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# Nitrogen-Air Battery

## Advanced Development Concept

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Sandia National Laboratories
Albuquerque, NM

presented to

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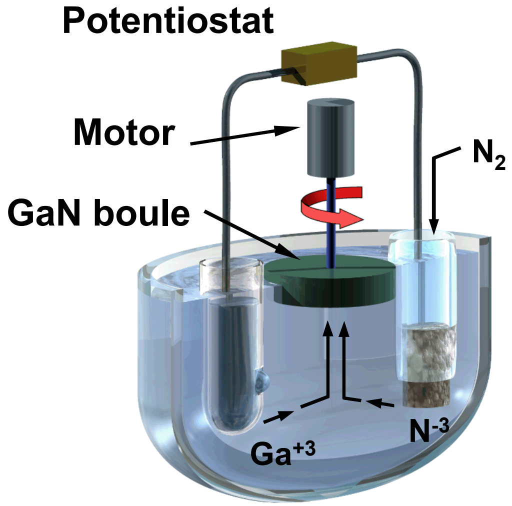
# Small Molecule Multielectron Transfer Reactions for Energy Storage

- Use the constituents found in the air as the battery active materials
  - Full air breathing battery
    - Oxygen cathode - four electrons per molecule: $O_2 + 4e^-$
    - Nitrogen anode – six electrons per molecule: $N_2 + 6e^-$
      - Large theoretical capacity 5.743 Ah/g
      - Safe
      - Low cost
- Enormous potential impact on stationary and mobile energy storage in both energy storage density and in economic value
- Initially appeared feasible based on our initial results, work done by K.Waldrip on the synthesis of GaN at SNL, and information available in the literature (e.g. Kyoto Univ. w/$Li_3N$ necessary)



Artistic rendering of synthesis of GaN through electrochemical generation of precursors:

$2Ga \rightarrow 2Ga^{+3} + 6e^-$

$N_2 + 6e^- \rightarrow 2N^{-3}$ ← nitrogen electrochemistry

$Ga + N_2 \rightarrow Ga^{+3} + N^{-3} \rightarrow GaN$

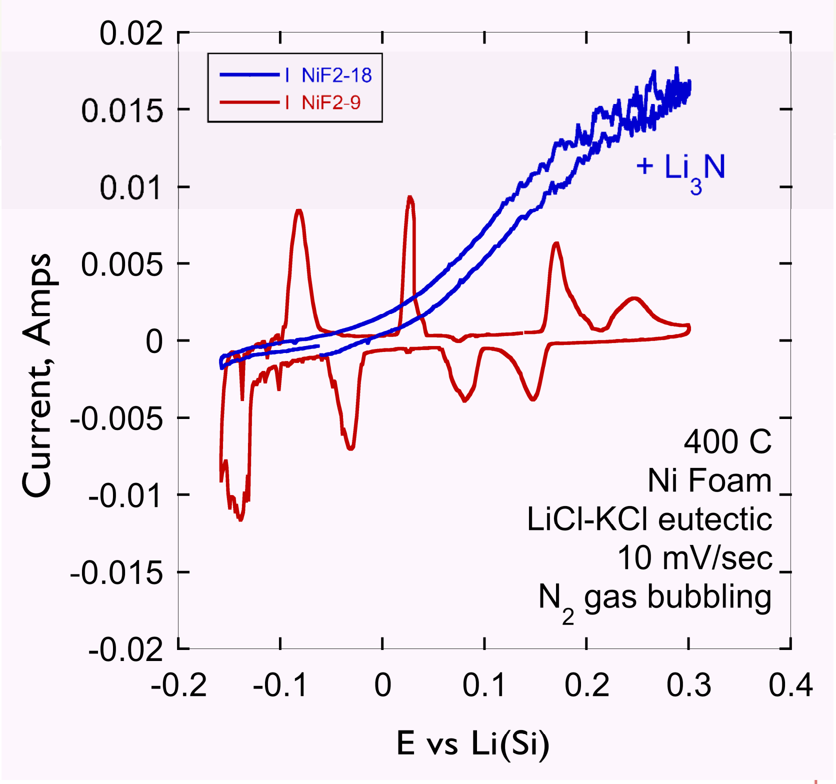
nitrogen to nitride as the anode for battery applications

***Karen Waldrip U.S. Patent Issued October 2008***

# Reduction of Nitrogen (Charge) & Oxidation of Nitride (Discharge)

- Reversible reduction of $N_2$
  - we routinely oxidize and reduce nitrogen species
  - $N_2 + 6e^- \Leftrightarrow 2N^{3-}$ E = 0.44 V vs Li

- Cell Design and electrode is moving forward
  - – flooded cell
  - – Ni foam electrode
    - – we do plan to evaluate other materials as active electrodes
  - – Electrode design currently under development (KW)

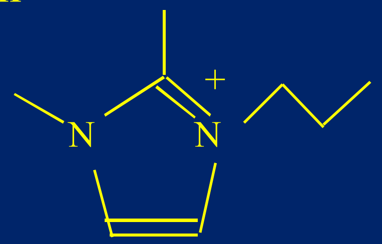


– Electrolyte
  - – High temperature molten salt electrolyte
  - – LiCl-KCl (45:55), 352 °C melting point

