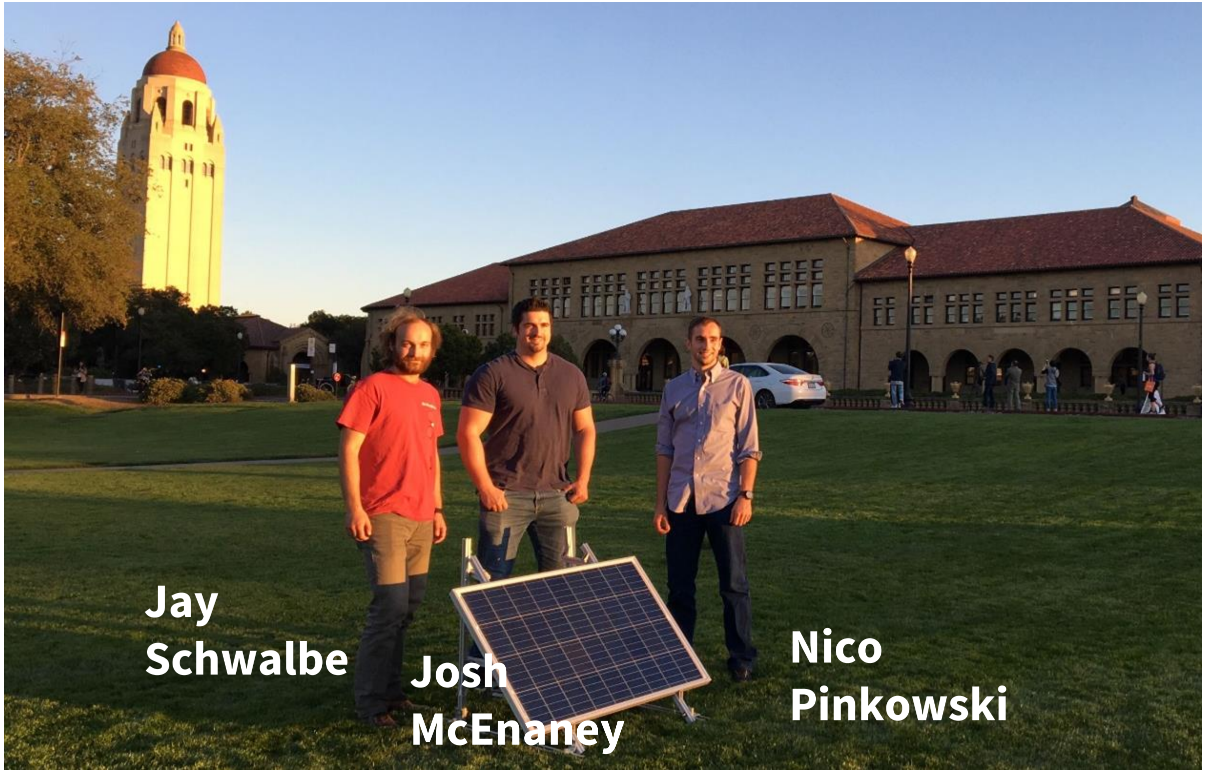
Nitricity


Nitricity produces distributed nitrogen fertilizer
using only air, water, and renewable electricity.

Nitricity in action | team



Notable Awards

Stanford University

Massachusetts Institute of Technology

FLOW first look west

TomKatCenter FOR SUSTAINABLE ENERGY STANFORD UNIVERSITY

StartX

Nitricity in action | on-farm system

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Stanford University

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StartX

Solar + Agriculture

India is pushing 31 GW of solar to help farmers offset pumping and electrical needs

BloombergNEF

PRODUCT BLOG ABOUT SUMMITS CONTACT LOGIN SEARCH

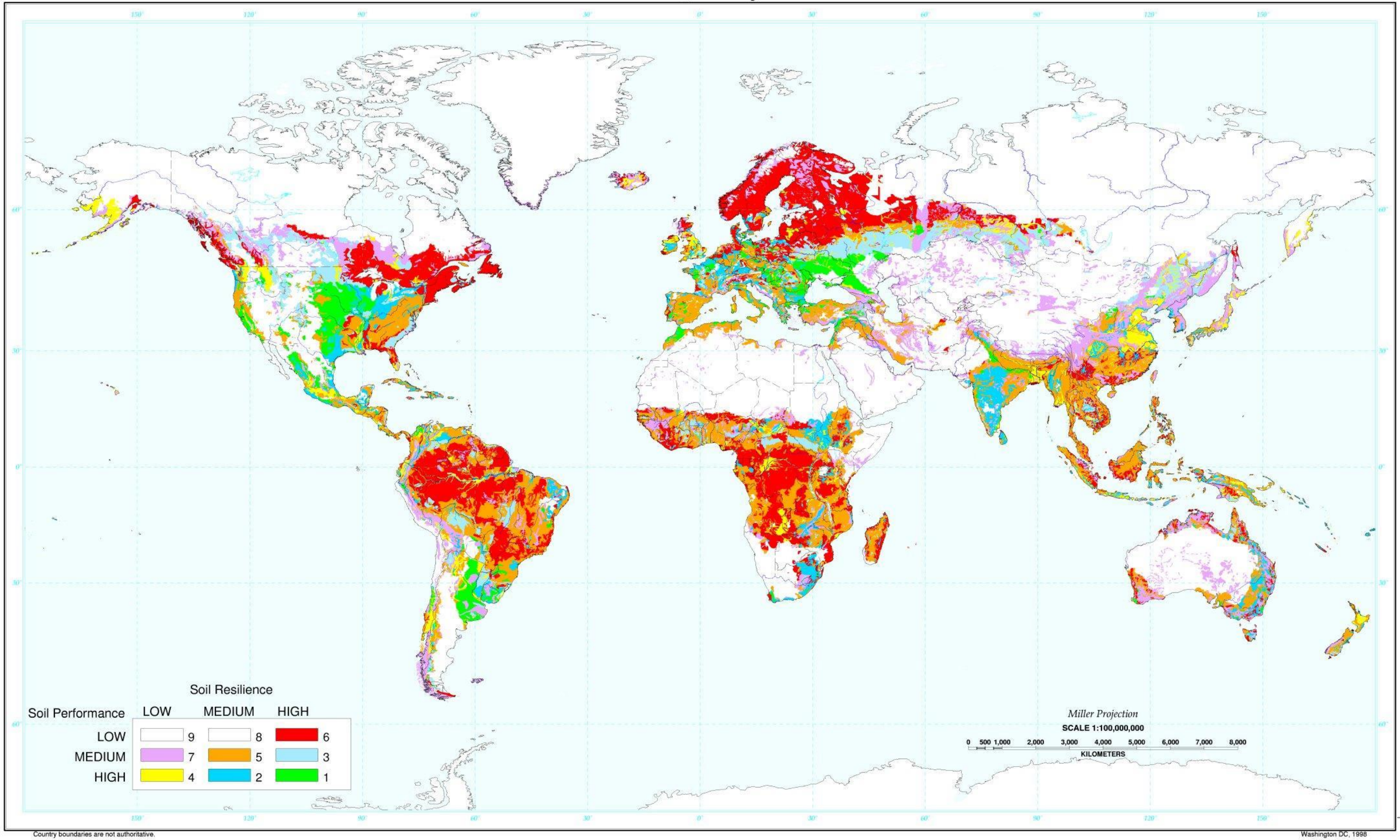
World's Largest Solarization of Agriculture Program Blooms: Q&A

January 28, 2021

By Vandana Gombar, BloombergNEF. This article first appeared on

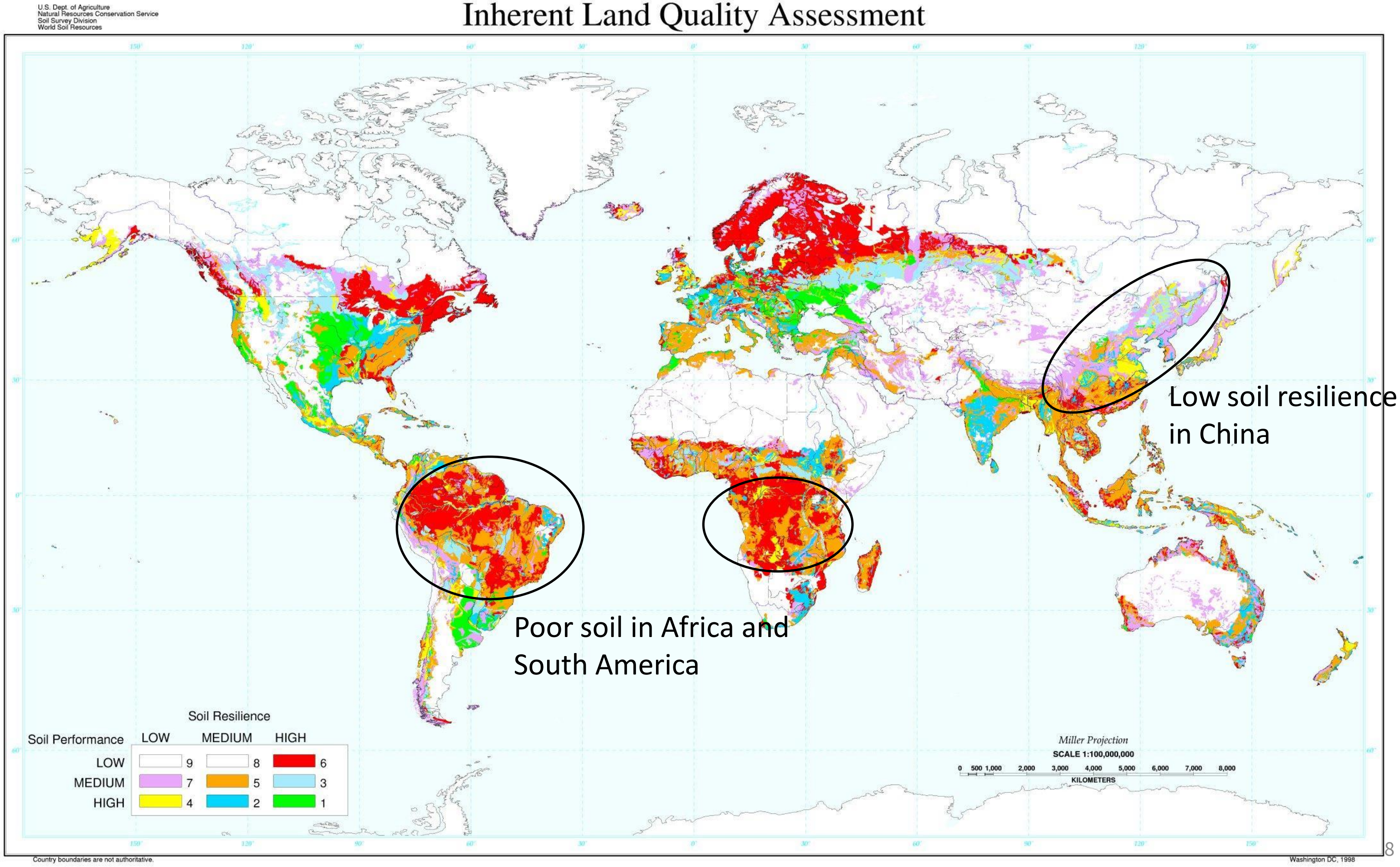
U.S. Dept. of Agriculture
Natural Resources Conservation Service
Soil Survey Division
World Soil Resources

Inherent Land Quality Assessment

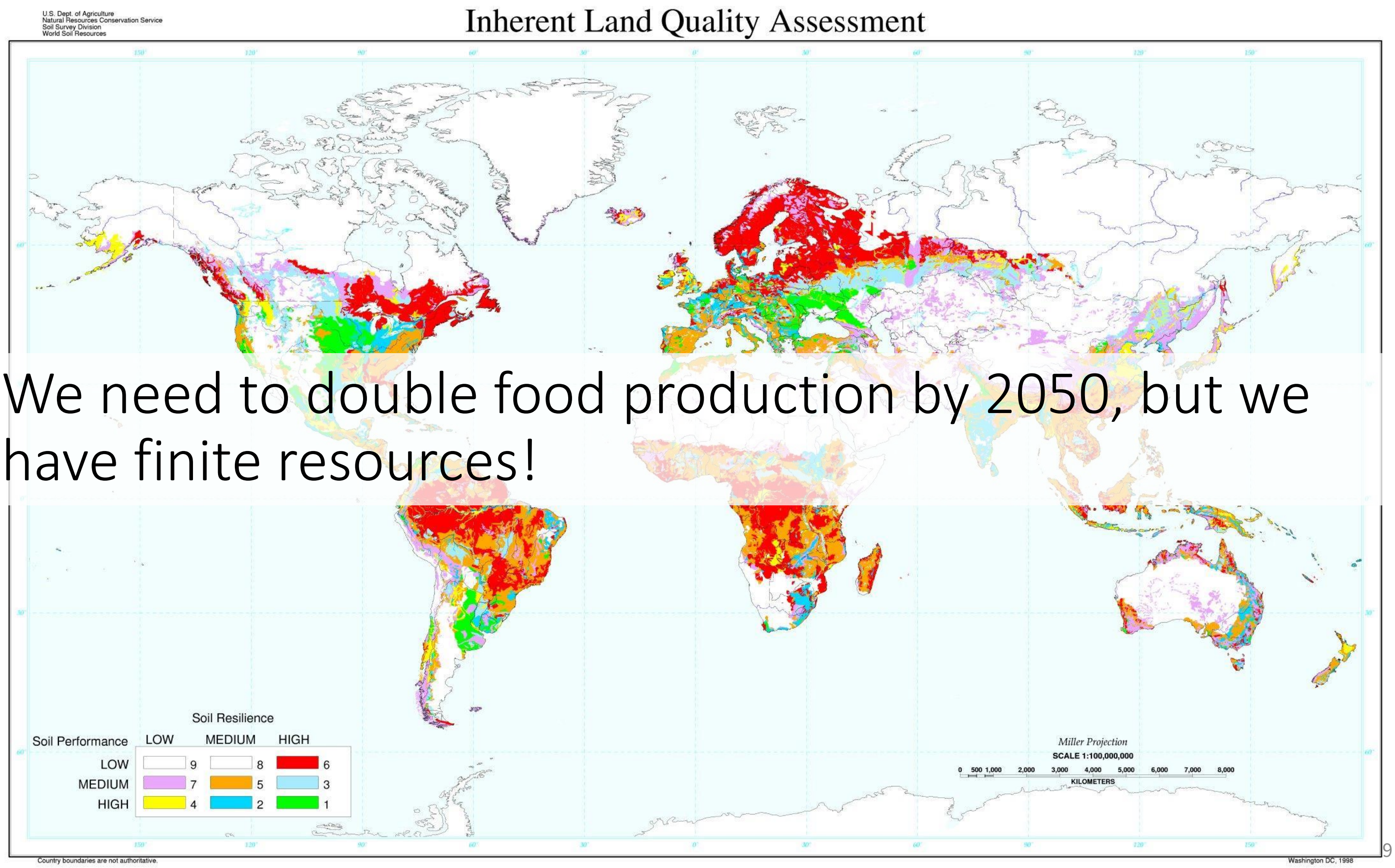


Country boundaries are not authoritative.

Washington DC, 1998

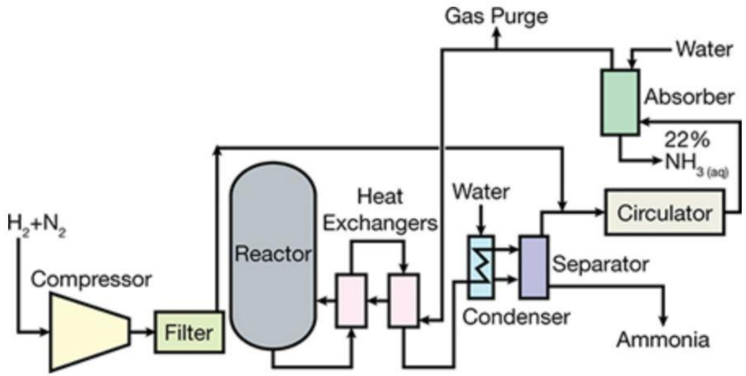

U.S. Dept. of Agriculture
Natural Resources Conservation Service
Soil Survey Division
World Soil Resources
Inherent Land Quality Assessment
Low soil resilience in China
Poor soil in Africa and South America
Soil Resilience
Soil Performance
LOW
MEDIUM
HIGH
LOW 9 8 6
MEDIUM 7 5 3
HIGH 4 2 1
Miller Projection
SCALE 1:100,000,000
0 500 1,000 2,000 3,000 4,000 5,000 6,000 7,000 8,000
KILOMETERS
Country boundaries are not authoritative.
Washington DC, 1998

We need to double food production by 2050, but we have finite resources!



