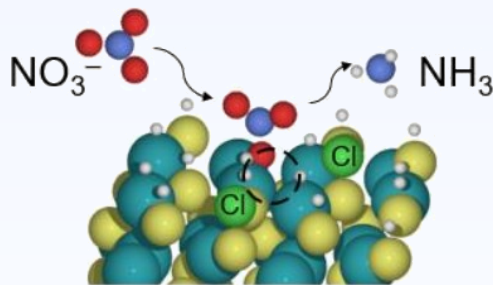
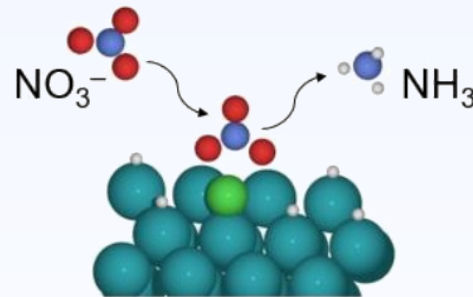


**Rh<sub>x</sub>S<sub>y</sub>/C** NO<sub>3</sub>RR Activity >  
Cl<sup>-</sup> Poison Resistance >

**Rh/C** NO<sub>3</sub>RR Activity  
Cl<sup>-</sup> Poison Resistance



Rh<sub>3</sub>S<sub>4</sub>(100) with Sulfur Vacancy



Rh(211)

# Rhodium Sulfide Electrocatalysts for Electrocatalytic Nitrate Reduction

Samuel D. Young

26 Aug 2021

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. *Catalysis Science and Technology*. In review.

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<http://cheresearch.engin.umich.edu/goldsmith/>

# Nitrate is a Major Water Pollutant

- Human N contribution to environment:  $10^8$  tonnes/yr.<sup>[1, 2]</sup>
  - Largest source: ammonia fertilizer (> 100 Tg N).
  - Makes  $\text{NO}_3^-$  is one of the most widespread water pollutants.
- Adverse health effects:<sup>[3-5]</sup>
  - Methemoglobinemia.
  - Ovarian and thyroid cancers.



Ammonia fertilizer in agriculture [1].

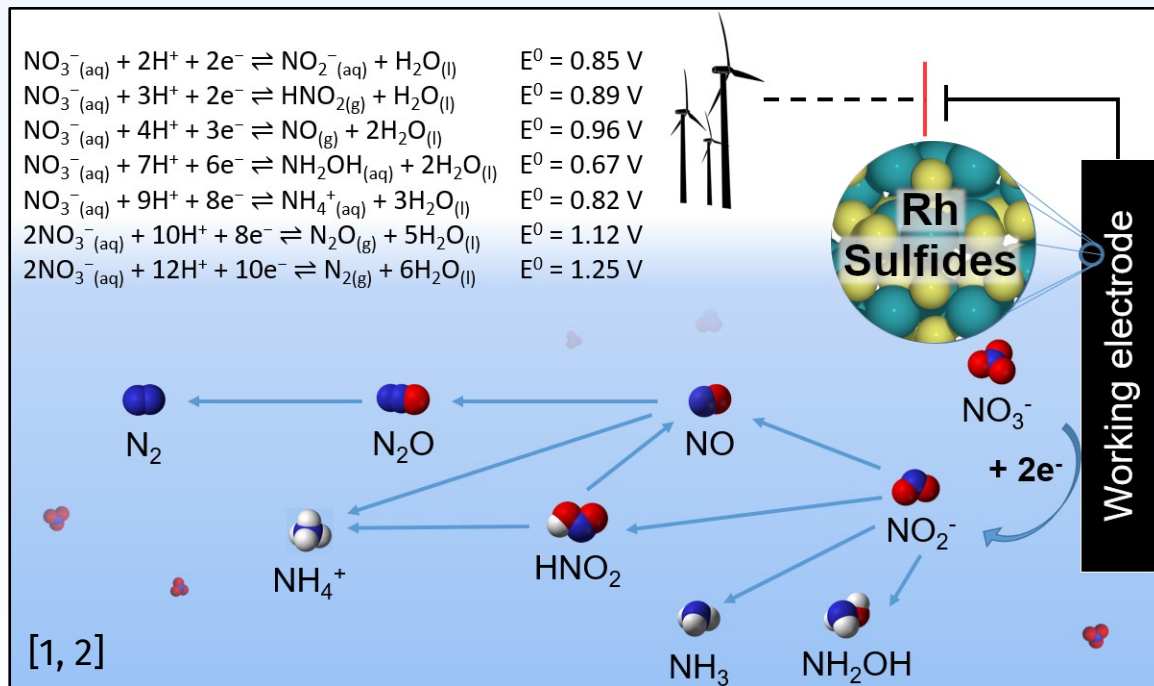


Methemoglobinemia patient (left) versus healthy patient (right) [5].

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).