# Other Molten Salt Electrolytes

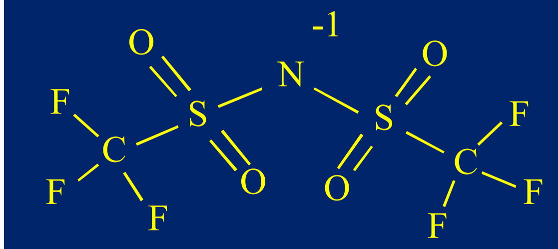
- Lowering the operating temperature
  - simplifies the cell and battery design and eases the engineering constraints
  - the operating temperature is currently defined by the electrolyte
- $N_2/N^{3-}$ couple
  - $N_2 + 6e^- \leftrightarrow 2N^{3-}$
  - – charge compensation
- We have investigated other inorganic salts, but have not identified a viable option
  - – e.g. alkali metal tetrachloroaluminates
- Ionic liquids
  - – previously determined that $Li_3N$ will form solutions with DMPI-Im at low concentration
  - – in our effort to characterize the solution, we determined that the IL is unstable against the nitride – occurs at elevated nitride concentrations
    - the imide decomposes

Cation



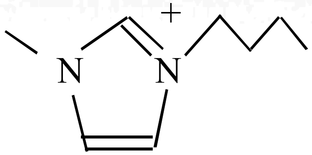
2,3-dimethyl-1-propylimidazolium
(DMPI)

Anion

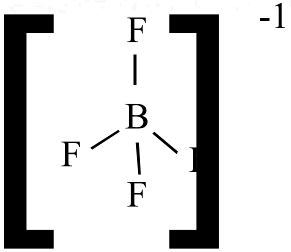


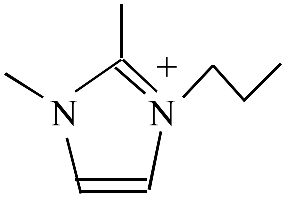
perfluoromethylsulfonyl imide
(Im)

# Room Temperature Ionic Liquids

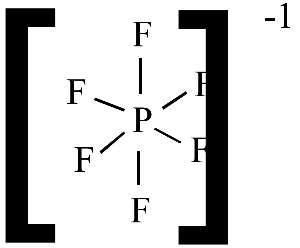


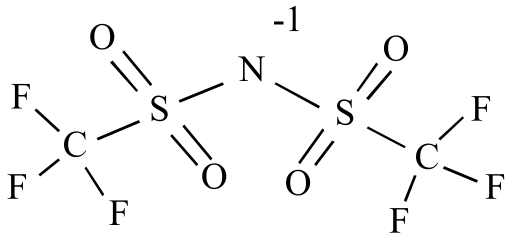
1-butyl-3-methylimidazolium
BMI





2,3-dimethyl-1-propylimidazolium
DMPI

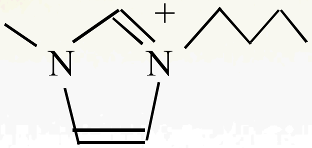




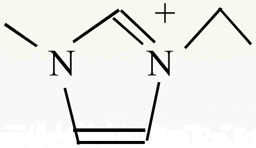
perfluoromethylsulfonyl imide
Im

|  | mp °C | + $H_2O$ |
|---|---|---|
| BMI-$BF_4$ | -71 | miscible |
| BMI-$PF_6$ | 10 | 11700 ppm |
| BMI-Im | 1 | 3280 ppm |
| DMPI-Im | 15 | hydrophobic |

