Sustainable NH_3 Production: New Tech and Techno economic Considerations

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Ammonia Energy Society Session
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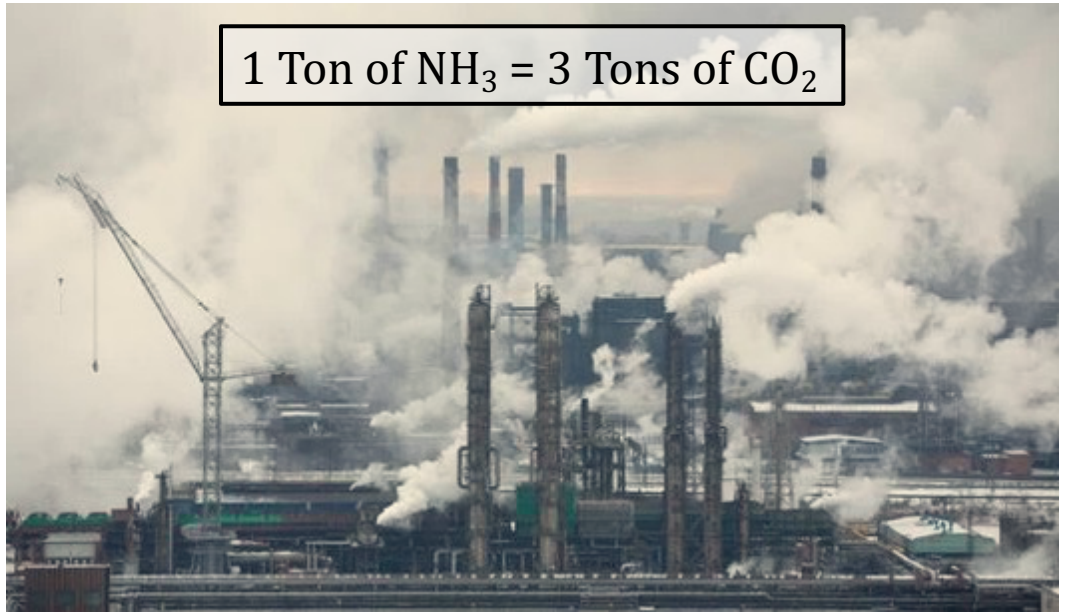
Overview

Background

Nitrogen fertilizer has been produced the same centralized way for 100 years via a carbon- and capital-intensive process.

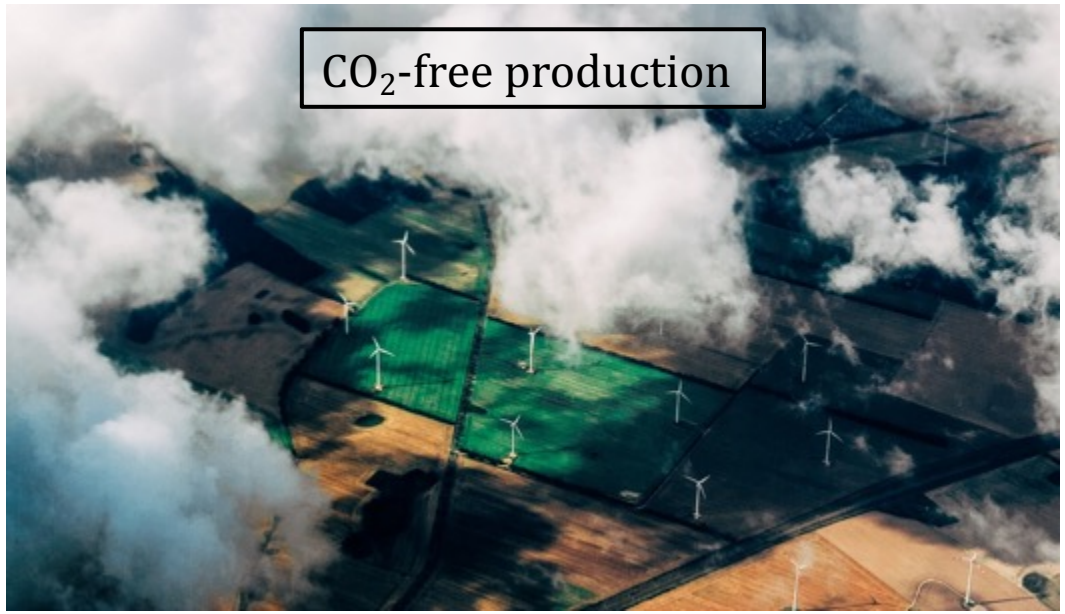


Billion-dollar, city-sized facilities

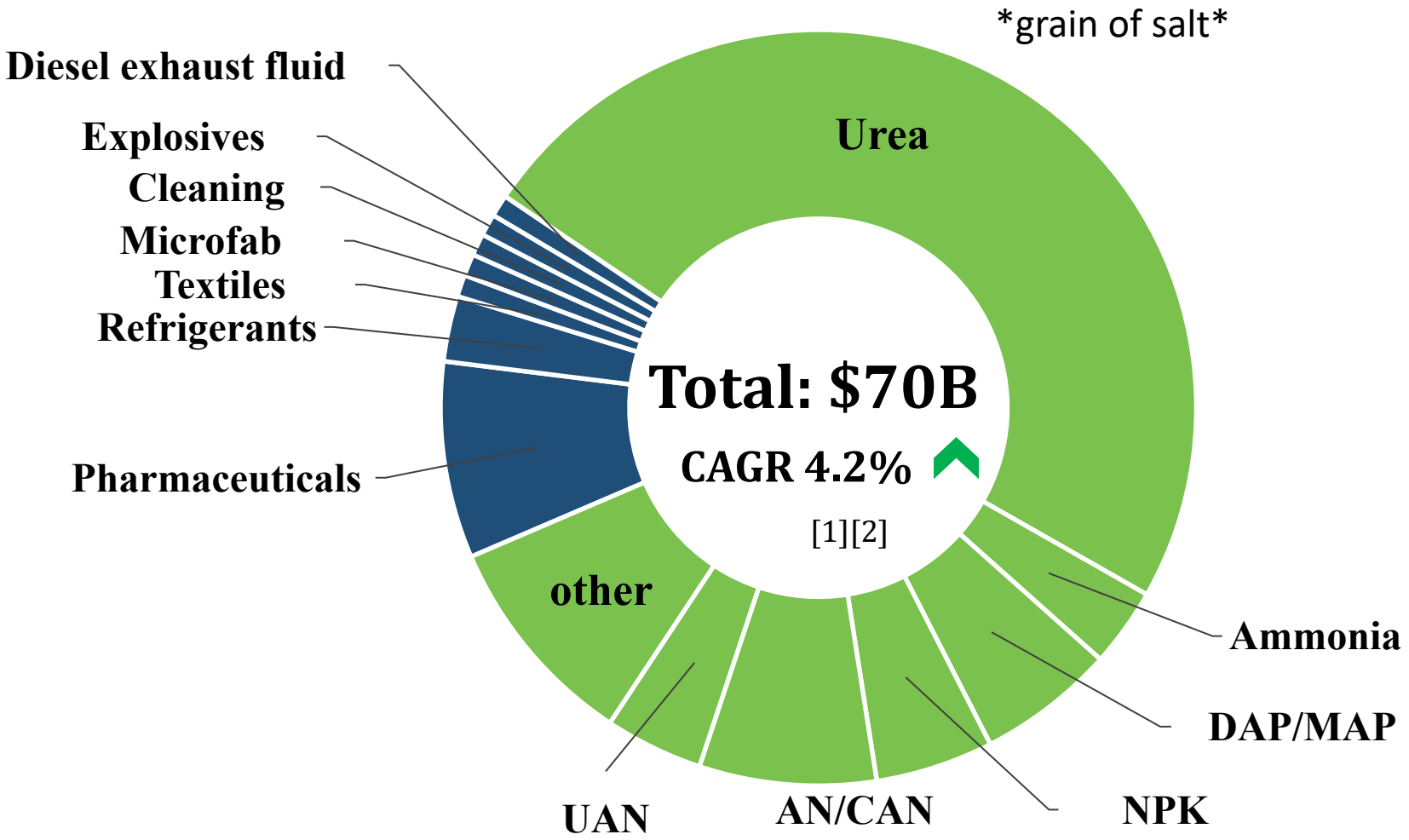
Image: Forbes.com

Goal

Carbon-free nitrogen closer to the end user using only air, water, and renewable electricity.



Ammonia market | overview



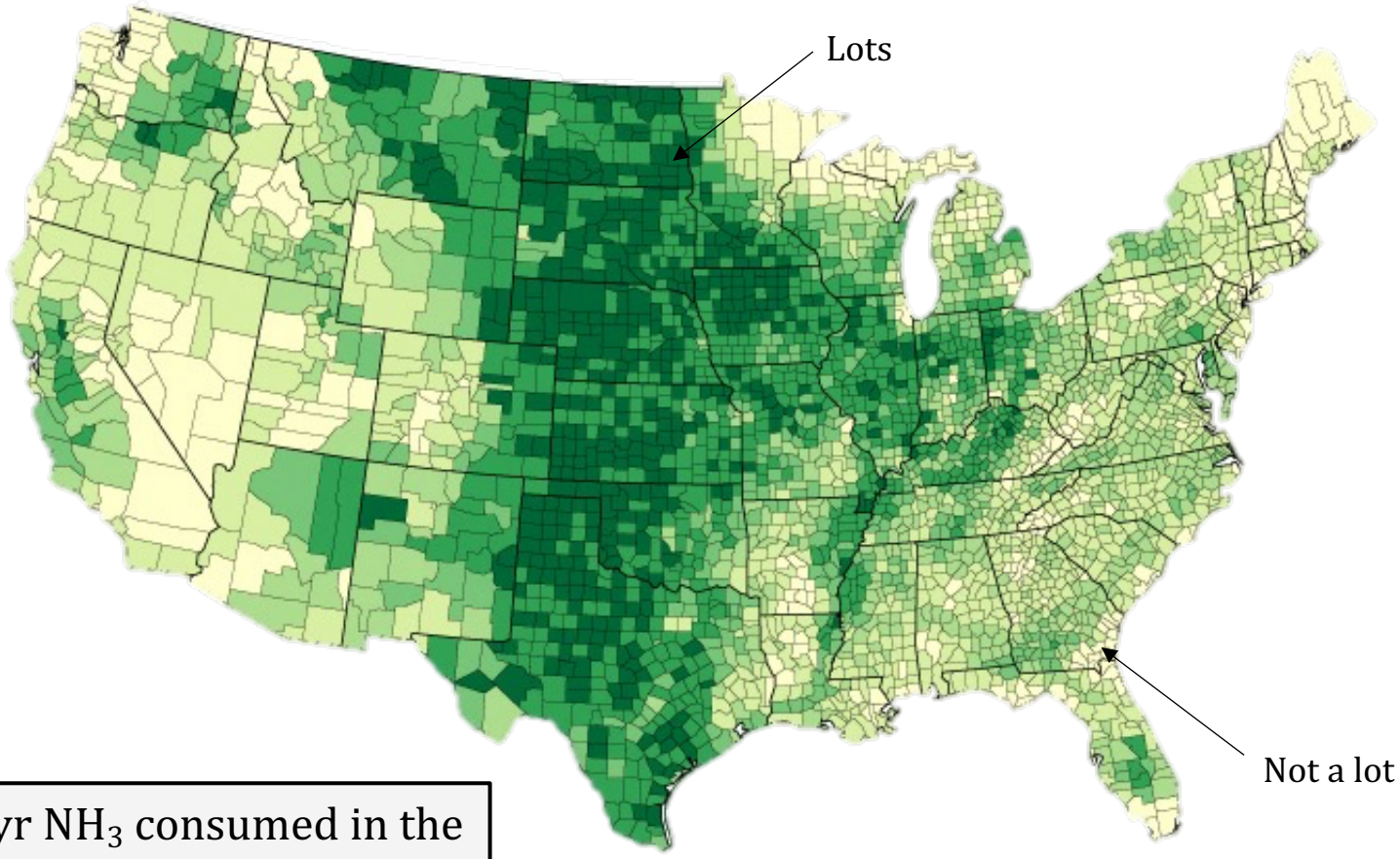
165M tons of ammonia produced in 2017 [3]

