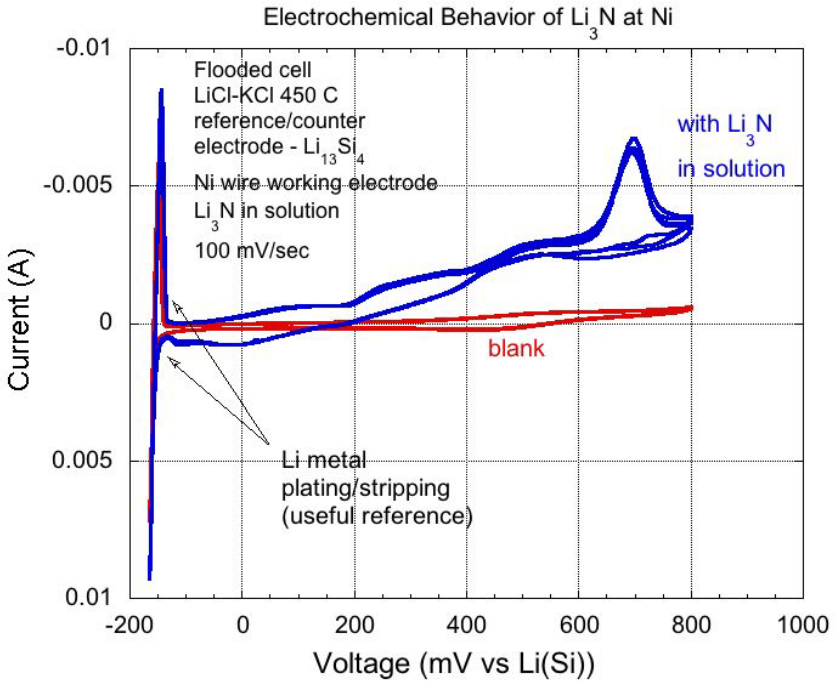


Electrochemistry of Nitrogen
Nitride Oxidation

- The electrochemical behavior of nitrogen species is most important
  - thermodynamics (voltage)
  - kinetics (power)
  - mechanism (power, reversibility, etc)
- Basic electrochemical process in aprotic media
  - $N_2 + 6e^- = 2N^{3-}$

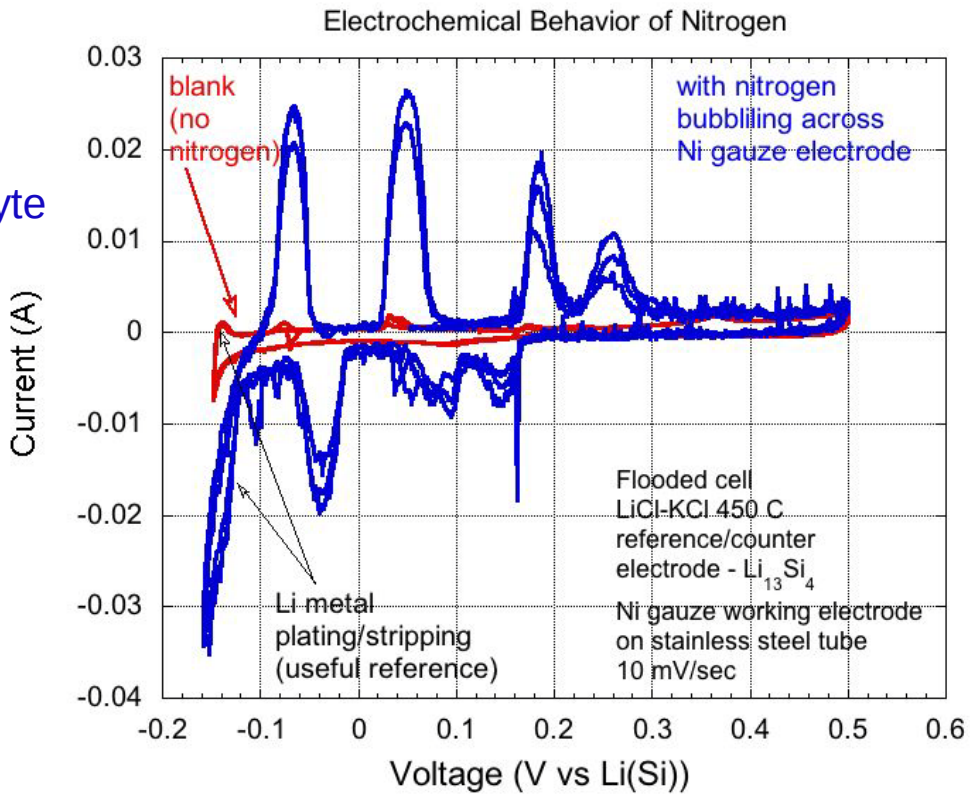
- We have completed preliminary electrochemical evaluation of nitride (N^{3-}) and nitrogen
  - Two cell configurations
    - flooded cell design
    - pressed pellet configuration
  - High temperature molten salt electrolyte
    - LiCl-KCl (45:55), 352 ° C melting point
  - $Li_{13}Si_4$ ref and counter electrode
    - solid at high temperature, stable reversible couple, 149.2 mV vs Li
    - also deposited Li at working to provide another reference
  - Ni foam and Ni wire working electrode





Electrochemistry of Nitrogen
Nitrogen Reduction

- Reduction of N_2
  - $N_2 + 6e^- = 2N^{3-}$
- Experimental Details
  - flooded cell design
  - Ni foam on stainless steel tube as the working electrode
  - High temperature molten salt electrolyte
  - LiCl-KCl (45:55), 352 ° C melting point
  - $Li_{13}Si_4$ ref and counter electrode
- nitrogen bubbled over Ni foam electrode
  - numerous redox process evident
  - reduction a very negative potentials
    - retain high energy



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Summary and Conclusions

- The electrochemistry of nitrogen is clearly non-trivial
- However, nitrogen can be reversibly reduced and oxidized at voltages consistent with high energy systems
- a path forward for increased solubility of gases in room temperature ionic liquids has been identified
- Select ionic liquids have the requisite electrochemical stability to allow their use as a room temperature electrolyte

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FY11 Proposed Work

- continue investigations of nitrogen electrochemistry
- continue low temperature electrolyte development
- develop oxygen cathode

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