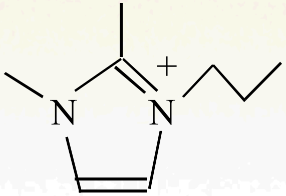
# Selected Imidazolium Ionic Liquids



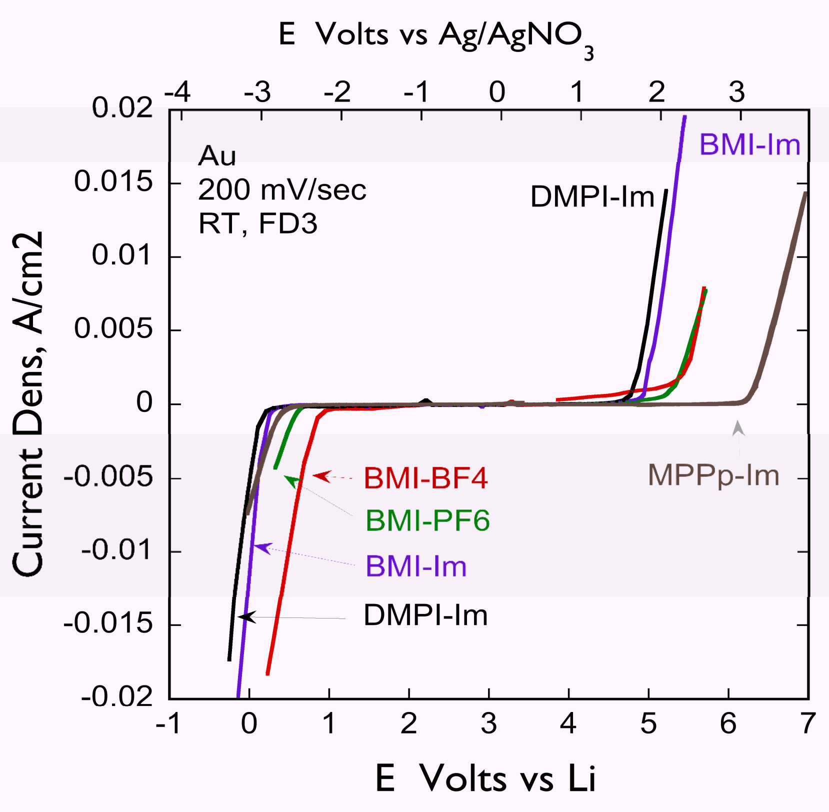
1-butyl-3-methylimidazolium
BMI

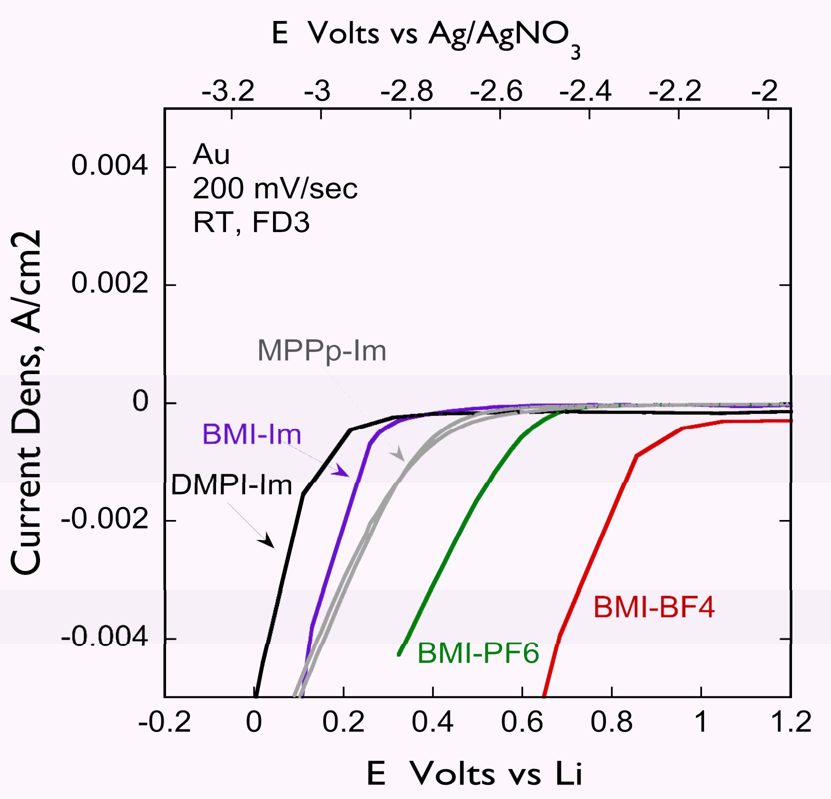


1-ethyl-3-methylimidazolium
EMI

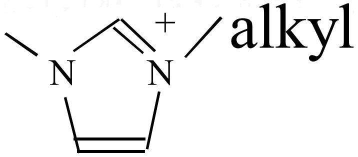


2,3-dimethyl-1-propylimidazolium
DMPI





# Alkyl Methylimidazolium - Im, $PF_6$, $BF_4$, $Cl^-$, $I^-$



1-alkyl-3-methylimidazolium
AMI

Huddleston *et. al.* (2001)

Choice of anion determines water miscibility.

For common anion, increasing alkyl chain length increases hydrophobisity

# Many Significant Science and Engineering Challenges

- There are many challenges with the individual cell elements as well as with the interactions between the cell elements in a complete cell configuration
  - electrode structure
  - electrode materials
  - cell design
  - solubility/stability of reactants and products
  - reactivity of intermediates and products – e.g $N^{3-}$
  - electrolyte composition
    - Low temp molten salt
    - High temp molten salt
    - Non-aqueous electrolyte
    - Aqueous electrolyte
  - electrolyte compatibility between anode and cathode
  - cross-over between anode and cathode
  - Interactions between cell constituents – e.g. passive layer formation on Ni electrodes in room temperature ionic liquids, solubility of Ni-oxides in chloride melts (no passivation), etc

- Given the complexity of the challenges faced for a full-cell design and based on the work done in FY10, in FY11 we focused solely on the anode - the $N_2$ reduction reaction
  - temperature of operation
  - electrolyte composition
  - catalyst
  - electrode material

# Another Approach to Lowering the Temperature

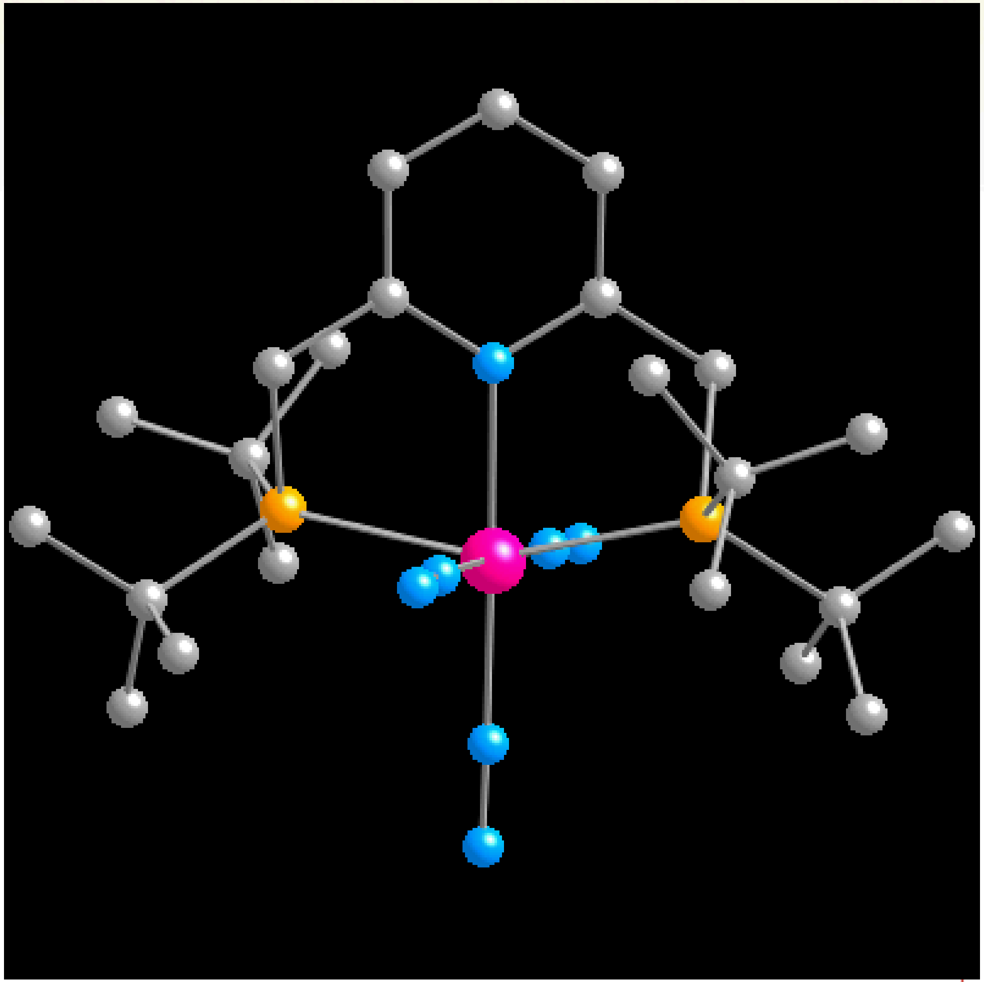
- Lowering the operating temperature
  - simplifies the cell and battery design and eases the engineering constraints
  - 
- Employ a different charge compensating ion
  - $N_2 + 6e^- + 6Li^+ \leftrightarrow 2NLi_3$ ($Li_3N$)
  - $N_2 + 6e^- + 6H^+ \leftrightarrow 2NH_3$
  - the lithium analog to ammonia
  - leads to a different reaction sequence for energy storage
  - will result in a lower battery voltage
- A catalyst will be needed for lower temperature reaction

