

Electrification and Decarbonization of Chemical Synthesis

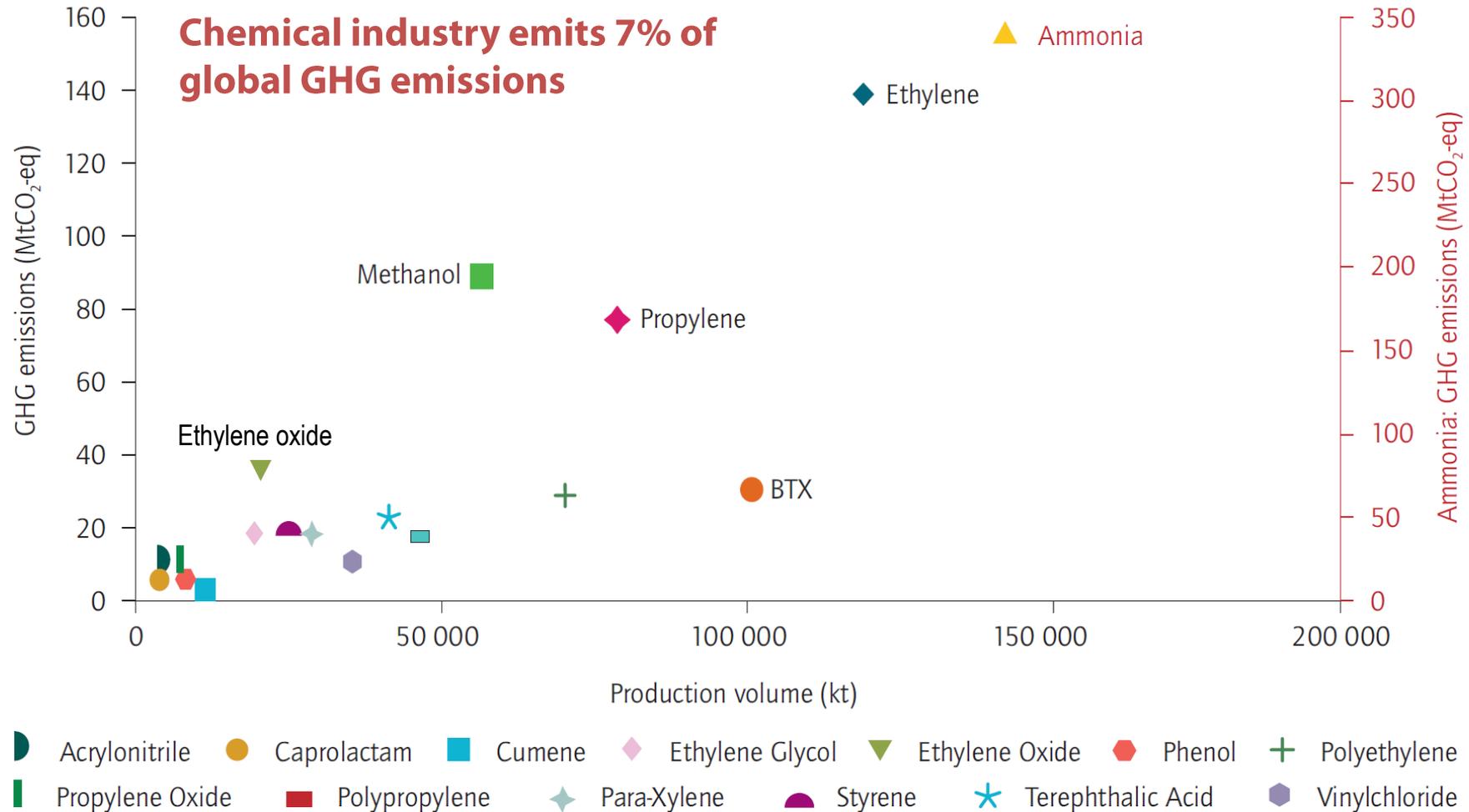
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Massachusetts Institute of Technology

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Carbon footprint of chemical manufacturing



Note: GHG emissions for olefins in this figure represent that of the steam cracking process. Ammonia is presented on a different axis on the right.

Source: DECHEMA

Defining Paradigms in Chemical Synthesis

Biosynthesis

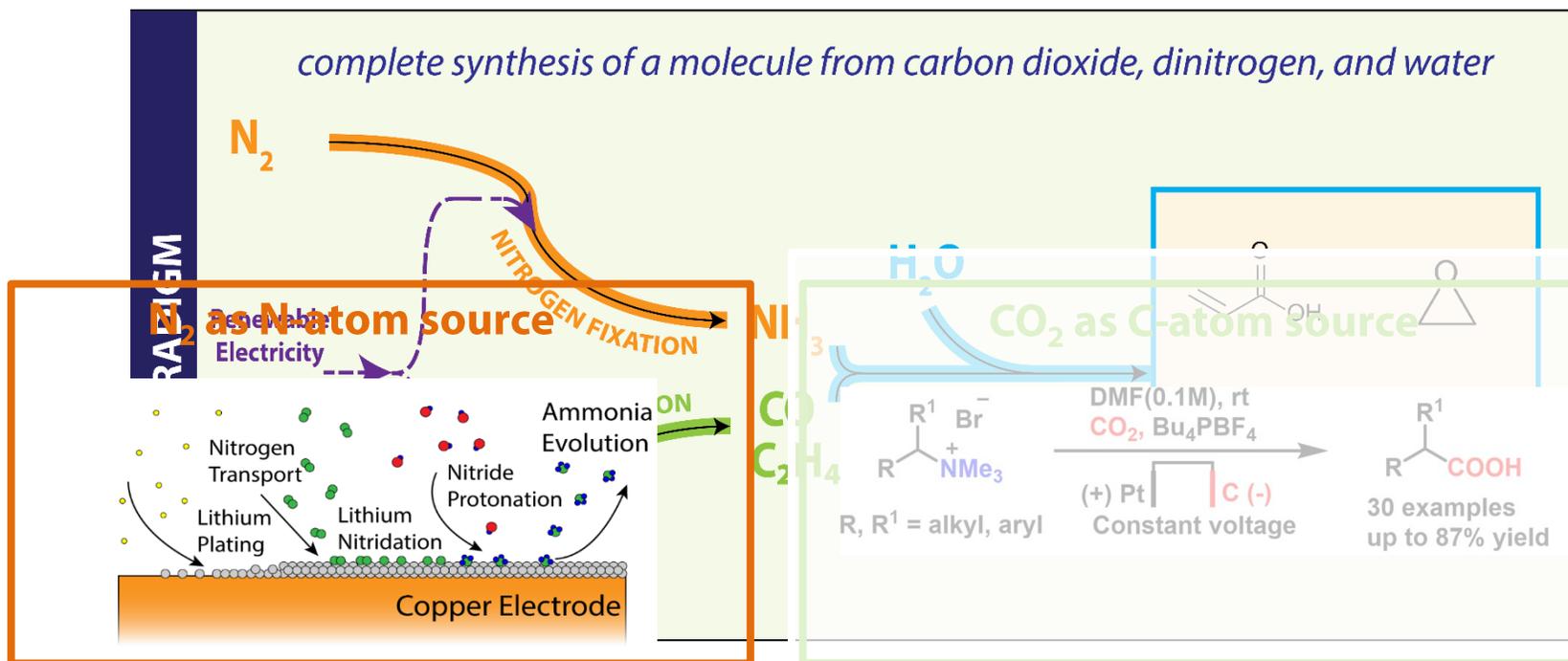
Nature's route for synthesizing a molecule

Semi-synthesis

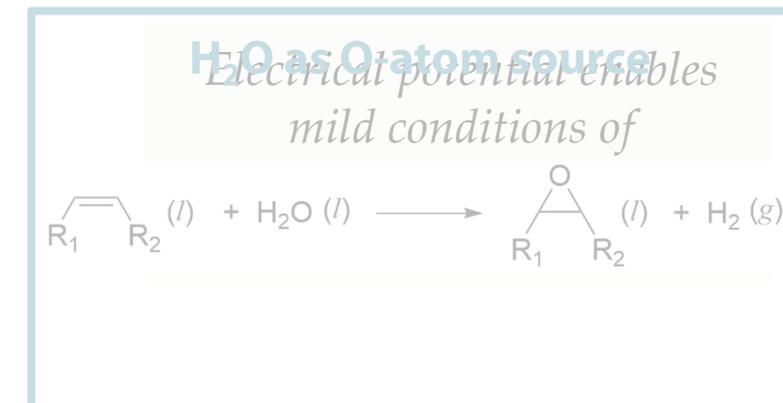
Synthesis of a molecule using a starting material isolated from a natural source

Total Synthesis

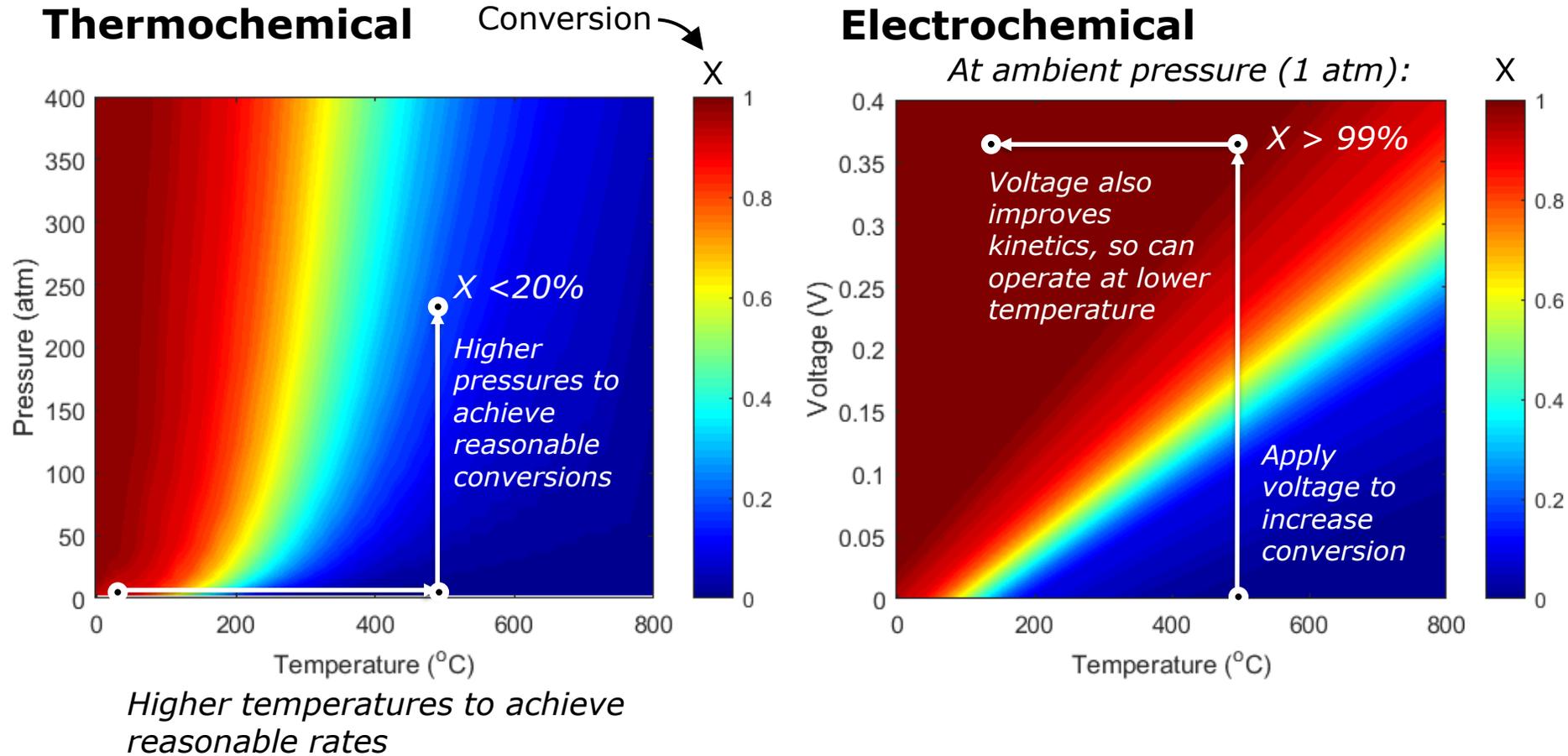
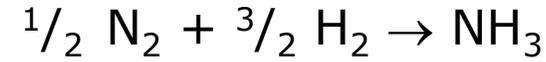
The preparation of a complex molecule beginning with simple, commercially available precursors



