

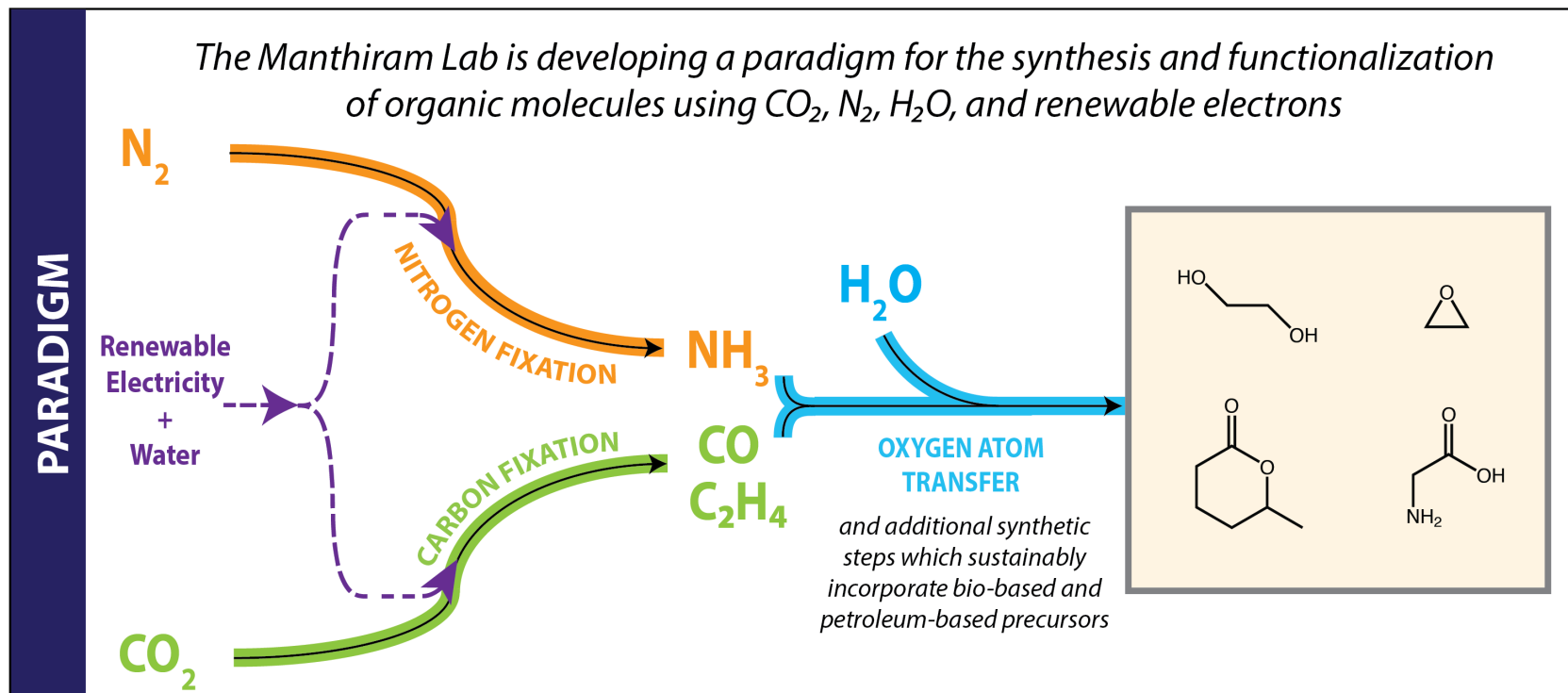
# Electrification of Ammonia Synthesis

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# Manthiram Lab: Electrifying and decarbonizing chemical transformations

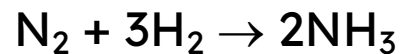


Air, water, and renewable electrons are distributed, sustainable resources

Electrical potential enables mild conditions of operation, replacing temperature and pressure

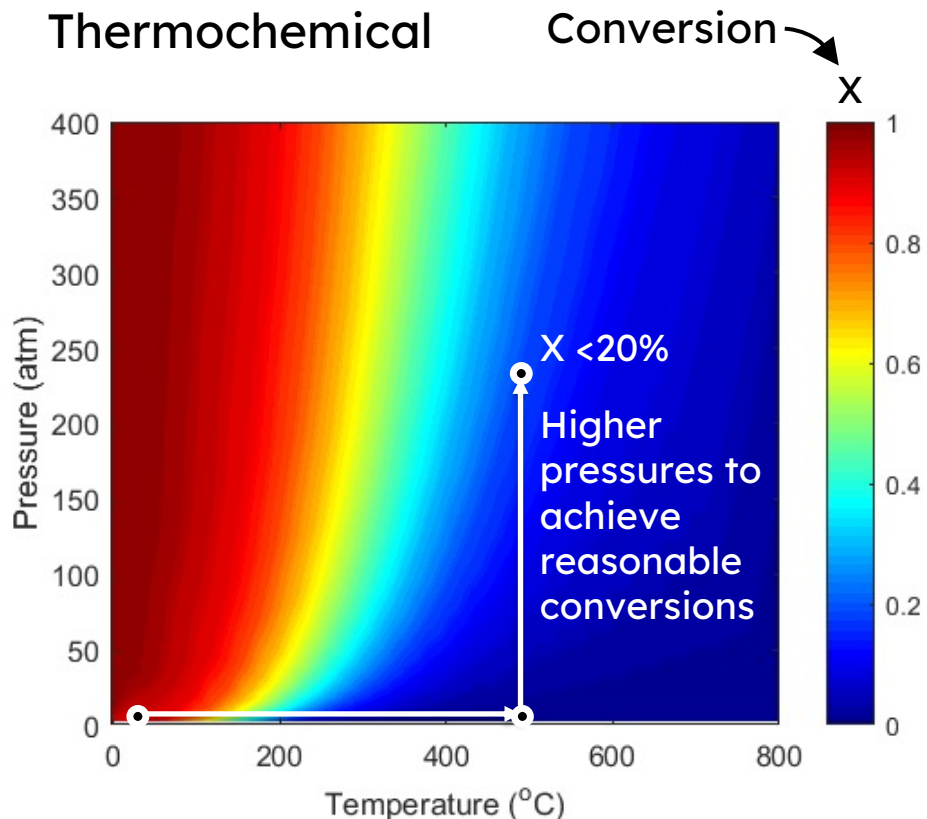
Our lab has developed new catalysts and integrated processes for electrically-driven ammonia synthesis, carbon dioxide fixation, and plastic production

