Green Energy: Electrochemical Synthesis of Ammonia For Energy Storage

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Energy Storage

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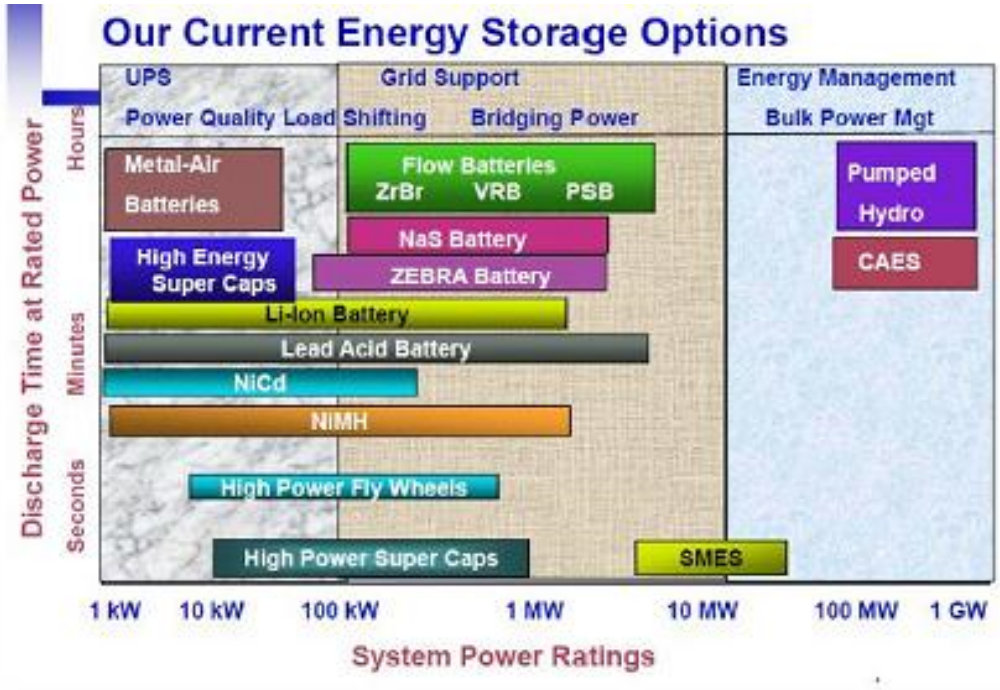
$$ LANL LDRD program - Energy Security

What are the options?



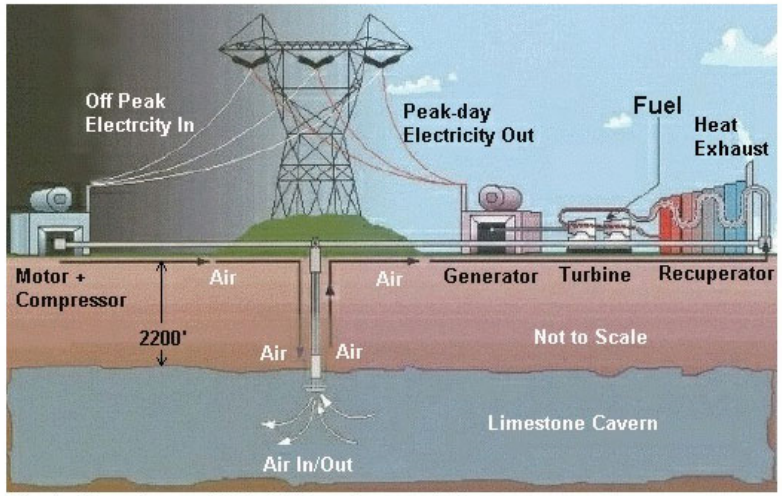
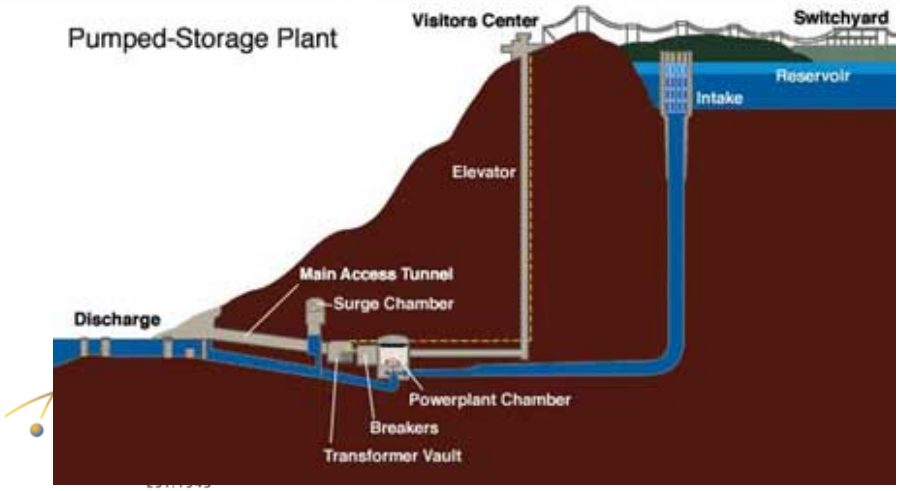


Photo Courtesy of CAES Development Company



Chemical fuels store ~ 10kWhr/liter!
About 100 times more than batteries

Water, Nitrogen, CO_2 feedstocks
CO_2- very dilute <400 ppm
Nature chose carbon dioxide reduction instead of nitrogen reduction for energy storage because of easier biocatalysis (Structural diversity of organic compounds)

Conventional Ammonia Synthesis

Haber-Bosh process

$$N_2(g) + 3H_2(g) \xrightleftharpoons[430\text{-}480^{\circ}C,\ 10\text{-}30MPa]{Fe\text{-}cat.} 2NH_3(g)$$

$$\Delta H = -92kJ/mol$$

Considered a landmark in het. cat. - led to three Nobel prizes (Haber 1918, Bosch 1931, Ertl 2007)

Thermodynamic limitations:

- Gas volume decreases in rxn → high pressures needed to push equilibrium to products
- Rxn is exothermic → efficient at low Temp, but to achieve industrially sufficient rxn rates high Temps (430-480˚C) are used
- Achieving industrially acceptable efficiencies (~70%) requires use of large-scale integrated facilities

What about Electrocatalysis?

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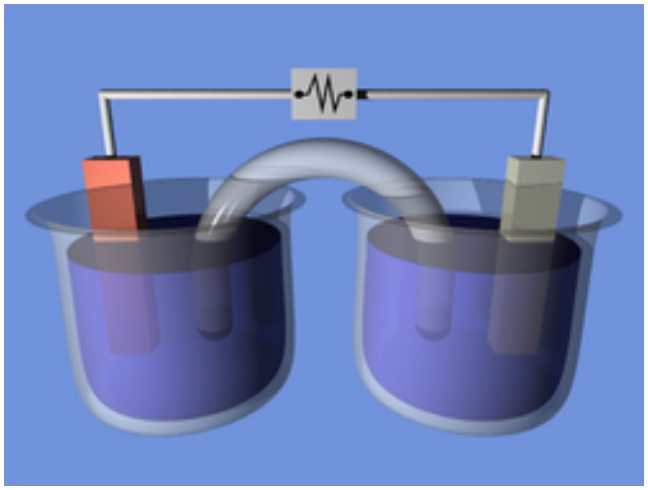
Energy Storage in Chemical Bonds – N as a Hydrogen Carrier

$H_2O \rightarrow H_2$

$CO_2 \rightarrow CH_3OH$

$N_2 \rightarrow NH_3$



$3H_2O \rightarrow 6H^+ + 6e^- + 3/2\ O_2$ Anode - water oxidation reaction

$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$ Cathode - nitrogen reduction reaction

---

$2N_2 + 6H_2O \rightarrow 4NH_3 + 3O_2$ Overall reaction

Theoretical potential ~0 V in aqueous media at room temperature!