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

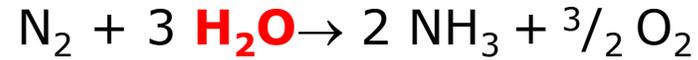


Replacing pressure with voltage

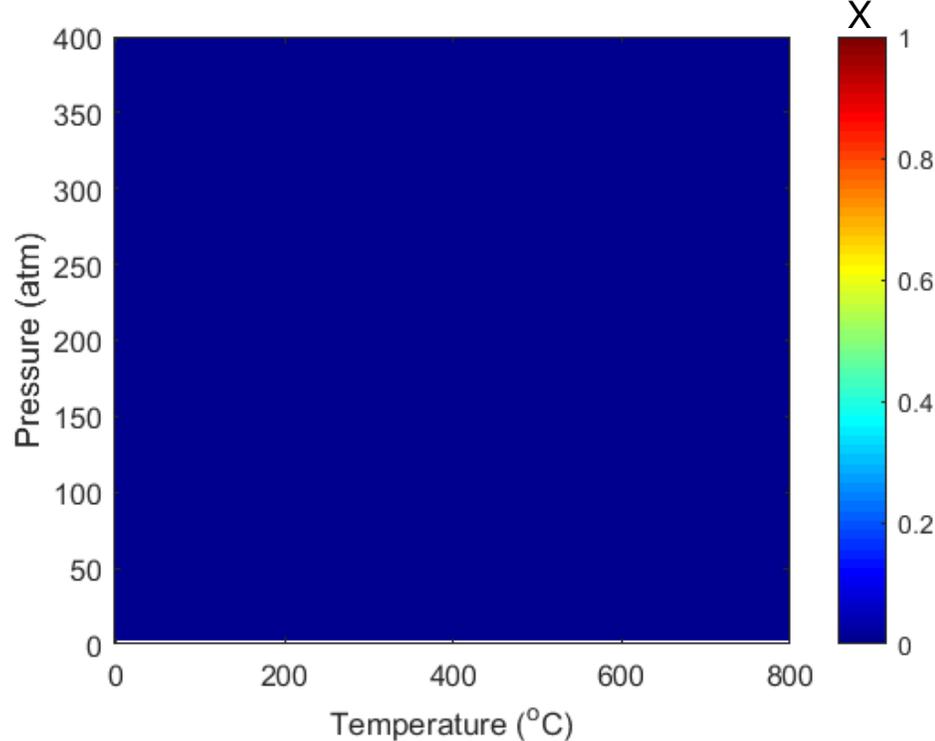


What happens if we replace hydrogen gas with water?

Can we react water and nitrogen to produce ammonia?

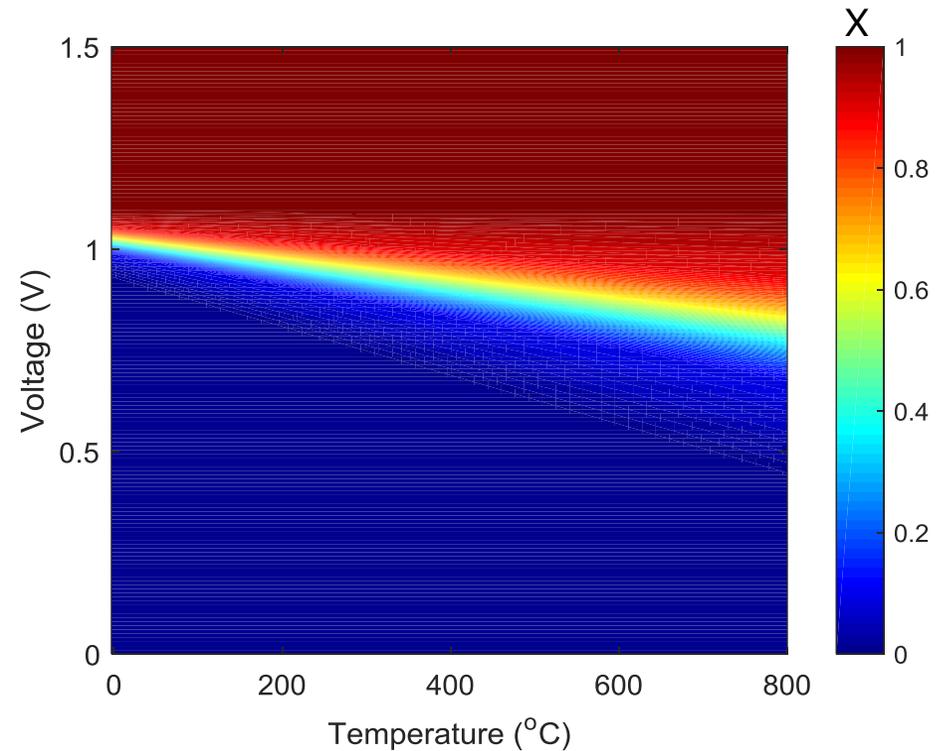


Thermochemical



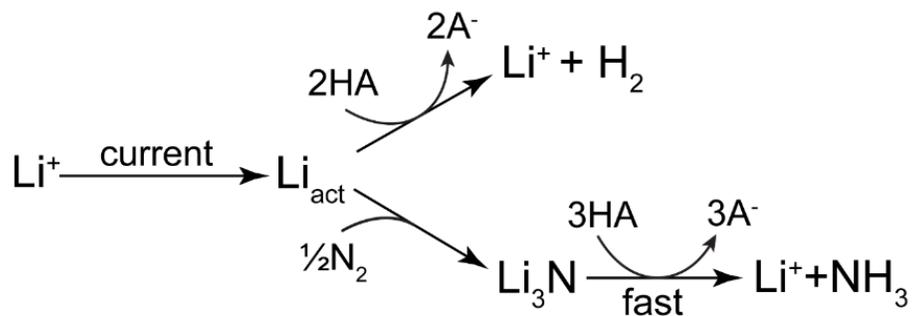
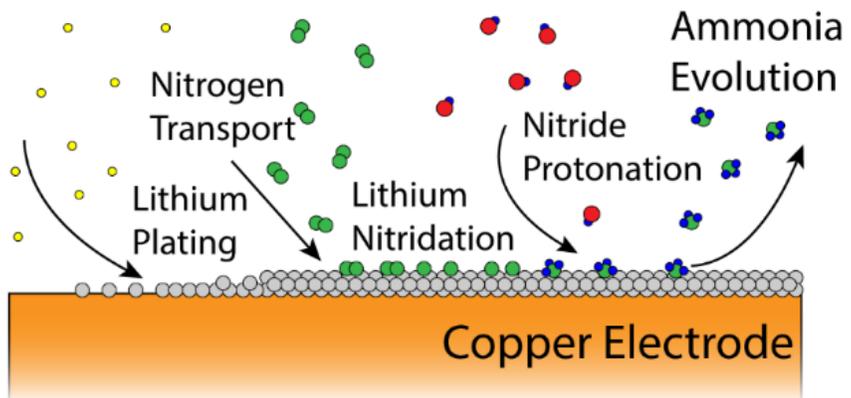
No conversion at reasonable temperatures

Electrochemical



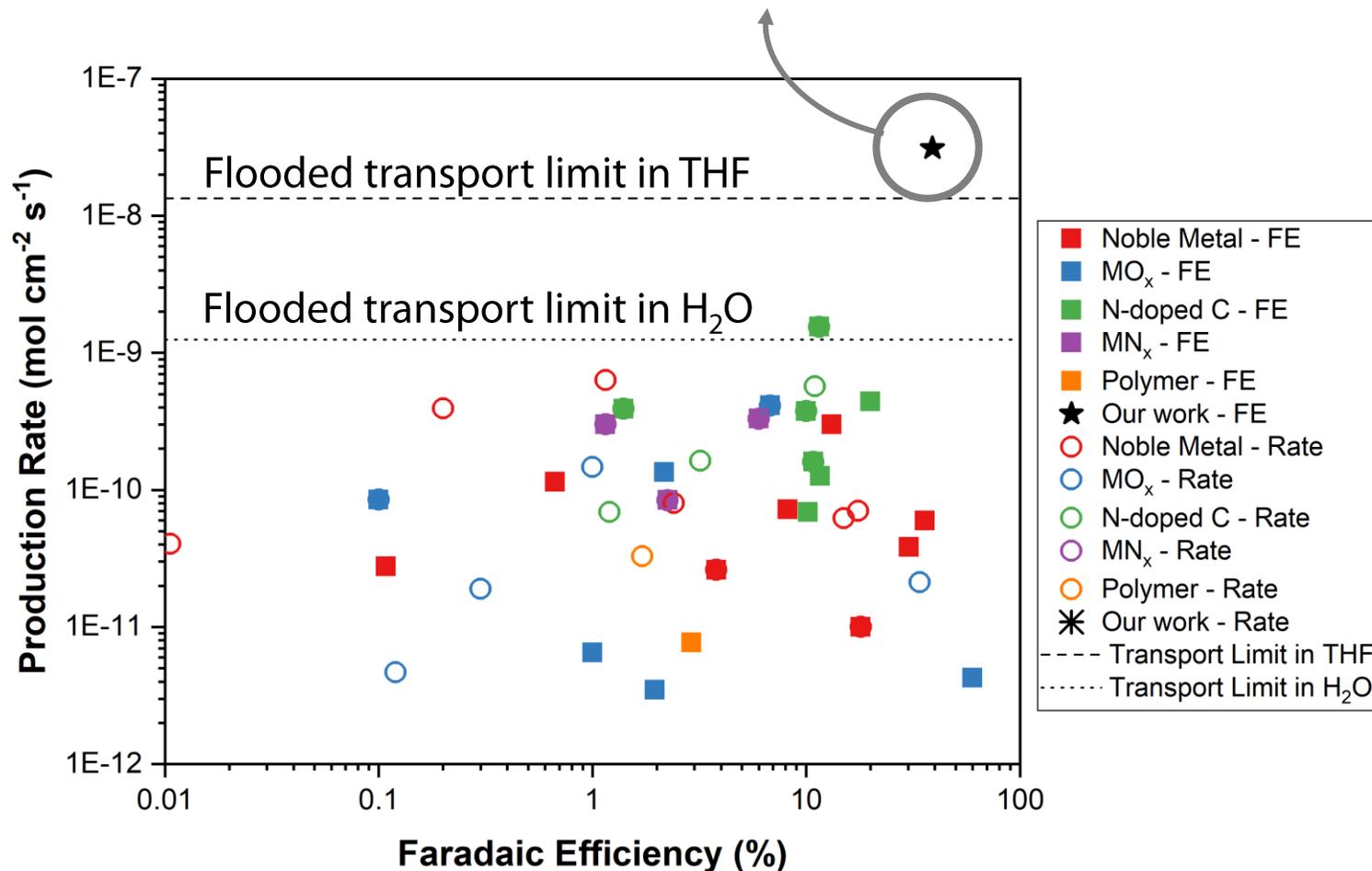
Can achieve reactivity at room temperature, with reduced voltage requirements at higher temperatures

