



# Electrocatalyst Discovery for the Ammonia Oxidation Reaction

Henry Northen<sup>1</sup>, J. Tyler Mefford<sup>1,\*</sup>

<sup>1</sup>Department of Chemical Engineering, University of California Santa Barbara

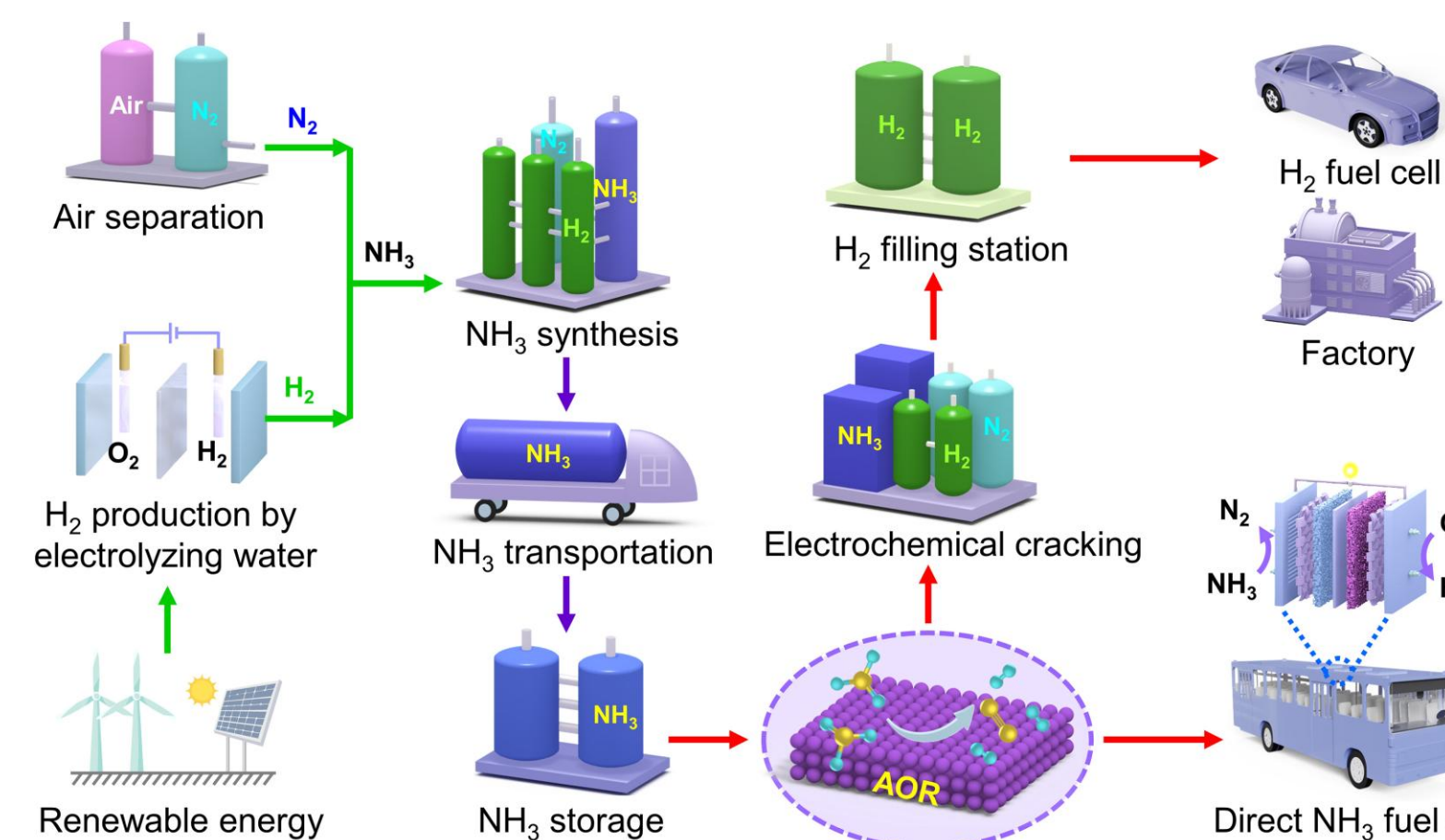
\*Corresponding author, Email: [tmefford@ucsb.edu](mailto:tmefford@ucsb.edu)

**Abstract:** Ammonia is a promising alternative to hydrogen for fuel cells due to its high energy density, simple storage, and existing global infrastructure for production and transport. Liquid hydrogen needs to be stored at either -253 Celsius or 350-700 Bar, which takes a substantial amount of energy and requires very specialized (and expensive) equipment to accomplish. Unlike hydrogen, ammonia can be stored as a liquid under mild conditions, reducing infrastructure barriers that have hindered hydrogen fuel cell adoption. However, ammonia oxidation reaction (AOR) kinetics are currently slow, relying heavily on scarce precious-metal catalysts that are susceptible to poisoning by nitrogen-containing intermediates. Overcoming these catalytic challenges is critical to realizing commercial ammonia fuel cells. Over the past year, I've used the Open Catalyst Project (OCP), a machine learning framework by Facebook AI Research, to perform calculations simulating Density Functional Theory (DFT). After screening over 11,500 materials, I compiled adsorption energies for the 173 most promising catalysts across 15 relevant AOR intermediates. This comprehensive dataset has enabled me to identify several promising non-precious-metal catalysts, as well as major trends that determine the preferred reaction pathways and decide the characteristics of optimal catalysts.