Fertilizer >75%

Industrial

[1] Yara Annual report 2017
[2] Marketwatch.com
[3] USGS annual ammonia report 2017

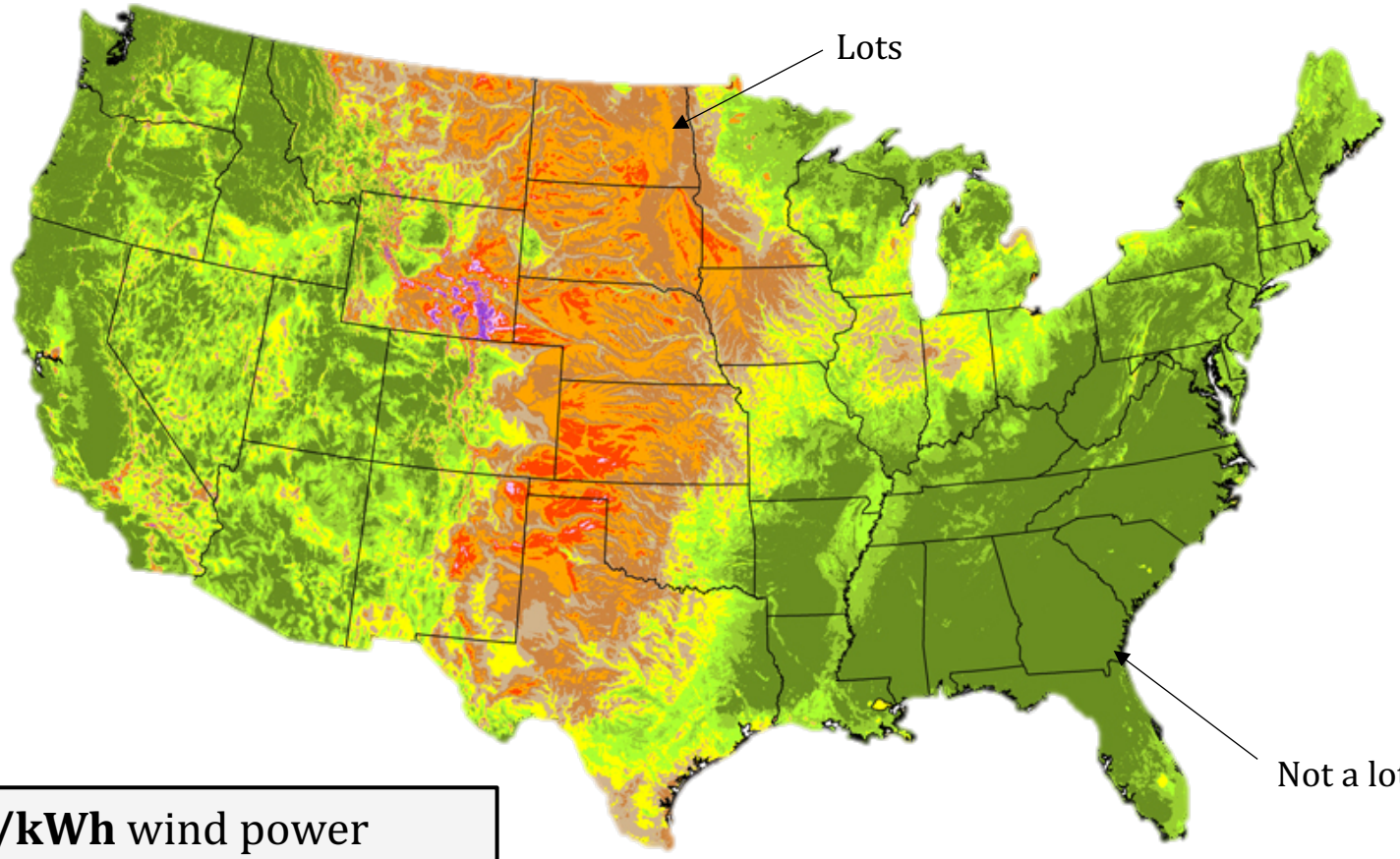
Farmland in the U.S.



7,000,000 tons / yr NH_3 consumed in the Midwest alone

Source: USDA

Wind Resources in the U.S.