Continuous electrically-driven ammonia synthesis

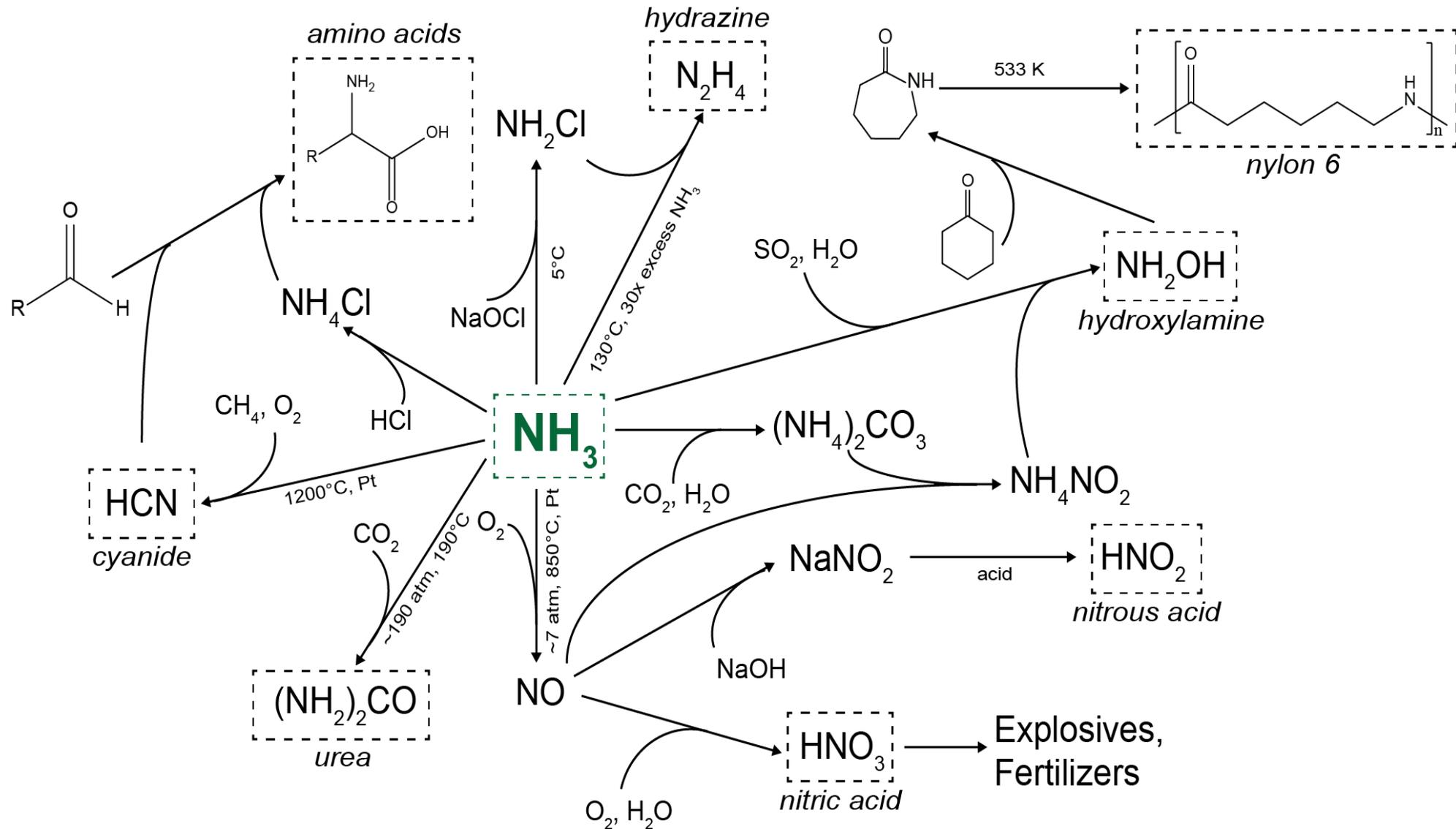


Understanding of coupled transport-kinetics is essential for a sparingly soluble reagent

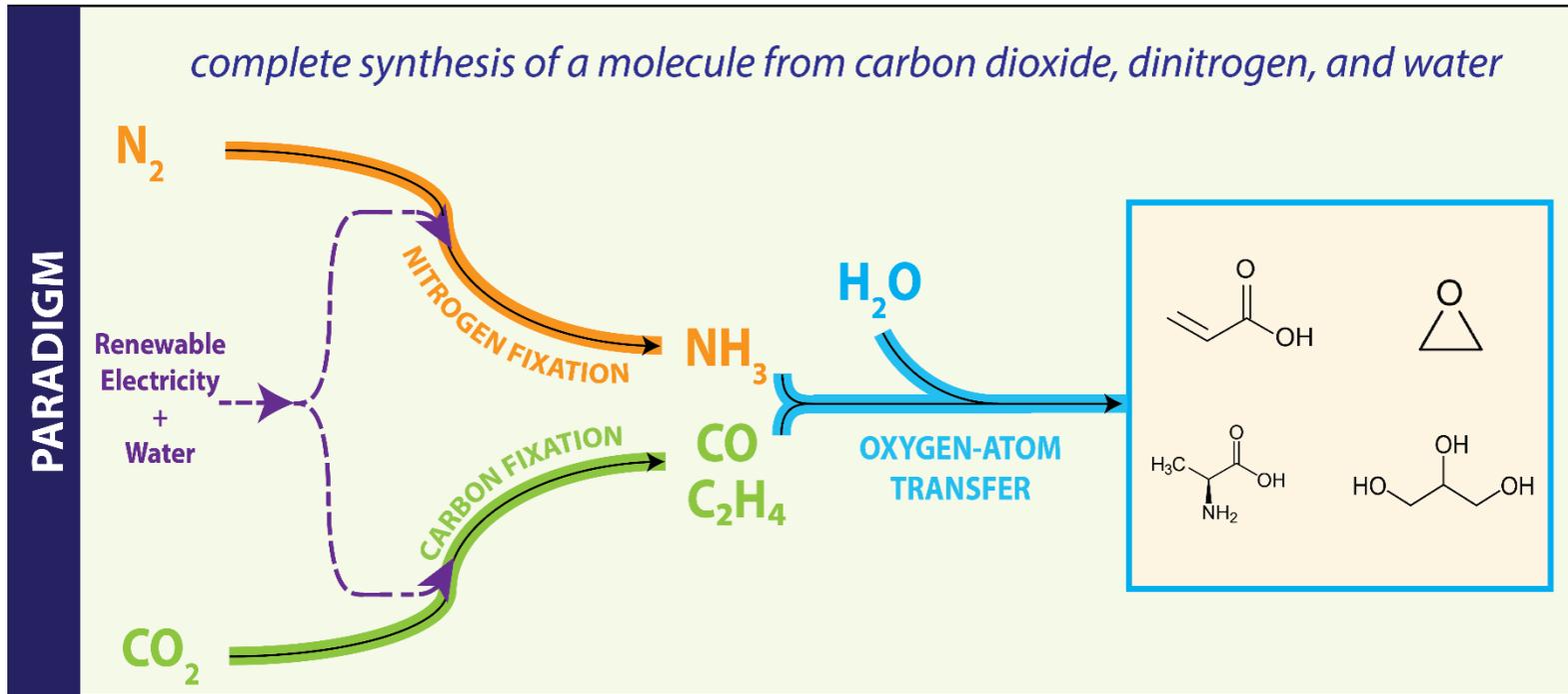
Our system achieves the highest rates for a continuous electrochemical process (quantitative ^{15}N confirmation)



Ammonia is a nexus molecule for chemical synthesis



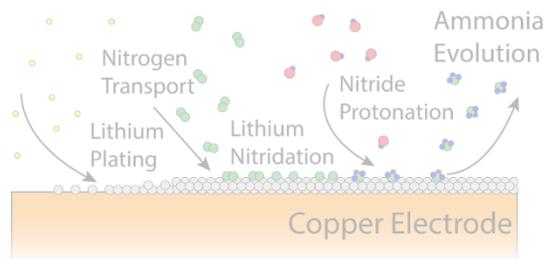
Outline



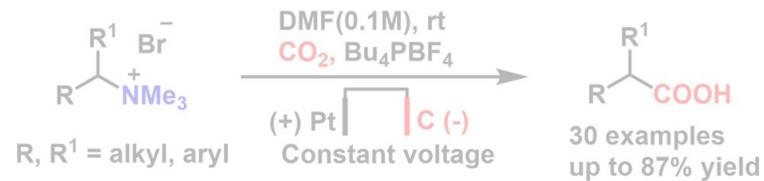
Air, water, and renewable electrons are distributed, sustainable resources

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

N_2 as N-atom source



CO_2 as C-atom source



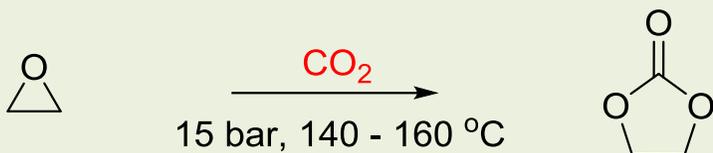
H_2O as O-atom source



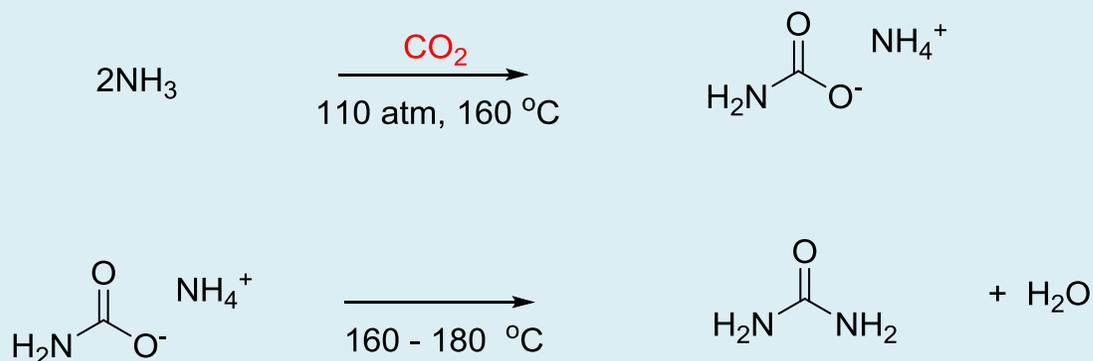
Direct use of CO₂ in chemical synthesis

Forming diverse C-C bonds using CO₂ directly remains underdeveloped for industrial use at large-scales

Forming C-O bonds (industry)



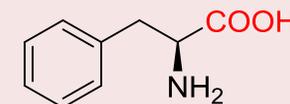
Forming C-N bonds (industry)



Forming C-C bonds (laboratory)



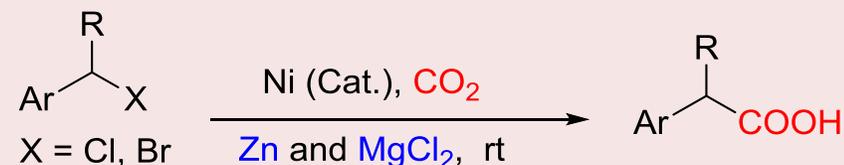
Terephthalic acid



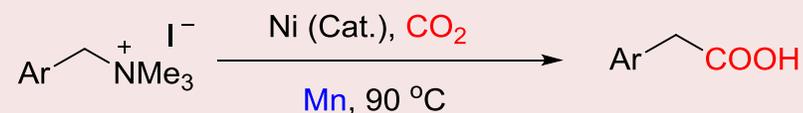
Phenylalanine



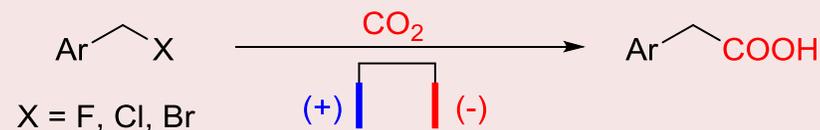
Require reactive and unstable organometallics