The problem: Kinetics, high over potentials … better catalysts are needed

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Back Conversion: Ammonia Oxidation Already Well Proven in Fuel Cells and Carnot Engines

Physical Chemistry & Materials Science

Electrolytes

- Structure-property relations for ion transport mechanisms in solid electrolytes,
- Physical chemistry and conductivity of ionic liquid/Acid salt systems
- Solubility of ammonia and influence on transport properties
- Electrocatalysis in ionic liquids, hydrogen oxidation, proton reduction,
- Electrochemical Stability Studies

Homogeneous Molecular Catalysts

- Chemical structure, reaction chemistry, charge transfer

Electrocatalyst Materials

- Surface properties, adsorption and catalysis, reaction mechanisms, electron conduction and charge transfer mechanism
- Control of particle size, nanostructure interfaces and electrode-electrolyte interactions

Experimental Plan

- Synthesize and Optimize Ionic Liquid Electrolytes
  - Measurement of proton transport properties, ammonia solubility
  - Measurement of proton transport as a function of ammonia content
  - Investigate Nitride ion formation in ionic liquids

- Synthesize and Optimize Solid Proton Conductors
  - Synthesis and Characterization of MP_2O_7 (M= Sn, W, Ti, Si, Ge, Ce and Zr)
  - Measurement of proton transport by AC impedance spectroscopy and INS
  - Theoretical Modeling of proton transport

- Synthesize and Optimize M-N Electrocatalysts
  - Characterize surface reaction chemistry
  - Heterogeneous and electrochemical methods
  - Theoretical Reaction modeling of catalysts

* Electrochemical Reactor Design and Optimization
  - Design and build high pressure nitrogen reduction electrochemical reactor
  - Solid Electrolyte and Liquid Electrolyte configurations
  - Characterize reactor behavior

Liquid Electrolytes or Solid State Ionic Conductors for Ion Transport?

Liquid Electrolytes :

Aqueous systems: Acid or Alkaline electrolytes: water oxidizes electrode-catalyst surface inhibits reaction, narrow stability window

Organic solvents/salt systems:

acetonitrile, propylene carbonate etc: limited temperature range,stability

Molten Salts:

molten borate, hydroxide, carbonate and chloride salts: corrosive

Ionic Liquids:

Immidizolium, phosphonium etc: many electrochemical and physical properties unknown … *Investigate ionic liquids as electrolytes for ammonia synthesis*

Solid Electrolytes:

Pervoskite oxides, beta aluminas, temperature limitations

Investigate metal pyrophosphates: High proton conductivity at lower T

Room Temperature Ionic Liquids

A salt consisting of an organic cation and (usually) hydrophobic anion that is a liquid at room temperature

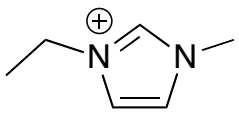
ADVANTAGES

- Low melting points
- High decomposition temperatures (~200 – 350^{o}C)
- High ionic conductivities (similar to 0.01M electrolyte in organic solvent)
- Extremely low volatilities (typically non-distillable)
- Large electrochemical windows when pure (5-6V)
- Viscosity decreases and conductivity increases with temperature
- Gases such as nitrogen and ammonia have reasonable to very high solubility
- Properties can be manipulated by changing cation/anion structure

DISADVANTAGES

- Room temperature viscosities are 2-4 orders of magnitude larger than organic solvents (reagent diffusion can be an issue)
- Purification the to extent necessary for echem experiments can be challenging

Ionic Liquids Being Investigated



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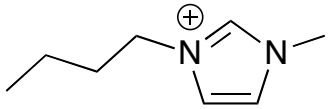

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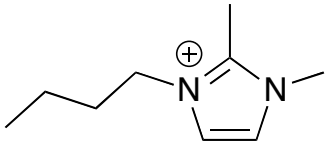

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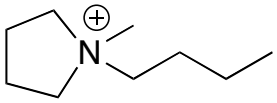

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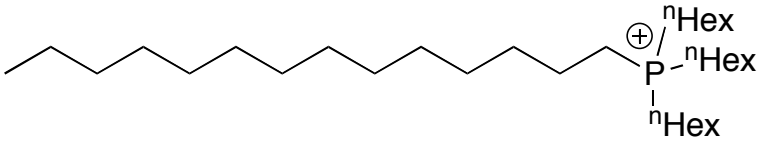
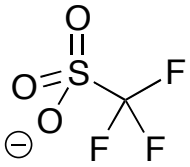
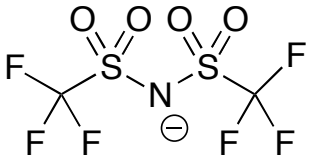
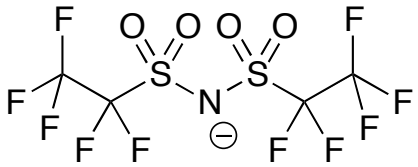




Tf



NTf_2



$N(EtTf)_2$

Mix and match various imidazolium, pyrrolidinium or phosphonium cations with hydrophobic anions gives a variety of RTILs having a range of properties.

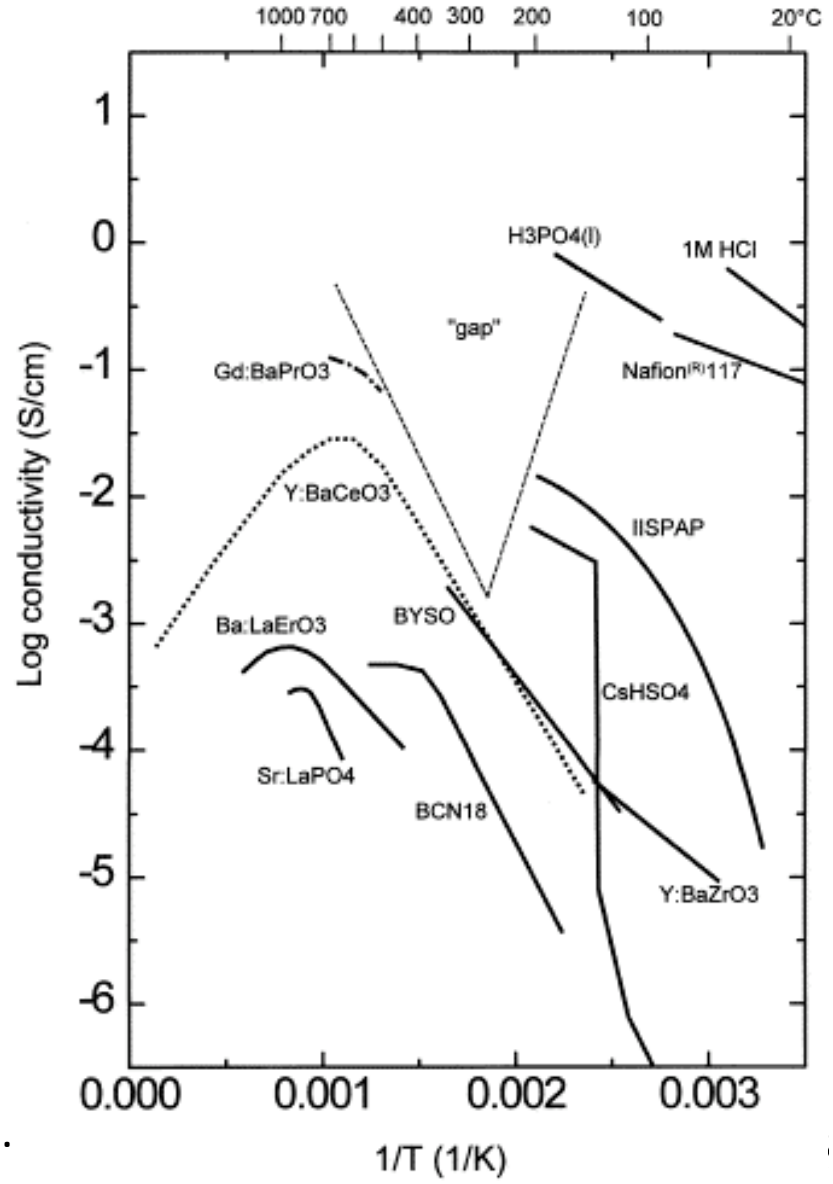
Intermediate temperature solid proton conducting electrolytes

- Each type of Fuel Cell has an operating temperature regime limited by its electrolyte
  - SOFC (700-1000˚C)
  - DMFC (50-120˚)
  - PAFC (150-200˚C)
  - PEM (50-100˚C)

- High temperature operation favors kinetics and alleviates water management difficulties