Incumbent technology

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$



Haber-Bosch:
400℃, 200 atm

Pattabathula, Venkat, and Jim Richardson. “Introduction to Ammonia Production.” *Back to Basics*, 2016, 7.

Incumbent technology - distribution

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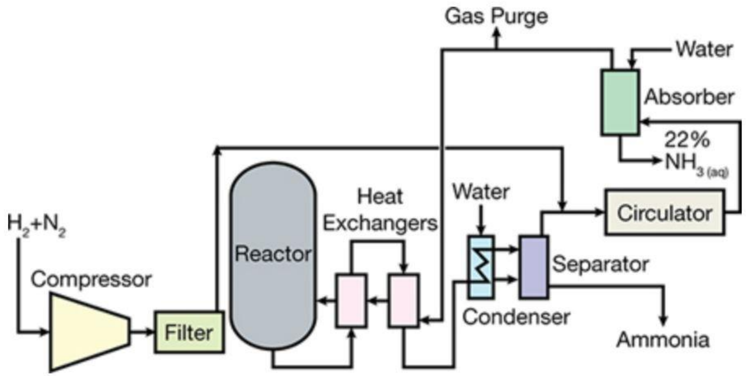
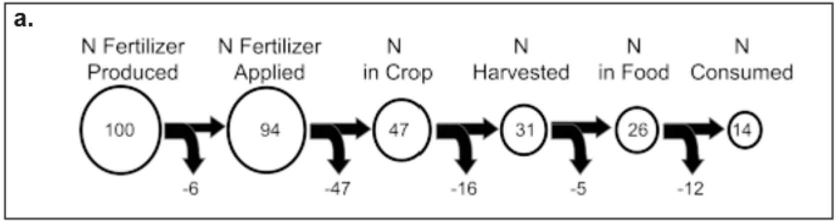
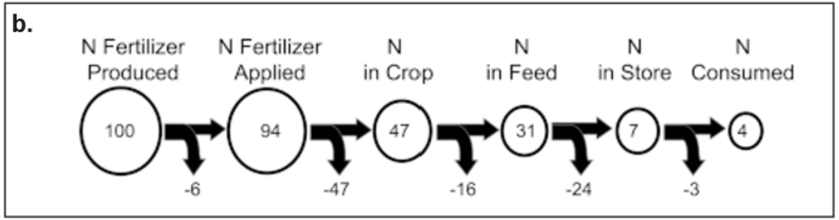


Haber-Bosch:
400℃, 200 atm

Vegetarian 14% N used



Carnivorous 4% N used



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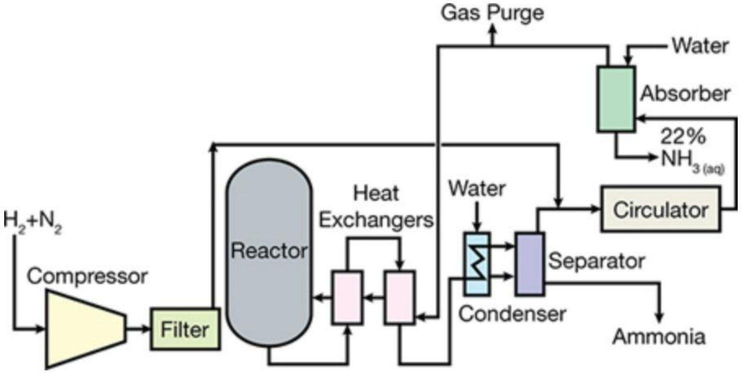
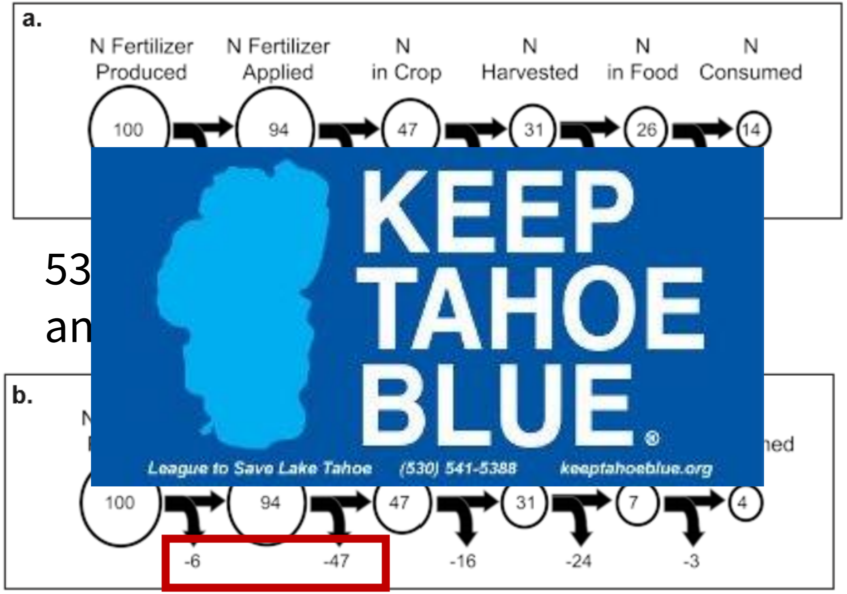


Haber-Bosch:
400℃, 200 atm



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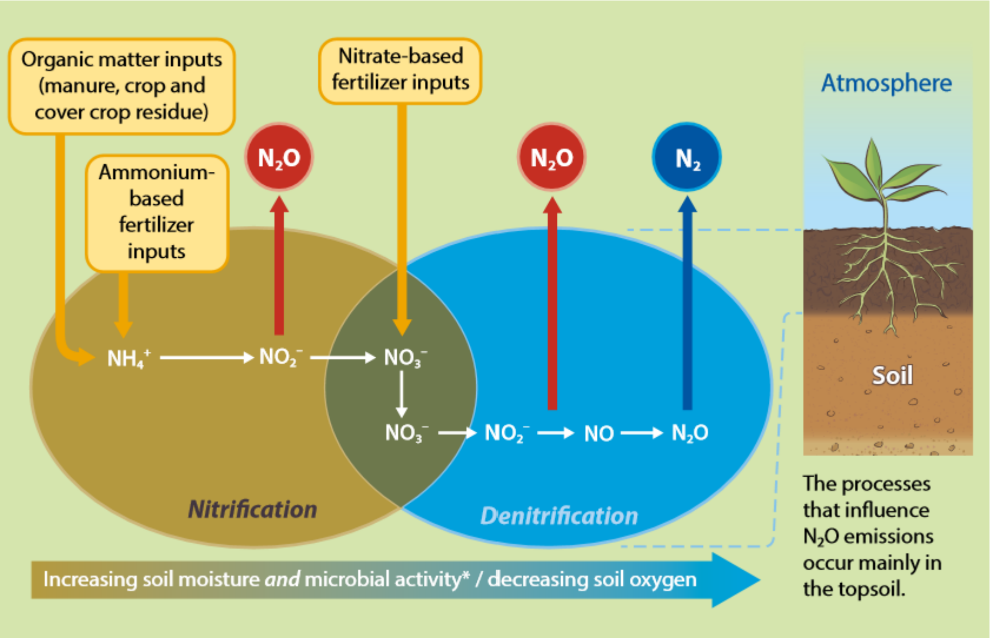
N_2O emissions



CALIFORNIA AGRICULTURE • VOLUME 71, NUMBER 3

N_2O emitted from microbial activity in both ammonia oxidation (nitrification) and nitrate reduction (denitrification)

Excess N increases emissions

Low oxygen increases denitrification

High frequency application has been shown to reduce N_2O

https://www.sciencedirect.com/science/article/abs/pii/S0167880916303954?via%3Dihub, Scientific RepoRts | 6:30349 | DOI: 10.1038/srep30349

Problems that require breakthrough solutions

Production
1.4% of global CO_2

Distribution
0.07% of global CO_2

Application
6.1% of global CO_2eq

Centralized, extreme CapEx

Farmers pay 3x-5x gate cost

Ineffective nutrient management

Problems that require breakthrough solutions

Production
1.4% of global CO_2

Centralized, extreme CapEx

Distribution
0.07% of global CO_2

2.88 Gt CO_2eq

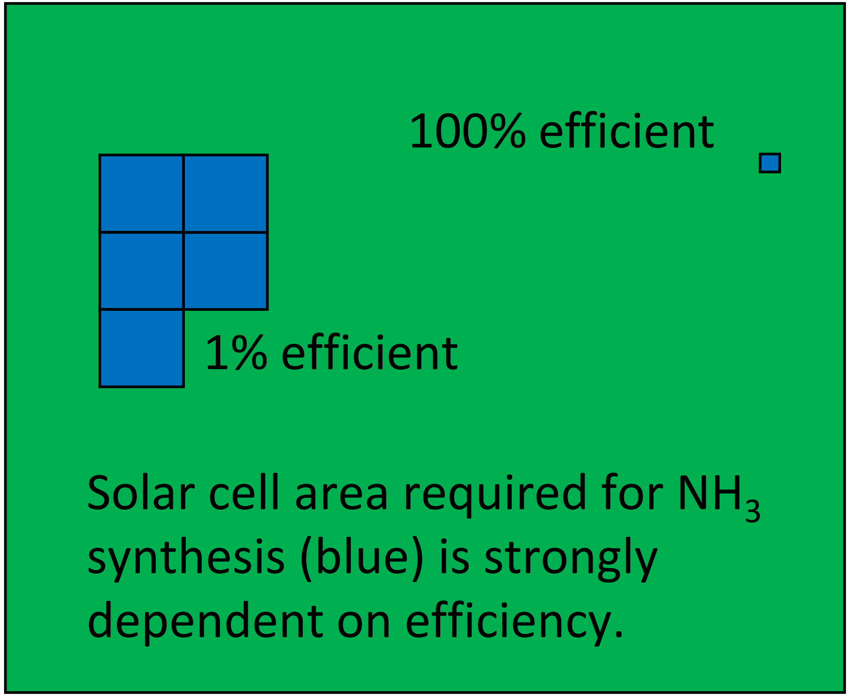
Farmers pay 3x-5x gate cost

Application
6.1% of global CO_2eq

Ineffective nutrient management

High $/acre

Potential for Electrification



approach	Cell potential [V]	Faradaic effeciency	kWh/kg NH_3
Haber-bosch + water splitting[1]	NA	NA	18.3
Electrochemical limit	1.23	100	6.9
Low FE electrochemical	1.23	1	690
High overpotential	4	100	22.4

[1]Cussler, Edward et. al. "Ammonia Synthesis at Low Pressure." *JoVE* no. 126 (August 23, 2017): e55691.

Electrochemistry – a possible distributed competitor

$$\boxed{N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3}$$

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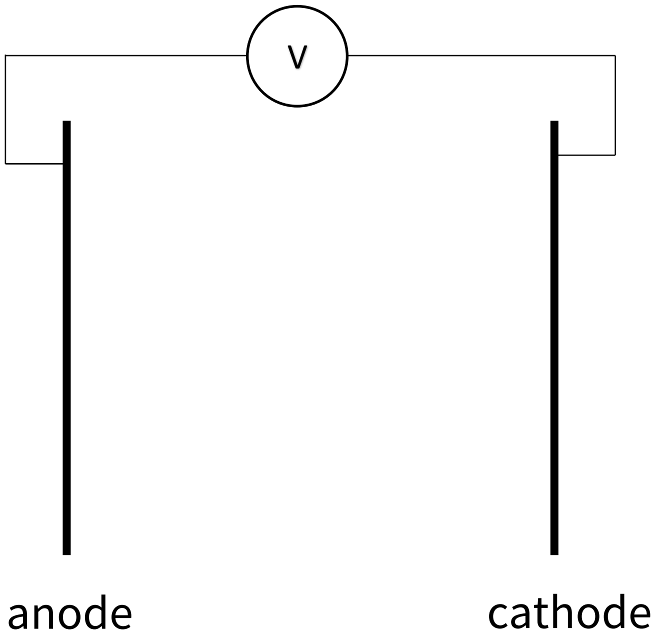

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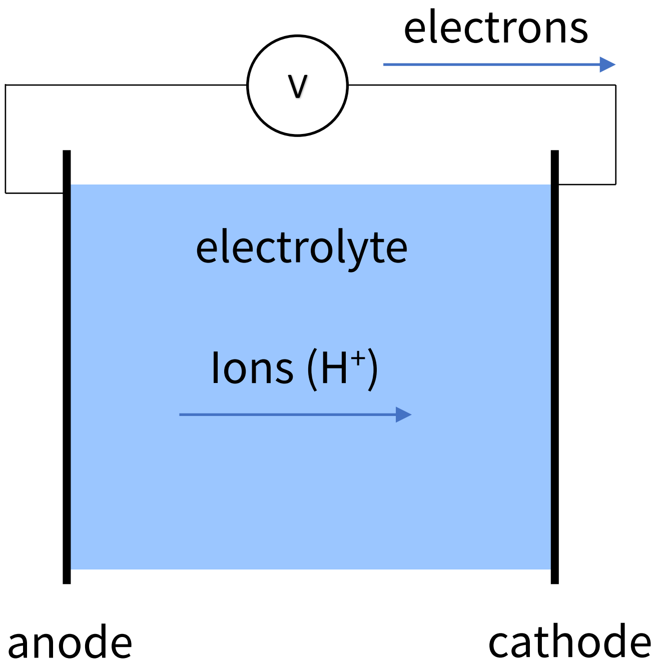

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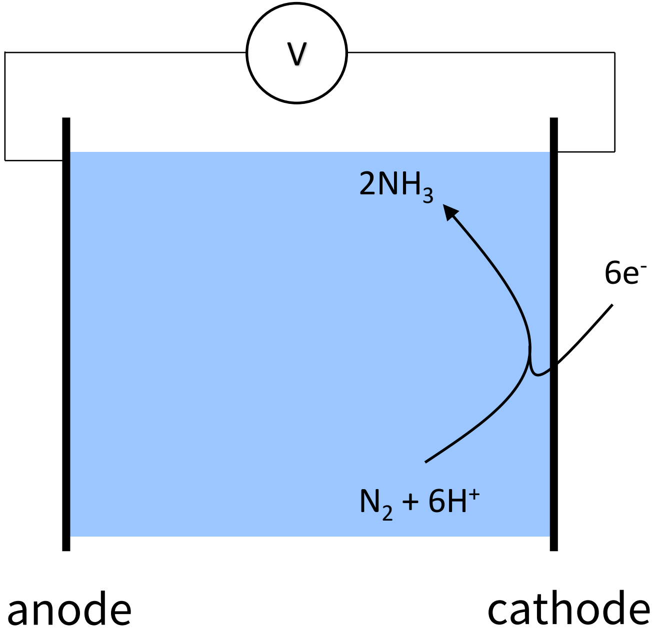

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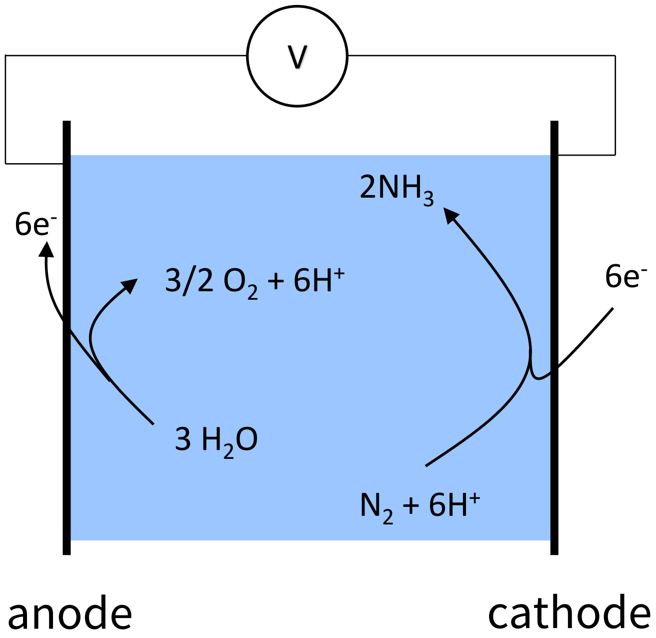
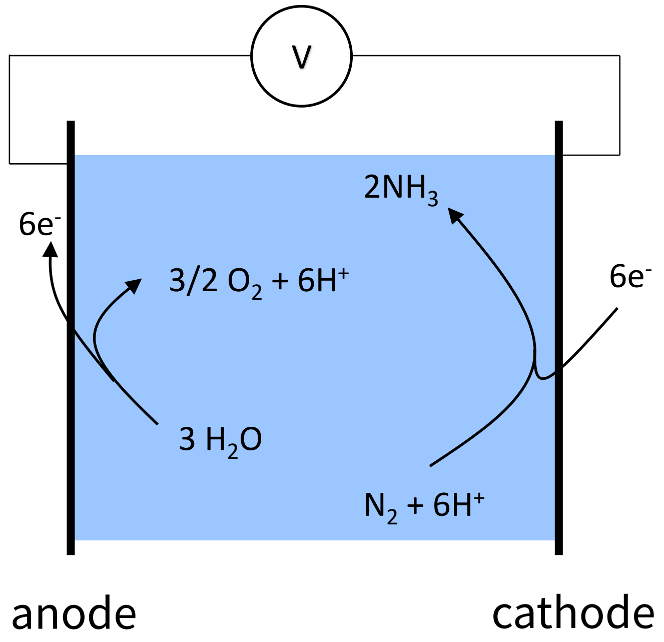


