Electrification of Ammonia Synthesis

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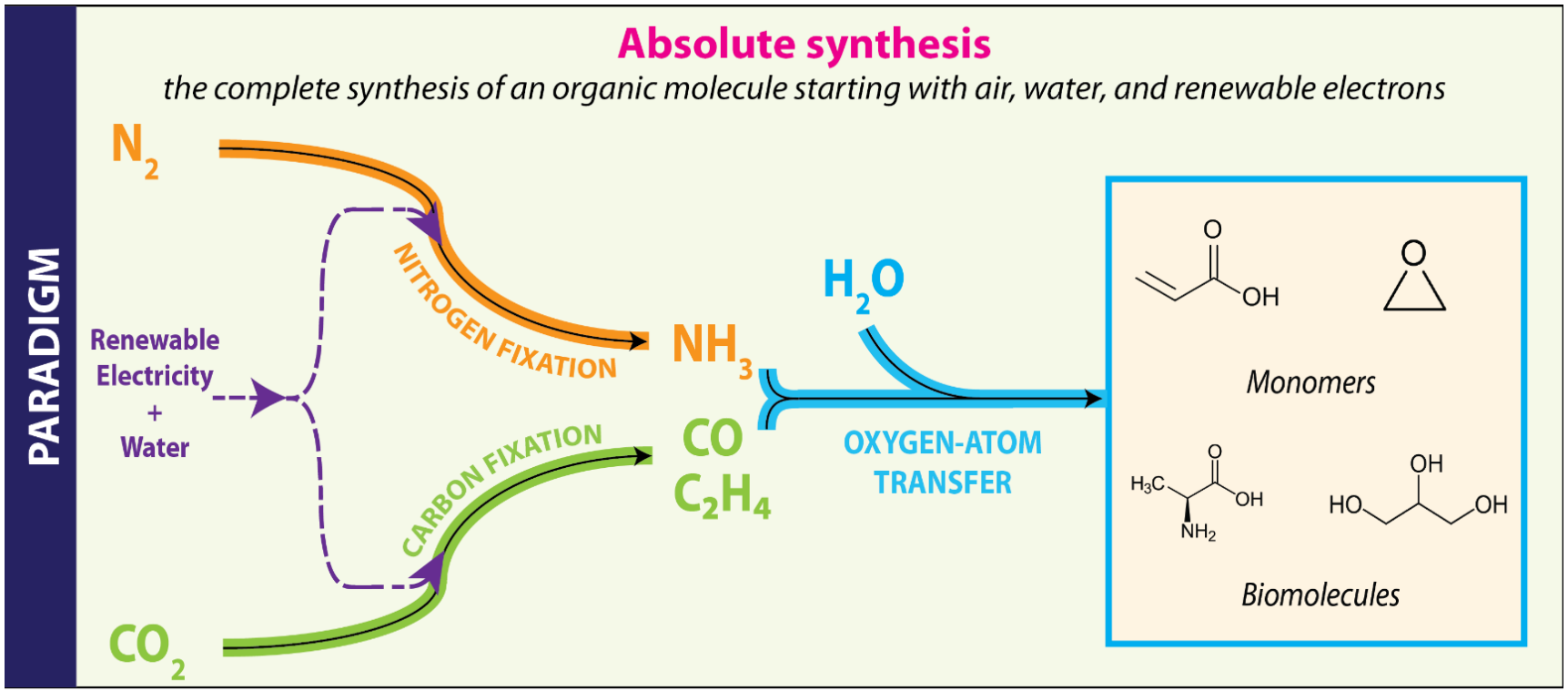
Manthiram Lab: Electrifying and decarbonizing chemical transformations



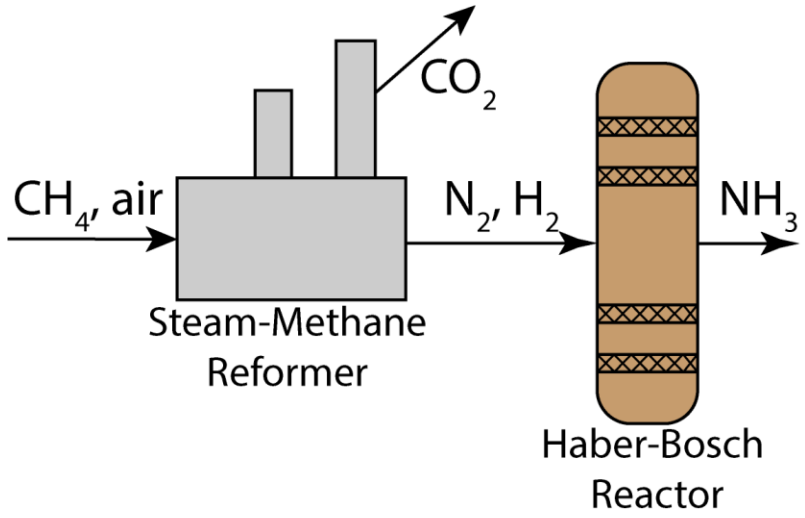
Air, water, and renewable electrons are distributed, sustainable resources

