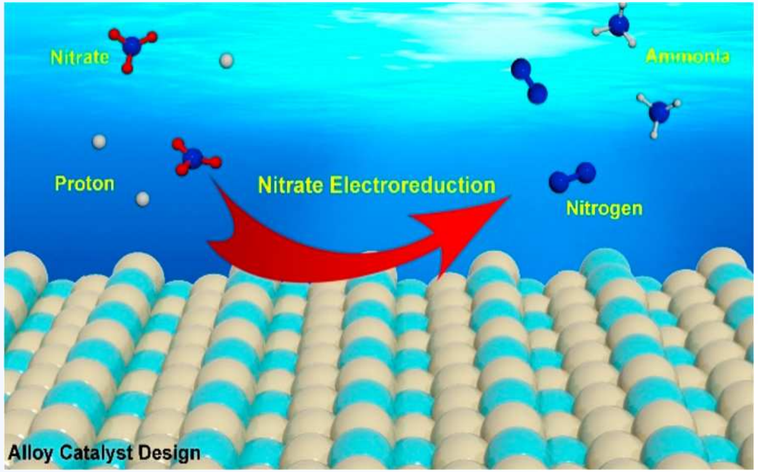

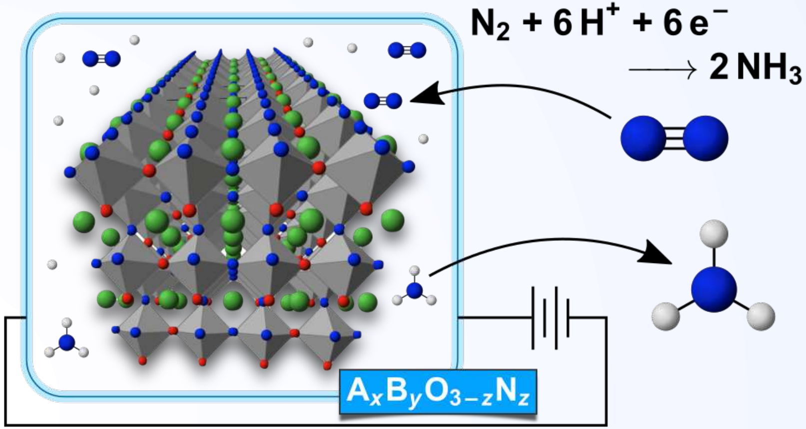

Heterogeneous Electrocatalysts for Aqueous Nitrate Reduction and Nitrogen Chemistry

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Oral Defense – 07 Aug 2023

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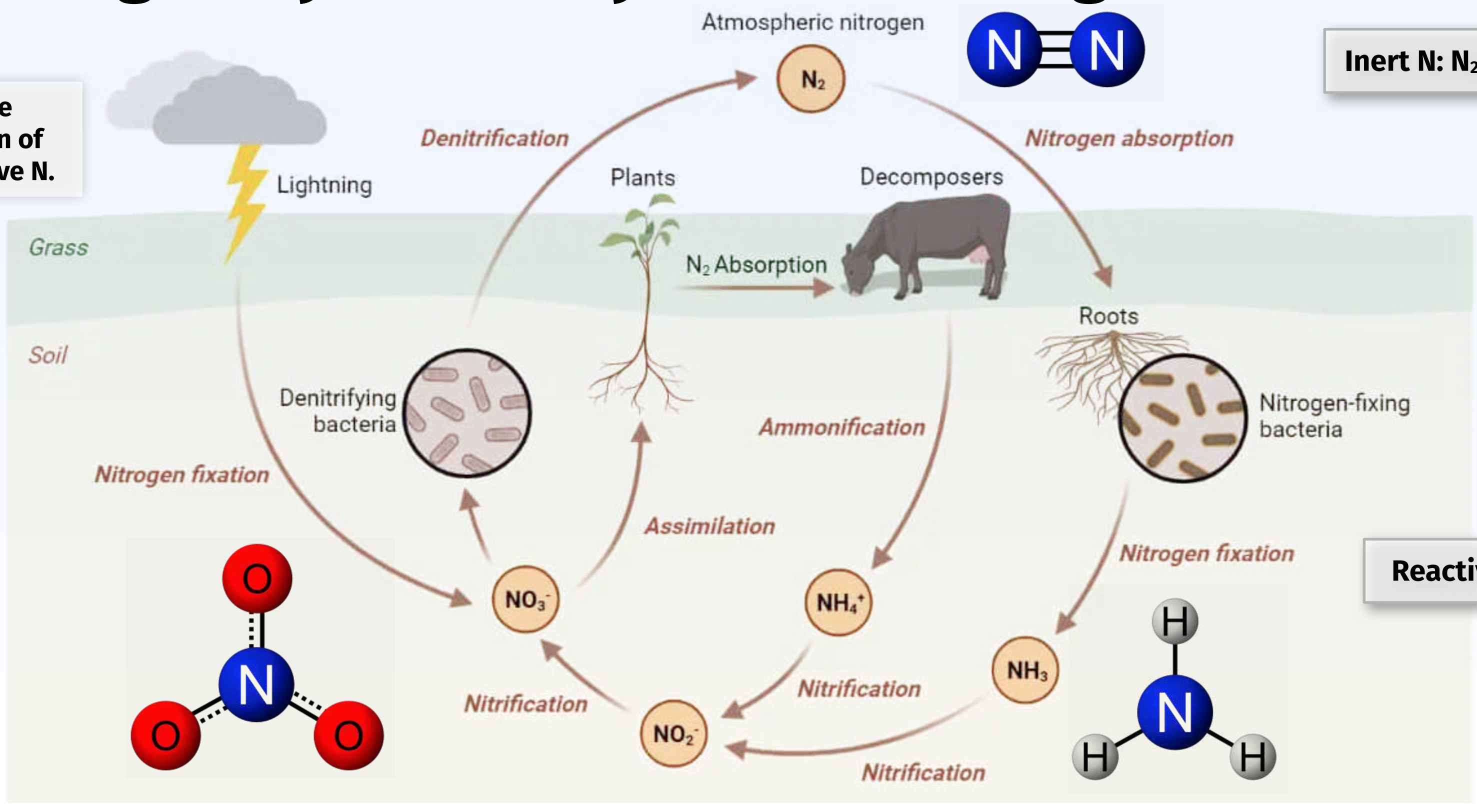
The Nitrogen Cycle is Key to Sustaining Life on Earth

Must balance interconversion of inert and reactive N.

Inert N: $N_2(g)$

Reactive N



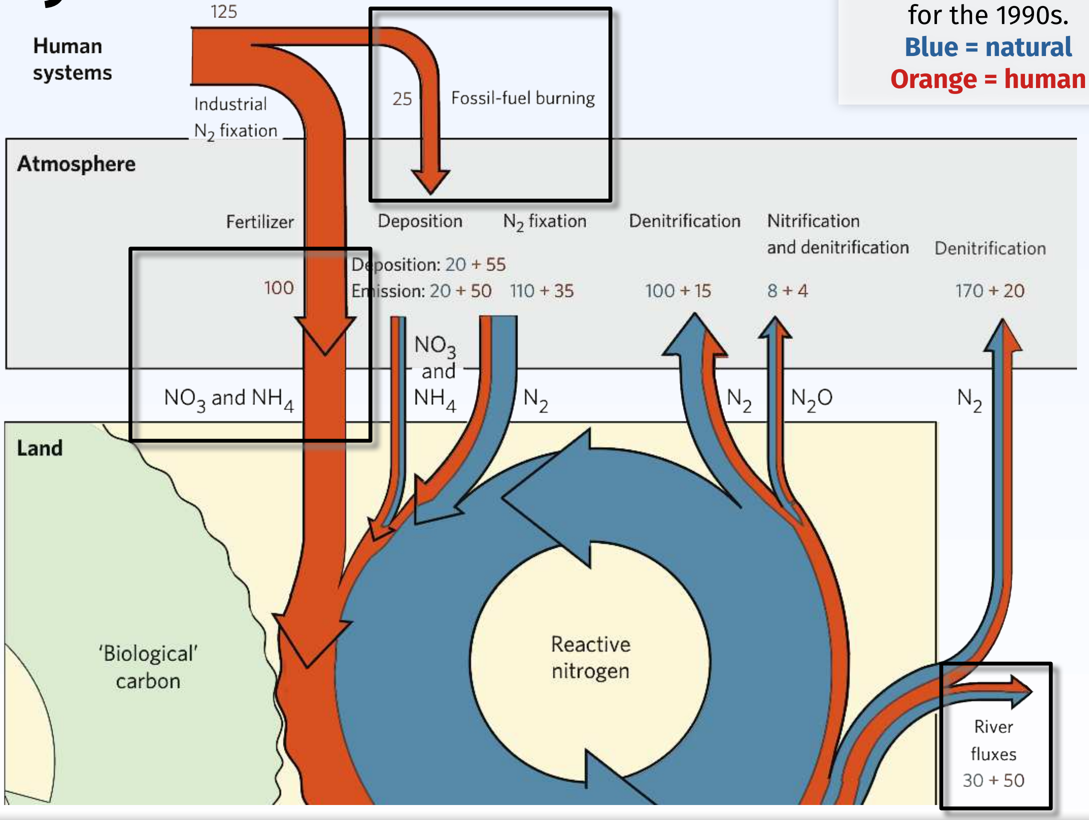
[1]

[1] Aryal, S. Nitrogen Cycle – Definition, Steps, Process, Significants. *The Biology Notes* **2023**. https://thebiologynotes.com/nitrogen-cycle-steps-and-significance/

The Global Nitrogen Cycle is Out of Balance

Numbers indicate approximate Tg N/year for the 1990s.
Blue = natural
Orange = human

- To balance the nitrogen cycle, we need to better understanding N chemistry.
- **How can we consume excess NO_3 from water systems?**
- **How can we produce NH_3 more efficiently?**



[1]

[1] Gruber, N.; Galloway, J. N. An Earth-System Perspective of the Global Nitrogen Cycle. *Nature* **2008**, *451* (7176), 293–296. https://doi.org/10.1038/nature06592.

Why Should We Care About Lowering Terrestrial Nitrate Levels?

Nitrate, NO_3^-

Nitrate is a major water pollutant

- Human N contribution to environment: 10^8 tonnes/yr.[1, 2]
  - Largest source: ammonia fertilizer (> 100 Tg N).
  - NO_3^- is one of the most widespread water pollutants.
- Adverse health effects:[3–5]
  - Methemoglobinemia.
  - Ovarian and thyroid cancers.
- Adverse environmental, economic effects:[2]
  - Eutrophication and aquatic death.
  - Impacts to fishing economies.

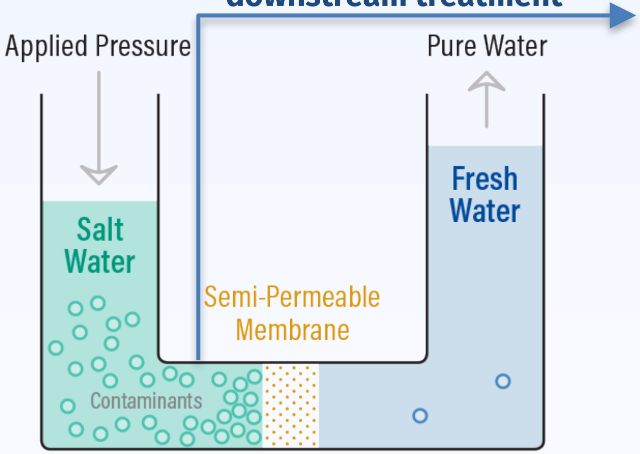
Ammonia fertilizer in agriculture [1].

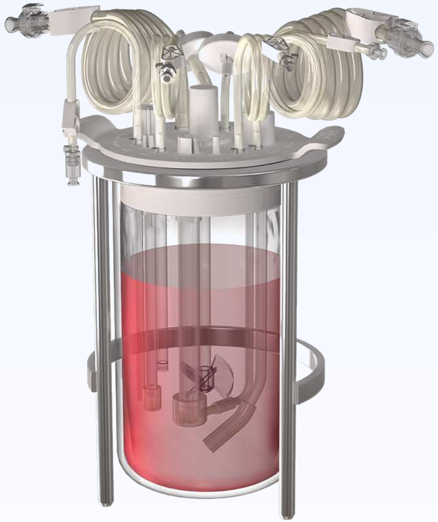
Methemoglobinemia patient (left) [5].

Algae bloom in nearby Lake Erie [2]

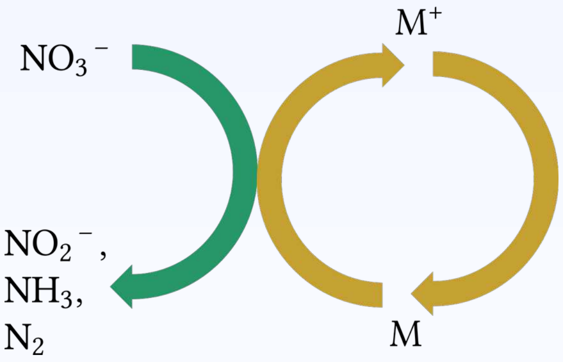
1. Fields, S. *Environmental Health Perspectives* **112**, A556–A563 (2004).
2. Duca, M. & Koper, M. T. M. *Energy Environ. Sci.* **5**, 9726–9742 (2012).
3. Farkas, J. Methemoglobinemia in *Internet Book of Critical Care* (2019).
4. Xie, L. *et al. Oncotarget* **7**, 56915–56932 (2016).
5. Soliman, D. S. & Yassin, M. Congenital methemoglobinemia misdiagnosed as polycythemia vera: Case report and review of literature. *Hematol Rep* **10**, (2018).