# Electrocatalytic Nitrate Reduction ( $\text{NO}_3\text{RR}$ ) is a Sustainable Route for Nitrate Remediation



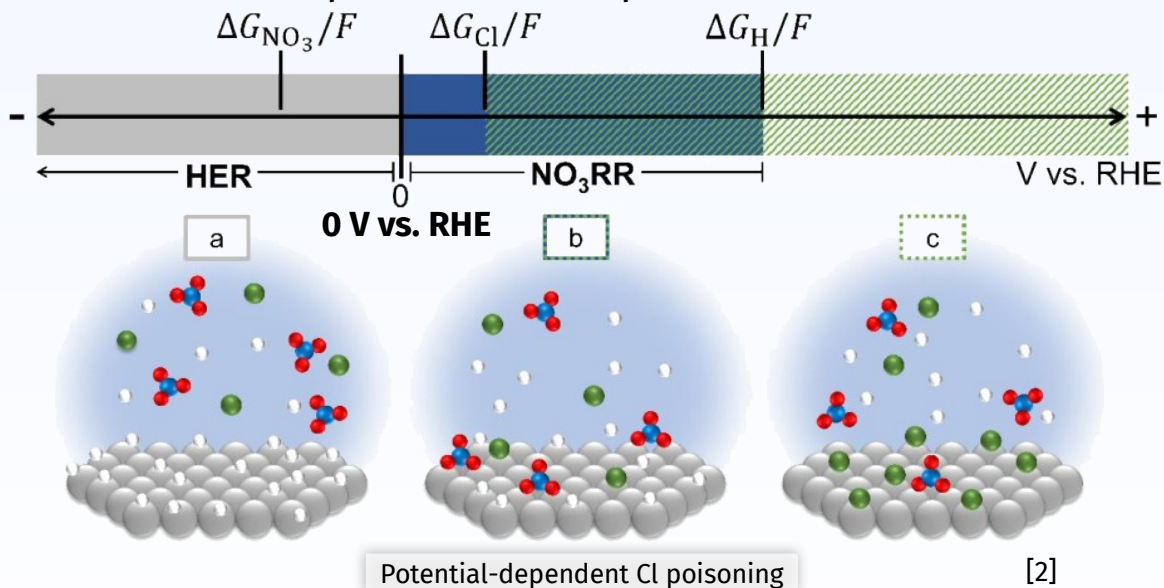
- Can be powered with renewable electricity.
- Don't need continuous reductant ( $\text{H}_2$ ) stream.
- Many benign or value-added products possible, especially  $\text{NH}_3/\text{NH}_4\text{NO}_3$ .
- Challenge: need more active, selective, and stable electrocatalysts.

[1] van Langevelde, P. H., Katsounaros, I. & Koper, M. T. M. Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production. *Joule* **5**, 290–294 (2021).

[2] Singh, N. & Goldsmith, B. R. Role of Electrocatalysis in the Remediation of Water Pollutants. *ACS Catal.* **10**, 3365–3371 (2020).

# Halide Poisoning Inhibits Many Electrocatalysts

- Halide poisoning is an understudied aspect of electrocatalyst design.
- Chloride ( $\text{Cl}^-$ ) poisons many potential  $\text{NO}_3\text{RR}$  catalysts<sup>[1]</sup> and is a very common pollutant.
- $\text{Cl}^-$  interferes with nitrate adsorption at  $\text{NO}_3\text{RR}$  potentials.<sup>[2]</sup>



[1] Juarez, F. et al. Why are trace amounts of chloride so highly surface-active? *Journal of Electroanalytical Chemistry* **847**, 113128 (2019).

[2] 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. *In review*.

[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).

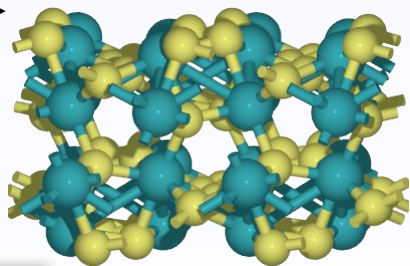
# Objective: Verify Whether Rh Sulfides Are Active Towards NO<sub>3</sub>RR And Resist Cl<sup>-</sup> Poisoning

- Rh is the most active pure metal for NO<sub>3</sub>RR.<sup>[1-2]</sup>
- Metal sulfides generally resist halide poisoning in HER.<sup>[3-4]</sup>
- Hypothesis: Rh sulfides should combine high Rh activity and poison resistance in NO<sub>3</sub>RR.

## • Questions:

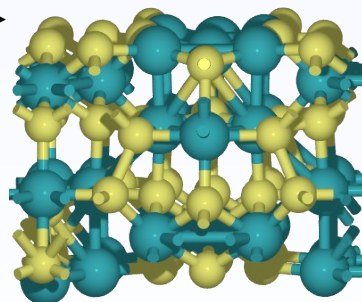
- What is the catalytic performance of Rh sulfides relative to Rh and Pt?
- Are Rh sulfides more poison-resistant than Rh and Pt?
- Which specific Rh sulfide phases or surfaces are the most active?

Surface →



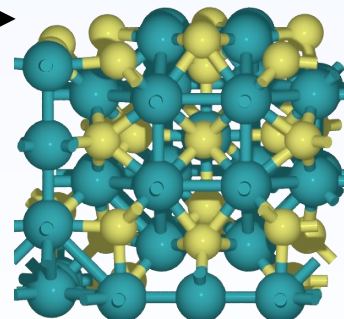
Rh<sub>2</sub>S<sub>3</sub>(001)

→



Rh<sub>3</sub>S<sub>4</sub>(100)

→



Rh<sub>17</sub>S<sub>15</sub>(100)

Three representative  
Rh sulfide facets

[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).