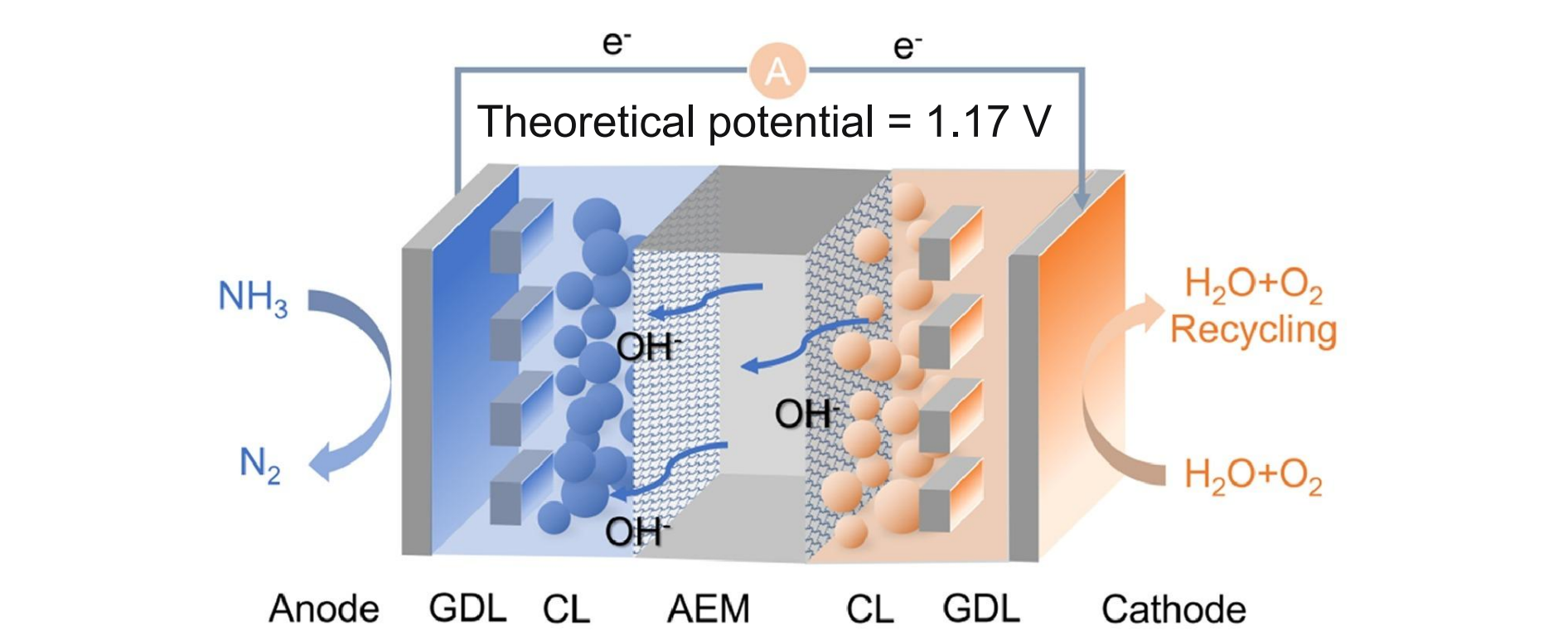
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## Project Motivations



Chem Catalysis, 2024

Ammonia is a promising potential fuel for clean power generation. It is easier and cheaper to store than hydrogen, has an existing global infrastructure for production and shipping, and can be a truly zero-carbon source of energy.