# Molybdenum Catalyst for $N_2$ Reduction to Ammonia

- Molybdenum phosphorous pincer ligand complex as a catalyst for $N_2$ reduction
  - In THF with an electron source, $MoPNP(N_2)_3$ was used as the catalyst to form $NH_3$

$$MoPNP(N_2)_3 + 6e^- + 6H^+ \leftrightarrow 2NH_3$$

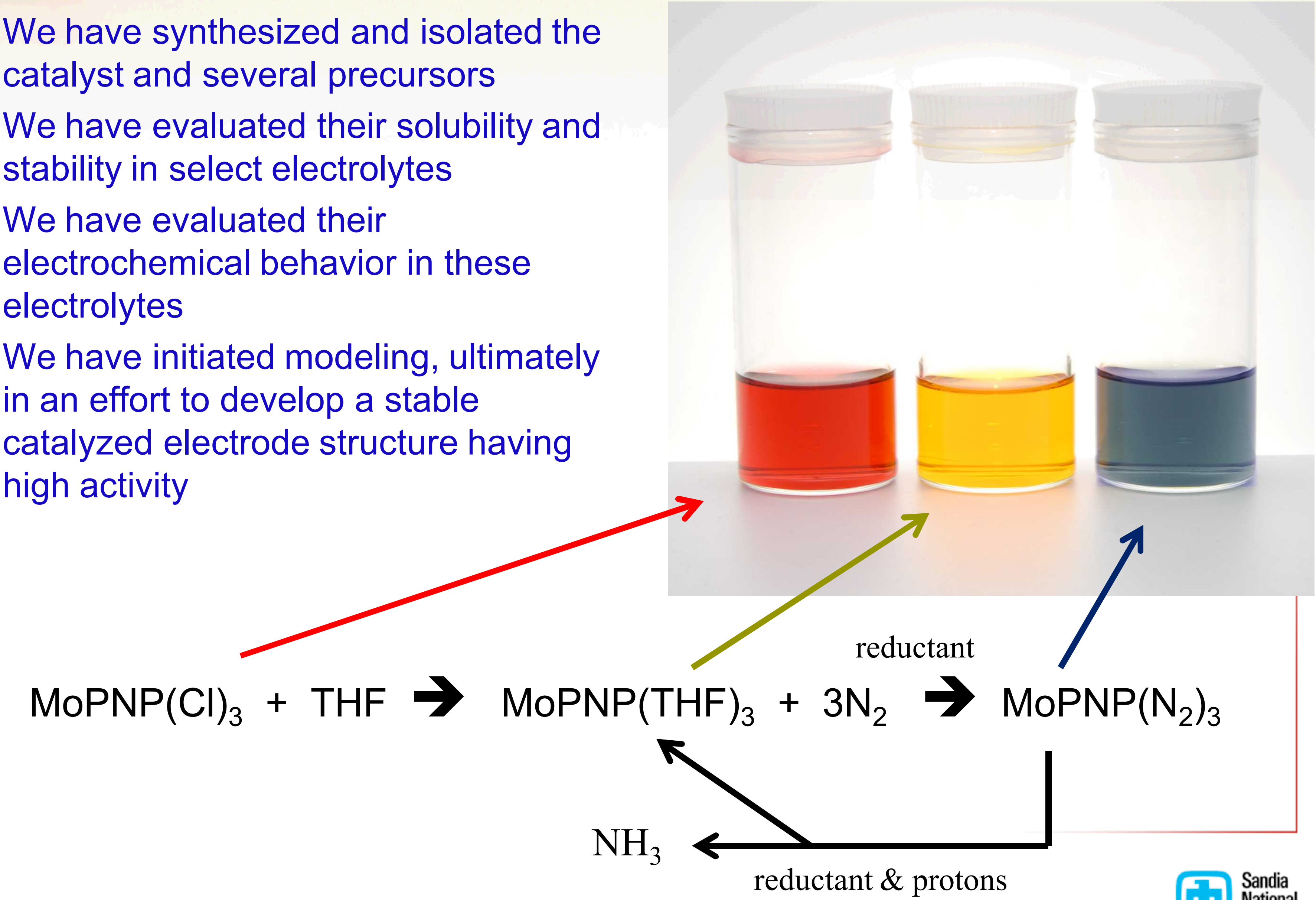
- THF is a battery solvent
- We will use an electrode in place of the chemical electron mediator source