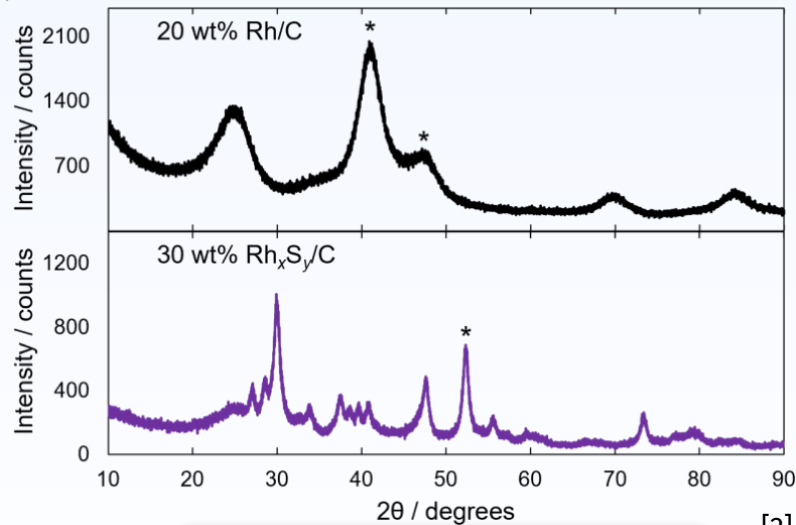
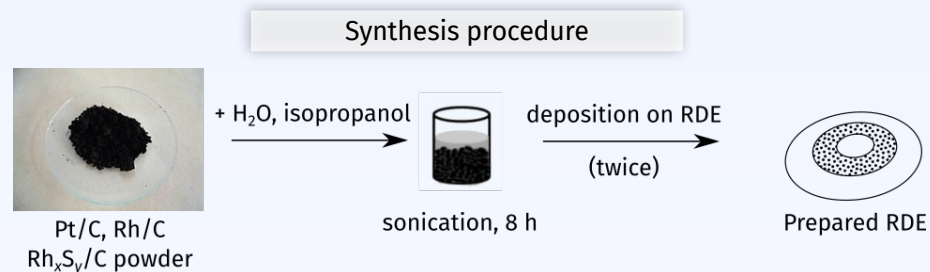
[2] Dima, G. E., de Vooy, A. C. A. & Koper, M. T. M. Electrocatalytic reduction of nitrate at low concentration. *Journal of Electroanalytical Chemistry* **554–555**, 15–23 (2003).

[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).

# Catalyst Synthesis

- Pt/C, Rh/C, and Rh<sub>x</sub>S<sub>y</sub>/C were prepared by catalyst ink impregnation on glassy carbon disks.
- Nanoparticle sizes range from 2.2 nm (Rh/C, Pt/C) to 12 nm (Rh<sub>x</sub>S<sub>y</sub>/C).
- We successfully synthesized a Rh sulfide phase, as shown in the XRD spectra.



Disappearance of Rh metal-specific peaks from XRD spectrum.

[1] Adapted from Wang, Z., Young, S. D., Goldsmith, B. R. & Singh, N. *Journal of Catalysis* **395**, 143–154 (2021).

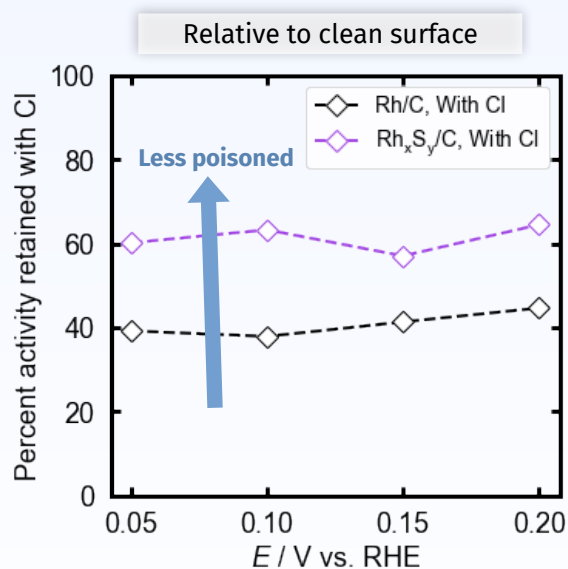
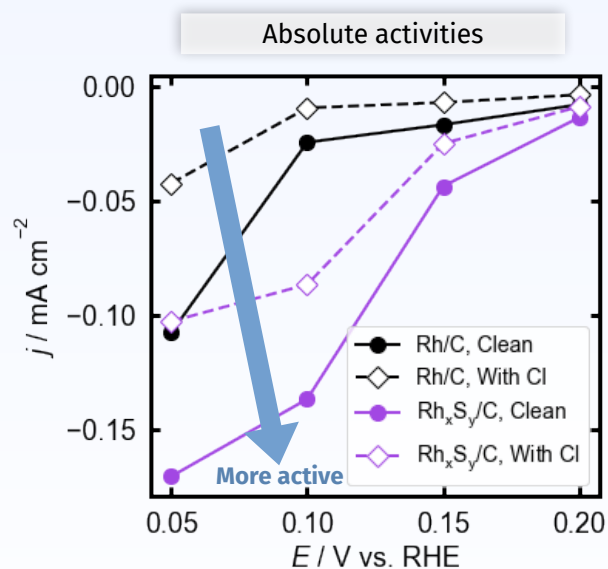
[2] Richards, D., Young, S. D., Goldsmith, B. R. & Singh, N. Electrocatalytic Nitrate Reduction on Rhodium Sulfide compared to Pt and Rh in the Presence of Chloride. *In review*.

[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).