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

Ammonia production is trending towards electrochemistry

Traditional Haber-Bosch

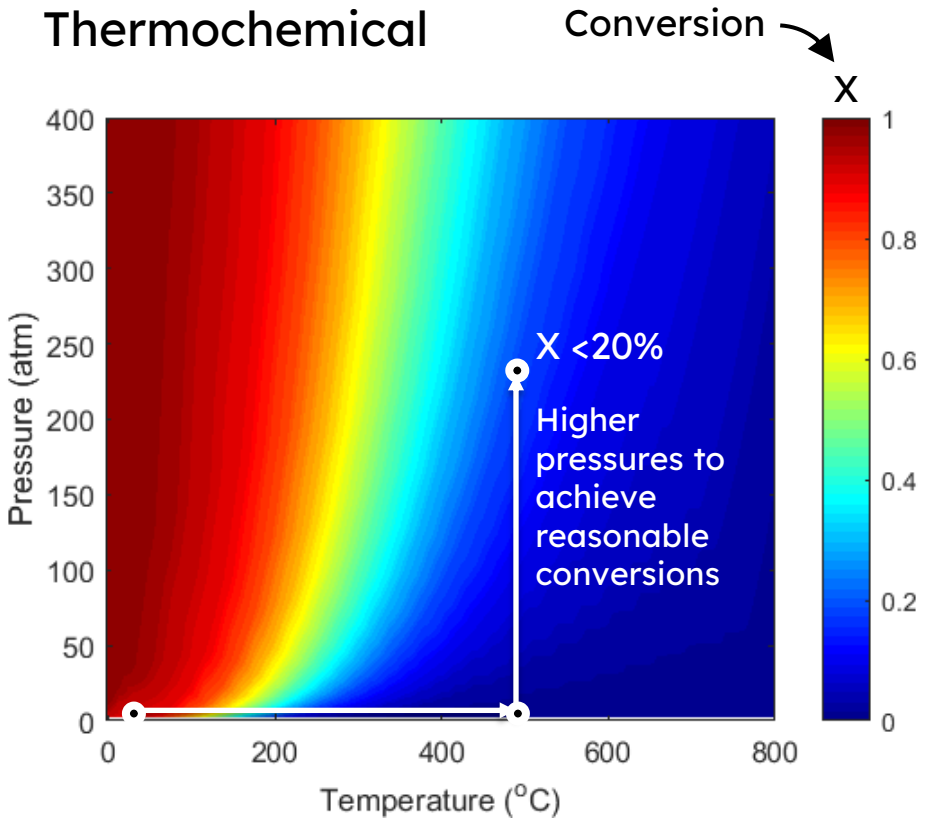


Replacing pressure with voltage

$^1/_2\ N_2 + {}^3/_2\ H_2 \rightarrow NH_3$

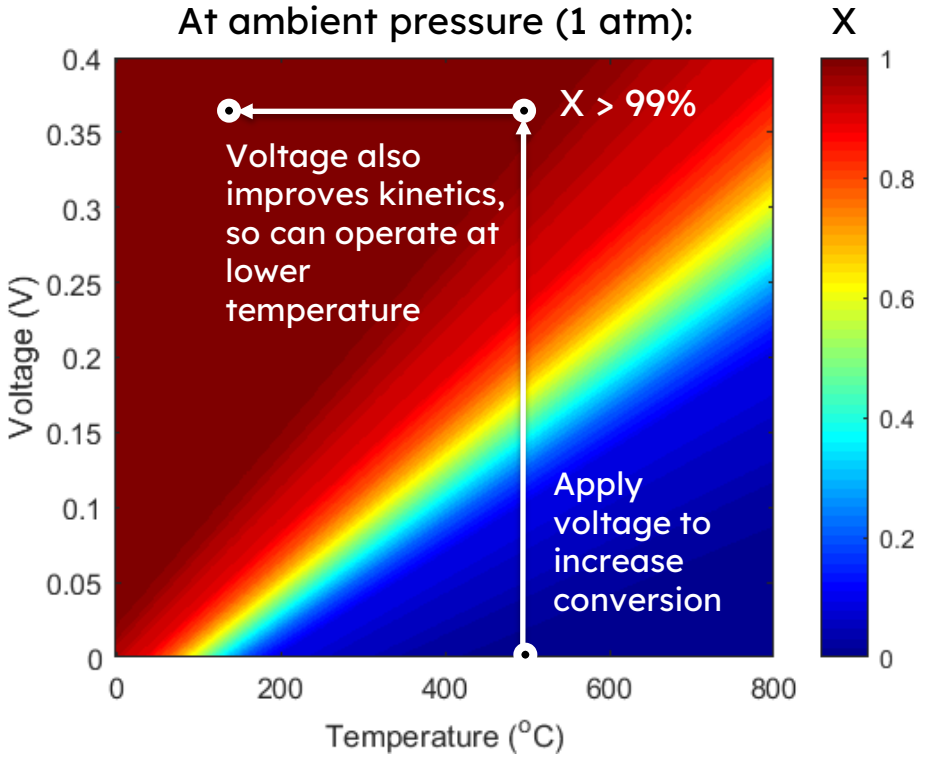
Zachary Schiffer

Thermochemical



Higher temperatures to achieve reasonable rates

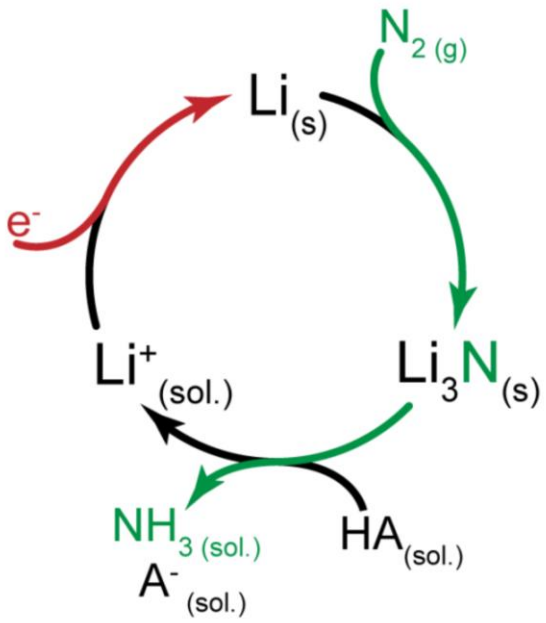
Electrochemical



