



# Nitrogen-Air Battery

## Advanced Development Concept

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presented to

U.S. DOE Energy Storage Systems Research Program

PEER Review

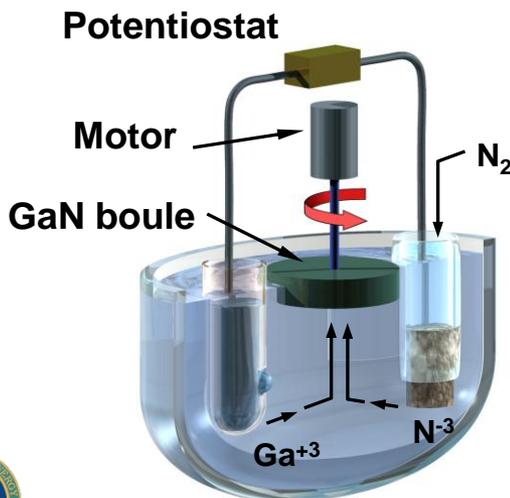
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# Small Molecule Multielectron Transfer Reactions for Energy Storage

- 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.Waldrup 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:



nitrogen to nitride as the anode for battery applications

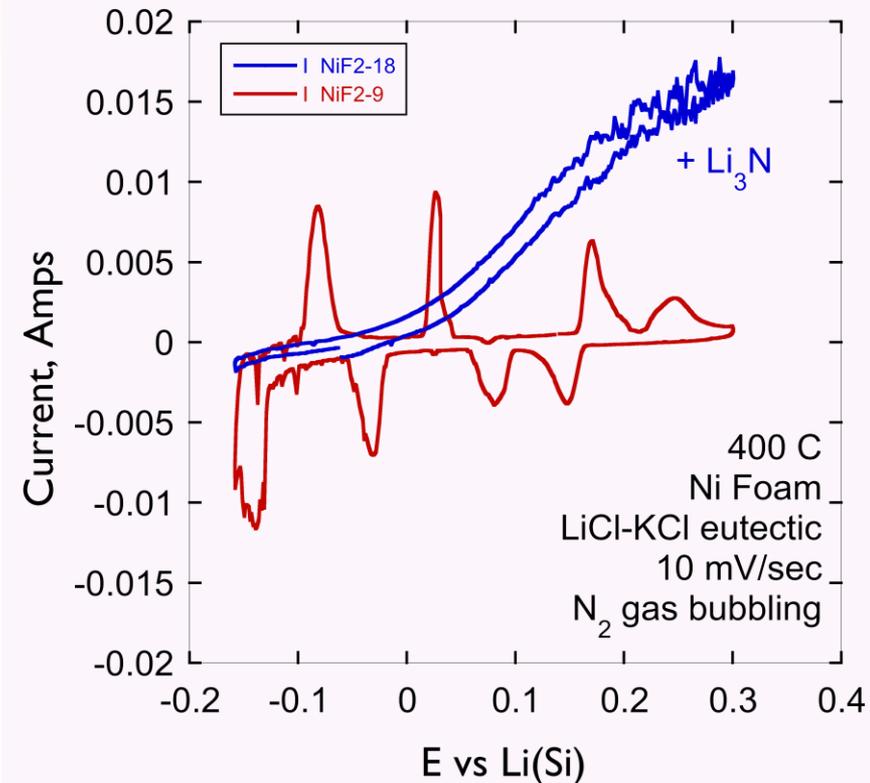


# Reduction of Nitrogen (Charge) & Oxidation of Nitride (Discharge)

- Reversible reduction of  $N_2$ 
  - we are now routinely oxidizing and reducing nitrogen species
  - $N_2 + 6e^- \leftrightarrow 2N^{3-}$   $E = 0.44$  V vs Li
- Cell Design
  - flooded cell
    - Ni foam electrode
  - Electrode is being redesigned
    - Metallic dispersion electrode with  $0.5 \mu$  porosity
    - Three porous electrode structures being evaluated
      - Ni
      - Ti
      - SS

This is a high temperature cell

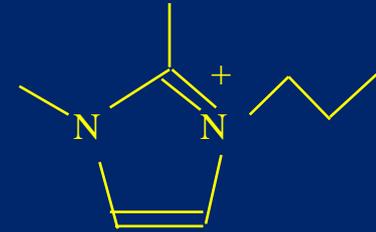
- High temperature molten salt electrolyte
- LiCl-KCl (45:55),  $352^\circ$  C melting point
  - Currently operating at  $400^\circ$  C
  - Have not determined the impact of the ternary mixture on phase diagram



# Toward Lowering the Operating Temperature

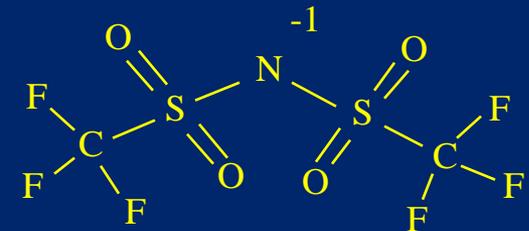
- Lowering the operating temperature
  - simplifies the cell and battery design, eases the engineering constraints, improves efficiency
- The operating temperature is currently dictated by the electrolyte
- Two parallel paths being pursued, both of which involve a different electrolyte solution
  1. Other molten salts
    - Other inorganic salts, but have not identified a viable candidate - e.g. alkali metal tetrachloroaluminates
    - Ionic liquids
      - previously determined that  $\text{Li}_3\text{N}$  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