# Steady-State Current Density Results

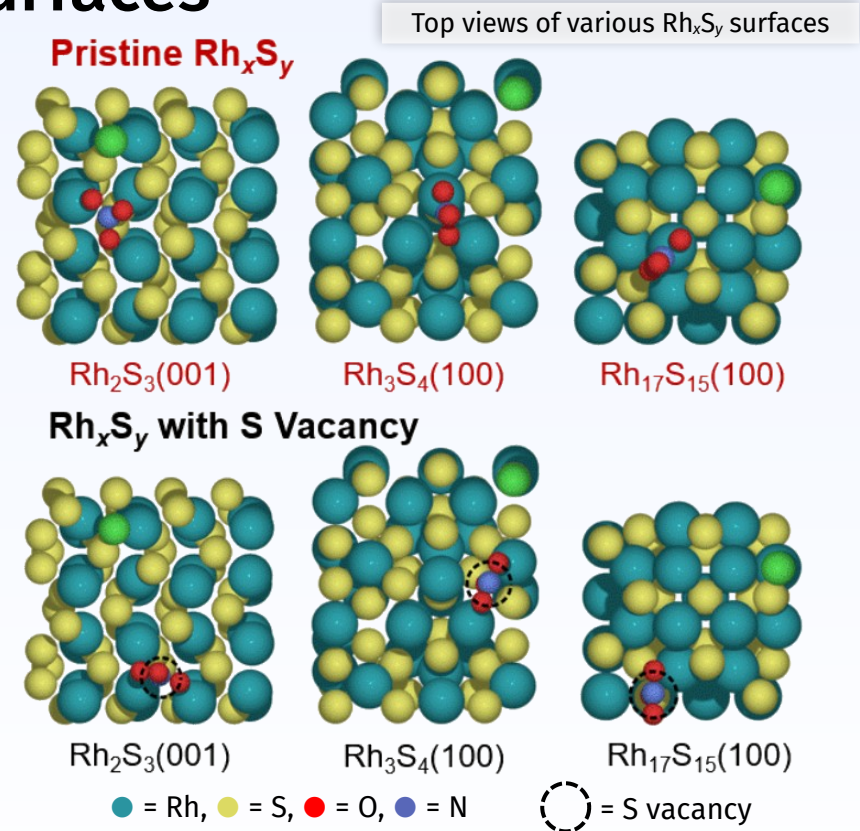
- $\text{Rh}_x\text{S}_y/\text{C}$  is more active than both  $\text{Rh}/\text{C}$  and  $\text{Pt}/\text{C}$ , both with and without  $\text{Cl}^-$  added.
- $\text{Pt}/\text{C}$  is much less active, likely due to very weak  $\text{NO}_3^-$  adsorption.
- $\text{Rh}_x\text{S}_y/\text{C}$  maintains 62% activity during poisoning, compared to 37% for  $\text{Rh}/\text{C}$ .
- **$\text{Rh}_x\text{S}_y/\text{C}$  is more poison-resistant than  $\text{Rh}/\text{C}$ , and more than  $\text{Pt}/\text{C}$  at more positive potentials.**



# DFT Modeling of Rh Sulfide Surfaces

- Modeled Rh sulfides using representative facet for each phase.<sup>[1]</sup>
- Density functional theory used to calculate binding energies and barriers.
- Central questions to answer:

- 1) How do adsorbates bind to different  $Rh_xS_y$  facets?
- 2) Which surface is most active?
- 3) Do S vacancies promote  $NO_3RR$  activity?

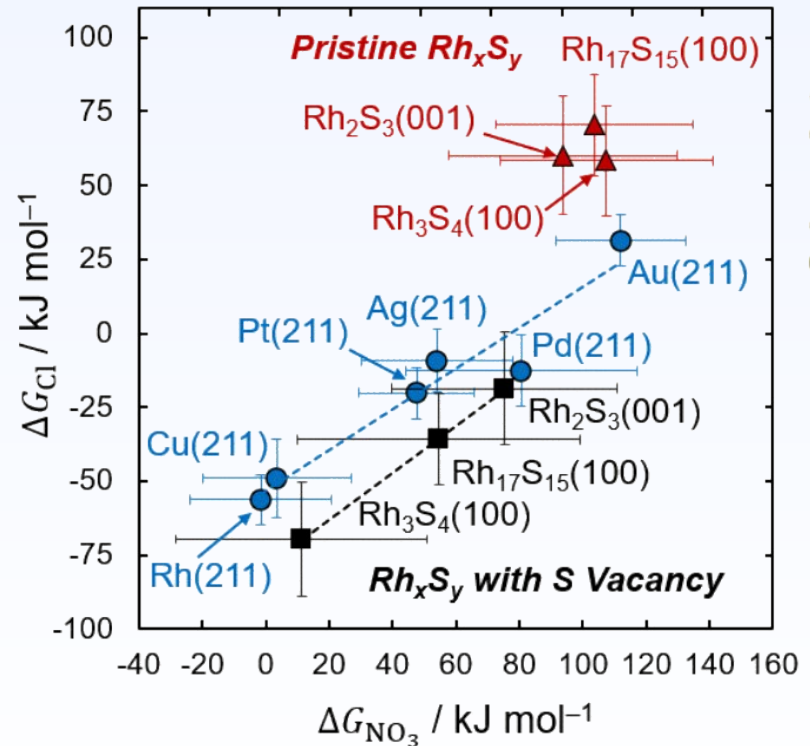


[1] Singh, N. et al. Investigation of the Active Sites of Rhodium Sulfide for Hydrogen Evolution/Oxidation Using Carbon Monoxide as a Probe. *Langmuir* 30, 5662–5668 (2014).

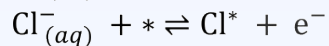
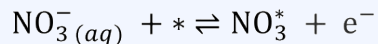
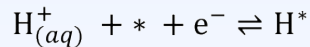


# 1) How do adsorbates bind to different $Rh_xS_y$ facets?

- Pristine sulfide surfaces adsorb much more weakly than transition metals – likely not active sites for  $NO_3RR$ .
- $Rh_xS_y$  with S vacancies follow scaling relationship similar to metals, but possibly more poisoned by  $Cl^-$ .
- **S-defected  $Rh_3S_4(100)$  predicted to bind both  $NO_3^-$  and  $Cl^-$  strongest.**

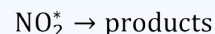
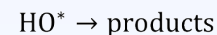
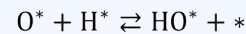
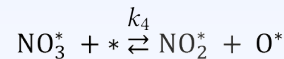
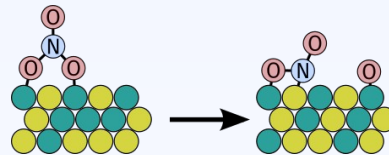