Stoichiometric metal reductant



Sacrificial anode (Mg, Al)
Limited scope of substrates

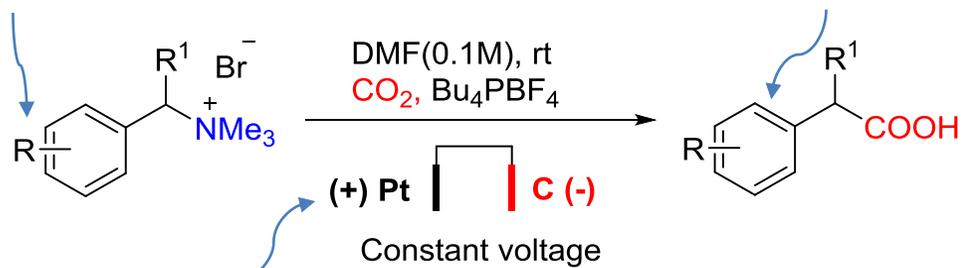


Electro-carboxylations without sacrificial anodes

Electrocarboxylation to form C-C bonds

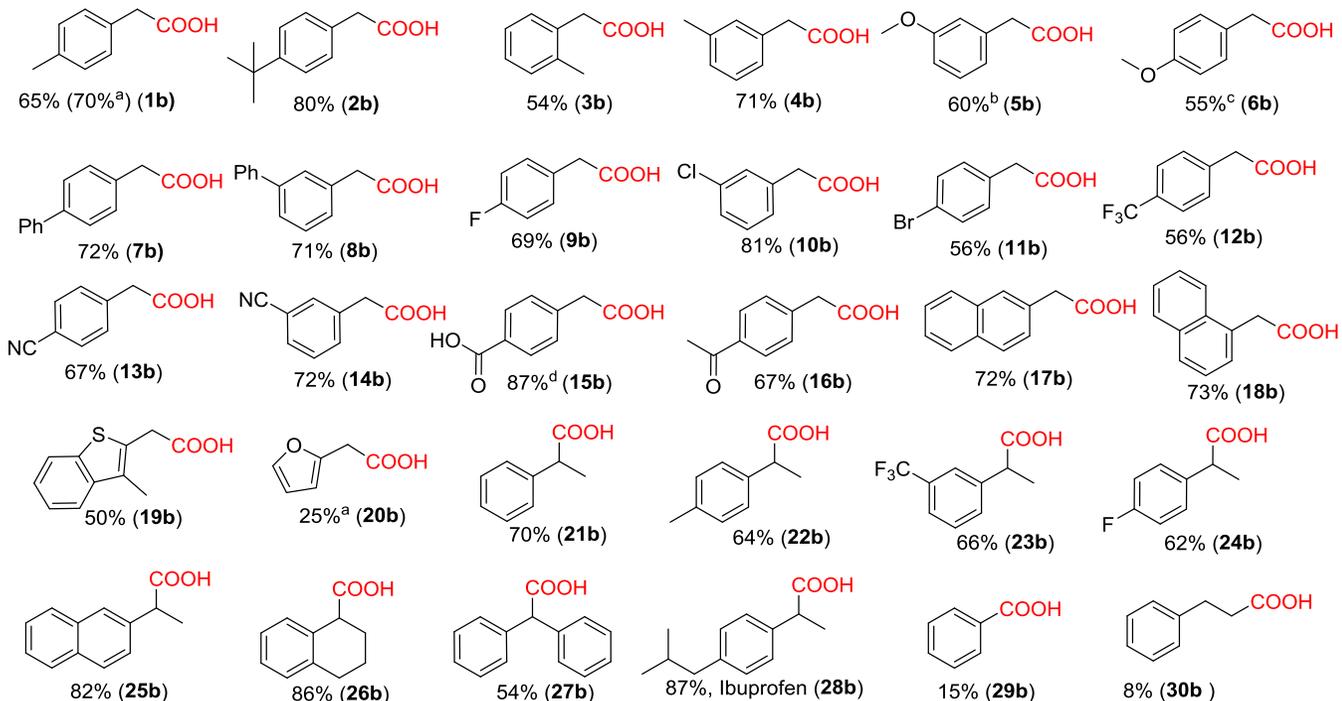
High functional group tolerance

No column chromatography



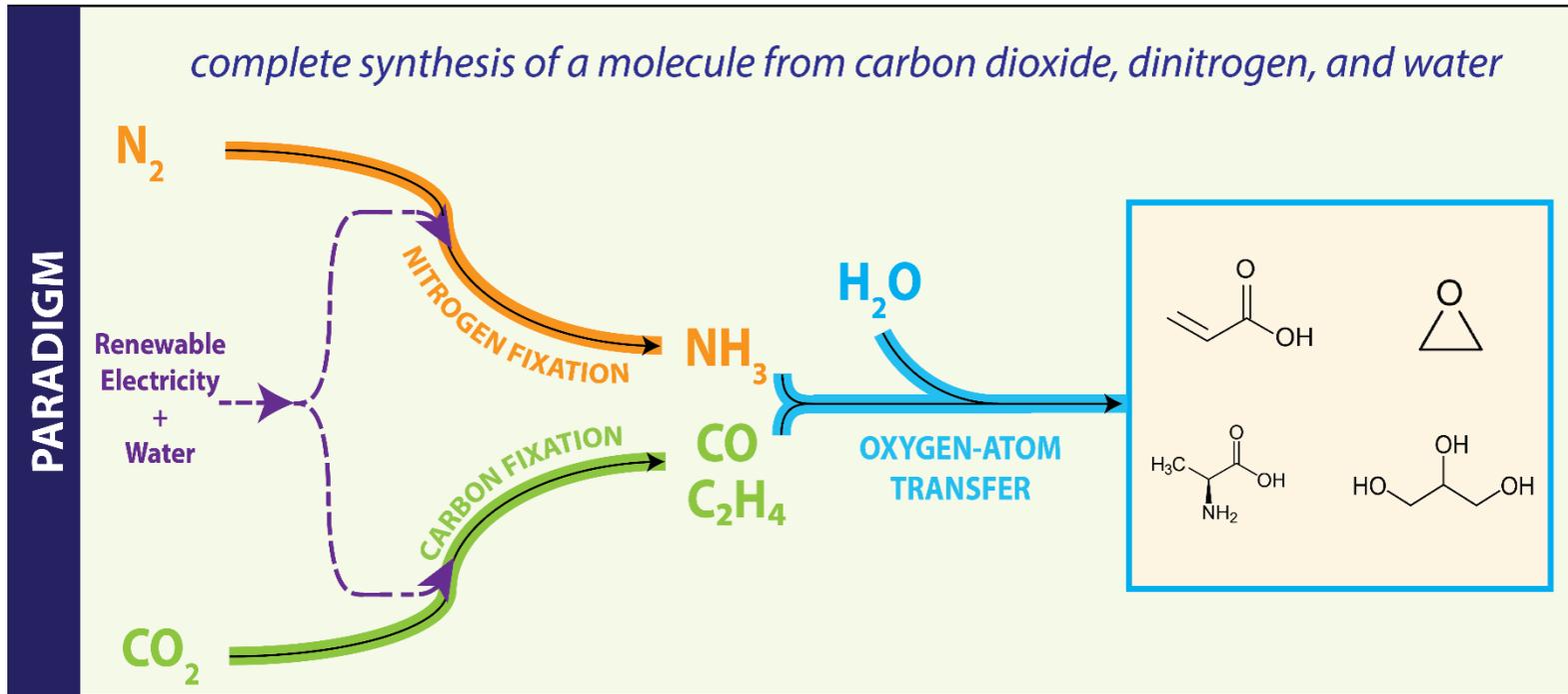
No sacrificial anodes and metal reductant (need to consider counter electrode chemistry for commodity chemicals)

Wide substrate scope



Starting with smaller-scale, fine chemical examples, and expanding to the more difficult commodity chemicals

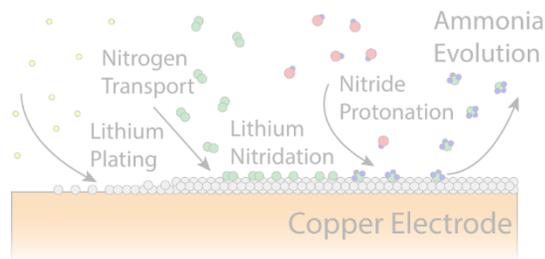
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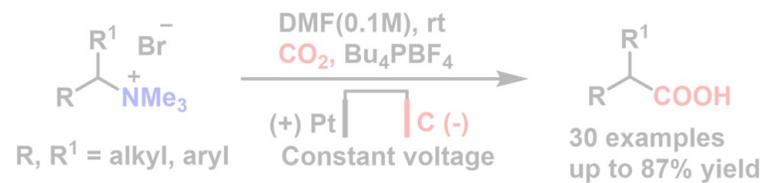
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N_2 as N-atom source