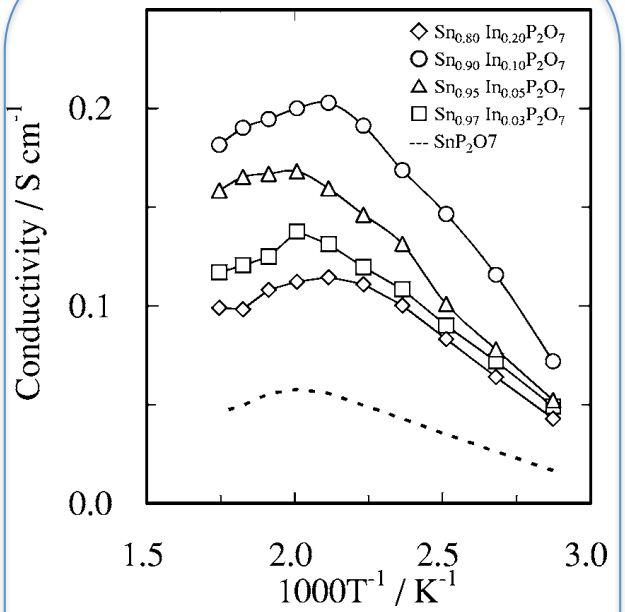
- Low temperature operation favors reduced assembly cost and improved durability

- Limited electrolyte materials available to bridge technologies in intermediate temperature range (100-400˚C)

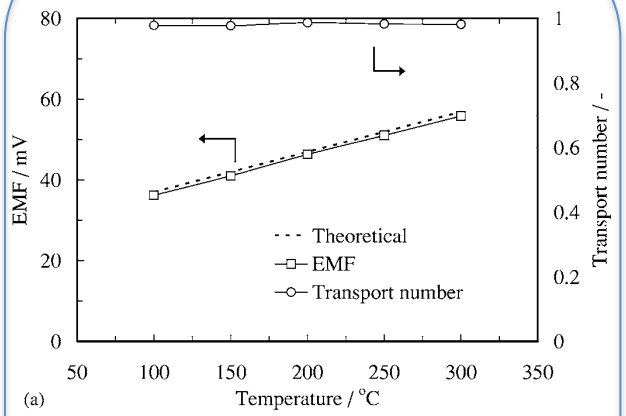


Norby *SSI*, **124**, 1999.

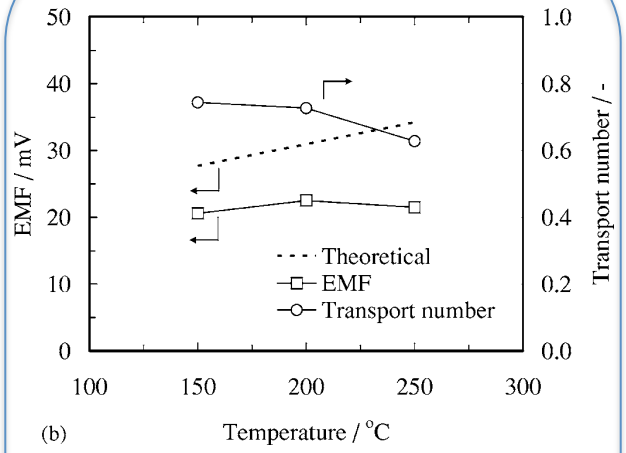
Intermediate Temperature Conductivity of SnP_2O_7



High σ in intermediate temperature range



σ_{ion} with transference number ~ 1



t_{H+} ~ 0.6-0.75

Doped-SnP_2O_7 materials are promising candidates for intermediate temperature proton conducting electrolytes

[1] Nagao et al., J Electrochem Soc, 2006

[2] Nagao et al. Electrochem Solid State Lett, 2006.

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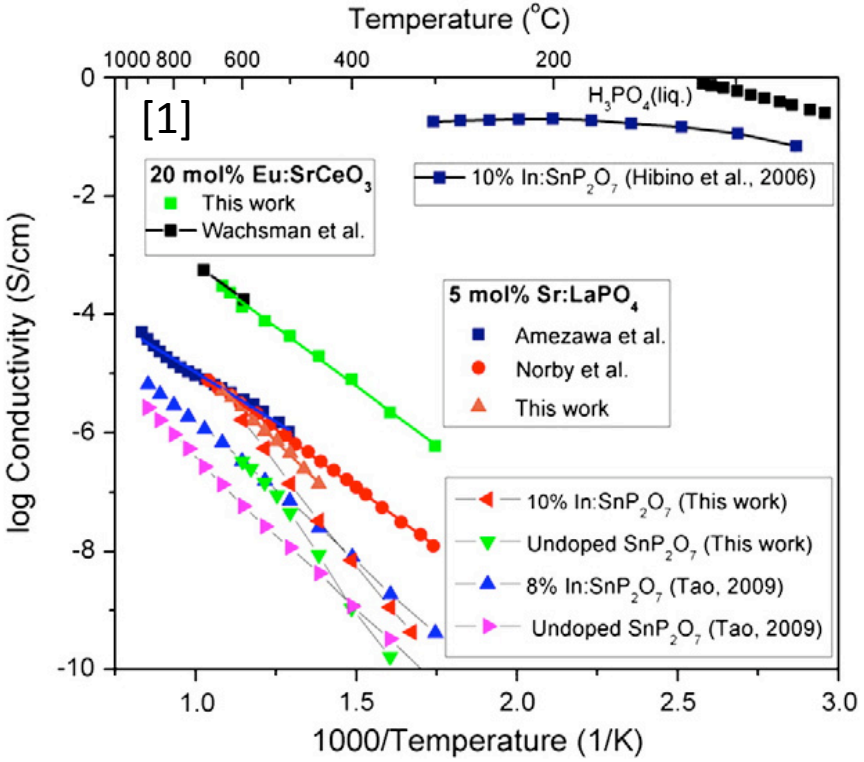
Origin of ionic conductivity in SnP_2O_7?

1. **Dopant induced defects provide sites for -OH incorporation- "Perovskite-like"**
2. **Facile grain-boundary pathway enabled by residual polyphosphate phase**



$$In_x\ Sn_{(1-x)}(P_2O_7)_{(1-x)}(HP_2O_7)_x$$

In^{3+} doping requires the presence of $[HP_2O_7]^{3-}$ for charge balance

[1] S.R Padke, C.R. Bowers, E.D. Wachsman, J.C. Nino, *Solid State Ionics*, **183** (2011)
[2] S. Tao, *Solid State Ionics*, **180** (2009)
[3] Xu, S. Tao, P. Wormald, J.T. Irvine, J Mat Chem, **20**, 2010

Systematically study conductivity and stability as a function of excess P:M ratio

Synthesis of $In_{0.1}Sn_{0.9}P_2O_7$ with varying P:M

"Solution Precipitation" w/ phosphate

In, Sn chlorides, diammonium phosphate $\xrightarrow{\text{pH adj.}}$ Gel $\xrightarrow[\text{Crucible}]{650^{\circ}C}$ ITPP

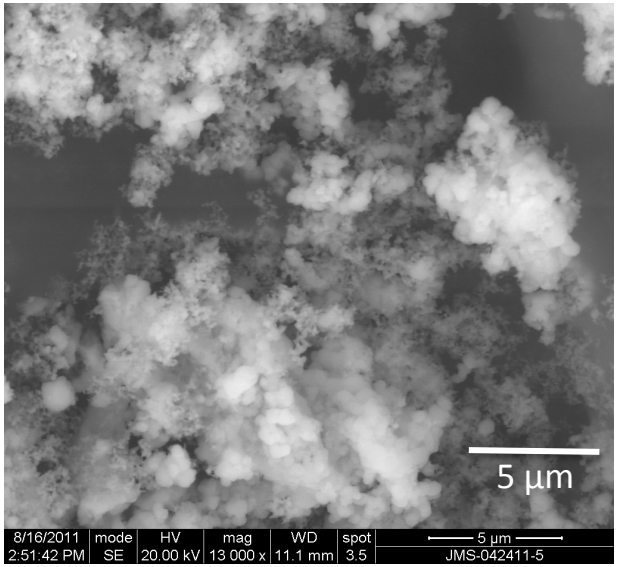
Results:

