High Efficiency Low Cost Electrochemical Ammonia Production

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NH3 Fuel Conference
Los Angeles, CA
September 20th 2016

PROTON
THE LEADER IN ON SITE GAS GENERATION.

Outline

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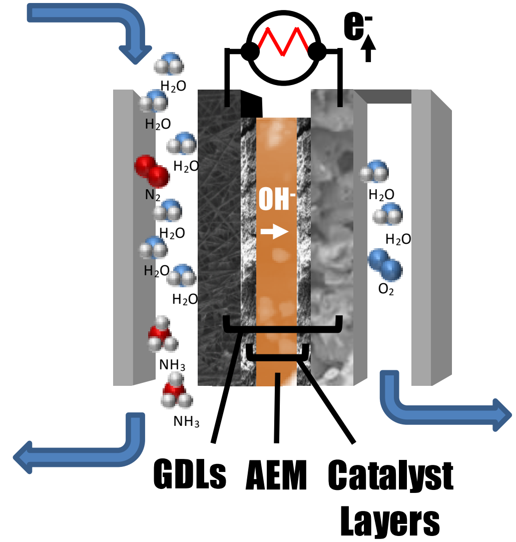
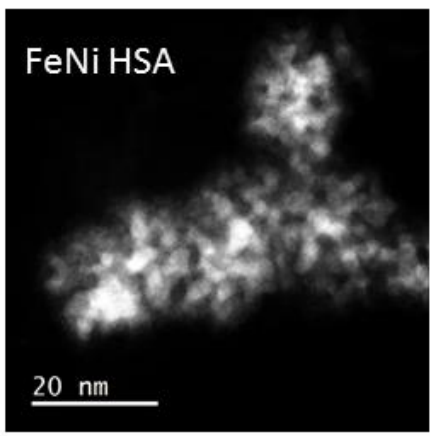
Proton OnSite Overview



Electrochemical Ammonia Synthesis



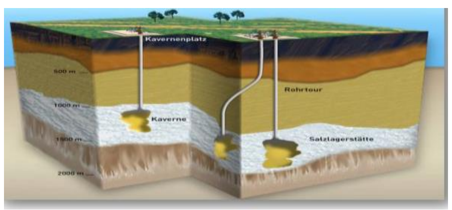
Results and Future Directions

Proton OnSite Overview

- Core technology in PEM electrolysis
- Founded in 1996, >2500 fielded units, 20 MW capacity shipped
- Continuing to scale manufacturing capability and output to address energy markets
- MW scale electrolyzer system now available

Headquarters in Wallingford, CT

Electrolyzer Applications:

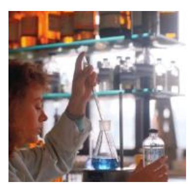


Renewable Energy Storage

Biogas

Power Plants

Heat Treating



Laboratories

Semiconductors

Government

Proton Fueling Station

Membrane-based Electrolysis

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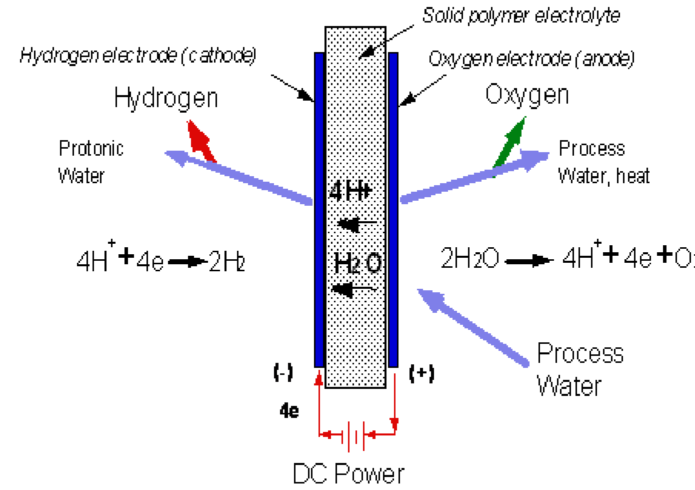
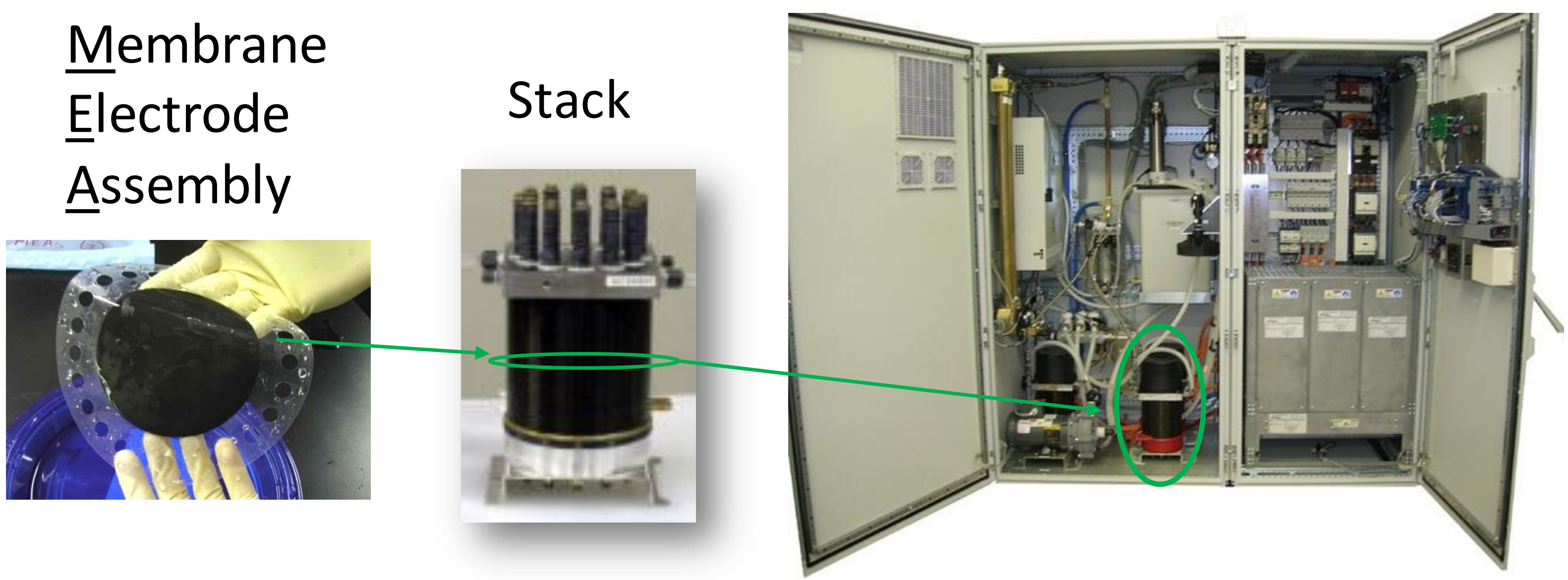
- "PEM" electrode = Proton Exchange Membrane
- Reaction occurs across a thin MEA
- Assembled into compact stacks and systems



