High Efficiency Low Cost Electrochemical Ammonia Production

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NH3 Fuel Conference
Chicago, IL
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PROTON
THE LEADER IN ON SITE GAS GENERATION.

Outline

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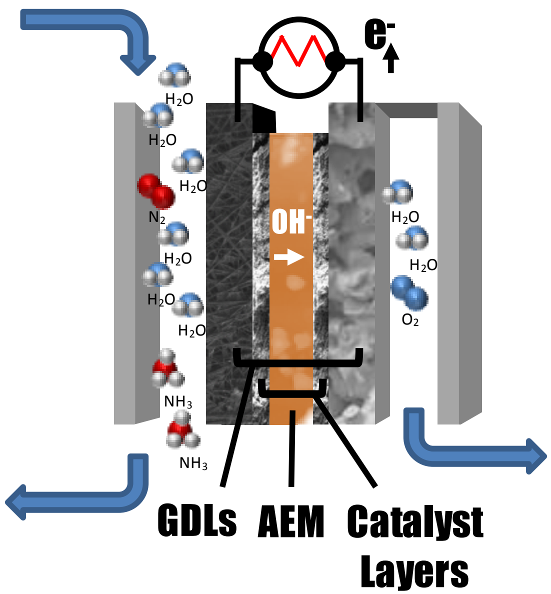
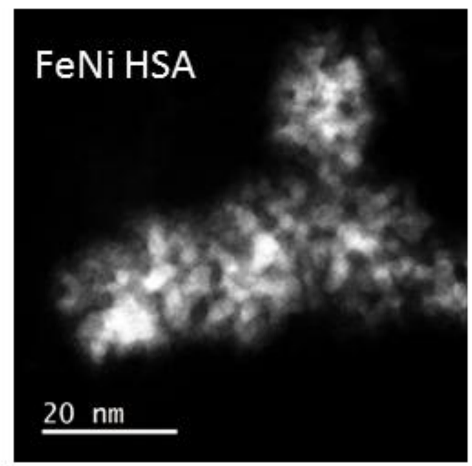
Proton OnSite Overview



Electrochemical Ammonia Synthesis



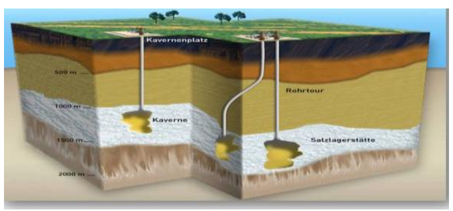
Results and Future Directions

Proton OnSite Overview

- Core technology in PEM electrolysis
- Founded in 1996, >2200 fielded units, 15 MW capacity shipped
- Continuing to scale manufacturing and output to address energy markets
- MW scale electrolyzer system now available

Headquarters in Wallingford, CT

Electrolyzer Applications:

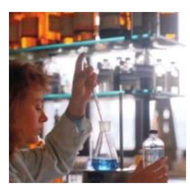


Renewable Energy Storage

Biogas

Power Plants

Heat Treating



Laboratories

Semiconductors

Government

Proton Fueling Station

Membrane-based Electrolysis

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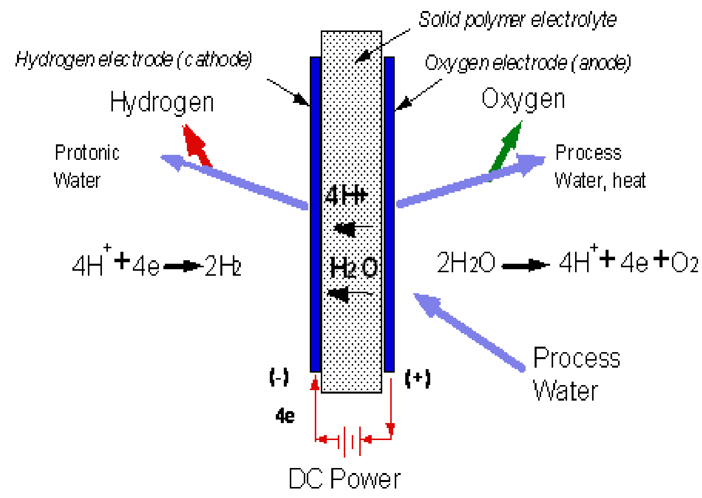
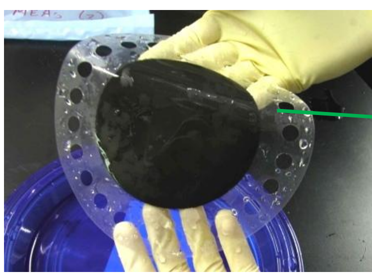
- “PEM” electrode = Proton Exchange Membrane
- Reaction occurs across a thin MEA
- Assembled into compact stacks and systems

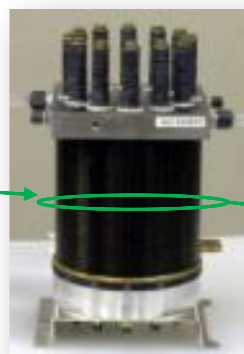


Hydrogen Generation Mode

Membrane Electrode Assembly



Stack



Scalable Technology

From Single to Multi-Stack Systems

HOGEN® GC

HOGEN® S Series

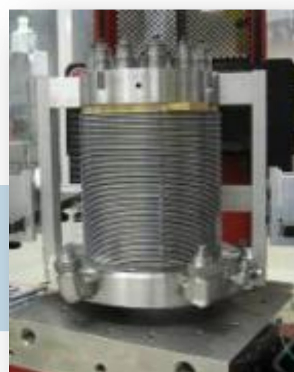
HOGEN® H Series

HOGEN® C Series

HOGEN® M Series

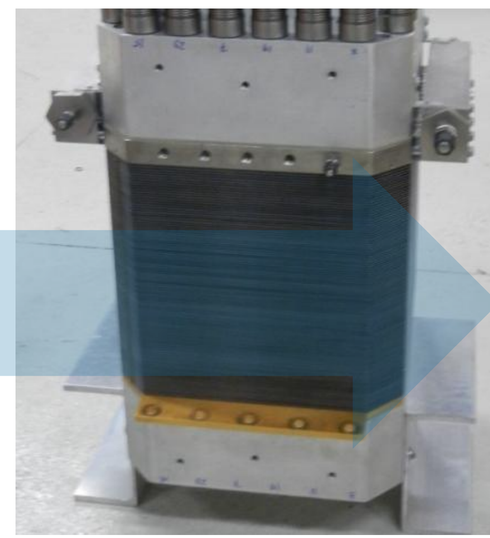
28 cm^2
0.05 Nm^3/hr
0.01 kg/day

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

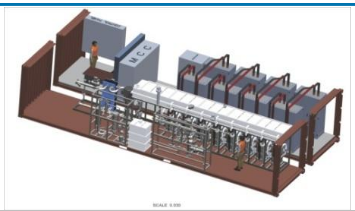


210 cm^2
10 Nm^3/hr
21.6 kg/day

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

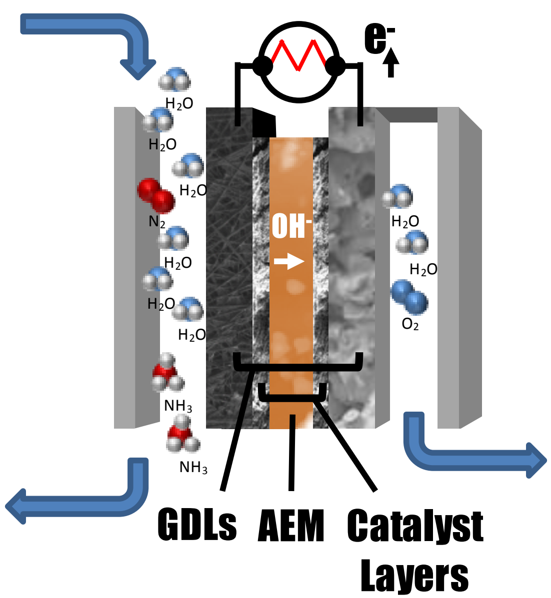


How Much Hydrogen Can We Make?