# Replacing pressure with voltage



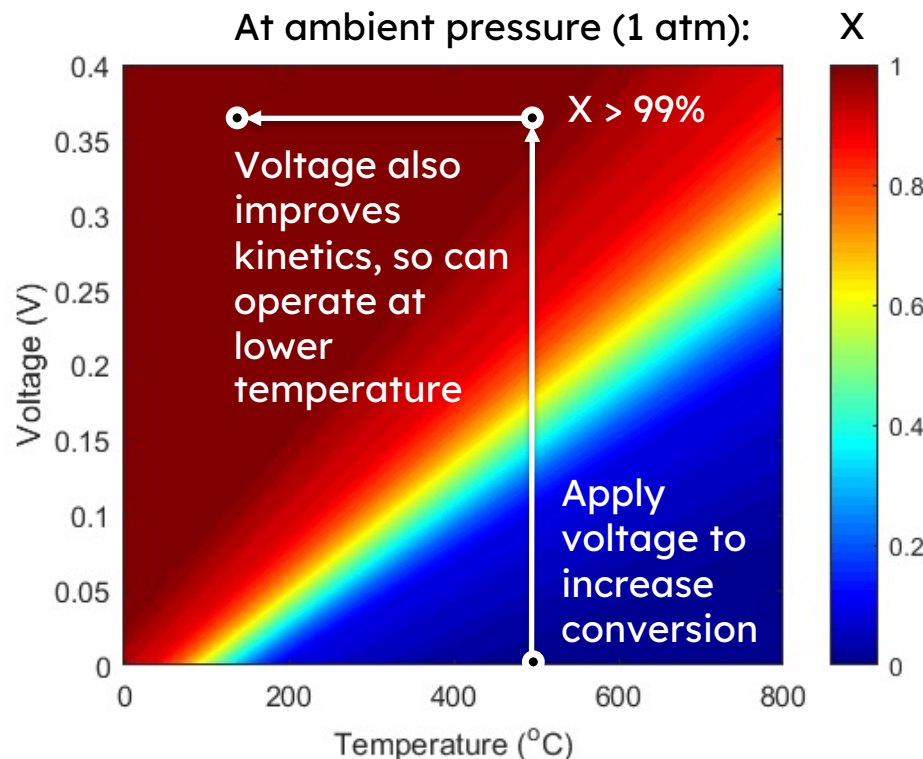
Zachary Schiffer

## Thermochemical

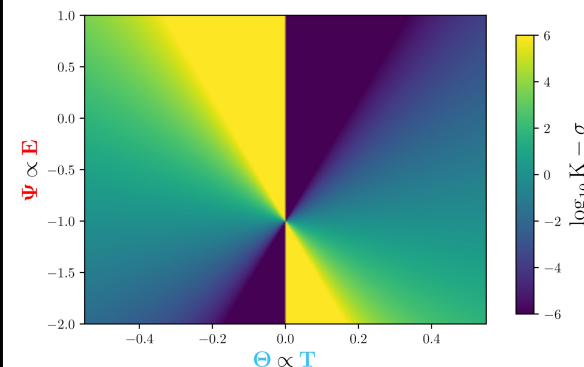
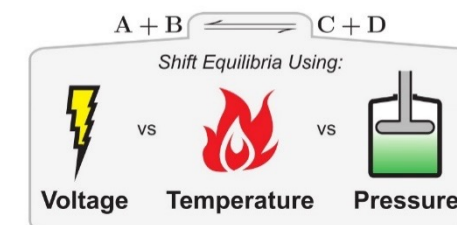


Higher temperatures to achieve reasonable rates

## Electrochemical



Should temperature, pressure, or voltage be used to drive a given chemical reaction?