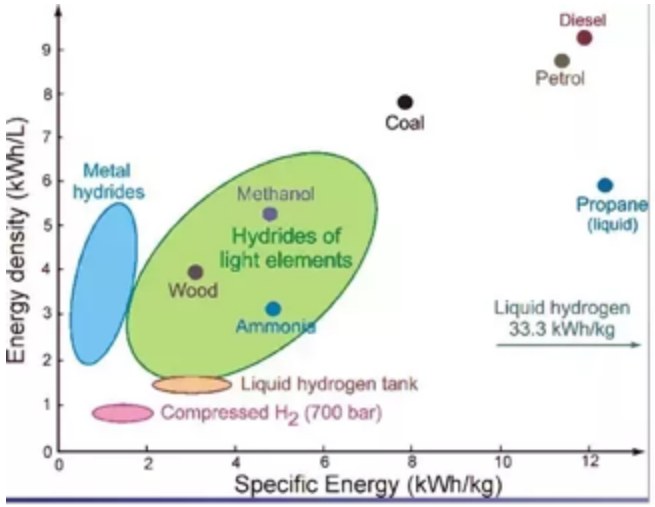


$0.02-$0.03/kWh wind power
in the Midwest

Source: NREL

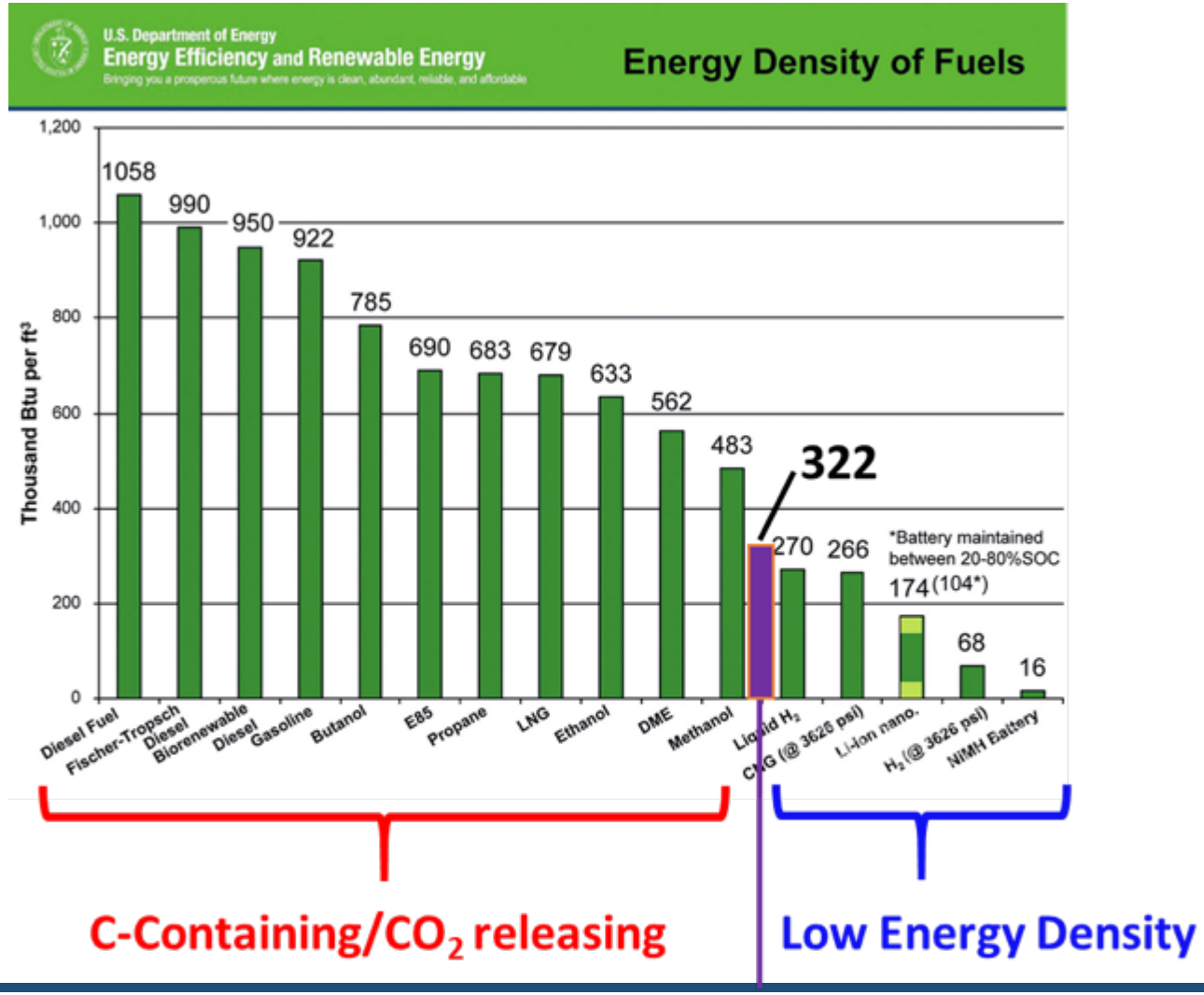
Ammonia to Feed and Fuel

Growing idea to use NH_3 as a fuel



- Clean, carbon free emissions

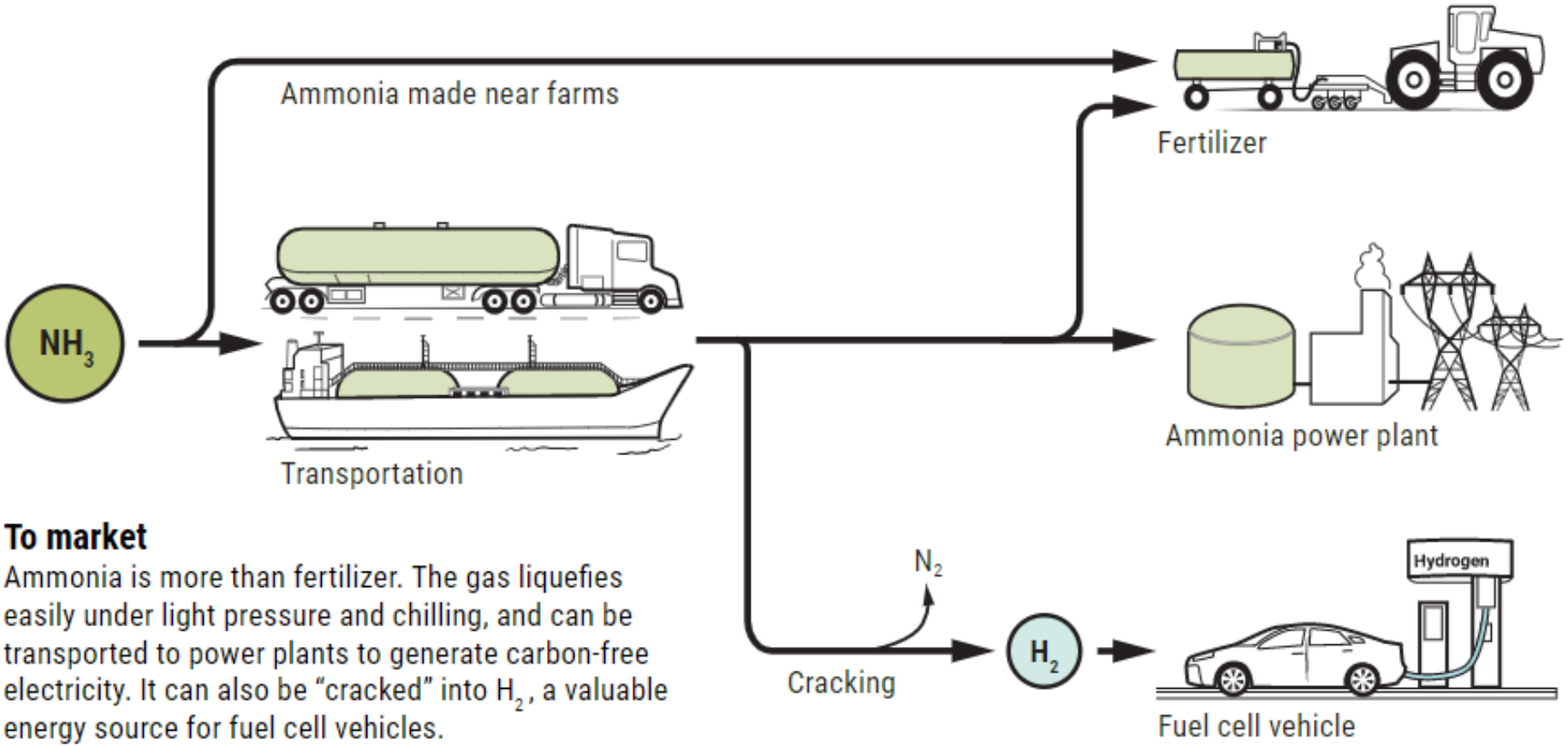
  $2NH_4 + 2O_2 \rightarrow N_2$ and $4H_2O$
- Proven safety record with strong infrastructure
- Flexible end-use



http://nh3fuelassociation.org
https://www.ammoniaenergy.org/
http://www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf

Ammonia
C-Free, Reasonable Energy Density

NH_3 Energy Economy



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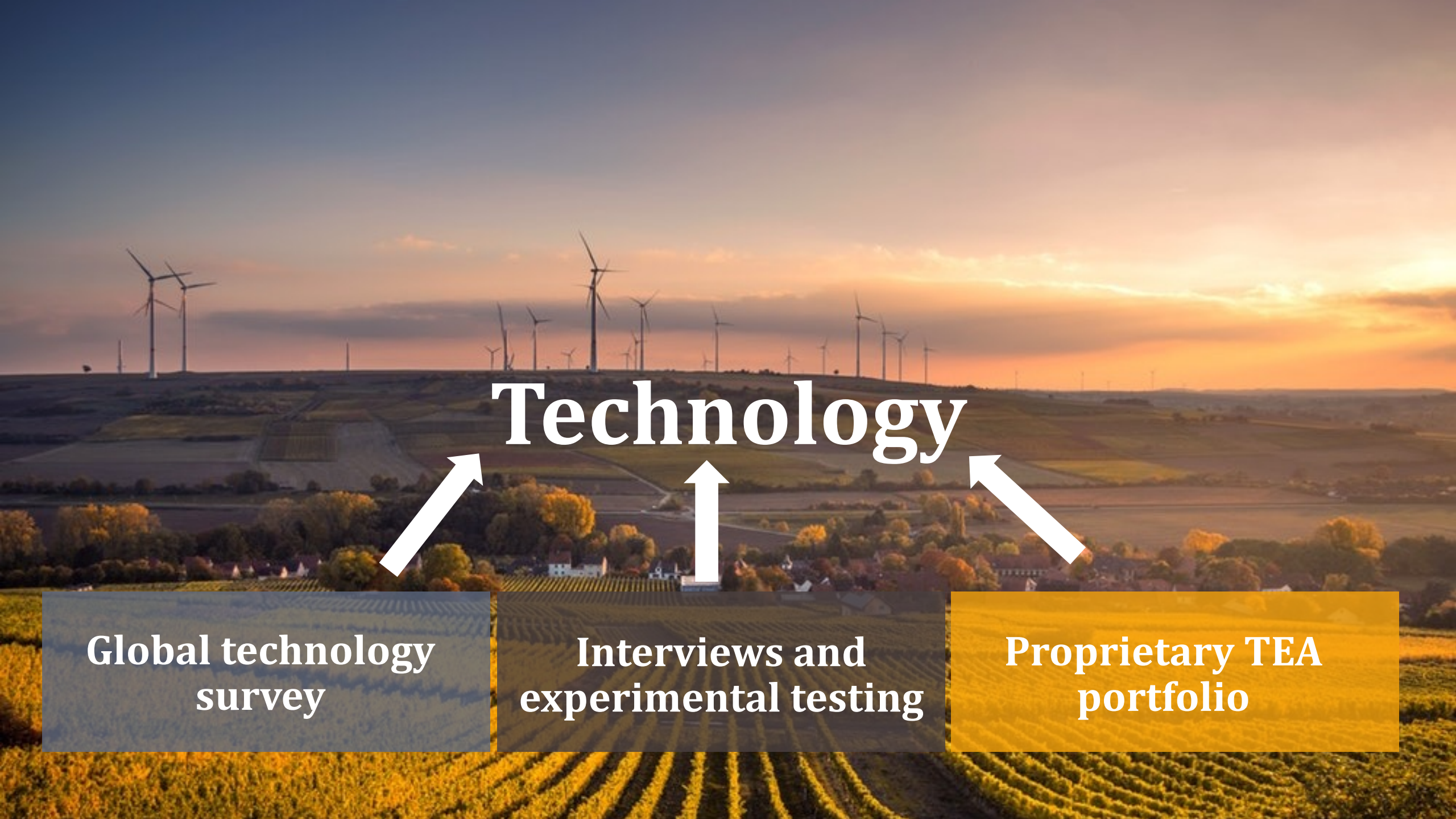

Technology
Global technology survey
Interviews and experimental testing
Proprietary TEA portfolio

NH_3 Technology Landscape

- Interviews and study of many groups around the world
- Included a study of key applied parameters and key risks
- Compiled and categorized technology into 3 major new-tech groups

[1] NH3 Report Jesse S.

fuelcellenergy · Molecule Works Inc. · Case Western Reserve University · University of Arkansas · CERAMATEC · Giner Labs · Monash University · Kansas State University · NREL · Starfire Energy · YARA · PROTON · Oak Ridge National Laboratory · STORAGENERGY · Chemical and Biological Engineering · Department of Bioproducts and Biosystems Engineering · The University of Utah · Stanford University · RTI International · BayoTech · WSU Wichita State University · Colorado School of Mines · parc

Improved Haber-Bosch

E-chem + Haber-Bosch

Electrochemical Methods

NH_3 Technology Landscape

- Techno-economic analysis indicates that e-chem presents an exciting technology pathway.

[1] NH3 Report Jesse S.

Improved Haber-Bosch

Moderate-pressure, CO_2 intensive

50-150 Bar, Still difficult to scale down

E-chem + Haber-Bosch

Requires intermediate H_2 production

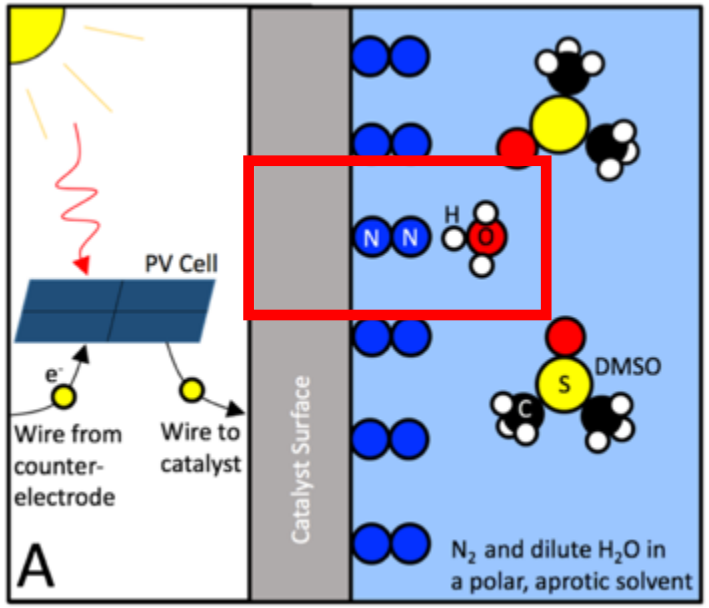
CapEx hurdles including H_2 compression and storage. H_2 production cost remains high. Promising

Electrochemical Methods

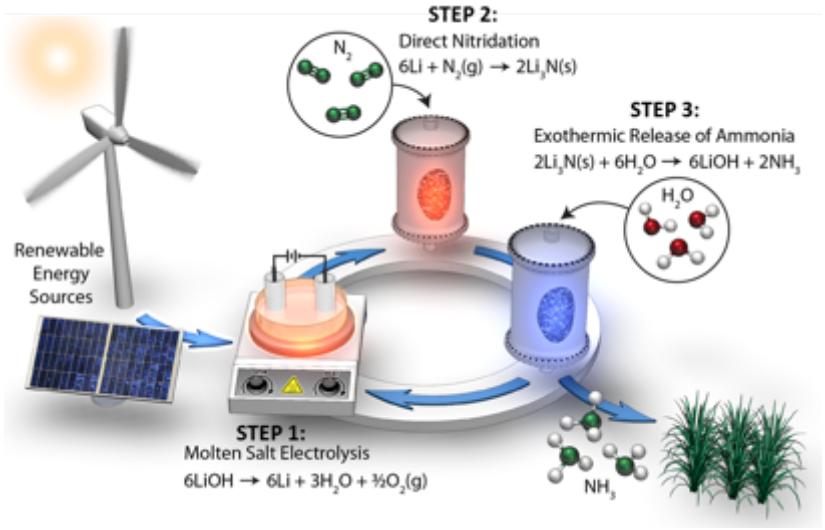
Exciting opportunity!