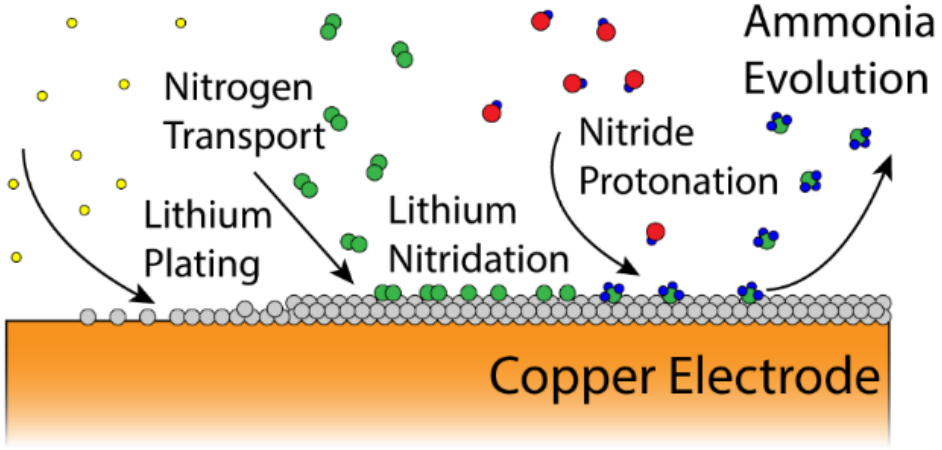
Z. J. Schiffer and K. Manthiram Joule 1 10-14 (2017).

Lithium mediated ammonia synthesis

Nikifar Lazouski



Cycle involving electrochemical and thermochemical steps

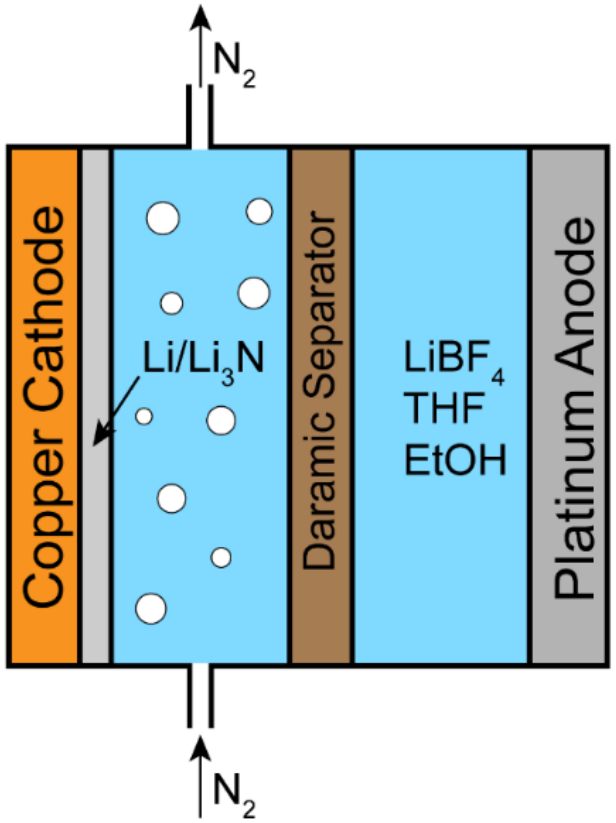


Reactions occur continuously at electrode surface

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).

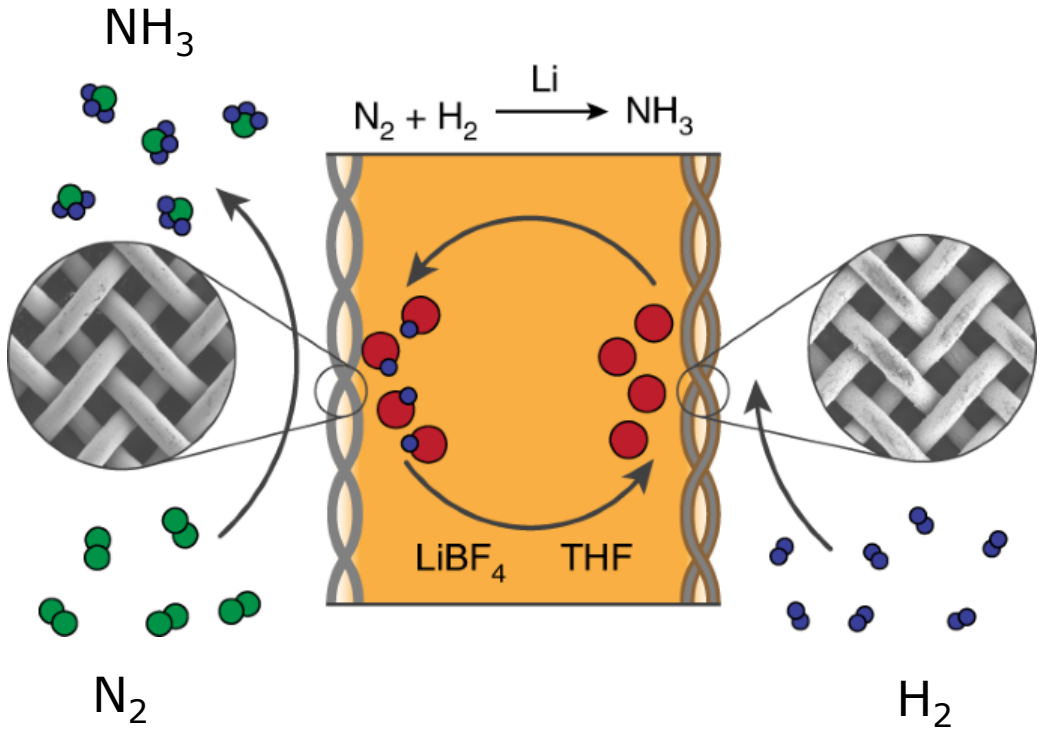
Overcoming transport limitations and undesired overall reaction