EnergyChem, 2023

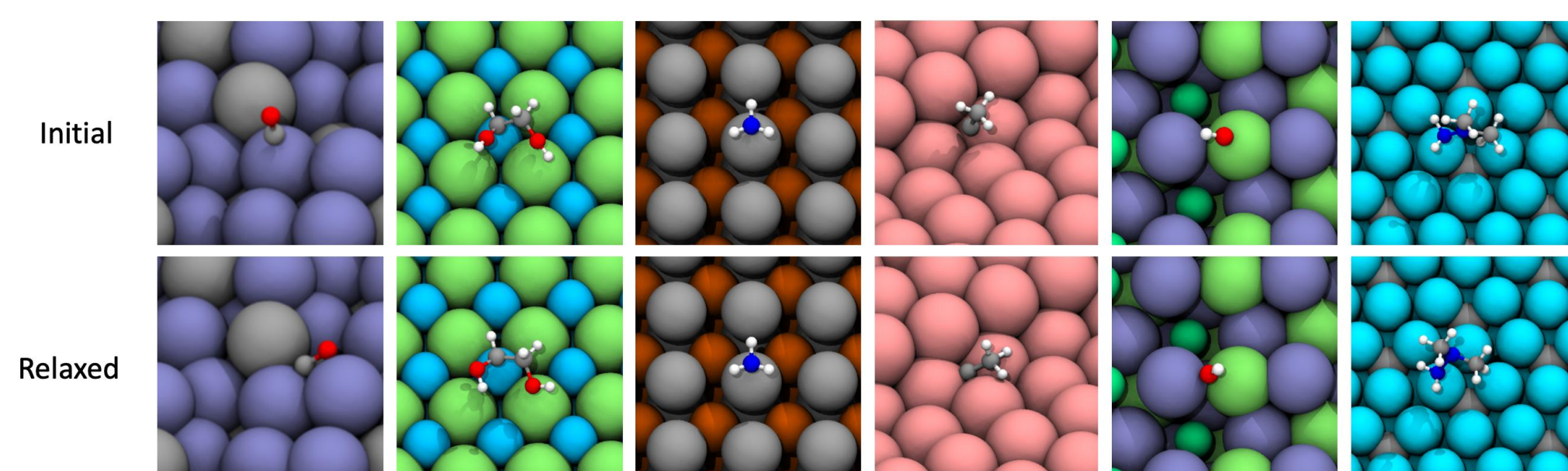
Current barriers to the ammonia oxidation reaction:

- Slow reaction kinetics
- Scarce and expensive catalysts
- Catalysts susceptible to poisoning by nitrogen-containing adsorbates

All these barriers are related to catalyst performance. To accelerate catalyst discovery, we've run calculations for tens of thousands of catalyst/adsorbate combinations, down-selecting from that to find electrocatalysts that fit our criteria.

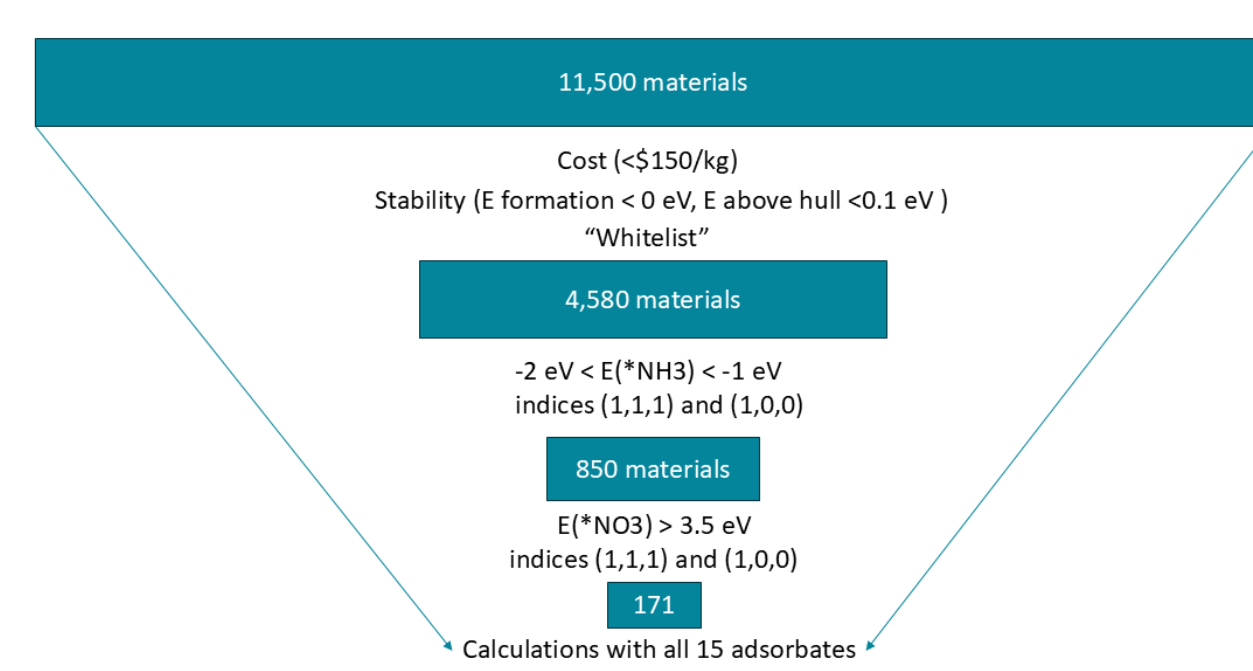
## Computational Catalysis

- Standard computational catalysis is done using Density Functional Theory (DFT)
- DFT is a computational modeling method that predicts chemical properties, energies, and structures based on electron densities
- Standard DFT calculations require significant computational resources and can take days to run
- The time and resource requirements make using DFT too challenging for extensive material screening
- The Open Catalyst Project (OCP) estimates DFT calculations using machine learning, taking calculation times down from days to just several minutes
- OCP allows us to calculate energies first, then narrow materials down based on characteristics of current catalysts**