Approaches to Balance Nitrogen Cycle Through NO_3^- Removal





Nitrate Reduction Reation (“NO3RR”)



Physical[1]

- Produces concentrated waste
- Need regular membrane/resin purging/regeneration

Bacterialogical[2]

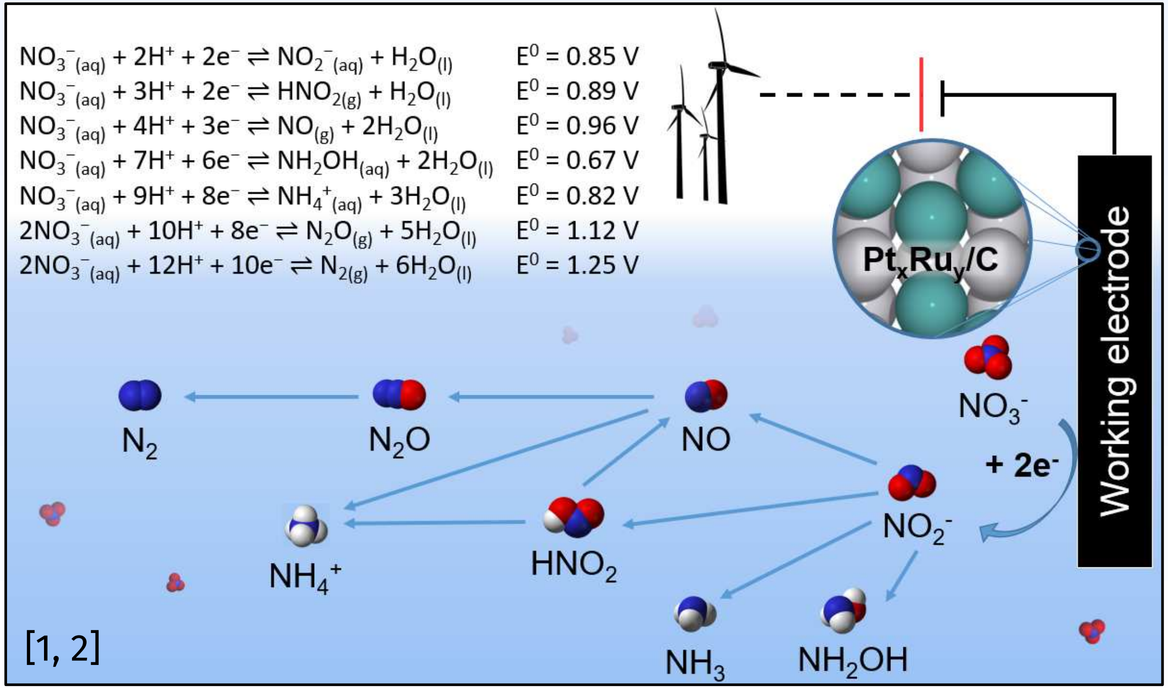
- Need carbon source and controlled conditions
- Can produce biotoxins

Catalytic[3]

- Catalyst can be poisoned
- Need electricity or reductant

[1] PureTec Industrial Water. What is Reverse Osmosis? https://puretecwater.com/reverse-osmosis/what-is-reverse-osmosis
[2] Distek, Inc. BIOne Single-Use Bioreactor System. https://www.distekinc.com/products/bione-single-use-bioreactor-system/
[3] Adapted from Hasnat, M. *et al.*, *J. Ind. Eng. Chem.* **28** (2015) 131–137

Electrocatalytic Nitrate Reduction (NO_3RR) is a Sustainable Route for Nitrate Remediation

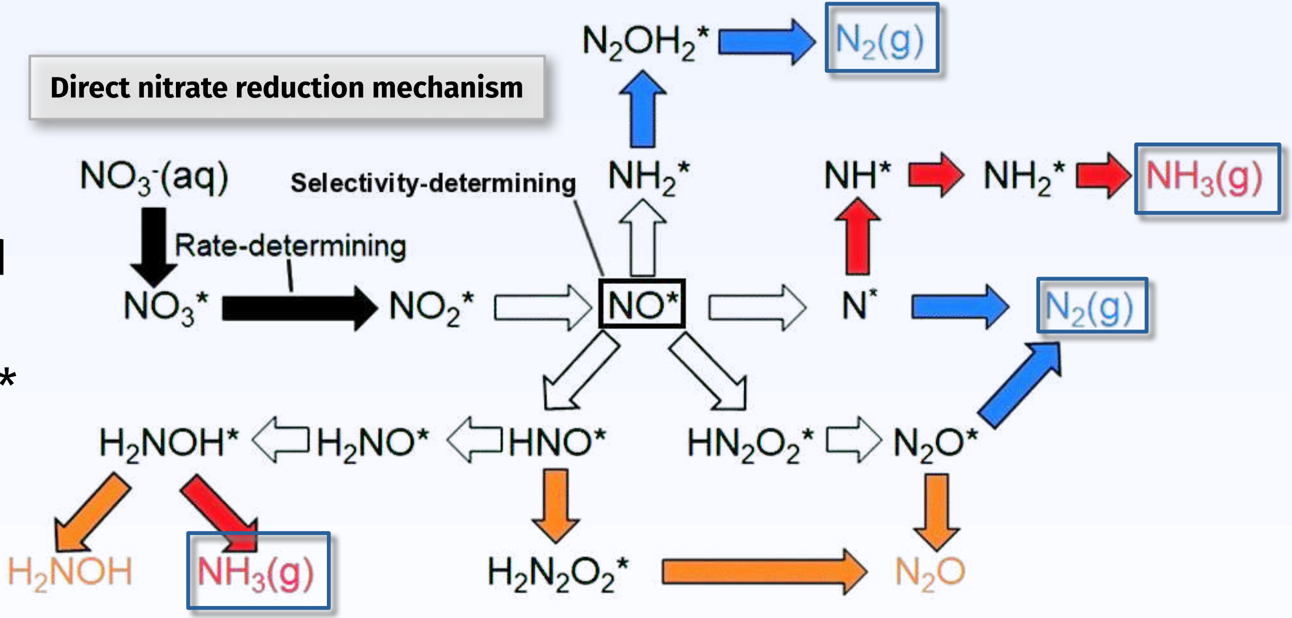


- Could be powered with renewable electricity
- Many benign or value-added products possible, especially NH_3, NH_4NO_3.
- **Challenge: need active, selective, and stable electrocatalysts.**

[1] Wang, Z., Young, S. D., Goldsmith, B. R. & Singh, N. Increasing electrocatalytic nitrate reduction activity by controlling adsorption through PtRu alloying. *Journal of Catalysis* **395**, 143–154 (2021).
[2] Singh, N. & Goldsmith, B. R. Role of Electrocatalysis in the Remediation of Water Pollutants. *ACS Catal.* **10**, 3365–3371 (2020).

NO_3RR Mechanism on Metals Informs Catalyst Design

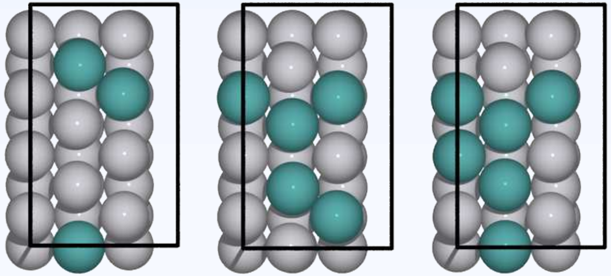
- On transition metals, rate-limiting step is[1]
  $NO_3^* \rightarrow NO_2^* + O^*$.
- Active catalysts should hold onto NO_3^- tightly.
- A low $NO_3^* \rightarrow NO_2^* + O^*$ barrier is important.



Pt-group metal activities: Rh > Ru > Ir > Pd ≈ Pt
Coinage metal activities: Cu > Ag > Au

[1] Dima, G. E.; de Vooys, A. C. A.; Koper, M. T. M. *Journal of Electroanalytical Chemistry* **2003**, 554–555, 15–23. DOI: 10.1016/S0022-0728(02)01443-2.
[2] Wang, Z.; Richards, D.; Singh, N. *Catalysis Science & Technology* **2021**, 11 (3), 705–725. DOI: 10.1039/D0CY02025G.

I Focus on Three Electrocatalyst Materials to Help Balance the Nitrogen Cycle



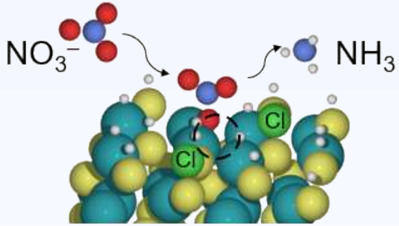
Pt Ru

Platinum–Ruthenium Alloys

Rh_xS_y/C

NO_3RR Activity

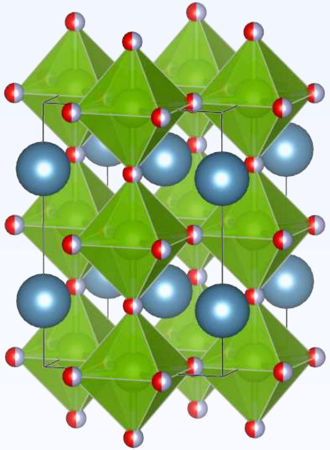
Cl^- Poison Resistance



$Rh_3S_4(100)$ with Sulfur Vacancy

Rh S

Rhodium Sulfides



A B O N

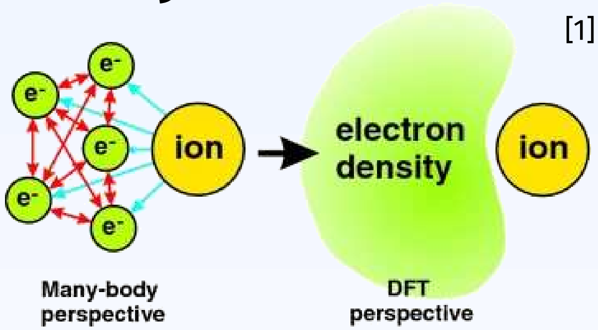
Perovskite Oxynitrides

Nitrate reduction

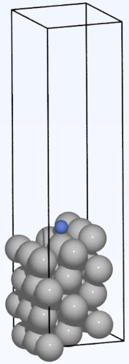
Ammonia synthesis

[1] Wang, Z., Young, S. D., Goldsmith, B. R. & Singh, N. *Journal of Catalysis* **395**, 143–154 (2021).
[2] Richards, D., Young, S. D., Goldsmith, B. R. & Singh, N. *Catal. Sci. Technol.* **11**, 7331–7346 (2021).
[3] Young, S. D., Chen, J., Sun, W., Goldsmith, B., Pilania, G. ACS Chemistry of Materials (2023). https://doi.org/10.1021/acs.chemmater.3c00943.

Density Functional Theory (DFT) Simulates Electron Behavior



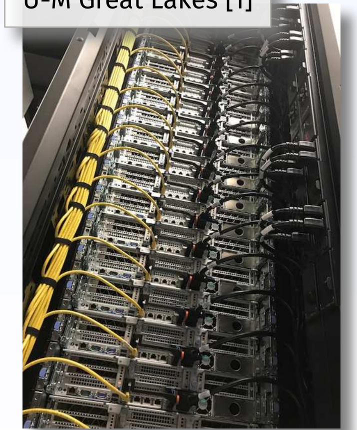
[1]



DFT → E = −43.873 eV

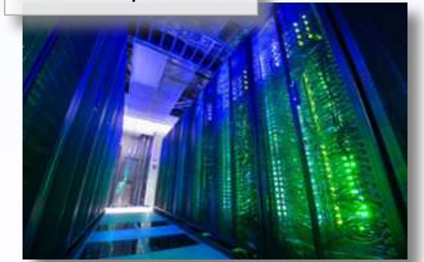
Vienna Ab-initio Simulation Package [2]

U-M Great Lakes [1]



NERSC Perlmutter [2]

XSEDE Expanse [3]



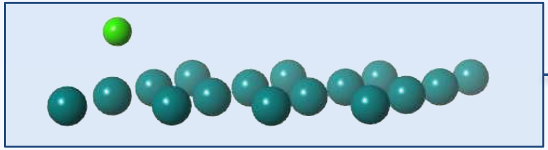
NERSC
XSEDE Extreme Science and Engineering Discovery Environment
NSF
ACCESS Advancing Innovation

[1] Bechstedt, F. (**2015**). Density Functional Theory. In: Many-Body Approach to Electronic Excitations. *Springer Series in Solid-State Sciences*, 181. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-662-44593-8_5

[2] Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Physical Review B* **1996**, 54 (16), 11169–11186. https://doi.org/10.1103/PhysRevB.54.11169.