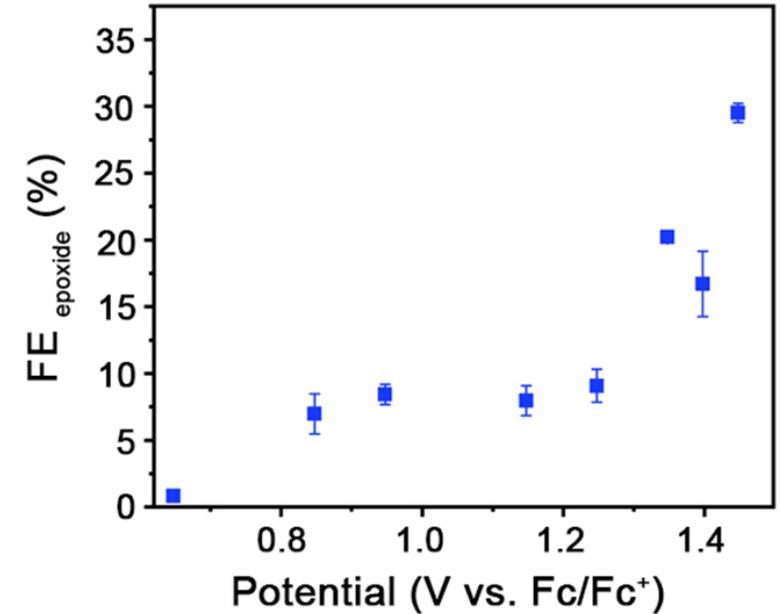
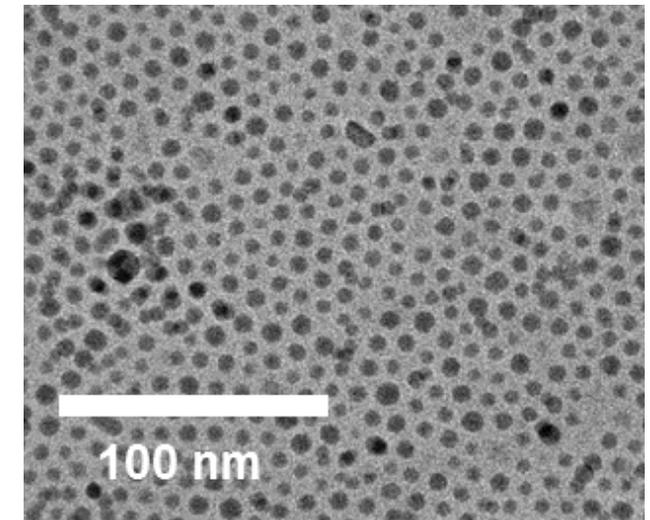
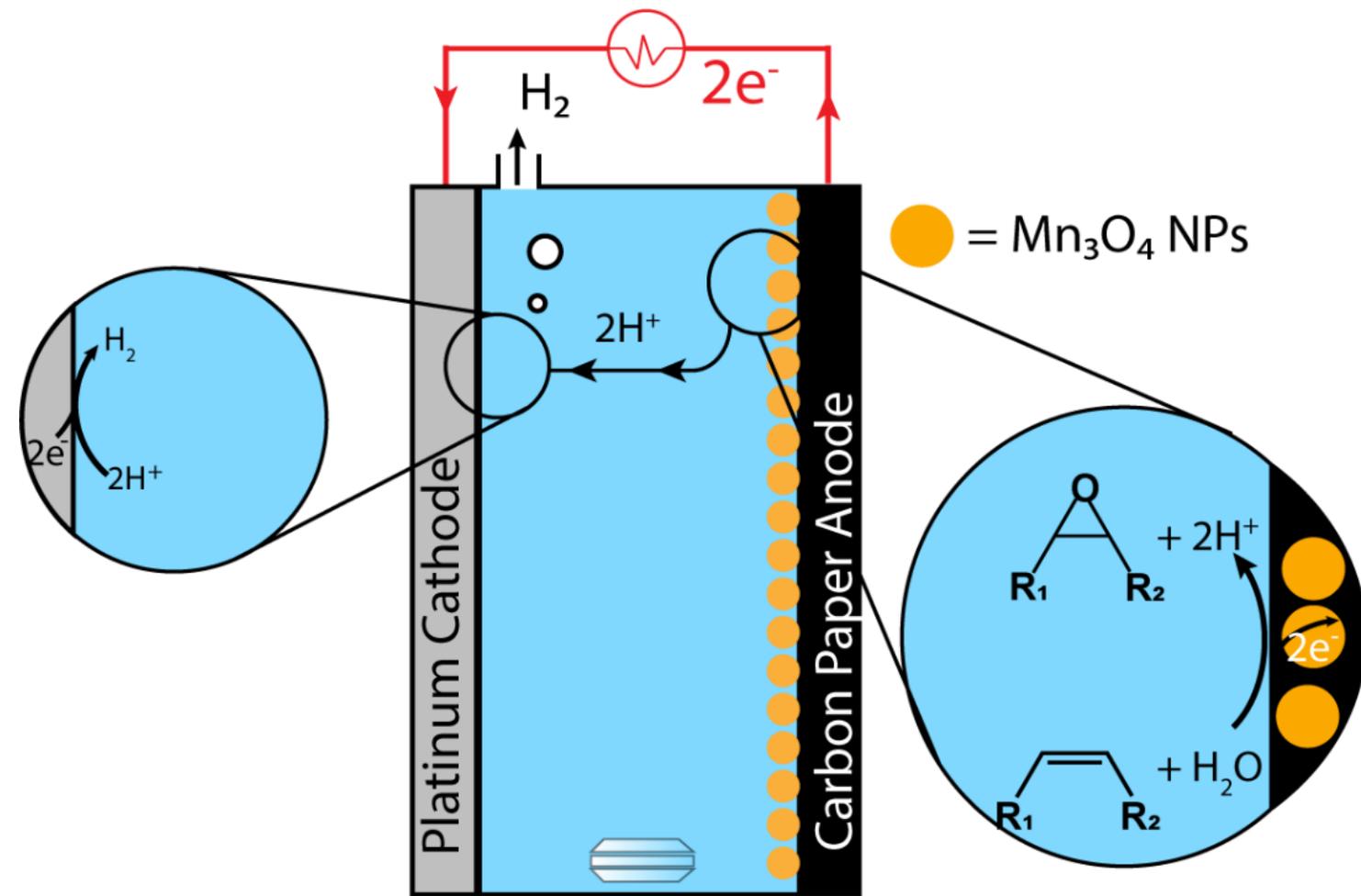
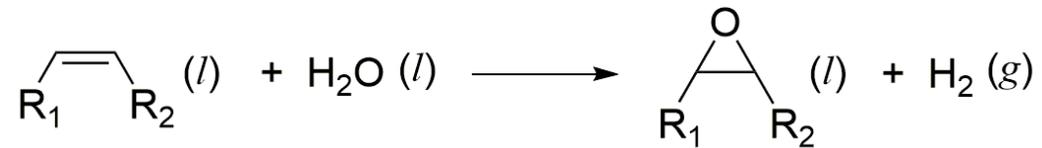
CO_2 as C-atom source



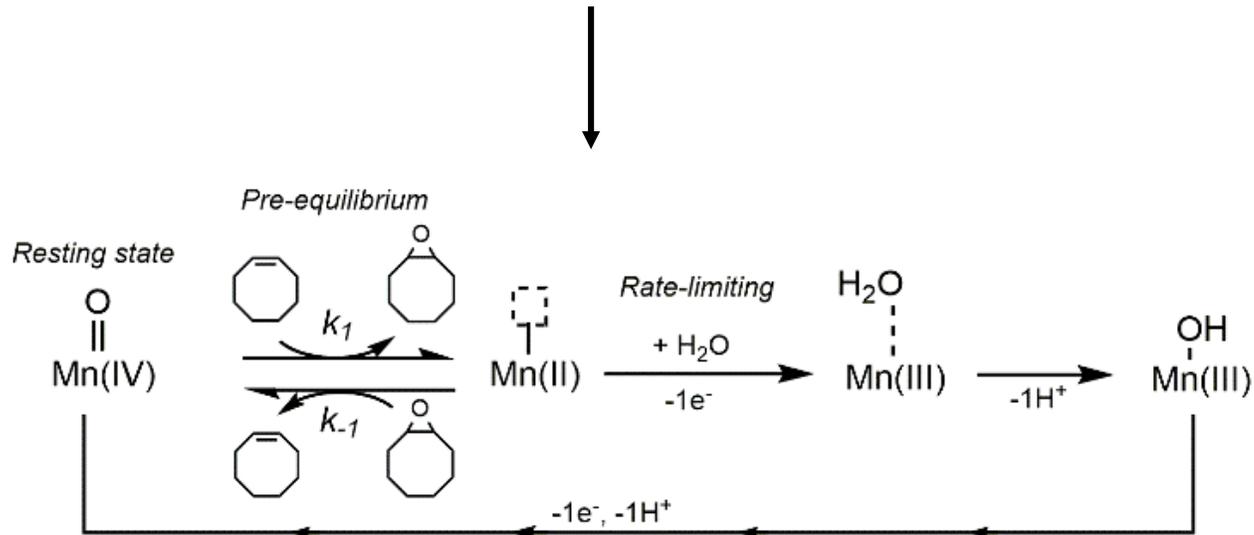
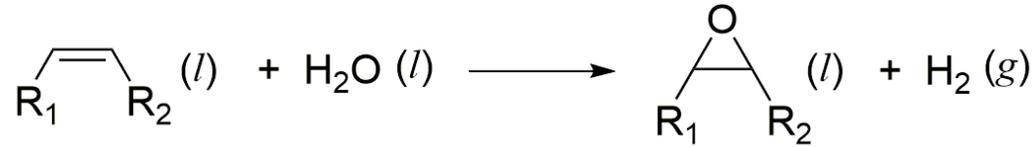
H_2O as O-atom source