## 2, 3) Which surface is most active? Do vacancies matter?



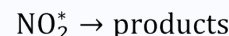
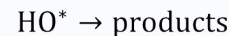
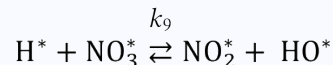
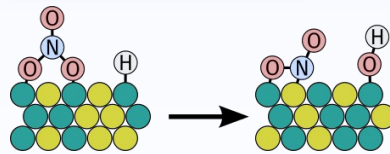
- Modeled competitive adsorption of H, Cl, and NO<sub>3</sub> on surface using Langmuir-Hinshelwood mechanisms.
- Combined coverages and barriers to get TOFs.
- Two likely mechanisms:
  - Direct NO<sub>3</sub> dissociation (transition metals,<sup>[1]</sup> previous computational models<sup>[2]</sup>)
  - H-assisted NO<sub>3</sub> dissociation (consistent with present data on Pt/C)

### Direct reduction



$$\text{rate} = \frac{k_4 K_{\text{NO}_3} [\text{NO}_3^-]_0}{(1 + K_{\text{H}} [\text{H}^+]_0 + K_{\text{NO}_3} [\text{NO}_3^-]_0 + K_{\text{Cl}} [\text{Cl}^-]_0)^2}$$

### H-assisted reduction



$$\text{rate} = \frac{k_9 K_{\text{NO}_3} [\text{NO}_3^-]_0 K_{\text{H}} [\text{H}^+]_0}{(1 + K_{\text{H}} [\text{H}^+]_0 + K_{\text{NO}_3} [\text{NO}_3^-]_0 + K_{\text{Cl}} [\text{Cl}^-]_0)^2}$$

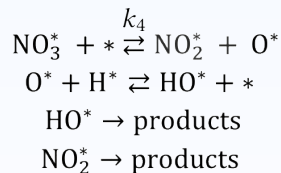
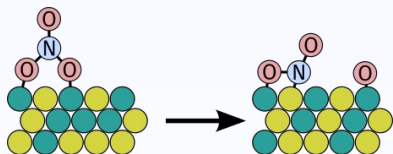
[1] Dima, G. E., de Voys, A. C. A. & Koper, M. T. M. Electrocatalytic reduction of nitrate at low concentration on coinage and transition-metal electrodes in acid solutions. *Journal of Electroanalytical Chemistry* **554–555**, 15–23 (2003).

[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).

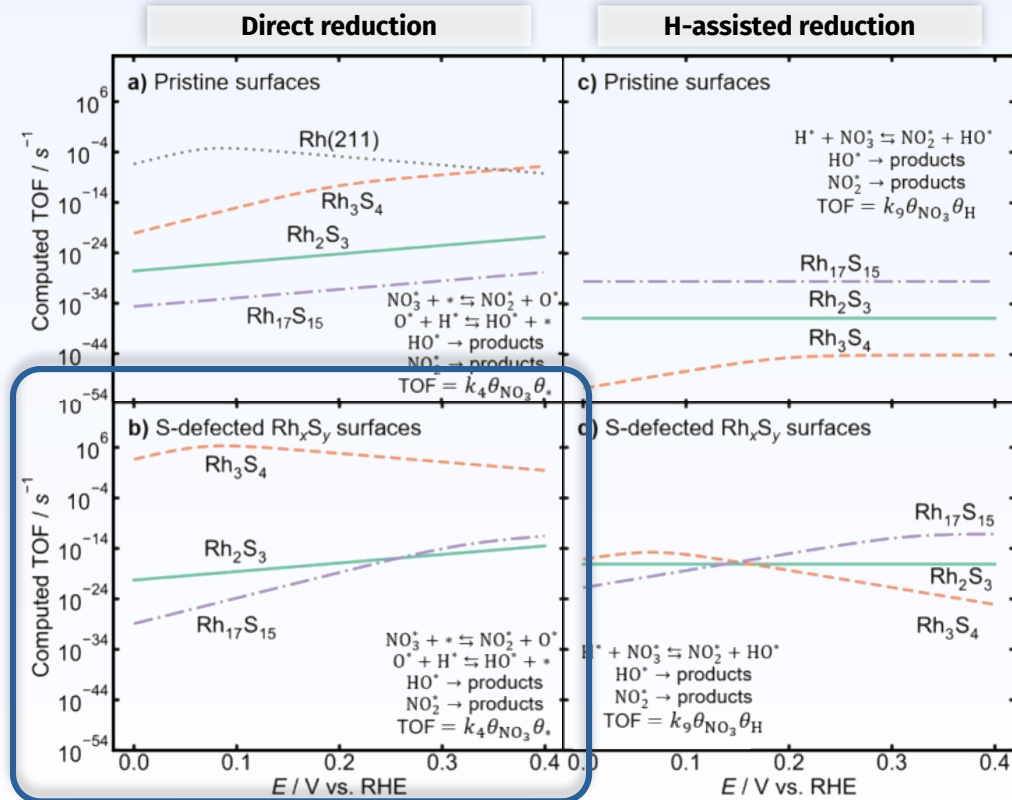
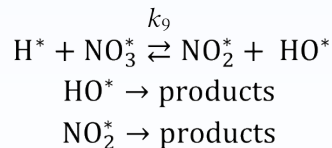
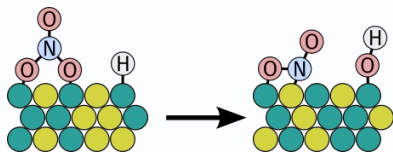
## 2, 3) Which surface is most active? Do vacancies matter?