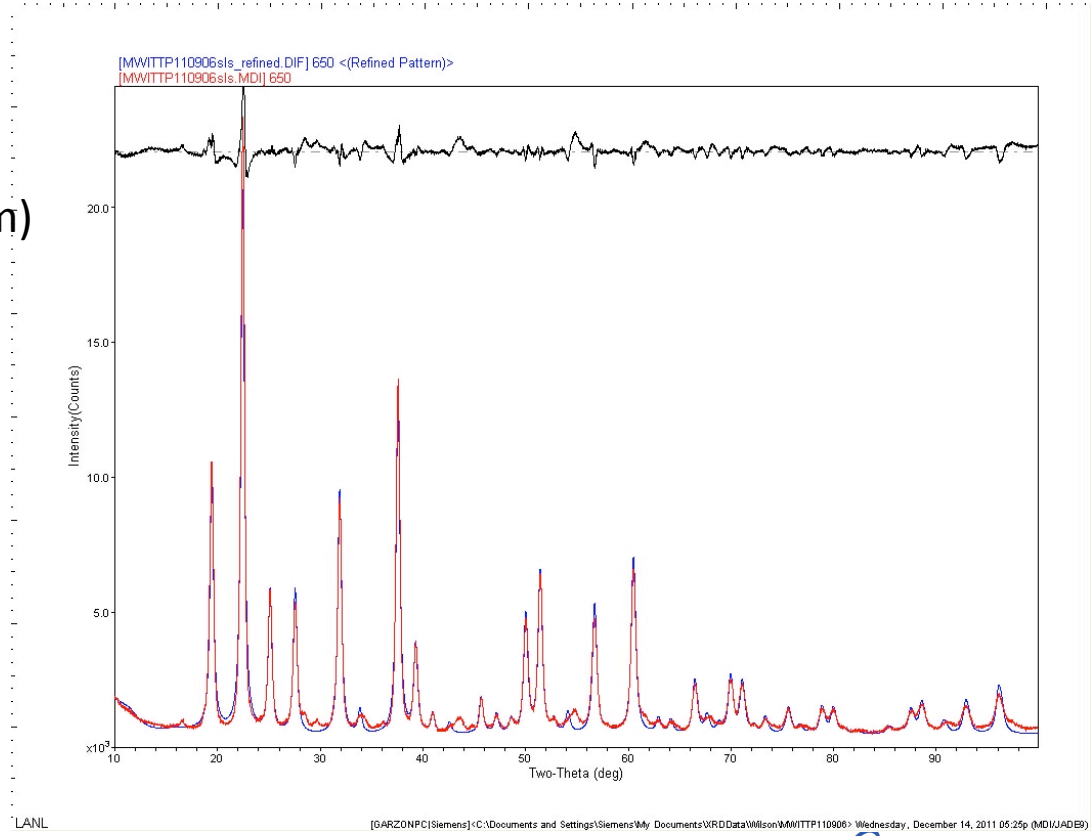
Rapid gel

650˚C crystallization

Small uniform crystallites (~ 20-30 nm)

Control of initial stoichiometry





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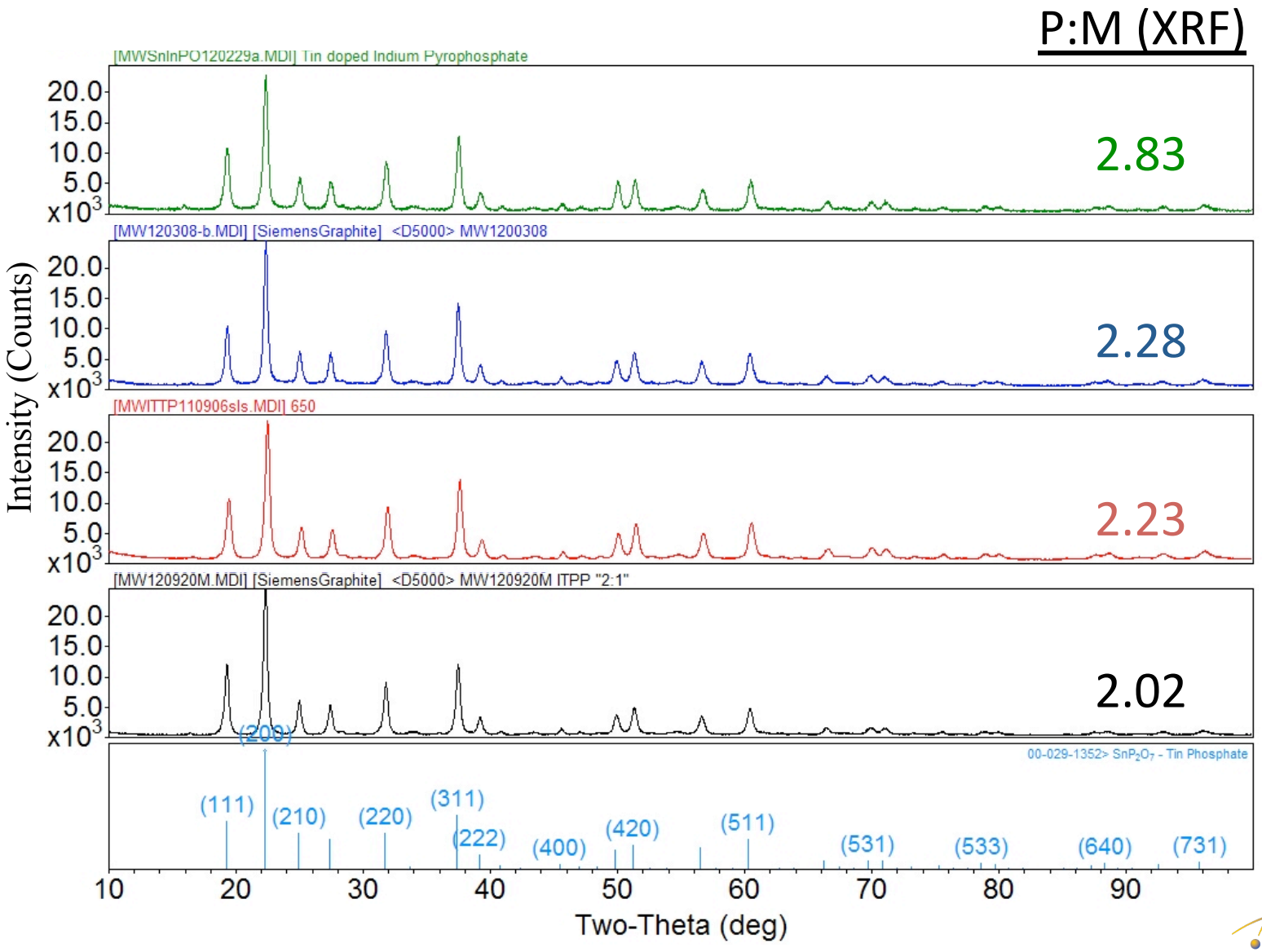
Characterization of $In_{0.1}Sn_{0.9}P_2O_7$ with varying P:M



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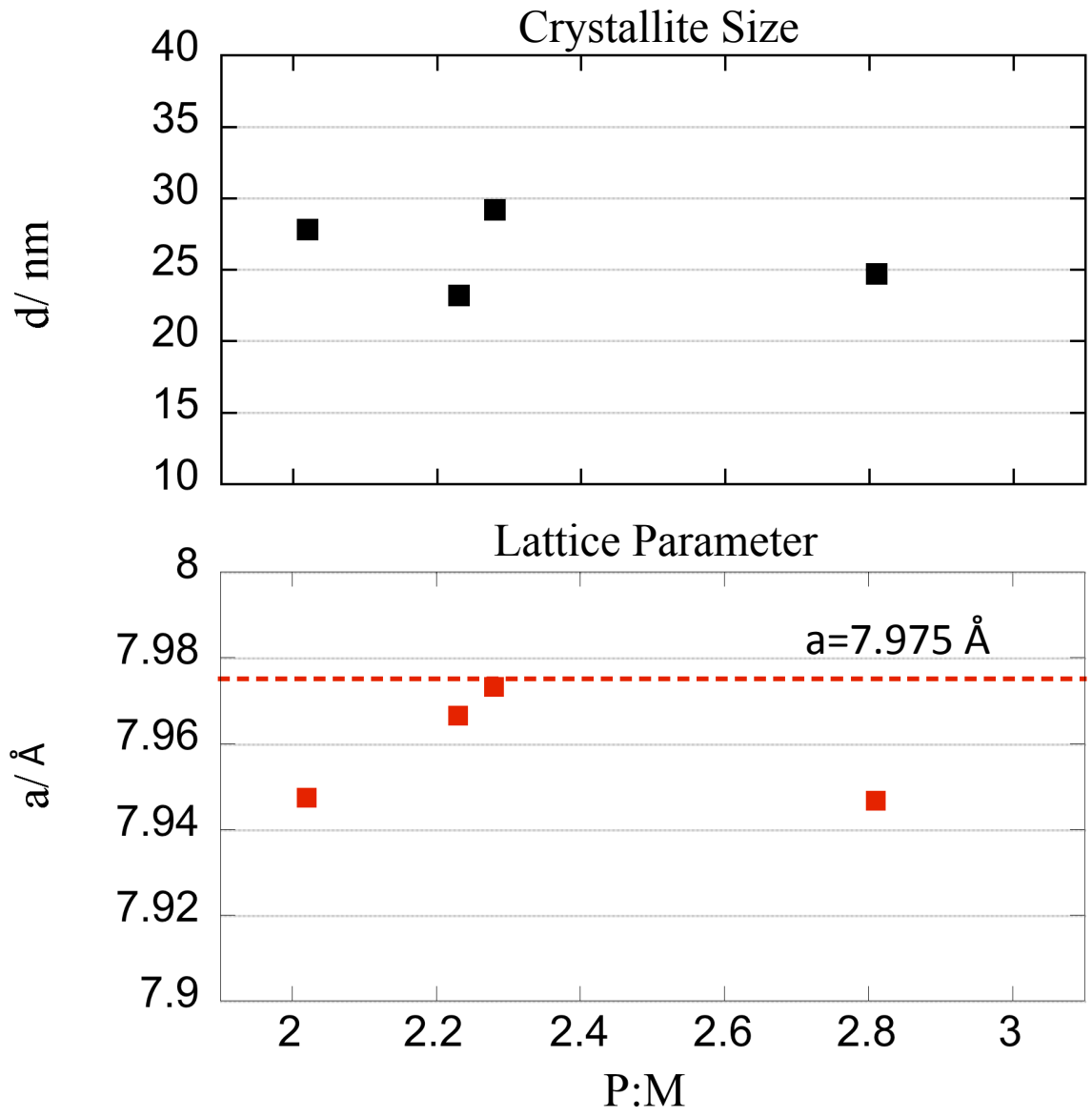