Hydrogen Generation Mode

Membrane Electrode Assembly

Stack



Scalable Technology

From Single to Multi-Stack Systems

HOGEN® GC

HOGEN® S Series

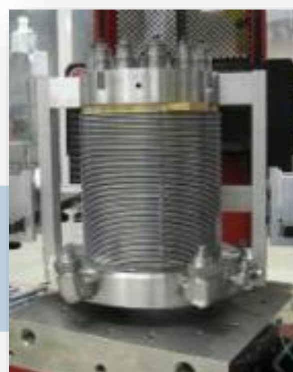
HOGEN® H Series

HOGEN® C Series

HOGEN® M Series

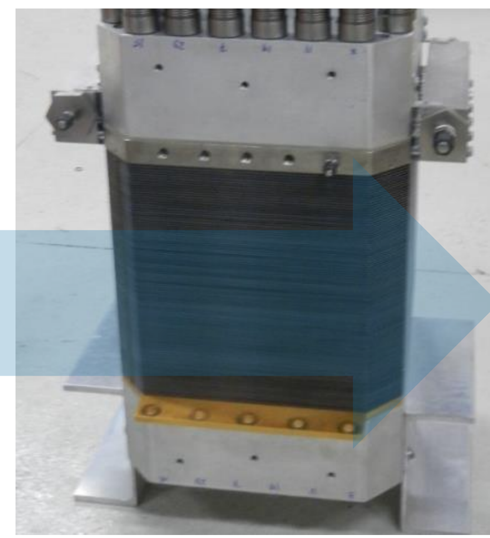
28 cm^2
0.05 Nm^3/hr
0.01 kg/day

86 cm^2
2 Nm^3/hr
4.3 kg/day



210 cm^2
10 Nm^3/hr
21.6 kg/day

680 cm^2
50 Nm^3/hr
100 kg/day



How much H_2 can we make?

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7 kW

1 day

40 kW

1 day

180 kW

1 week

1,000 kW

1 day

Outline

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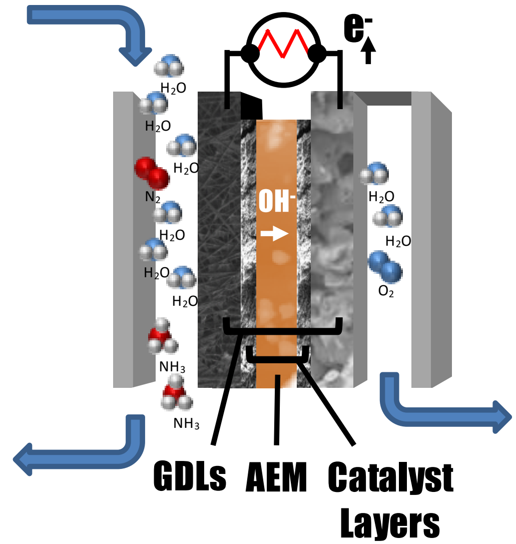
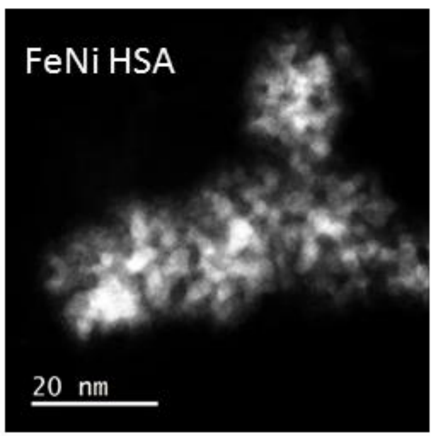


Proton OnSite Overview

Electrochemical Ammonia Synthesis

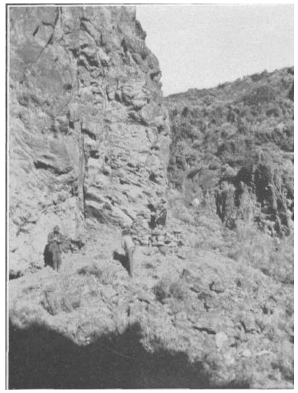


Results and Future Directions

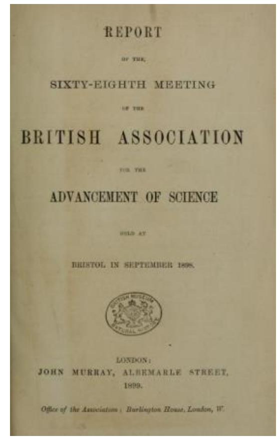
Ammonia Production History

mid 1800's: mining **1899:** Crooks raises alarm **1913:** Haber-Bosch

Guano mining[1]



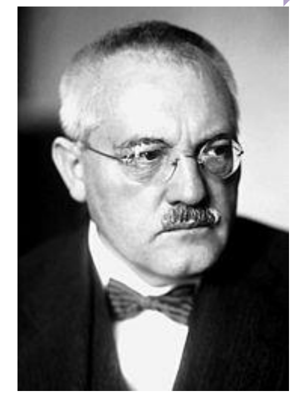
Nitrate salt mining[2]



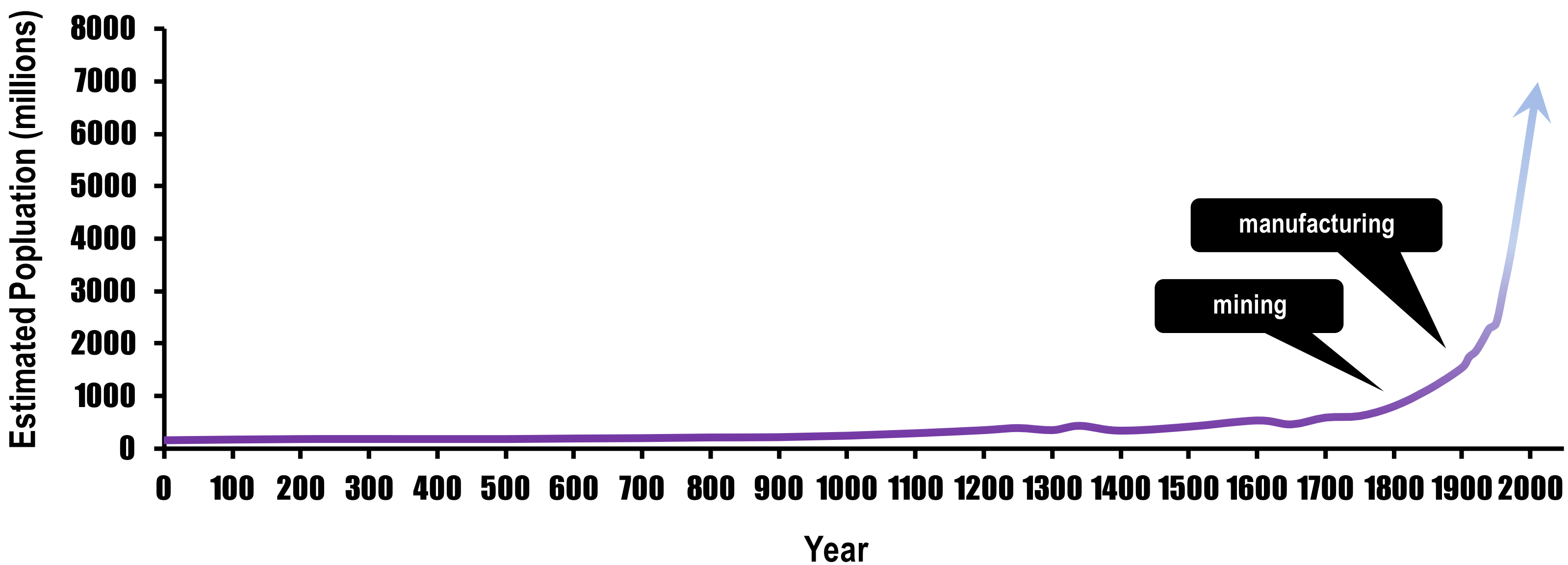
REPORT
OF THE
SIXTY-EIGHTH MEETING
OF THE
BRITISH ASSOCIATION
FOR THE
ADVANCEMENT OF SCIENCE
HELD AT
BRISTOL IN SEPTEMBER 1898.