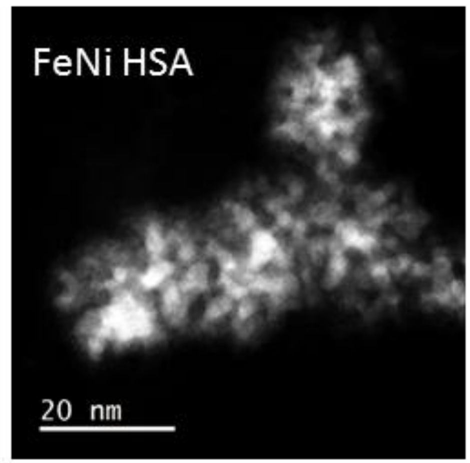
$/kW vs. S-Series	100%	43%	28%	13%E
	S-Series	**H-Series**	**C-Series**	**Megawatt**
Product Type				
Year Introduced	2000	2004	2012	2015
Units Sold	450+	200+	22+	NA
H2 output (Nm³/hr)	1	6	30	200–400
Generates	1 Day 	1 Day 	1 Week 	1 Day 
Replaces	 Six Pack	 Tube Trailer	 Jumbo Tube Trailer	 Jumbo Tube Trailers

Outline

Proton OnSite Overview



Electrochemical Ammonia Synthesis

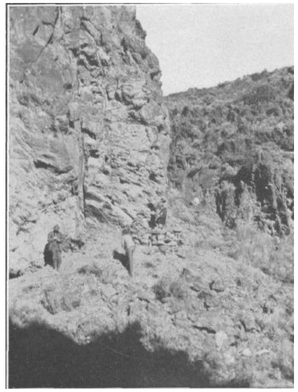


Results and Future Directions

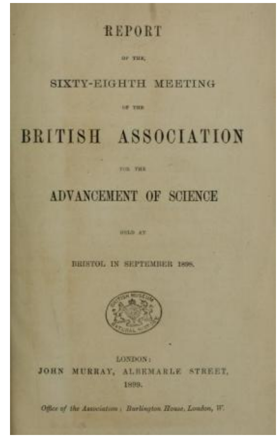
Ammonia Production History

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

Guano mining[1]



Nitrate salt mining[2]



REPORT

SIXTY-EIGHTH MEETING

BRITISH ASSOCIATION

ADVANCEMENT OF SCIENCE

BRISTOL IN SEPTEMBER 1898.

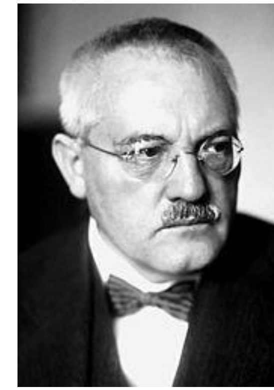
LONDON:

JOHN MURRAY, ALBEMARLE STREET,

1899.

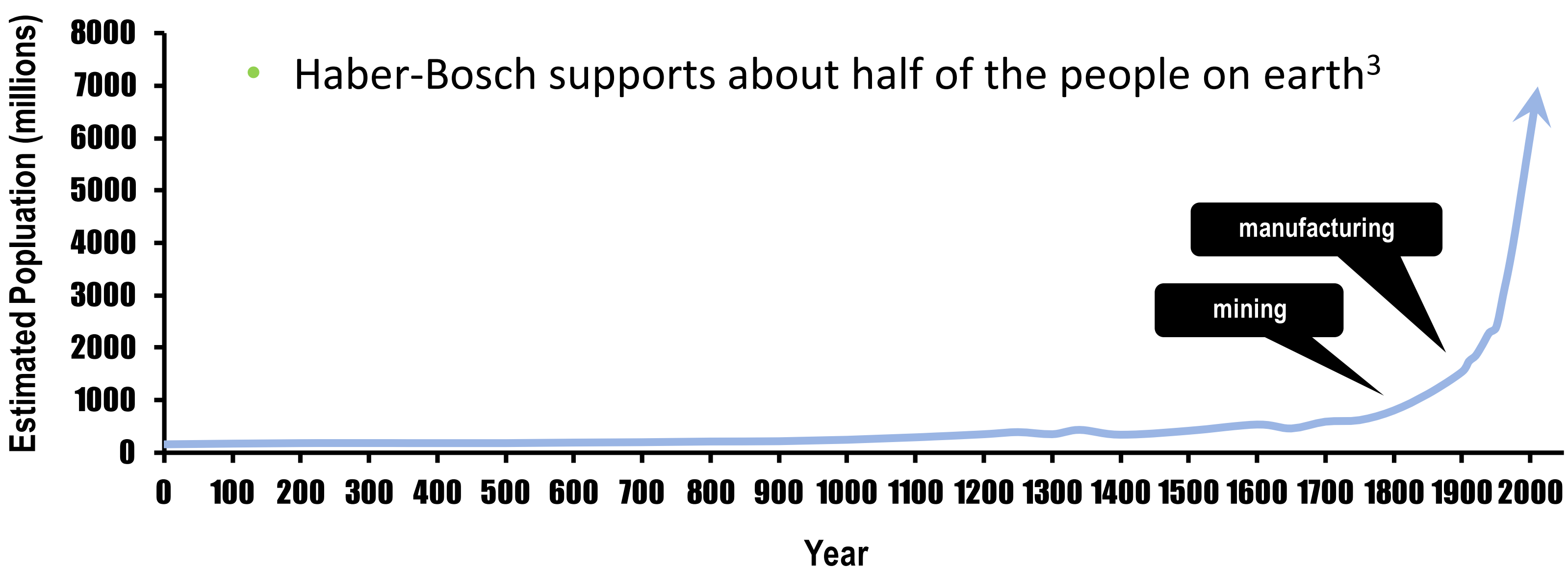
Office of the Association: Burlington House, London, W.