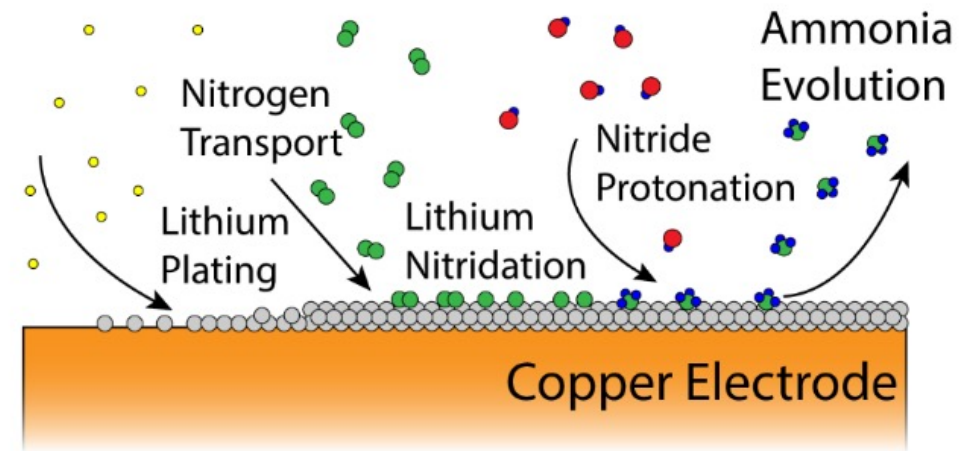
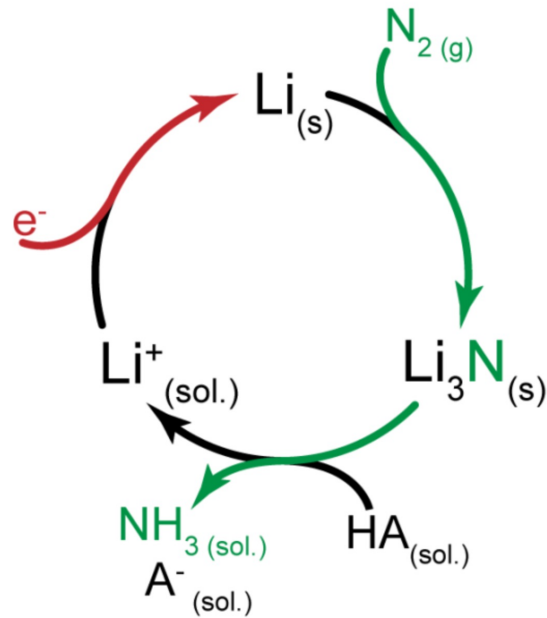
Z. J. Schiffer, A. Limaye, and K. Manthiram, *Joule* 5, 135-148 (2021).

Z. J. Schiffer and K. Manthiram *Joule* 1, 10-14 (2017).

# Lithium mediated ammonia synthesis



Nikifar Lazouski



Cycle involving electrochemical and thermochemical steps

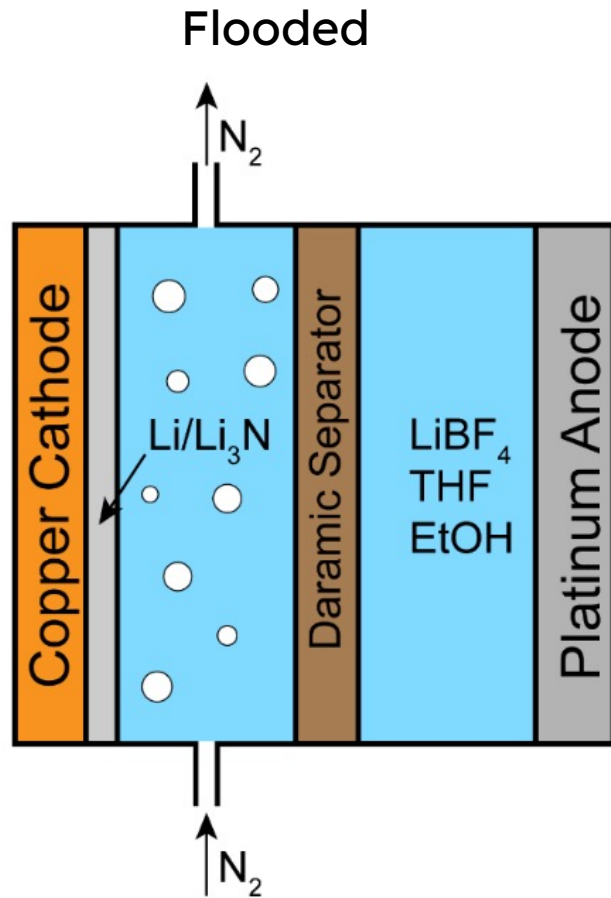
Reactions occur continuously at electrode surface

Fichter, P. G. F, Erlenmeyer, H. *Helv. Chim. Acta* (1930)

Tsuneto, A. J. *Electroanal. Chem.* (1994)