LONDON:
JOHN MURRAY, ALBEMARLE STREET,
1899.
Office of the Association: Burlington House, London, W.

Fritz Haber



Carl Bosch



(1) History Today Volume 30 Issue 6 June 1980
(2) Dept. of the Interior US Geological Survey Bulletin 523, 1912

Haber-Bosch (HB) Process

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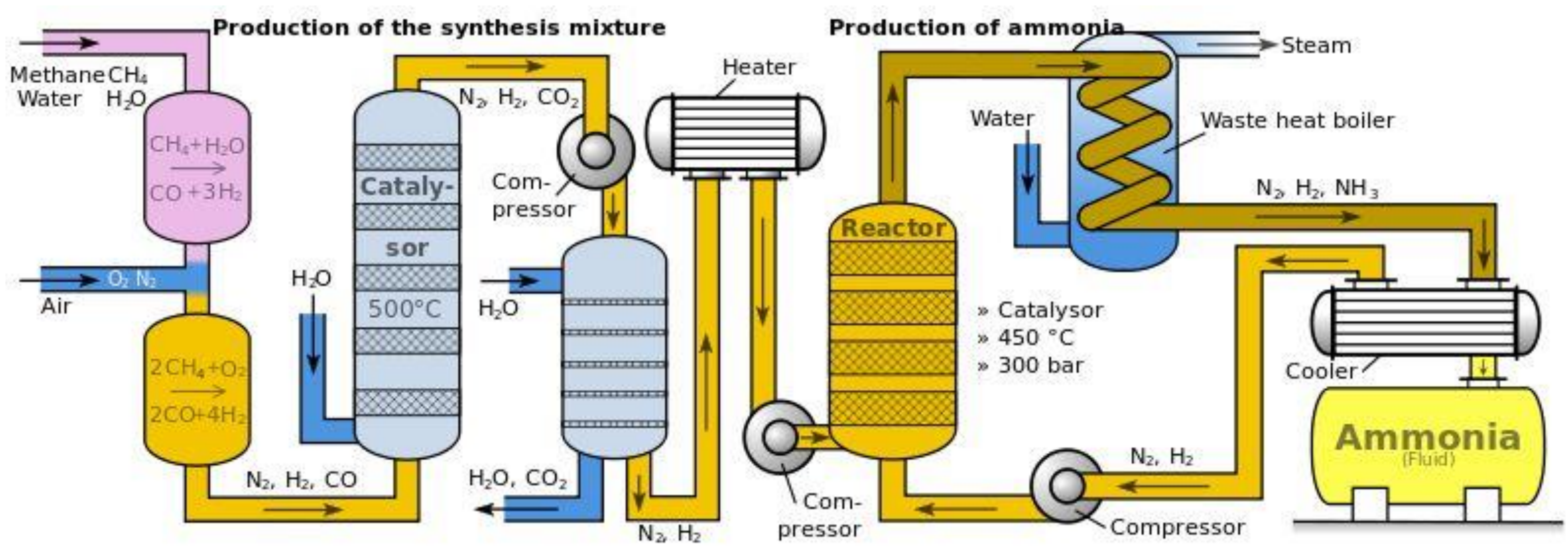


- H_2 obtained from fossil fuels, high temp and high pressure, high capital cost
- Supports about half of the people on earth

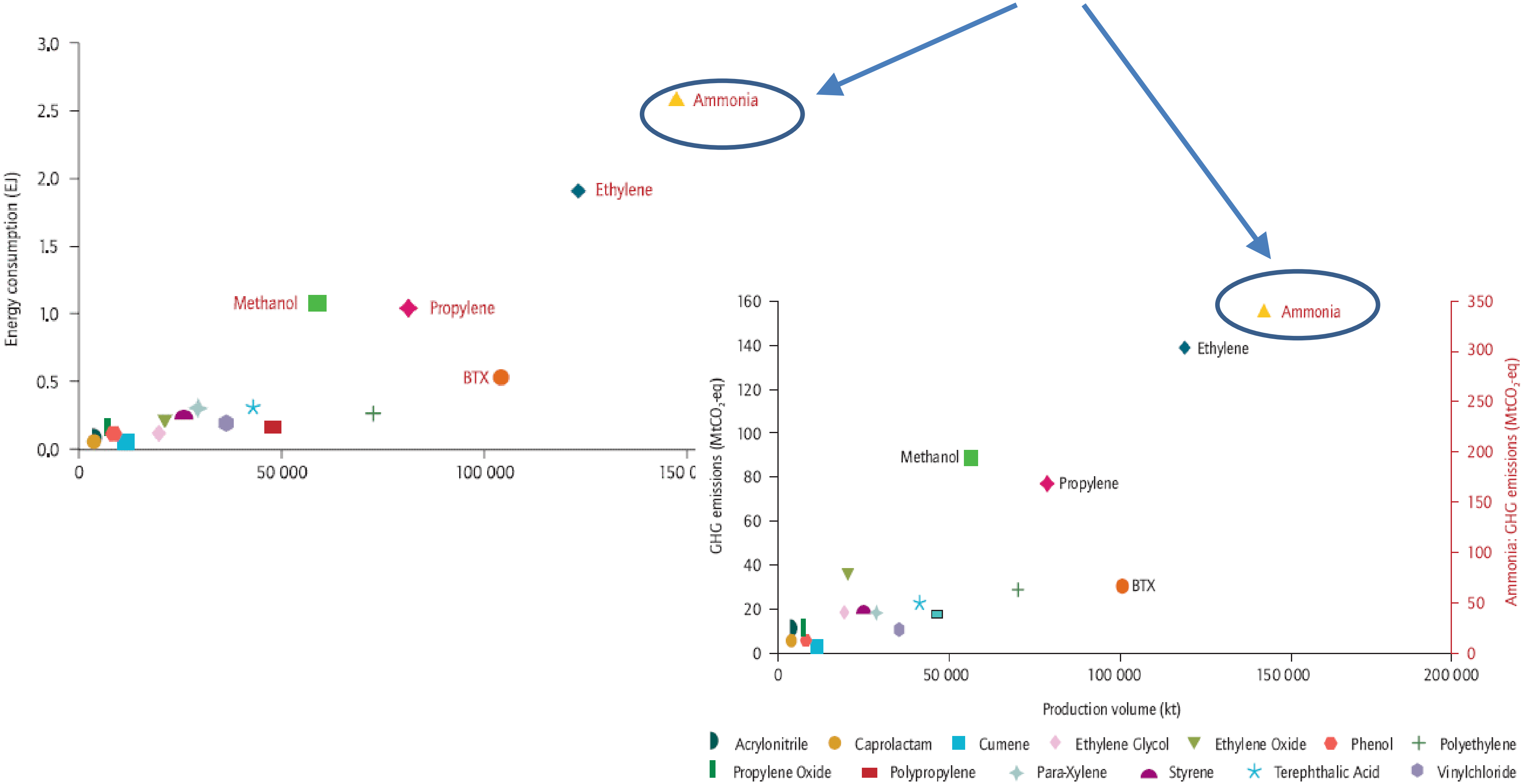
  J.W. Erisman, M.A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, Nat. Geosci., 1 (2008) 636-639.
- Inefficient (consumes ~1% of the worlds energy)

  Ammonia Production: Moving Towards Maximum Efficiency and Lower GHG Emissions http://www.fertilizer.org/, 2014.
- High-polluting (~3% GHG emissions)

  Feeding the Earth, International Fertilizer Industry Association, http://www.fertilizer.org/, 2009.