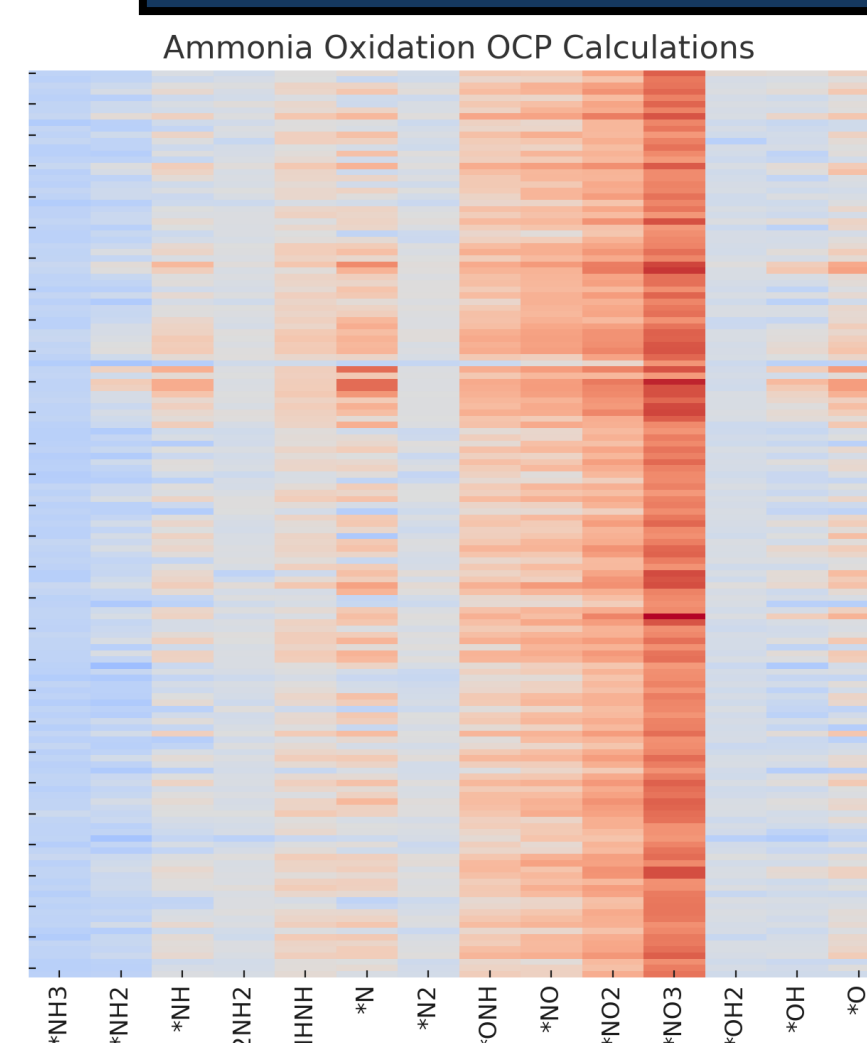
## Methods

We used OCP to create an extensive dataset of adsorption energies, enabling us to identify several promising non-precious-metal catalysts that have theoretically better thermodynamics than Pt and investigate trends and mechanisms of the AOR.



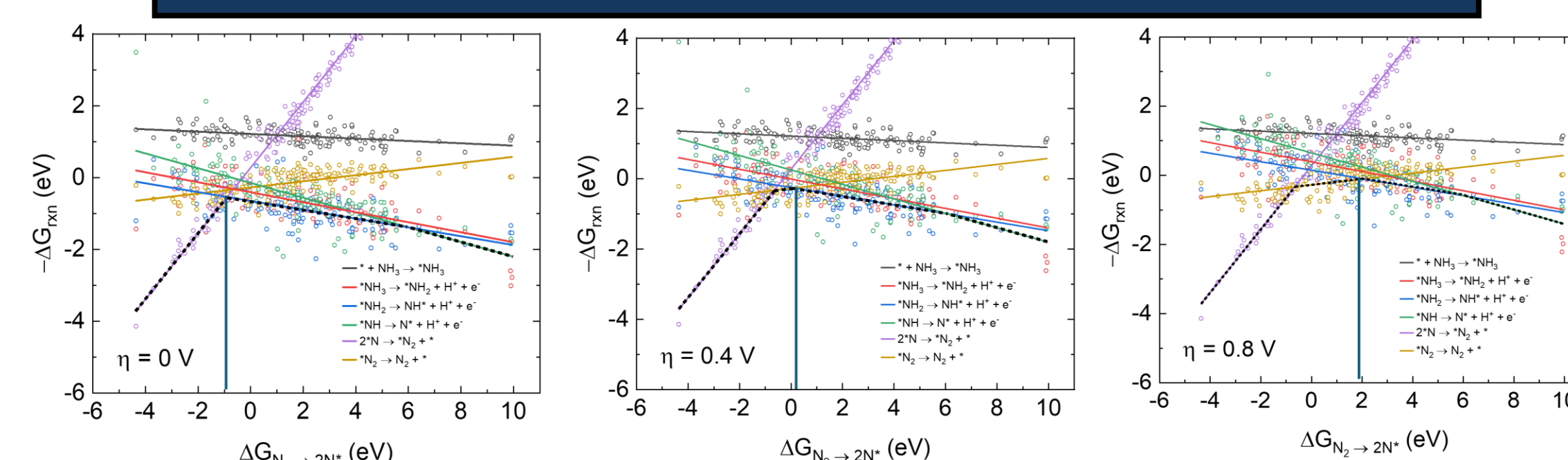
- OCP calculations still take about 5 minutes per adsorbate/material/miller index combination.
- 15 adsorbates, 11,500 materials, and 2 miller indices = 1200 days to finish.
- To shorten calculations, we set up the above filters, which shortened the calculation run time from several years to several months
- These calculations would have taken 958 years to do using traditional DFT methods**