Fritz Haber



Carl Bosch

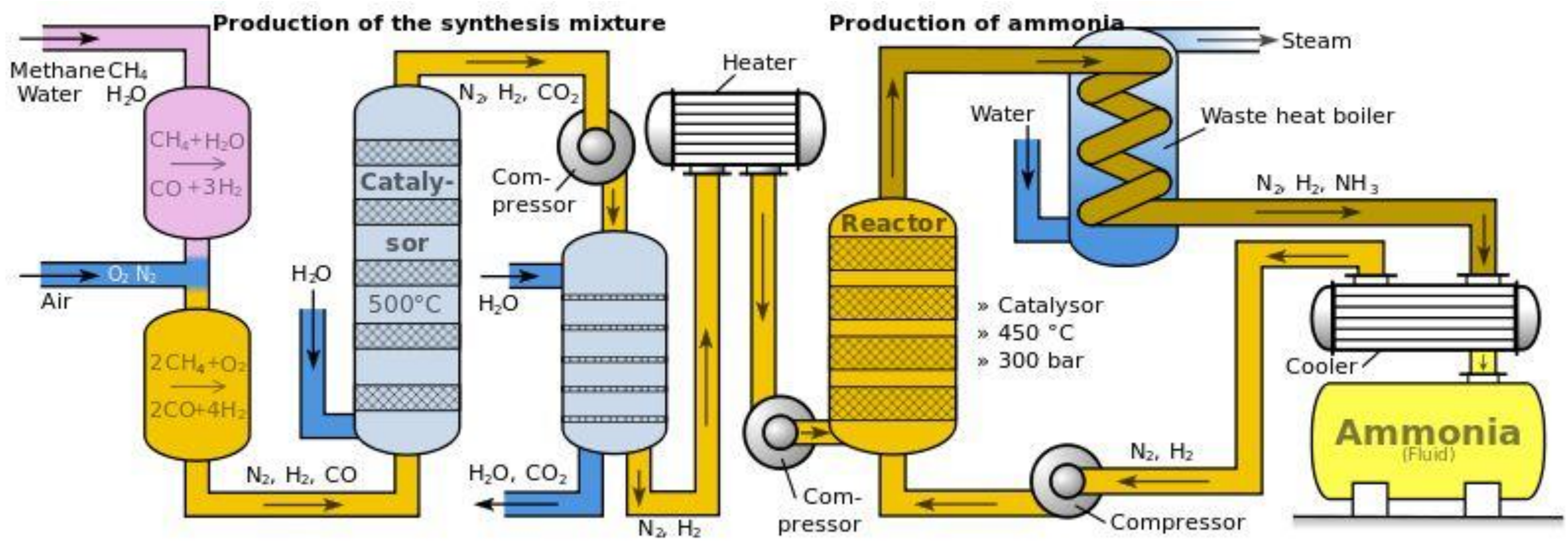
- Haber-Bosch supports about half of the people on earth[3]



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

(3) J.W. Erisman, M.A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, Nat. Geosci., 1 (2008) 636-639.

Haber-Bosch (HB) Process



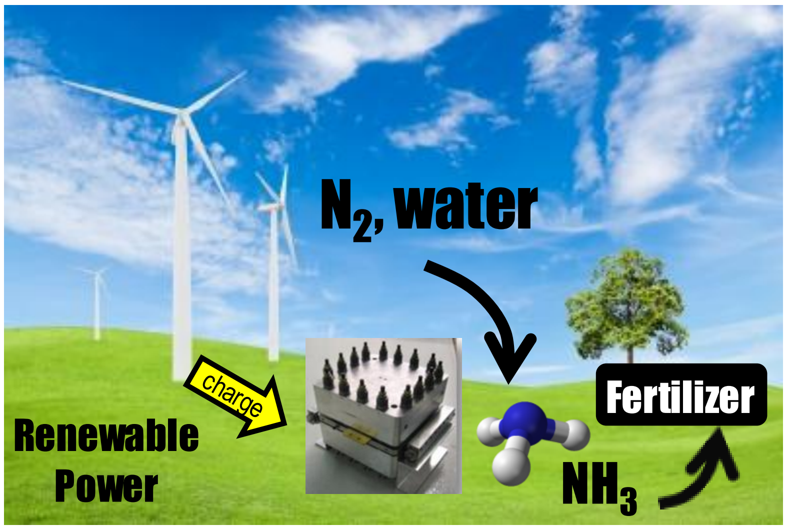
- H_2 obtained from fossil fuels, high temp and high pressure, high capital cost
- Inefficient (consumes ~1% of the worlds energy)

  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.

Vision for Electrochemical Ammonia Production

Ammonia Synthesis



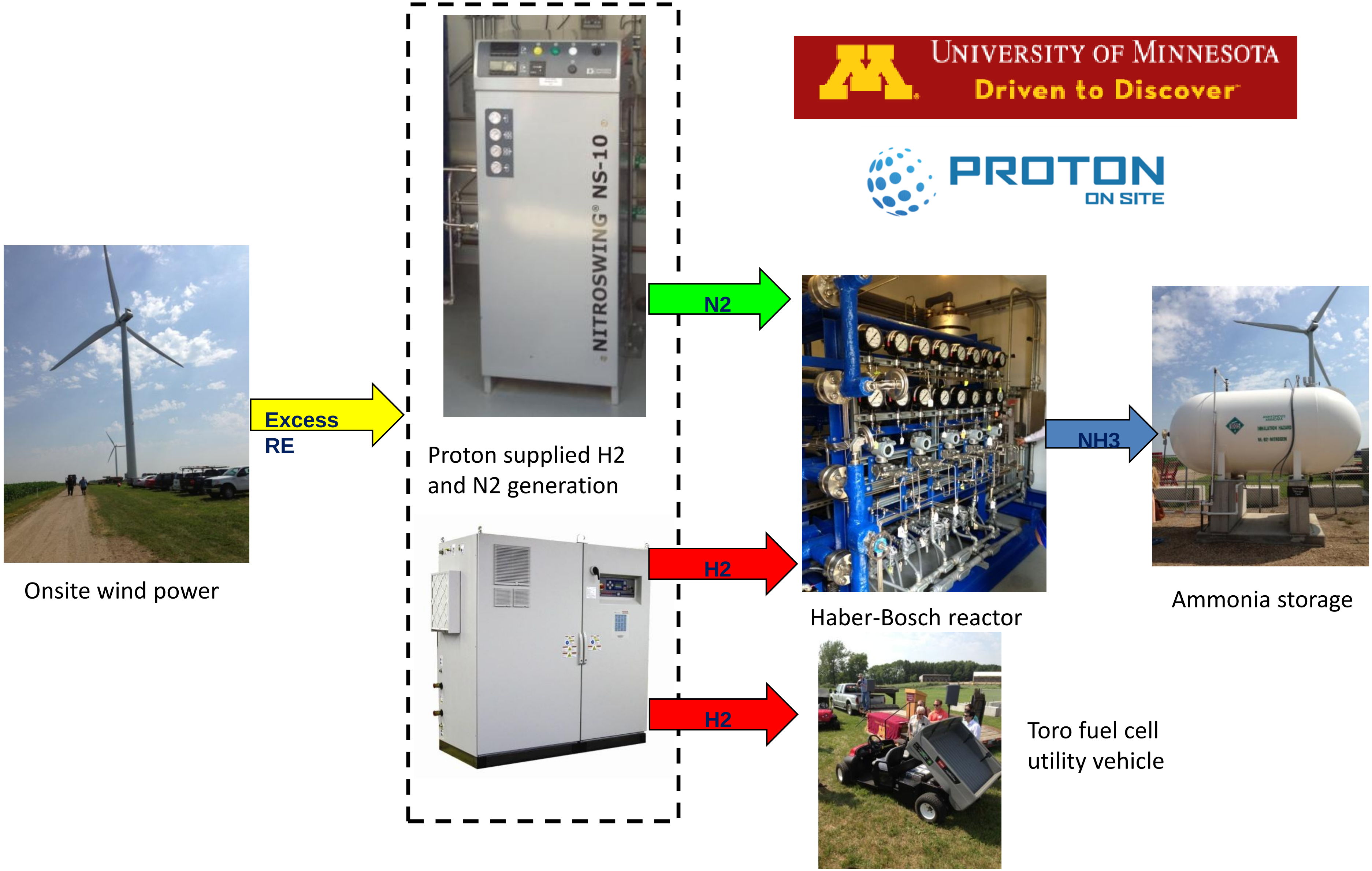
Industrial Uses: chemical synthesis, emissions scrubbing, refrigeration