Less tech-ready

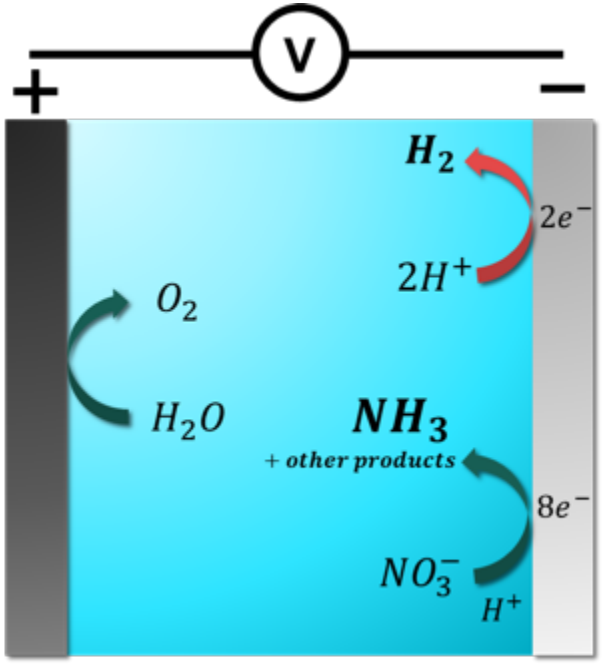
3 Electrochemical Tech Highlights



"Direct electrochemical"

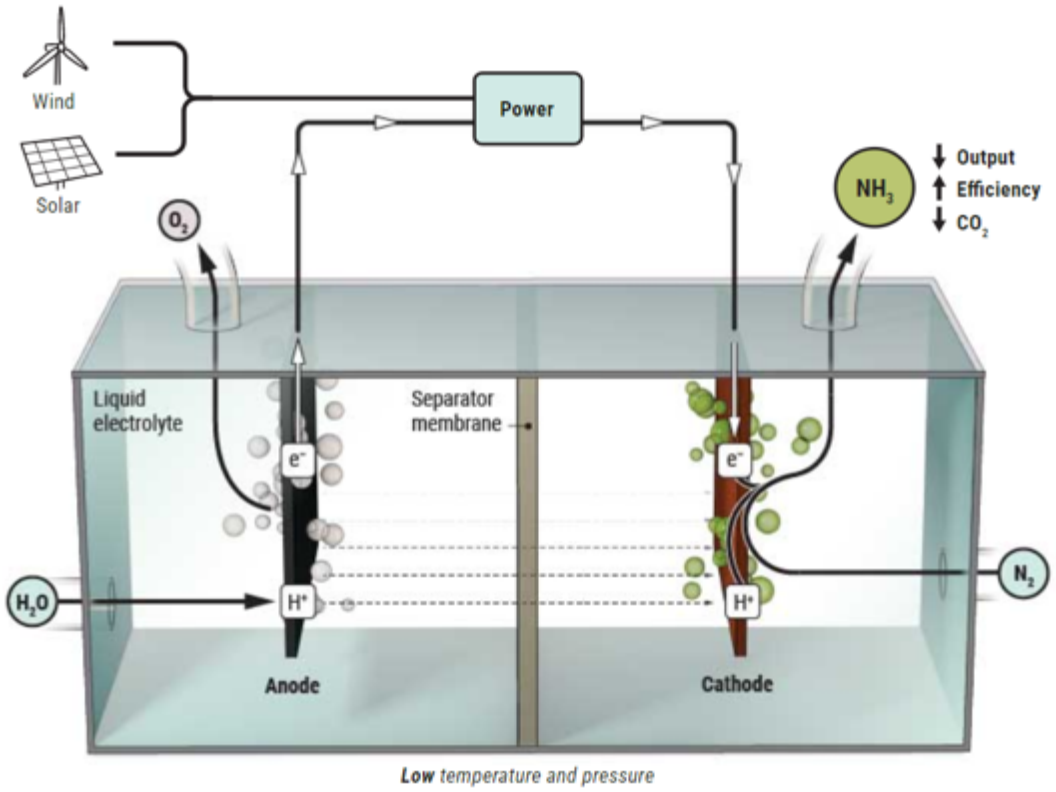


Electrochemical metal cycling



Nitrate reduction

New Tech Highlights: **Direct e-chem**



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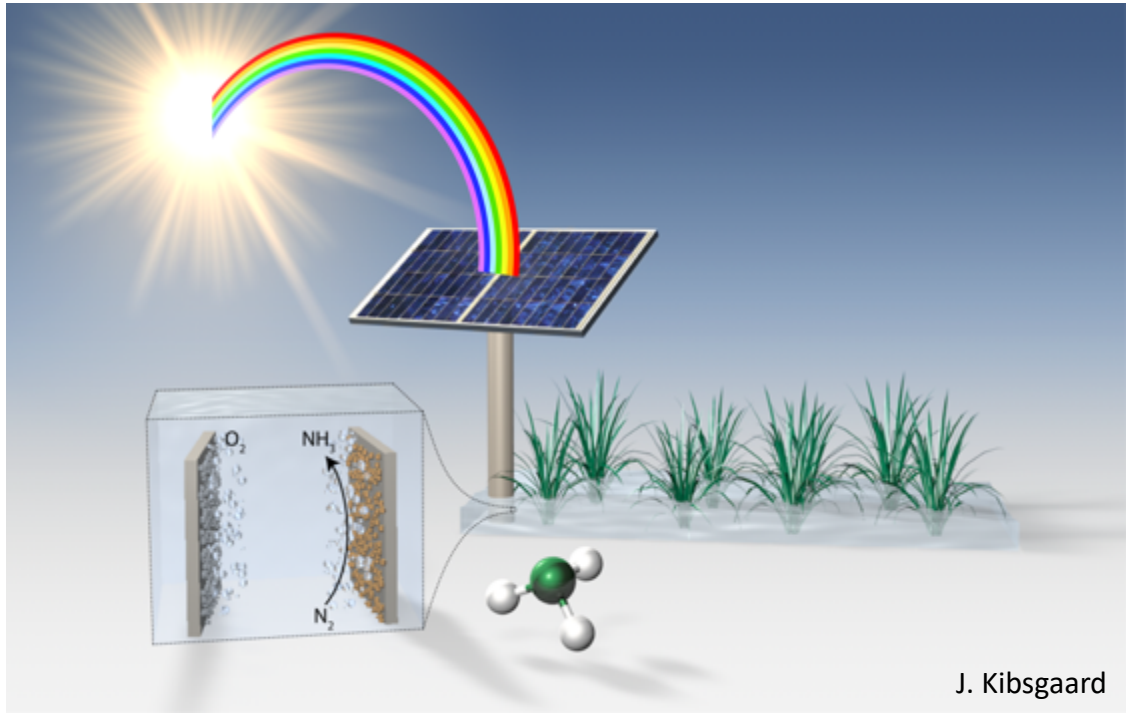
The "Ideal"

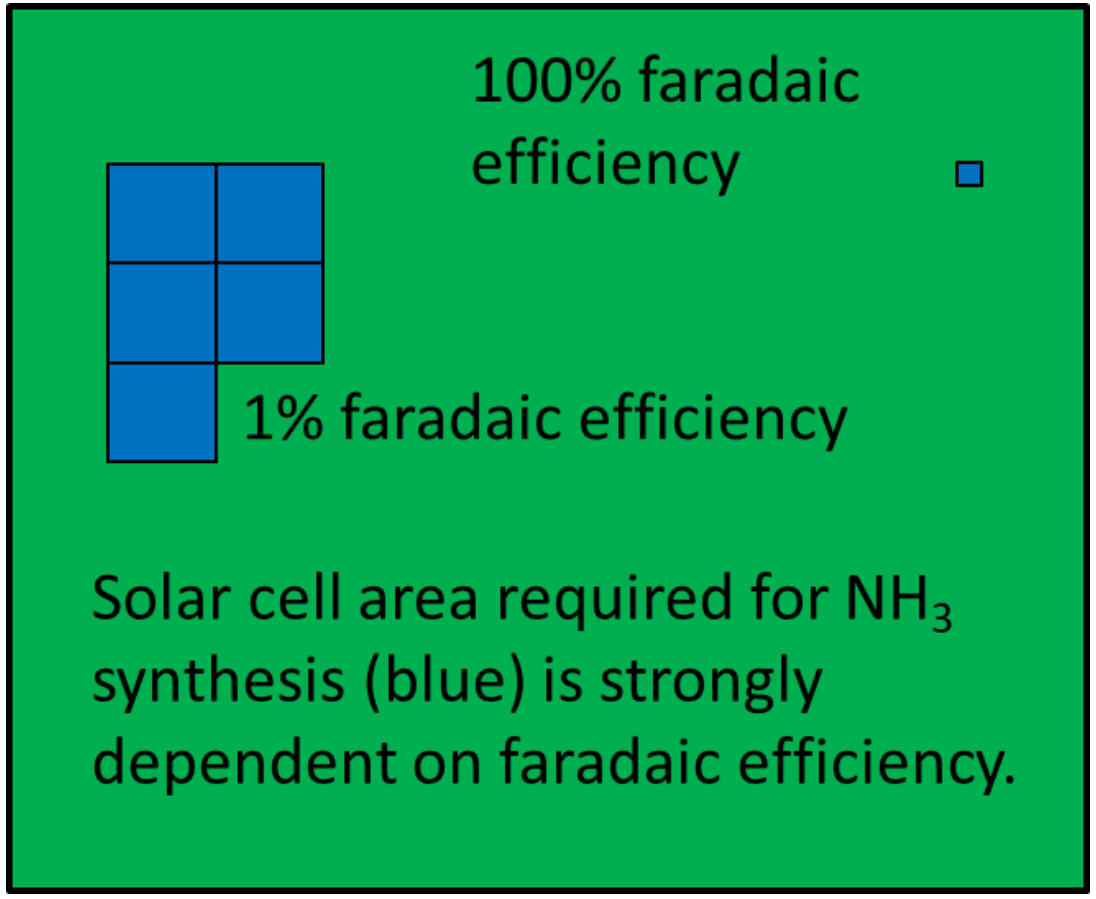


J. Kibsgaard

- Sustainable production from air, water, electricity
- Produced when sun is shining, as needed
- Ambient pressure and temp conditions possible
- Low capital cost gives entitlement for broad use