## Cation



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

## Anion



perfluoromethylsulfonyl imide  
(Im)

# The Other Approach to Lowering the Temperature of Operation

- Employ a different charge compensating ion
- The current half-cell reaction employs an alkali metal cation as the charge compensating specie:



–  $\text{NLi}_3$  the lithium analog to ammonia

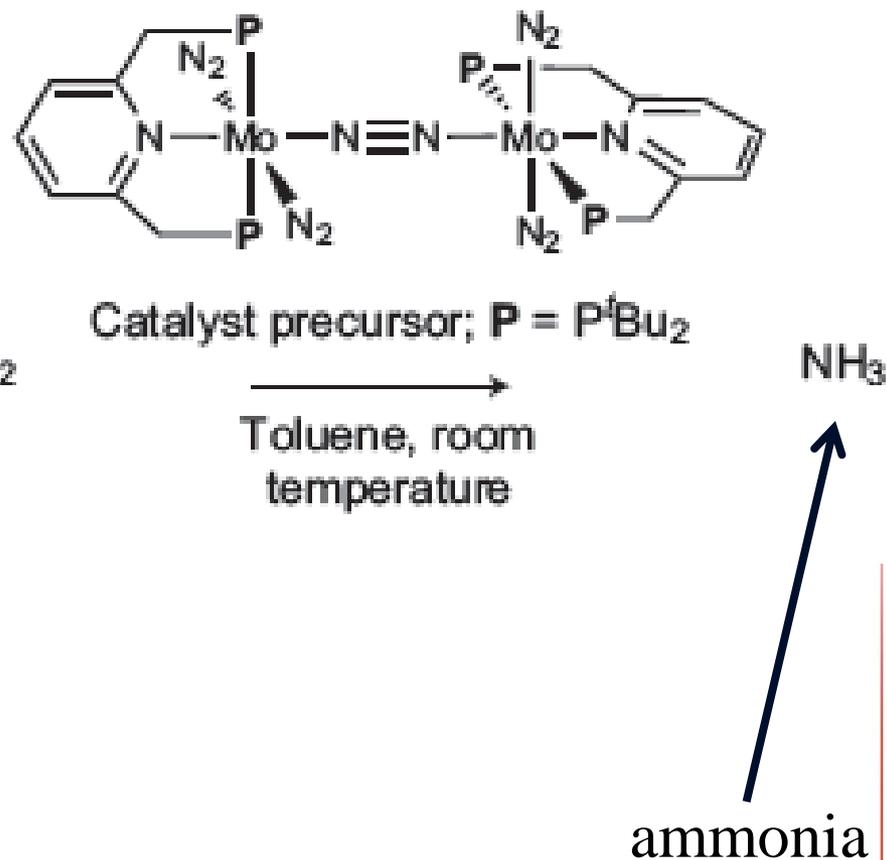
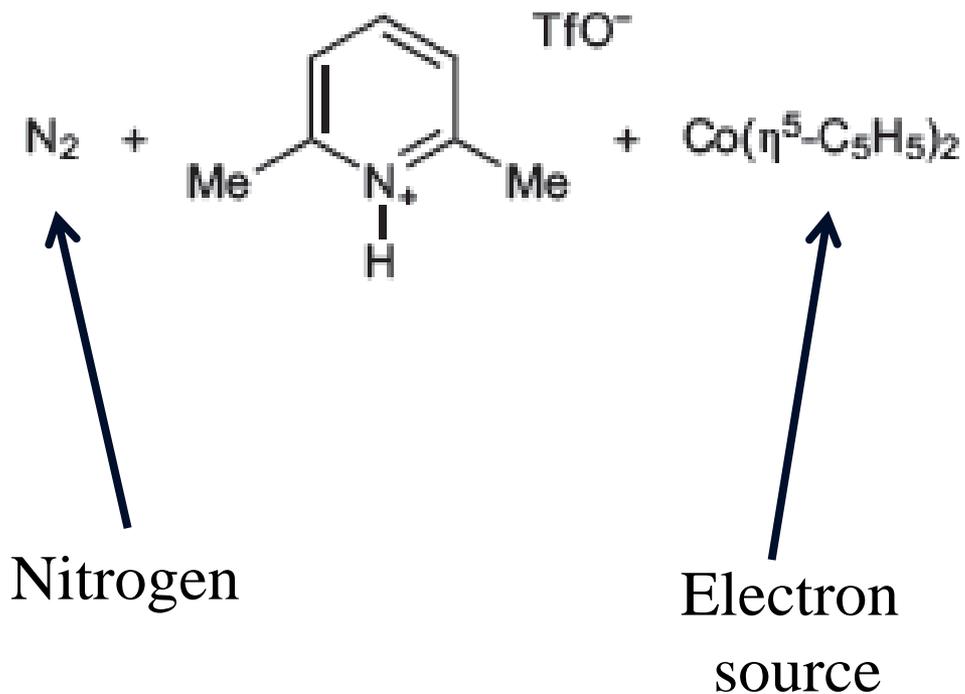