The NH_3 energy problem

- 18 of major chemical products use 80% of energy and produce 75% of GHGs for the chemical industry
- Ammonia is largest by far (mainly from H_2 via SMR)



Transitioning to Renewable NH_3

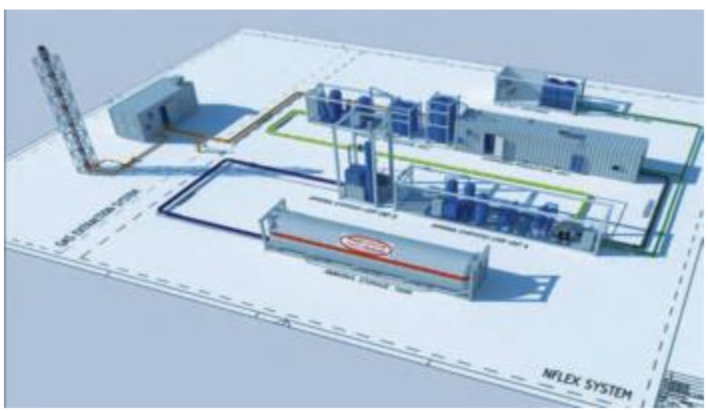
- Current process drives centralized production

Haber Bosch plant
2000+ metric tons NH_3/day

~1,000 MW H_2 equivalent
Steam methane reforming for H_2

http://www.bbc.co.uk/schools/gcsebitesize/science/triple_edexcel/gases_equilibria_ammonia/ammonia/revision/1/

- Options for distributed production:



http://www.protonventures.com/wp-content/uploads/2016/04/2016.4.15-Brochure-Proton-Ventures.pdf

Small Haber Bosch: 3-50 metric tons NH_3/day
~1-20 MW H_2 equivalent; renewable electrolysis

Electrochemical NH_3: g-kg NH_3/day
Small scale electrolysis
Proof of concept

Vision for Electrochemical Ammonia Production

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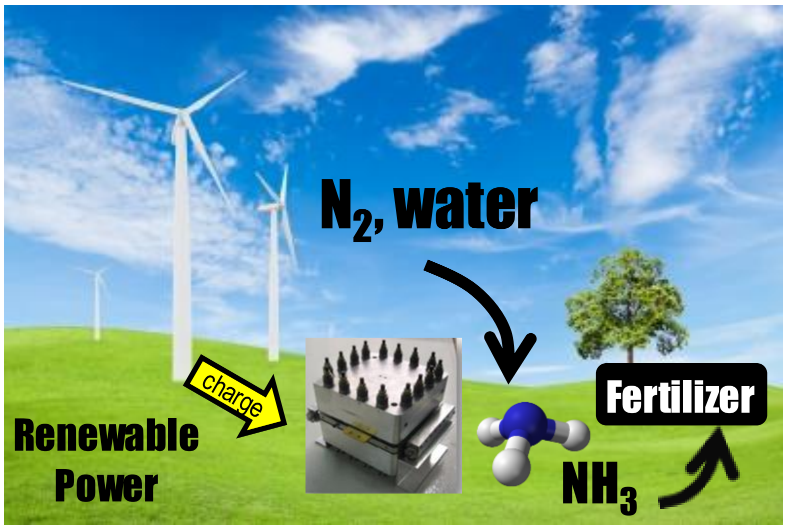
Ammonia Synthesis



Industrial Uses: chemical synthesis, emissions scrubbing, refrigeration

J.N. Renner, L.F. Greenlee, A.M. Herring, K.E. Ayers, Electrochemical Synthesis of Ammonia: A Low Pressure, Low Temperature Approach, in: The Electrochemical Society Interface, Summer 2015.

- Electrically driven process for low temp/pressure/emissions
- Compatible with intermittent operation
- High regional demand for fertilizer co-located with renewables

Scalable Technology

Ammonia Production Technology Plan

Bench Scale Size: 25 cm^2

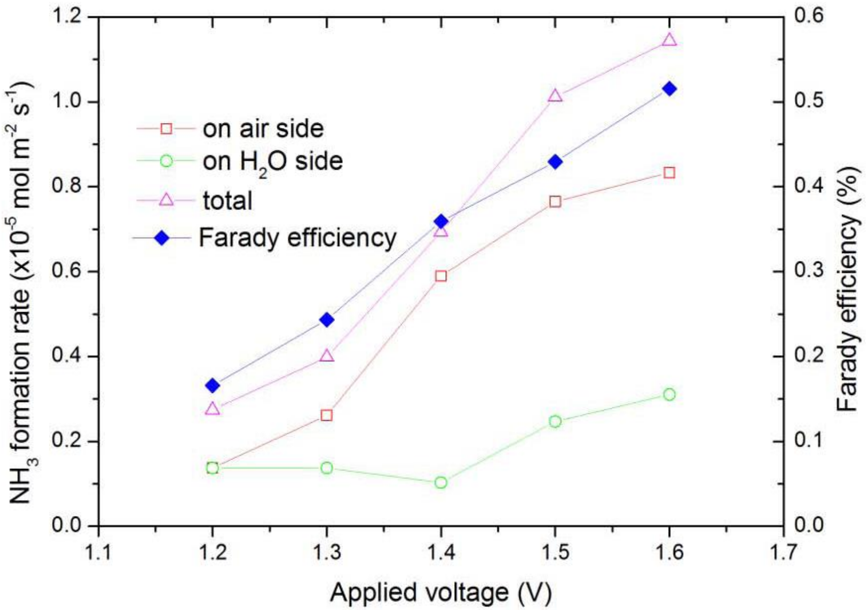
GC Size: 28-84 cm^2

M Series: 400,000 cm^2

PHASE I	PHASE II	FUTURE
Proof-of-Concept Phase Bench Scale	Breadboard Phase Garden Capacity (100 g/year)	Product Phase Small Farm (260 acres – 12,500 kg/year)
<u>Targets</u> Current Efficiency: > 1%	<u>Targets</u> Current Efficiency: 10% Current Density: 10 mA/cm^2	<u>Targets</u> Current Efficiency: 50% Current Density: 50 mA/cm^2

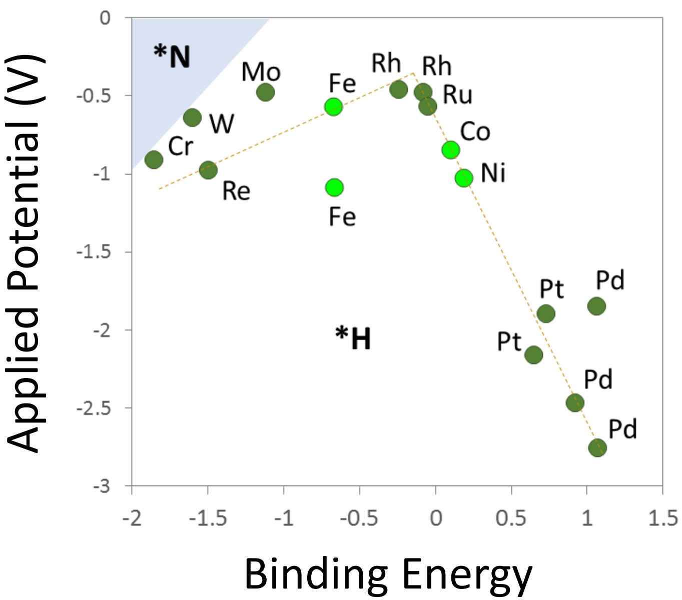
- Enables networks of distributed scale and near point-of-use
- Proton developing MW-scale