Arashiba et al., Nature Chemistry, 3, 120, (2011)

# Molybdenum Catalyst

1. We have synthesized and isolated the catalyst and several precursors
2. We have evaluated their solubility and stability in select electrolytes
3. We have evaluated their electrochemical behavior in these electrolytes
4. We have initiated modeling, ultimately in an effort to develop a stable catalyzed electrode structure having high activity



$$\mathrm{MoPNP(Cl)_3} + \mathrm{THF} \rightarrow \mathrm{MoPNP(THF)_3} + 3\mathrm{N_2} \xrightarrow{\text{reductant}} \mathrm{MoPNP(N_2)_3}$$

$$\mathrm{MoPNP(N_2)_3} \xrightarrow{\text{reductant \& protons}} \mathrm{NH_3} + \mathrm{MoPNP(THF)_3}$$

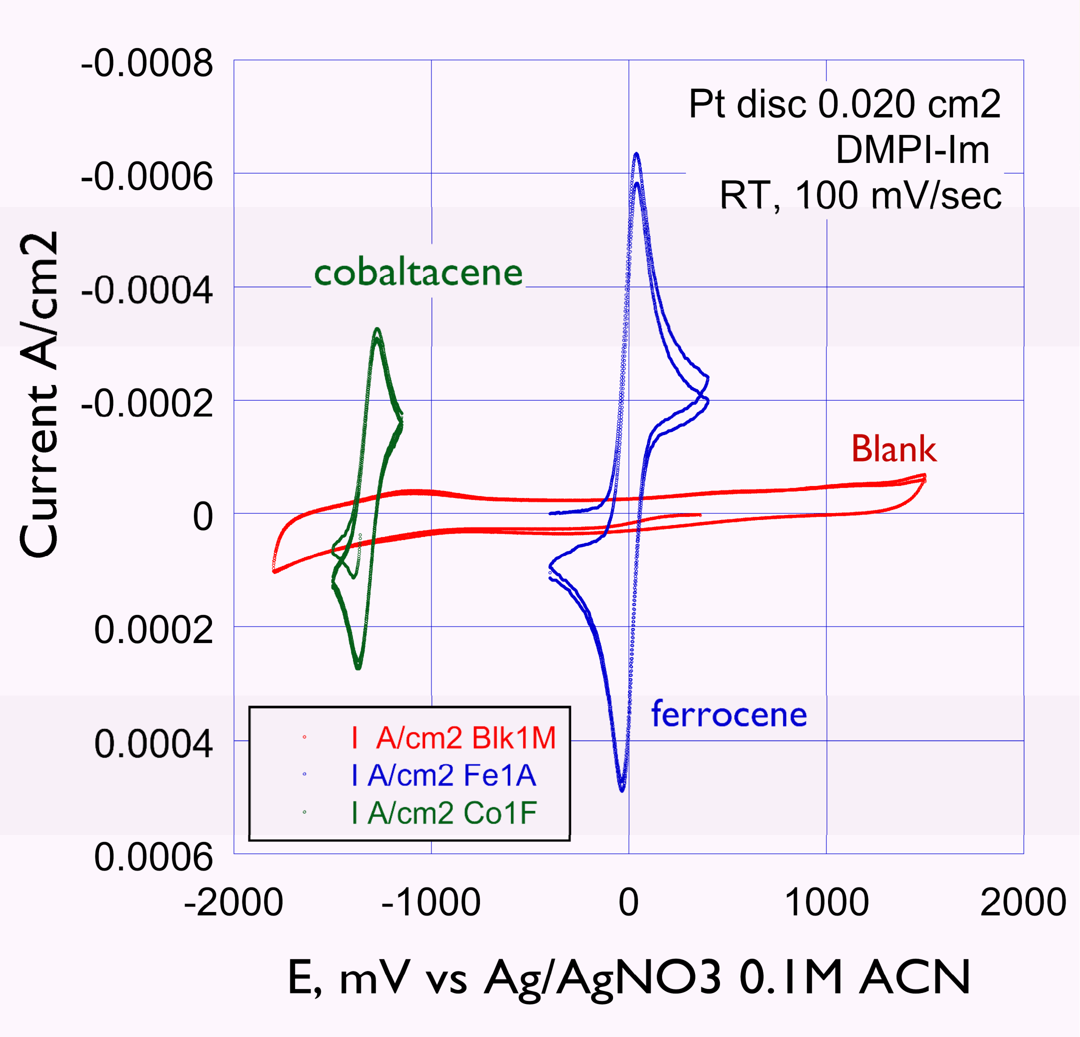
# Catalyst is Electroactive at a Solid Electrode

- Have demonstrated the catalyst is electroactive at a solid electrode
  - Need to couple to an electrode structure in the battery
- Have demonstrated that the catalyst and precursors are electroactive in different electrolytes
- Catalyst and precursors are soluble, stable, and electrochemically active in:
  - THF – original solvent used.
    - High vapor pressure and flammable
  - Dimethoxyethane (DME) – traditional standard battery solvent
    - High vapor pressure and flammable
  - Aromatic Ionic Liquids – imidazolium quaternary ammonium ions
    - Non-flammable, room temperature molten salt with low vapor pressure
  - nonAromatic Ionic Liquids – assymetric alkyl ammonium ions
    - Non-flammable, room temperature molten salt with low vapor pressure