New Tech Highlights: **Direct e-chem**

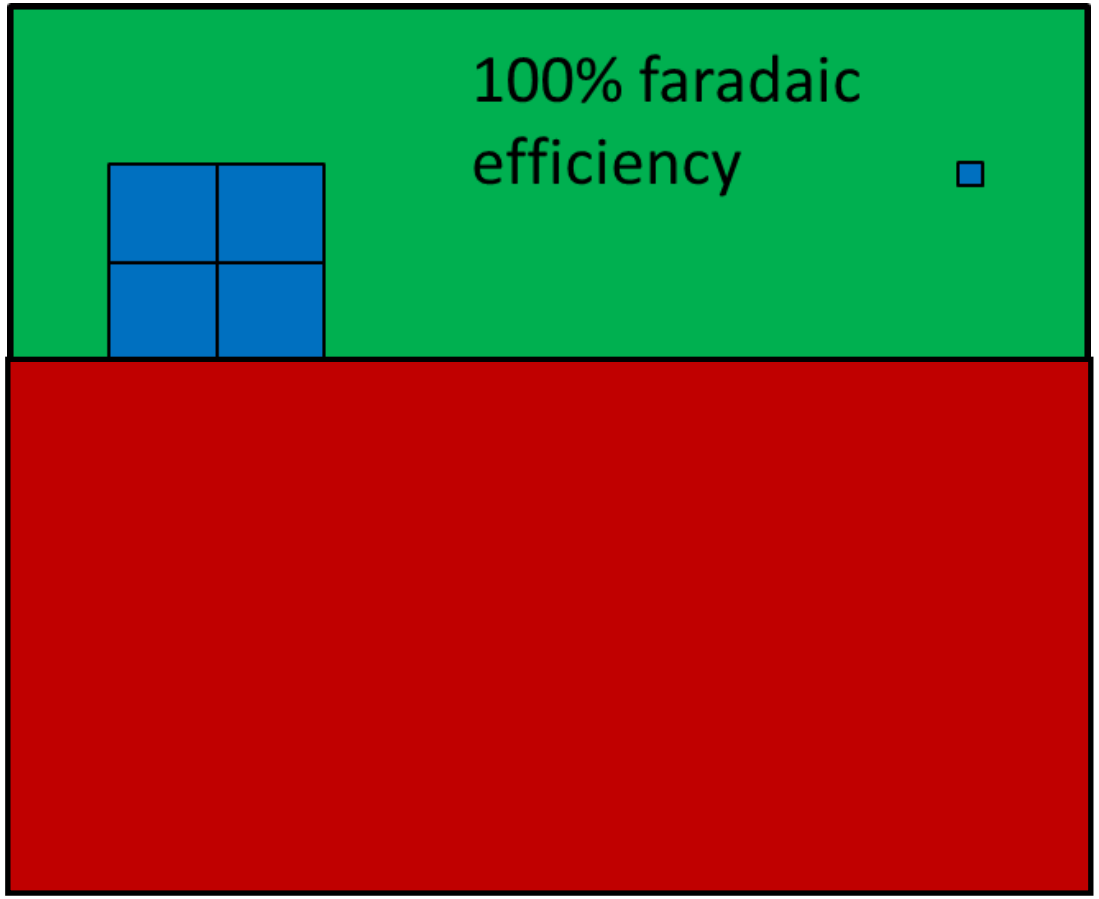
Average farm



- If efficient, requires very little solar area per farm land
- However, most efficient reports operate at only a few uA/cm^2 current densities… (or several mg NH_3/m^2 h)

New Tech Highlights: **Direct e-chem**

Average farm

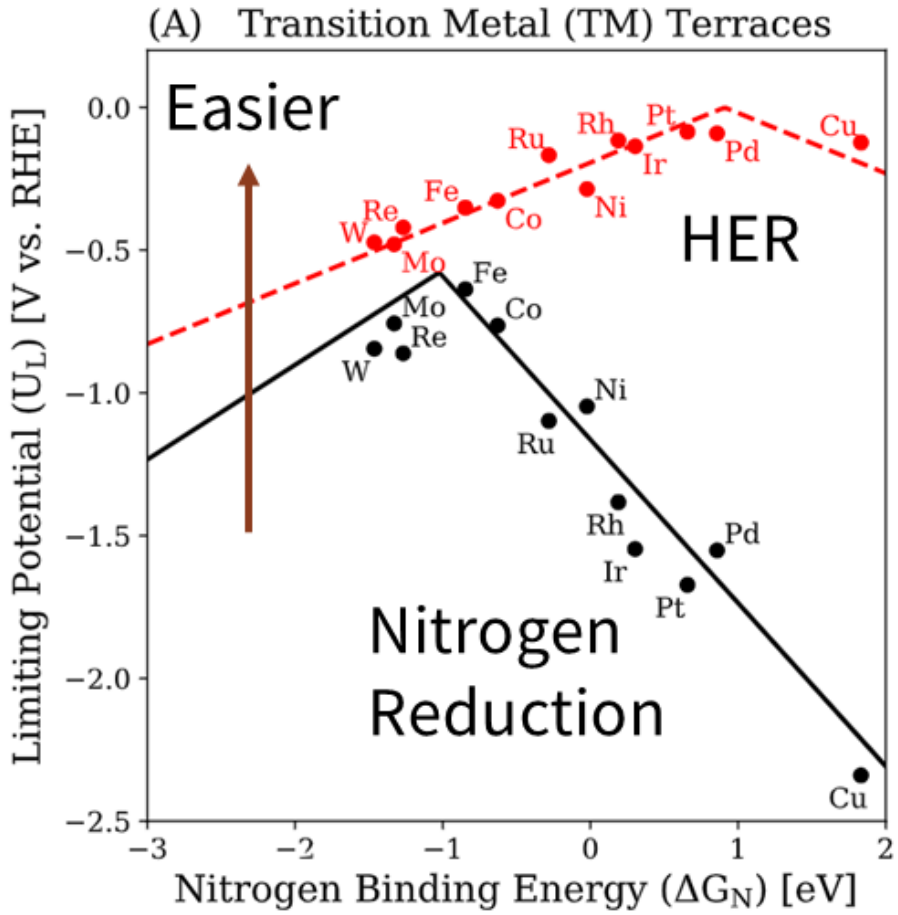


- If efficient, requires very little solar area per farm land
- However, most efficient reports operate at only a few uA/cm^2 current densities… (or several mg NH_3/m^2 h)

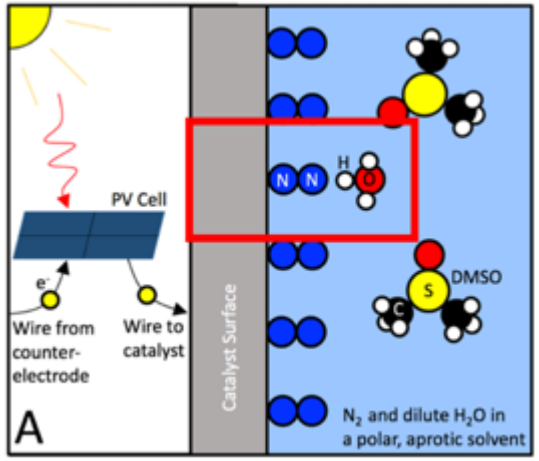
— Approx. geometric area of catalyst required at this rate

Equates to high capital costs – rate must improve!

New Tech Highlights: **Direct e-chem**



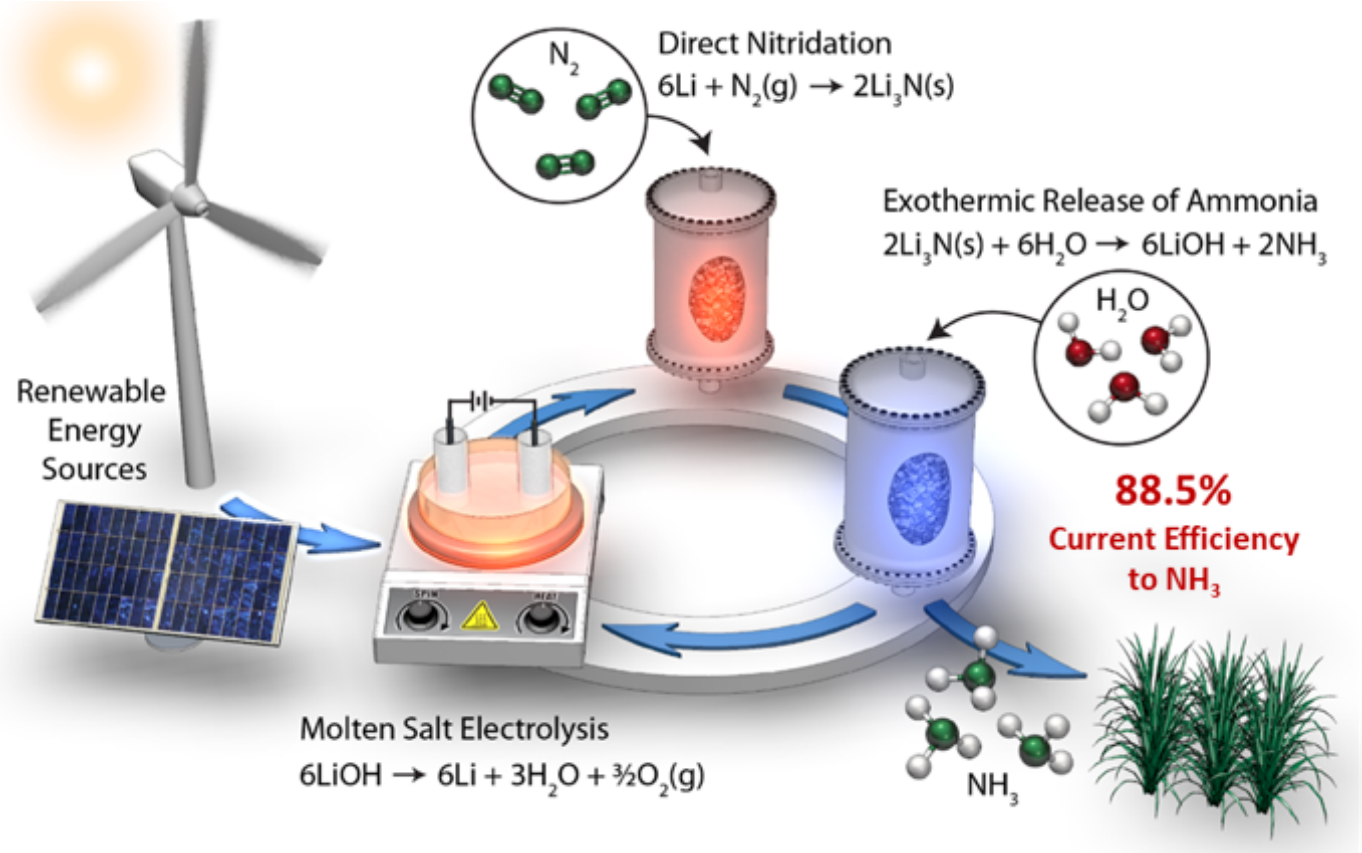
- Hydrogen evolution dominates with water present
- Literature prone to false positives
- Most less than 1% FE and/or very low current densities (<1mA/cm^2)