Flooded



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

Gas diffusion electrodes

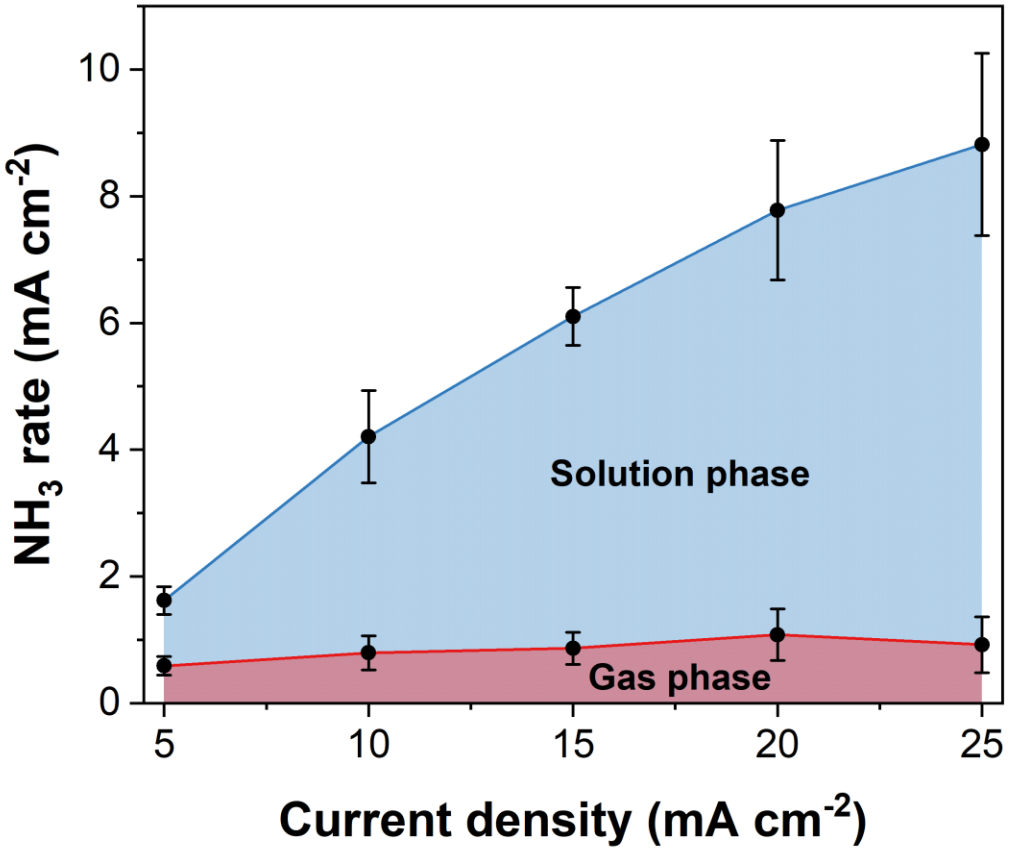


Gas diffusion electrodes to enable

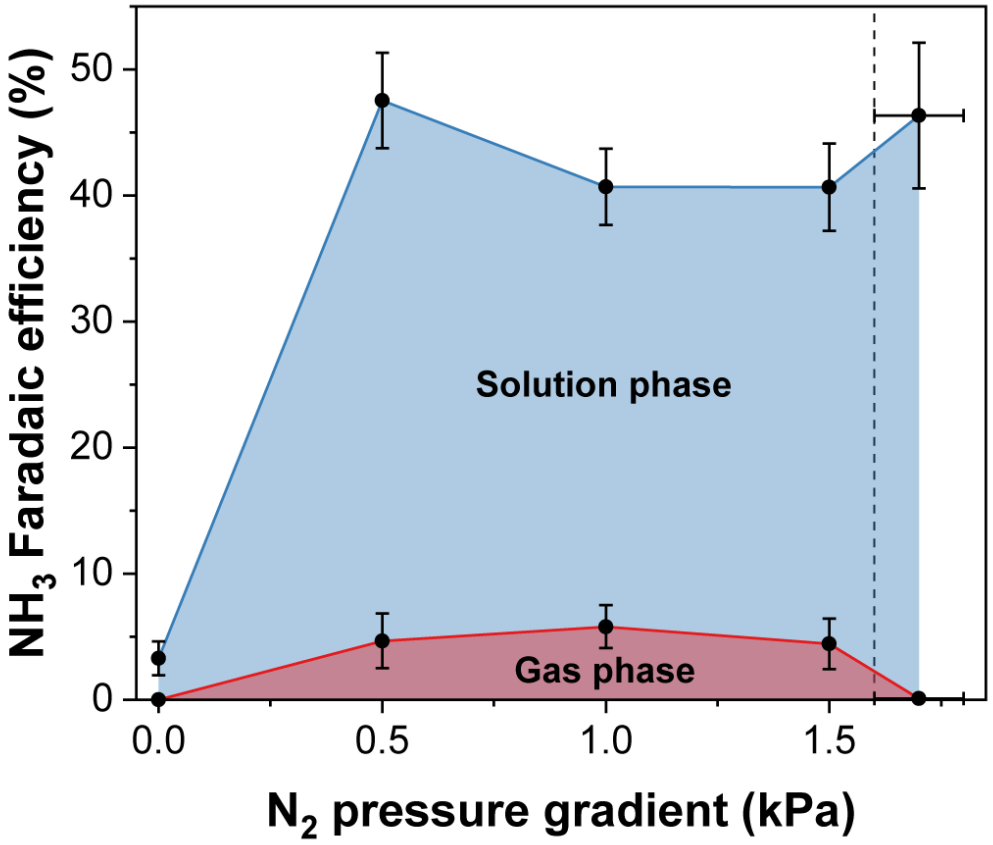
$N_2 + 3H_2 \rightarrow 2NH_3$

N. Lazouski, M. Chung, K. Williams, M. Gala, and K. Manthiram, *Nature Catalysis* 3 (2020)

Rates of ammonia synthesis above the flooded transport limit