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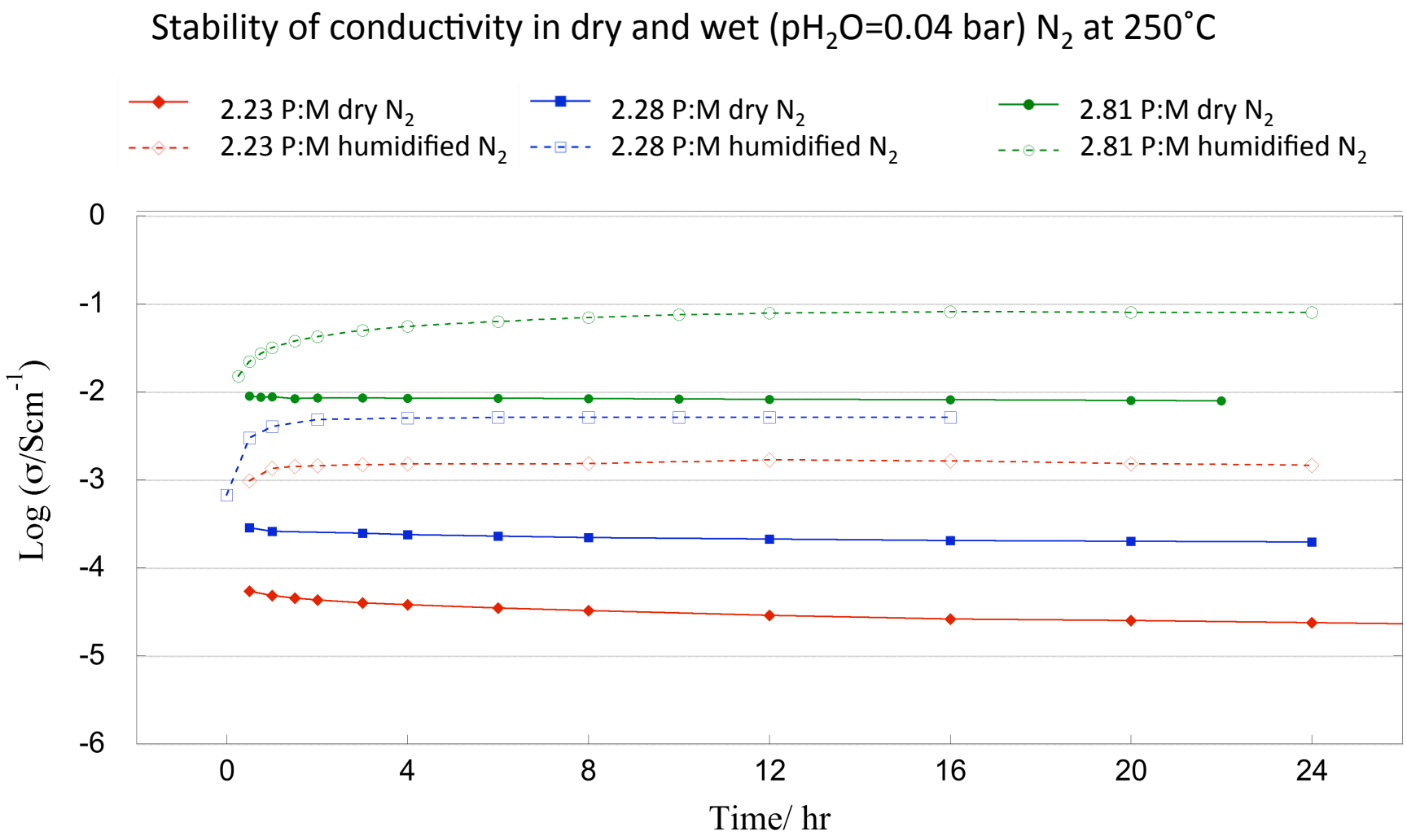
4-pt conductivity measurement of ITPP

- Difficult to obtain dense pellets
  - Press pellets uniaxially, then isostatically
  - $\rho_{\text{high excess P:M}}$ (75%) > $\rho_{\text{low exess P:M}}$ (65%)
  - Did not sinter, except for 2.02 P:M
- Spring loaded compression to Pt foil
- Measured impedance, calculated conductivity

Conductivity of $In_{0.1}Sn_{0.9}P_2O_7$ with varying P:M



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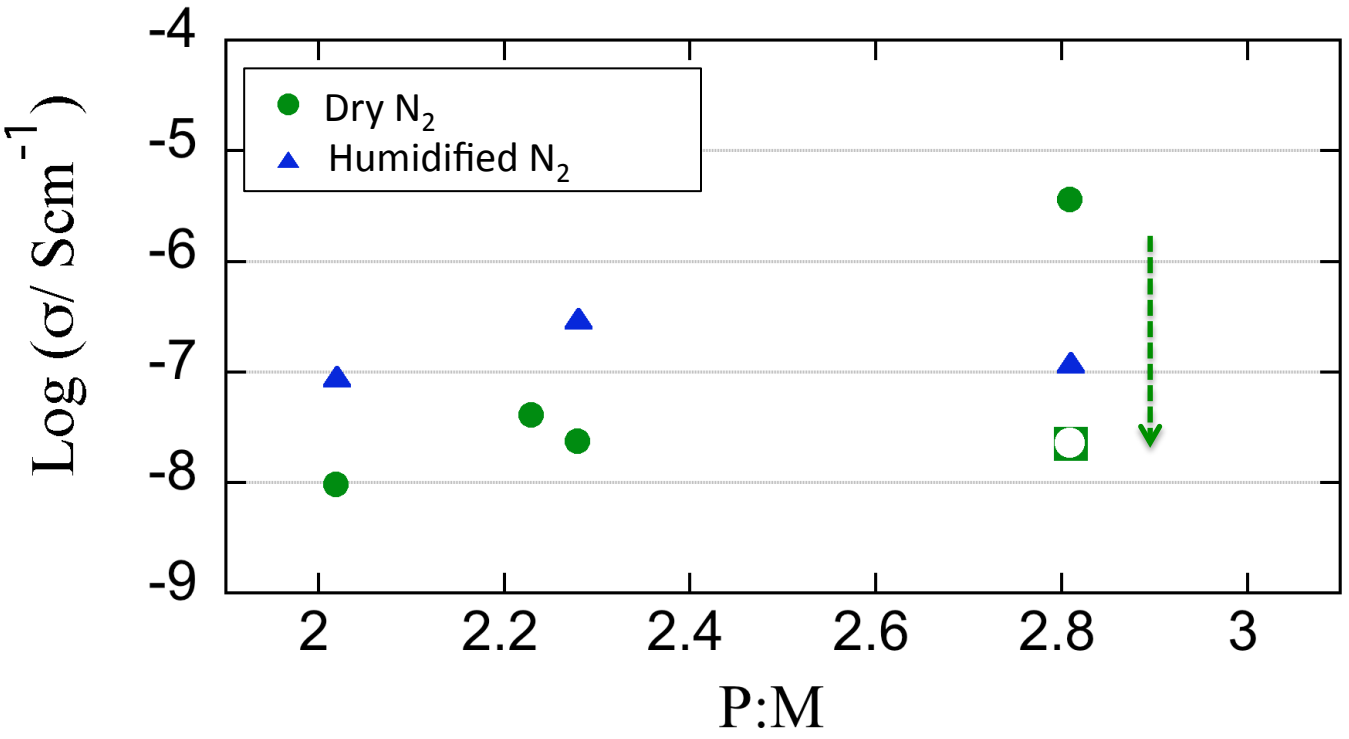
Conductivity of $In_{0.1}Sn_{0.9}P_2O_7$ with varying P:M