- leads to a different reaction sequence for energy storage
- Changes the energetics of storage
  - will result in a lower battery voltage
- A catalyst will be needed for lower temperature operation



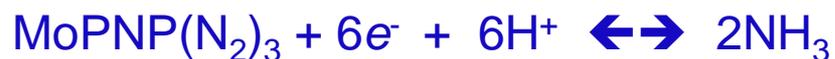
# Mo-based catalyst

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

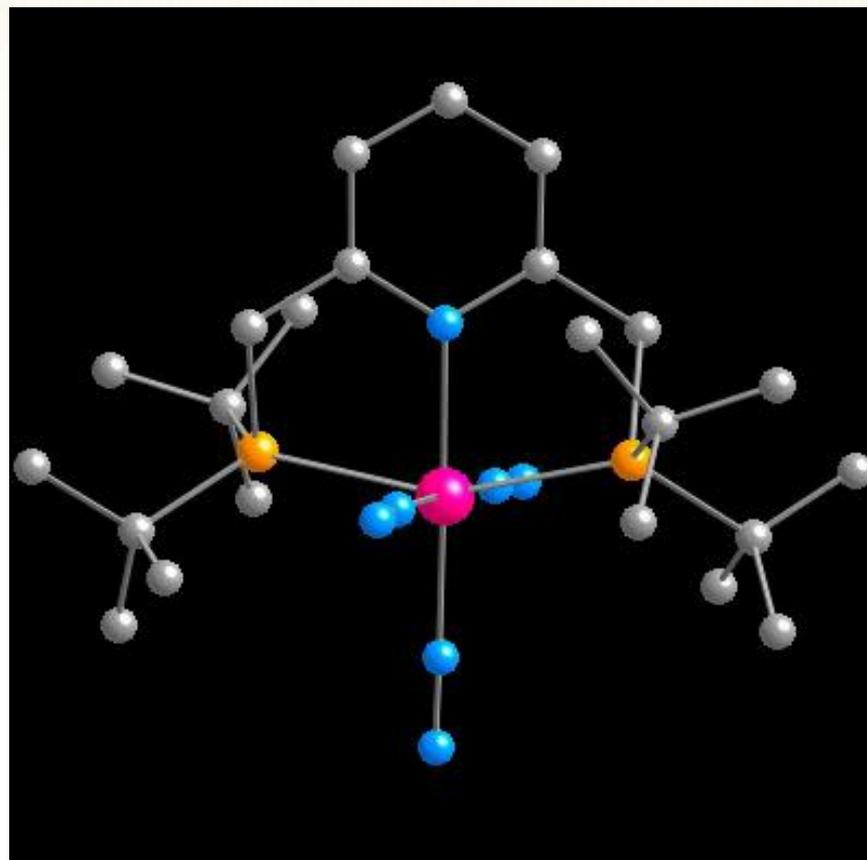


# Molybdenum Catalyst for N<sub>2</sub> Reduction to Ammonia

- Molybdenum phosphorous pincer ligand complex as a catalyst for N<sub>2</sub> reduction
  - In toluene with an electron source, MoPNP(N<sub>2</sub>)<sub>3</sub> was used as the catalyst to form NH<sub>3</sub>



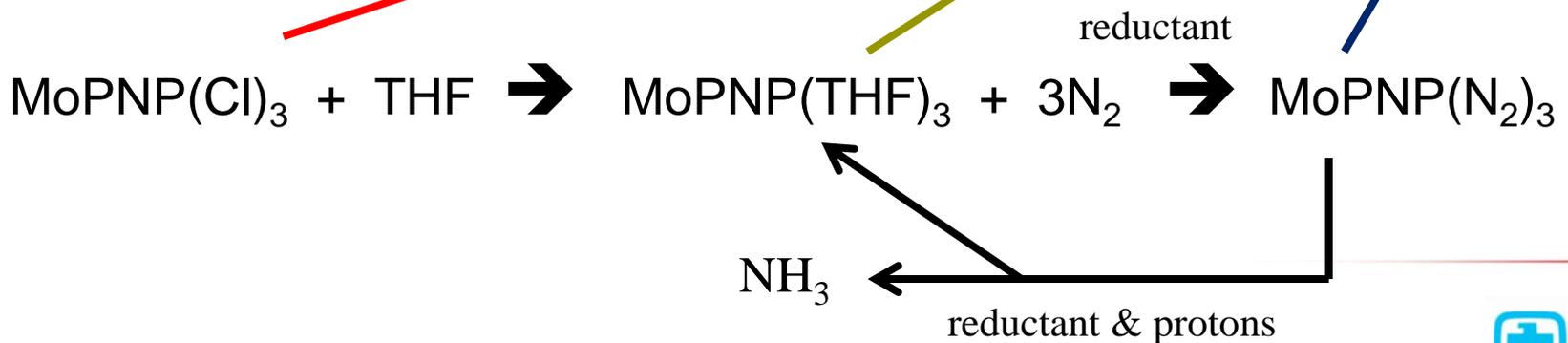
- We will use an electrode in place of the chemical electron mediator source
- The catalyst (MoPNP(N<sub>2</sub>)<sub>3</sub>) was synthesized in THF
- Provides a route to a different electrolyte solution