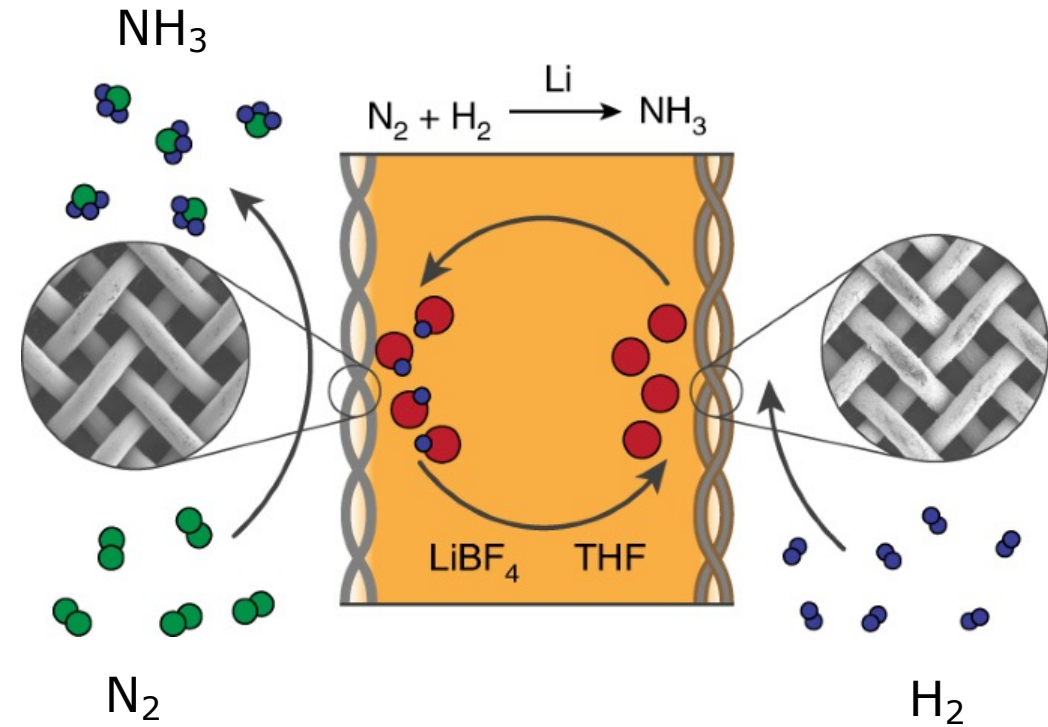
N. Lazouski, Z. J Schiffer, K. Williams, and K. Manthiram, *Joule* 3, 1127-1139 (2019).

# Overcoming transport limitations and undesired overall reaction



Rates limited by transport,  
undesirable proton source,  
and low energy efficiency