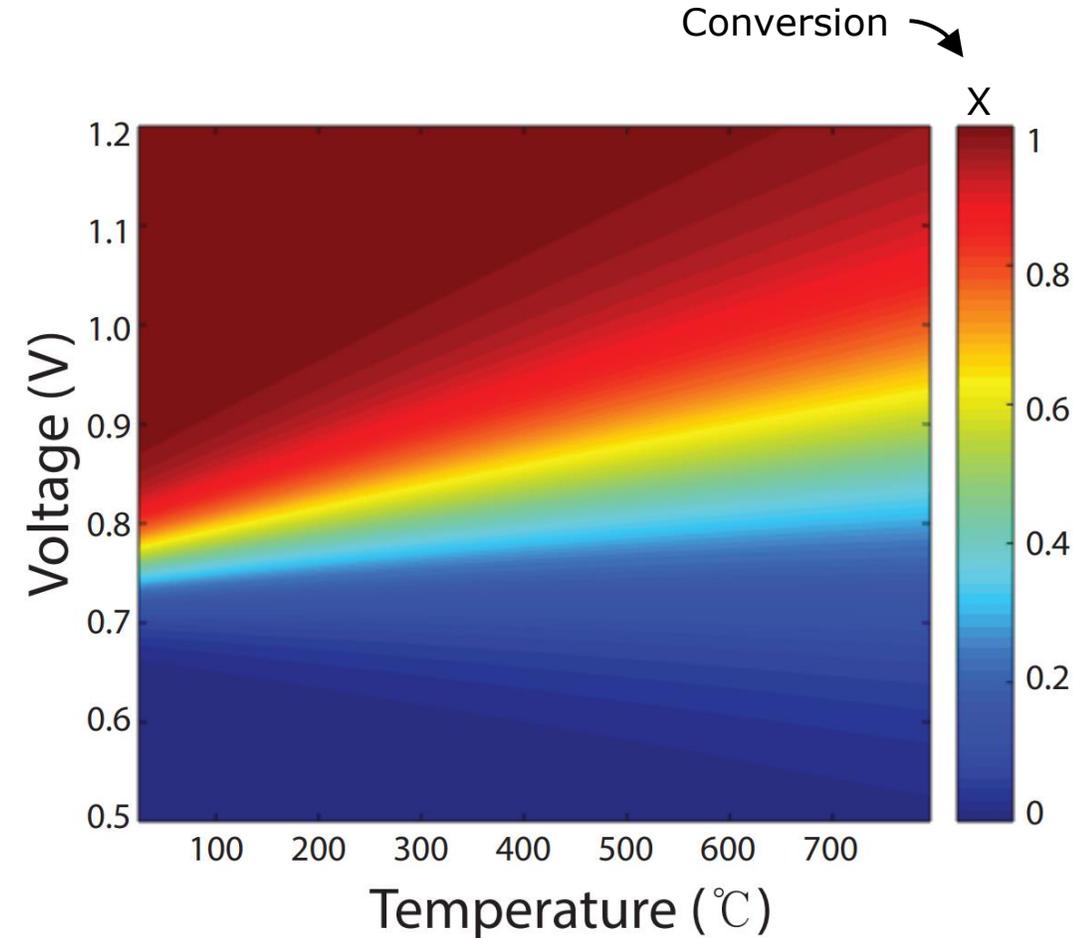
Sustainable O-atom transfer reactions



Energy landscape for O-atom transfer reactions

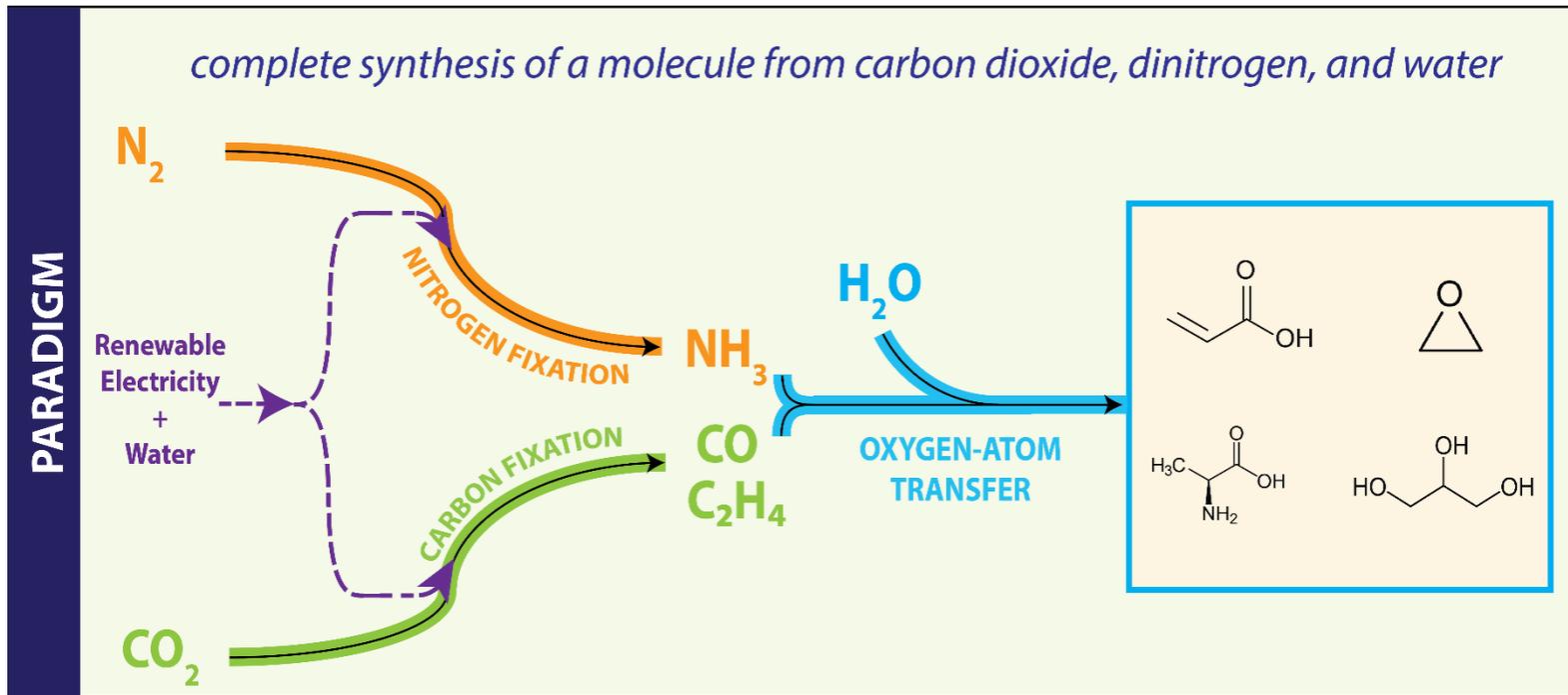


Mechanism is much like water splitting,
without formation of oxygen-oxygen bond



Thermodynamic cell voltage for epoxidation using water is 0.8 V, as compared to 1.2 V for water splitting – can lower the energy footprint of water splitting

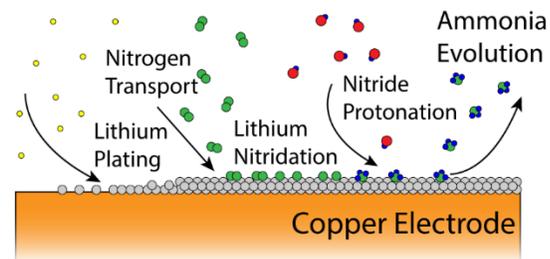
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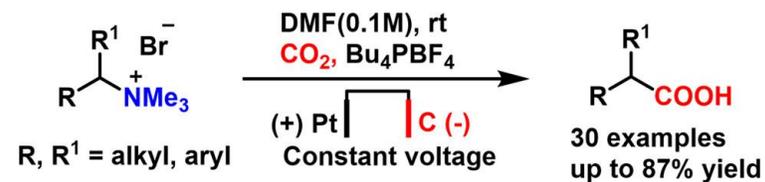
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CO_2 as C-atom source



H_2O as O-atom source

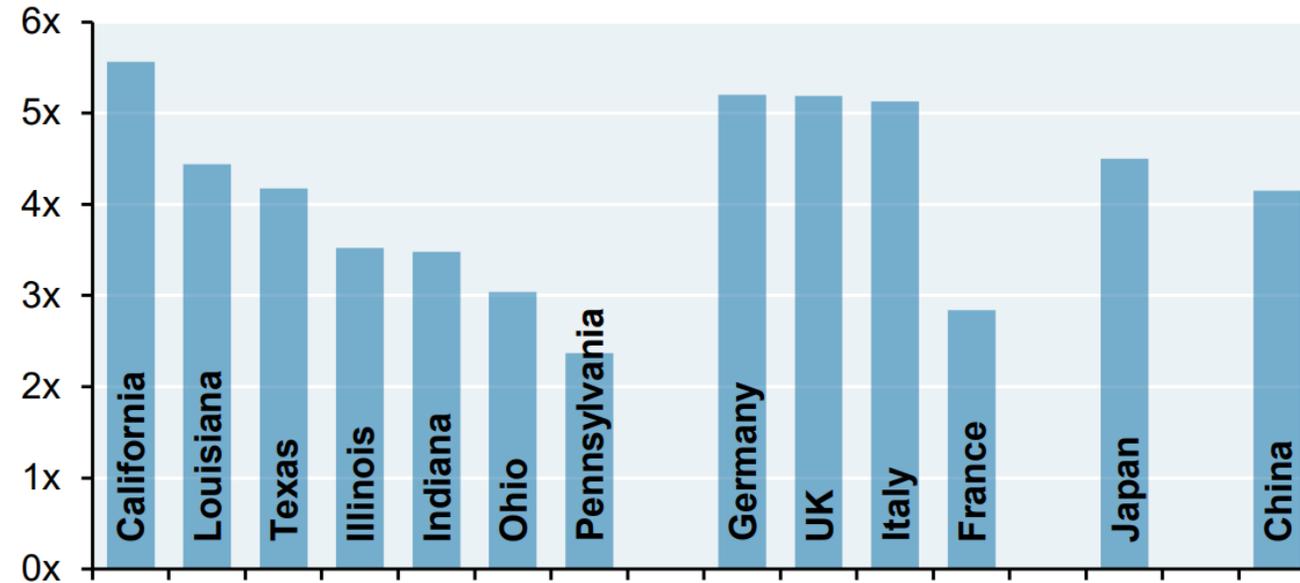


Chemical synthesis needs methane-parity

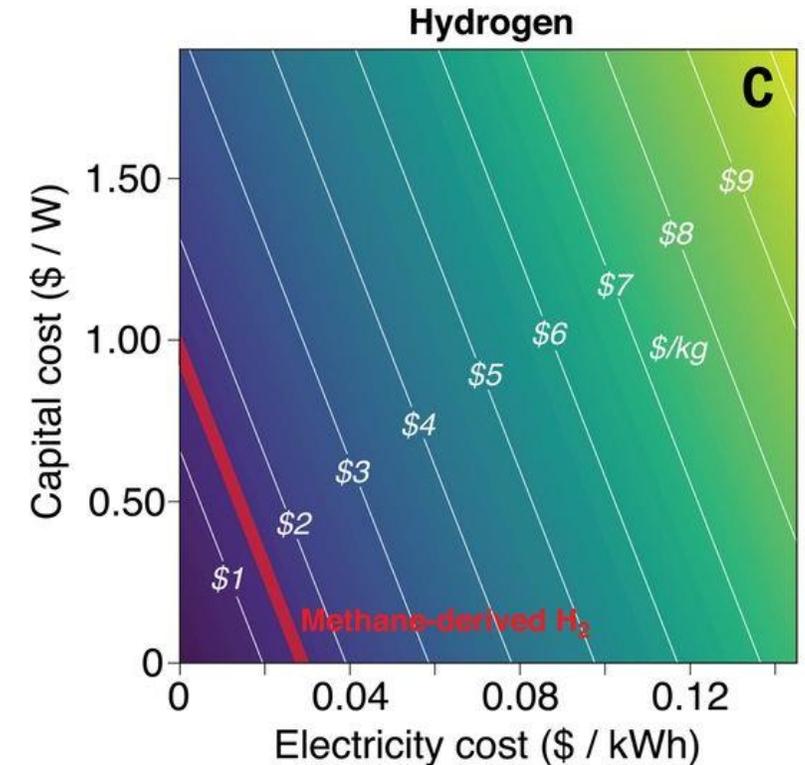
We often hear about grid-parity, but commodity chemical synthesis methane-parity is important

Electricity is 3x-5x more expensive than natural gas

Ratio of electricity price to natural gas price for industrial users per MJ of energy

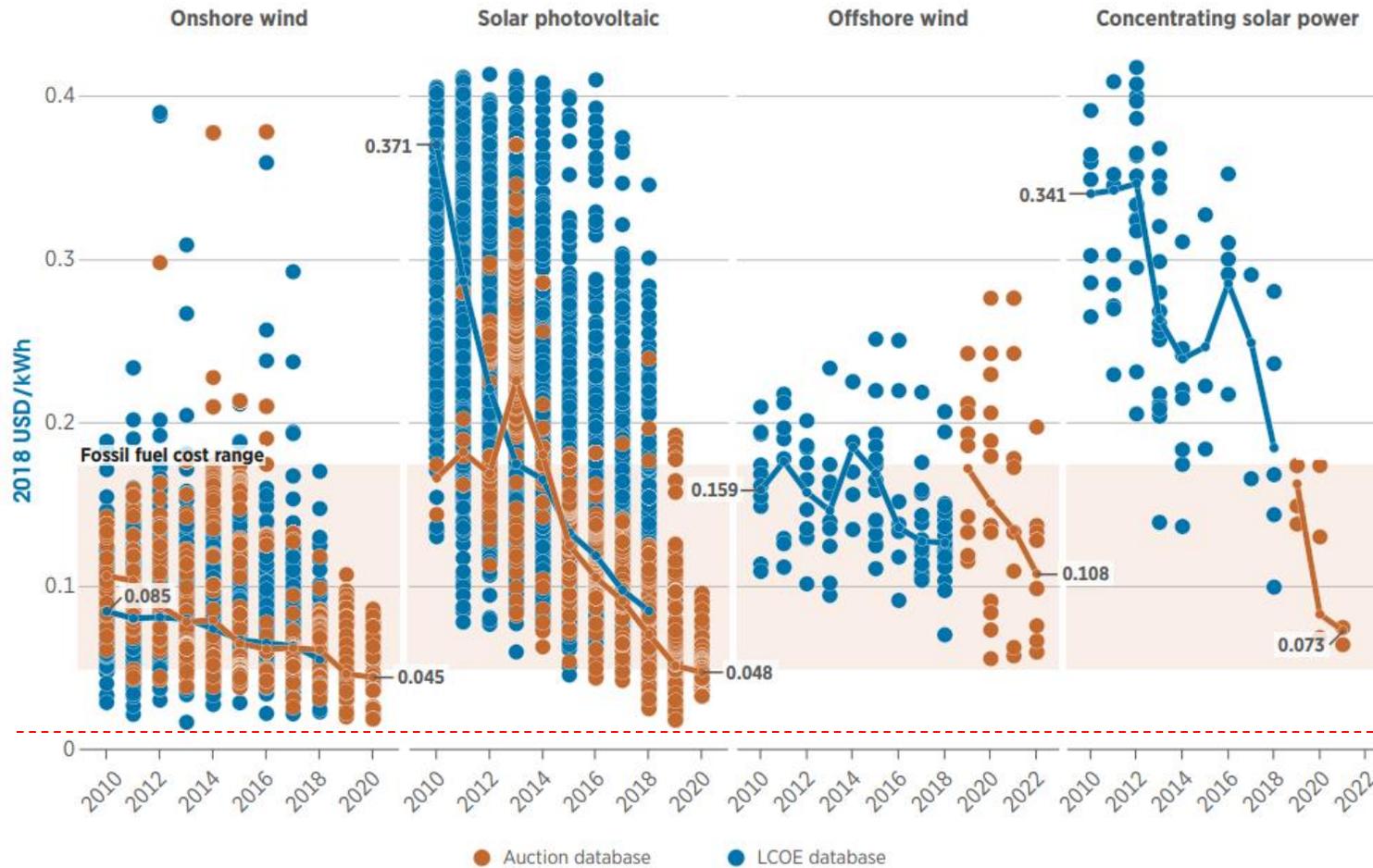


Source: EIA, Eurostat, IAEE, CEIC, IFPEN, JPMAM. 2018. The 7 US states shown are the largest industrial users of US primary energy.



