



Stability Assessment of Graphene-Based Single-Atom Electrocatalysts for CO₂ Reduction

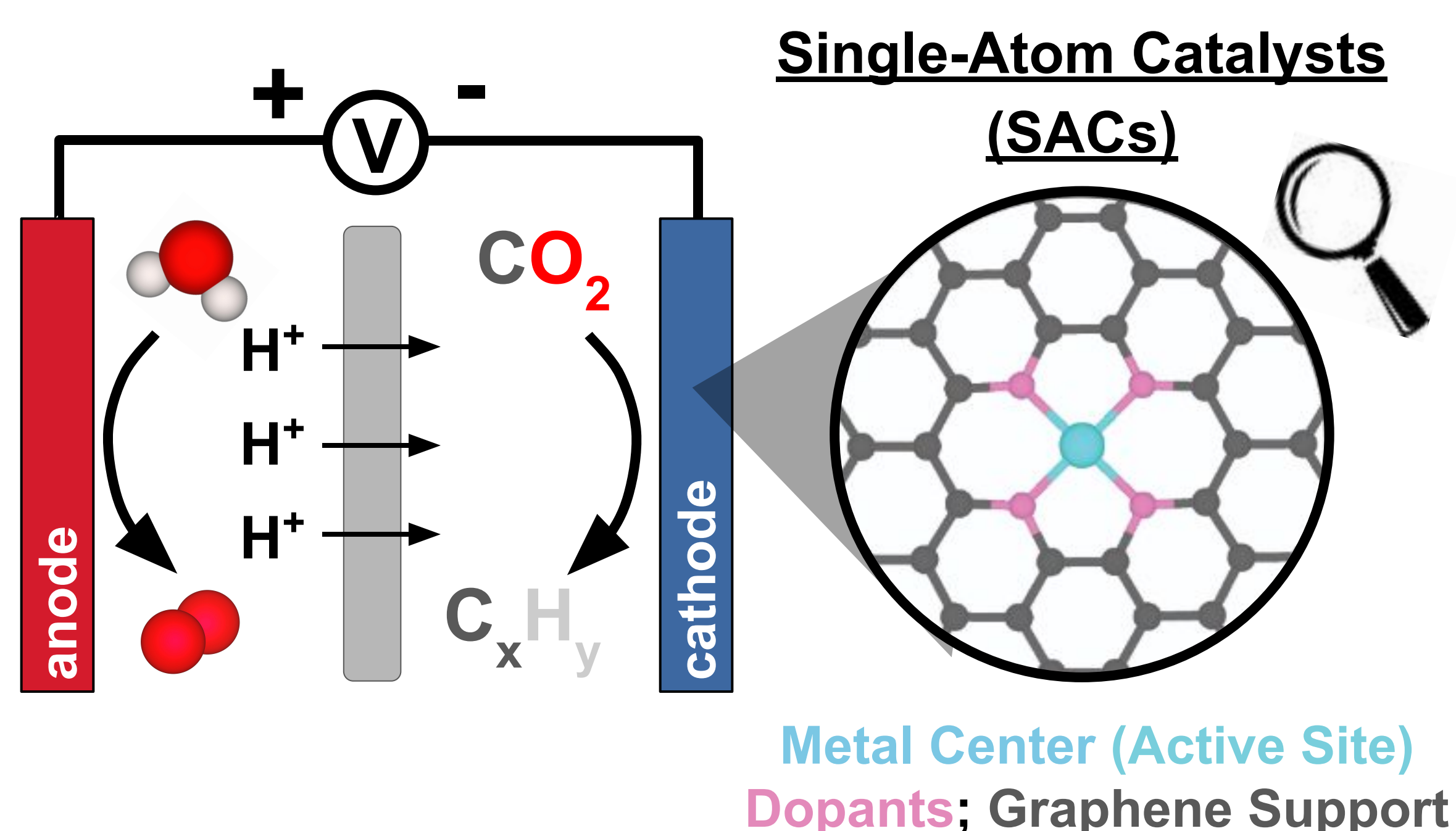
Rohan Harrison, YSP Student, *Newton South*
Lee Van Voorhis, YSP Student, *Cambridge Rindge and Latin*
Colin Gallagher, Chemical Engineering, *Northeastern University*
Dr. Qing Zhao, Chemical Engineering, *Northeastern University*



Background

Unsustainable CO₂ emissions pose several ecological and humanitarian challenges. **Electrochemical CO₂ reduction (CO₂R) has been proposed as a solution.**

Traditional CO₂R catalysts suffer from several practical limitations. Graphene-based catalysts featuring isolated metal centers, namely **single-atom catalysts, provide a platform for new CO₂R catalysts** that can outperform traditional cathode materials.