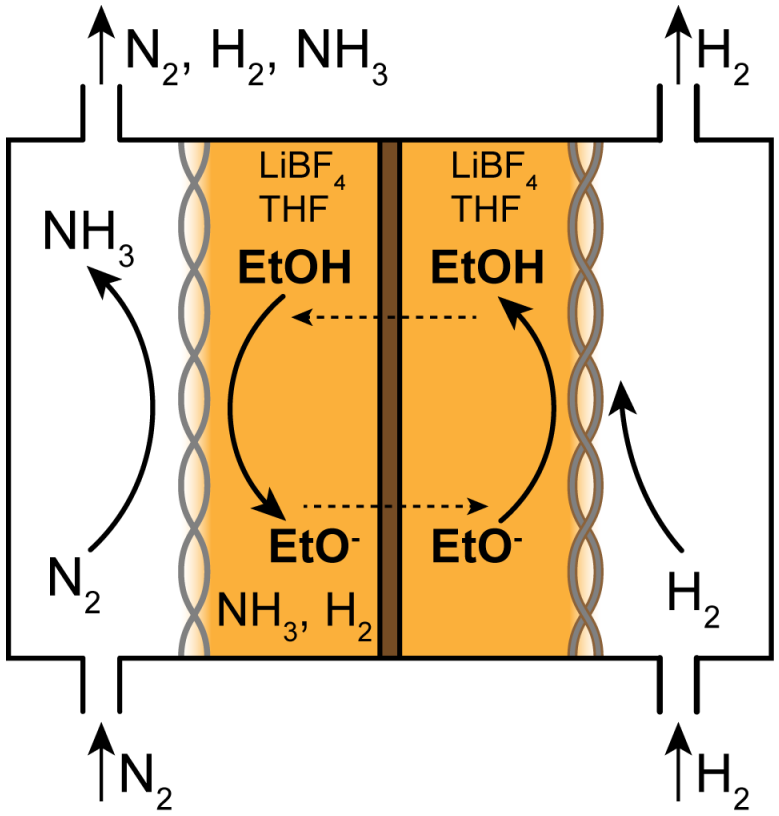
The rate of nitrogen reduction is increased significantly, with some produced ammonia found in the gas phase

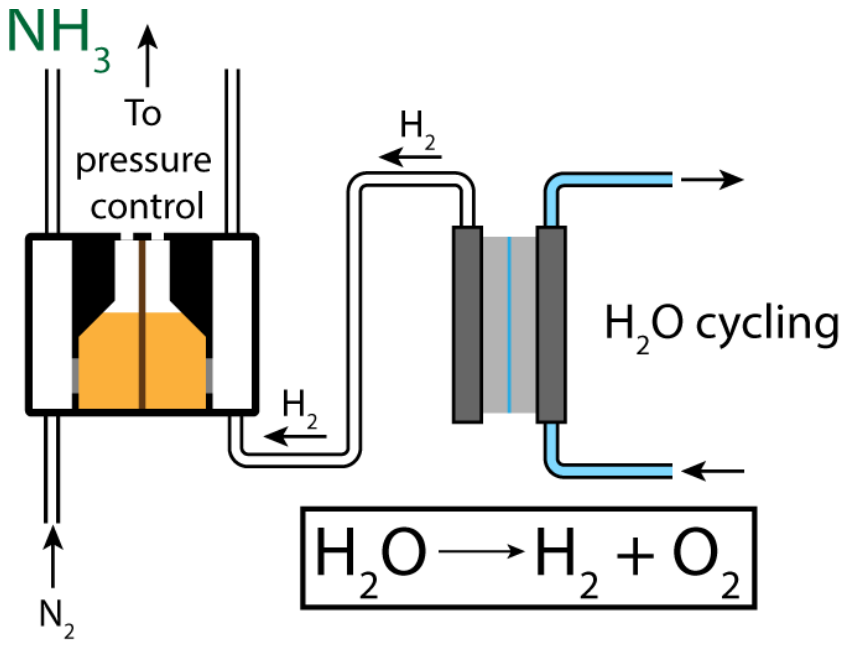


High FEs can be obtained at 15 mA cm^{-2} at non-zero pressure gradients across the GDE

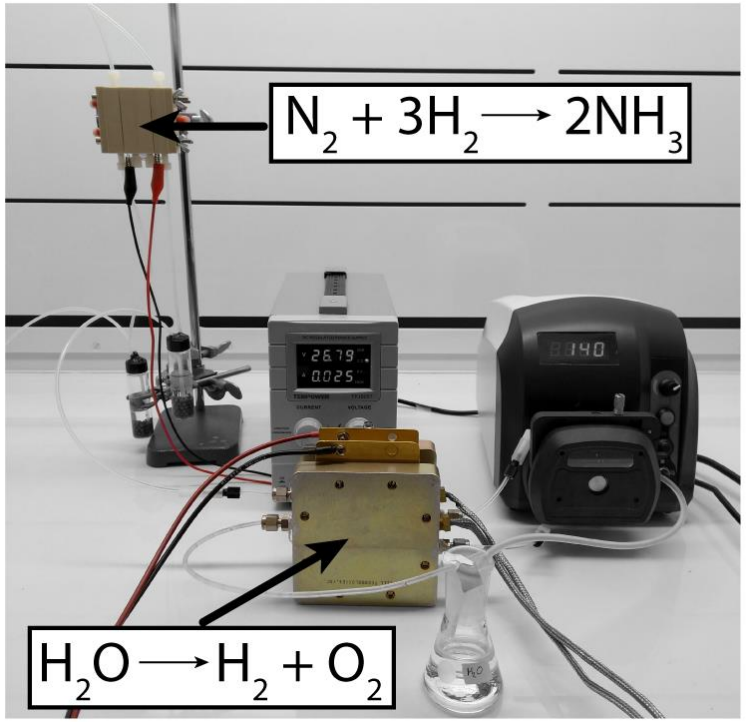
N. Lazouski, M. Chung, K. Williams, M. Gala, and K. Manthiram, *Nature Catalysis* 3 (2020)