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



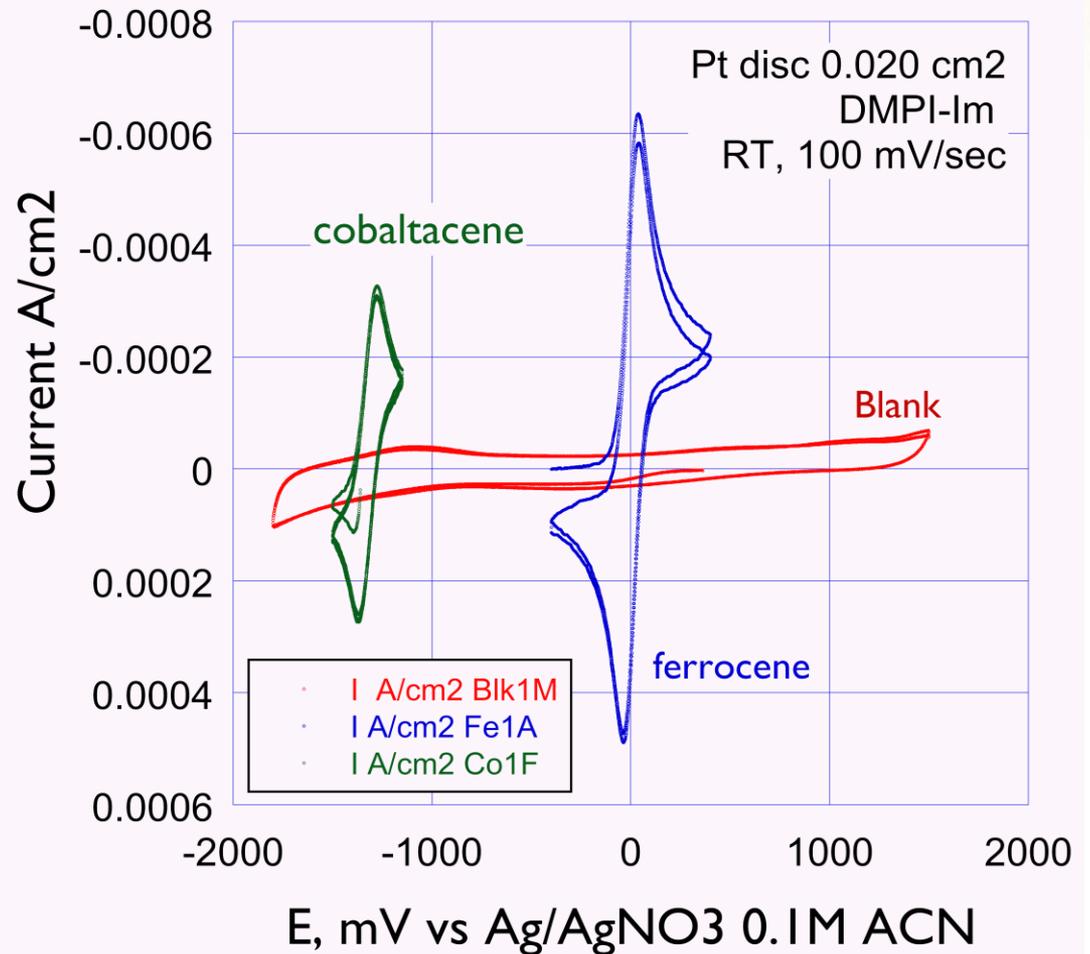
# Catalyst is Electroactive at a Solid Electrode

- Catalyst and precursors are soluble and stable in low temperature (room temperature) electrolyte solutions. Lithium triflate in:
  - THF – original solvent used to synthesize the catalyst.
    - 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
    - Selects ILs exhibit high solubility for  $\text{NH}_3$
  - nonAromatic Ionic Liquids – assymetric alkyl ammonium ions
    - Non-flammable, room temperature molten salt with low vapor pressure
- Have demonstrated that the catalyst and precursors are electroactive in different electrolytes
- This provides a path forward to safe electrolyte system
  - High molecular weight analogs to DME (glymes, diglyme)
  - Ionic liquids