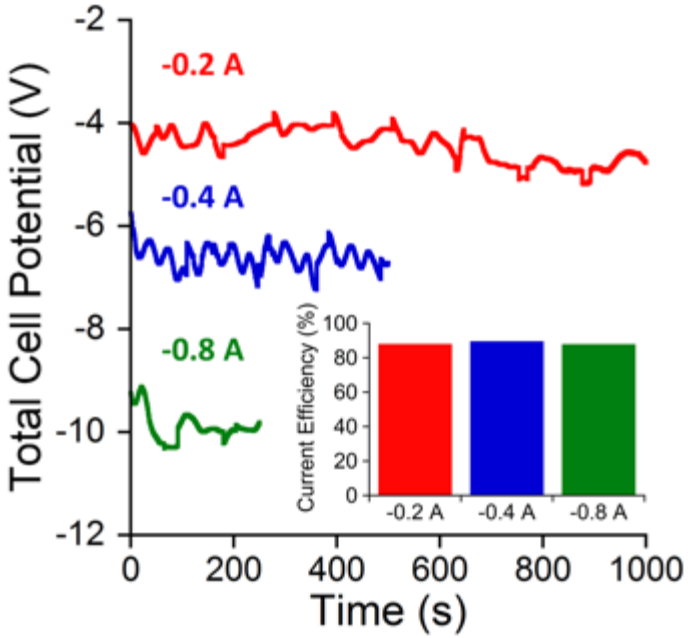


- Limiting protons can improve efficiency
- Stability not yet a focus
- Low “tech-readiness”, long term promise

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.

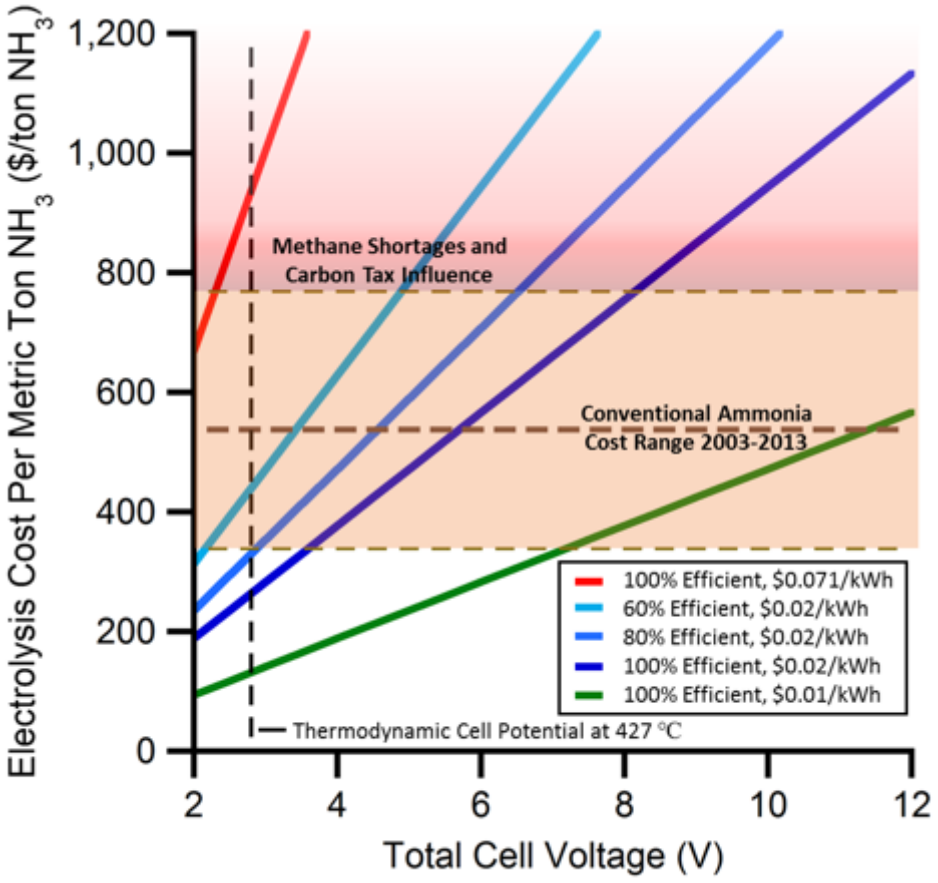
New Tech Highlights: **Electrochemical metal cycling**





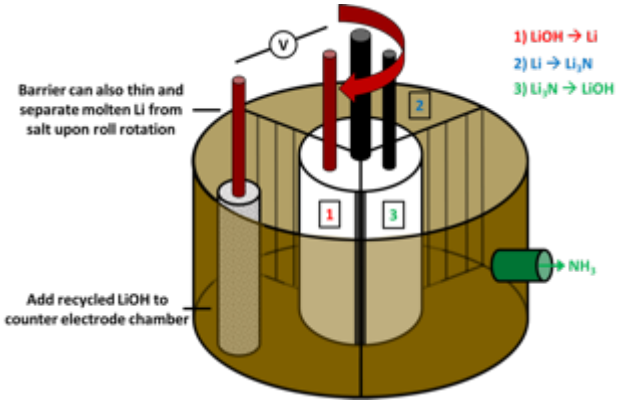
J. M. McEnaney, A. R. Singh, J. A. Schwalbe, J. Kibsgaard, J. C. Lin, M. Cargnello, Thomas F. Jaramillo, J. K. Nørskov *Energy Environ. Sci.* **10** 1621 (2017).

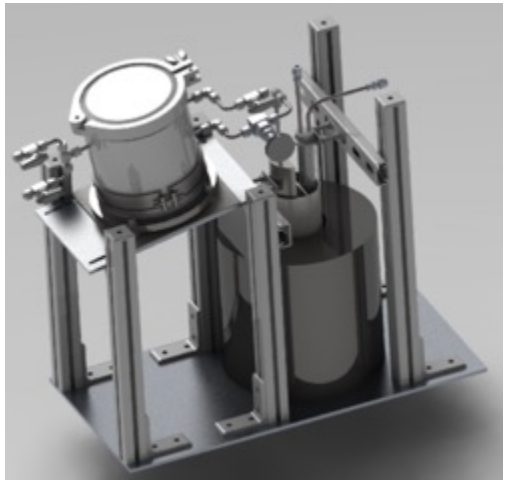
New Tech Highlights: **Electrochemical metal cycling**



- 1000x the rate of "direct electrochemical" methods today (2 A)
- ~90% current efficiency to NH_3 product demonstrated
- Ambient pressure, moderate temperature (350 C)

- Designed and built prototypes for continuous operation and practical implementation