Basic Definitions

$$\text{Faradaic Efficiency} = \frac{Charge\ to\ NH_3}{Total\ Charge}$$

$$N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3$$



The Voltage Determines the Driving Force

$$N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3$$

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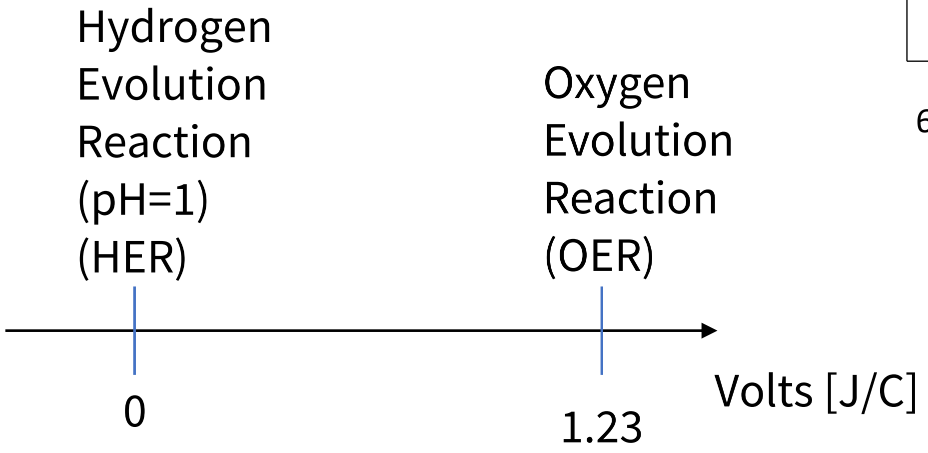

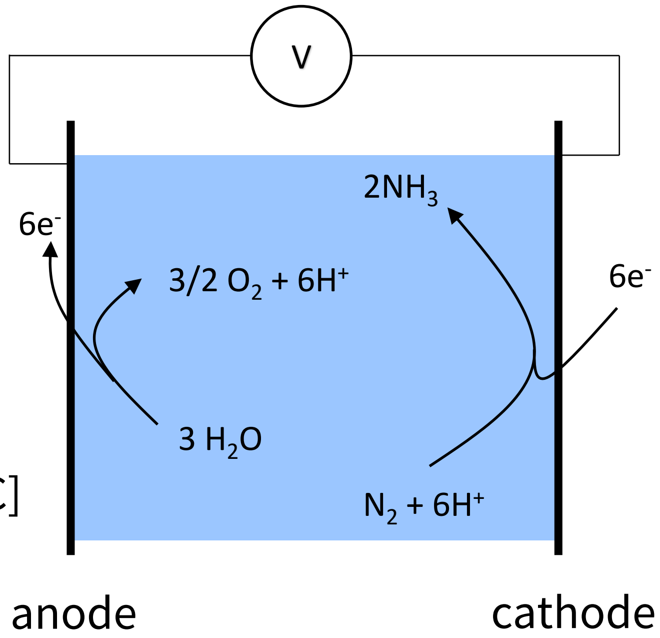

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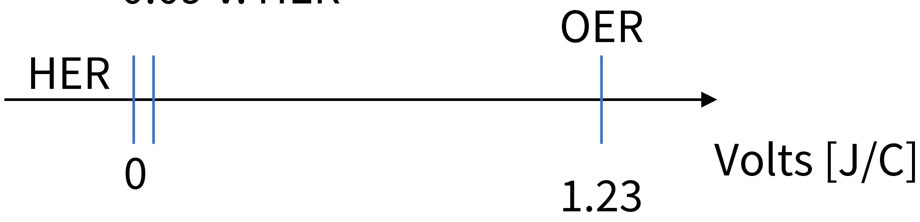
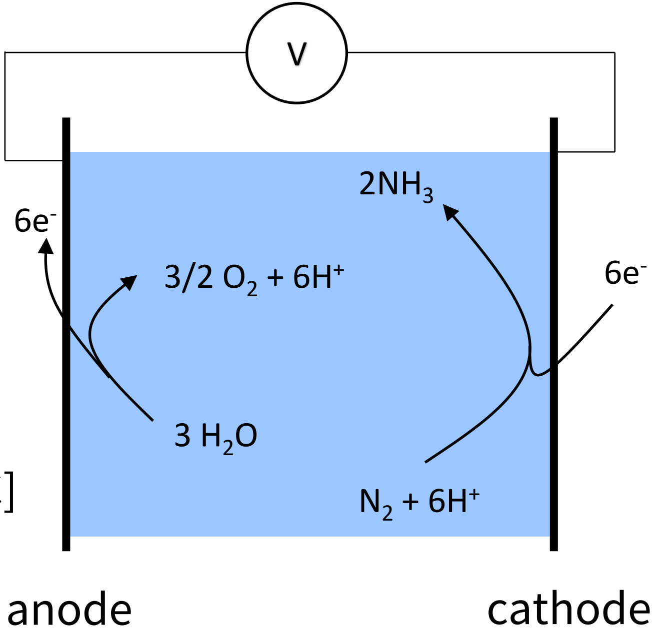
Nitrogen Reduction (N2RR)
0.09 v. HER





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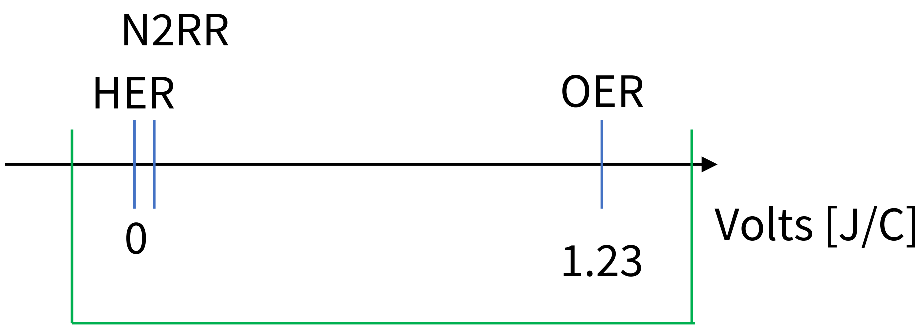
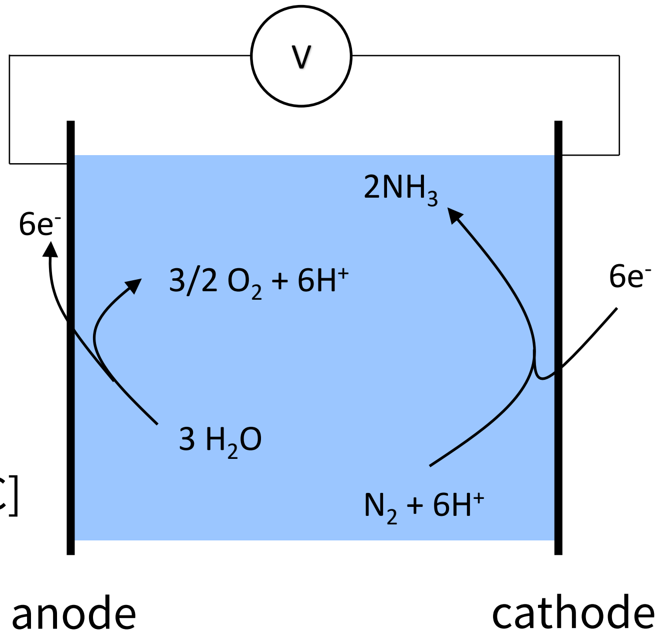
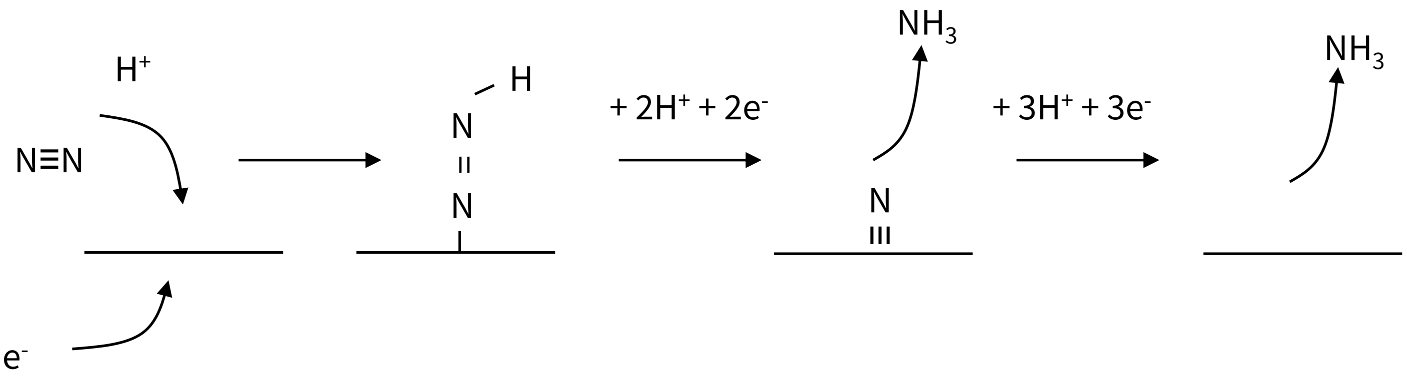


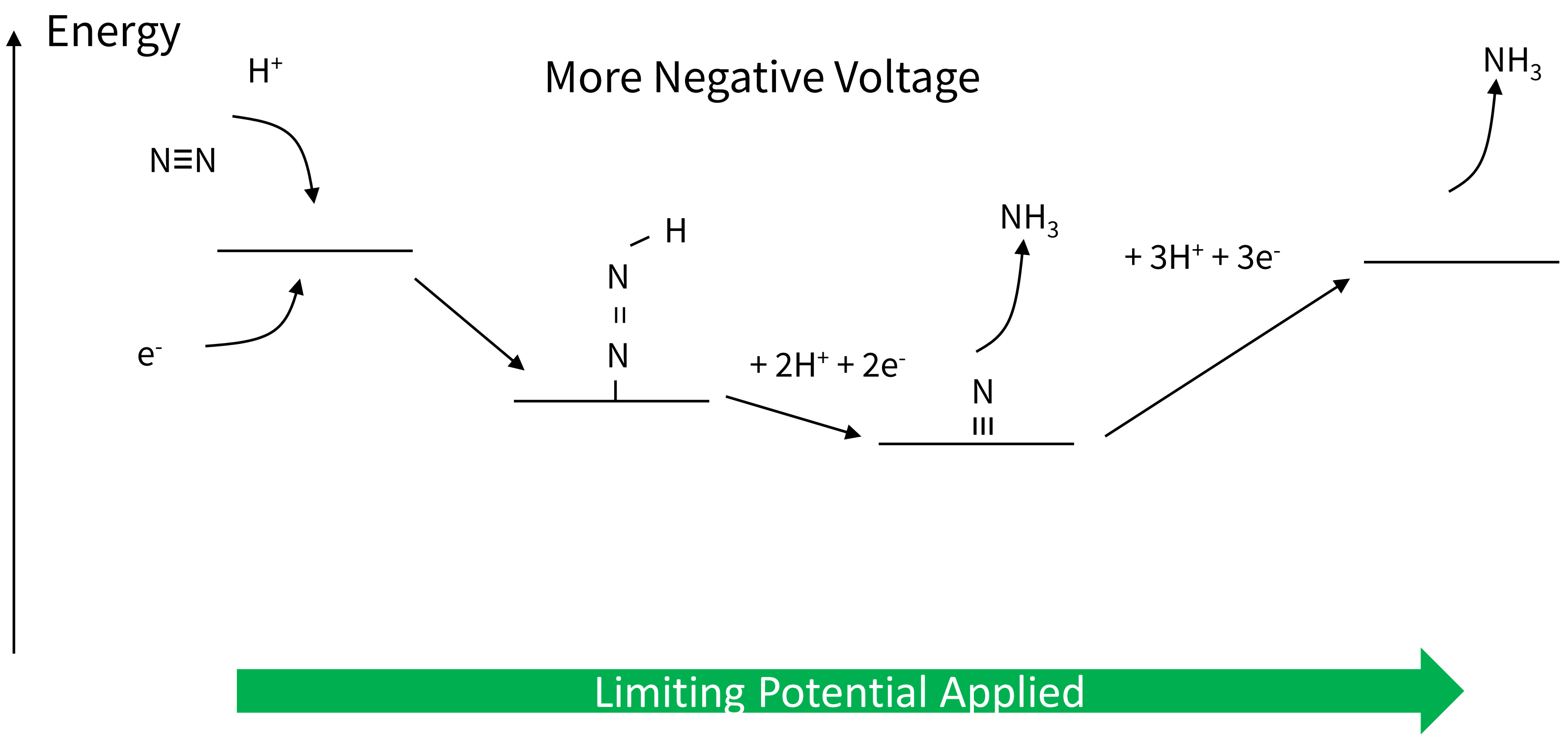


Simplified Mechanism of Ammonia Synthesis



Singh, Aayush R., Brian A. Rohr, Michael J. Statt, **Jay A. Schwalbe**, Matteo Cargnello, and Jens K. Nørskov. "Strategies toward Selective Electrochemical Ammonia Synthesis." *ACS Catalysis*, July 29, 2019, 8316–24.

Simplified Version of the Energetic Landscape



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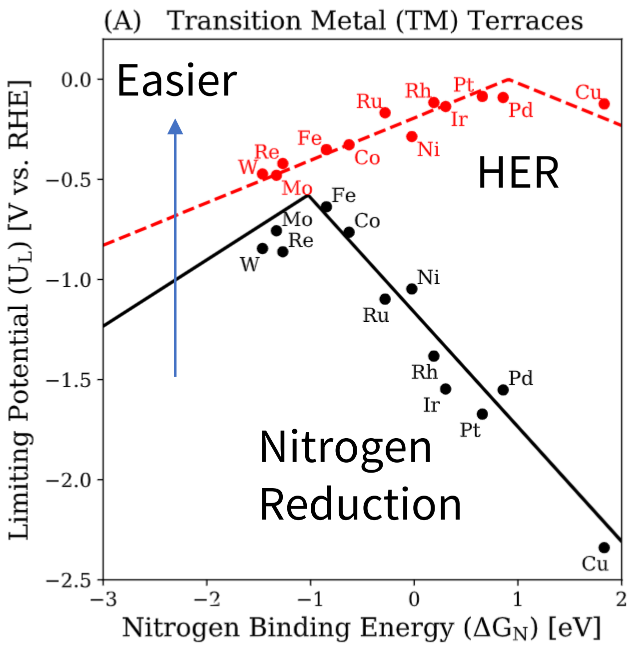
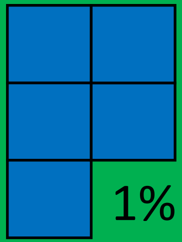
The Hydrogen evolution reaction presents a fundamental challenge



100% faradaic efficiency



1% faradaic efficiency

Solar cell area required for NH_3 synthesis (blue) is strongly dependent on faradaic efficiency.