- Provides a path forward to safe electrolyte system
  - High molecular weight analogs to DME (glymes, diglyme)
  - Ionic liquids

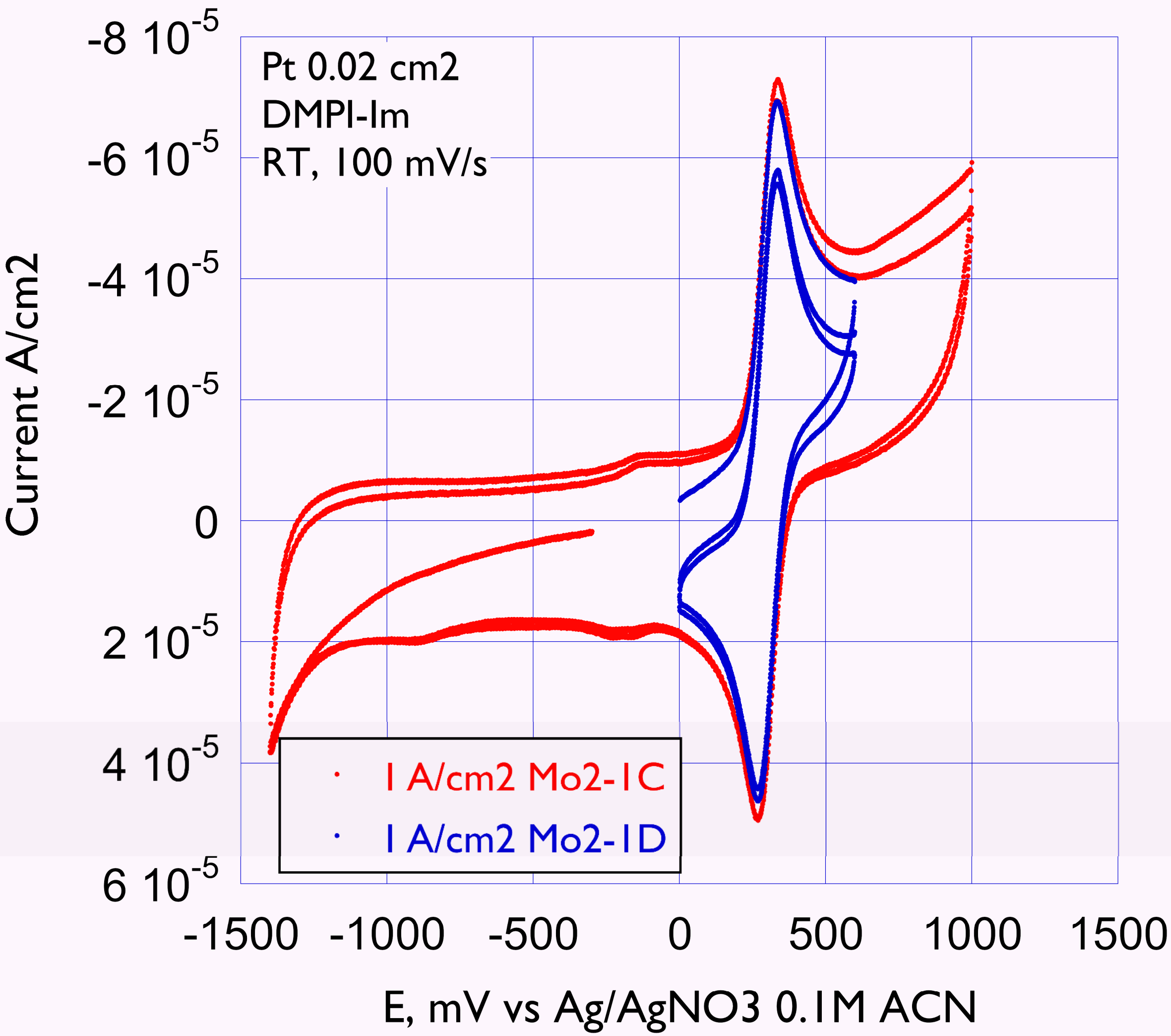
# Electrochemical Behavior of Mo Species

- Redox behavior of blank and select couples
- Cobaltocene is the electron transfer compound used for the Arashiba $NH_3$ synthesis

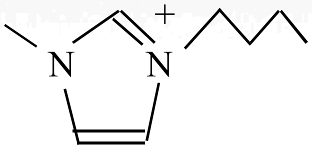


# MoPNP(THF)$_3$

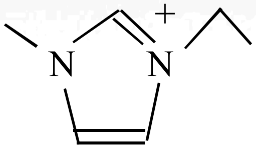
- the MoPNP(THF)3 exhibits reversible redox behavior
- All of the MoPNP compounds exhibit rich electrochemical behavior at solid electrodes
- All of the MoPNP compounds are stable in a variety of solvents
- All of the MoPNP comppounds exhibit the same electrochemical behavior in these different solvent systems