- Electricity cost of electrolysis, not prohibitive with cheap electricity

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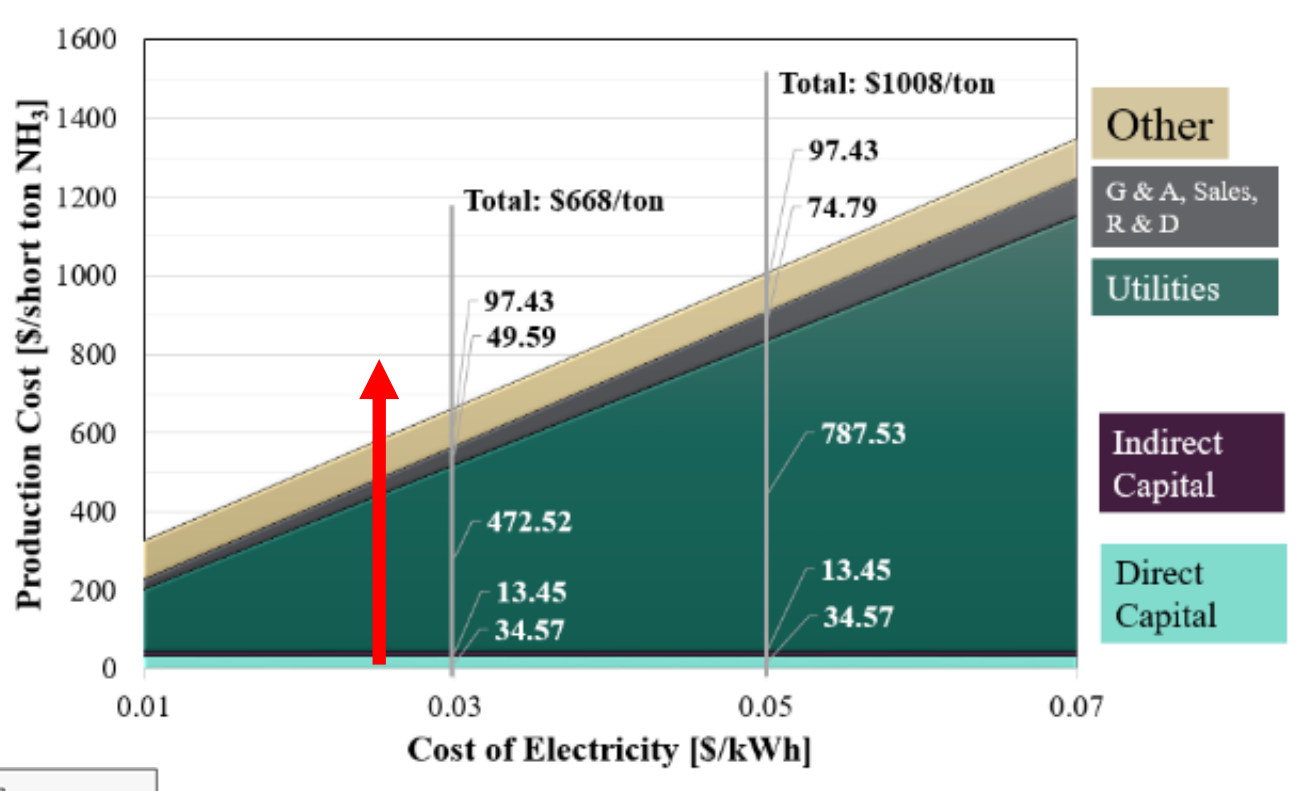
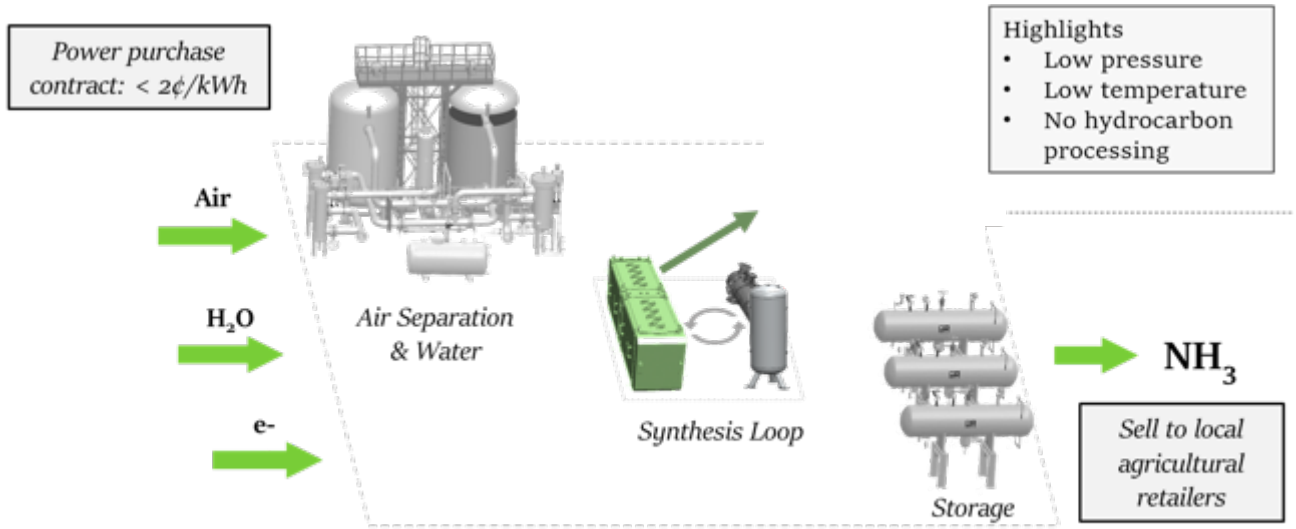
Electrochemical metal cycling

- Detailed plant modeling and TEA





- 10 TPD scale
- ~~10 year depreciation~~ → 2 year depreciation (Li Cells Today)
- Not too far off – need dirt cheap electricity

Li cell stability requires innovation to decrease CapEx

[1] McEnaney J. et al. (2017). Energy Environ. Sci 2017. 10, 1610.
[2] Stratasys

New Tech Highlights: **Nitrate reduction**

Nitrate waste is an environmental pollutant

- Algal blooms/Habitat loss
- Birth defects/Health issues
- Significant denitrification research

to form N_2 gas…

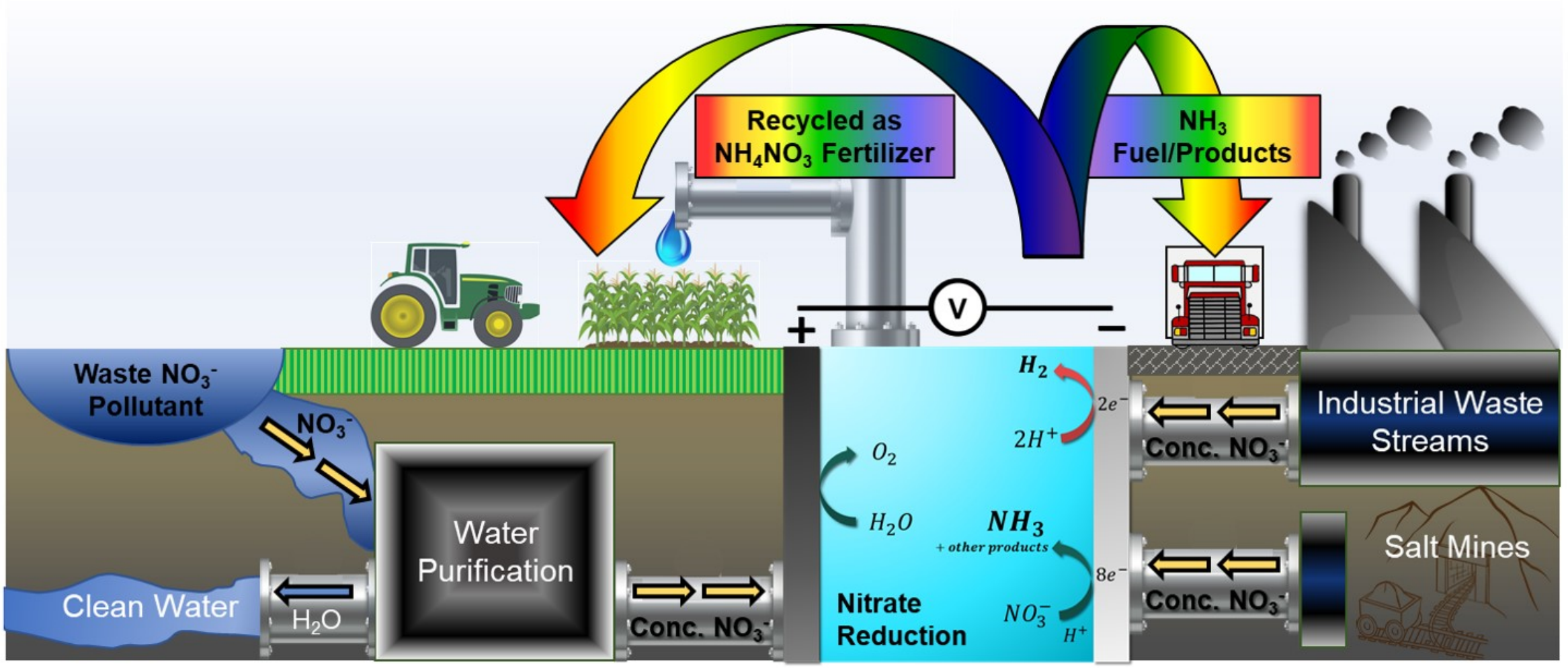
Nitric acid is made from NH_3

- Source of NH_4NO_3 fertilizer
- N_2O byproduct is a potent GHG (300x CO_2)
- 118 MmTCO_2e GHG emissions
- ~1% of all non CO_2e from HNO_3

What if we could turn waste nitrates into a useful product?

J. M. McEnaney, S. J. Blair, A. C. Nielander, J. A. Schwalbe, M. Cargnello, Thomas F. Jaramillo, *ACS Sustainable Energy and Fuels,* 2019 Submitted manuscript

New Tech Highlights: **Nitrate reduction**



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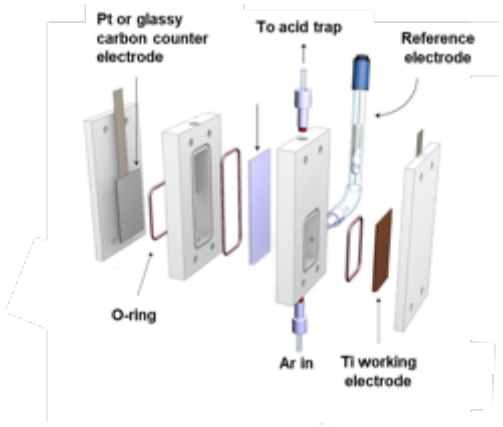
New Tech Highlights: **Nitrate reduction**

Electrolyte engineering for selectivity to NH_3: Success!

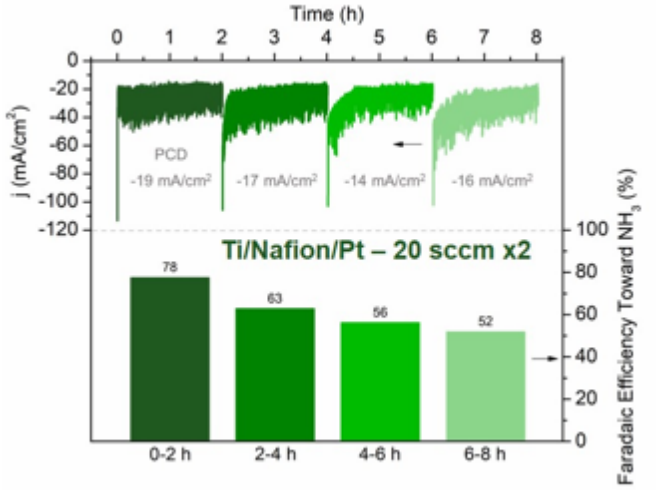
Literature Comparison

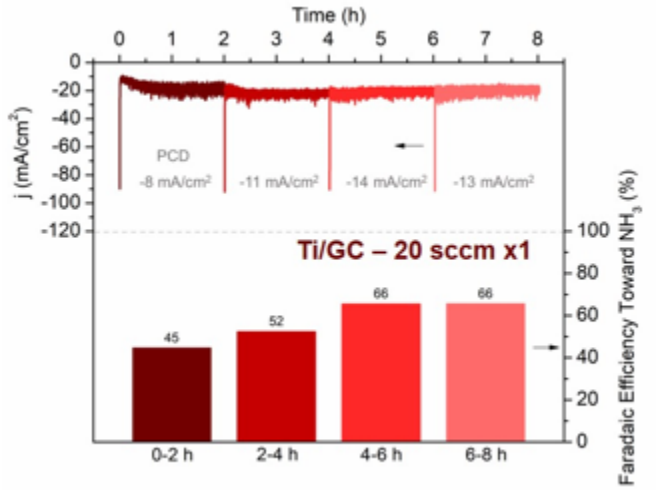
Cathode	Conditions	Max Faradaic Efficiency to NH_3 Reported	Partial Current Density to NH_3 (mA/cm^2)	Reference
Fe Cu Ti	100 mg/L (1.2 mM) $NaNO_3$ -20 mA/cm^2 applied Neutral pH	11 % 3.2 % 2.5 %	-2.2 -0.6 -0.5	*Electrochimica Acta* **2009,** *54* (20), 4600-4606.
Al Bi Zn Sn In Pb	0.050 M $NaNO_3$ -1.8 V vs Ag/AgCl Variable pH (0.16-13.7)	12 % <10 % <10 % <10 % <10 % <10 %	N/A	*Environmental Technology* **2013,** *34* (3), 373-381.
Ti	50 mg/L (0.6 mM) $NaNO_3$ -38 mA/cm^2 applied Neutral pH	5.6 %	-2.1	*J Electroanal Chem* **2016,** *782*, 270-277.
Sn	0.05 M $NaNO_3$ (2 M NaCl) -2 V vs Ag/AgCl Neutral pH	14.5 %	~-5	*Electrochimica Acta* **2007,** *52* (23), 6412-6420.
Rh/graphite	1 M $NaNO_3$ (1 M NaCl) -4mA/cm^2 Neutral pH	24 %	-1	*Electrochimica Acta* **2007,** *52* (21), 6237-6247.
Ti	**0.3 M KNO_3 0.1 M HNO_3 -1 V vs RHE Acidic pH**	**82 %**	**-22**	***This work***