- Conductivity at 600 ˚C similar regardless of starting P:M
- Presence of H_2O has strong influence on stability

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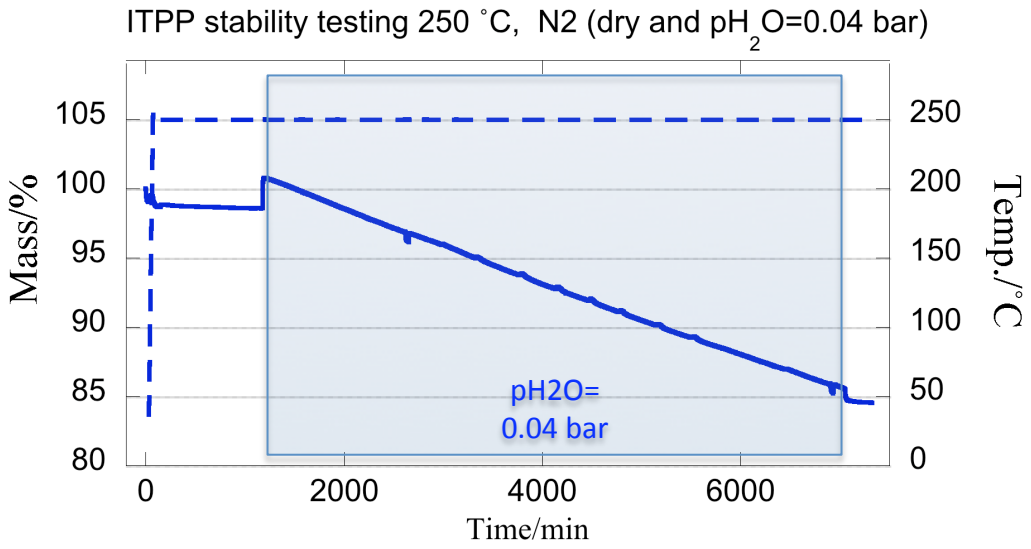
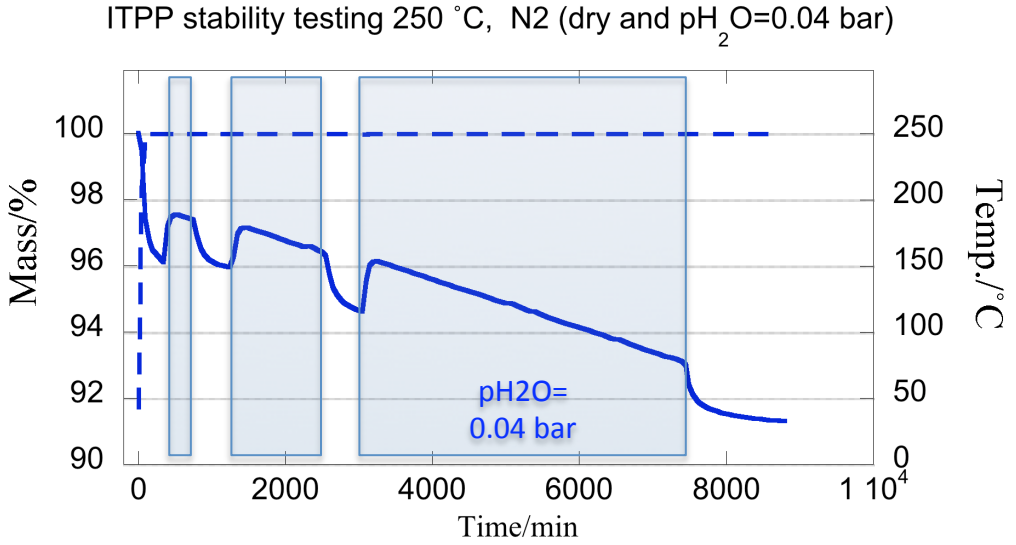
Stability of $In_{0.1}Sn_{0.9}P_2O_7$ with excess P:M

Loose Powder



	Δ%/hr
Dry N_2	-0.016
Humidified N_2	-0.16

Pressed Pellet
ρ/ρ_{th}~0.75



	Δ%/hr
Dry N_2	-0.017
Humidified N_2	-0.045

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Indium Tin PyroPhosphate (ITPP) Conductivity

- Study indicates that excess phosphoric acid phase, likely residing at grain boundaries, has strong positive influence on conductivity

- While crystalline phase and overall composition were confirmed with XRD and XRF, we have not unequivocally determined that crystalline ITPP phase is stoichiometric in all cases
  - Possibly phosphate deficient ITPP with additional excess amorphous phosphorous phase
  - Substoichiometric ITPP has been shown to have reduced conductivity

- Future work:
  - Probe *crystalline* P:M (occupancy) using Neutron Powder Diffraction
  - Study protonic environment for varying P:M by probing vibrational states using Inelastic Neutron Scattering
  - Address mechanical limitations- formulate dense pellets and/or incorporate ITPP into membranes

Catalysis of Nitrogen Reduction

Nitrogen triple bond energy 226 kcal/mole ~ 1MJ/mole!

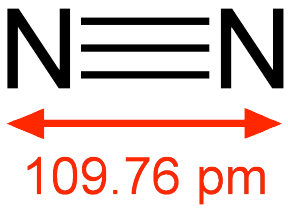
Homogeneous phase molecular catalysts *Associative* (bond proton to N_2 then break N_2 bond…nitrogenase) Reaction has not been driven electrochemically.

Heterogeneous catalysis on Ru surfaces *Dissociative* (split triple bond then react…Haber-Bosch)

Heterogeneous catalysis MoN_x surfaces ?
(little work has been performed on metal nitride surfaces…must suppress H_2 formation)

Electrocatalysis has not been explored in detail

High pressure studies are advantageous to shift equilibrium



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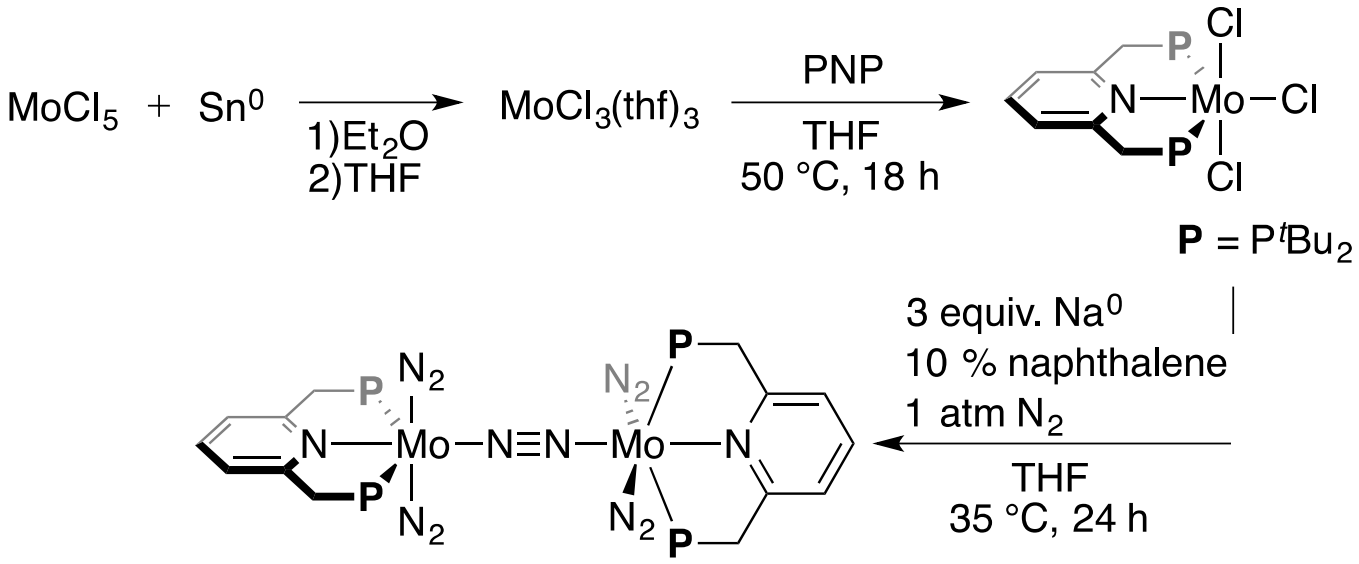
Synthesis of dinuclear dinitrogen complex