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

Wind to Ammonia Pilot Plant:

University of Minnesota / Morris (West Central Research & Outreach Center)



Scalable Technology

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Ammonia Production Technology Plan

Bench Scale Size: 25 cm²

GC Size: 28-84 cm²

M Series: 250,000-500,000 cm²

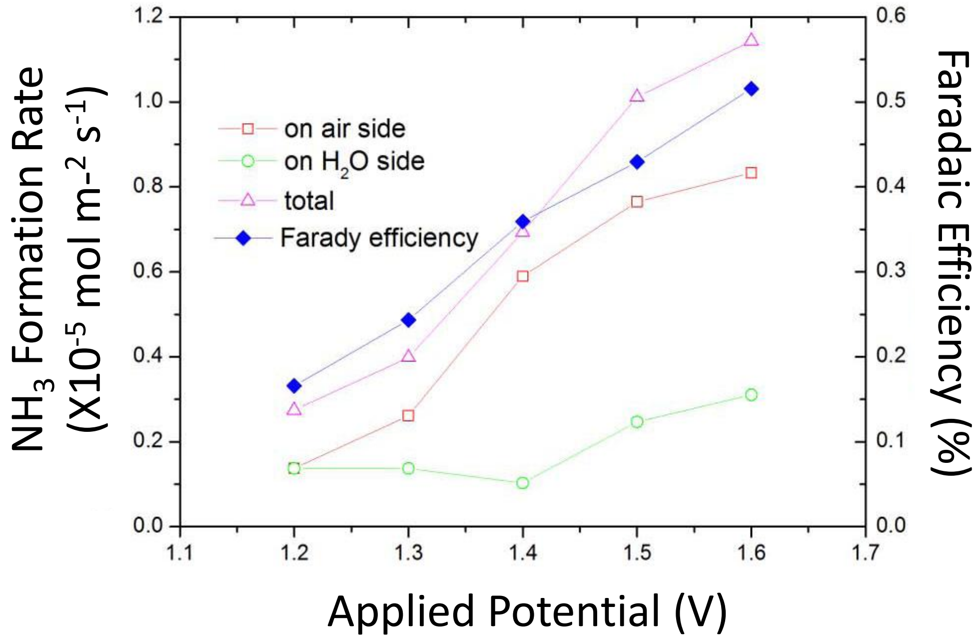
PHASE I	PHASE II	FUTURE
Proof-of-Concept Phase Bench Scale	Breadboard Phase Garden Capacity (100 g/year)	Product Phase Small Farm (260 acres – 12,500 kg/year)
Targets Current Efficiency: > 1%	Targets Current Efficiency: 10% Current Density: 10 mA/cm²	Targets Current Efficiency: 50% Current Density: 50 mA/cm²

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

A 5 MW system could produce 10 tons/day ammonia

(@ 500 mA/cm², 50% efficiency, 1.5 V)

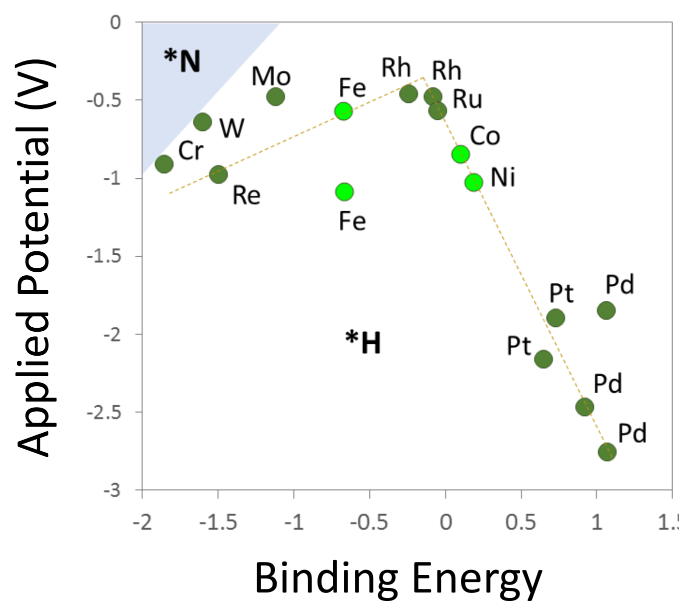
Background/Key Obstacles



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

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

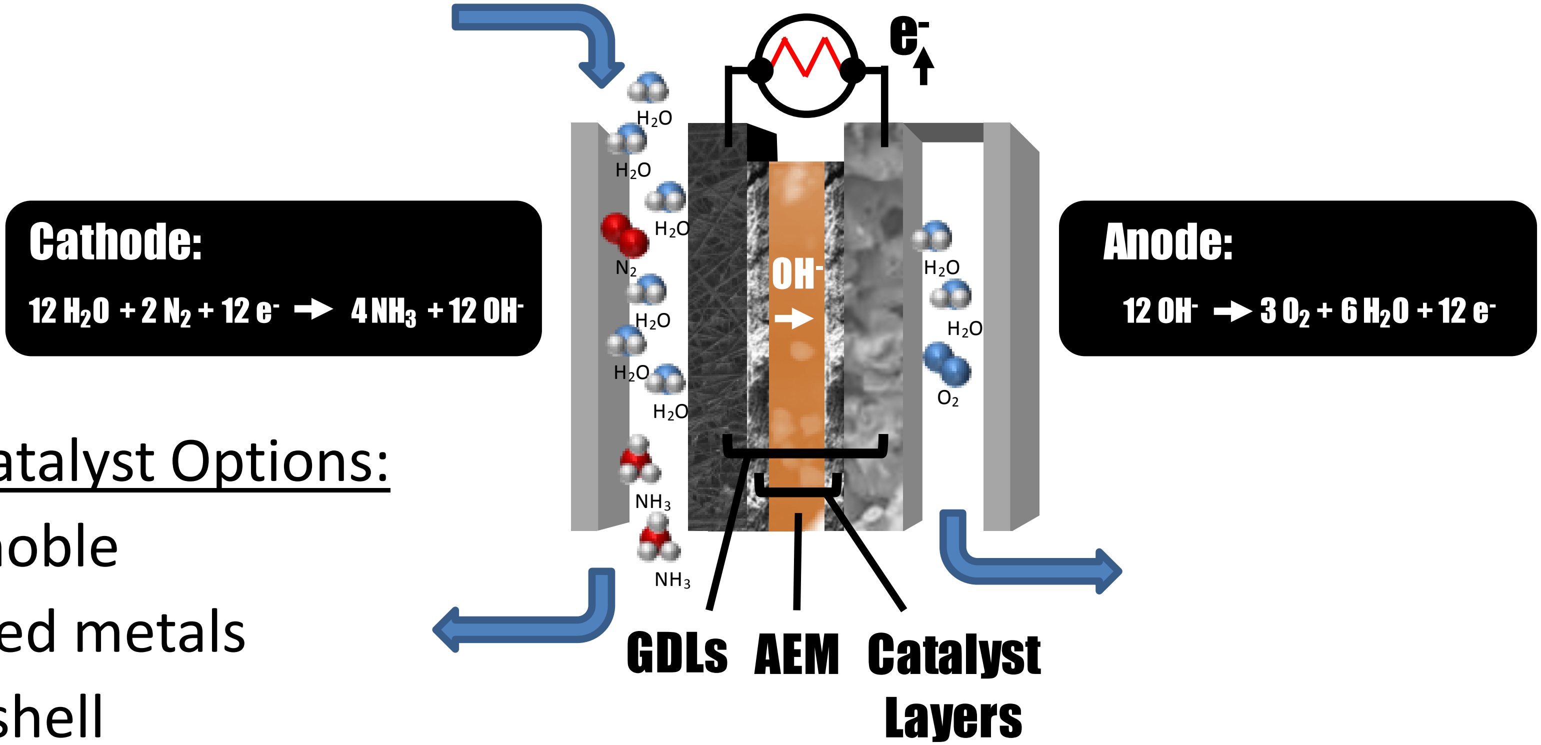
- PEM demonstrated feasibility
- At 1.5 V and below, need ~50% Faradaic efficiency to match HB