Background/Key Obstacles



R. Lan, J.T.S. Irvine, S. Tao, Scientific Reports, 3 (2013).

- PEM demonstrated feasibility
- At 1.5 V and below, need ~50% Faradaic efficiency to match HB

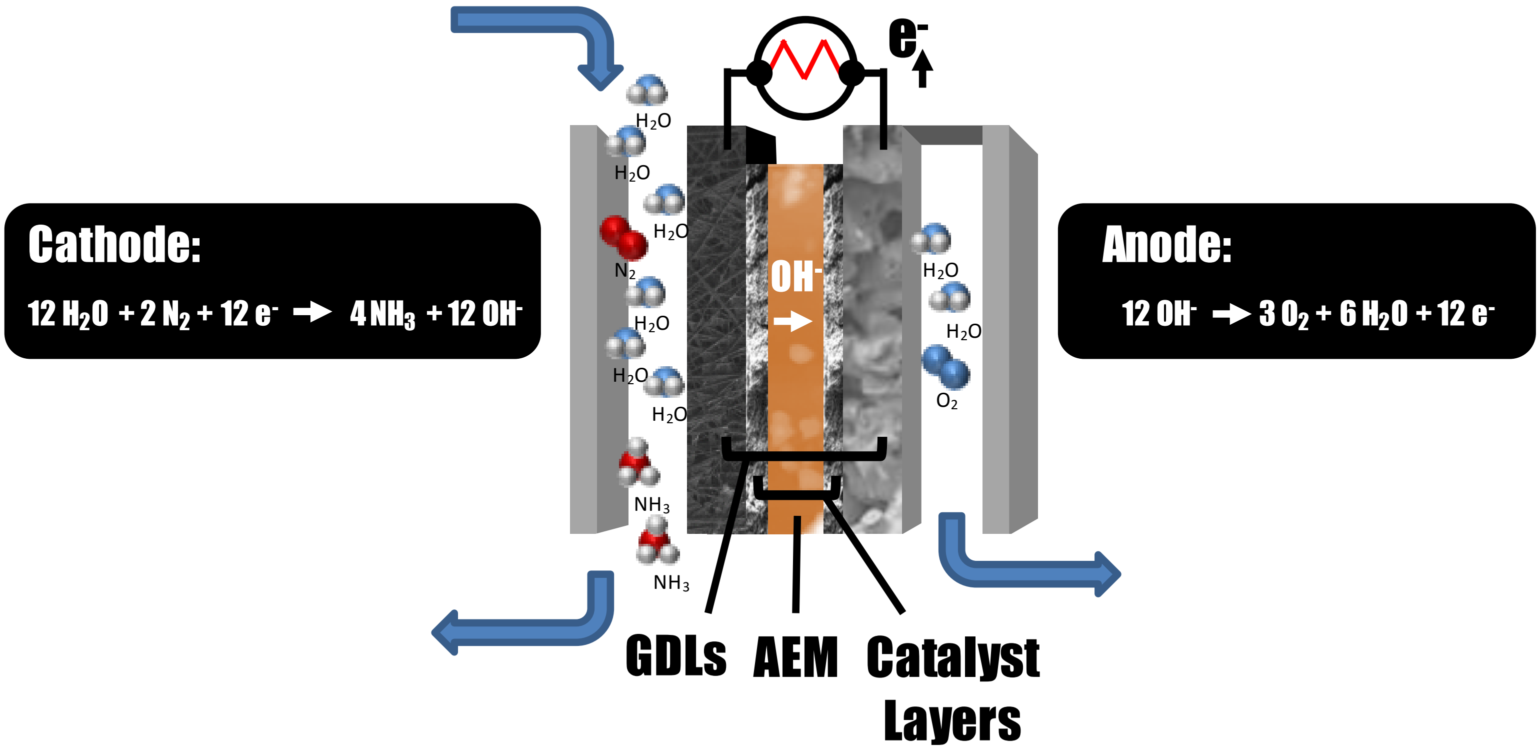


A volcano plot predicting metal performance for nitrogen electroreduction[1]

E. Skúlason, *et. al*, Phys. Chem. Chem. Phys., 14 (2012).

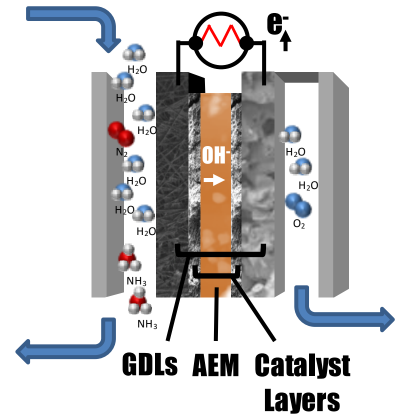
- Key obstacle: selective catalyst
  - low NH_3 overpotential
  - high H_2 overpotential

AEM-based Approach



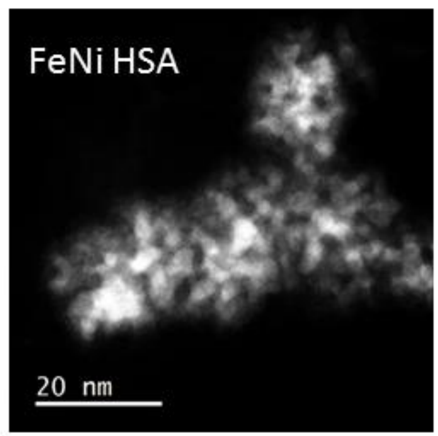
- AEM enables wider range of efficient catalysts vs. PEM
- Lower cost materials of construction in alkaline environment

Outline



Proton OnSite Overview

Electrochemical Ammonia Synthesis



Results and Future Directions

Ammonia Generation Rig

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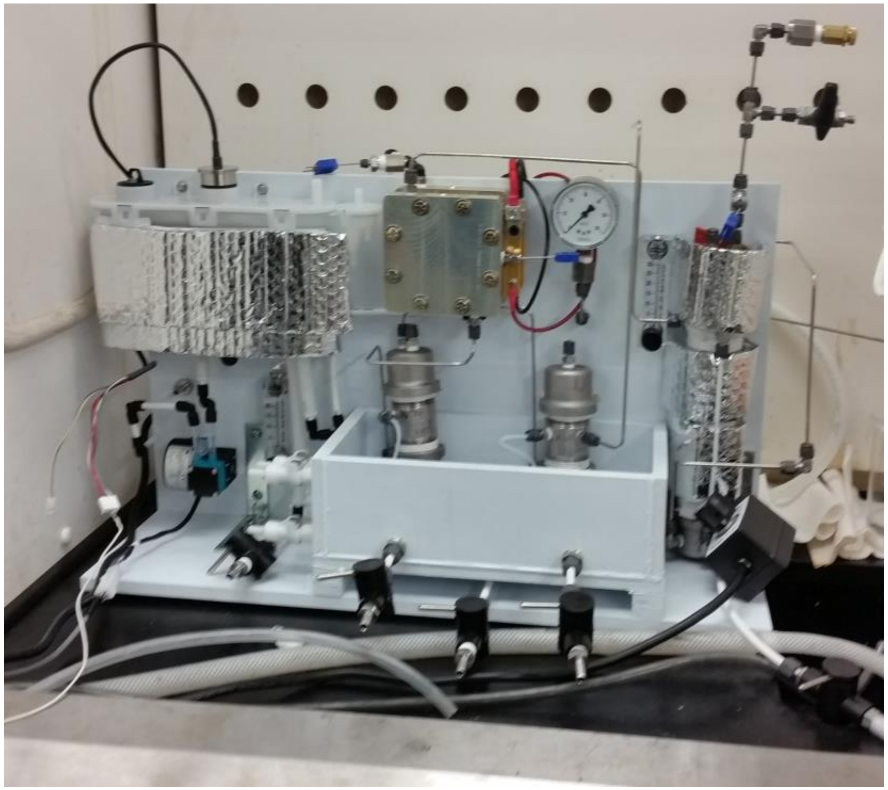
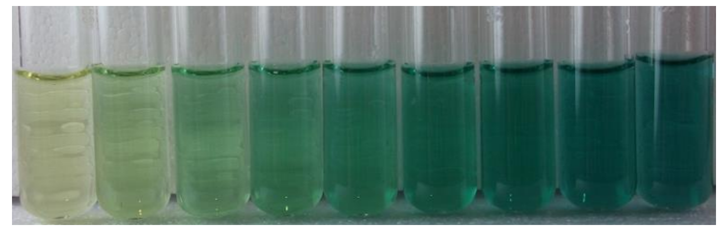