DFT Can Calculate Adsorption Energies

Adsorption energy[3]: $E_A = E_{\mathrm{A}^*} - E_* - E_{\mathrm{A\,(g)}}$

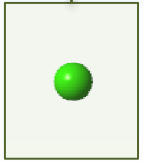


Surface + Adsorbate

A

Surface

Bare surface



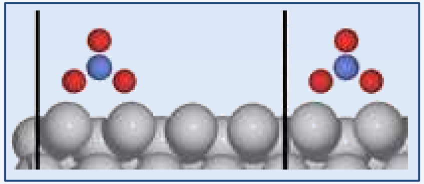
Adsorbate alone

VASP (Vienna Ab-initio Simulation Package)[1] (using PBE and BEEF-vdW functionals[2, 3])

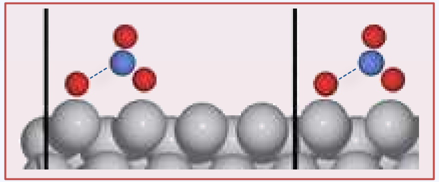
[1] The VASP Site. https://www.vasp.at/index.php/about-vasp/59-about-vasp
[2] Wellendorff, J. *et al. Phys. Rev. B* **85**, 235149 (2012).
[3] Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
[4] Liu, J.-X., Richards, D., Singh, N. & Goldsmith, B. R. *ACS Catal.* **9**, 7052–7064 (2019).

DFT Can Calculate Activation Barriers

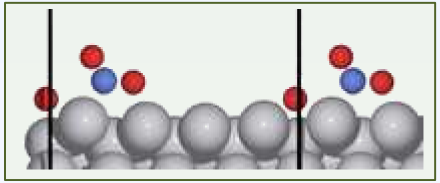
$$NO_3^* \longrightarrow NO_2^* + O^*$$



Initial State ("I")



Transition State ("‡")

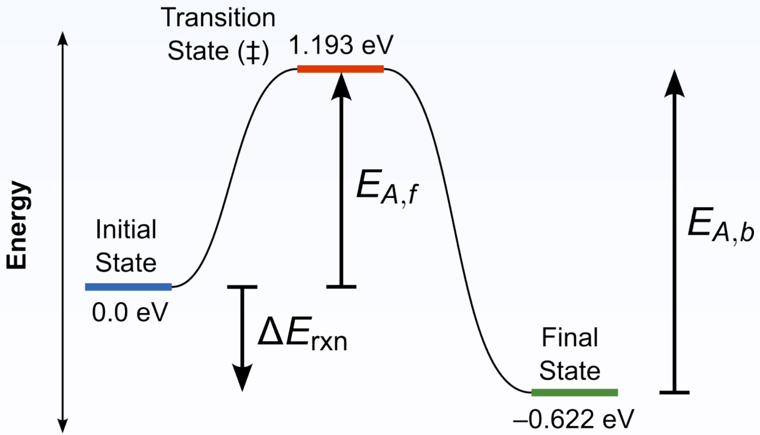


Final State ("F")

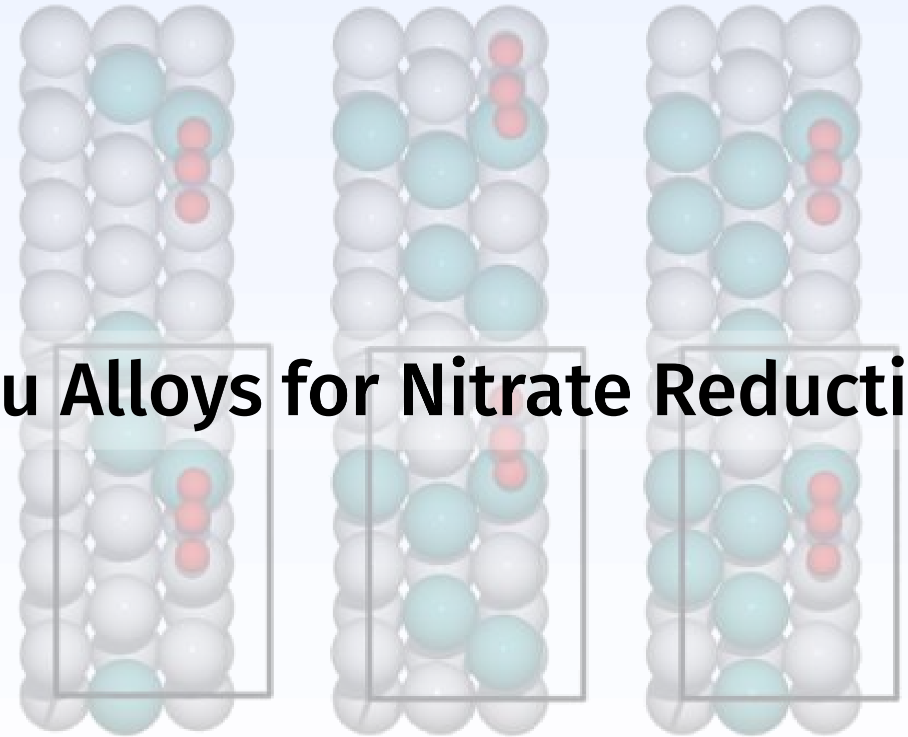
Forward barrier: $E_{A,f} = E_{\ddagger} - E_I$

Backward barrier: $E_{A,b} = E_{\ddagger} - E_F$

Reaction energy: $\Delta E_{\mathrm{rxn}} = E_F - E_I$



PtRu Alloys for Nitrate Reduction



NO_3^- adsorbed on PtRu surface alloys

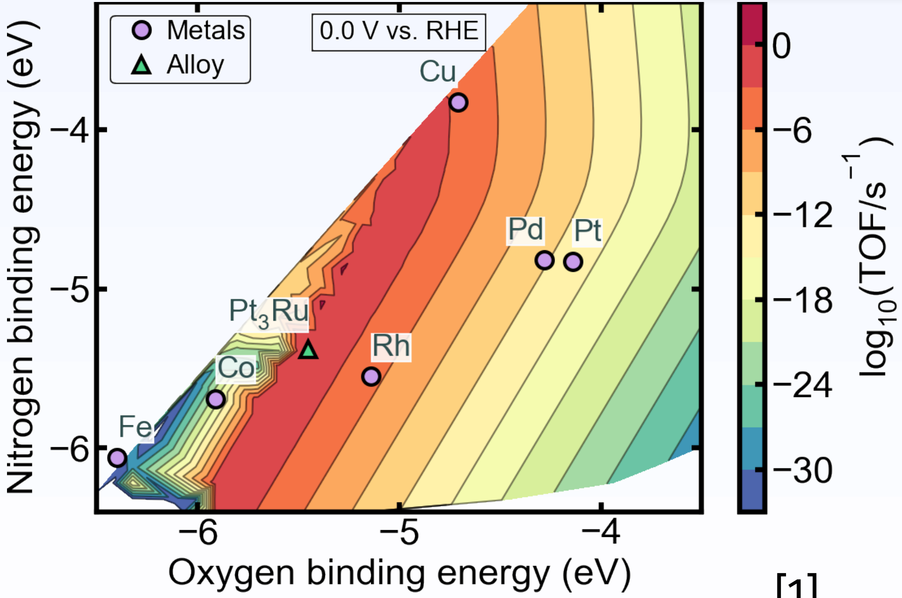
Objective: Verify Whether Pt_3Ru Alloy Predicted Using Pure Metal Microkinetics is Active Towards NO_3RR

- Previous study of pure metals found N, O binding energies as thermodynamic descriptors.
- Pt_3Ru alloys predicted to be promising.[1, 2]
- **Questions:**
  - **Is Pt_3Ru more active than Pt?**
  - **Can we systematically tune NO_3RR kinetics through alloying?**
  - **Can we use *pure metal* microkinetics to predict *alloy* activity?**

Jin-Xun Liu

Danielle Richards

TOF = "turnover frequency", or intrinsic reaction rate

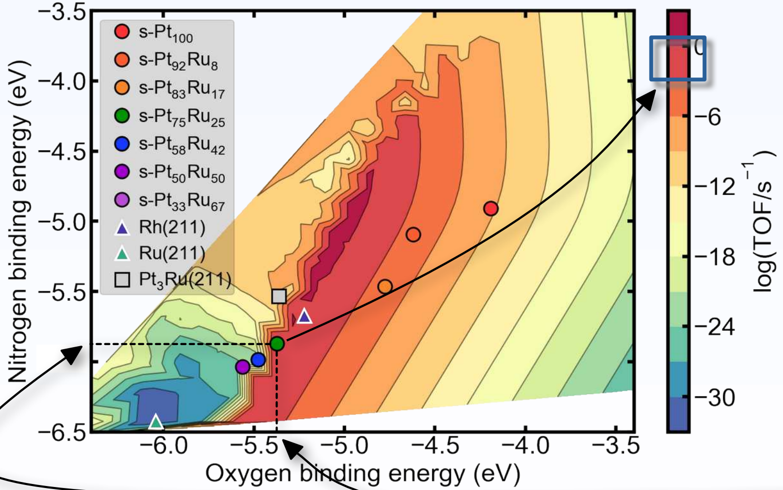


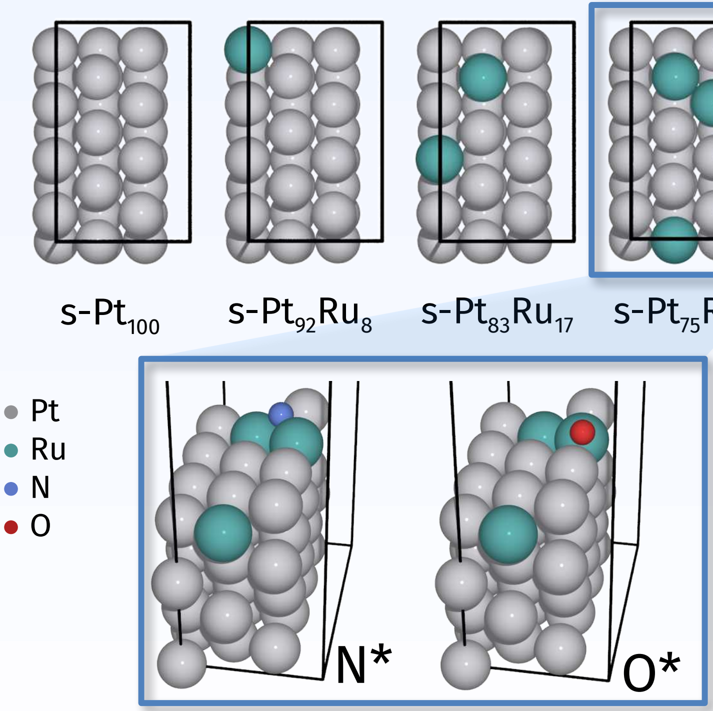
[1]

[1] Liu, J.-X., Richards, D., Singh, N. & Goldsmith, B. R. Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals. *ACS Catal.* **9**, 7052–7064 (2019).
[2] All potentials are relative to the reversible hydrogen electrode (RHE).

DFT Modeling of Pt_xRu_y Adsorption Energies

- How to control surface compositions? Alloy the surface.
- Computed N and O binding energies correspond to a TOF on the volcano chart.



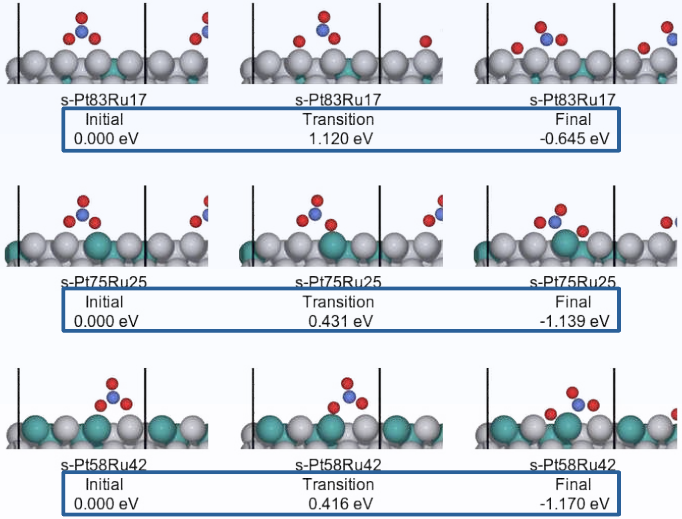


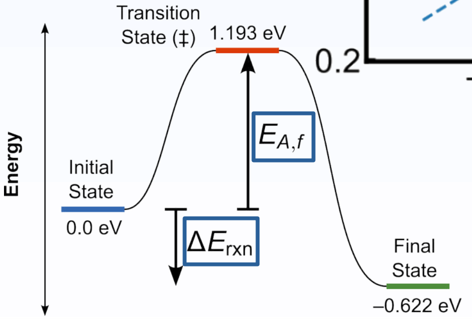
ΔE_N = −5.869 eV

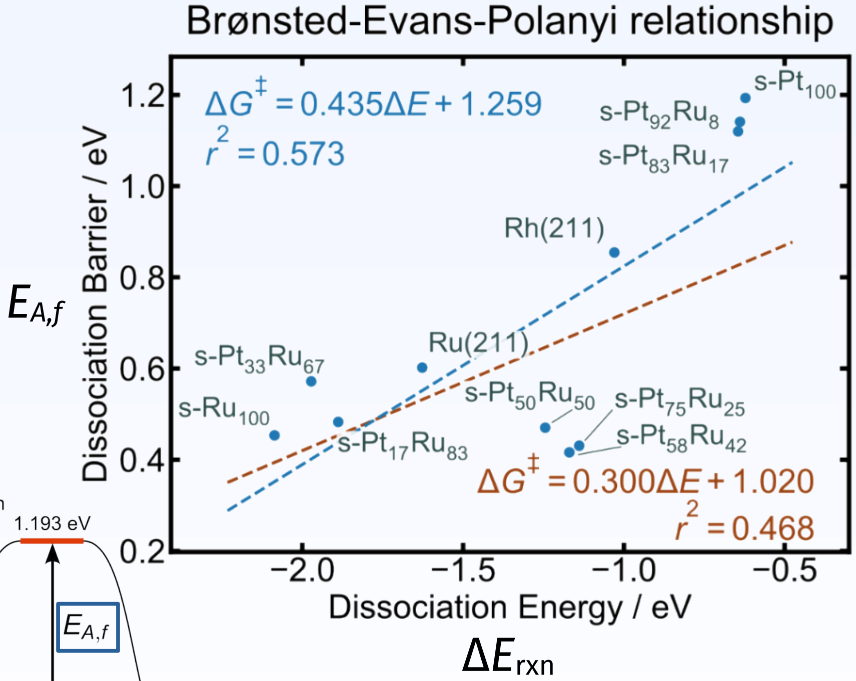
ΔE_O = −5.373 eV

DFT Modeling of Pt_xRu_y Nitrate Dissociation Barriers

- Okay to use transition metal volcano chart on Pt_xRu_y alloys?
- Compare $NO_3^* \rightarrow NO_2^* + O^*$ barriers.