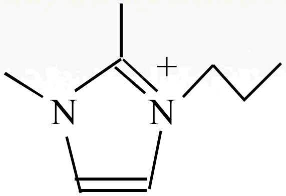
# Selected Imidazolium Ionic Liquids



1-butyl-3-methylimidazolium
BMI



1-ethyl-3-methylimidazolium
EMI



2,3-dimethyl-1-propylimidazolium
DMPI

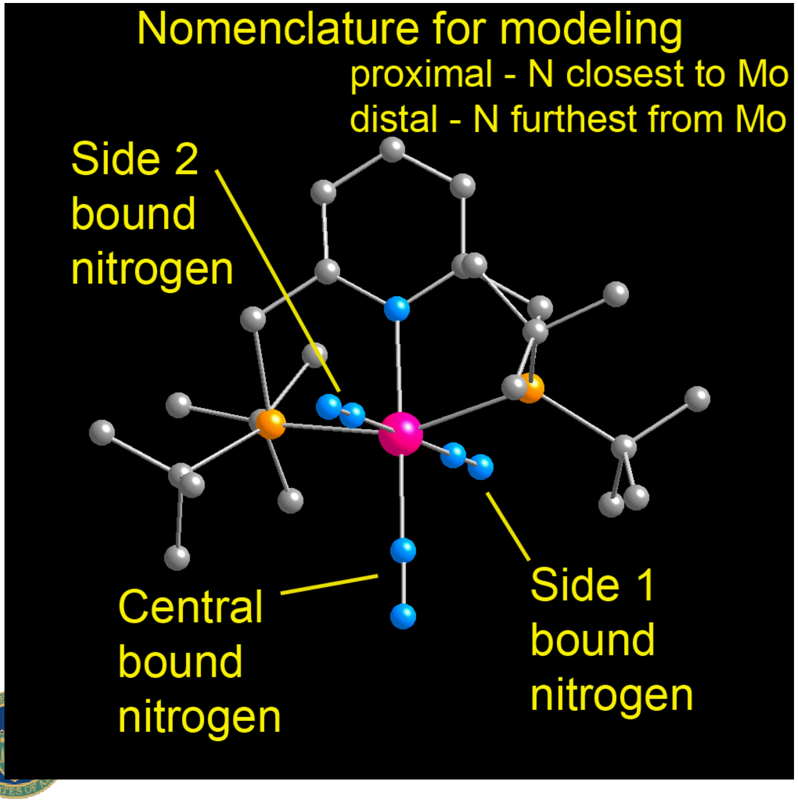
Seki *et. al* (2006) reduction of imidazolium cation occurs at C2 proton
DMPI-Im more stable than EMI-Im, DMPI-Im much more suited to $Li^+$ reduction.

Yokozeki *et. al.* (2007) BMI-$PF_6$, BMI-$BF_4$, EMI-Im**, exhibit high solubility for $NH_3$ at** room Temp. 20-40 mole/o (adsorption cooling/heating cycle)

Shi *et. al.* (2009) Osmotic Ensemble Monte Carlo Simulations compare solubilities of CO
$SO_2$, $N_2$, **$O_2$ and $NH_3$ in EMI-Im**
**Solubility of $NH_3$ result of hydrogen bonding to C2 proton.**
Solubility of $SO_2$, $CO_2$**, $N_2$ and $O_2$ result from anion interactions**

# Modeling the Catalyst

- Understand the electrocatalytic reaction to:
  - improve the catalyst
  - improve electrocatalytic performance
  - determine if the electronic structure at the surface of metallic electrodes (including alloys) will provide a structure consistent with the Mo-$N_2$ catalytic structure



Nomenclature for modeling

proximal - N closest to Mo

distal - N furthest from Mo

Normalized Binding Energies and Spin of Lone H Addition to Various Metal-PNP-N2 Complexes

| No. H added | Side | Central | m | B.E./H-atom |
|---|---|---|---|---|
| Mo Complex | | | | |
| 1 | | distal | 1 | 0.82 |
| **1** | distal | | **1** | **0.95** |
| W Complex | | | | |
| 1 | | distal | 1 | 1.00 |
| **1** | distal | | **1** | **1.04** |
| V Complex | | | | |
| **1** | | distal | **0** | **1.95** |
| 1 | distal | | 0 | 1.41 |

- Notice that substituting V for Mo makes the pincer molecule much more attractive for the 1st H atom addition. We don't yet know what will happen when subsequent H's added. Also notice that addition to the central $N_2$ is more attractive in the V complex, which is opposite than for both Mo and W.
  - We plan to synthesize the V complex to evaluate this catalyst
- We have completed modeling of 1, 2, 3, and 4 H atom additions in various locations and positions

# Normalized Binding Energy for Addition of H Atoms

| No H-atoms | $N_2$ Location | | | spin m | B.E. / H-atom |
|---|---|---|---|---|---|
| | Side 1 | Side 2 | Central | | |
| 1 | | | distal | 1 | 0.82 |
| 1 | | | proximal | 1 | 0.06 |
| **1** | **distal** | | | **1** | **0.95** |
| 1 | proximal | | | 1 | 0.00 |
| | | | | | |
| 2 | | | distal | 0 | 1.47 |
| 2 | distal | | | 0 | 1.68 |
| **2** | | | **trans** | **0** | **1.86** |
| 2 | trans | | | 0 | 1.80 |
| 2 | | | cis | 0 | 1.77 |
| 2 | cis | | | 0 | 1.65 |
| 2 | distal | distal | | 0 | 1.31 |
| | | | | | |
| 3 | | | $NH-NH_2$ | 1 | 1.96 |
| 3 | trans | distal | | 1 | 1.61 |
| 3 | trans | | distal | 1 | 1.64 |
| **3** | **$NH-NH_2$** | | | **1** | **2.01** |
| 3 ($NH_3$ eliminated) | | | $N-NH_3$ | 1 | 1.99 |
| 3 ($NH_3$ stays on) | $N-NH_3$ | | | 1 | 1.48 |
| 3 | distal | distal | distal | 1 | 1.10 |
| **3 $NH_3$ H bonds** | **$NHNH_2$** | **$N_2$ off** | | **1** | **>2.17** |
| | | | | | |
| 4 | | | $NH_2NH_2$ | 0 | 2.16 |
| **4 ($N_2H_4$ eliminated)** | | **$NH_2NH_2$** | | **0** | **2.22** |
| 4 | | | $NH-NH_3$ | ~0 | 1.88 |
| 4 | trans | trans | | 0 | 1.74 |
| 4 | | trans | trans | 0 | 1.77 |
| 4 | | cis | trans | 0 | 1.79 |