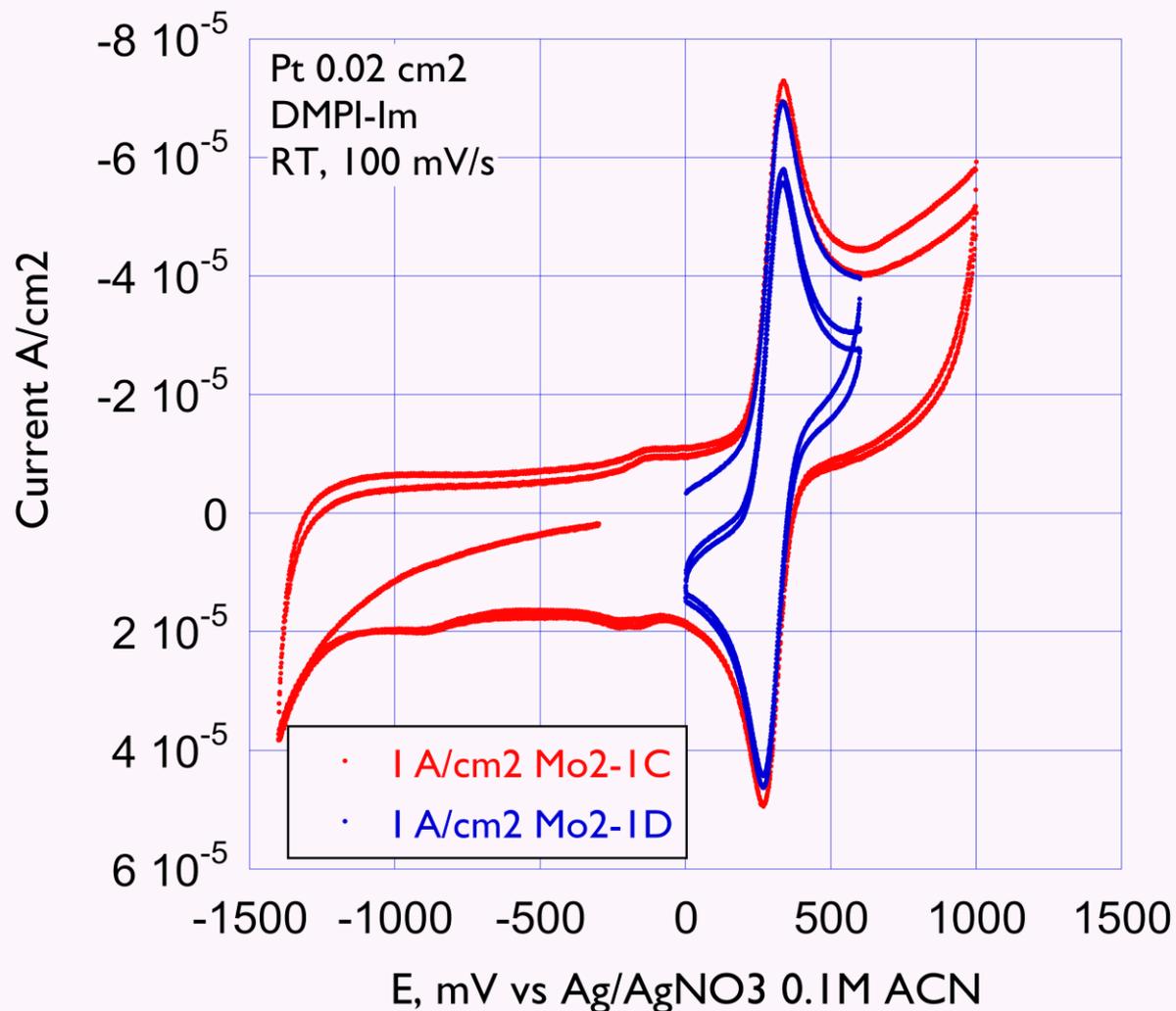
# Electrochemical Behavior of Mo Species

- Redox behavior of blank and select couples
- Cobaltocene is the electron transfer compound used by Arashiba for  $\text{NH}_3$  synthesis



# MoPNP(THF)<sub>3</sub>

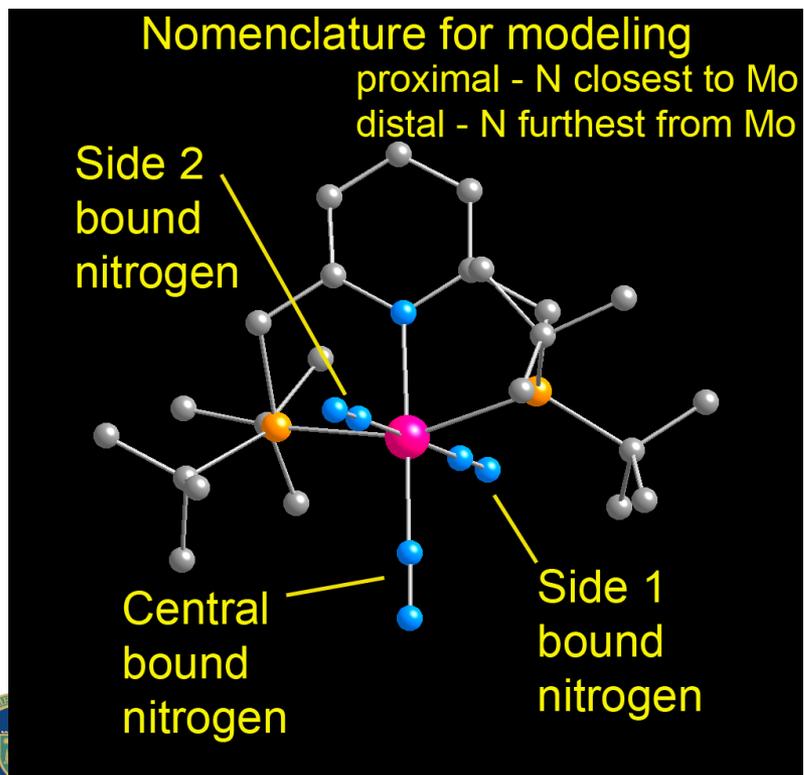
- the MoPNP(THF)<sub>3</sub> exhibits reversible redox behavior
- All of the MoPNP compounds exhibit rich electrochemical behavior at solid electrodes
- All of the MoPNP compounds are stable in a variety of solvents
- All of the MoPNP compounds exhibit the same electrochemical behavior in these different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