A volcano plot predicting metal performance for nitrogen electroreduction

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

AEM-based Approach



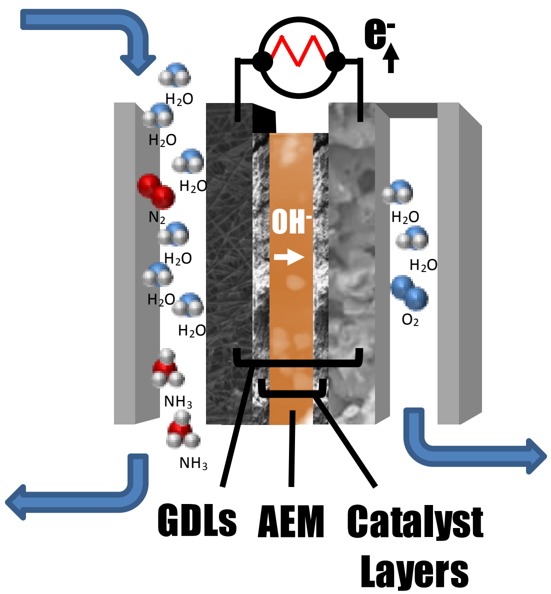
<u>More Catalyst Options:</u>

- Non-noble
- Blended metals
- Core-shell
- Ligands

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

Outline

Proton OnSite Overview



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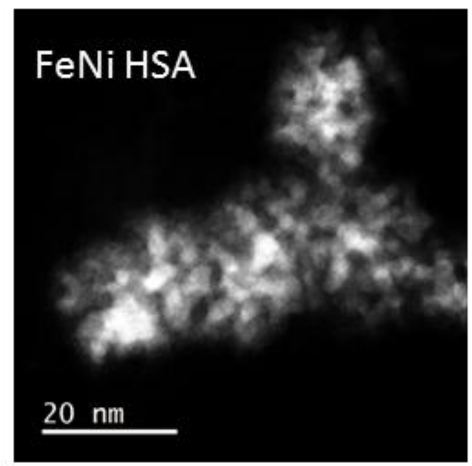
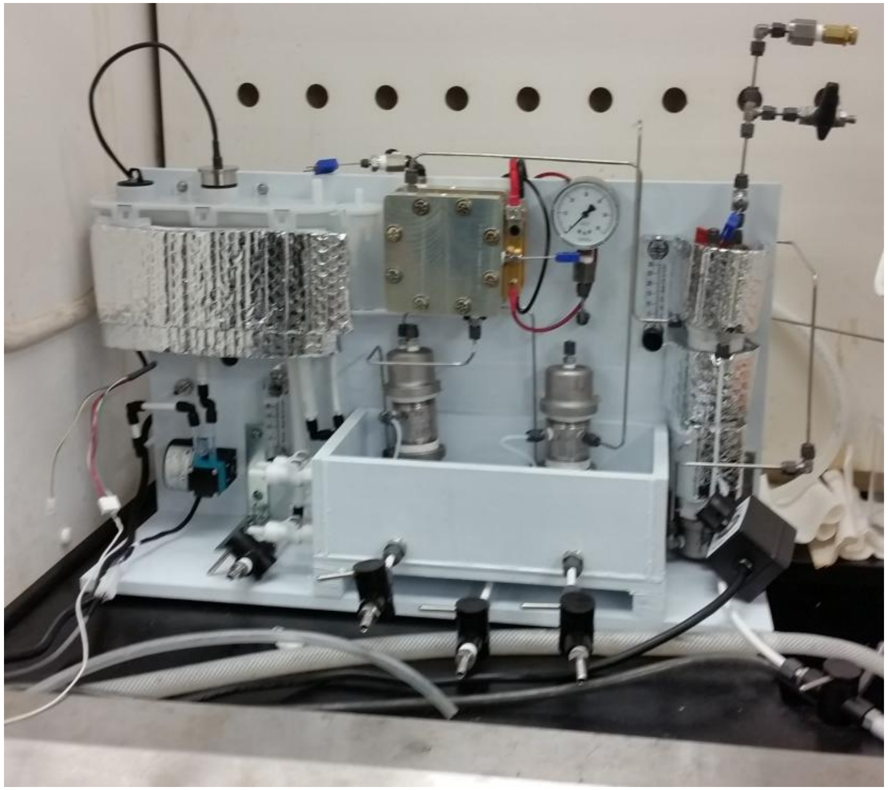
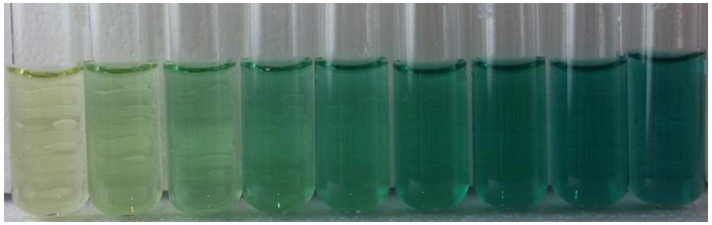