- With barriers and potential-dependent coverages, can calculate potential-dependent TOFs.
- **S-defected  $Rh_3S_4(100)$  is predicted to be most active, through direct mechanism.**
- **S vacancies facilitate  $NO_3RR$ .**

### Direct reduction

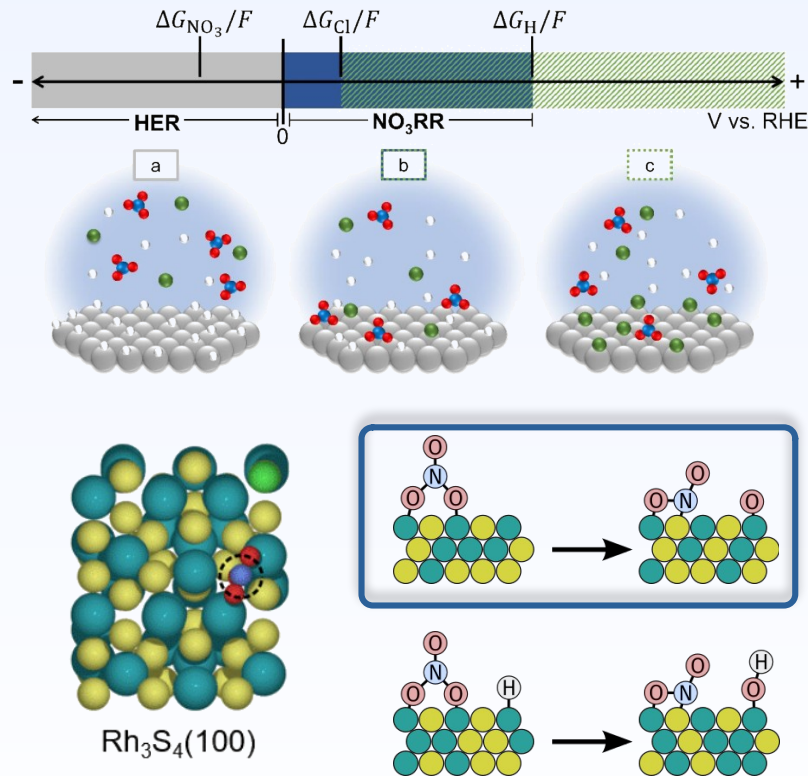


### H-assisted reduction



# Conclusions

- $\text{Rh}_x\text{S}_y/\text{C}$  is  $\sim 4x$  as active as Rh and  $\sim 15x$  as active as Pt at 0.1 V vs. RHE.
- $\text{Rh}_x\text{S}_y/\text{C}$  maintains maintains 62% activity during poisoning, compared to 37% for Rh/C.
- S-defected  $\text{Rh}_3\text{S}_4(100)$  is most active surface, through direct reduction.
- Future research:
  - Synthesize specific facets and defects to confirm activity predictions.
  - Isotopic labeling to confirm reaction mechanism.
  - Core-shell or nanoparticle size engineering to reduce Rh used.

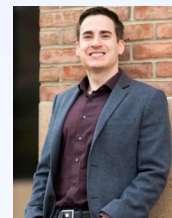


# Acknowledgements

- Danielle Richards and Prof. Nirala Singh for experimental work and insights
- Dr. Jin-Xun Liu for previous computational work on pure metals
- Prof. Bryan R. Goldsmith – Advisor
- Michigan Institute for Computational Discovery and Engineering
- National Energy Research Scientific Computing Center
- XSEDE – San Diego Supercomputing Center



Danielle Richards



Bryan R. Goldsmith



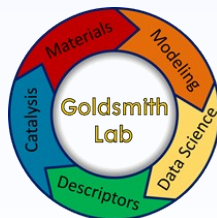
Nirala Singh



Jin-Xun Liu



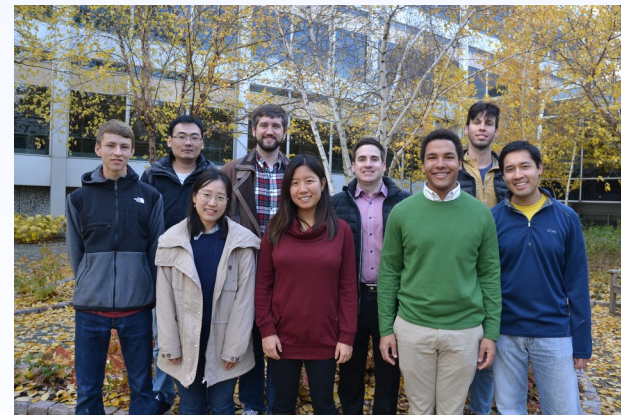
Extreme Science and Engineering  
Discovery Environment