# 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<sub>2</sub> catalytic structure



Normalized Binding Energies and Spin of Lone H Addition to Various Metal-PNP-N<sub>2</sub> Complexes

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

- Notice that substituting V for Mo makes the pincer molecule much more attractive for the 1<sup>st</sup> H atom addition. We don't yet know what will happen when subsequent H's added. Also notice that addition to the central N<sub>2</sub> 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

# 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 in a high temperature molten salt
- 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 that have the potential to operate at room temperature



# Future Tasks

- complete design and development of the gas diffusion electrode and cell for use in the high temperature molten salt electrolyte
- Complete the cell design for the Mo-catalyzed reduction of  $N_2$  for room temperature operation.
- Complete the ionic liquid half-cell studies



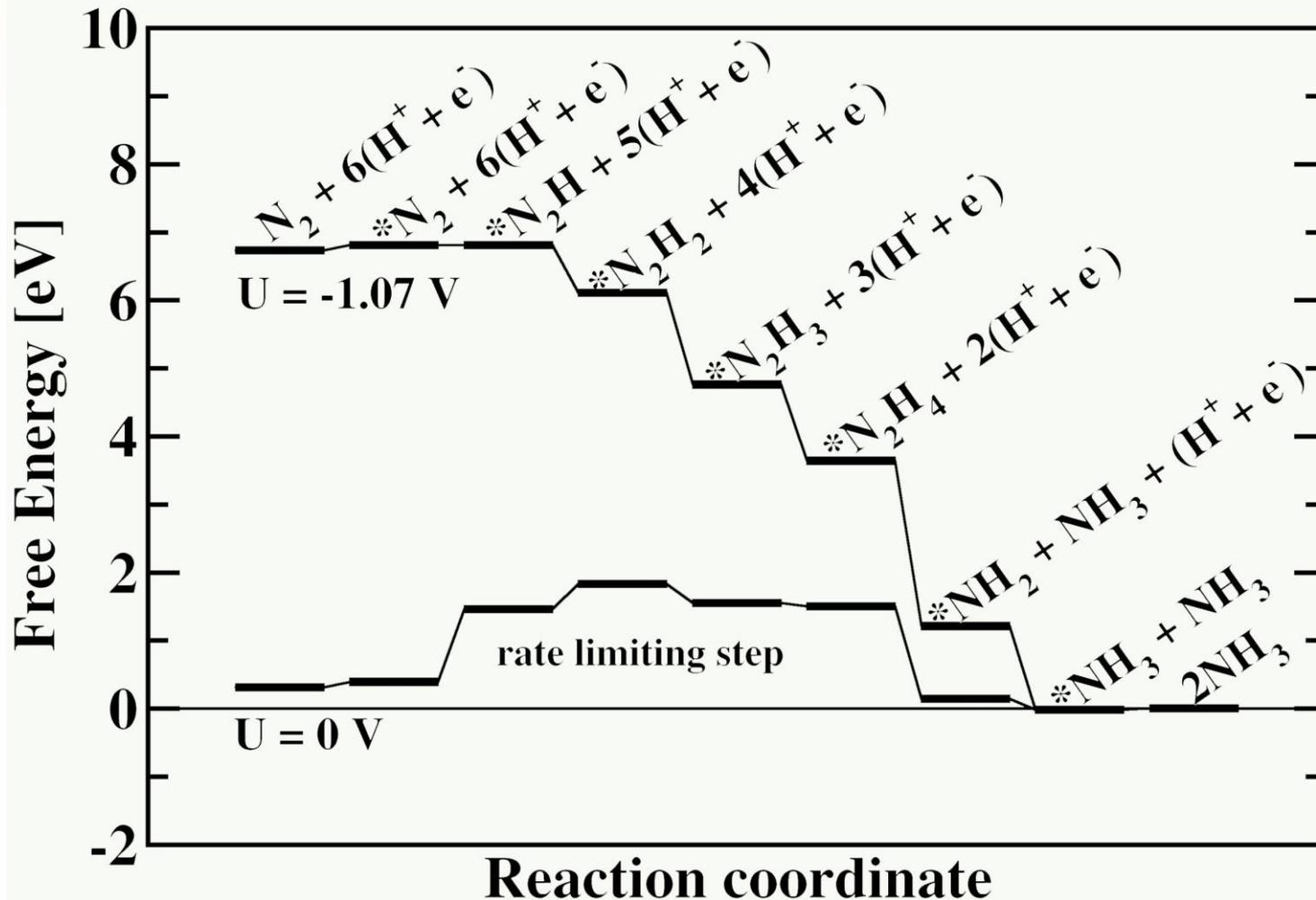
# Acknowledgements

- Dr. Imre Gyuk
  - Office of Electricity Delivery and Energy Reliability
  - Department of Energy
  
- Preparation and synthesis of Mo-catalysts and ILs
  - Harry Pratt
  - Travis Anderson