Results and Future Directions

Ammonia Generation Rig



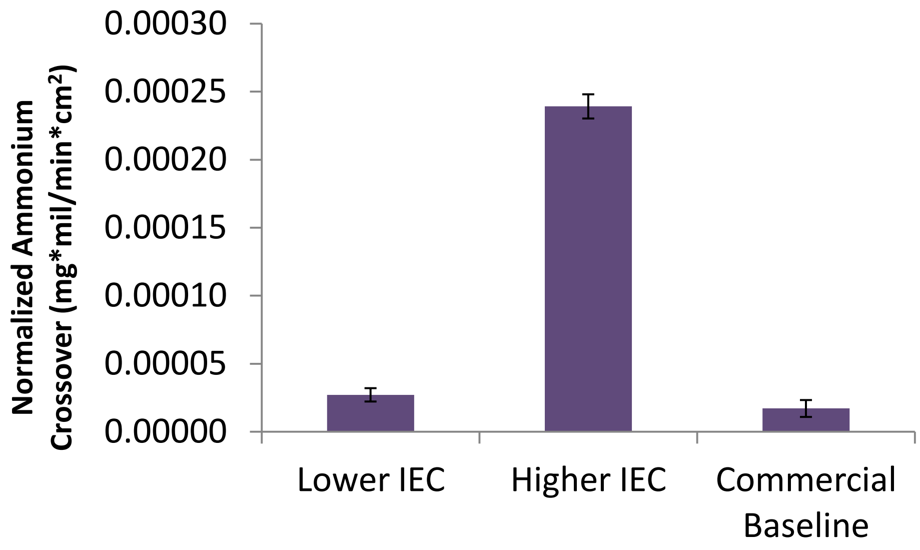
Ammonia Capture via Acid Trap and Determination via Colorimetric Assay:

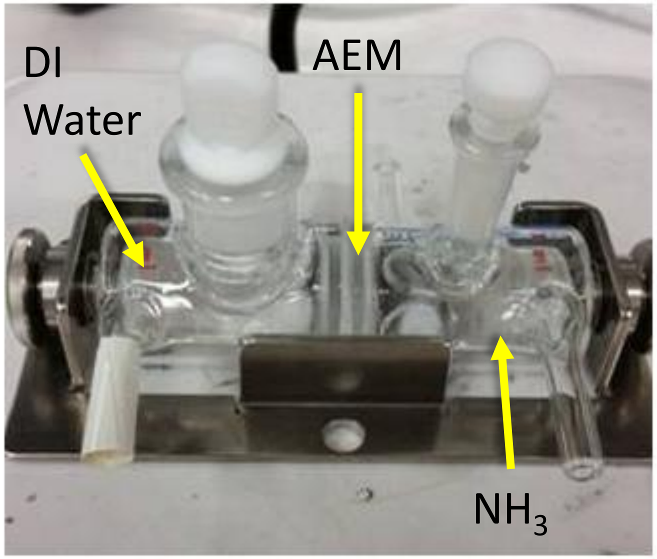


Increasing ammonia concentration

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

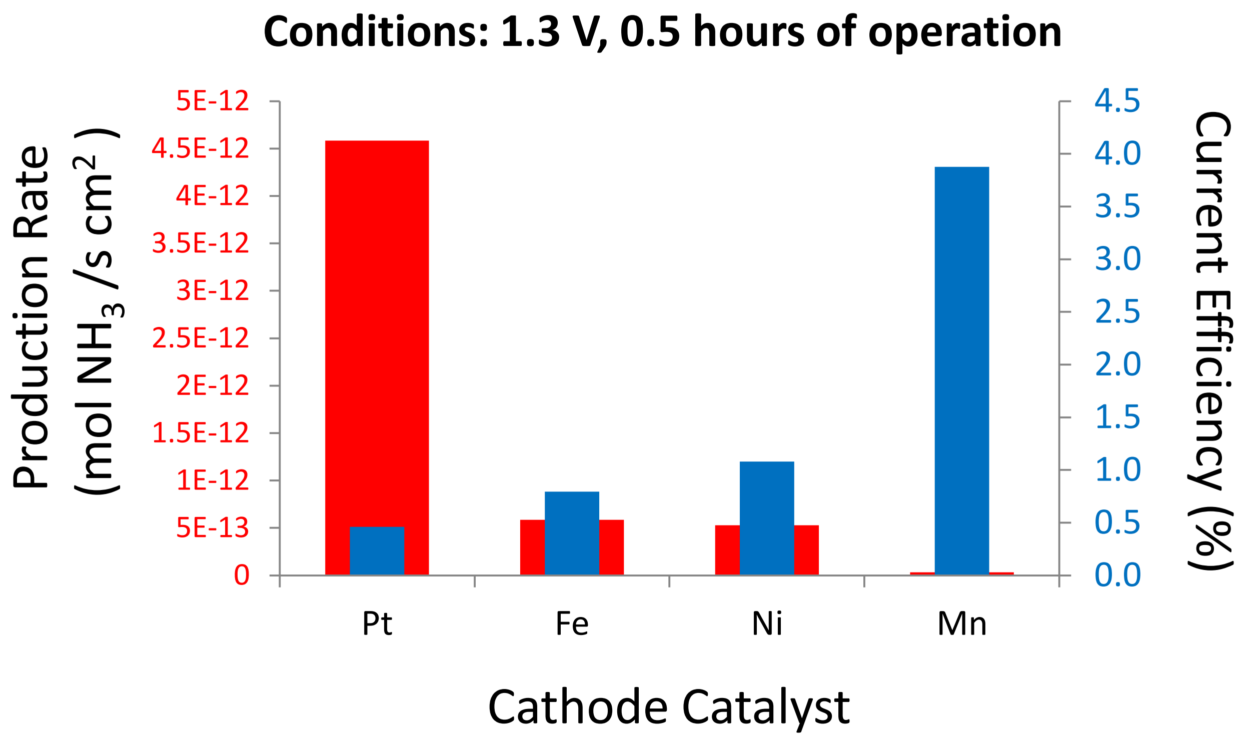
Membrane Screening





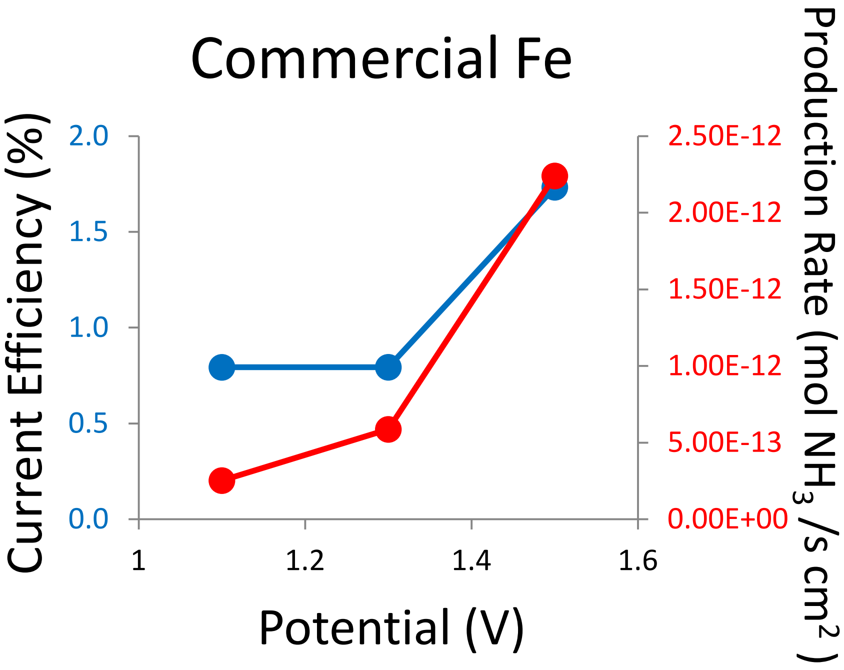
- 9X greater diffusion through higher IEC material
- May indicate hydrophobicity/swelling in limiting ammonia crossover
- Good performing membranes have an order of magnitude less crossover than baseline production rates
  - Commercial baseline material good starting point