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# Summary and Conclusions

- The electrochemistry of nitrogen is clearly non-trivial.
- nitrogen can be reduced to nitride ($N^{-3}$) and the nitride can be oxidized back to nitrogen at voltages consistent with high energy batteries.
- the Arashiba catalyst provides a low temperature approach for nitrogen reduction to $NH_3$.
- the Arashiba catalyst is compatible with electrolyte solvents amenable to large-scale systems.

# Future Tasks

- complete design and development of the gas diffusion electrode for use in the high temperature molten salt
- demonstrate Mo-catalyzed reduction of $N_2$ in half-cells.
- complete IL half-cell studies

# Acknowledgements

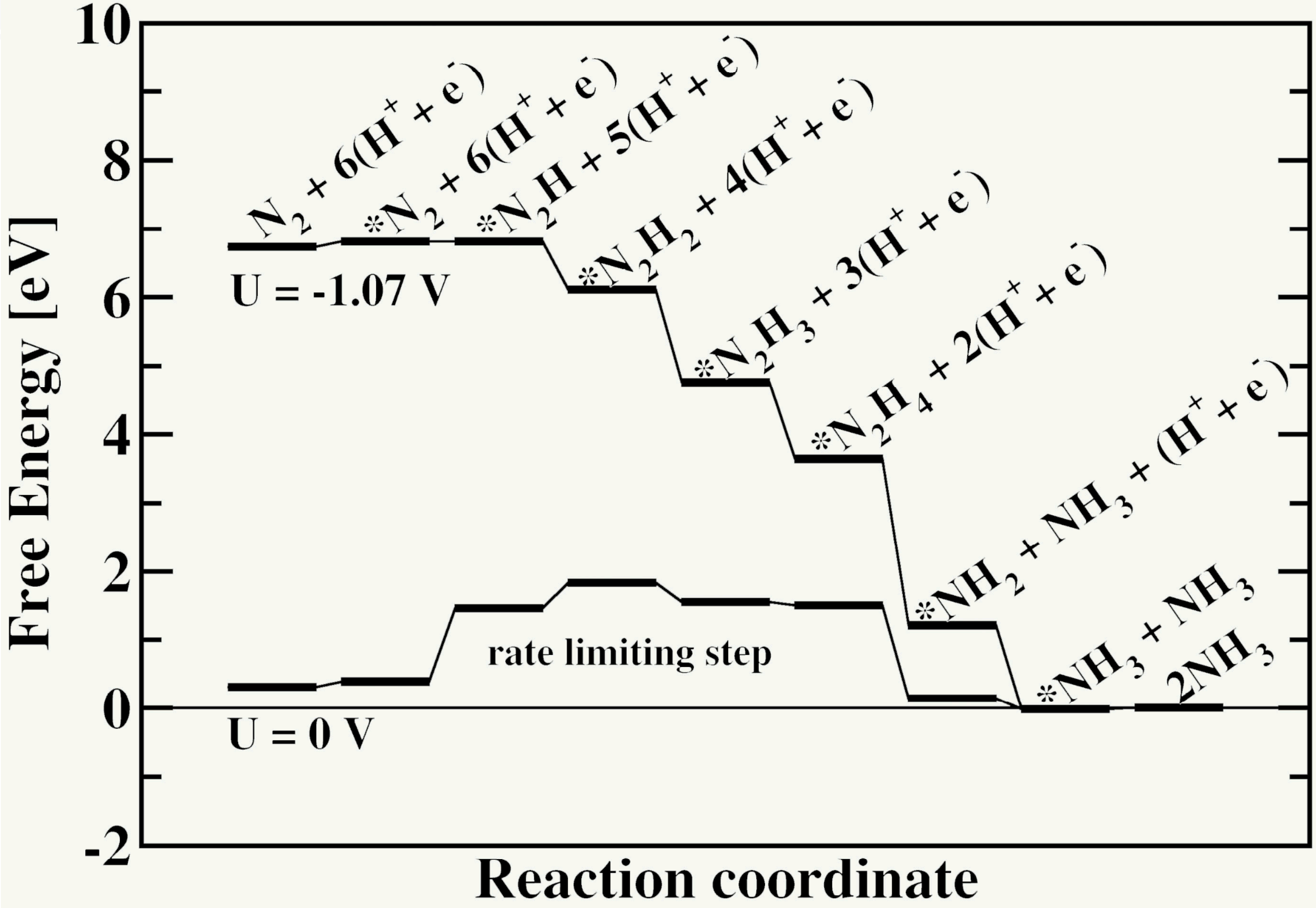
- Dr. Imre Gyuk
  - Office of Electricity Delivery and Energy Reliability
  - Department of Energy

- synthesis and characterization of Mo-catalysts and ILs
  - Travis Anderson
  - Harry Pratt

# Backup

Theoretical Calculations for the 6-$e^-$ 6-$H^+$ Reduction of Nitrogen

Half-reaction $N_2 + 6e^- + 6H^+ = 2NH_3$



E.Skulason, T.Bligaard, J.Rossmeisl, A.Logadottir, J.K. Norskov, H.Jonsson, University of Iceland, Center for Atomic-scale Materials Physics,