## Adsorbate Trends

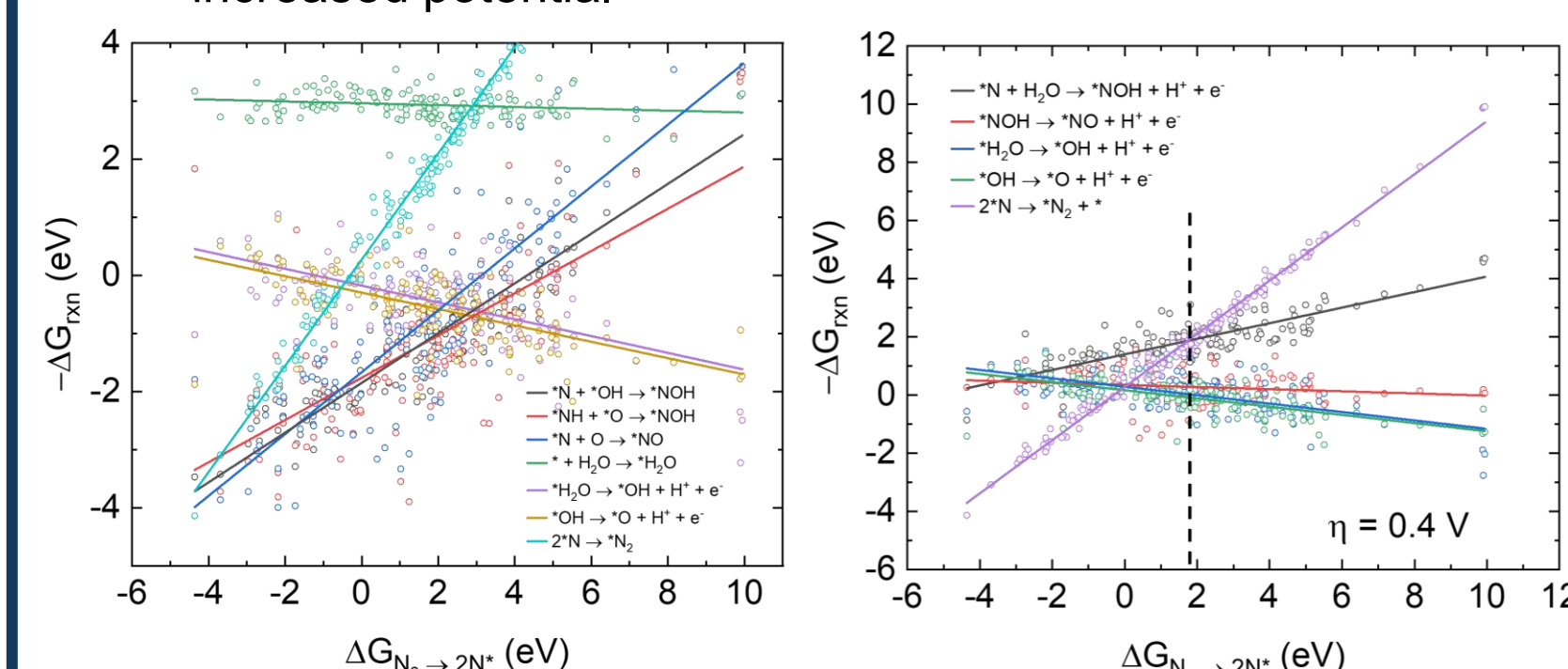


- In general, we see low energies for NHx species and high energies for NOx species
- This is what we want to see!
- NHx species should adsorb to the catalyst to dehydrogenate, then desorb to N2 gas when done
- Want "Goldilocks" slight negative energy
- We do not want to form NOx species, as they are toxic and lead to losses in fuel cell efficiency
- Want very positive energies for NOx
- These trends also confirm that filtering based on NH3 and NO3 (above) was successful