Source: Davis S. J. et al. *Science* **2018**, 360.

Dramatic drop in levelized cost of electricity

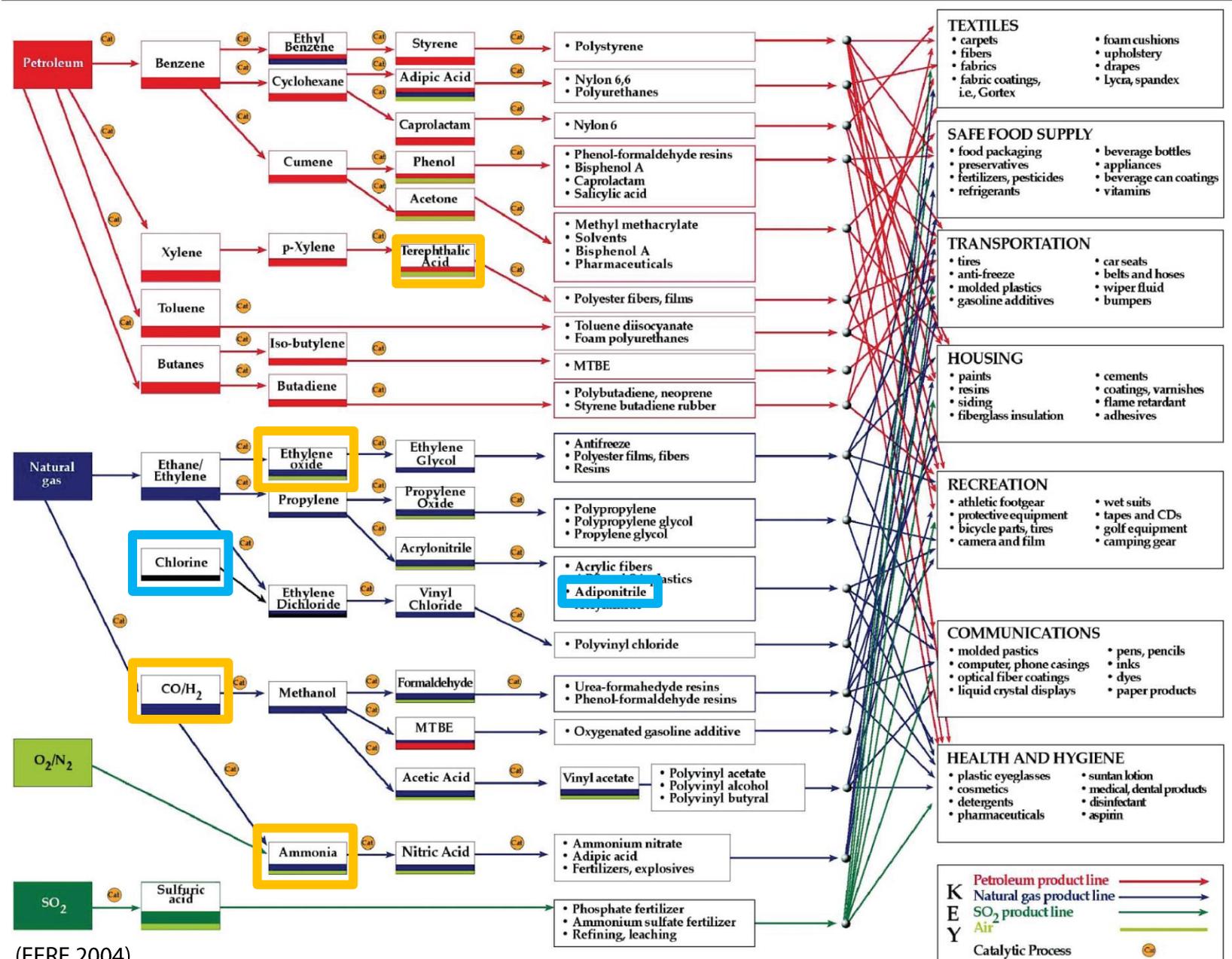


Source: IRENA

Reaching methane-parity may be on the horizon

Electrochemical unit operations

Raw materials Commodity chemicals Secondary commodity chemicals Intermediates Finished Products and Consumer Goods



Acknowledgements



Aditya
Limaye



Joy
Zeng



Sierra
Brooks



Nikifar
Lazouski



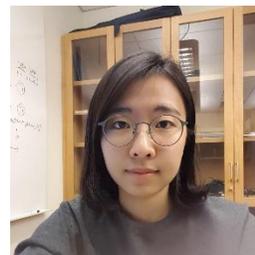
Dengtao
Yang



Kindle
Williams



Nathan
Corbin



Minju
Chung



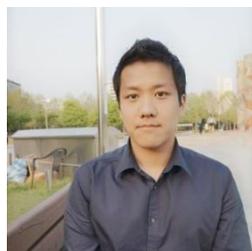
Joseph
Maalouf



Zachary
Schiffer



Michal
Gala



Kyoungsuk
Jin



Jess
Cohen

Funding



John Bradley

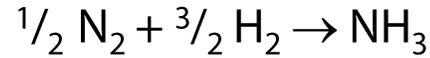


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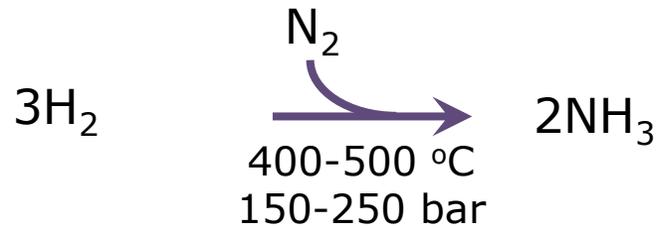
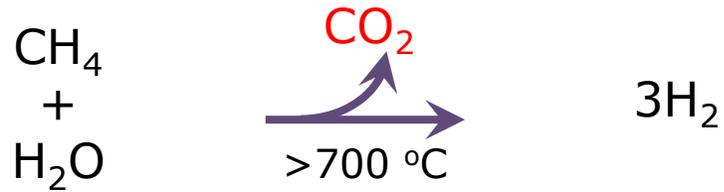


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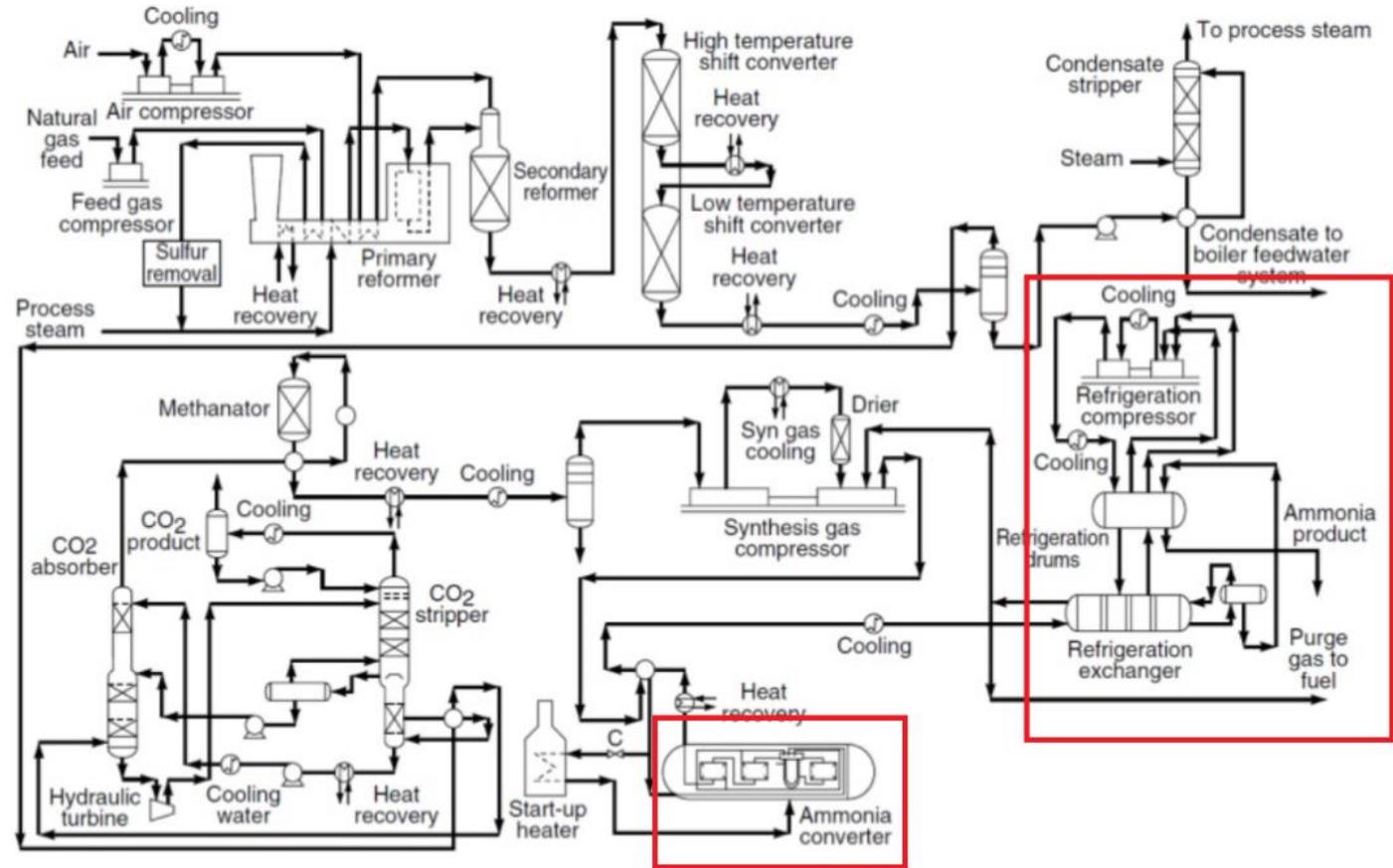
Haber Bosch process leads to large carbon dioxide emissions