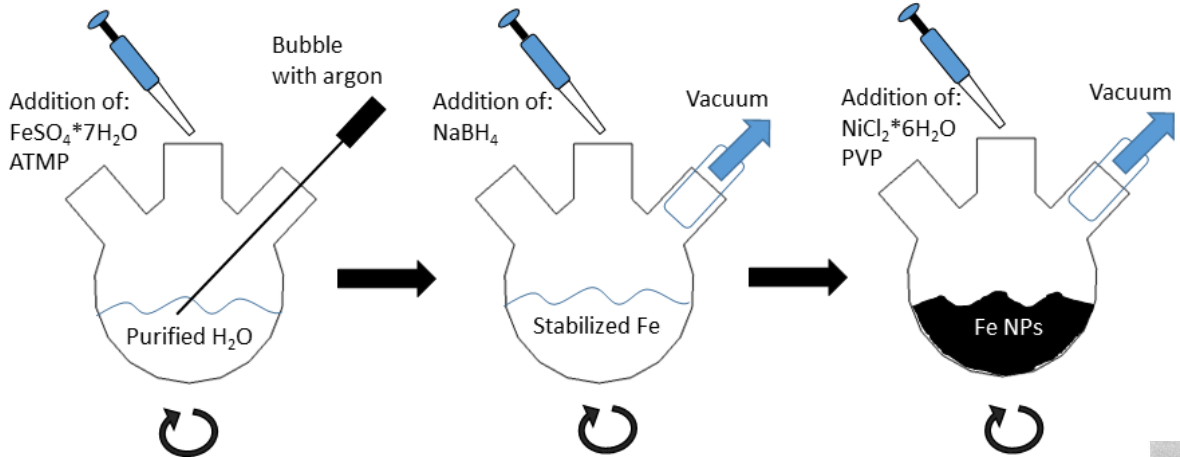
Ammonia Capture via Acid Trap and Determination via Colorimetric Assay:

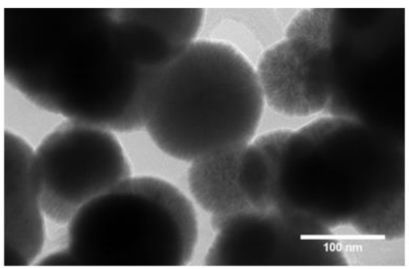


Increasing ammonia concentration

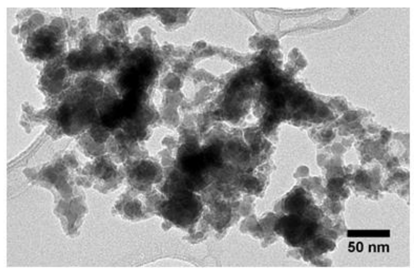
- Design reviewed by senior engineers, safety qualified
- Test bed to compare multiple configurations and catalysts
- Sensitive colorimetric assay for ammonia (verified independently)

Catalyst Synthesis

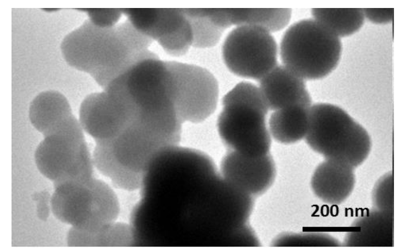




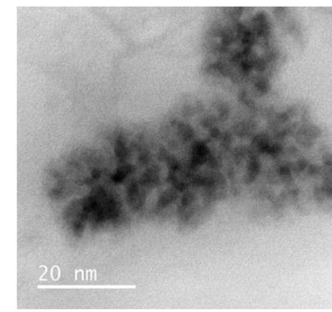
Large Fe-only



Small Ni-only



FeNi
Low SA

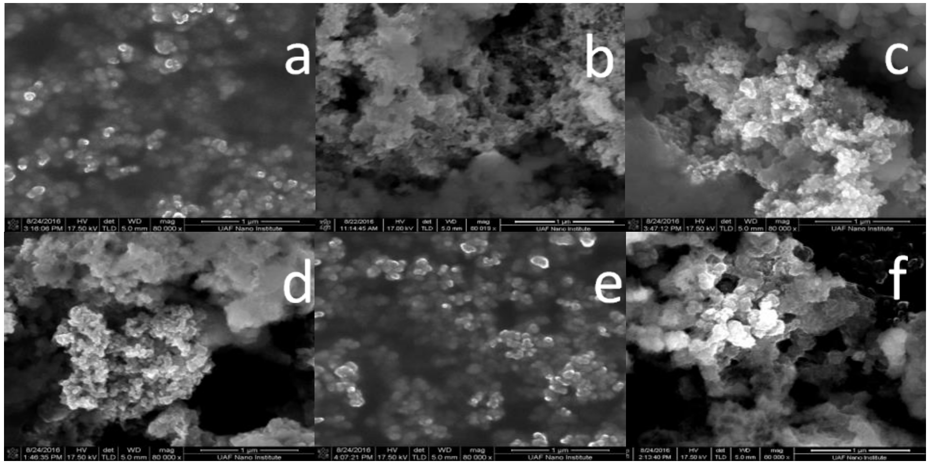


FeNi
High SA

- Exquisite control over nanoparticle morphology and composition for Ni and Fe compounds
- Compared to commercial Pt

Phase I Summary

- Synthesized FeNi core-shell and alloy nanocatalysts
- Demonstrated detectable ammonia generation in AEM cell

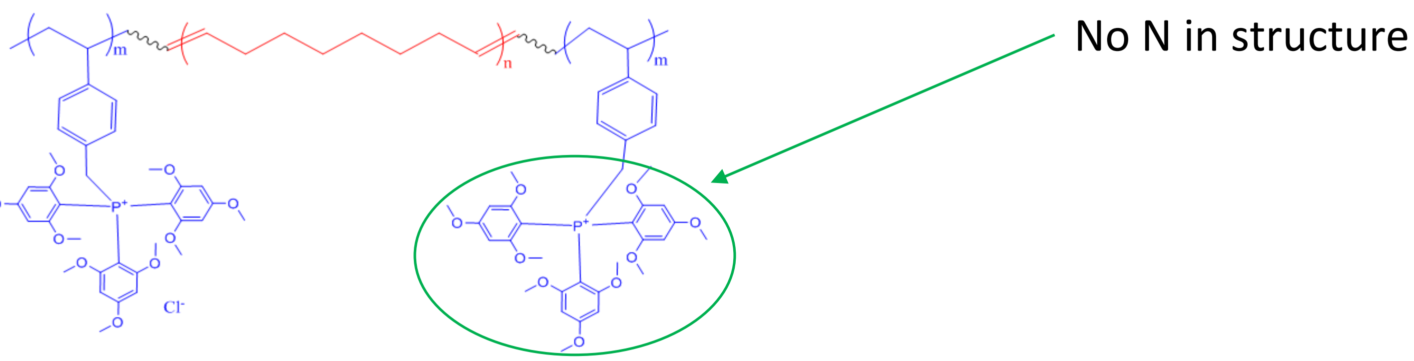


SEM images at 80,000 magnification for a) 1:1 FeNi core-shell, b) 1:1 FeNi alloy, c) 1:3 FeNi core-shell, d) 1:3 FeNi alloy, e) 3:1 FeNi core-shell, and f) 3:1 FeNi alloy.