## Nitrogen Scaling Relations

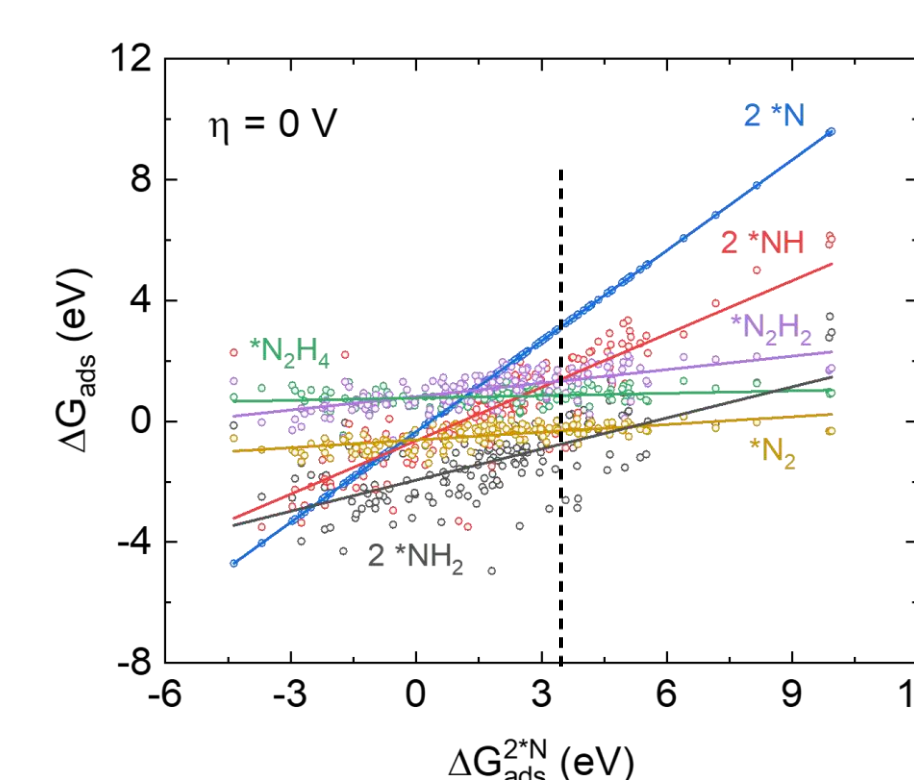
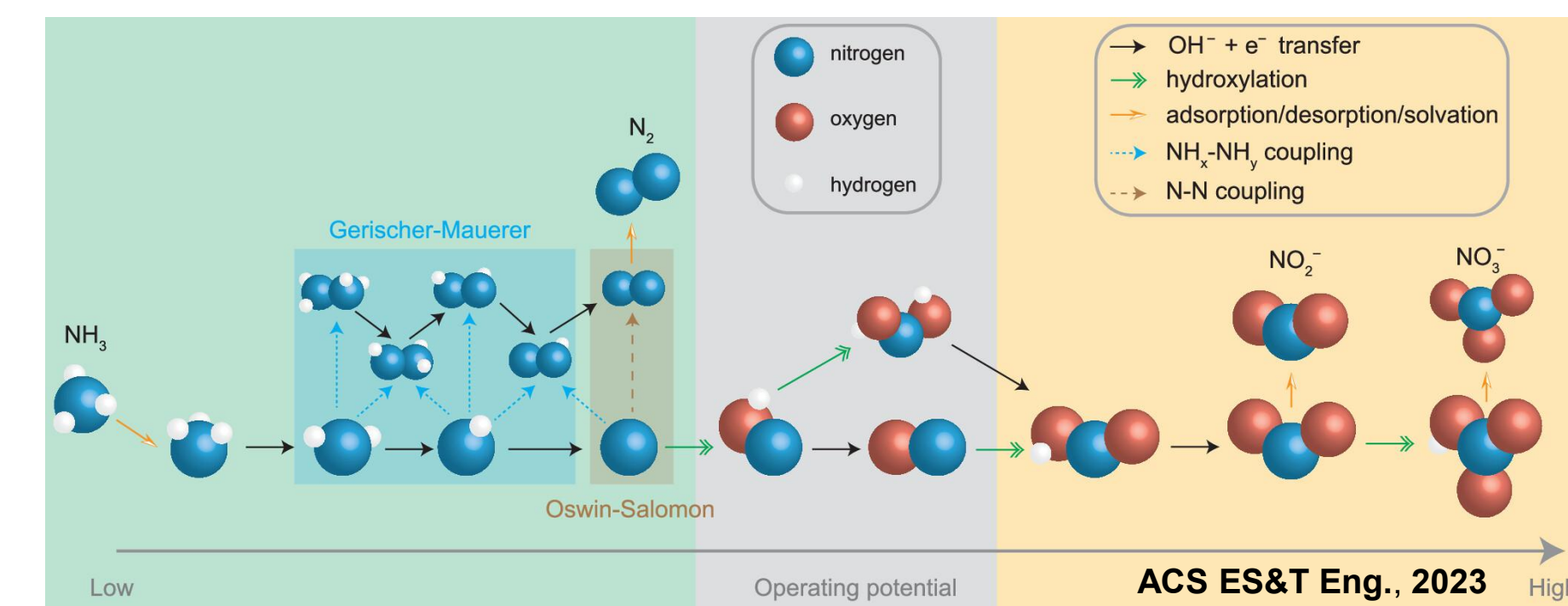


- How does the ideal catalyst scale with the strength of nitrogen binding and the applied potential?
- Ideal catalyst is at the peak of the "volcano" made by the black dotted line
- Represents the catalyst with the lowest barrier for the rate limiting step
- At 0 V, the ideal catalyst has stronger \*N binding, and shifts to weaker \*N binding with increased potential