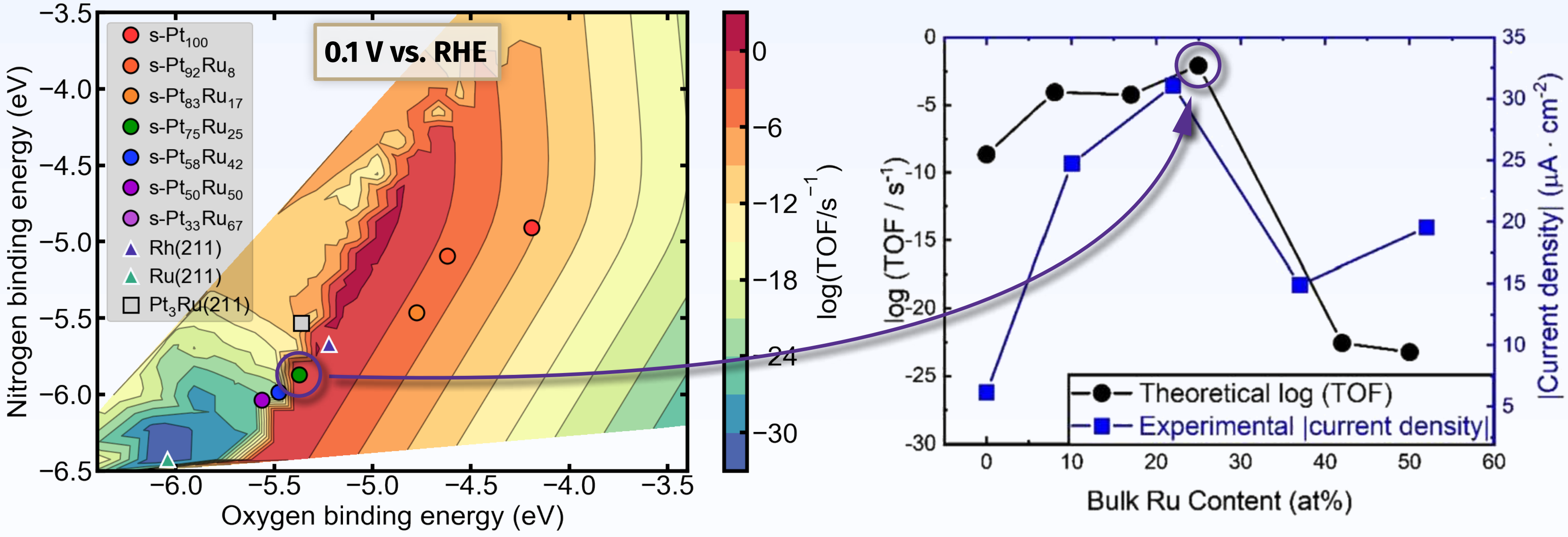


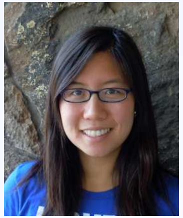




Close agreement rationalizes using transition metal volcano plot.

Tuning PtRu Composition Systematically Changes NO_3RR Activity



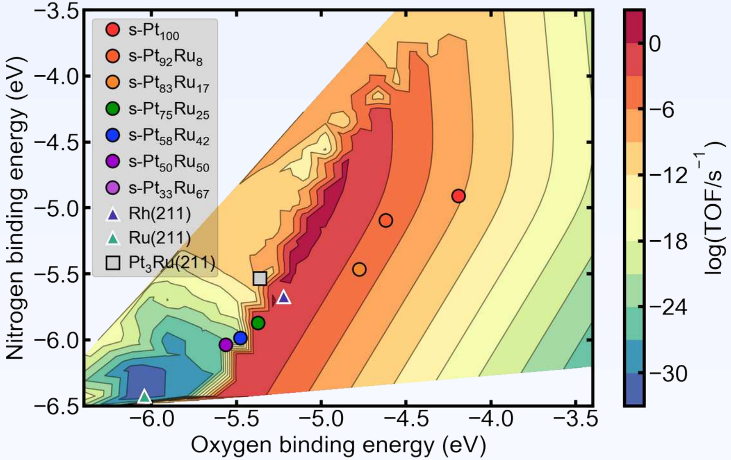


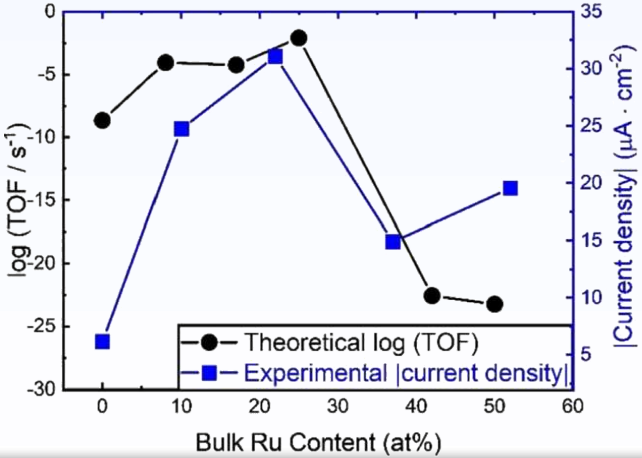
Zixuan Wang

We hypothesize that the maximum in activity arises from a shift in the rate-determining step from nitrate dissociation to another step.

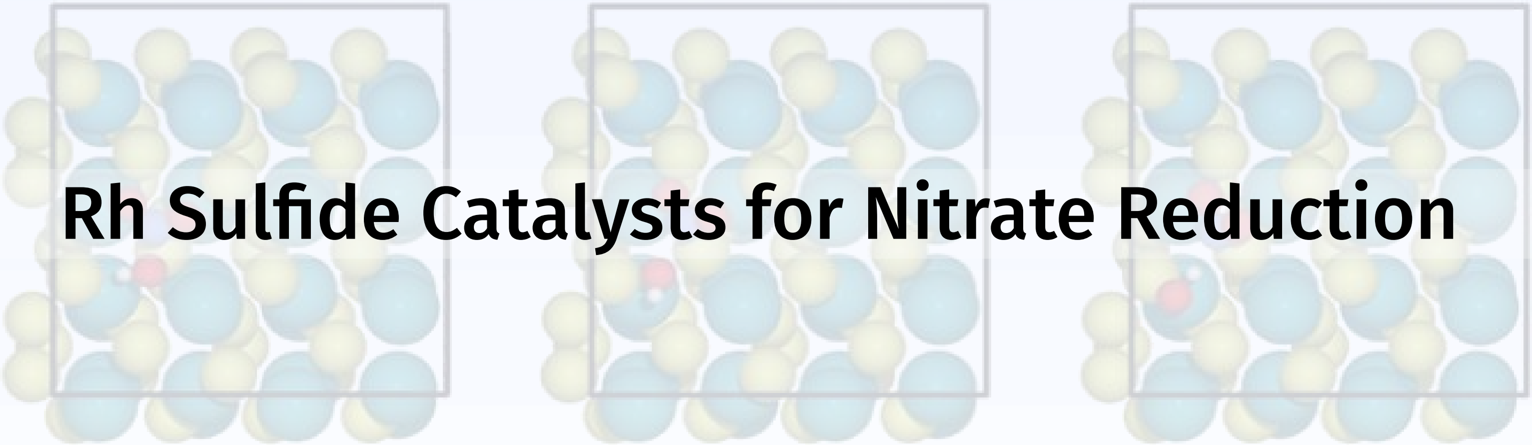
Conclusions and Implications

- Pt_3Ru ($Pt_{78}Ru_{22}$/C) is more active for NO_3RR than Pt/C.
- Pure metal microkinetics rationalize activity trends of alloys (Pt_xRu_y/C).
- *One can potentially save calculations when screening alloy electrocatalysts.*





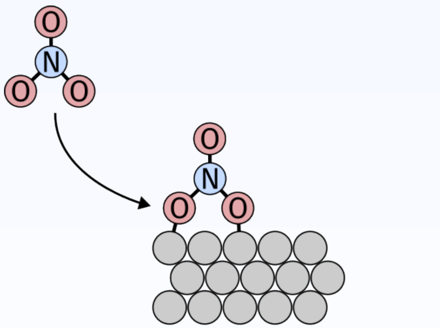
Rh Sulfide Catalysts for Nitrate Reduction

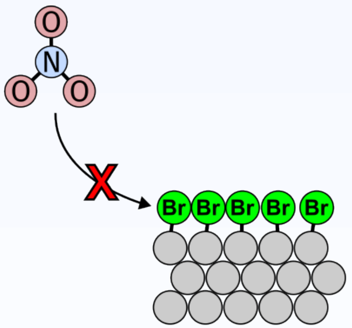


$Rh_{17}S_{15}(100)$ surfaces

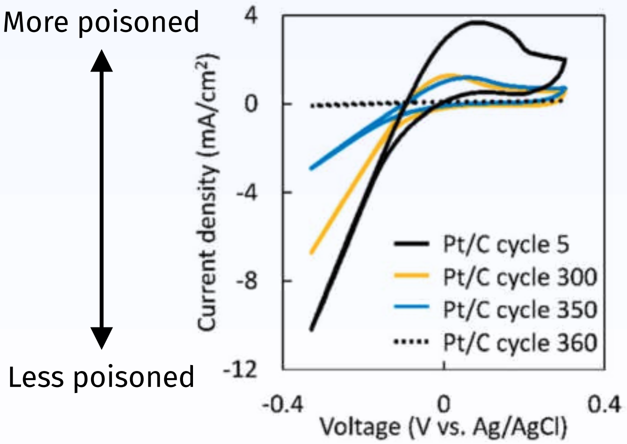
Halide Poisoning Limits Catalyst Effectiveness

- Poisoning: sites on surface blocked by non-reactant molecules, decreasing activity.
- Cl^-, Br^-, I^-, and other halides are common in concentrated wastewater.
- Halides poison electrocatalysts for many electrocatalytic reactions.





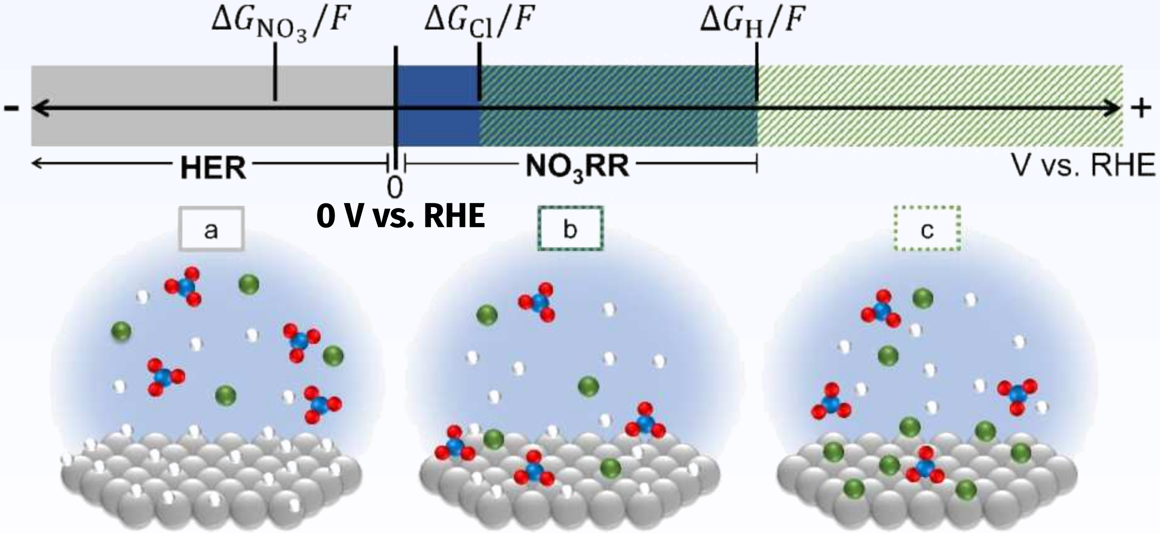
Pt for hydrogen evolution, poisoned by Br^- [1]



[1] Singh, N. et al. Stable electrocatalysts for autonomous photoelectrolysis of hydrobromic acid using single-junction solar cells. *Energy Environ. Sci.* **7**, 978–981 (2014).
[2] PureTec Industrial Water. What is Reverse Osmosis? https://puretecwater.com/reverse-osmosis/what-is-reverse-osmosis