- Improved selectivity towards ammonia generation over hydrogen evolution compared to Pt catalysts
- Catalysts containing higher concentrations of Fe to Ni have shown higher ammonia generation rates

Key Issues for Electrochemical Ammonia Generation

- Production rates are low – small sources of interference can confuse results
  - Can detect ammonia from non-N2 sources
    - Degradation of N-containing materials
    - Impurities/contamination
- Need to eliminate/correct for ammonia from non-electrocatalytic sources
  - Approach 1: Elimination of N-containing side groups in membrane
    - Shift to materials containing phosphonium cations

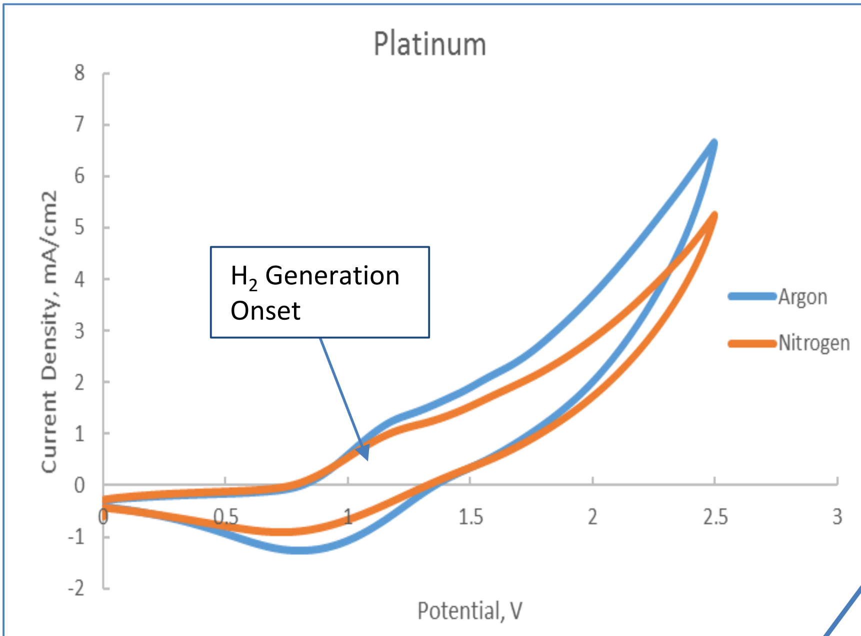


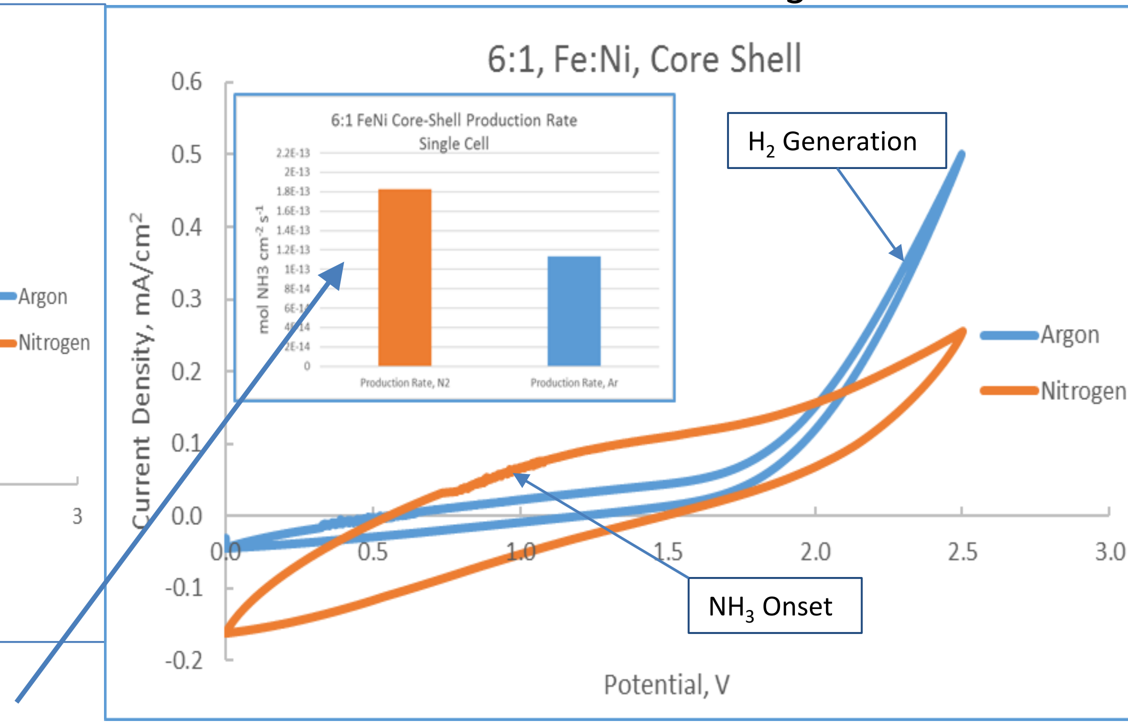
  - Approach 2: Argon controls to compare to N2 results
- Similar issues noted in DOE roundtable discussion[1]

[1]Norskov, J. K., *et el., Sustainable Ammonia Synthesis: Exploring the scientific challenges associated with discovering alternative, sustainable processes for ammonia production*; Department of Energy: A report from the Roundtable Discussion held February 16, 2016, March 25, 2016.

Effect of Catalyst Composition

Commercial Pt catalyst - Increased levels of H_2 generation	FeNi core-shell catalyst – Increased levels of NH_3 generation



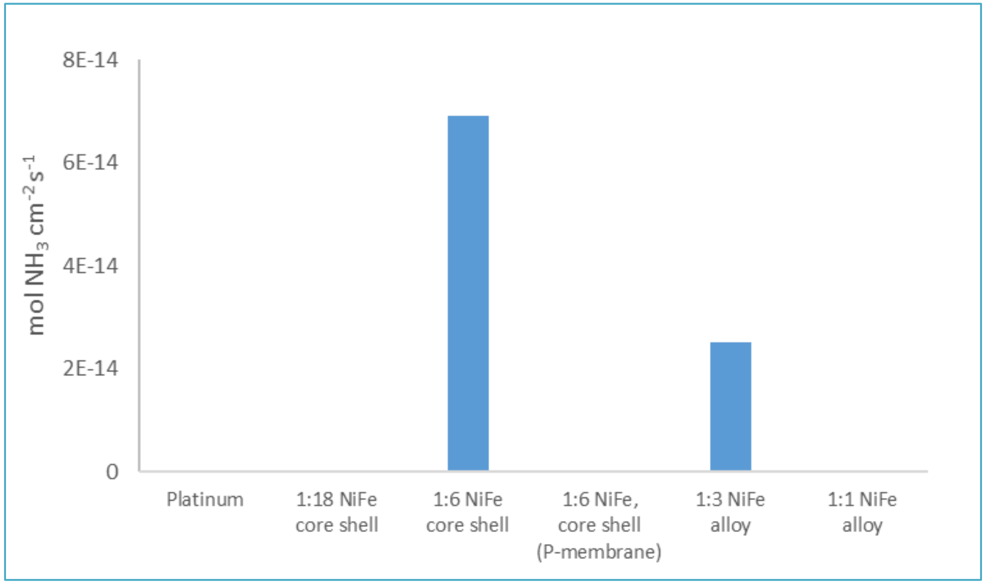


Net ammonia production observed with N_2 (orange) vs. argon control (blue)