Coupling to water splitting





$N_2 + 3H_2 \longrightarrow 2NH_3$



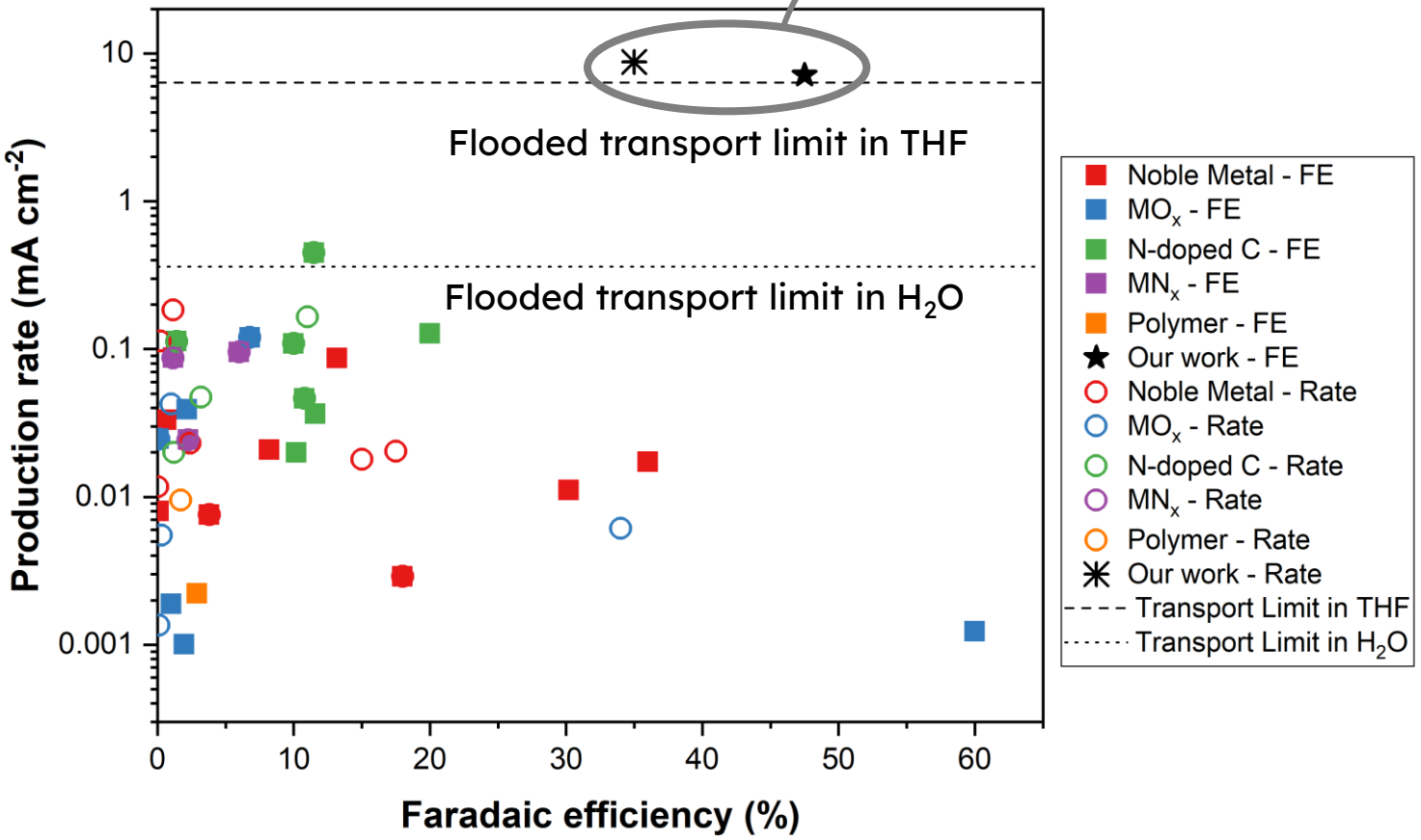
Hydrogen oxidation at the anode can replenish protons in the electrolyte

Water splitting-derived hydrogen can be used at the anode to have overall ammonia production from N_2 and H_2O

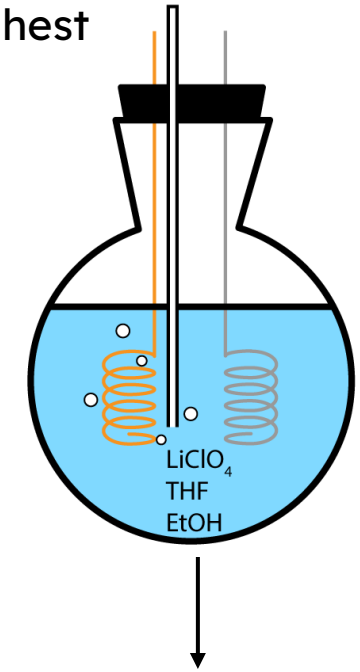
N. Lazouski, M. Chung, K. Williams, M. Gala, and K. Manthiram, *Nature Catalysis* 3 (2020)