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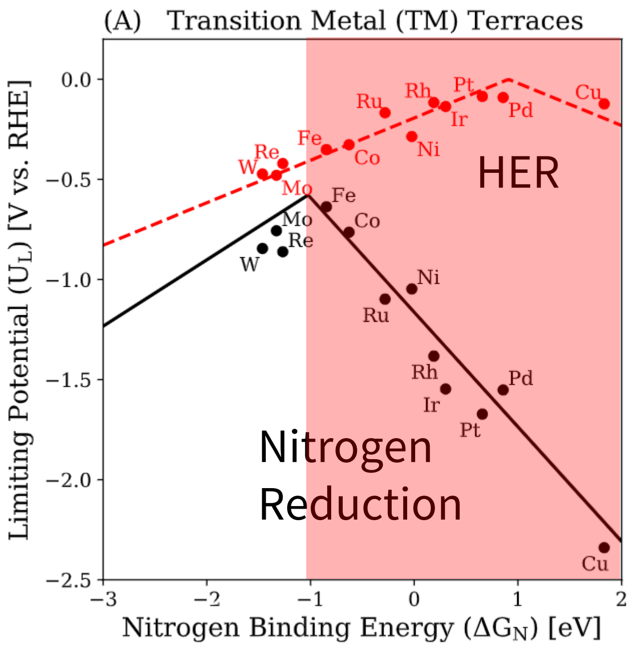
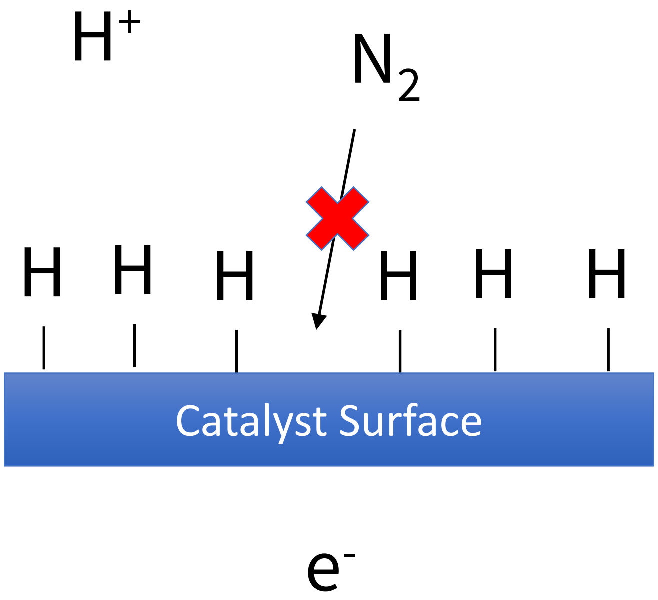
DFT Gives us a Starting Point





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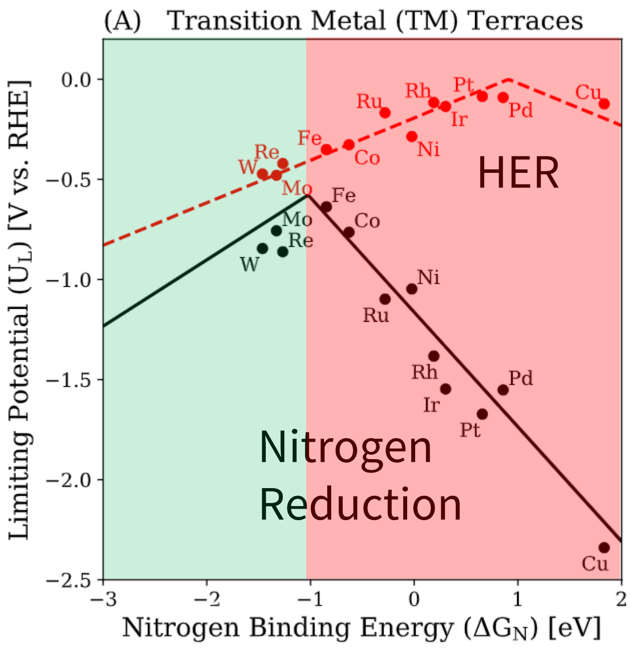

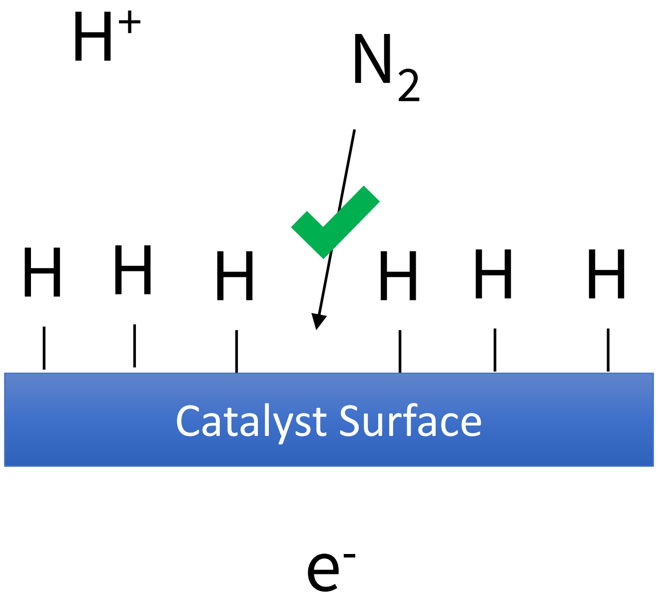

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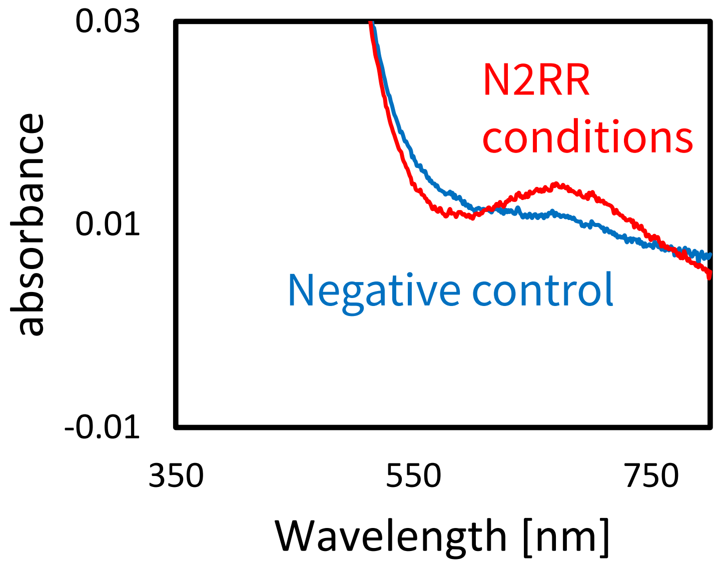
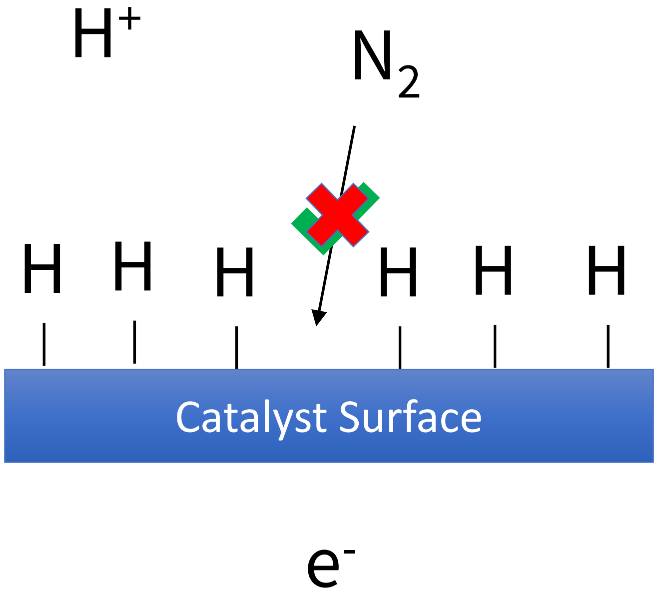
Even the Most Exciting Cases Don't Work in Water

FE<1% - Not Statistically Significant





Jay Schwalbe, unpublished data
Andersen et. al. nature 1, 2019

Even the Most Exciting Candidates Don’t Work in Water

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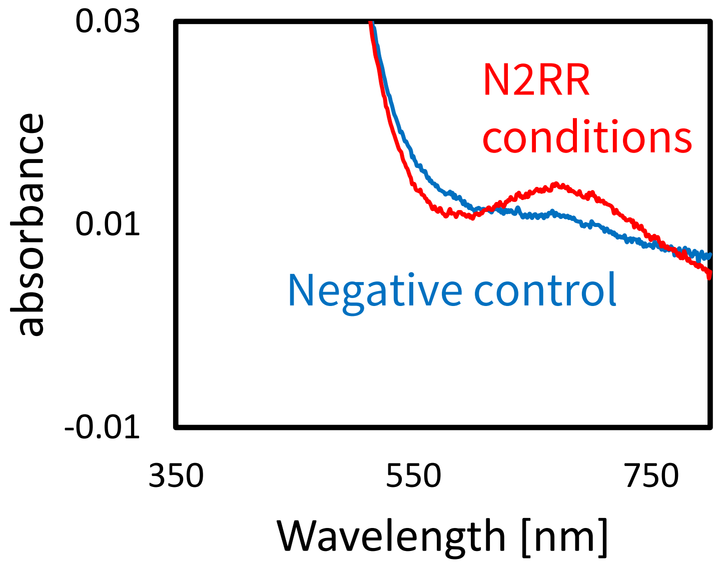

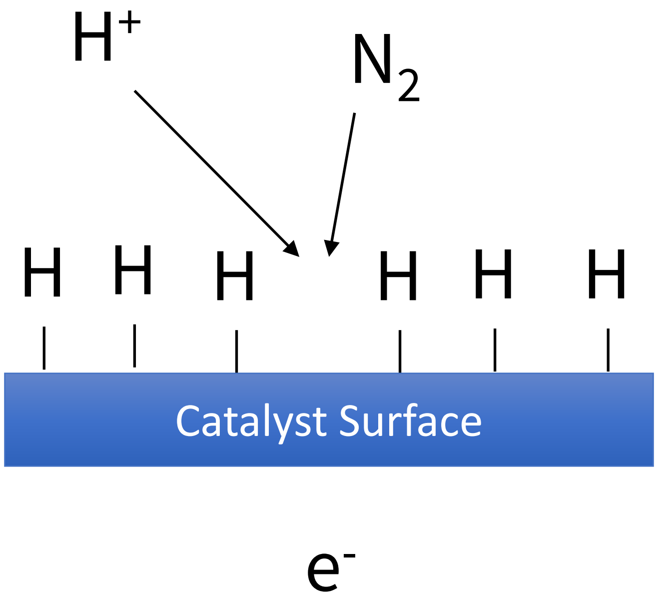

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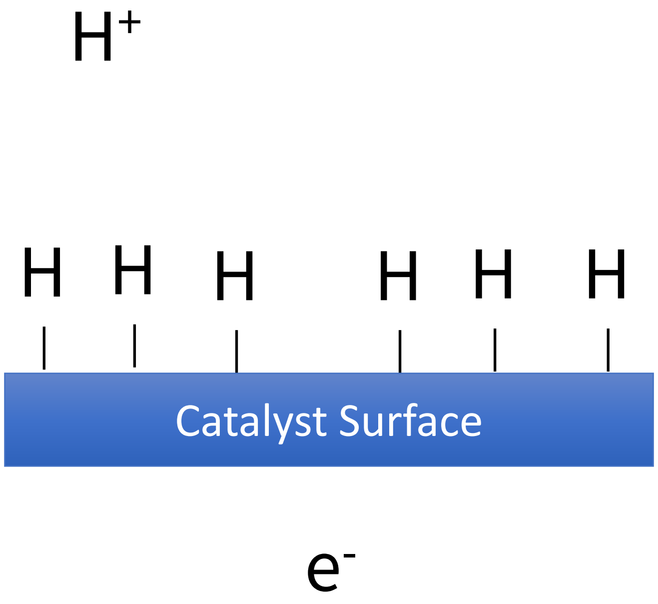
Model Development

$$r_H = k_H \theta_H \tilde{c}_{H^+} \tilde{c}_{e^-} \cong k_H \tilde{c}_{H^+} \tilde{c}_{e^-}$$



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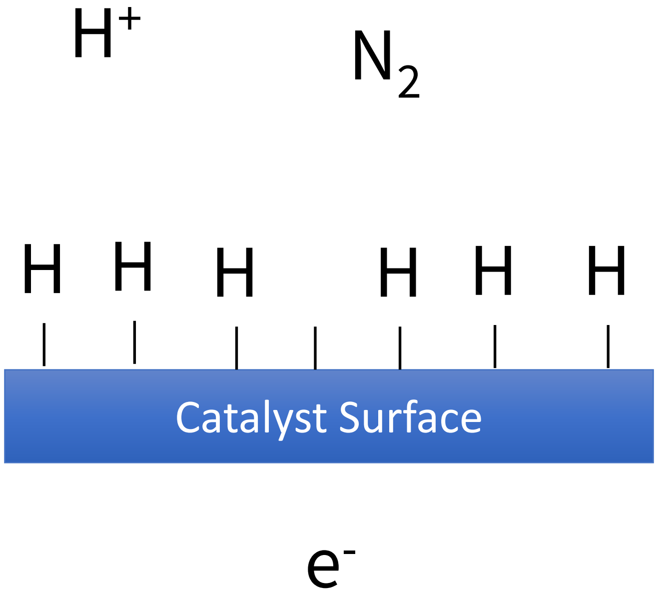
$$r_N = k_N \theta_{N_2} \boxed{\tilde{c}_{H^+}} \tilde{c}_{e^-}$$

$$\theta_{N_2} = \frac{K_N \tilde{c}_{N_2}}{1 + K_H \tilde{c}_{H^+} \tilde{c}_{e^-} + K_N \tilde{c}_{N_2}} \cong \frac{K_N \tilde{c}_{N_2}}{K_H \boxed{\tilde{c}_{H^+}} \tilde{c}_{e^-}}$$



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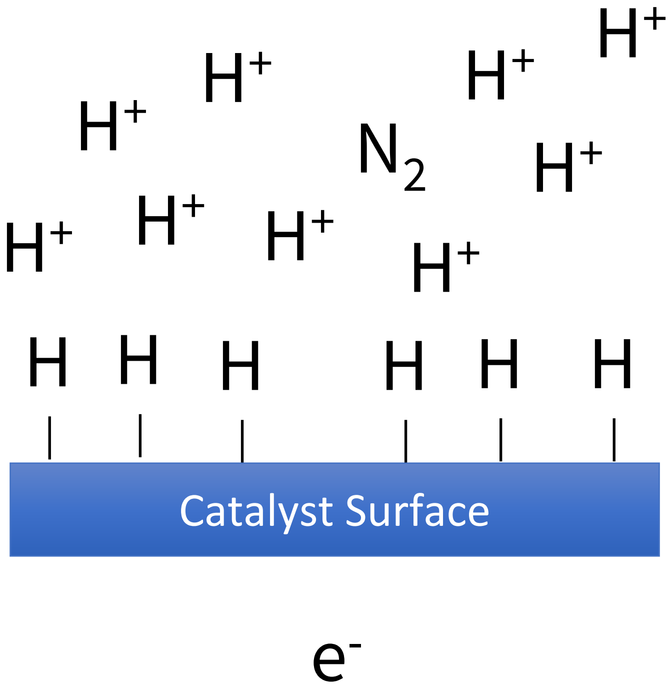
Model Development

Water has too many protons!

$$r_H = k_H \theta_H \tilde{c}_{H^+} \tilde{c}_{e^-} \cong k_H \tilde{c}_{H^+} \tilde{c}_{e^-}$$

$$r_N = k_N \theta_{N_2} \tilde{c}_{H^+} \tilde{c}_{e^-} \cong k_N \frac{K_N}{K_H} \tilde{c}_{N_2}$$

$$\frac{r_N}{r_H} = \frac{k_N}{k_H} * \frac{K_N}{K_H} * \frac{\tilde{c}_{N_2}}{\tilde{c}_{H^+} \tilde{c}_{e^-}}$$



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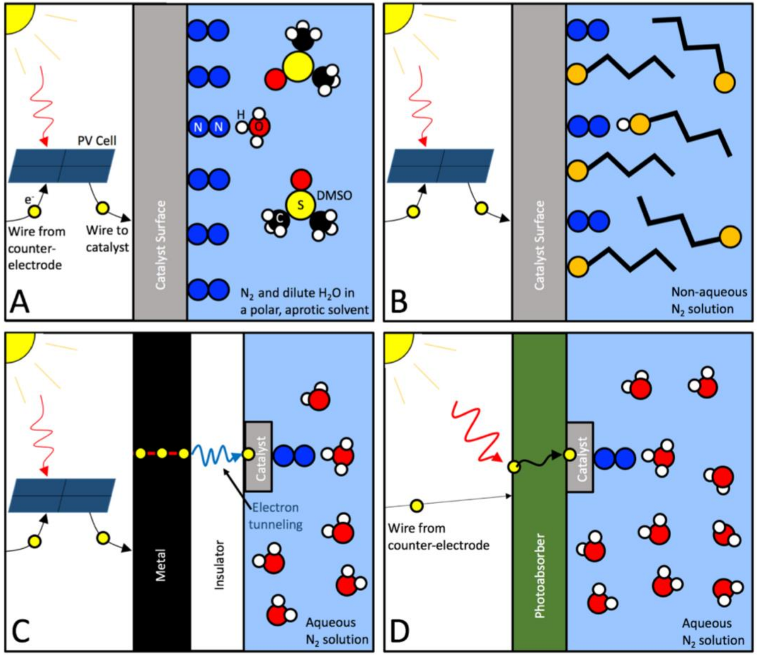
Proposed Strategies

$$r_H = k_H \theta_H \tilde{c}_{H^+} \tilde{c}_{e^-} \cong k_H \tilde{c}_{H^+} \tilde{c}_{e^-}$$

$$r_N = k_N \theta_{N_2} \tilde{c}_{H^+} \tilde{c}_{e^-} \cong k_N \frac{K_N}{K_H} \tilde{c}_{N_2}$$

$$\frac{r_N}{r_H} = \frac{k_N}{k_H} * \frac{K_N}{K_H} * \frac{\tilde{c}_{N_2}}{\tilde{c}_{H^+} \tilde{c}_{e^-}}$$