Chloride (Cl^-) Poisons Many Potential NO_3RR Catalysts

- Cl^- adsorption competes with nitrate adsorption at NO_3RR potentials.[1]
- Even trace amounts of Cl^- can poison electrocatalysts.[2]



Potential-dependent Cl^- poisoning

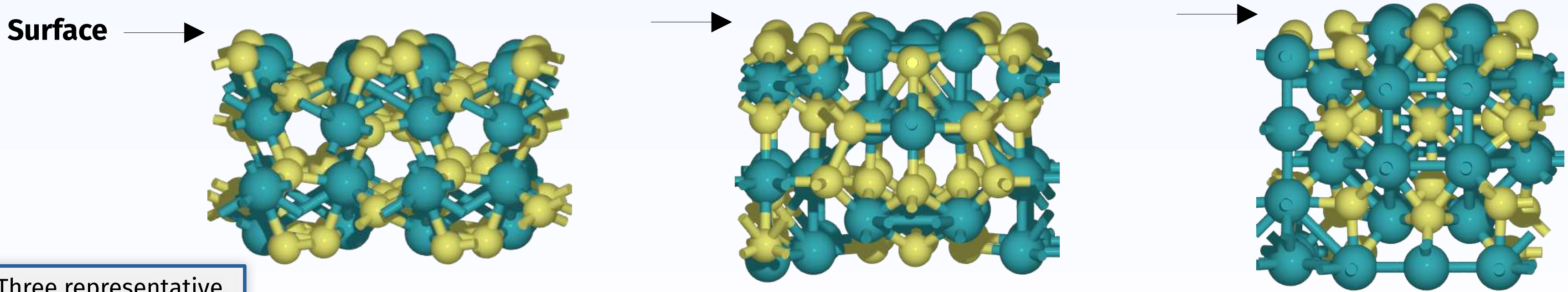
[1]

[1] Richards, D.; Young, S. D.; Goldsmith, B. R.; Singh, N. *Catal. Sci. Technol.* **2021**, 11 (22), 7331–7346.
[2] Juarez, F. et al. Why are trace amounts of chloride so highly surface-active? *Journal of Electroanalytical Chemistry* **847**, 113128 (2019).

Objective: Understand Rh Sulfide NO_3RR Activity and Cl^- Poisoning

- Rh active for NO_3RR.[1–2] Sulfides often resist halide poisoning.[3–4]
- Hypothesis: Rh sulfides will be active and resistant to Cl^- poisoning.

- **Questions:**
  - **What is the NO_3RR mechanism on Rh sulfides?**
  - **How does the presence of Cl^- affect NO_3RR performance?**



Three representative Rh sulfide facets

$Rh_2S_3(001)$ $Rh_3S_4(100)$ $Rh_{17}S_{15}(100)$

[1] Liu, J.-X., Richards, D., Singh, N. & Goldsmith, B. R. Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals. *ACS Catal.* **9**, 7052–7064 (2019).
[2] Dima, G. E., de Vooys, A. C. A. & Koper, M. T. M. Electrocatalytic reduction of nitrate at low concentration. *Journal of Electroanalytical Chemistry* **554–555**, 15–23 (2003).
[3] Ivanovskaya, A. et al. Transition Metal Sulfide Hydrogen Evolution Catalysts for Hydrobromic Acid Electrolysis. *Langmuir* **29**, 480–492 (2013).
[4] Singh, N. et al. Stable electrocatalysts for autonomous photoelectrolysis of hydrobromic acid using single-junction solar cells. *Energy Environ. Sci.* **7**, 978–981 (2014).

DFT Modeling of Rh Sulfide Surfaces

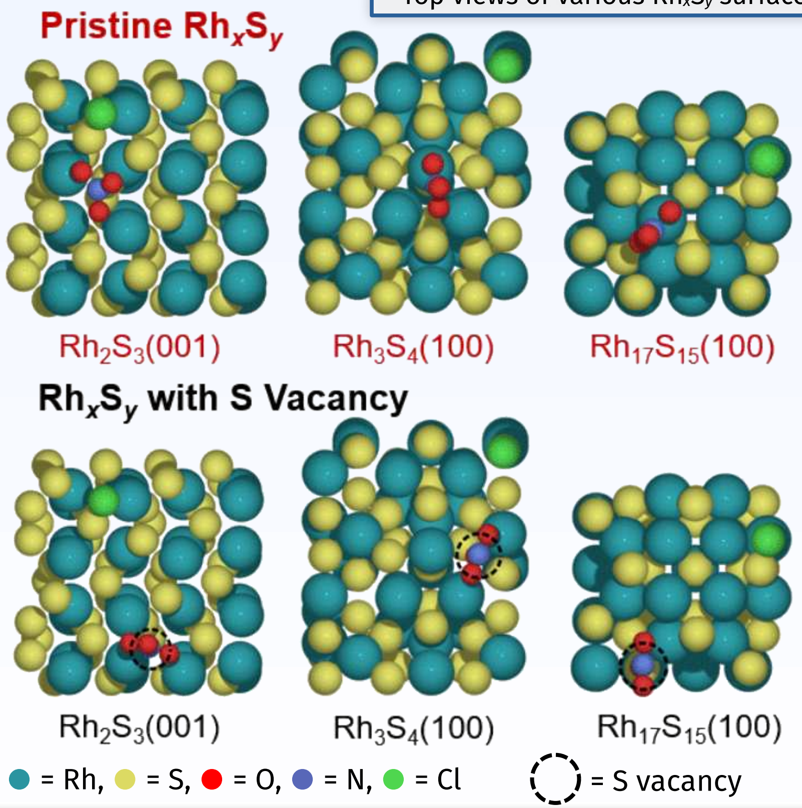
- Rh sulfides are modeled using Rh_2S_3(001), Rh_3S_4(100), and $Rh_{17}S_{15}$(100).[1]
- Density functional theory used to calculate binding energies and barriers.
- Central questions to answer:

(1) Do Rh_xS_y facets break unfavorable NO_3^-–Cl^- scaling relationship?

(2) What is the mechanism on Rh_xS_y?

(3) Do S vacancies improve NO_3RR?

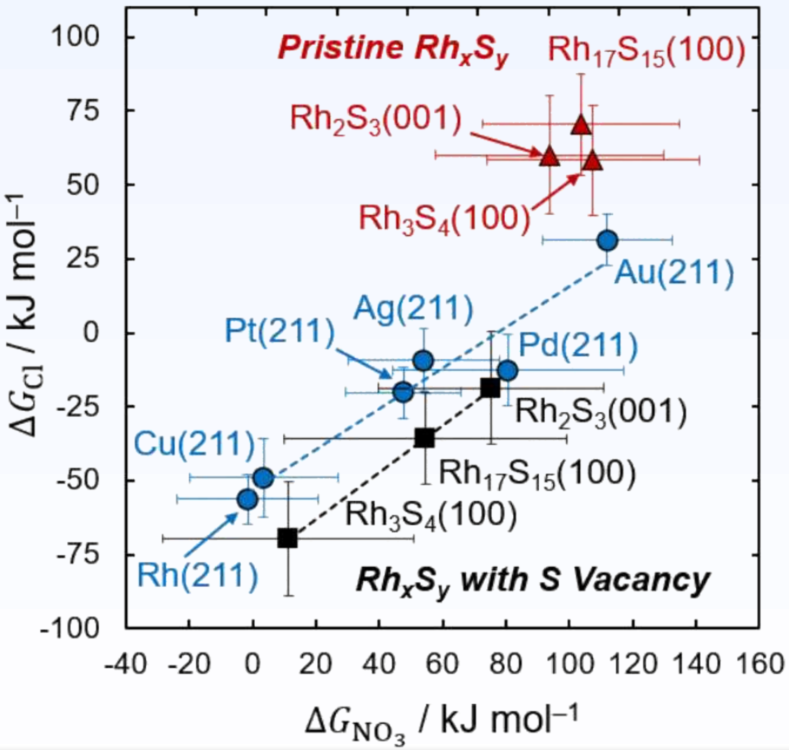
Top views of various Rh_xS_y surfaces



[1] Singh, N. et al. Investigation of the Active Sites of Rhodium Sulfide for Hydrogen Evolution/Oxidation Using Carbon Monoxide as a Probe. *Langmuir* **30**, 5662–5668 (2014).

How Do Adsorbates Bind to Different Rh_xS_y Facets?

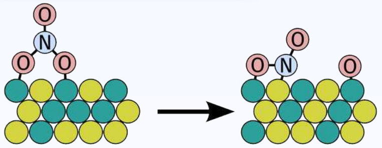
- Pure transition metals: **blue** line. Want Rh_xS_y to be above **blue** line.
- Pristine sulfide surfaces: **red**. Binds NO_3^- and Cl^- very weakly.
- S-defected Rh_xS_y: **black**. Follows same trend as transition metals.
- S-defected $Rh_3S_4(100)$ should have fastest NO_3RR rate, but also be poisoned by Cl^-.



Which Site is The Active Site? Which Mechanism is Happening?

- Assume H^+, Cl^-, and NO_3^- compete to adsorb on Pt, Rh, and Rh_xS_y surfaces.
- NO_3RR can proceed through a direct[1–2] or H-assisted mechanism.

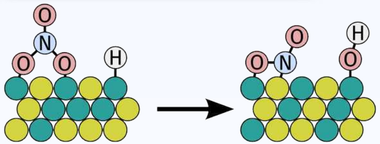
Direct reduction



$$NO_3^* + * \overset{k_4}{\rightleftarrows} NO_2^* + O^*$$
$$O^* + H^* \rightleftarrows HO^* + *$$
$$HO^* \rightarrow \text{products}$$
$$NO_2^* \rightarrow \text{products}$$

$$\text{rate} = \frac{k_4 K_{NO_3}[NO_3^-]_0}{\left(1 + K_H[H^+]_0 + K_{NO_3}[NO_3^-]_0 + K_{Cl}[Cl^-]_0\right)^2}$$

H-assisted reduction



$$H^* + NO_3^* \overset{k_9}{\rightleftarrows} NO_2^* + HO^*$$
$$HO^* \rightarrow \text{products}$$
$$NO_2^* \rightarrow \text{products}$$

$$\text{rate} = \frac{k_9 K_{NO_3}[NO_3^-]_0 K_H[H^+]_0}{\left(1 + K_H[H^+]_0 + K_{NO_3}[NO_3^-]_0 + K_{Cl}[Cl^-]_0\right)^2}$$

k_4, k_9: rate constants

K_{NO_3}, K_{Cl}, K_H: equilibrium constants

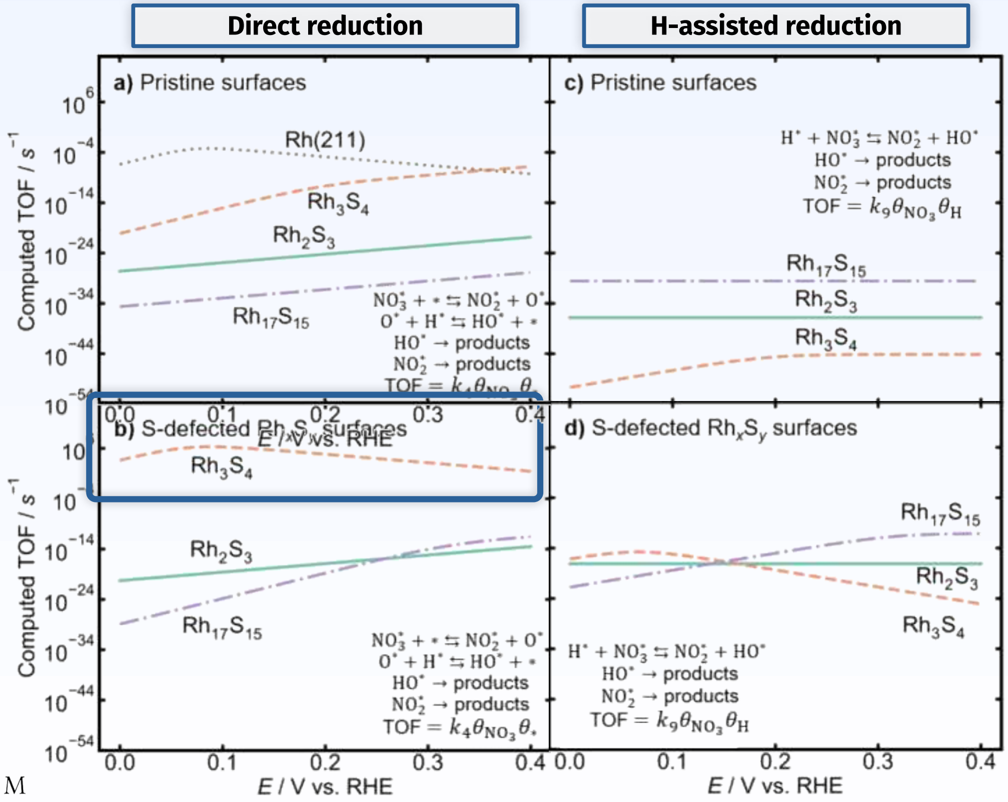
$[NO_3]_0, [H^+]_0, [Cl^-]_0$: initial molar concentrations

Pt undergoes H-assisted reduction, but exact mechanism is unknown for Rh and Rh_xS_y.