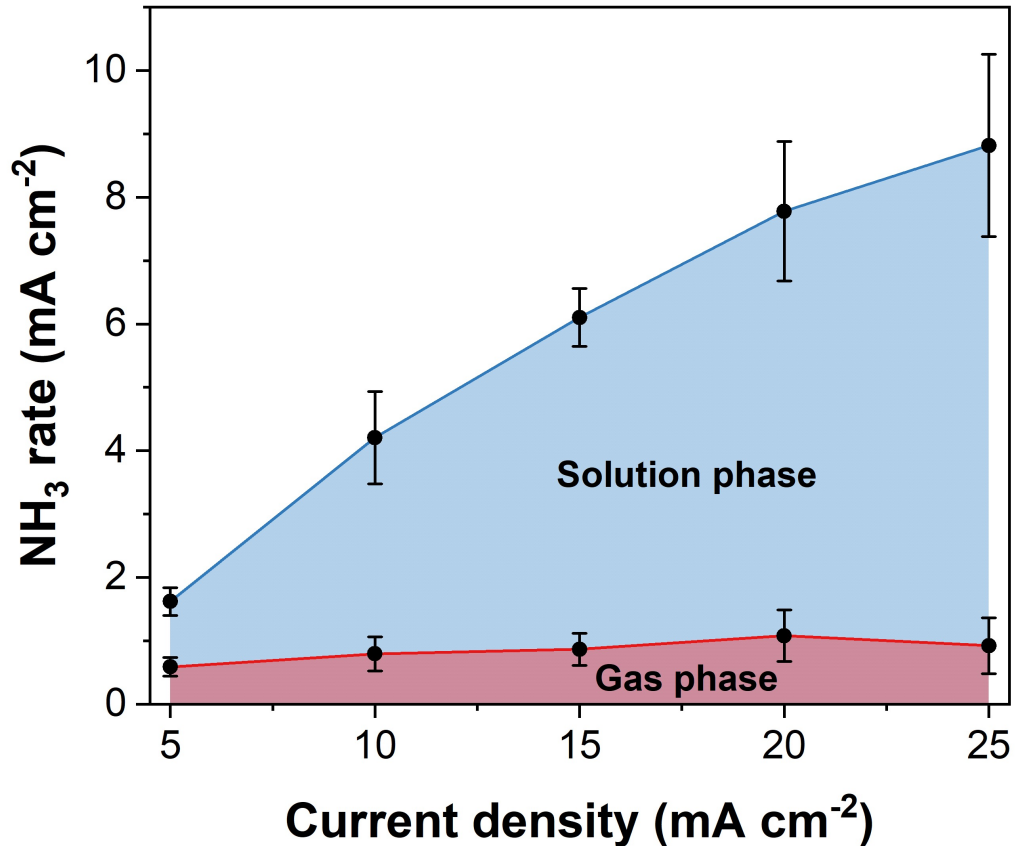
## Non-aqueous gas diffusion electrodes



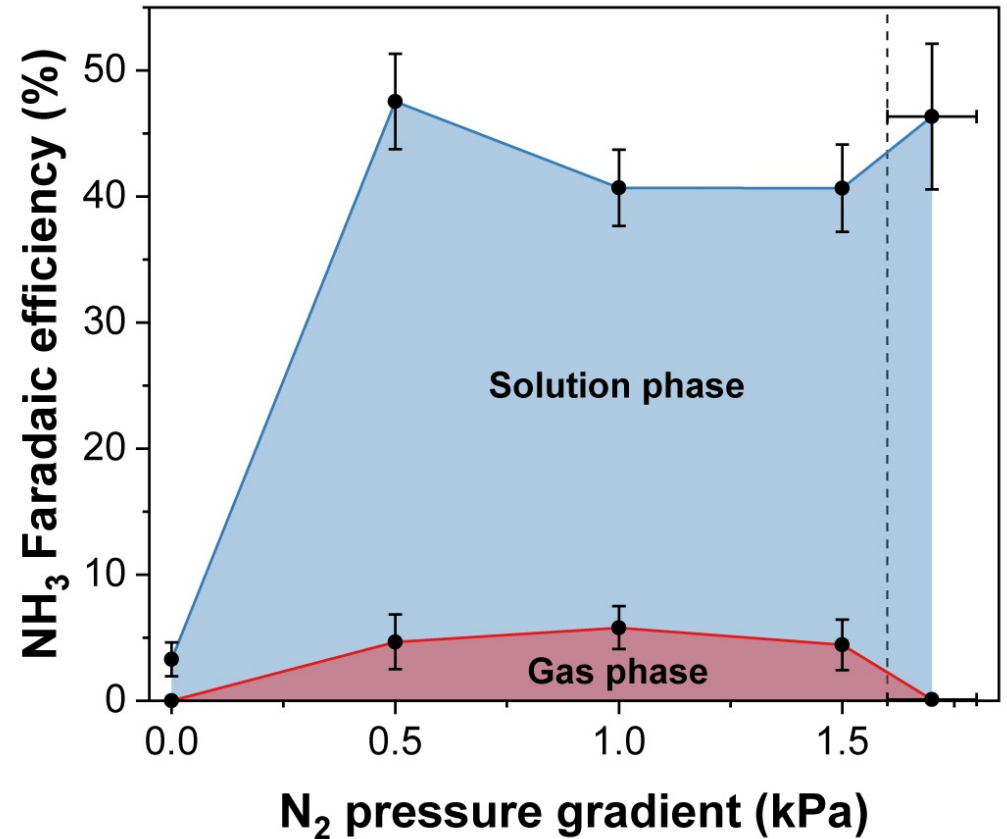
Metal cloth-based gas diffusion  
electrodes to enable



# Rates of ammonia synthesis above the flooded transport limit

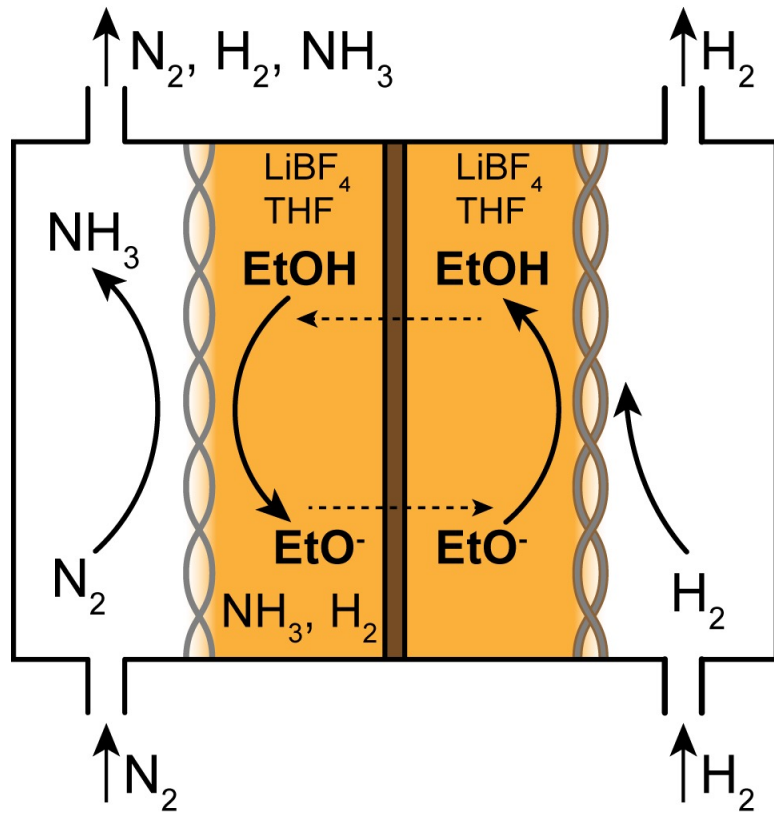


The rate of nitrogen reduction is increased significantly, with some produced ammonia found in the gas phase