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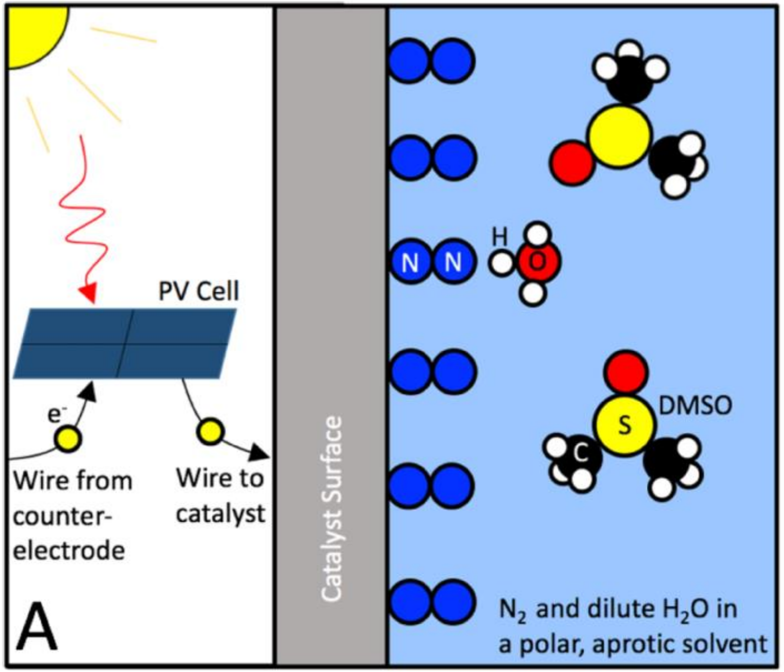
$$\frac{r_N}{r_H} = \frac{k_N}{k_H} * \frac{K_N}{K_H} * \frac{\tilde{c}_{N_2}}{\tilde{c}_{H^+} \tilde{c}_{e^-}}$$



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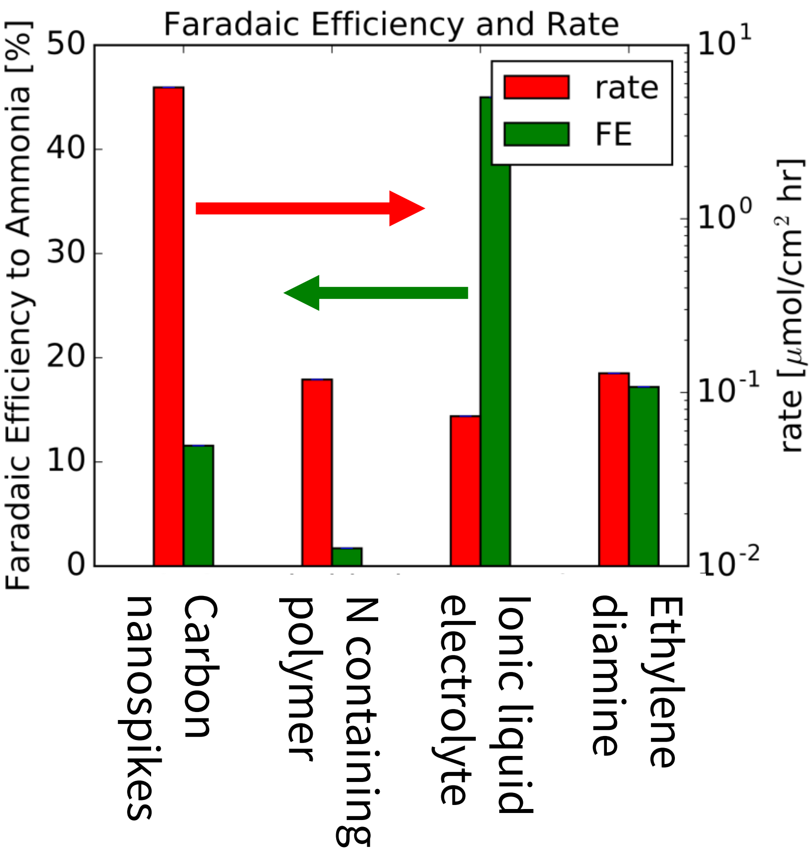
Experimental Measurements of Ammonia Synthesis

Ammonia rates are observed to be low



"A Physical Catalyst for the Electrolysis of Nitrogen to Ammonia." *Science Advances* 4, no. 4 (April 2018): e1700336.

"Ammonia Electrosynthesis with High Selectivity under Ambient Conditions via a Li+ Incorporation Strategy." *Journal of the American Chemical Society* 139, no. 29 (July 26, 2017): 9771–74.

"Electro-Synthesis of Ammonia from Nitrogen at Ambient Temperature and Pressure in Ionic Liquids." *Energy & Environmental Science* 10, no. 12 (2017): 2516–20.

"Electrochemical Synthesis of Ammonia from Water and Nitrogen in Ethylenediamine under Ambient Temperature and Pressure." *J. Electrochem. Soc.* 163 (2016).

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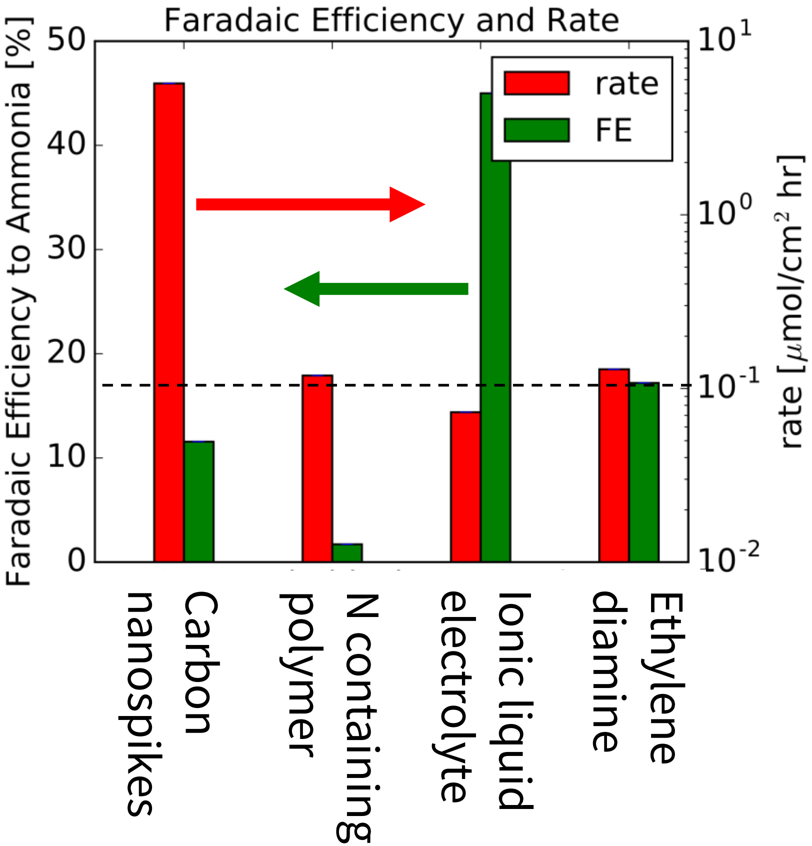
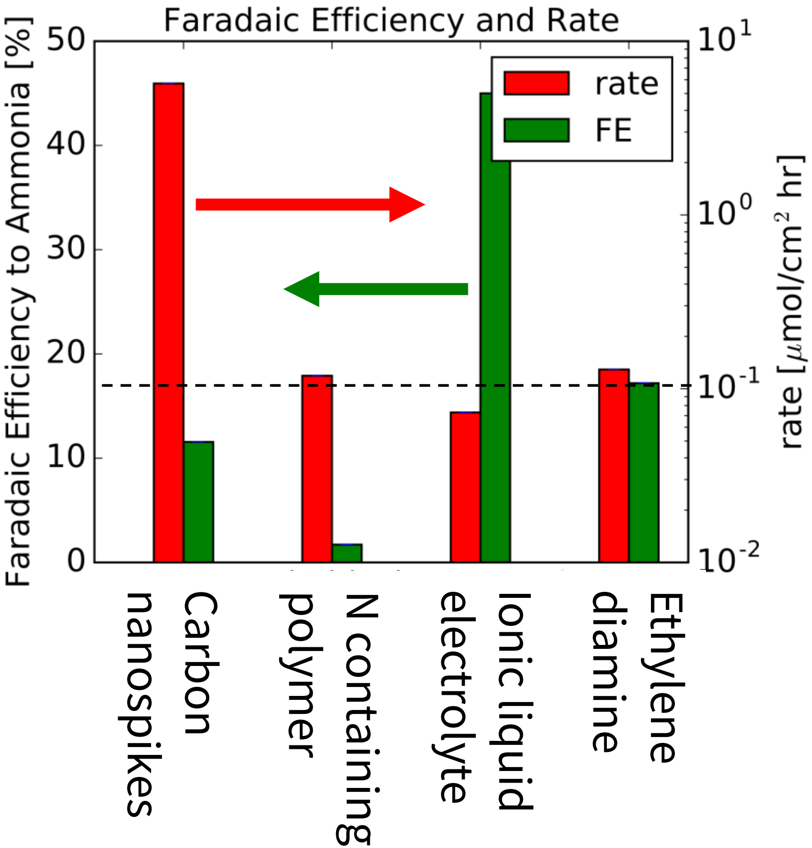


$$0.1\,\frac{\mu mol}{cm^2 hr} * 1cm^2 * 4hrs * \frac{1}{.01\ l} = 40\mu M$$

$$40\ \mu M\ \approx 1ppm$$

Low enough to be in the range of common contamination



$$0.1\,\frac{\mu mol}{cm^2 hr} * 1cm^2 * 4hrs * \frac{1}{.01\ l} = 40\mu M$$

$$40\ \mu M \ \approx 1ppm$$

Left: >5ppm ~ 275uM contamination from adhesive on vial top

Some critical literature

Detect ammonia with N_2 supplied

Amount greater than with Argon or no Current?

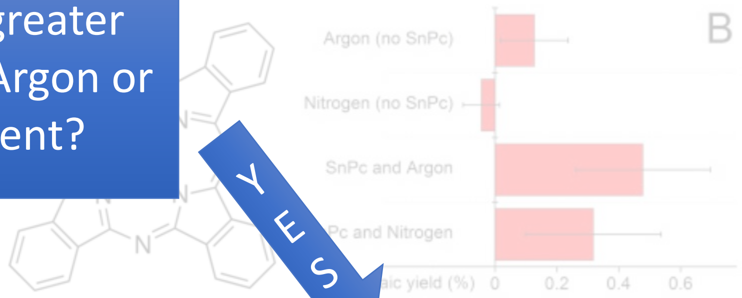
YES

Verify with purified $^{15}N_2$ experiment

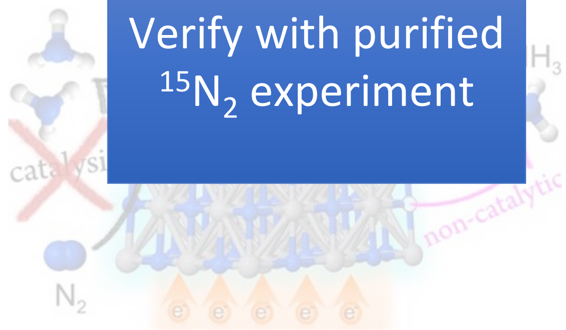
NO ☹

Eliminate sources of contamination

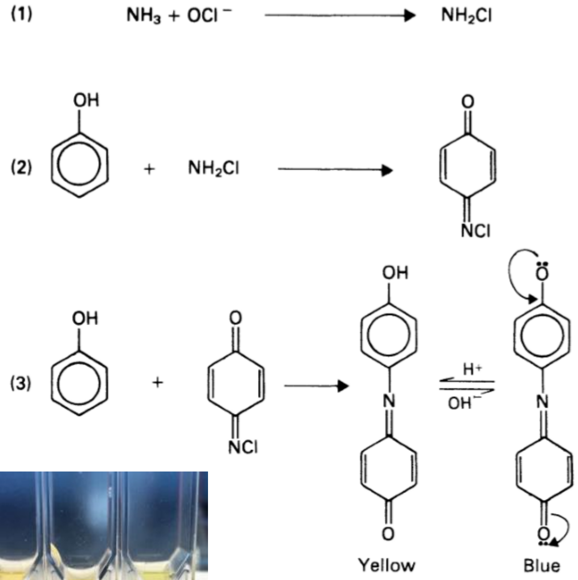
“A ... Phthalocyanine ... Catalyst for the Electrosynthesis of Ammonia.” *Electrochimica Acta* 258 (December 2017): 618–22.

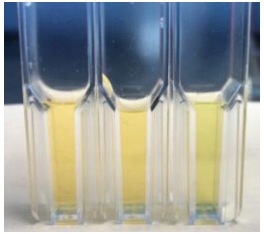


“Critical Assess... of the Electrocatalytic Activity of Vanadium a... ward Dinitrogen Red... *...S Sustainable Chemistry & En...* ...019.



Ammonia detection is possible with a number of techniques - Colorimetric





0 µM 55 µM 165 µM

Searle, Phillip L. "The Berthelot or Indophenol Reaction and Its Use in the Analytical Chemistry of Nitrogen. A Review." *Analyst* 109, no. 5 (January 1, 1984): 549–68.

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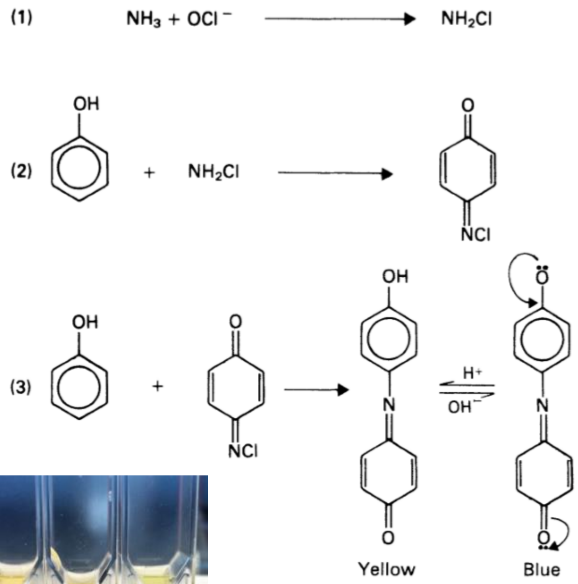

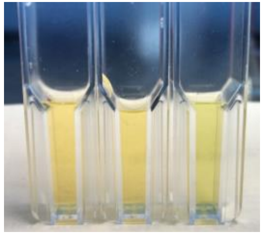

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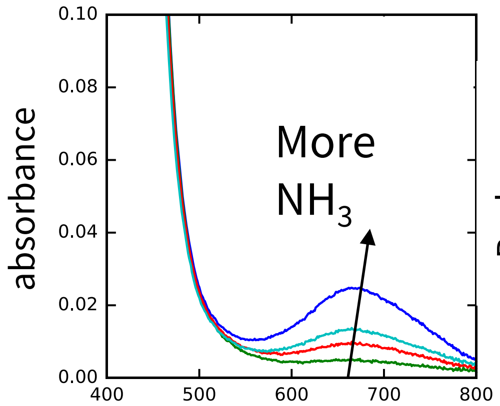

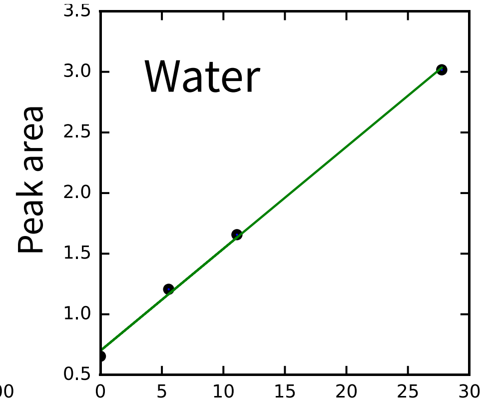

Searle, Phillip L. “The Berthelot or Indophenol Reaction and Its Use in the Analytical Chemistry of Nitrogen. A Review.” *Analyst* 109, no. 5 (January 1, 1984): 549–68.