N_2 reduction catalysis with
1 equiv $[(PNP)Mo(N_2)_2]_2(N_2)$:

72 equiv Cp_2Co
96 equiv [LutH][OTf]
ca. 1 atm N_2
solvent
20 hr, room temperature

Solvent	Equiv NH_3/cat
Toluene (Nishibayashi)	11.8
Toluene (Our work)	13.1
Various ILs	*ca.* 0.5

H_2 is also formed

Echem experiments ongoing …

Mo_2N as a catalyst

- γ-Mo_2N is known to catalyze a number of reactions such as hydrogenolysis, and methanol steam reforming

- It is one of the most active non-group 8 catalysts for ammonia synthesis

- γ-Mo_2N is electrically conductive, which makes it an appealing candidate for use as an electrocatalyst

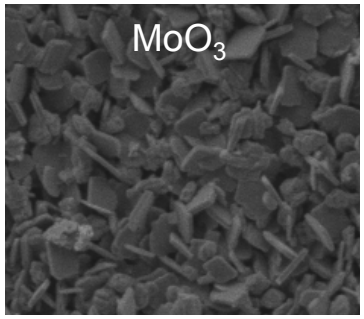
- Empirical relationships exist correlating sample preparation conditions and surface treatment and catalytic activity

- However, correlation between the catalytic activity and chemical structure is poorly understood

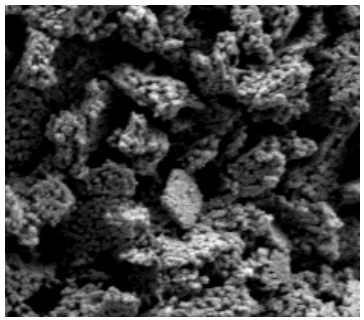
Mo_2N synthesis – powders

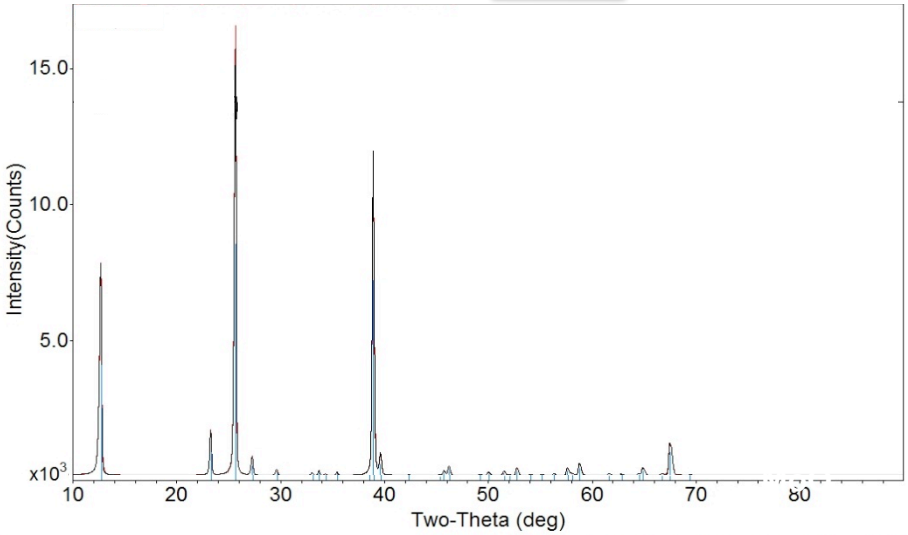
$$MoO_3(s) + NH_3(g) \xrightarrow{\Delta} Mo_2N(s)$$

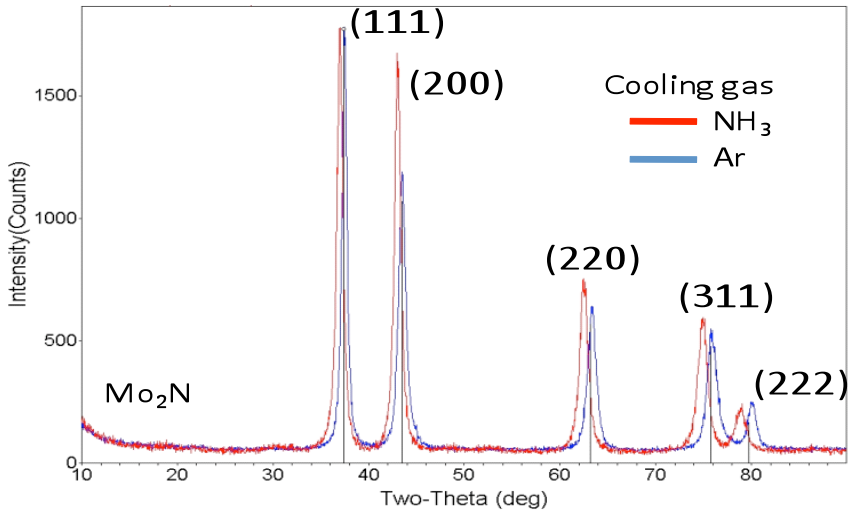
γ-Mo_2N



pseudomorphic rxn →







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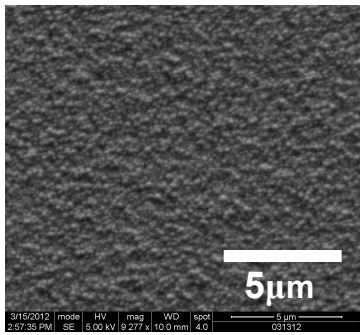
Very sensitive to possible presence of O_2 or water

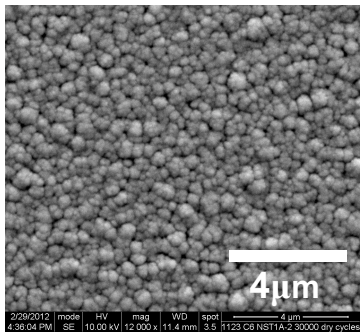
Mo_2N synthesis – films

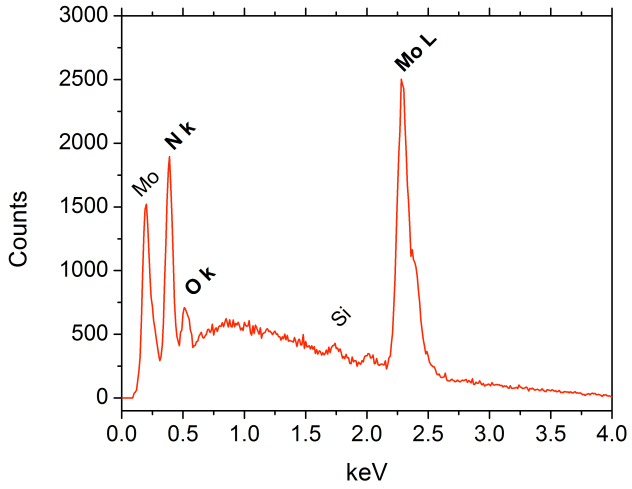
Reactive ion beam sputtering

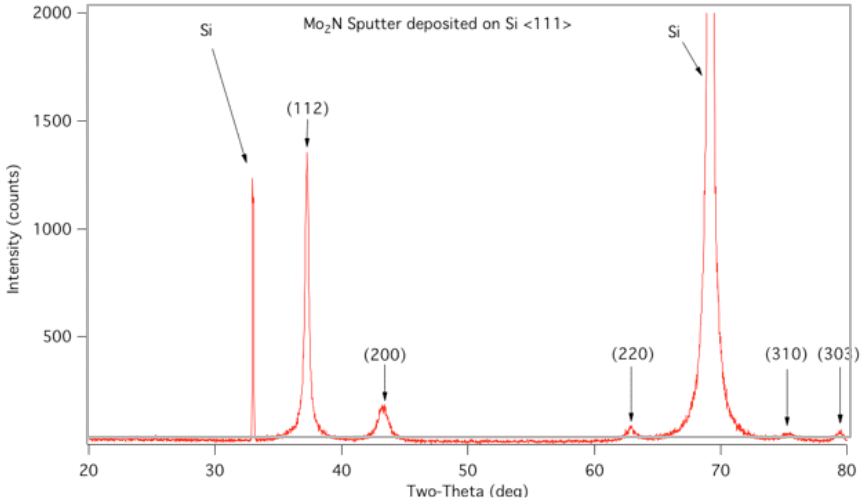
$Mo(g) + (10\text{-}50\%)N_2/Ar(g) \longrightarrow Mo_2N(s)$