# Backup

Theoretical Calculations for the 6-e<sup>-</sup> 6-H<sup>+</sup> Reduction of Nitrogen  
Half-reaction  $\text{N}_2 + 6\text{e}^- + 6\text{H}^+ = 2\text{NH}_3$



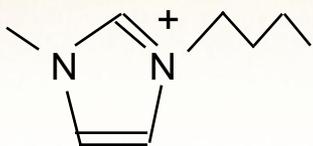
E.Skulason, T.Bligaard, J.Rossmeisl, A.Logadottir, J.K. Norskov, H.Jonsson, University of Iceland, Center for Atomic-scale Materials Physics,

## Normalized Binding Energy for Addition of H Atoms

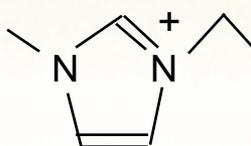
No H-atoms	N <sub>2</sub> Location			spin m	B.E. / H- atom
	Side 1	Side 2	Central		
1			distal	1	0.82
1			proximal	1	0.06
<b>1</b>	<b>distal</b>			<b>1</b>	<b>0.95</b>
1	proximal			1	0.00
2			distal	0	1.47
2	distal			0	1.68
<b>2</b>			<b>trans</b>	<b>0</b>	<b>1.86</b>
2	trans			0	1.80
2			cis	0	1.77
2	cis			0	1.65
2	distal	distal		0	1.31
3			NH-NH <sub>2</sub>	1	1.96
3	trans	distal		1	1.61
3	trans		distal	1	1.64
<b>3</b>	<b>NH-NH<sub>2</sub></b>			<b>1</b>	<b>2.01</b>
3 (NH <sub>3</sub> eliminated)			N-NH <sub>3</sub>	1	1.99
3 (NH <sub>3</sub> stays on)	N-NH <sub>3</sub>			1	1.48
3	distal	distal	distal	1	1.10
<b>3 NH<sub>3</sub> H bonds</b>	<b>NHNH<sub>2</sub></b>	<b>N<sub>2</sub> off</b>		<b>1</b>	<b>&gt;2.17</b>
4			NH <sub>2</sub> NH <sub>2</sub>	0	2.16
<b>4 (N<sub>2</sub>H<sub>4</sub> eliminated)</b>		<b>NH<sub>2</sub>NH<sub>2</sub></b>		<b>0</b>	<b>2.22</b>
4			NH-NH <sub>3</sub>	~0	1.88
4	trans	trans		0	1.74
4		trans	trans	0	1.77
4		cis	trans	0	1.79



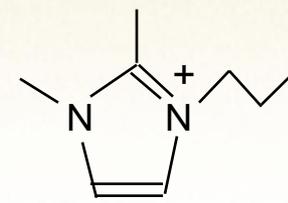
# Selected Imidazolium Ionic Liquids



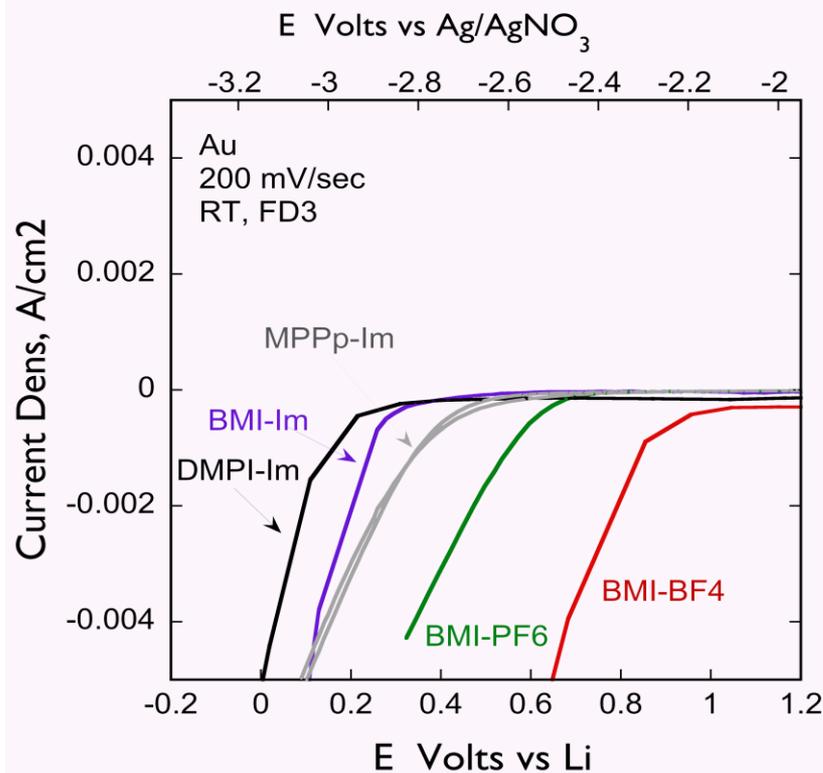
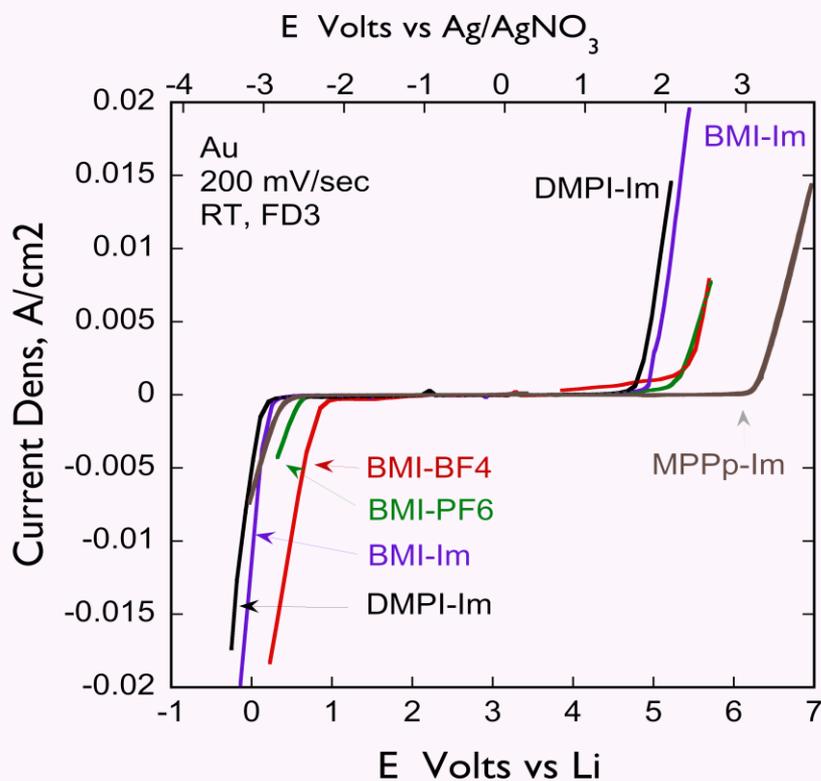
1-butyl-3-methylimidazolium  
BMI