Thanks, Chenshuang Zhou!

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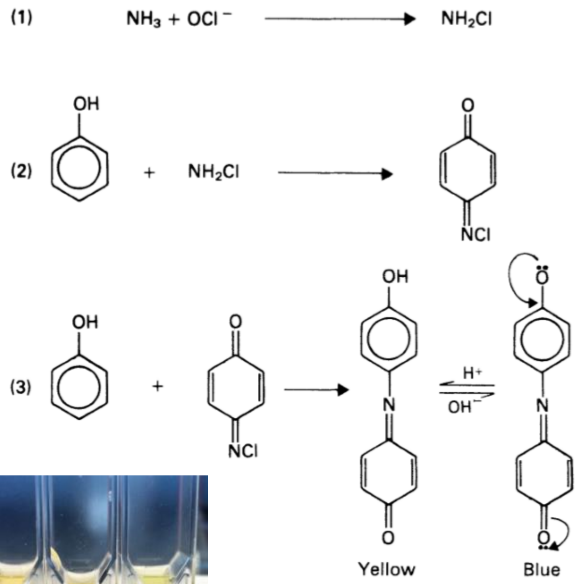

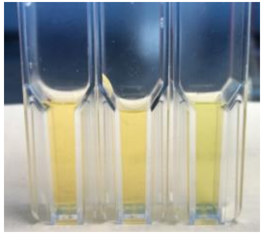

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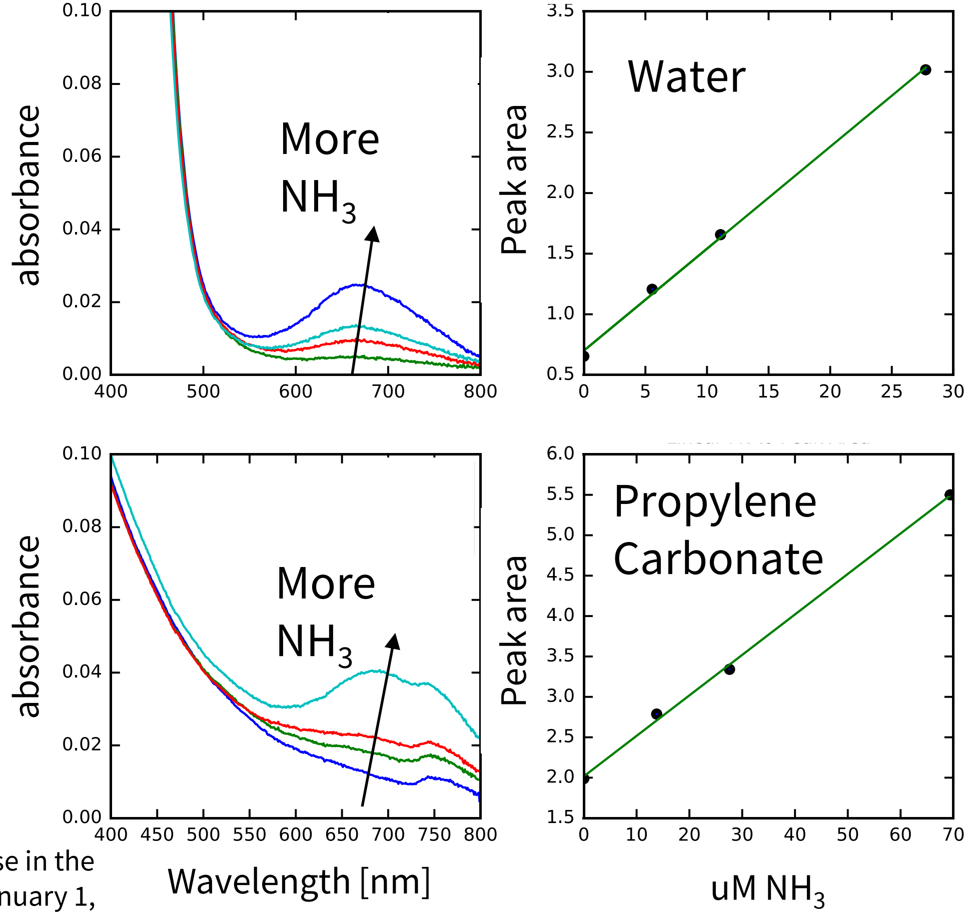

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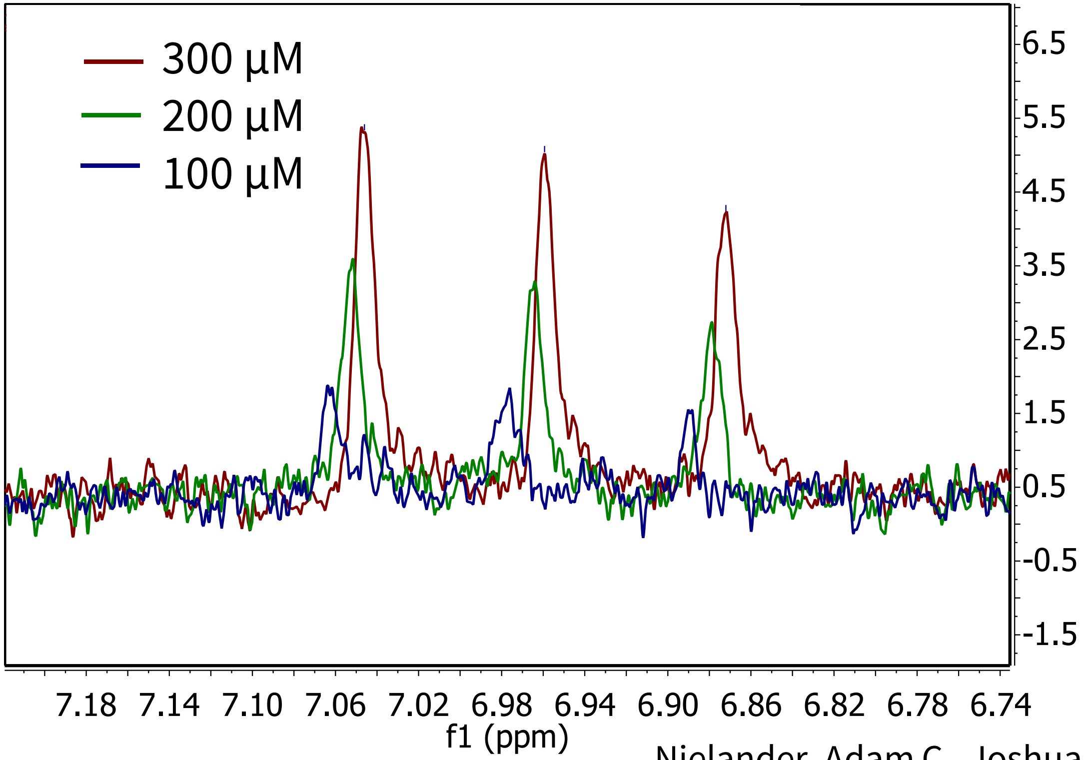
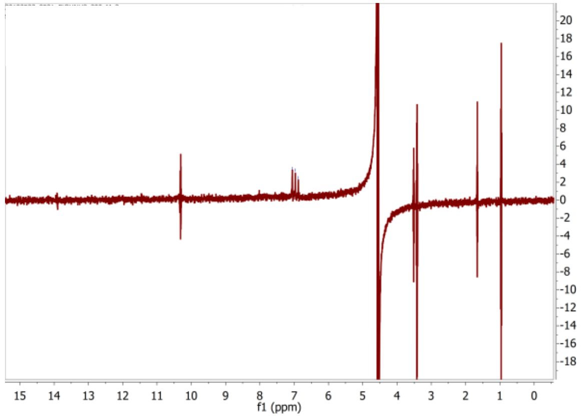
Ammonia detection is possible with a number of techniques - NMR





Selective excitation of ammonia

Nielander, Adam C., Joshua M. McEnaney, **Jay A. Schwalbe**, et. al. *ACS Catalysis* 9, no. 7 (July 5, 2019): 5797–5802.

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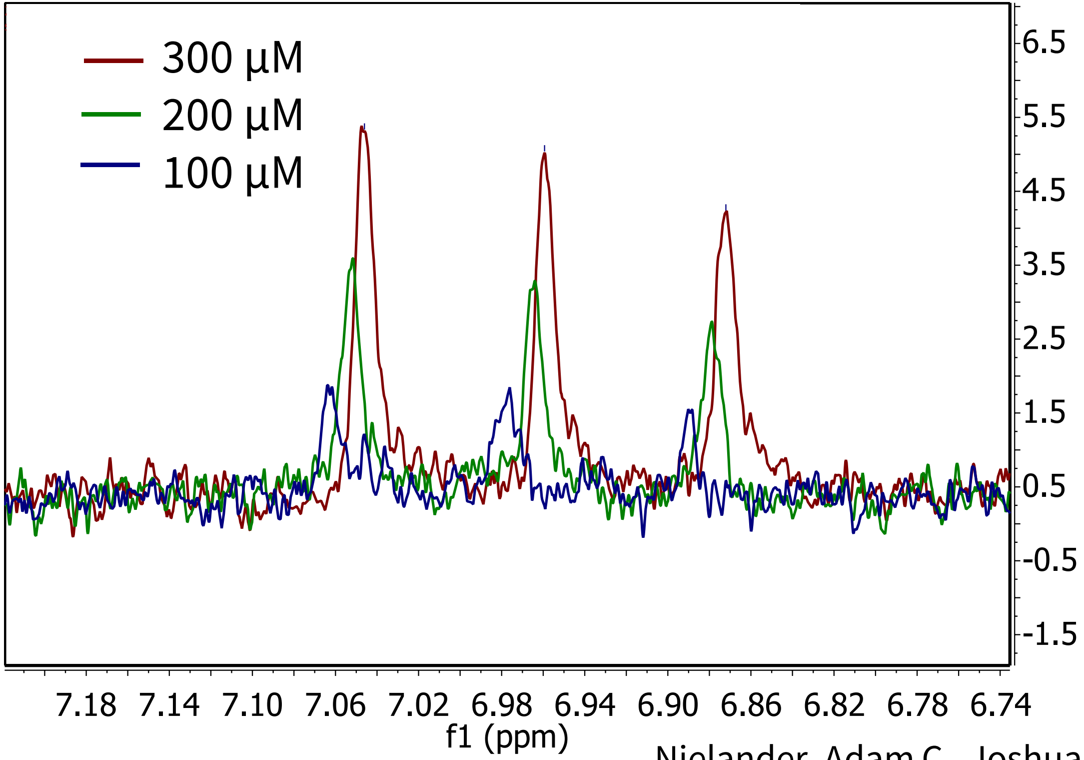

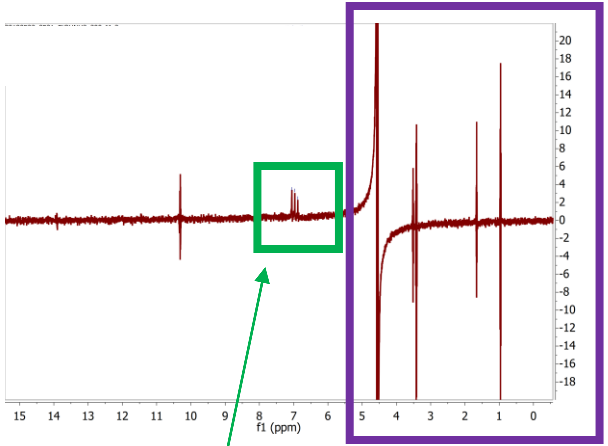

Selective excitation of ammonia

Solvent not strongly detected

Nielander, Adam C., Joshua M. McEnaney, **Jay A. Schwalbe**, et. al. *ACS Catalysis* 9, no. 7 (July 5, 2019): 5797–5802.

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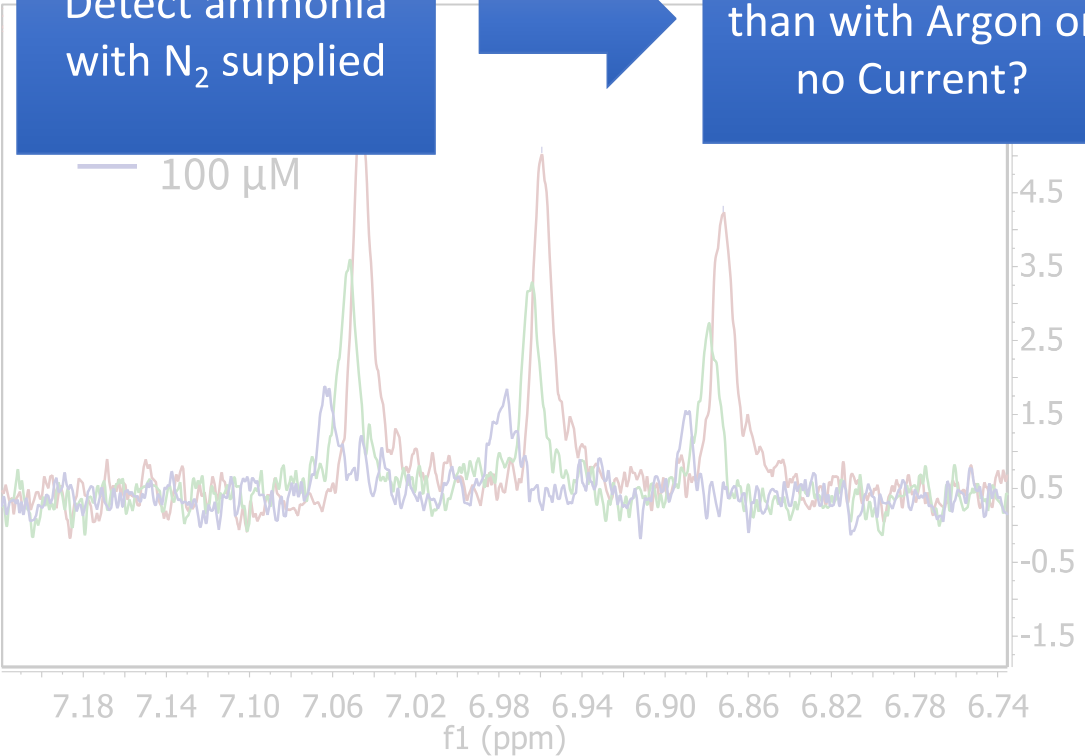
Detect ammonia with N_2 supplied

Amount greater than with Argon or no Current?