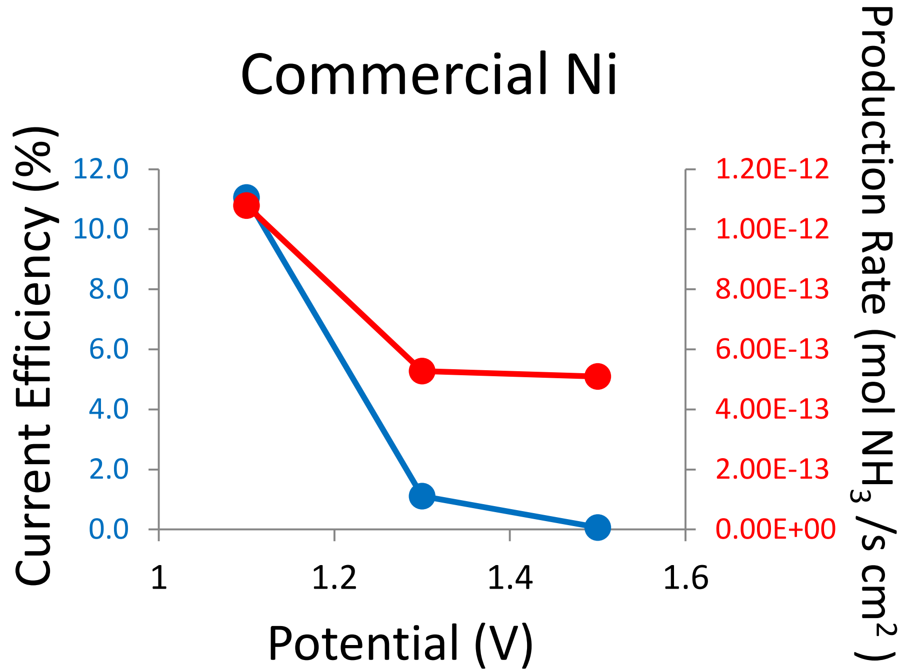
Commercial Catalyst Screening



- Platinum consistently had <1% efficiencies (similar to PEM), performance degrades after an hour
- Order of magnitude increase in efficiencies with non-noble metal
- Increased efficiency seems to correlate with decreased production
  - Indicates competition between HER and NH_3 production

Effect of Voltage

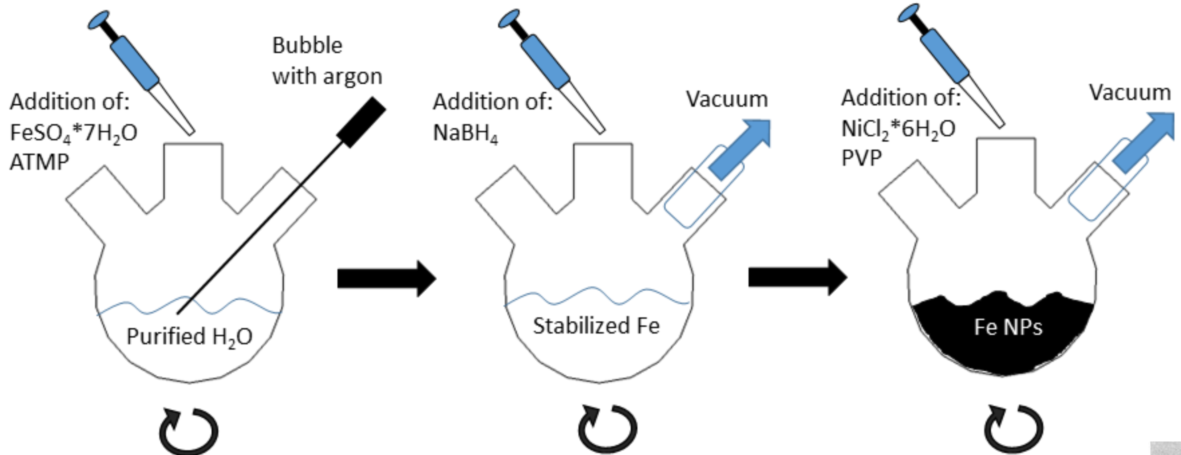


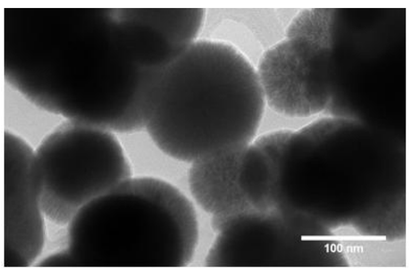


- Increasing production rate and efficiency with increasing potential using Fe (opposite effect with Ni)
- High current efficiencies possible with Ni
- Provides further evidence for competition between HER and NH_3 production

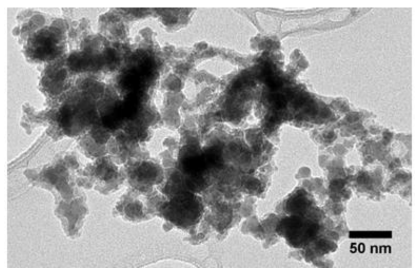
Conditions: 1 hour of operation at each voltage step