Comparing our system to reported catalysts

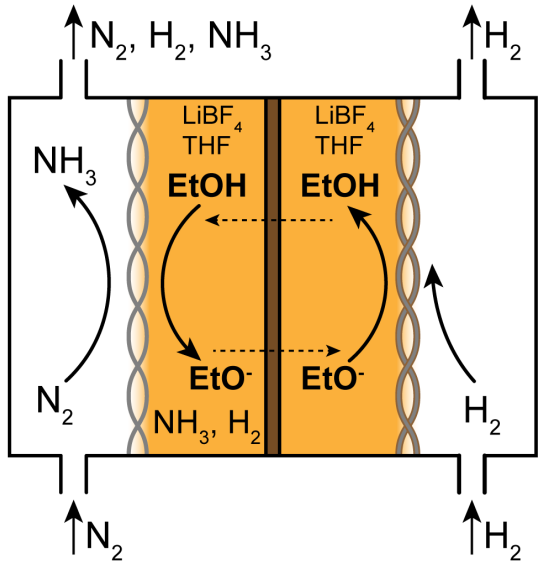
Our approach achieves the highest rates for a semi-batch process



Energy efficiency of 2% - critical barrier to overcome



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



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

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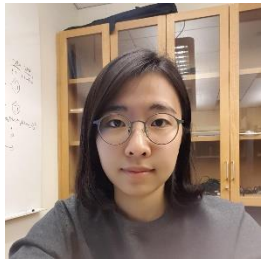

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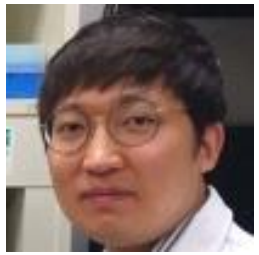

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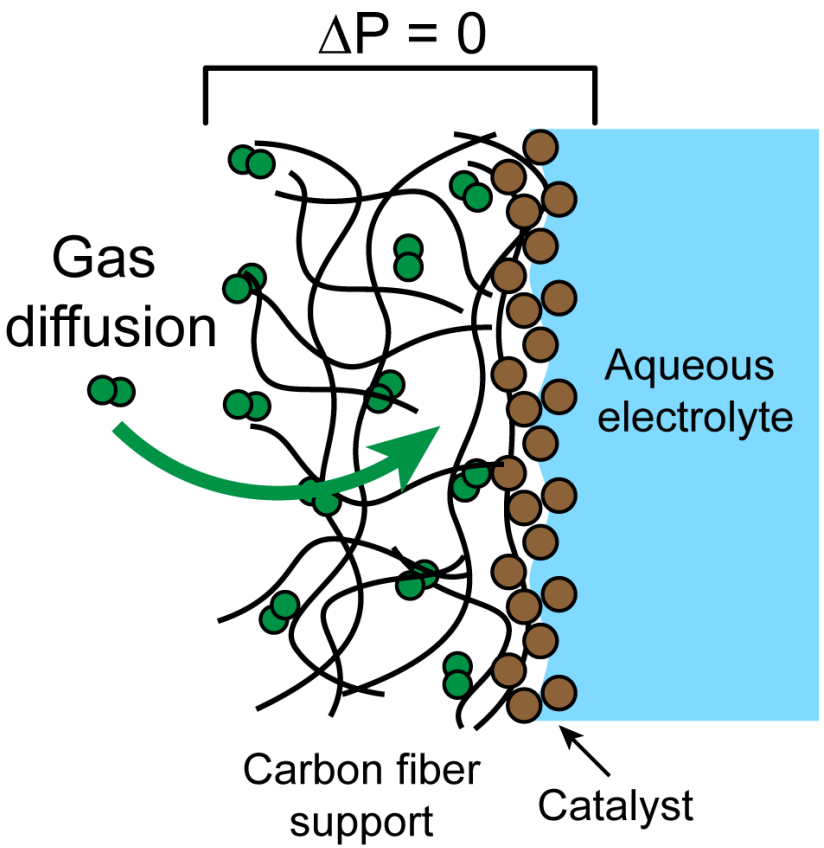
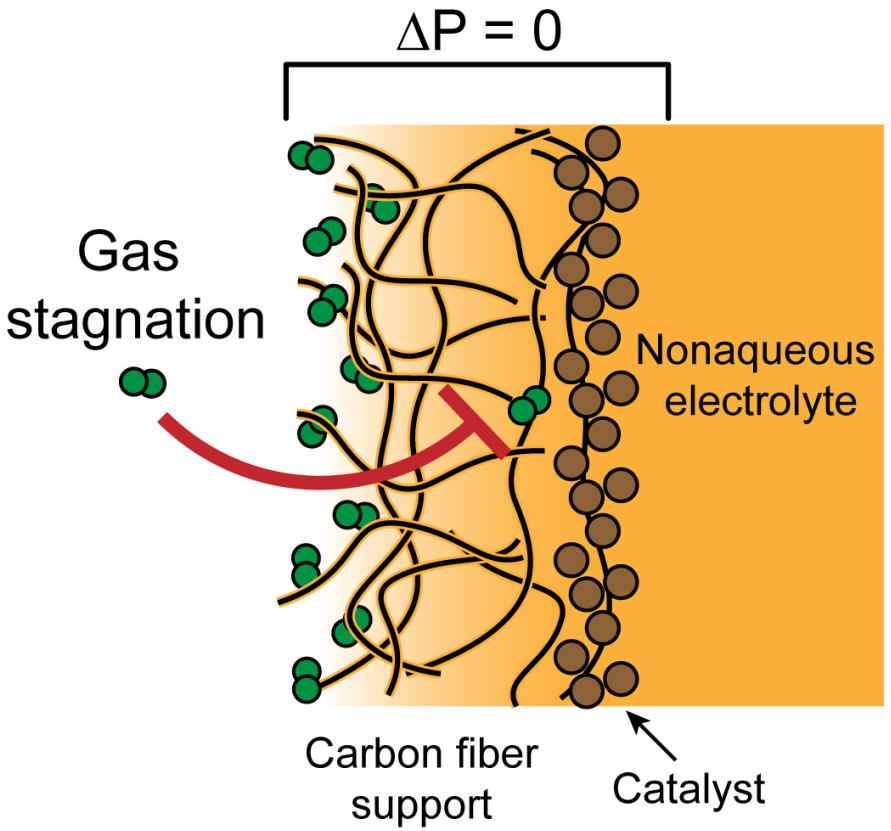
Conventional gas diffusion electrodes are not viable