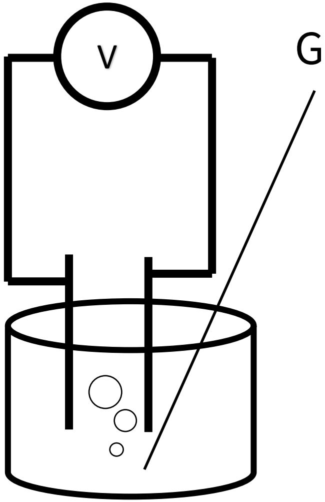
Selective excitation of ammonia

Solvent not strongly detected

Schematic of Electrochemical Experiment

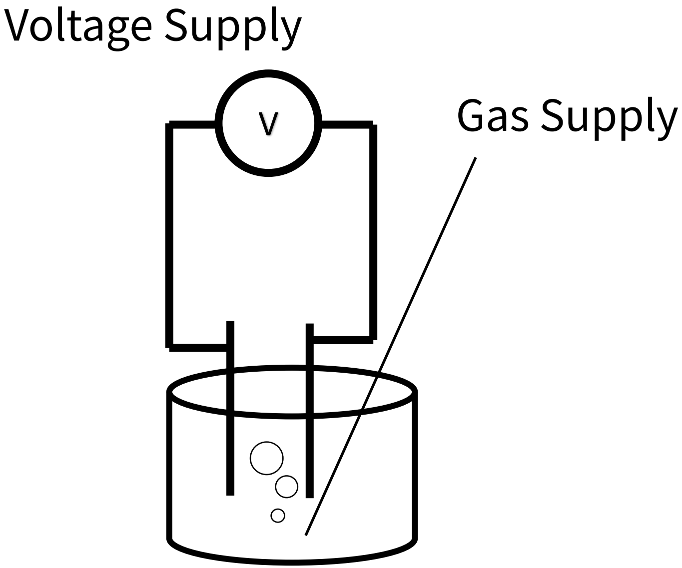
Voltage Supply

Gas Supply



Electrolyte:
THF, 0.1M $LiClO_4$,
1 v% Ethanol
Mo cathode

Schematic of Electrochemical Experiment



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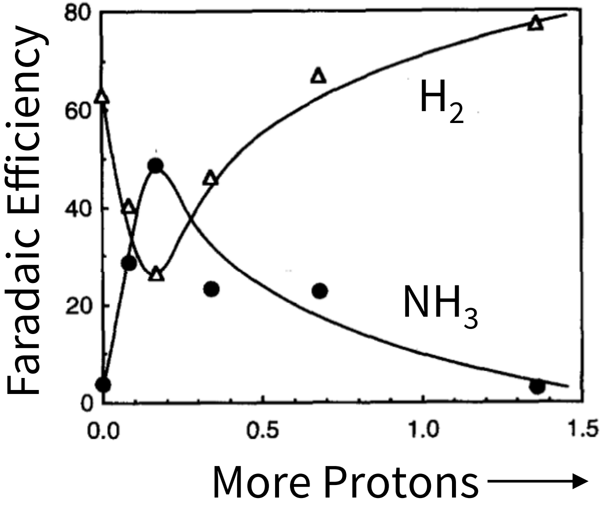
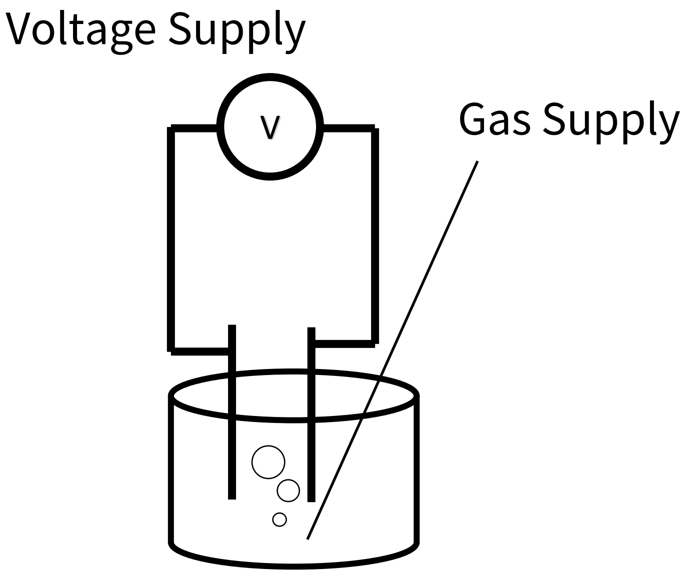


Tsuneto, Akira, Akihiko Kudo, and Tadayoshi Sakata. *Chemistry Letters* 22, no. 5 (May 1, 1993): 851–54.

Schematic of Electrochemical Experiement



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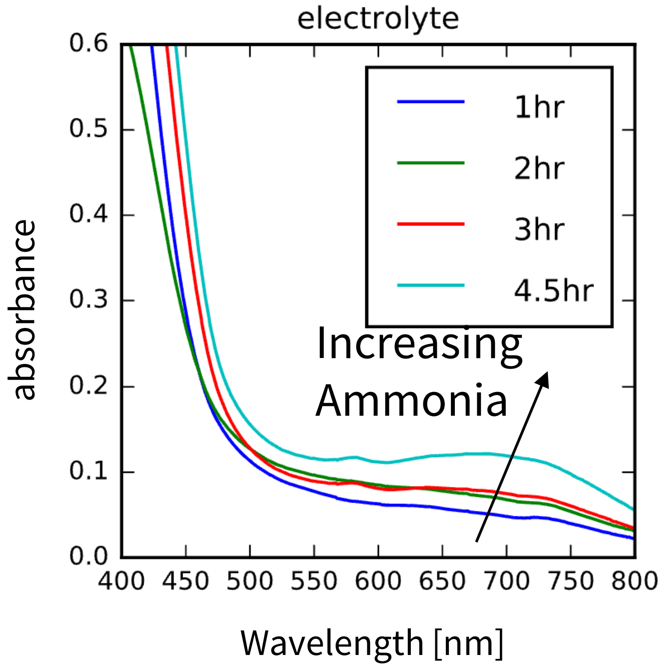

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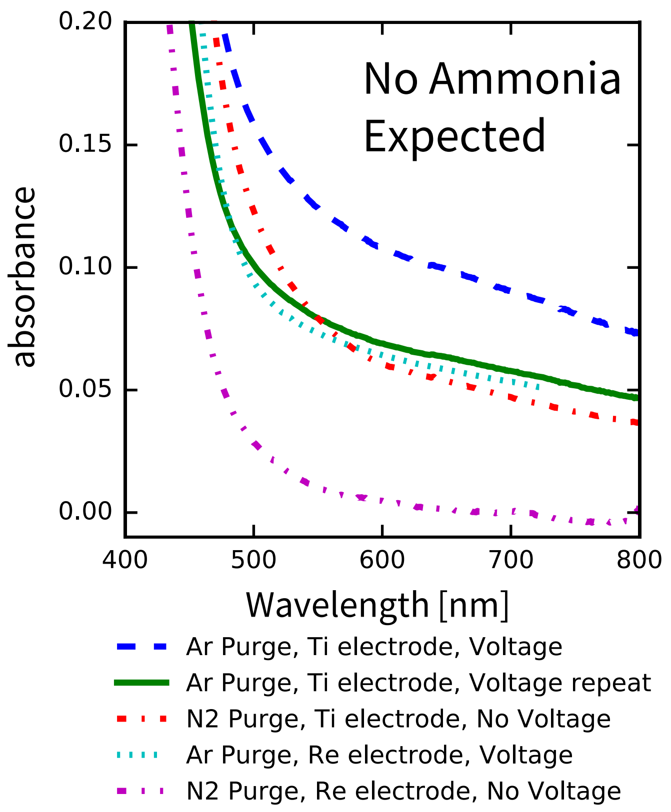
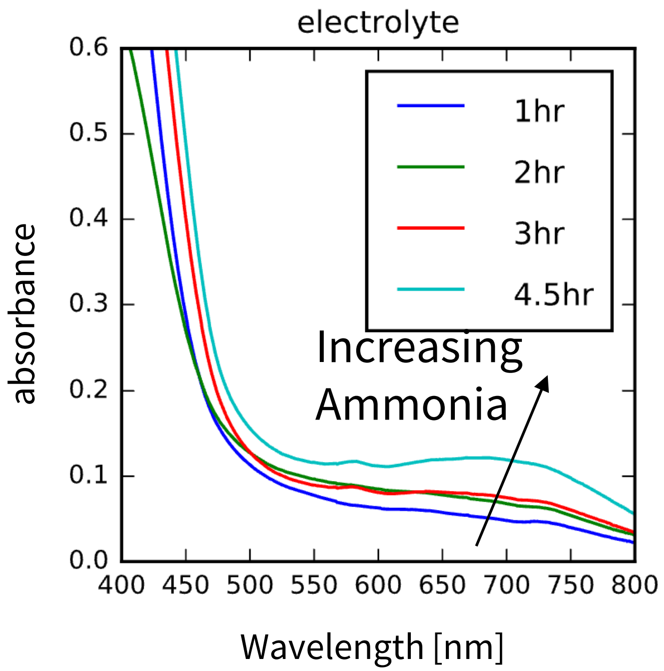
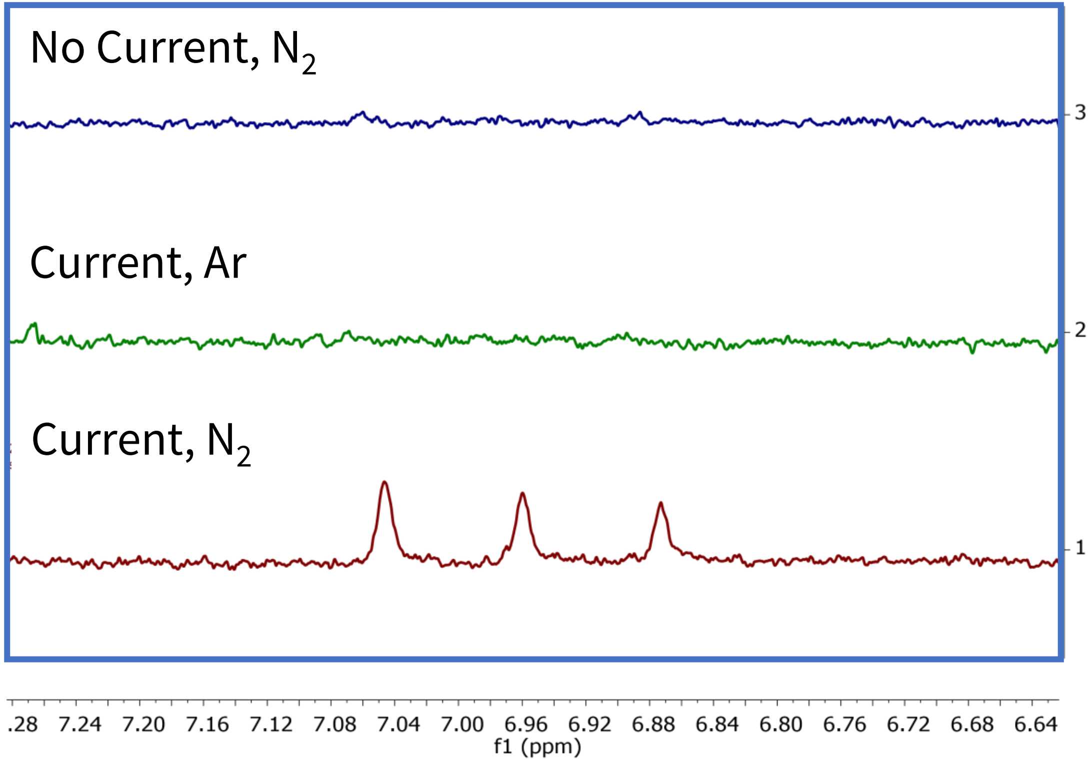




NMR Has Less Baseline Variation



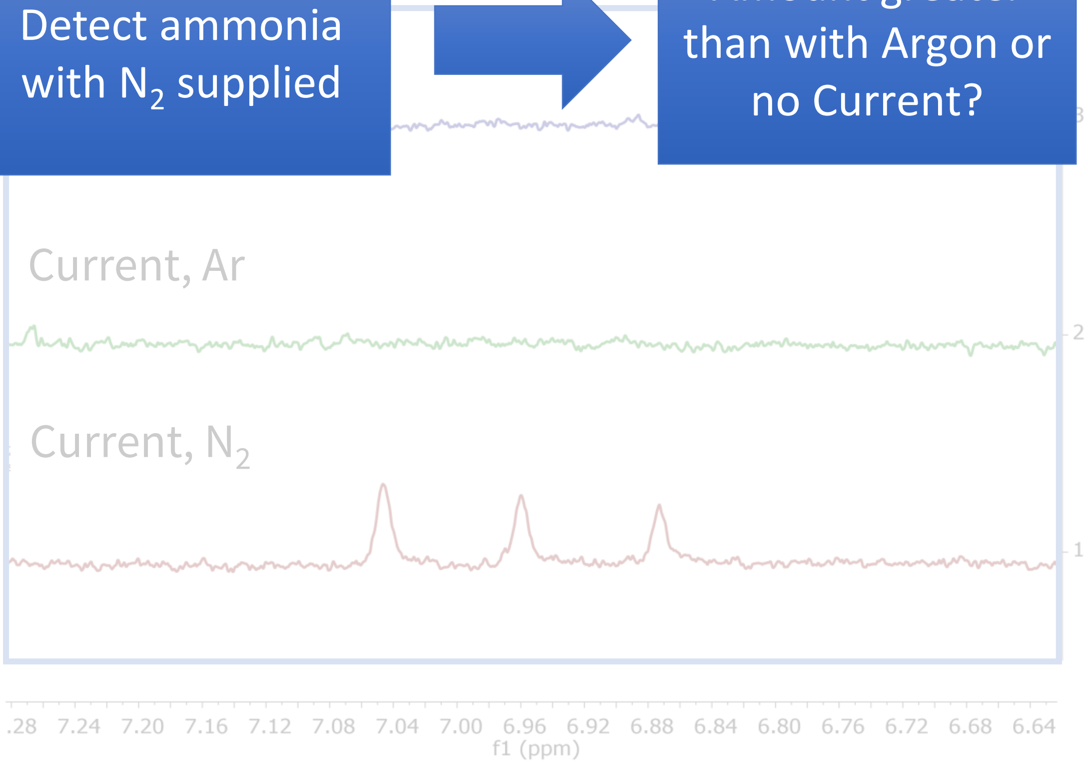
NMR Gives More Clear Results

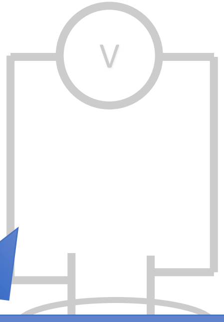
Detect ammonia with N_2 supplied

Amount greater than with Argon or no Current?