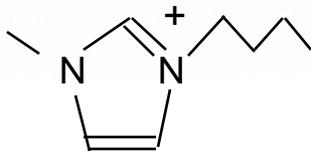
1-ethyl-3-methylimidazolium  
EMI



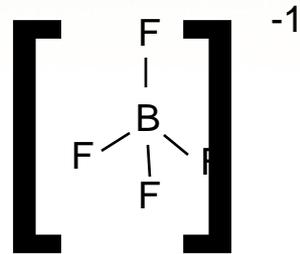
2,3-dimethyl-1-propylimidazolium  
DMPI



# Room Temperature Ionic Liquids



1-butyl-3-methylimidazolium  
BMI

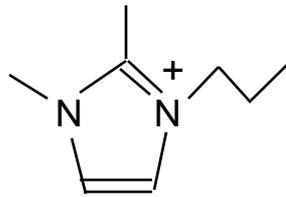


BMI-BF<sub>4</sub>

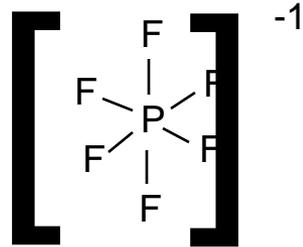
mp °C

-71

+  
H<sub>2</sub>O  
miscible



2,3-dimethyl-1-propylimidazolium  
DMPI



BMI-

10

11700 ppm

PF<sub>6</sub>

BMI-Im

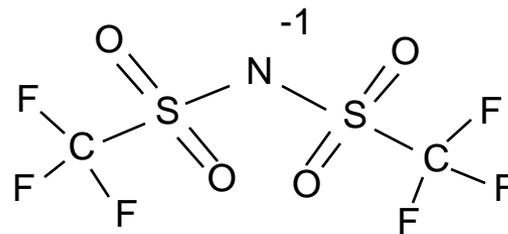
1

3280 ppm

DMPI-Im

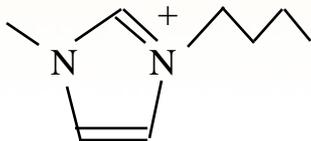
15

hydrophobic

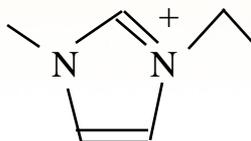


perfluoromethylsulfonyl imide  
Im

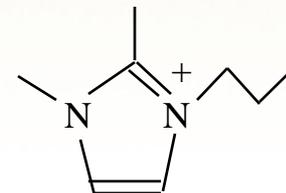
## Selected Imidazolium Ionic Liquids



1-butyl-3-methylimidazolium  
BMI



1-ethyl-3-methylimidazolium  
EMI



1,3-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<sup>+</sup> reduction.

Yokozeki *et. al.* (2007) BMI-PF<sub>6</sub>, BMI-BF<sub>4</sub>, EMI-Im, **exhibit high solubility for NH<sub>3</sub> at room Temp. 20-40 mole/o (adsorption cooling/heating cycle)**

Shi *et. al.* (2009) Osmotic Ensemble Monte Carlo Simulations compare solubilities of CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and NH<sub>3</sub> in EMI-Im  
**Solubility of NH<sub>3</sub> result of hydrogen bonding to C2 proton.**  
**Solubility of SO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> result from anion interactions**