[1] Dima, G. E., de Vooys, A. C. A. & Koper, M. T. M. Electrocatalytic reduction of nitrate at low concentration on coinage and transition-metal electrodes in acid solutions. *Journal of Electroanalytical Chemistry* **554–555**, 15–23 (2003).
[2] Liu, J.-X., Richards, D., Singh, N. & Goldsmith, B. R. Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals. *ACS Catal.* **9**, 7052–7064 (2019).

S-defected Rh_3S_4(100) is Predicted to be Most Active

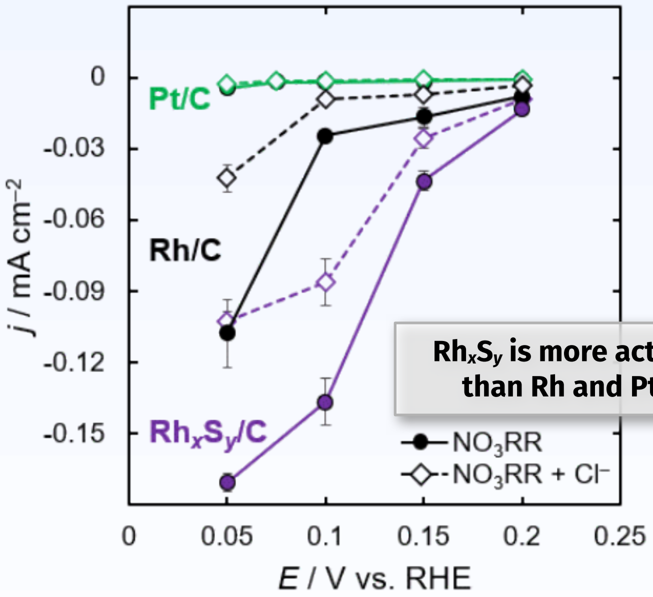
- My computational results predict the highest activity for **S-defected Rh_3S_4(100)** under the **direct mechanism**.
- S vacancies facilitate NO_3RR.



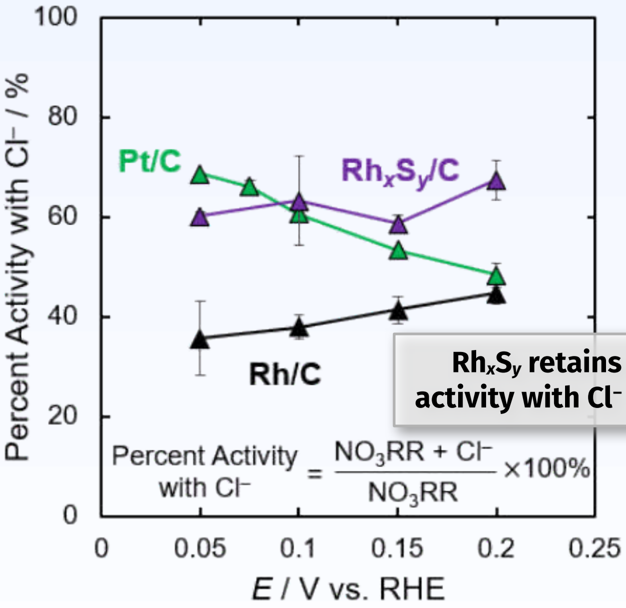
$[NO_3]_0 = [H^+]_0 = 1$ M; $[Cl^-]_0 = 0$ M

Rh_xS_y Retains Activity in Presence of Chloride

Danielle Richards



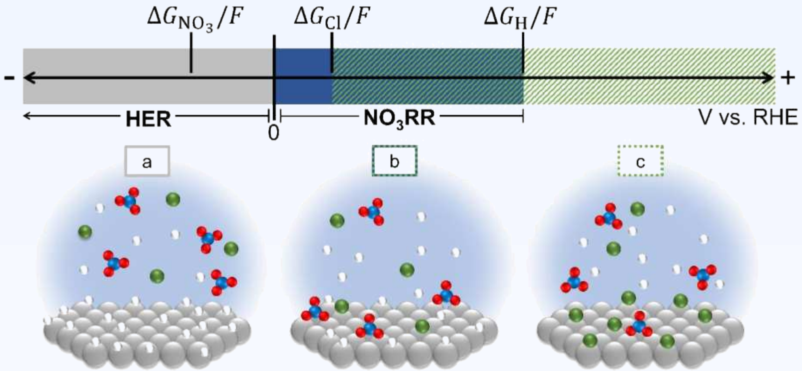
Rh_xS_y is more active than Rh and Pt.

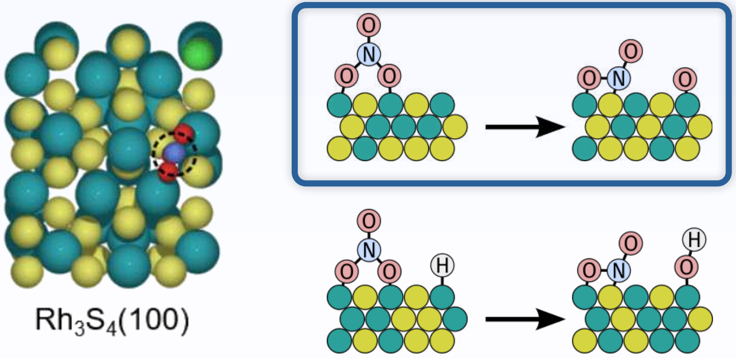


Rh_xS_y retains ~60% activity with Cl^- present.

Rh_xS_y is Promising for Cl^--Resistant NO_3RR

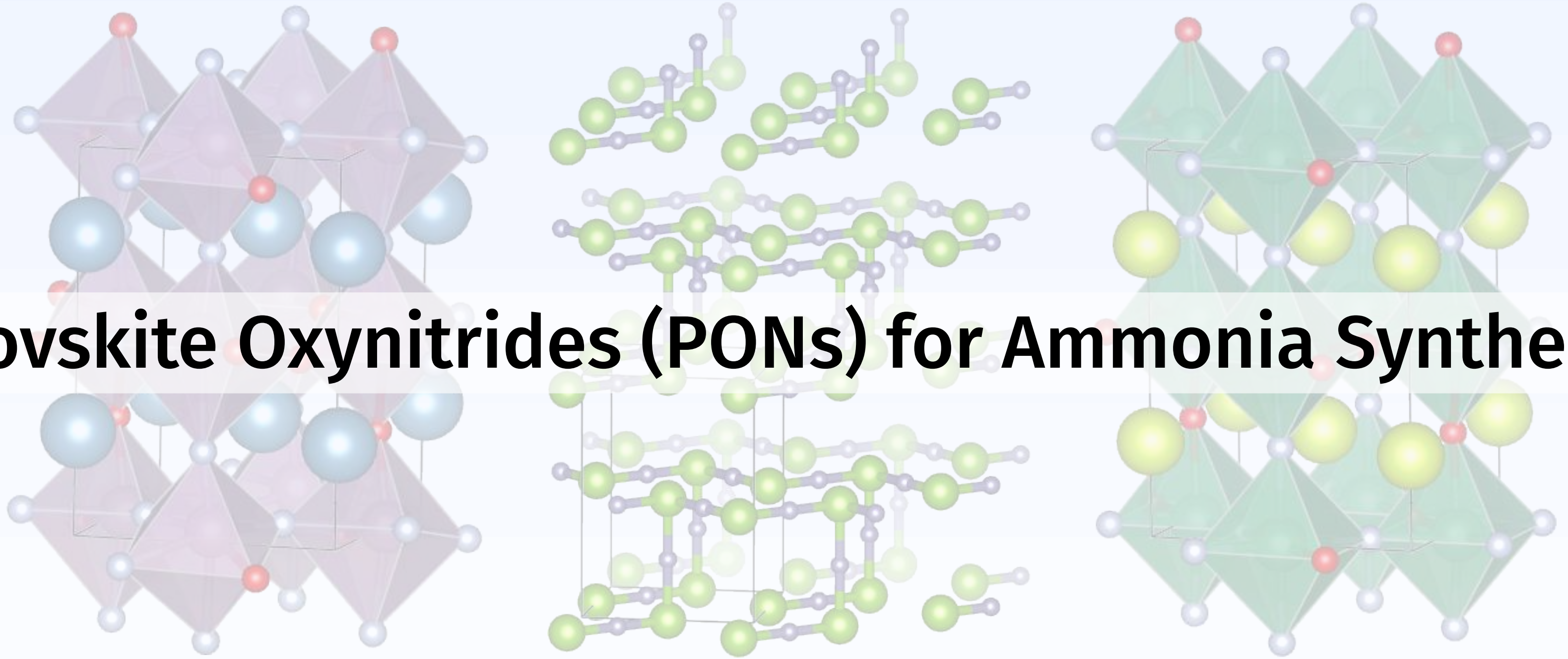
- **Rh_xS_y/C is active for NO_3RR and exhibits Cl^- poison resistance.**
- **We predict S-defected Rh_3S_4(100) to be the active site.**
- Future experiments:
  - EPR spectroscopy.
  - Isotopic labeling.
  - Core-shell or nanoparticle engineering.





Richards, D.; Young, S. D.; Goldsmith, B. R.; Singh, N. Electrocatalytic Nitrate Reduction on Rhodium Sulfide Compared to Pt and Rh in the Presence of Chloride. Catal. Sci. Technol. 2021, 11 (22), 7331–7346. https://doi.org/10.1039/D1CY01369F.

Perovskite Oxynitrides (PONs) for Ammonia Synthesis

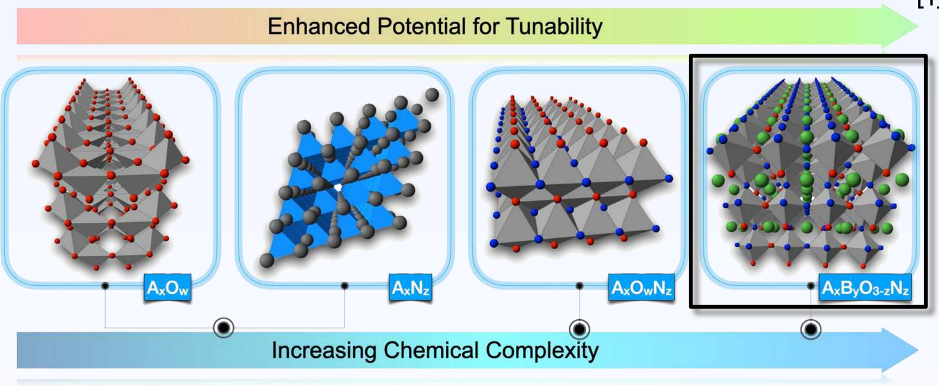


Perovskite oxynitride crystals

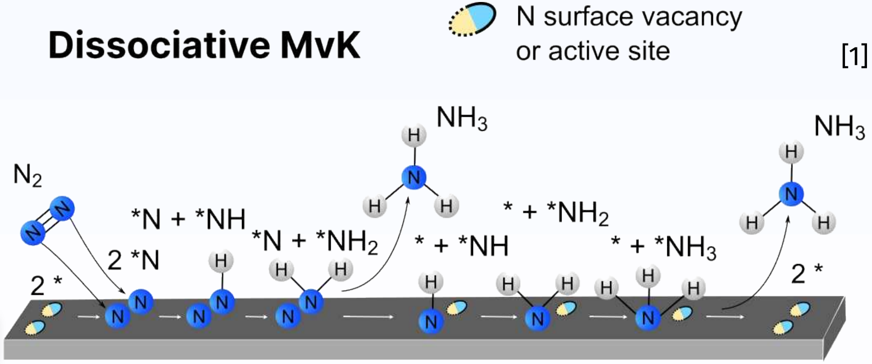
PONs Are Tunable Materials With Potential Use for N Chemistry

- Metal oxynitrides have been used for many electrochemical reactions.[1–2]
- PONs may be useful for N chemistry, such as for efficient NH_3 synthesis.[2]
- **Which factors govern PON stability during N chemistry reactions?**

[1]



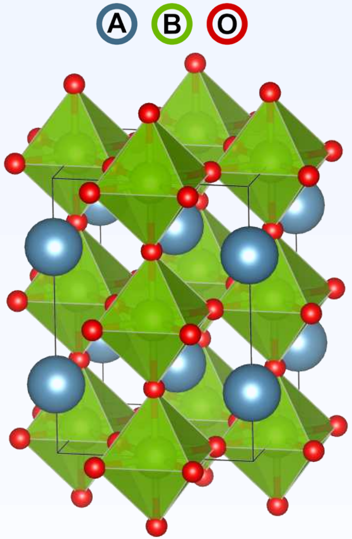
[1]



Possible PON surface

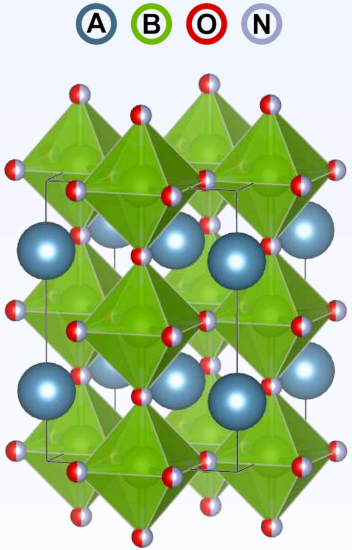
[1] Young, S. D.; Ceballos, B. M.; Banerjee, A.; Mukundan, R.; Pilania, G.; Goldsmith, B. R. Metal Oxynitrides for the Electrocatalytic Reduction of Nitrogen to Ammonia. *J. Phys. Chem. C* **2022**, 126 (31), 12980–12993.
[2] Young, S. D.; Banerjee, A.; Pilania, G.; Goldsmith, B. R. Perovskite Oxynitrides as Tunable Materials for Electrocatalytic Nitrogen Reduction to Ammonia. *Trends in Chemistry* **2021**, 3 (9), 694–696.
[3] Wang, Z.; Richards, D.; Singh, N. Recent Discoveries in the Reaction Mechanism of Heterogeneous Electrocatalytic Nitrate Reduction. *Catalysis Science & Technology* **2021**, 11 (3), 705–725.