- Increasing selectivity for ammonia generation with FeNi core-shell catalyst over hydrogen evolution compared to Pt catalyst

Conditions: 3 hour of operation at voltage, IrOx counter electrodes

Phase II performance



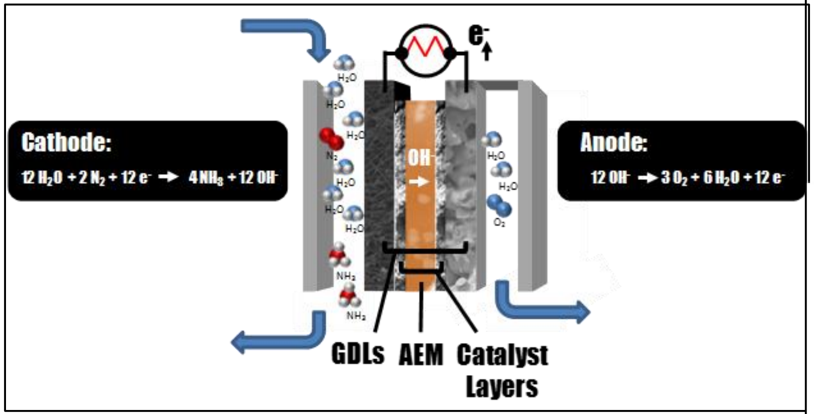
Ammonia generation rate, with argon background rate subtracted, for each catalyst in Phase II screening effort.

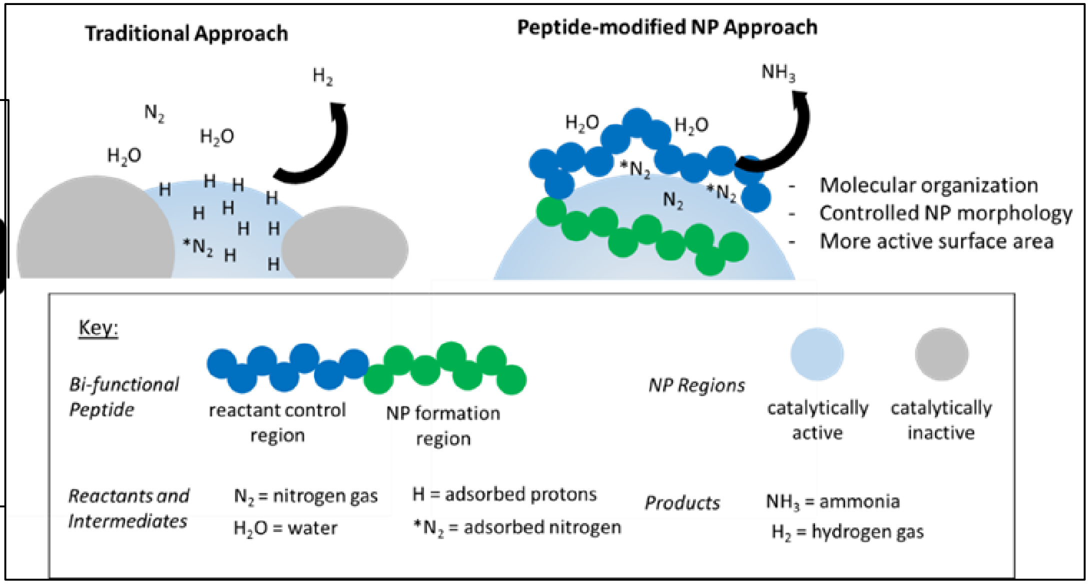
- Only FeNi catalysts with 1:6 and 1:3 NiFe ratios show ammonia production vs. control
  - Down selected for catalyst layer optimization for improved performance
- Work ongoing to refine catalyst structure and combine with N-free membranes

Conditions: 3 hour of operation at 2.5 V, IrOx counter electrodes

Bio-inspired Catalysts for Ammonia Generation

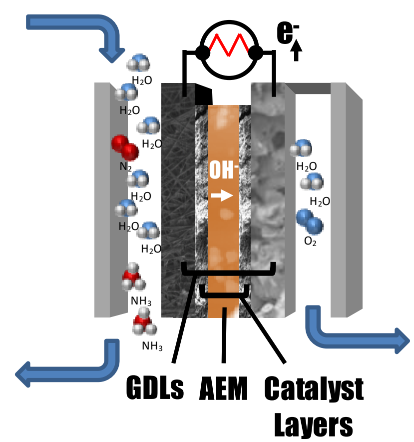
- Catalyst structures inspired by nitrogenase enzymes are being developed for improved electrochemical ammonia generation
- Peptides can be used to improve the catalytic activity of the catalyst through:
  - Control of reactants at catalyst surface and active sites
  - Formation of structured catalyst nanoparticles



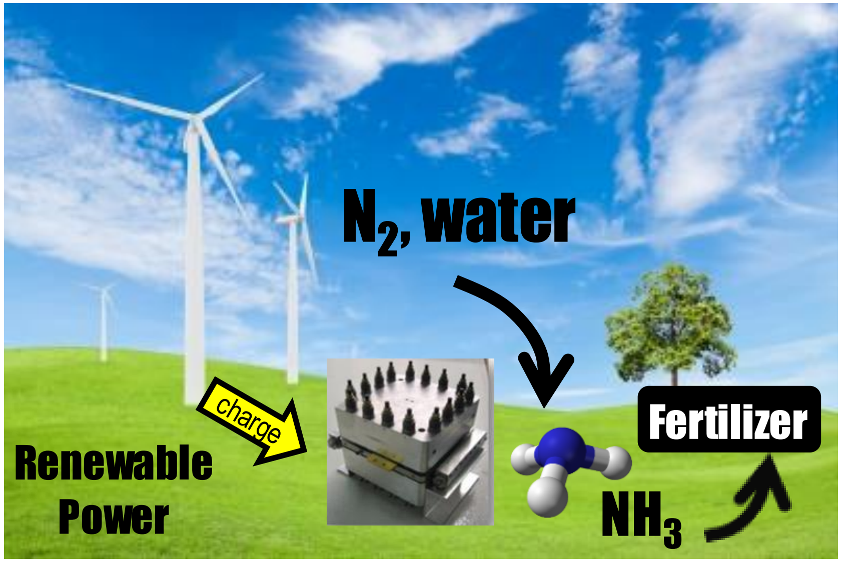


Conclusions

- The developed system provides an adequate test bed
- Proof-of-concept was established for AEM-based ammonia generation
- Careful experiments are required to prove electrocatalytic generation vs. contamination
- Continued understanding and control of catalyst sites is needed for efficient low temperature ammonia generation



How do we achieve our vision?



Phase II Work:

- Upgrading ammonia rig
- More detailed product analysis
- NiFe and other nanocatalysts
- Membrane/ionomer/electrode optimization
- Demonstrate increased current density and durability

Future Work:

- Fundamental studies on reaction mechanisms
- Bio-inspired catalysts for selectivity
  - Use of catalyst surface peptides to facilitate improved ammonia generation
  - DOE SBIR Phase I project
- Purification and systems work
- Scale-up

Acknowledgements

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