Catalyst Synthesis

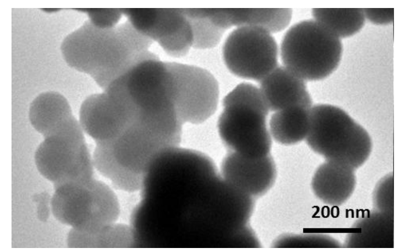




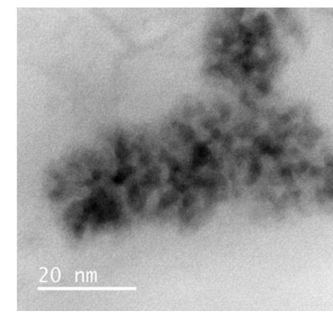
Large Fe-only



Small Ni-only



FeNi
Low SA



FeNi
High SA

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

Nanoparticle performance

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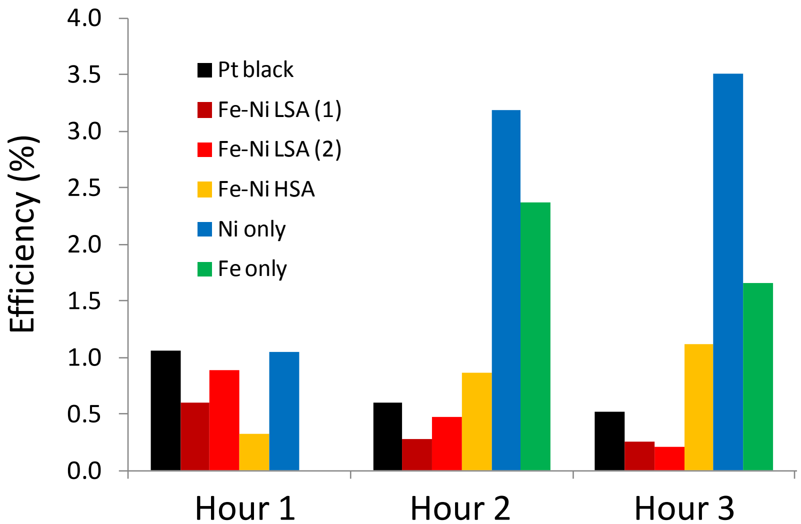
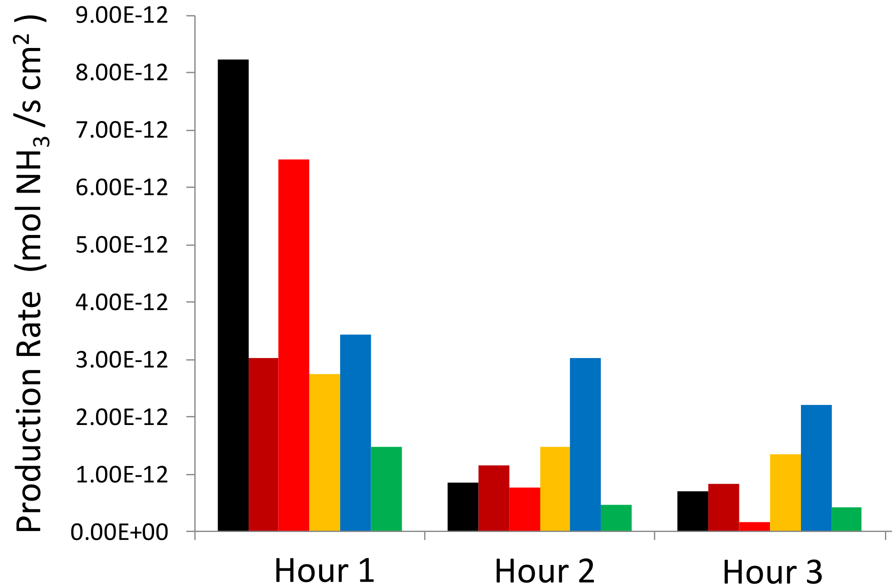
Conditions: 1.2 V, 1 hour of operation





* Fe-only efficiency at hour 1 is non-zero, estimated >10%

- Performance of Ni-Fe materials are affected by surface area
- LSA more Fe like
- HAS more Ni like
- Ni materials have higher stability and efficiency
- Pt performance degrades

Comparison

Process	Catalyst	Energy Consumption (kwh/kg NH_3)	Ammonia Production Rate (mol NH_3/cm^{2}s)	Faradaic Efficiency (%)	Cell Potential (V)	Temp (°C)
Haber-Bosch[1]	Typically Fe-based	13.2	N/A	N/A	N/A	300-500
PEM Electrochemical[2]	Pt	1600-3600	6.20×10^{-10} – 2.80×10^{-10}	0.16-0.36	1.2-1.4	25
Mixed Electrolyte Electrochemical[3]	perovskite oxide	130 - 1140	3.1×10^{-11} – 1.71×10^{-10}	0.5-4.5	1.2-1.4	400
Molten Hydroxide Electrochemical[4]	Fe_2O_3	16	2.40×10^{-9}	35	1.2	200
AEM Electrochemical	Pt, Fe, Ni, FeNi	14-520	1.33×10^{-12} – 3.80×10^{-12}	1.1 - 41	1.2	50

- Orders of magnitude increase in current efficiency compared to PEM
- Similar efficiencies at lower temperatures than molten hydroxide
- Production rates need to be increased

(1) W. Leighty, The Leighty Foundation, Energy Storage with Anhydrous Ammonia: Comparison with other Energy Storage, October 2008.

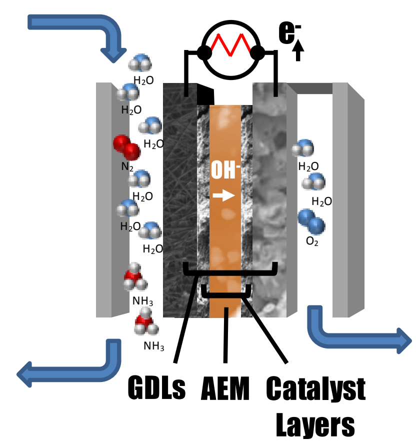
(2) R. Lan, J.T.S. Irvine, S. Tao, Scientific Reports, 3 (2013)

(3) R. Lan, S.W. Tao, RSC Adv., 3 (2013) 18016-18021.

(4) S. Licht, B.C. Cui, B.H. Wang, F.F. Li, J. Lau, S.Z. Liu, Science, 345 (2014) 637-640.

Conclusions

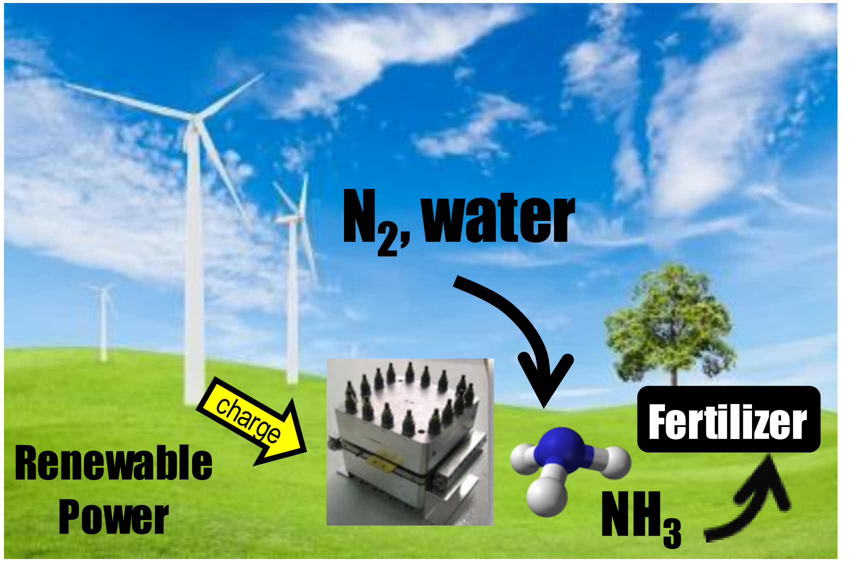
- The developed system provided an adequate test bed
- Proof-of-concept was established for AEM-based ammonia generation
- An order of magnitude increase in efficiency was observed compared literature at similar conditions
- AEM-based technology is promising for efficient ammonia production at low temperatures



How do we achieve our vision?

Phase II Work:

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



Future Work:

- Fundamental studies on reaction mechanisms
- Bio-inspired catalysts for selectivity
- Purification and systems work
- Scale-up

Acknowledgements

Proton OnSite:

- Kathy Ayers
- Nemanja Danilovic
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- Arie Havasov (co-op)
- Wolfgang Grassmann (co-op)

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NIST/Univ. of Arkansas

- Andrew Herring
Colorado School of Mines

- Douglas Tiffany
University of Minnesota

Questions and Discussion

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- NSF/ASEE Postdoctoral Fellowship