What is a Perovskite Oxynitride (PON)?



Perovskite oxide

ABO_3



$\sqrt{2} \times \sqrt{2} \times 2$ PON supercell

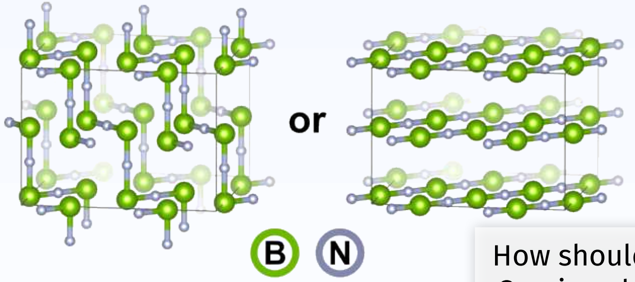
ABO_2N or $ABON_2$

ABO_xN_{3-x}

Which cations should go in the A and B spots?

A	Ca	Ca	La	La	⋯	?
B	Ti	Cr	Cr	Re	⋯	?

Mostly *cis* or Mostly *trans* or ?



How should the N and O anions be arranged around the cell?

The structure and composition of a PON strongly impacts its performance and stability.

[1] Fuertes, A. Chemistry and applications of oxynitride perovskites. *J. Mater. Chem.* **22**, 3293–3299 (2012).
[2] Young, S. D.; Banerjee, A.; Pilania, G.; Goldsmith, B. R. Perovskite Oxynitrides as Tunable Materials for Electrocatalytic Nitrogen Reduction to Ammonia. *Trends in Chemistry* **2021**, 3 (9), 694–696.

Goal: Determine Thermodynamic Stability and Anion Ordering In ABO_2N And $ABON_2$ Perovskite Oxynitrides

(a) Cation Pair Selection

- Select elements from periodic table
- Enumerate all permutations of cations
- Filter based on geometric factors

(b) Anion Ordering Selection

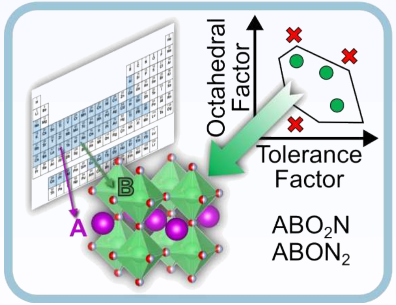
- Enumerate distinct anion orderings with selected cation pairs
- Evaluate relative energies of anion orderings

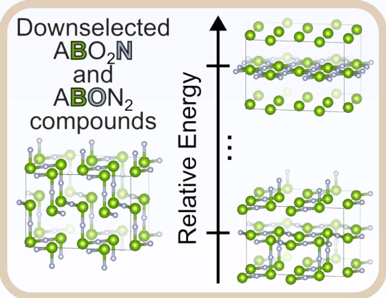
(c) Energy-Above-Hull Analysis

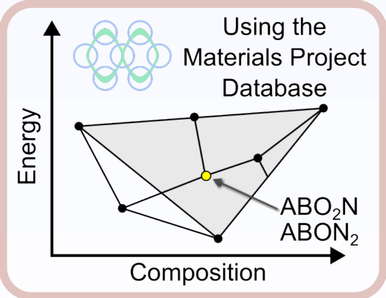
- Pair 295 cation pairs with optimal anion ordering
- Calculate energies above hull using Materials Project

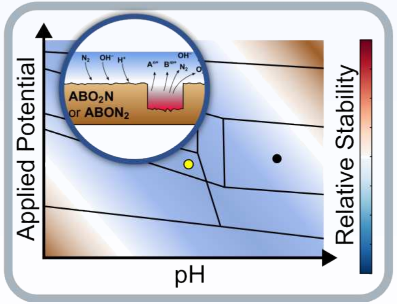
(d) Electrochemical Stability Analysis

- Construct multidimensional Pourbaix diagrams
- Identify regions of stability and corresponding operating conditions









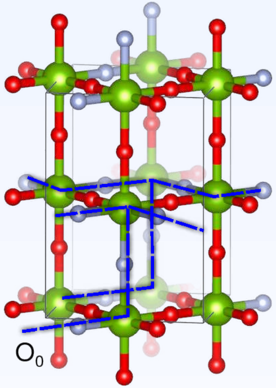
We Aim to Identify Preferred Anion Orderings

- For $\sqrt{2} \times \sqrt{2} \times 2$ supercell, there are 32 total symmetrically distinct anion orderings.[1]

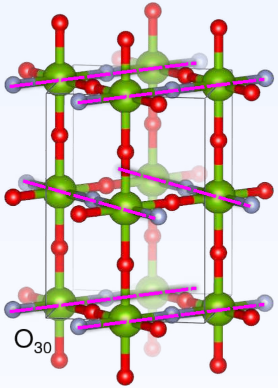
ABO_2N

B O N

Low energy



...30 more structures...



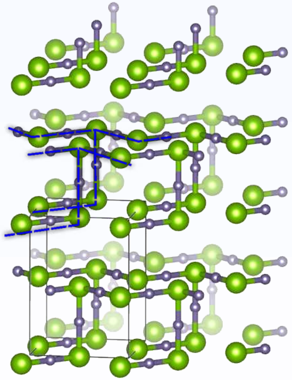
High energy

Topology

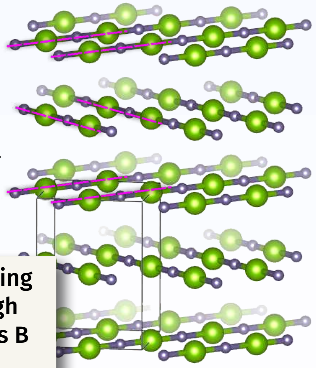
B M

M = minority composition anion

Low energy



...30 more structures...

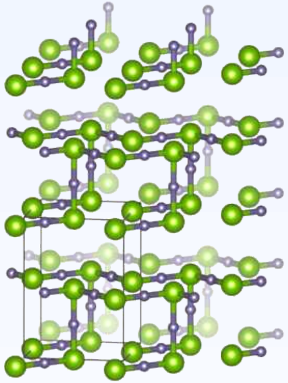


High energy

The most stable anion ordering (ordering O_0) contains a high degree of *cis* bonding across B atoms.

[1] Hart, G. L. W., Nelson, L. J. & Forcade, R. W. Generating derivative structures at a fixed concentration. *Computational Materials Science* **59**, 101–107 (2012).

Combine Optimal Anion Ordering with Cation Pairs

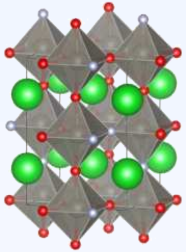


Prototypical anion ordering O_0

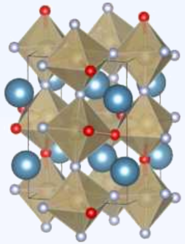
+

295 charge-independent cation pairs

→

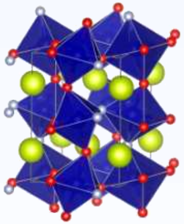


$BaWO_2N$

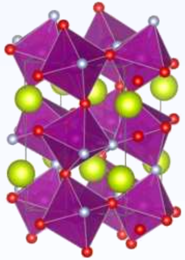


$CaOsON_2$

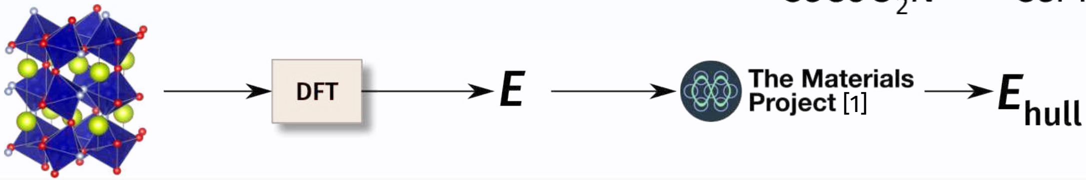
+ 291 more...



$CeCoO_2N$



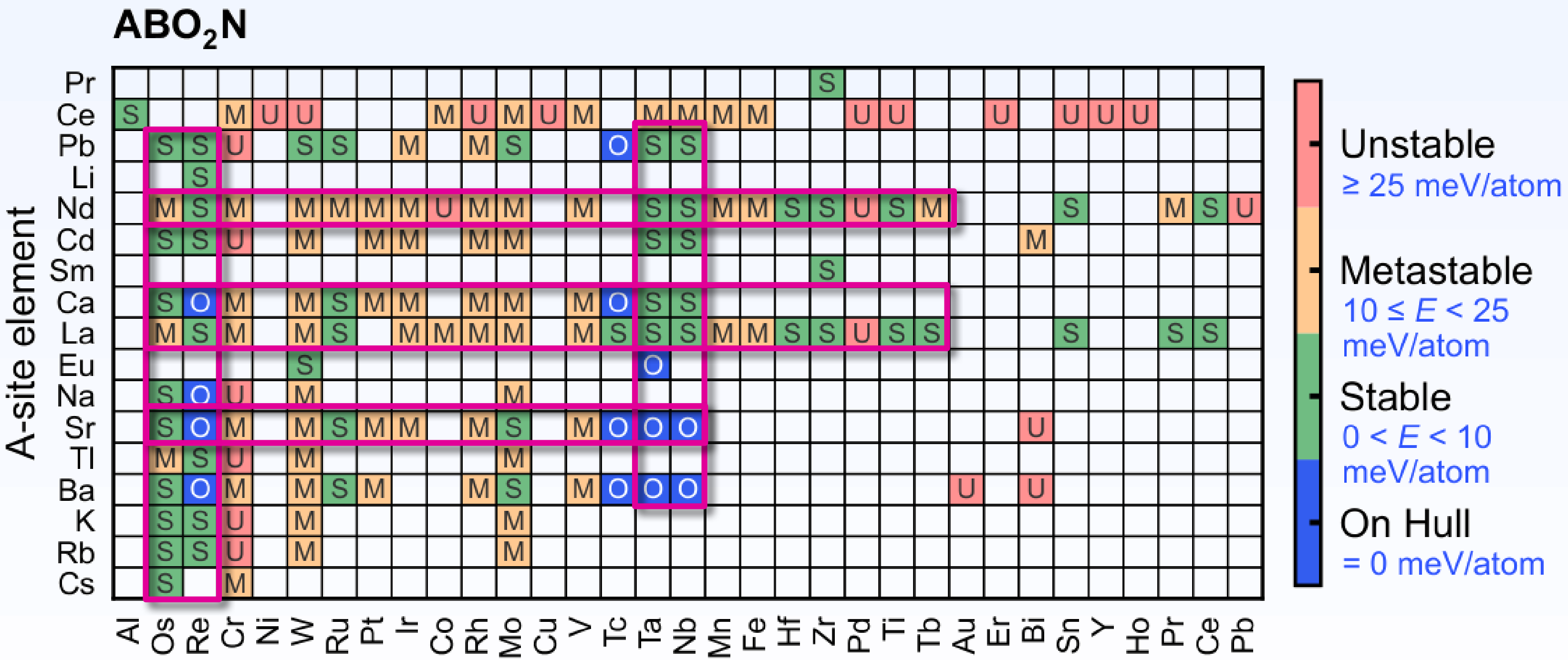
$CeMnO_2N$



E_{hull} measures likelihood of decomposition.

[1] Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Materials* **2013**, 1 (1), 011002. DOI: 10.1063/1.4812323.