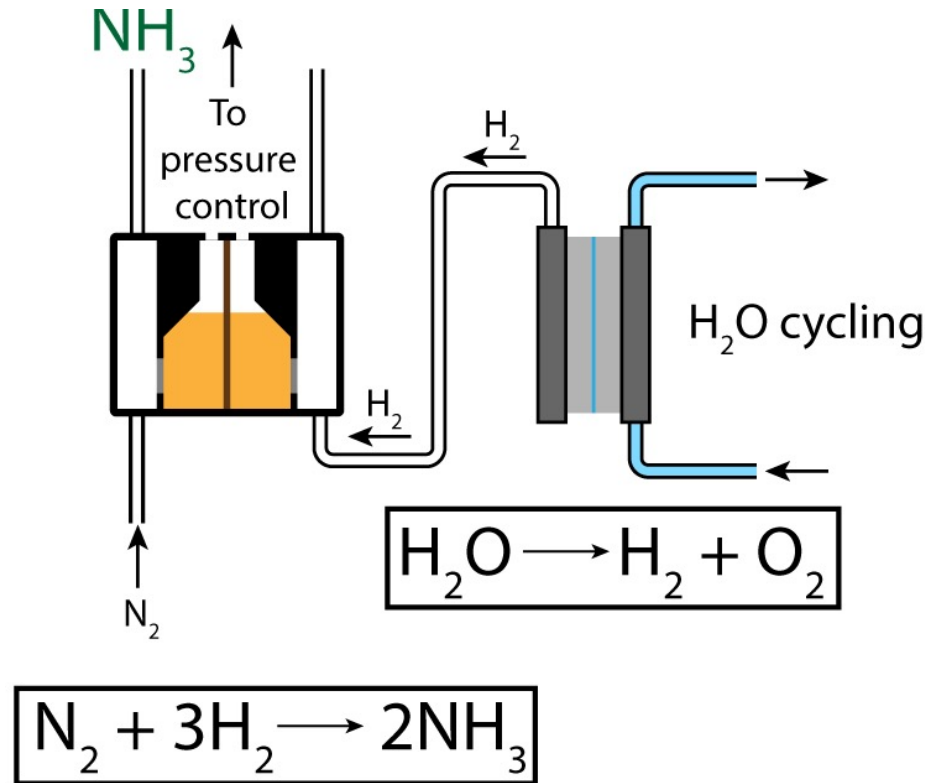


High FEs can be obtained at 15 mA cm<sup>-2</sup> at non-zero pressure gradients across the GDE