Haber Bosch process



Large carbon footprint and harsh conditions

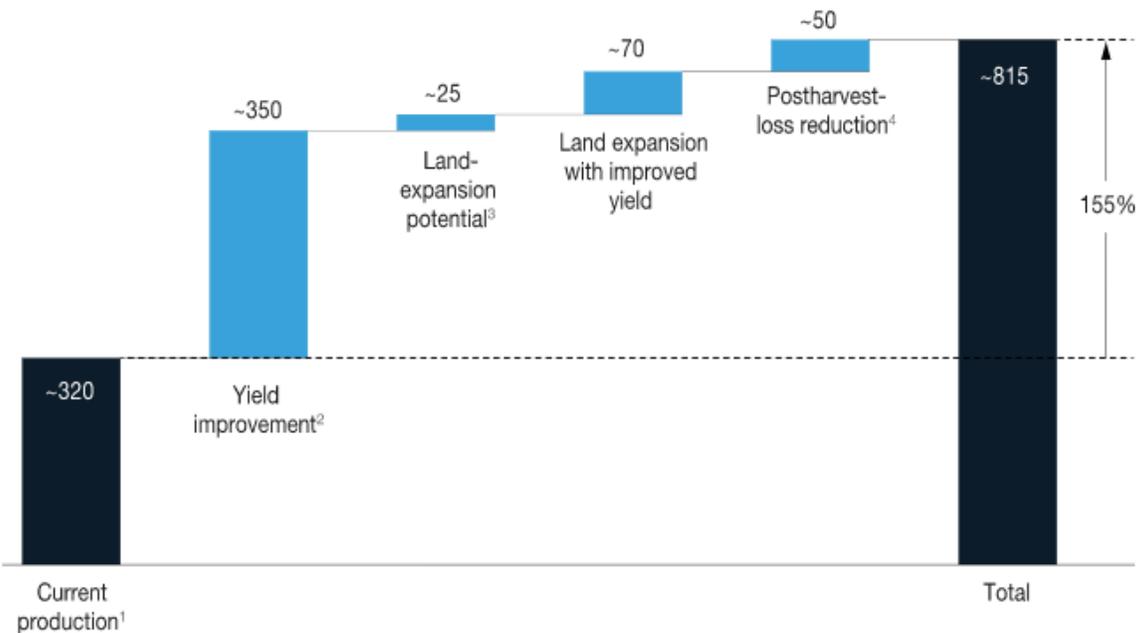


Ahmad, S.D. 2015

Need sustainable, modular production methods for ammonia

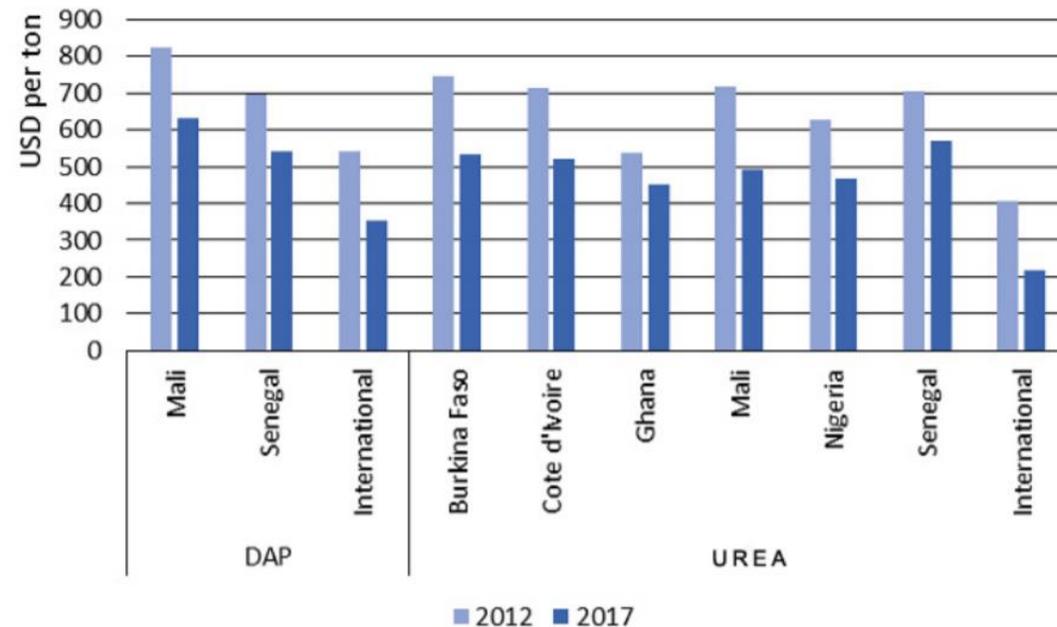
Distribution can contribute significantly to fertilizer prices

Cereal and coarse-grain production potential in Africa (millions of tons)

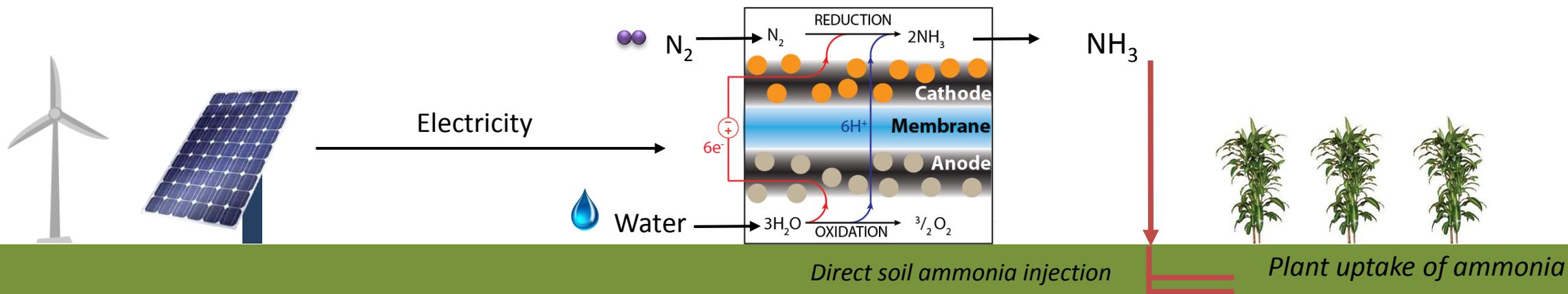


McKinsey&Company | Source: FAO; Global Yield Gap Atlas; McKinsey analysis

Urea and DAP fertilizer prices by country



Source : AfricaFertilizer.org ; World Bank Pink Sheet

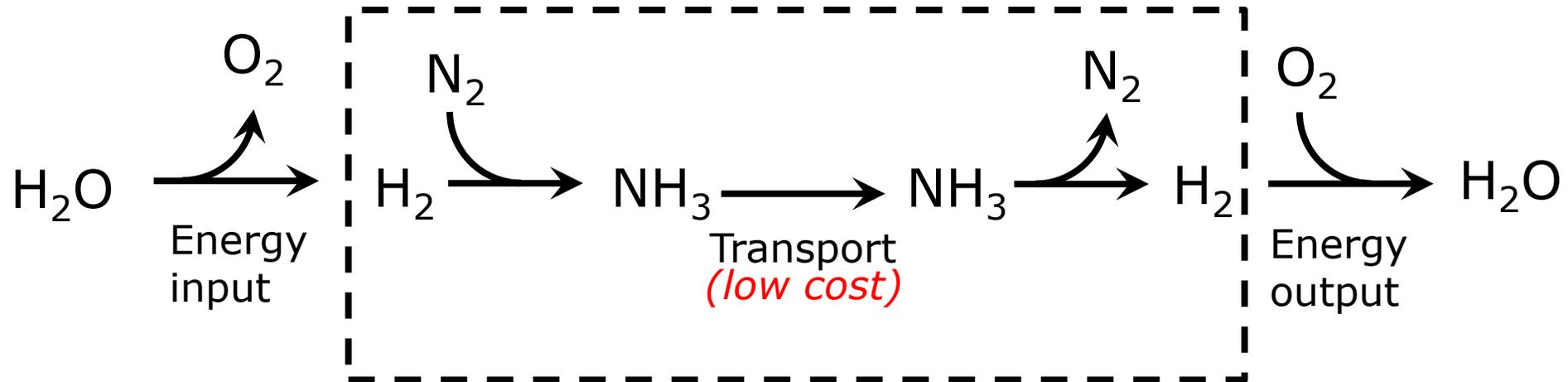


Ammonia is a nexus molecule: food, health, plastics, *and* energy



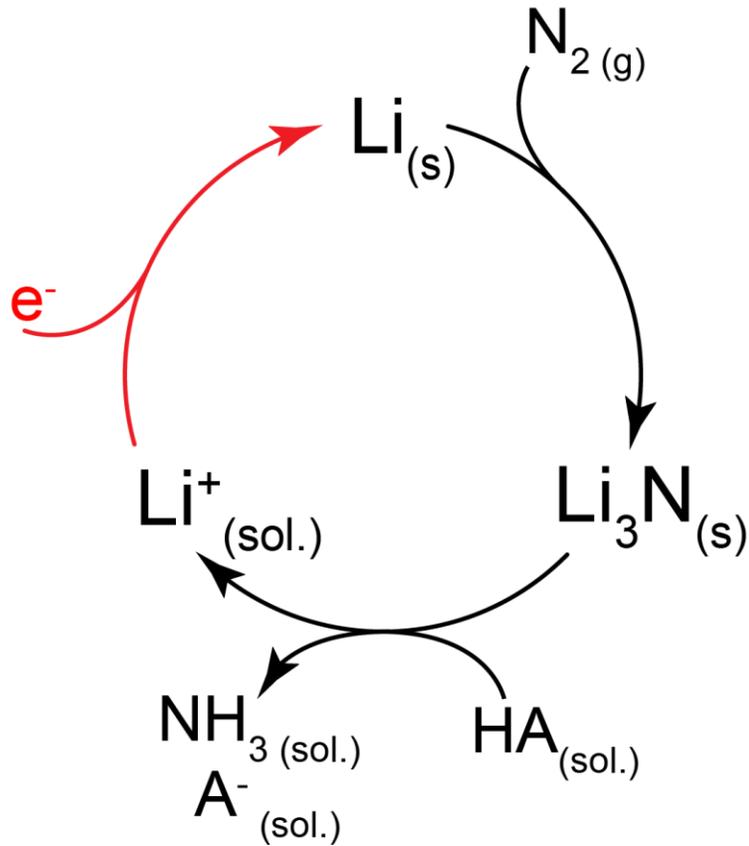
H₂ Fuel Station

	Hydrogen 
Energy density	0.03 kWh/L at 1 bar 1.3 kWh/L at 700 bar
Compression losses	7-19%
Transport and storage	\$0.1/kWh

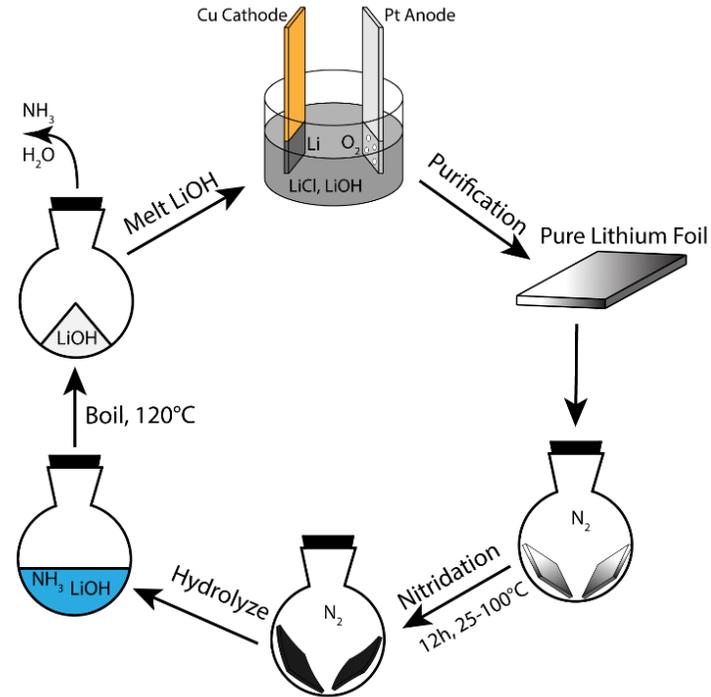


Ammonia functions as hydrogen carrier

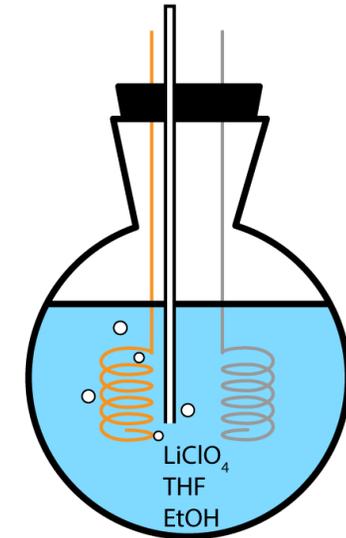
Lithium mediated ammonia synthesis



Cycle involving electrochemical and thermochemical steps



McEnaney, *J. Energ. Environm. Sci.* **2017**



8.4% FE

$0.55 \text{ nmol cm}^{-2} \text{ s}^{-1}$

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

Proof of concept studies are promising but limited