We Identify 85 Stable PON Materials



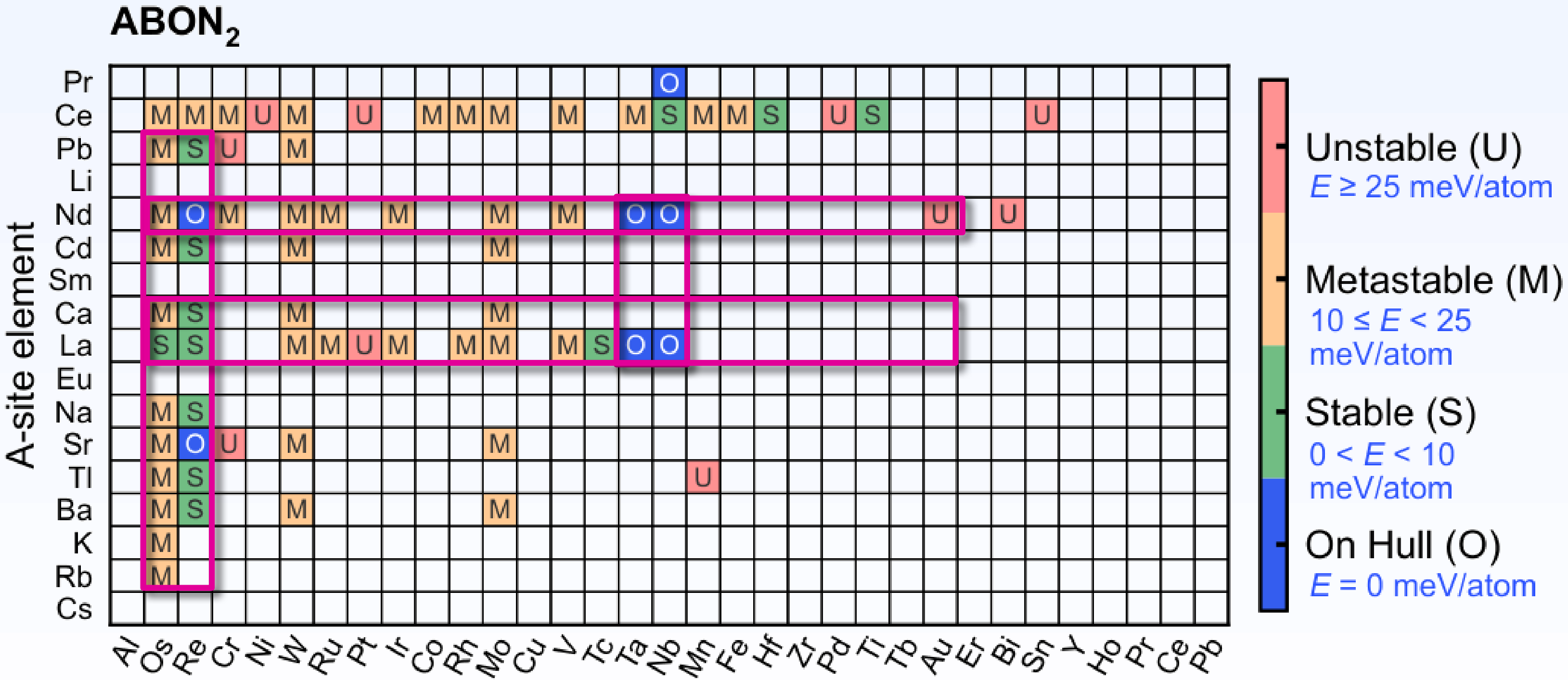
A = {Nd, Ca, La, Sr, Ba}

B-site element

B = {Os, Re,[1] W, Mo, Ta, Nb}

Young, S.; Chen, J.; Sun, W.; Goldsmith, B.; Pilania, G. Thermodynamic Stability and Anion Ordering of Perovskite Oxynitrides. *ACS Chemistry of Materials* **2023**. DOI: 10.1021/acs.chemmater.3c00943.

We Identify 85 Stable PON Materials



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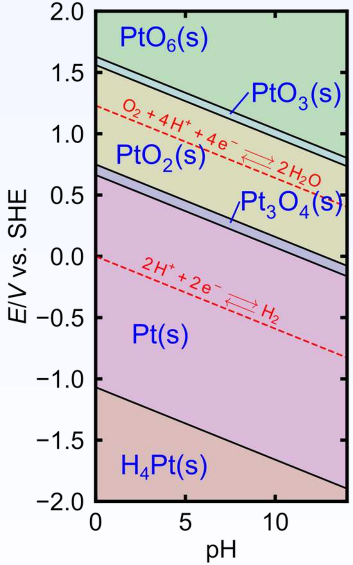
Young, S.; Chen, J.; Sun, W.; Goldsmith, B.; Pilania, G. Thermodynamic Stability and Anion Ordering of Perovskite Oxynitrides. *ACS Chemistry of Materials* **2023**. DOI: 10.1021/acs.chemmater.3c00943.

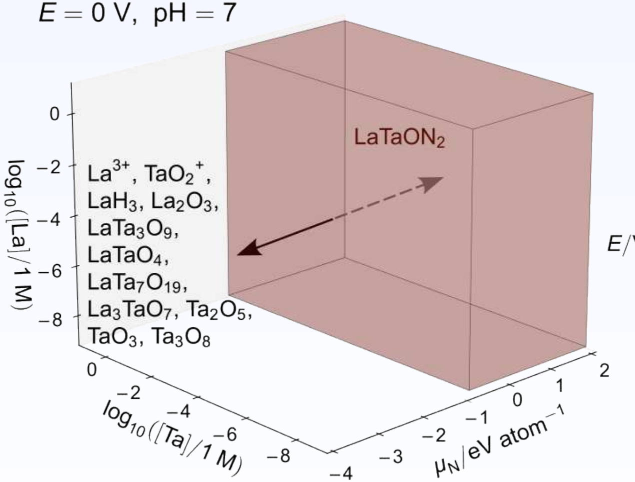
We Generate a Pourbaix Diagram for $LaTaON_2$

Jiadong Chen
Materials Science
Wenhao Sun Lab
University of Michigan

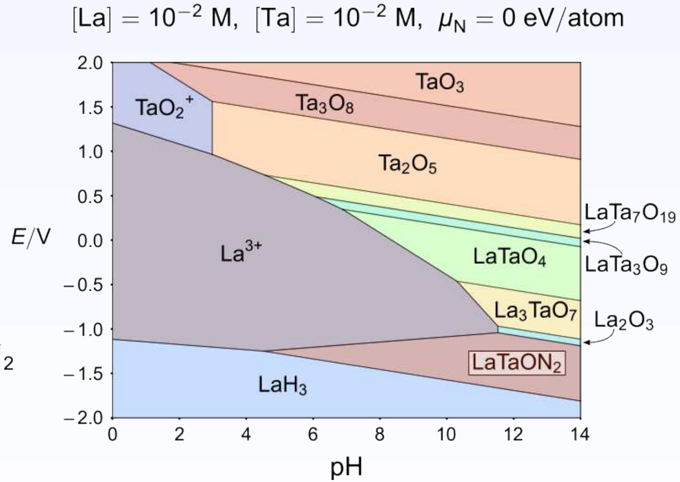
Pourbaix diagram, Pt-O-H system



Stability processing diagram for the La-Ta-O-N-H system



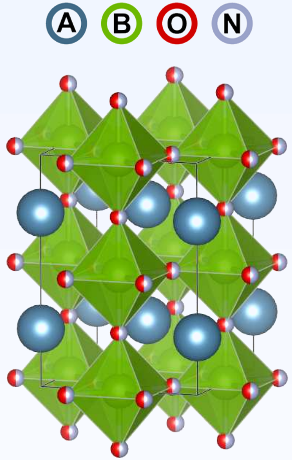
Pourbaix diagram, La-Ta-O-N-H system, $\mu_{La} = \mu_{Ta} = 0$



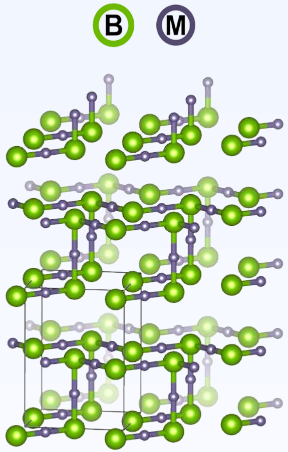
$LaTaON_2$ potentially synthesizable with N-rich precursors; stable in alkaline conditions.

Young, S.; Chen, J.; Sun, W.; Goldsmith, B.; Pilania, G. Thermodynamic Stability and Anion Ordering of Perovskite Oxynitrides. *ACS Chemistry of Materials* **2023**. DOI: 10.1021/acs.chemmater.3c00943.

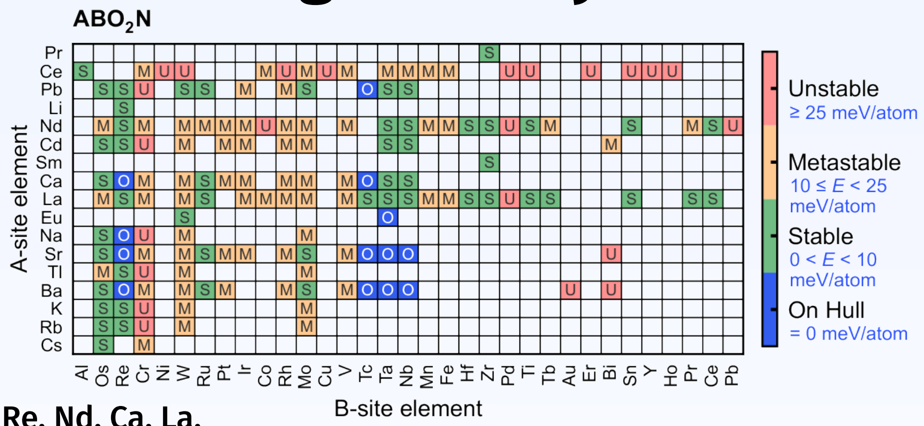
We Predict Many PONs That Are Waiting to be Synthesized



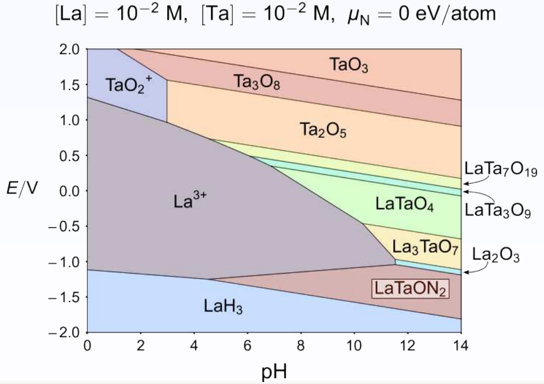
PONs are highly tunable in chemistry and ion ordering.



The optimal anion ordering has a high degree of M–B–M *cis* bonding.



Os, Re, Nd, Ca, La, Sr, Ba, among others, correlate to PON stability.

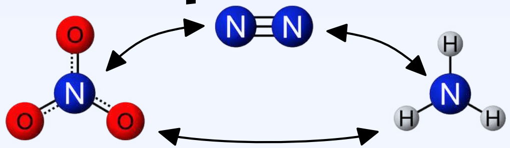


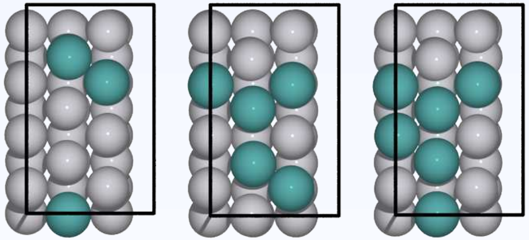
$LaTaON_2$ is potentially stable in alkaline, reducing conditions.

Ion-ordering-sensitive analysis could also be applied to complex perovskites, spinels, etc.

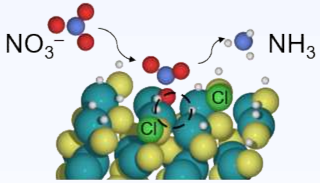
Young, S.; Chen, J.; Sun, W.; Goldsmith, B.; Pilania, G. Thermodynamic Stability and Anion Ordering of Perovskite Oxynitrides. *ACS Chemistry of Materials* **2023**. DOI: 10.1021/acs.chemmater.3c00943.

Effective Electrocatalysts Can Help Balance the Global Nitrogen Cycle

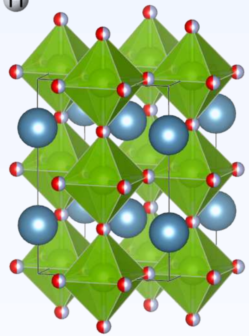




Rh_xS_y/C
NO_3RR Activity
Cl^- Poison Resistance



$Rh_3S_4(100)$ with Sulfur Vacancy



Pt_3Ru_1 more active and cheaper than Pt for NO_3RR.[1]

Tuning alloy composition enables higher catalyst activity. Analysis of alloys can exploit results from pure metal studies.

Rh sulfide more active, less poisoned than Rh for NO_3RR.[2]

As in other reactions, sulfur can help reduce halide poisoning. Surface vacancies may enable higher activity then on pure metals.

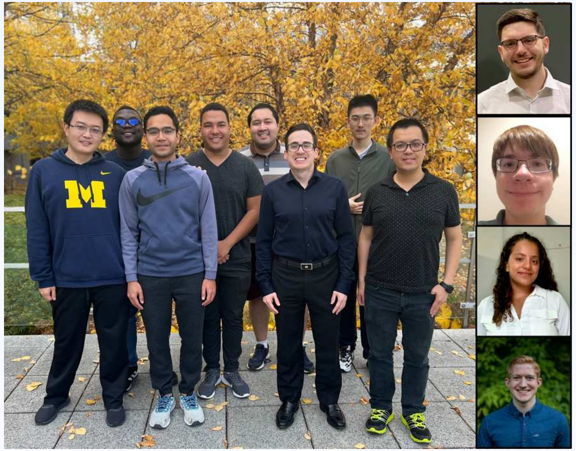
Cation chemistry correlates with stability; *cis* ordering is important.[3]

Strategic searching in a combinatorial materials space can elucidate design guidelines without exhaustive calculations.

Computational chemistry aids experimentalists and accelerates discovery of new catalyst materials.

[1] Wang, Z.; Young, S. D.; Goldsmith, B. R.; Singh, N. *Journal of Catalysis* **2021**, 395, 143–154.
[2] Richards, D.; Young, S.; Goldsmith, B. R.; Singh, N. *Catal. Sci. Technol.* **2021**, 11 (22), 7331–7346.
[3] Young, S.; Chen, J.; Sun, W.; Goldsmith, B.; Pilania, G. *ACS Chemistry of Materials* **2023**.

Acknowledgements

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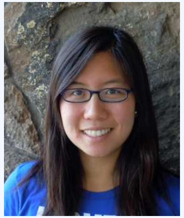
Zixuan Wang


Danielle Richards

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