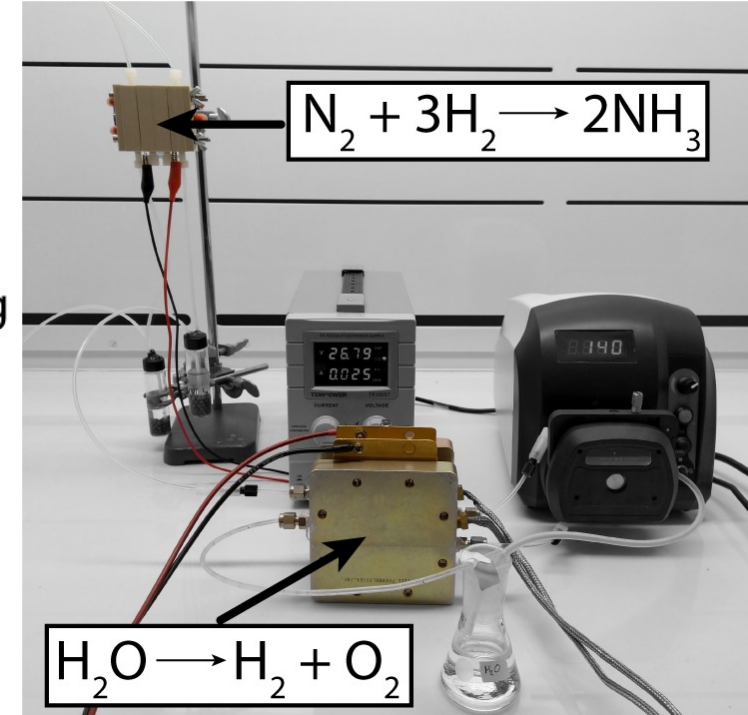
# Coupling to water splitting



Hydrogen oxidation at the anode can replenish protons in the electrolyte

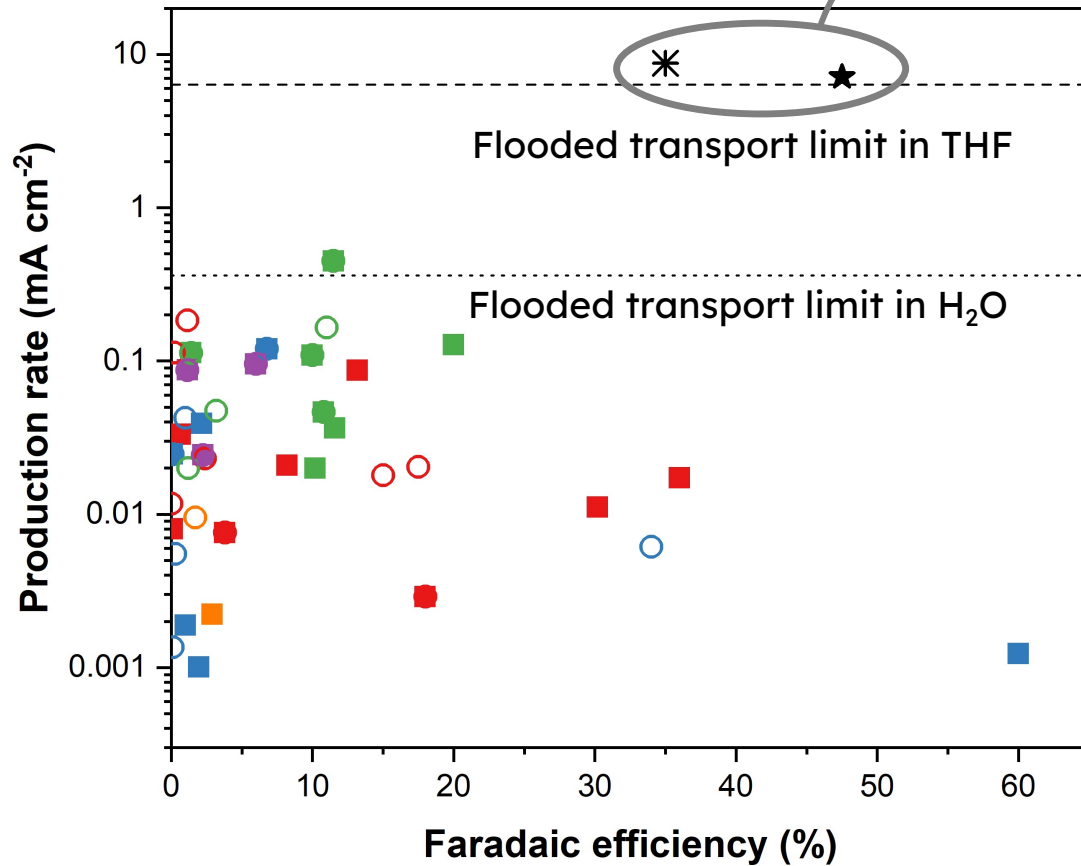


Water splitting-derived hydrogen can be used at the anode to have overall ammonia production from  $\text{N}_2$  and  $\text{H}_2\text{O}$

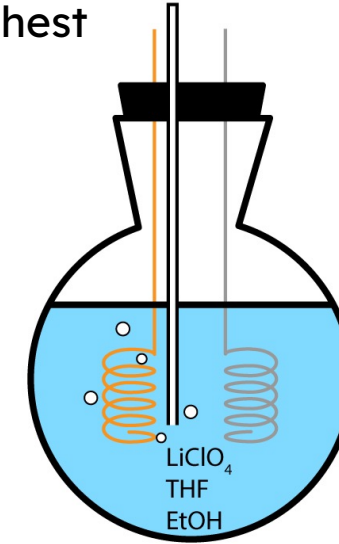


# Comparing our system to reported catalysts

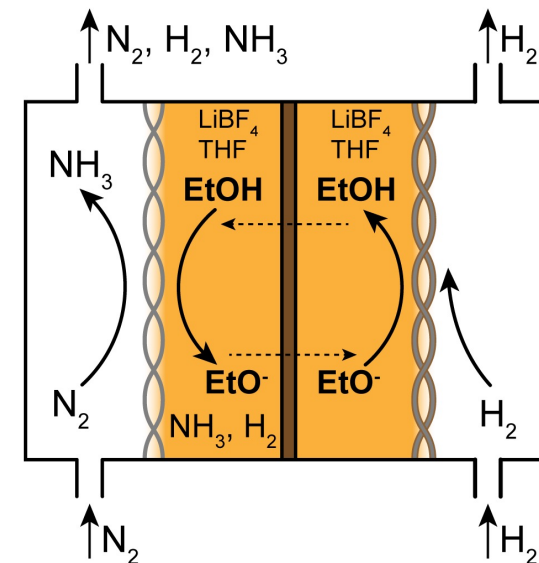
Our approach achieves the highest rates for a semi-batch process