See paper updates or  
view these slides



<https://samuelyd.github.io>

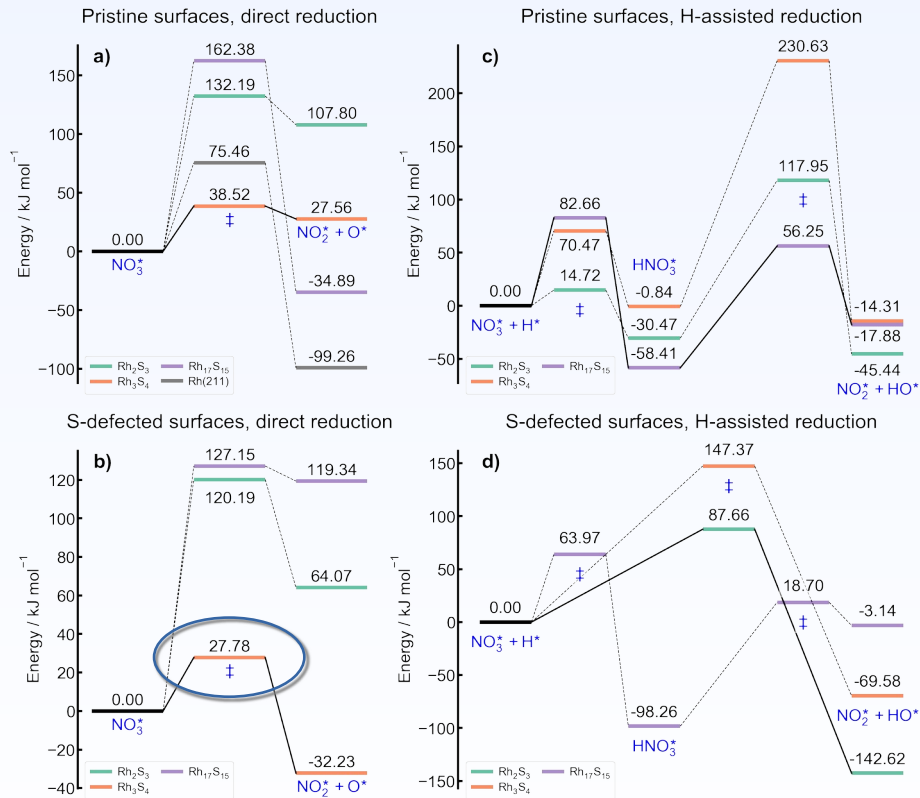


Questions?

# Backup slides

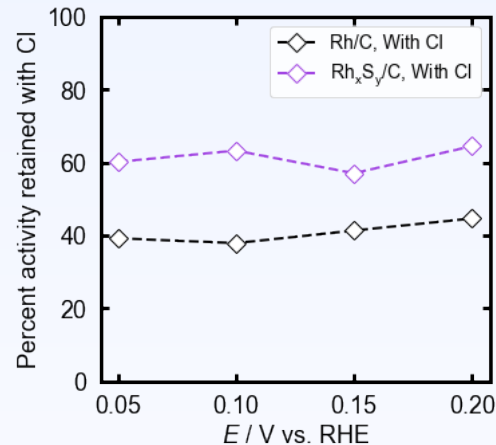
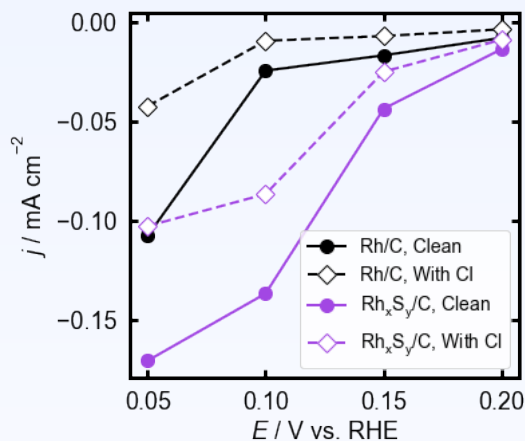
## 2, 3) Which surface is most active? Do vacancies matter?

- Computed barriers for each sulfide surface, for each proposed mechanism.
- **Lowest barrier is S-defected  $\text{Rh}_3\text{S}_4(100)$  through the direct mechanism.**
- H-assisted mechanism tends to have higher effective barriers – likely not the active mechanism on  $\text{Rh}_x\text{S}_y$ .



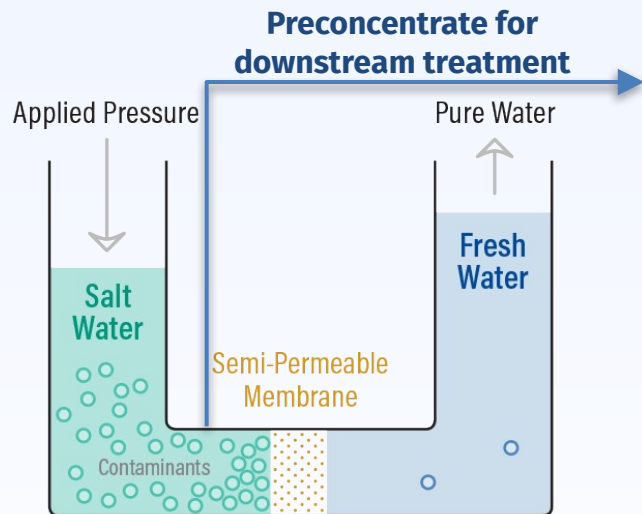
# Faradaic Efficiency

- At 0.1 V vs. RHE, 0.1 M HNO<sub>3</sub>, Rh<sub>x</sub>S<sub>y</sub>/C has 67% FE to NH<sub>4</sub><sup>+</sup> (compared to 92% for Rh/C).
- **Rh<sub>x</sub>S<sub>y</sub>/C has lower FE than Rh/C, but about 3 times the absolute NH<sub>4</sub><sup>+</sup> yield.**



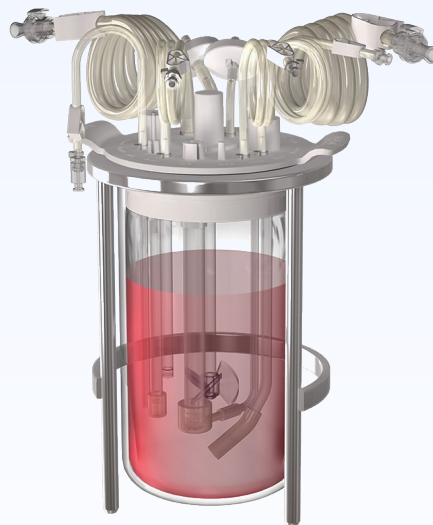


# Approaches to Nitrate Removal



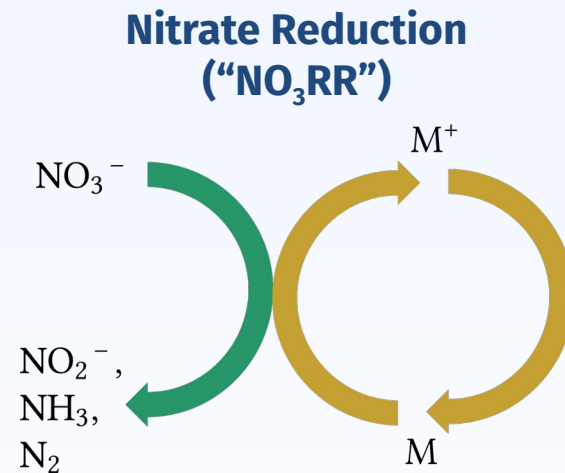
## Physical<sup>[1]</sup>

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



## Biological<sup>[2]</sup>

- Need carbon source
- Can produce biotoxins



## Catalytic<sup>[3]</sup>

- Catalysts easily poisoned by other contaminants
- Need electricity or reductant