Literature denitrification focus (H_2 and N_2 products)

Optimization toward NH_3 production





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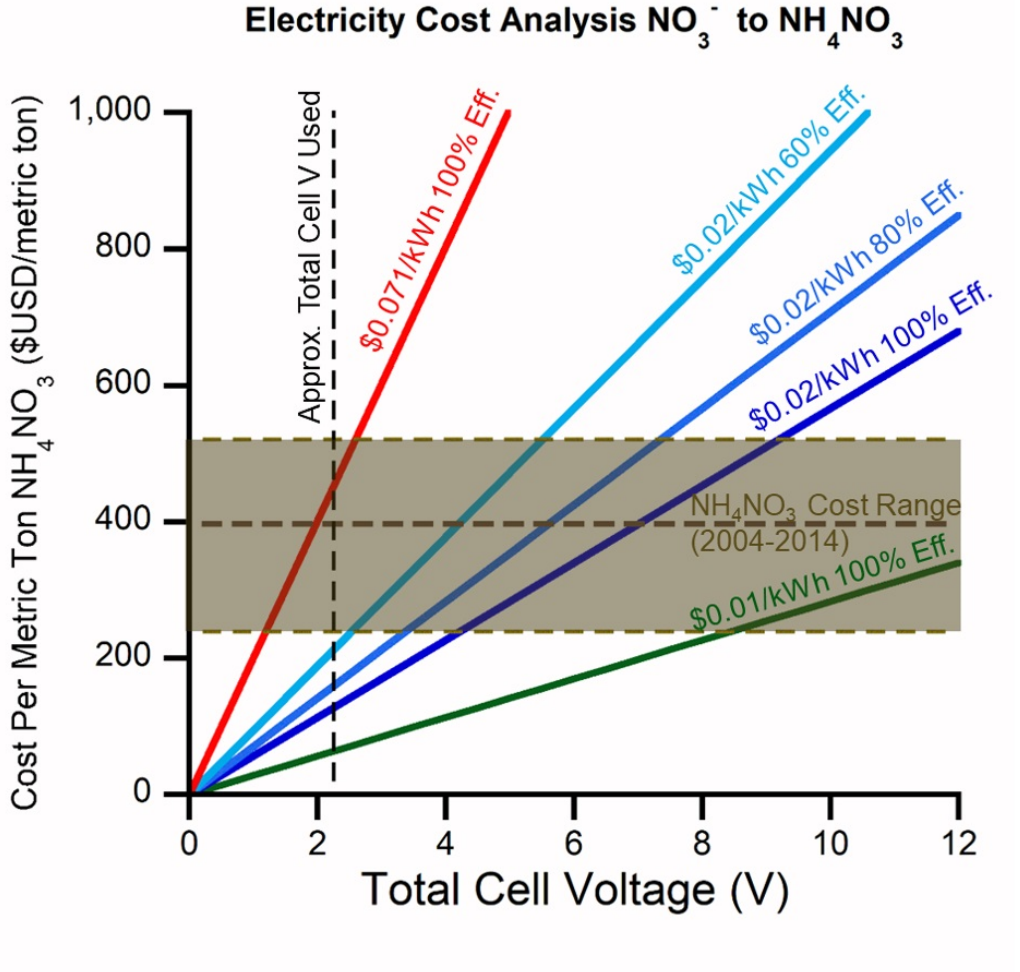
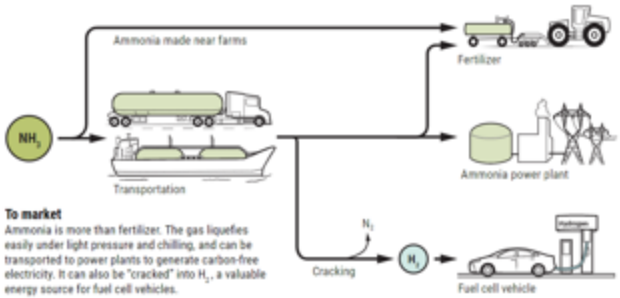
New Tech Highlights: **Nitrate reduction**

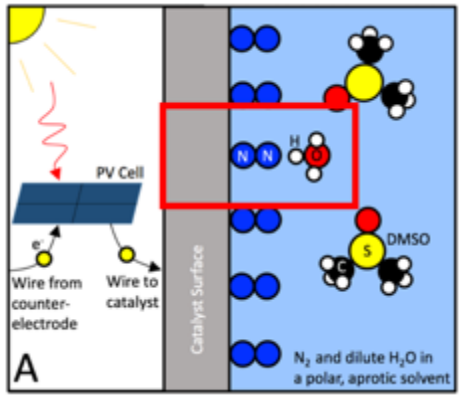


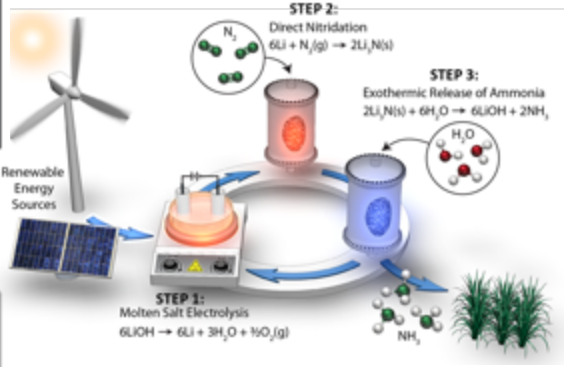
- Despite $8e^-$ reduction process, the electricity cost to produce NH_4NO_3 is not prohibitive
- Dependent on ability to concentrate waste nitrate source
- Need to mitigate electrode stability issues
- If electricity were cheap enough, could convert all to NH_3

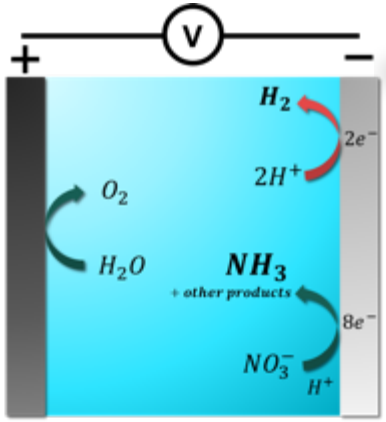
J. M. McEnaney, S. J. Blair, A. C. Nielander, J. A. Schwalbe, M. Cargnello, Thomas F. Jaramillo, *ACS Sustainable Energy and Fuels,* 2019 Submitted manuscript

Summary









New tech development to build NH_3 economy

- Direct Electrochemical (improvements)
  - Ideal, low-cost opportunity
  - Low rates and efficiencies
- Electrochemical Metal Cycling
  - Great rate and efficiency
  - Cell stability issues
- Electrochemical Nitrate Reduction
  - Great environmental opportunity
  - Electrode stability issues

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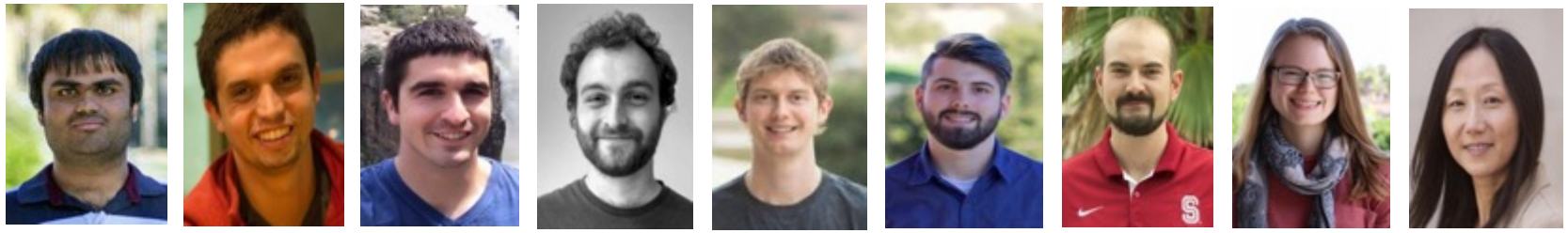
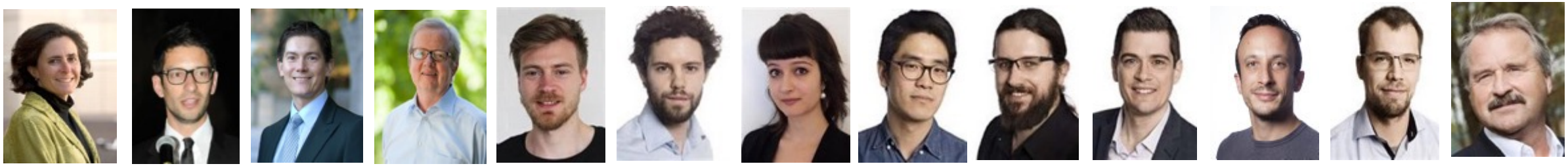




Nitricity Team

Nico Pinkowski | co-founder

Josh McEnaney | co-founder

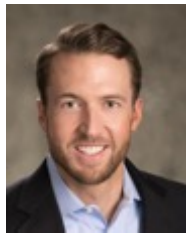
Brian Rohr | operations

Jay Schwalbe | VP of tech

Mentors

Business

Cody Friesen
CEO Zero Mass Water



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Finance

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Engineering Scale-up

GJ Ia O'
Primus Power

Scientific Advisory Council

Jens Nørskov
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Tom Jaramillo
Professor, Stanford University


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