Energy efficiency of 2% -  
critical barrier to overcome



Tsuneto (1994)  
8.4% FE  
 $0.16 \text{ mA cm}^{-2}$

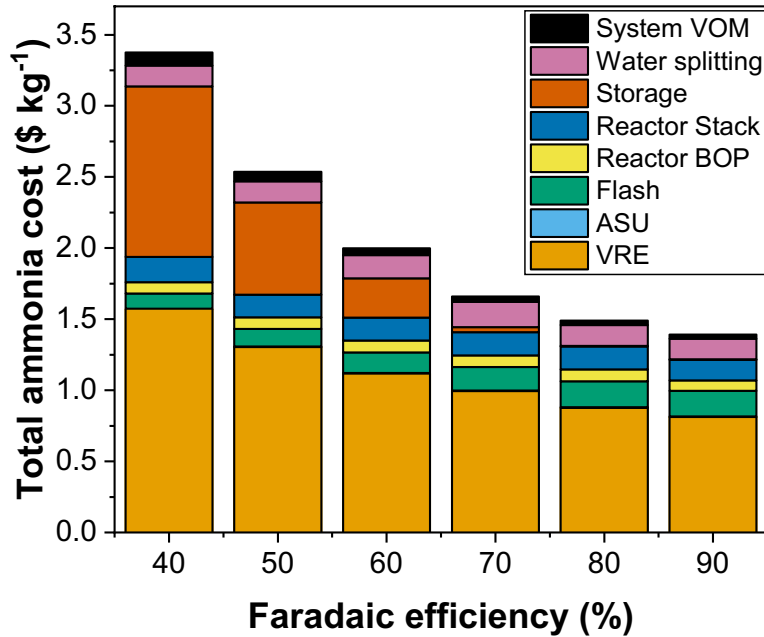


Our work (2020)  
47% FE  
 $8.7 \text{ mA cm}^{-2}$

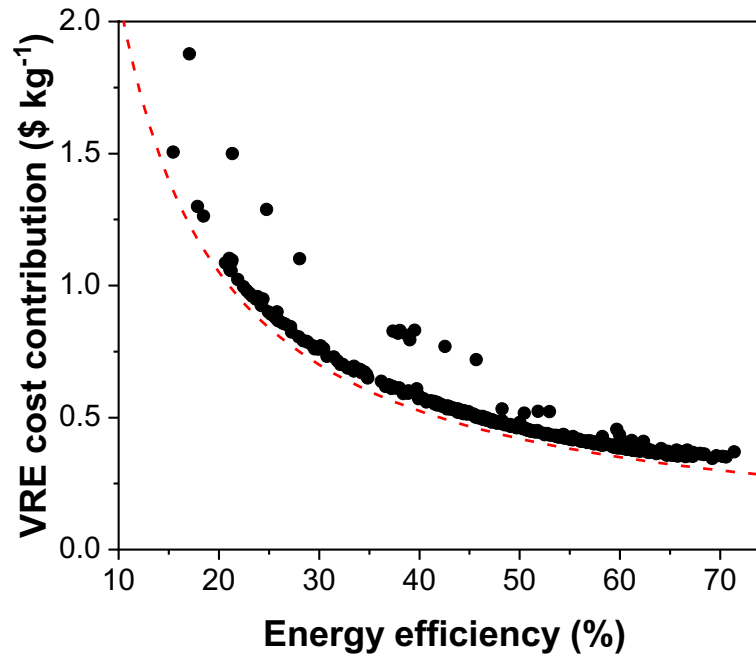


# Further improvements in rate and energy efficiency are necessary

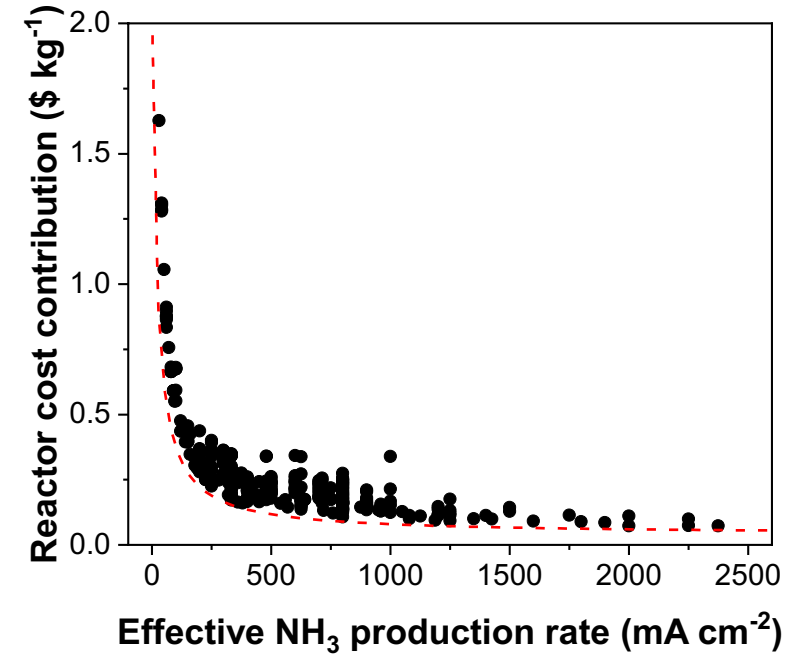
(with D. Mallapragada, MIT Energy Initiative)



Detailed technoeconomic analysis of large-scale process can determine optimal NH<sub>3</sub> cost given process characteristics



Energy efficiency of NH<sub>3</sub> reactor predicts VRE (and storage) costs well; ~40% efficiency is necessary



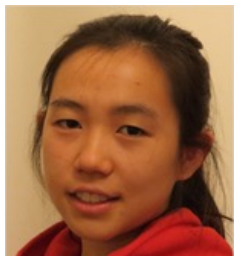
Capital cost of reactor can be predicted by production rate of ammonia; ~400 mA cm<sup>-2</sup> partial current is necessary

250 tons/day  
VOM: Variable Operating and Maintenance Costs  
ASU: Air Separation Unit  
BOP: Balance of Plant  
VRE: Variable Renewable Energy

# Acknowledgements



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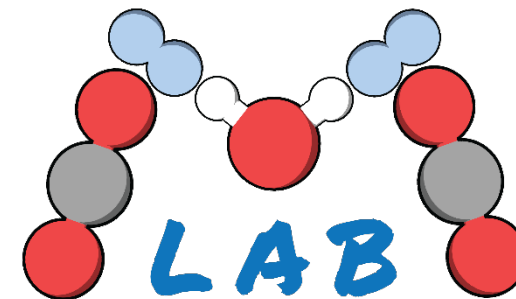
Nikifar  
Lazouski



Trent  
Weiss



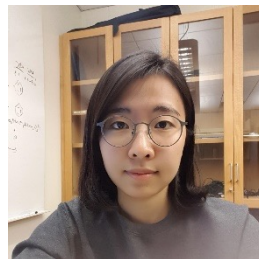
Zachary  
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Corbin



Minju  
Chung



Joseph  
Maalouf



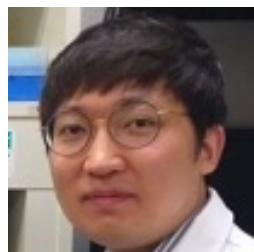
Sayandeep  
Biswas



Fang-yu  
Kuo



Simar  
Mattewal



Hee Jo  
Song

## Funding



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