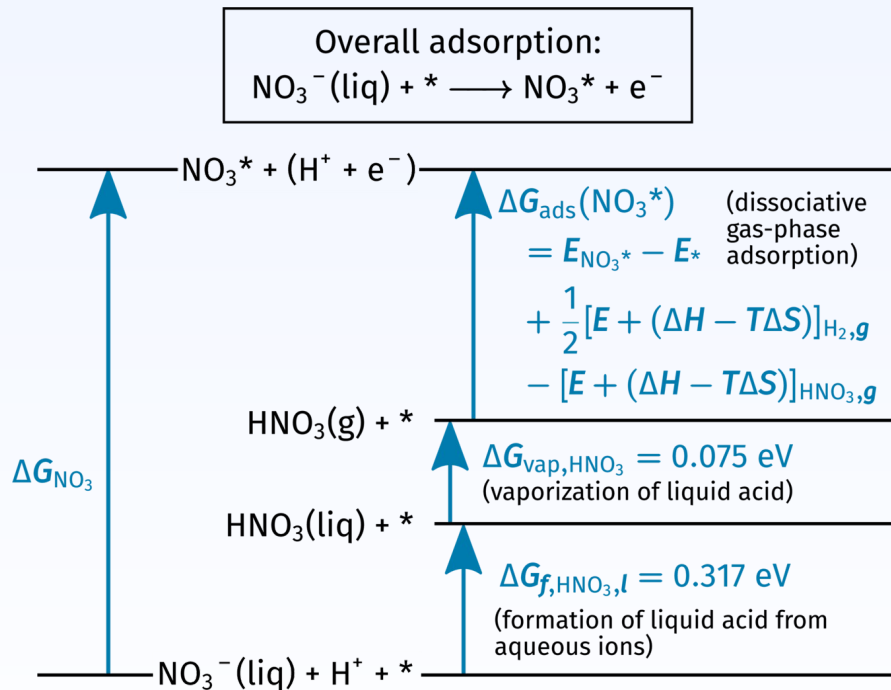
[1] PureTec Industrial Water. What is Reverse Osmosis? <https://puretecwater.com/reverse-osmosis/what-is-reverse-osmosis>

[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

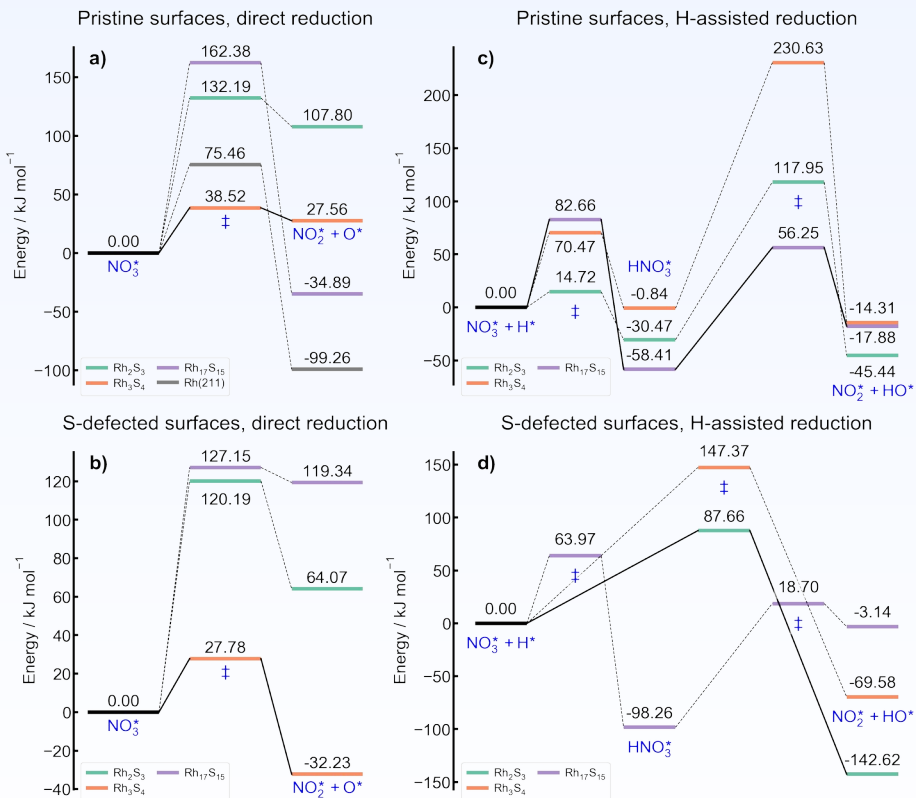
# Nitrate binding energies adjusted with a thermodynamic cycle

- Plane-wave DFT cannot model single point charges—they would multiply infinite with periodic boundary conditions.
- Strategy: compute binding energies using neutral  $\text{NO}_3$ , then compute equivalent energy of  $\text{NO}_3^-$  using a thermodynamic cycle.<sup>[1]</sup>



[1] Calle-Vallejo, F., Huang, M., Henry, J. B., Koper, M. T. M. & Bandarenka, A. S. Theoretical design and experimental implementation of Ag/Au electrodes for the electrochemical reduction of nitrate. *Physical Chemistry Chemical Physics* **15**, 3196 (2013).

# All computed barriers



# All computed TOFs