Product crystallinity, structure, deposition rate and surface area vary with: gas composition, pressure, type of substrate









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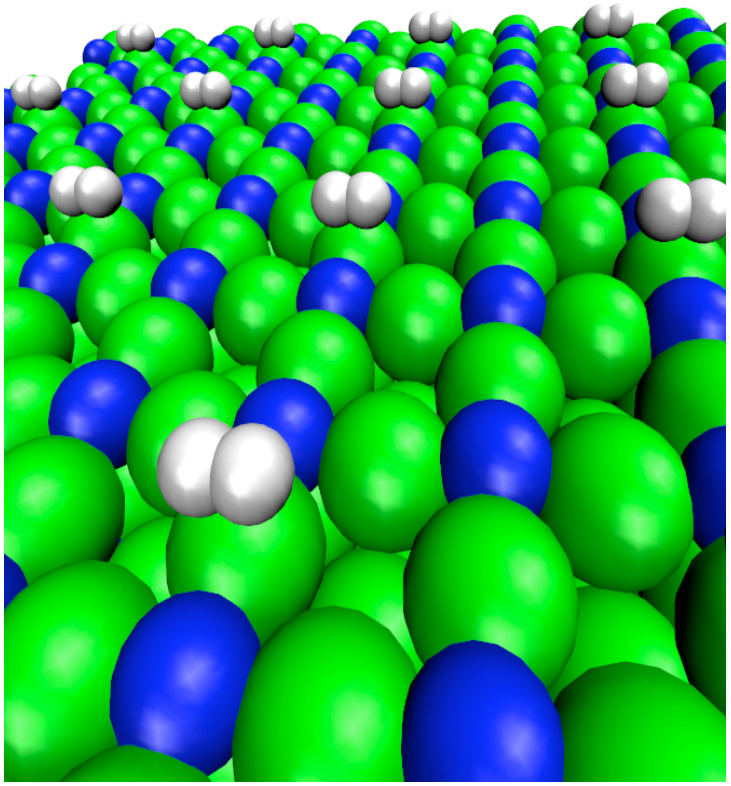
Idealized surface structure of Mo_2N



fcc structure with ½ N positions vacant

THEORY: DFT N_2 binds to surface Mo atoms in side-on fashion

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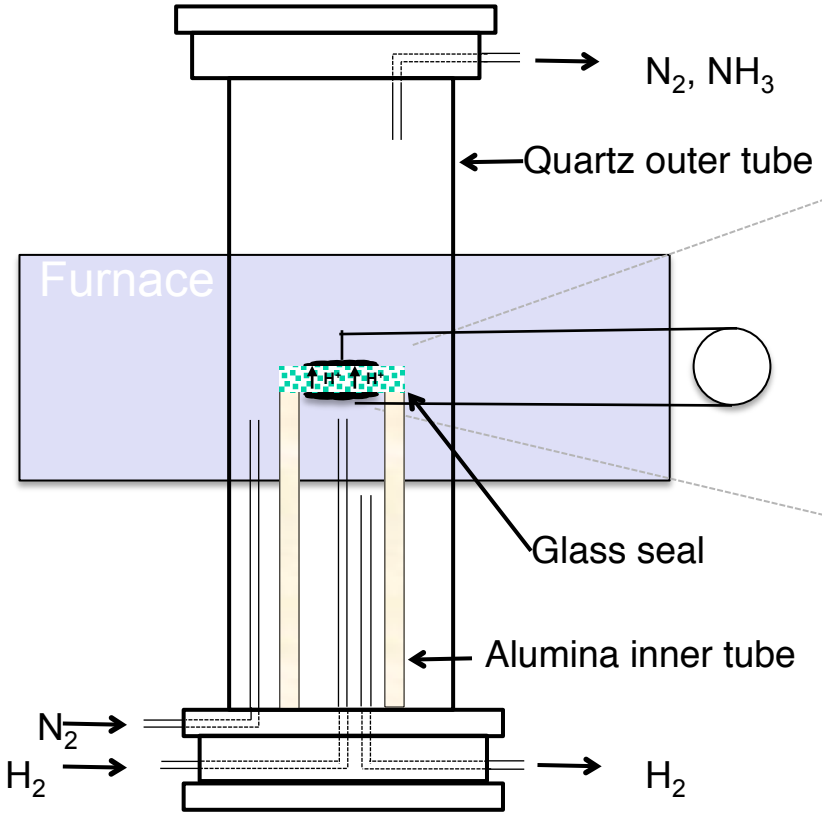
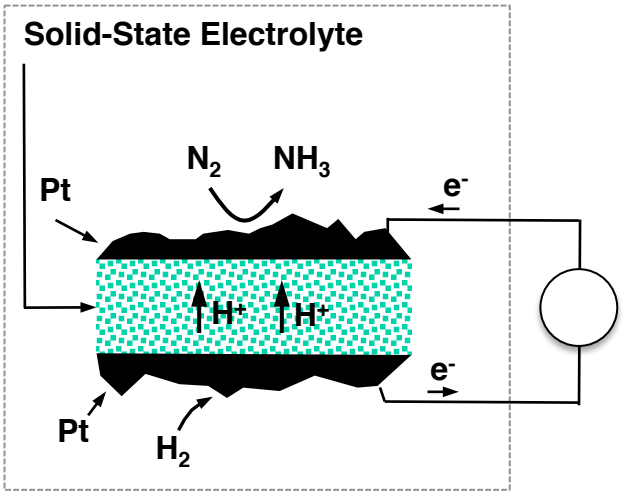
Gas Phase Echem Cell: Experimental Set-up

2-Chamber reactor cell



Electrochemical Cell



- Atmospheric pressure
- 550-750 ˚C

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Solid state electrochemical NH_3 synthesis

Proton Conductor	Cell	Temp	NH_3 Formation Rate (mol s^{-1} cm^{-2})
SCY	H_2,Pd|SCY|Pd, N_2, NH_3, He	570˚C	4.5×10^{-9} [1]
SCY	Steam H_2O,Pd|SCY|Ru-based, N_2, NH_3, He	650˚C	9.1×10^{-14} [2]
BCGO	H_2,Ag-Pd|BCGO|Ag-Pd, N_2, NH_3	480˚C	3.09×10^{-9} [3]
Nafion	H_2,Pt|Nafion|Ru, N_2, NH_3	80 ˚C	1.13×10^{-8} [4]
SCY	**H_2,Pt|SCY|Pt, N_2, NH_3**	**650˚C**	**2×10^{-9} Our work**

1. Marnellos, *Science*, 1998
2. Skodra, *Solid State Ionics*, 2009
3. Li, *J Solid State Electrochem*, 2005
4. Xu, *Sci China Ser B:Chem*, 2009

Conclusions

- Tin pyrophosphate proton conductors are promising membrane materials for intermediate temperature (~ 250^{o}C) electrochemical ammonia synthesis
- Ionic liquids may have promise
- Mo_2N studies are feasible with synthetic procedures for film formation
- Homogeneous Mo catalysts perform ammonia synthesis in ionic liquids, but development will require understanding of solvent effects and further investigation
- Electrochemical ammonia synthesis at 250^{o}C is lowest temp prep using solid membrane material.

NEXT UP

Optimization of electrochemical cell design…catalyst, electrode fabrication, etc.