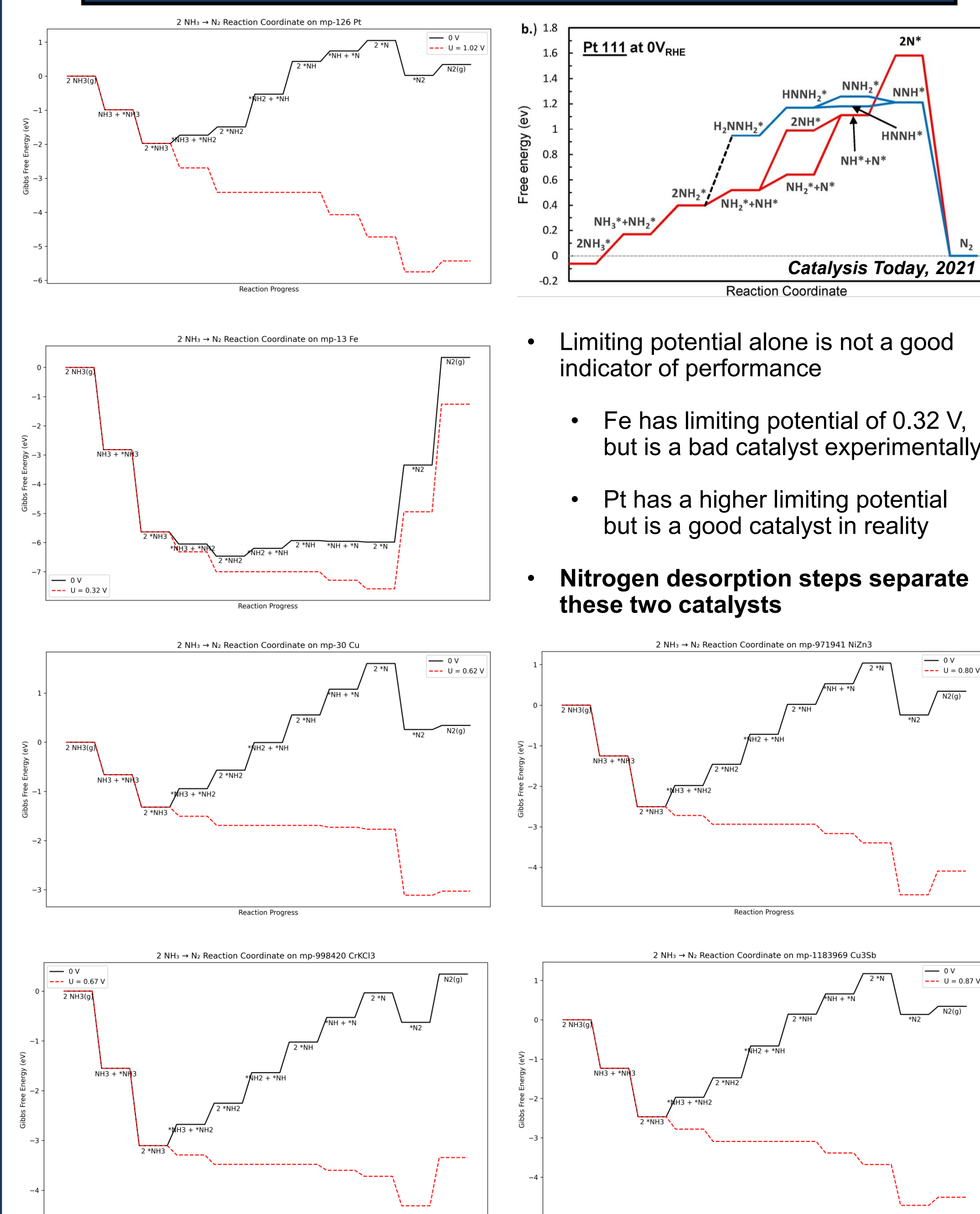
- Need catalyst with weak \*N binding to avoid forming \*NOx species
- With 0 V applied, \*N2 formation is always favored over \*NOx

## Mechanisms



- For weak \*N binding the G-M mechanism is preferred
- For strong \*N binding O-S is favored
- We concluded earlier that catalysts with weak \*N binding were necessary to avoid forming \*NOx species
- Therefore, the G-M mechanism is necessary to avoid the formation of \*NOx species**