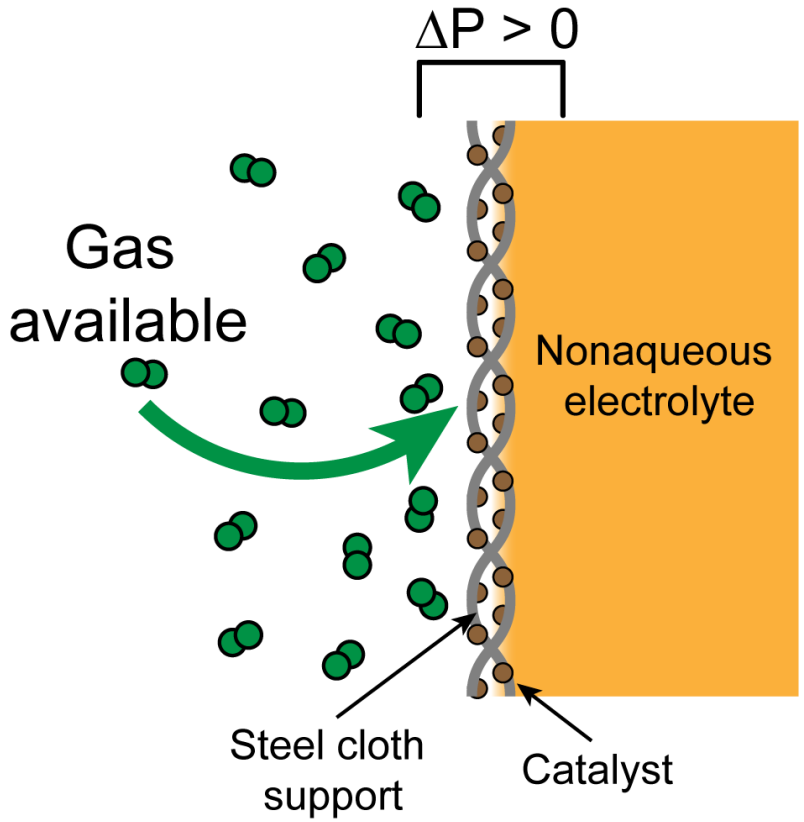


A stable gas-liquid interface, stabilized by hydrophobic interactions, can increase gas transfer rates

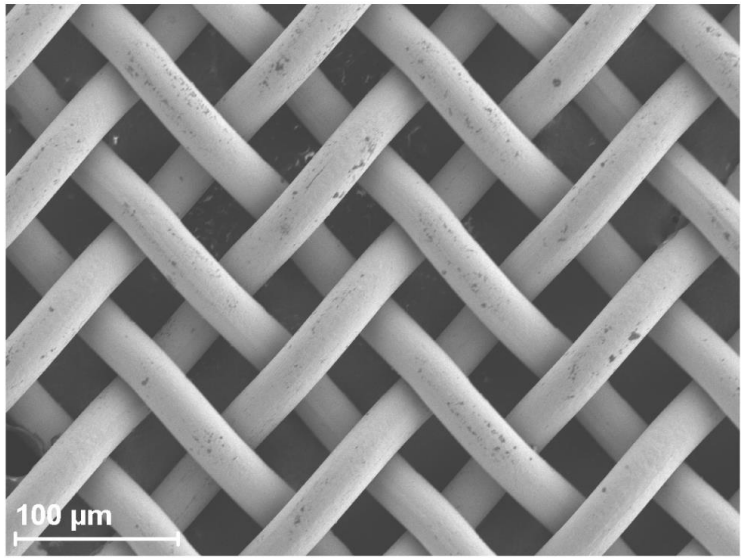


Hydrophobic interactions are absent in nonaqueous electrolytes, leading to electrode flooding and loss of gas-liquid interface

Using metallic meshes can overcome flooding

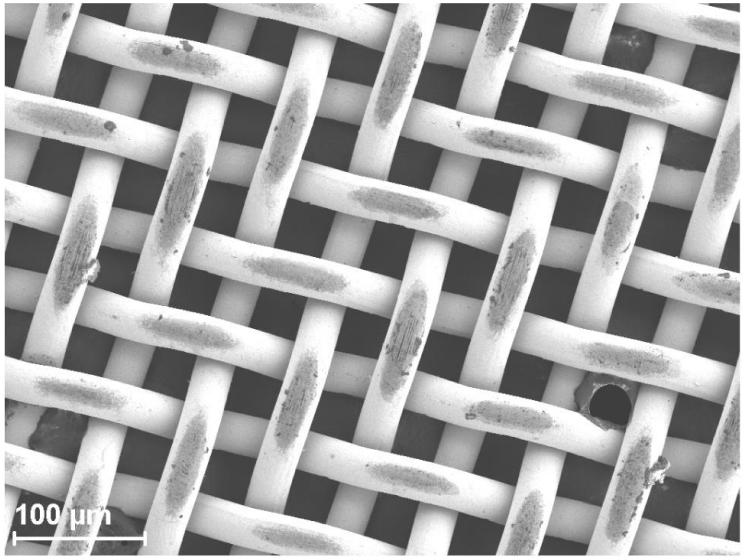


Gas-liquid interface at metallic mesh support allows for rapid transport; metal meshes don't pull in electrolyte by capillary action due to less favorable surface interactions



Stainless steel cloths can be used as GDEs directly for nitrogen reduction

Catalysts can be deposited for use in other chemistries



N. Lazouski, M. Chung, K. Williams, M. Gala, and K. Manthiram, *Nature Catalysis* 3 (2020)