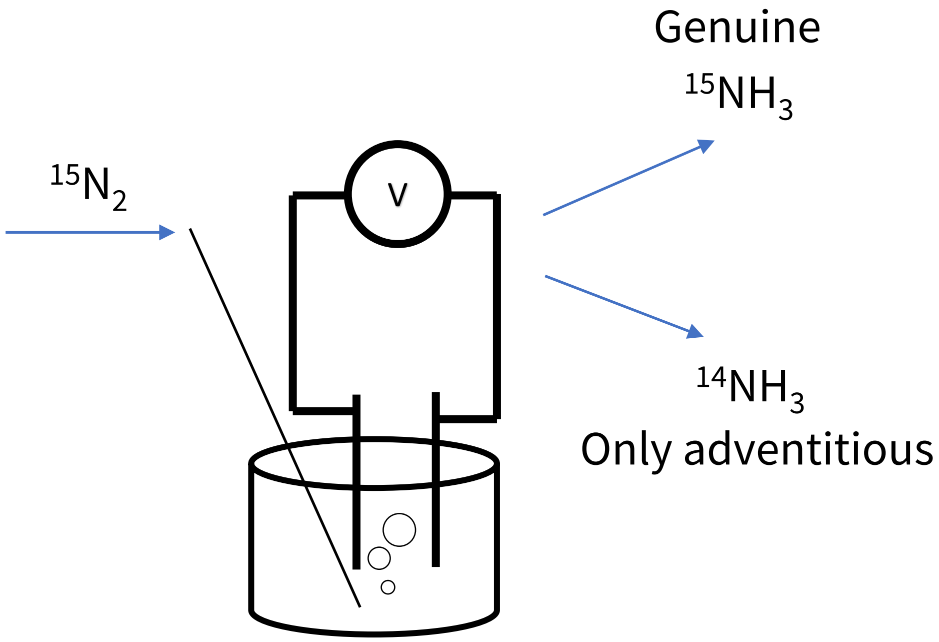
YES

Verify with purified $^{15}N_2$ experiment

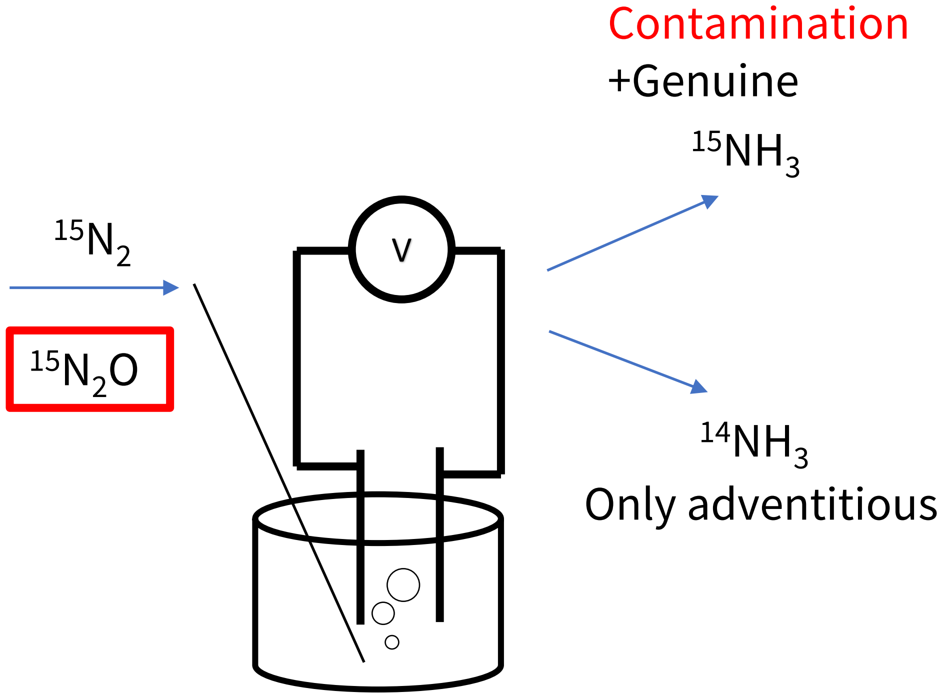




^{15}N labelling experiments



Contamination in $^{15}N_2$



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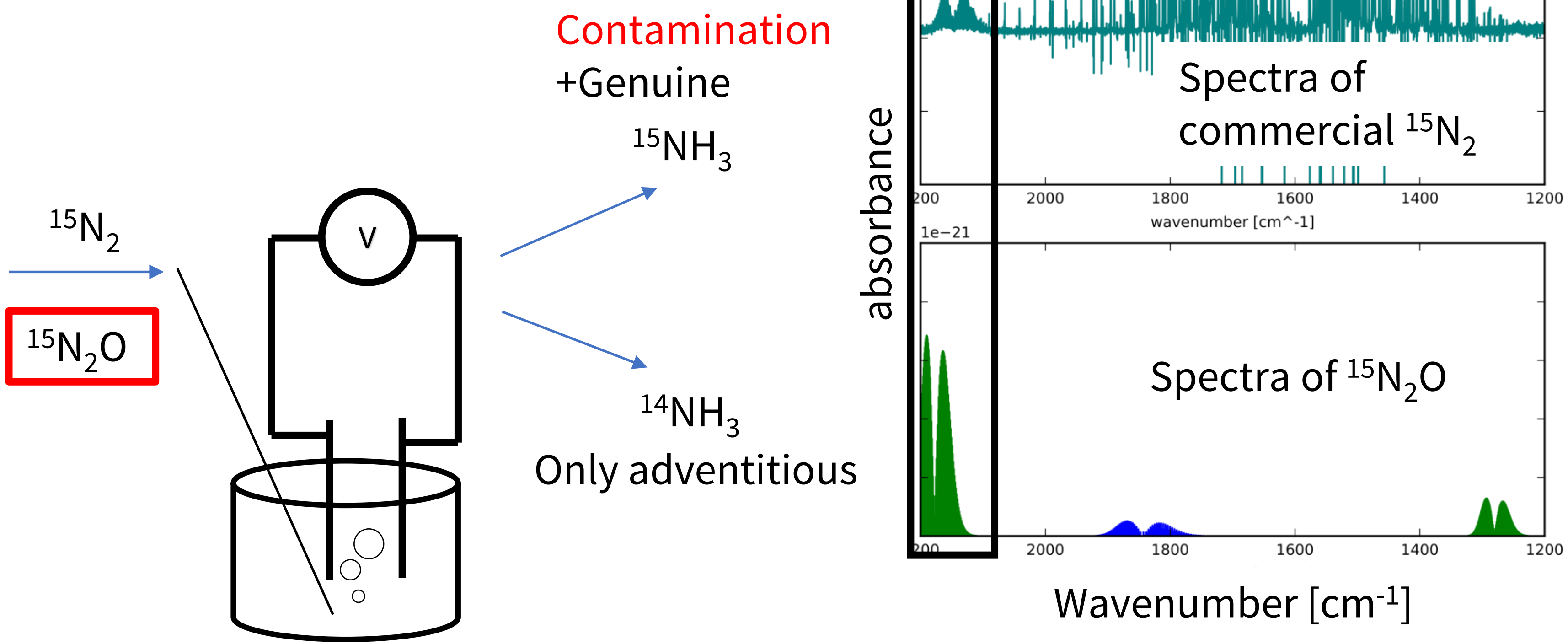
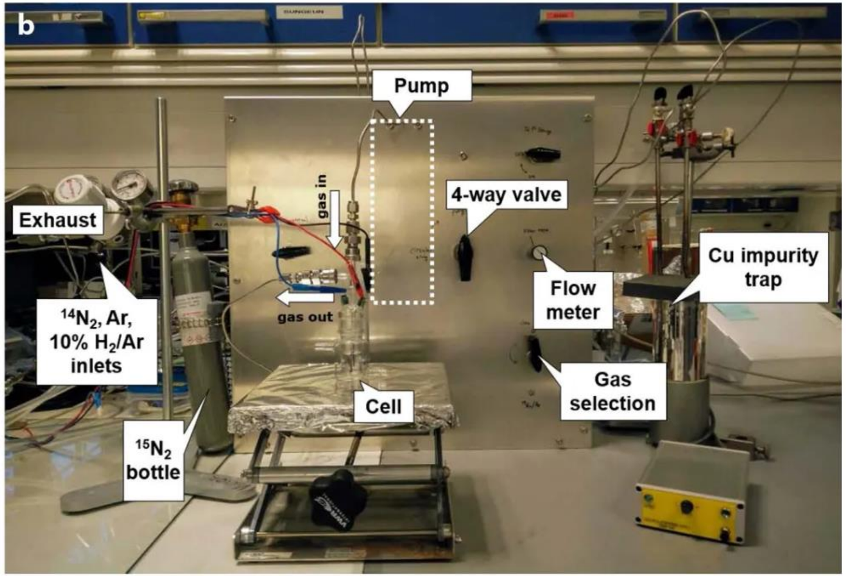


“The Contamination of Commercial 15N2 Gas Stocks with 15N–Labeled Nitrate and Ammonium and Consequences for Nitrogen Fixation Measurements.” *PLoS ONE* 9, no. 10 (October 17, 2014): e110335.

Gas must be purified and quantitative agreement achieved



Gas purification and recycling set-up at DTU

Andersen, Suzanne Z., Viktor Čolić, Sungeun Yang, **Jay A. Schwalbe**, Adam C. Nielander, Joshua M. McEnaney, Kasper Enemark-Rasmussen, et al. "A Rigorous Electrochemical Ammonia Synthesis Protocol with Quantitative Isotope Measurements." *Nature*, May 22, 2019, 1.

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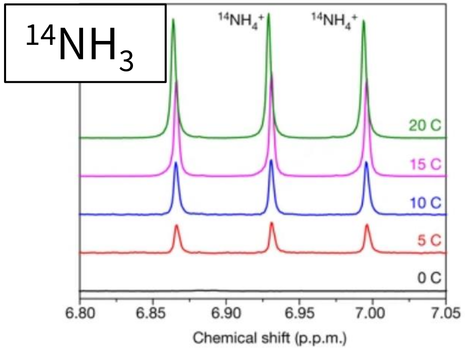

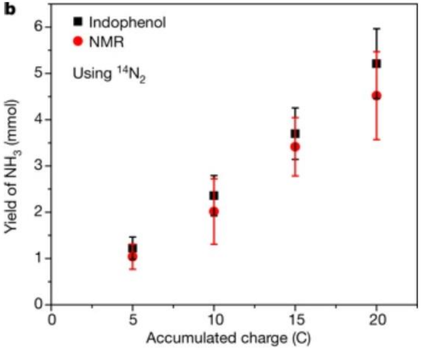

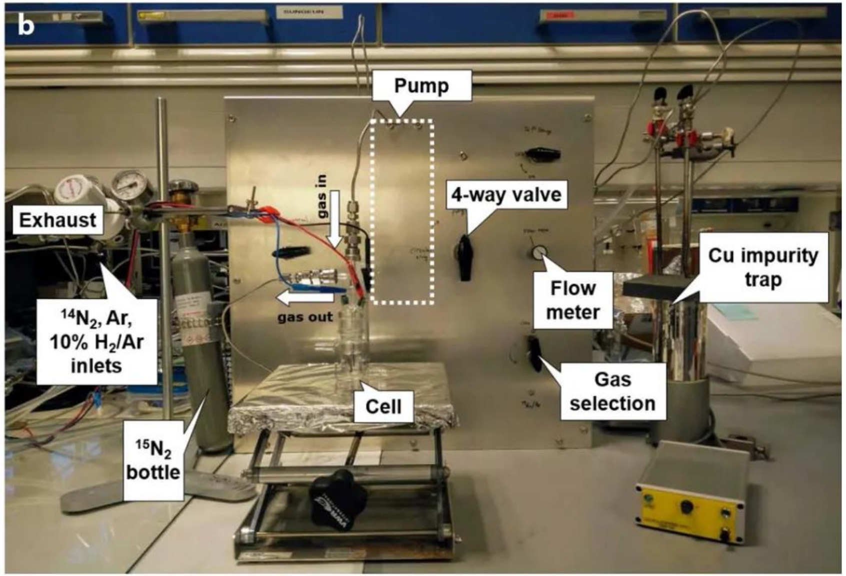

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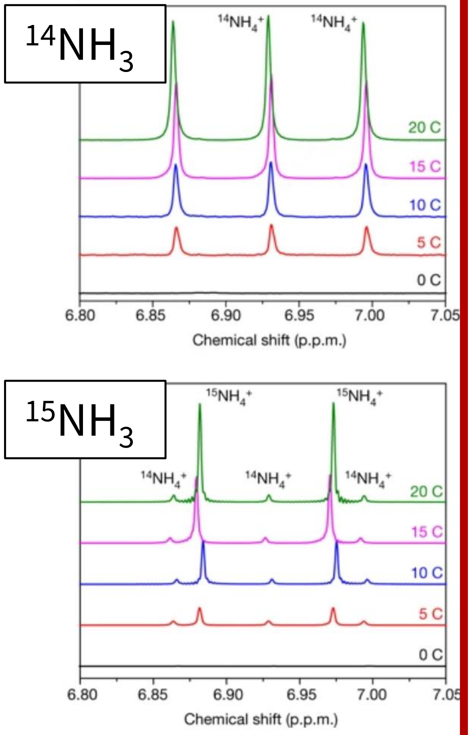

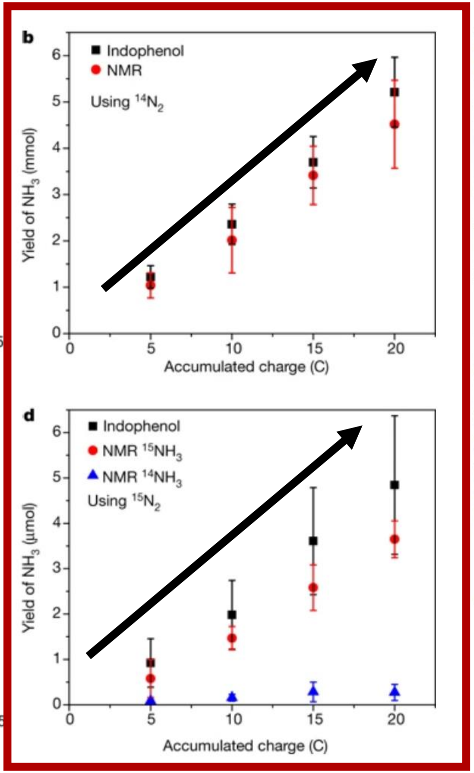

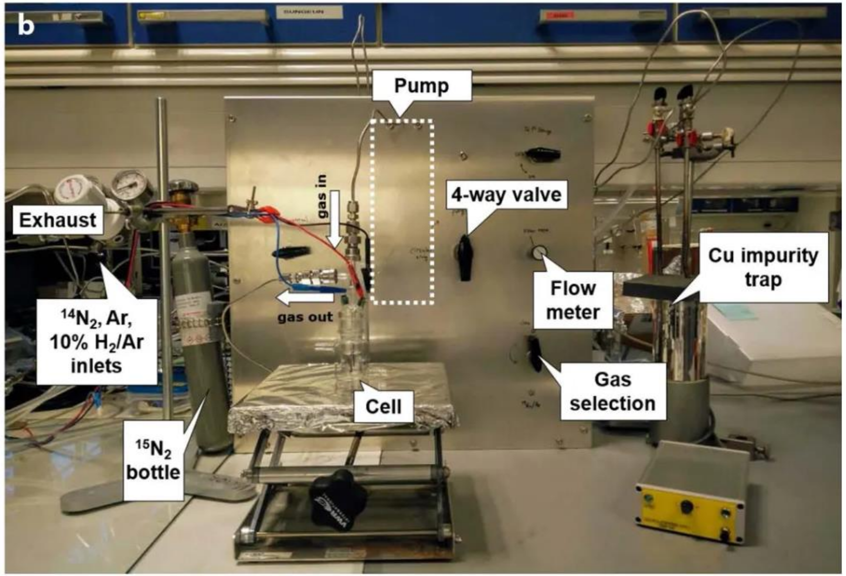

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Detect ammonia with N_2 supplied

Amount greater than with Argon or no Current?

YES

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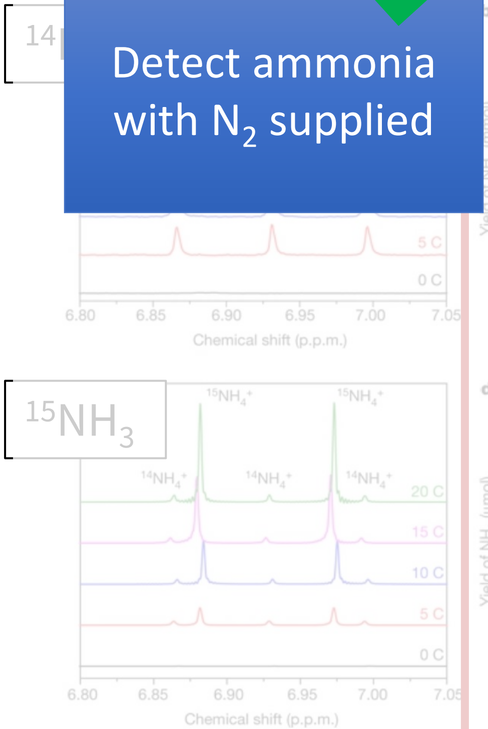

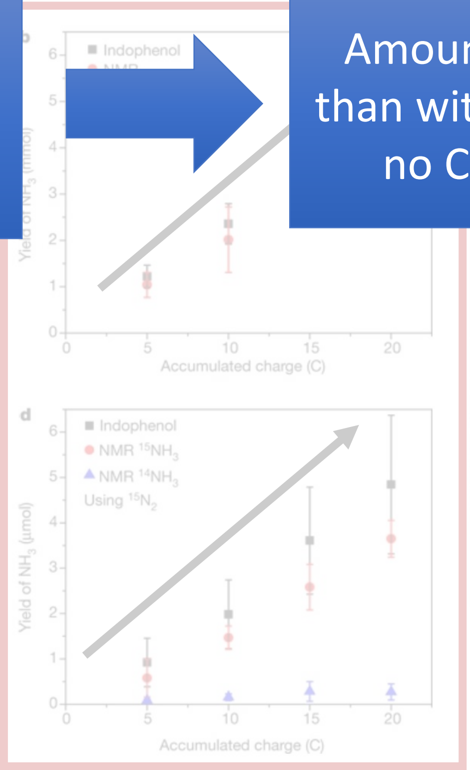

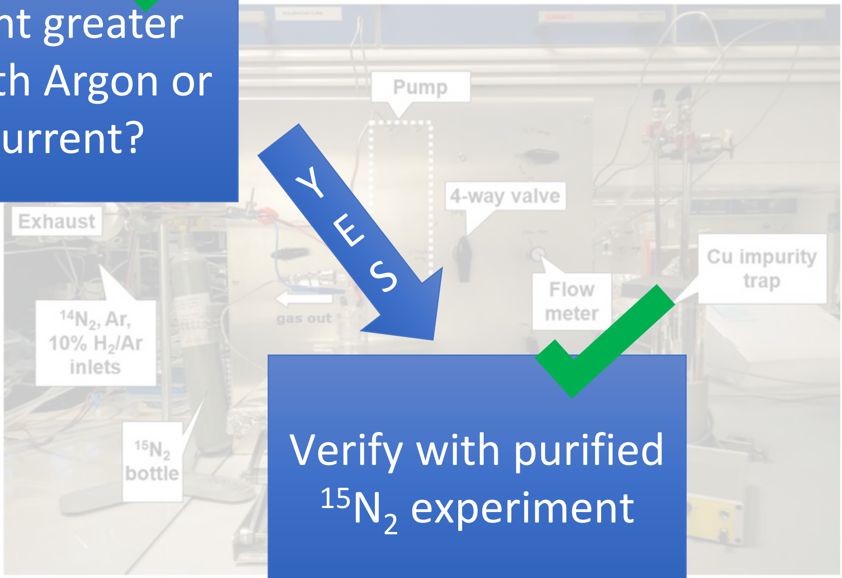

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Questions?