## Reaction Coordinates

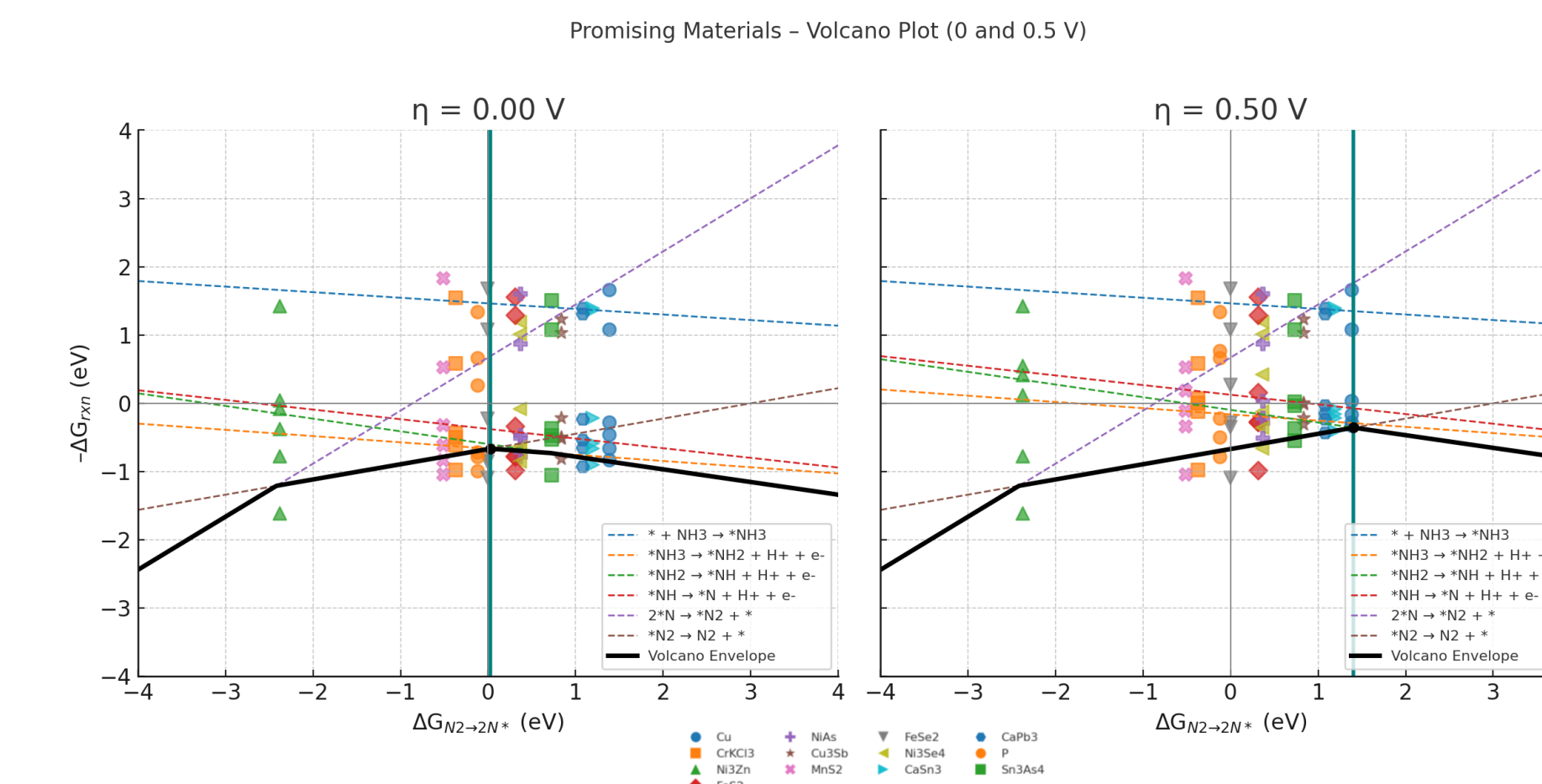


- Limiting potential alone is not a good indicator of performance
- Fe has limiting potential of 0.32 V, but is a bad catalyst experimentally
- Pt has a higher limiting potential but is a good catalyst in reality
- Nitrogen desorption steps separate these two catalysts**

These reaction coordinates show the energetics of some of the more promising non-precious-metal catalysts. They have lower limiting potentials than Pt while still having somewhat favorable nitrogen desorption energetics.

Copper is especially interesting, as previous DFT studies have not identified its low theoretical overpotential. OCP could have possibly found a lower energy configuration or used different miller index when calculating.

## Promising Materials



- Among the materials screened, Fe-based chalcogenides (FeSe2 and FeS2) identified as promising
- Interestingly, these materials are analogous to the FeS2 domains in the FeMo cofactor in nitrogenase – the natural enzyme responsible for N2 → NH3 conversion
- The chalcogenides of metals seem to have much better nitrogen desorption energetics than the pure metal, although they conversely have higher limiting potentials**

## Conclusions

- Ammonia is a promising alternative to hydrogen, and if improvements can be made in the electrocatalysts for the AOR, it is well positioned to be adopted globally
- OCP provides a new way to search for catalysts and has allowed us to shorten the computational time from nearly 1000 years to several months
- The G-M mechanism is necessary to avoid the formation of \*NOx species, which limits catalyst activity but increases selectivity
- Nitrogen desorption is the biggest predictor of catalyst performance → Fe-chalcogenides identified as promising direction for experimental validation

## Future Work

- Perform DFT calculations to verify OCP data
- Calculate the full range of adsorbates for the G-M mechanism
- Start experimental work to test computationally identified catalysts

## References

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## Acknowledgements