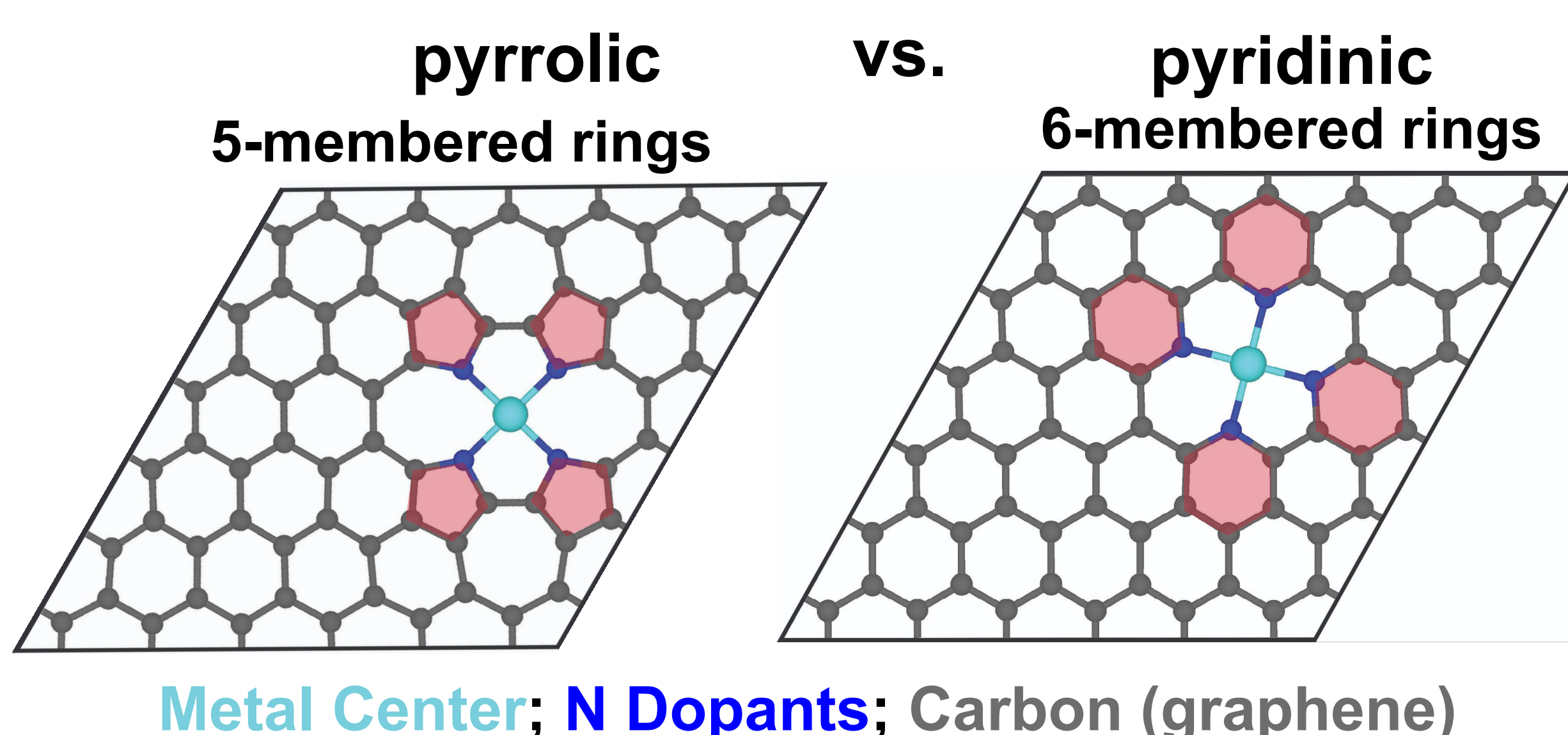
Abstract

The true coordinating environment of SACs is difficult to confirm experimentally. Computational models allow us to compare the stability of different active sites.

Objectives: Use computational models to...

- (1) Compare the relative stability of different 3d-transition metals in doped-graphene SACs
- (2) Compare the relative stability of different dopant coordination environments (pyrrolic vs. pyridinic)

Computational Models



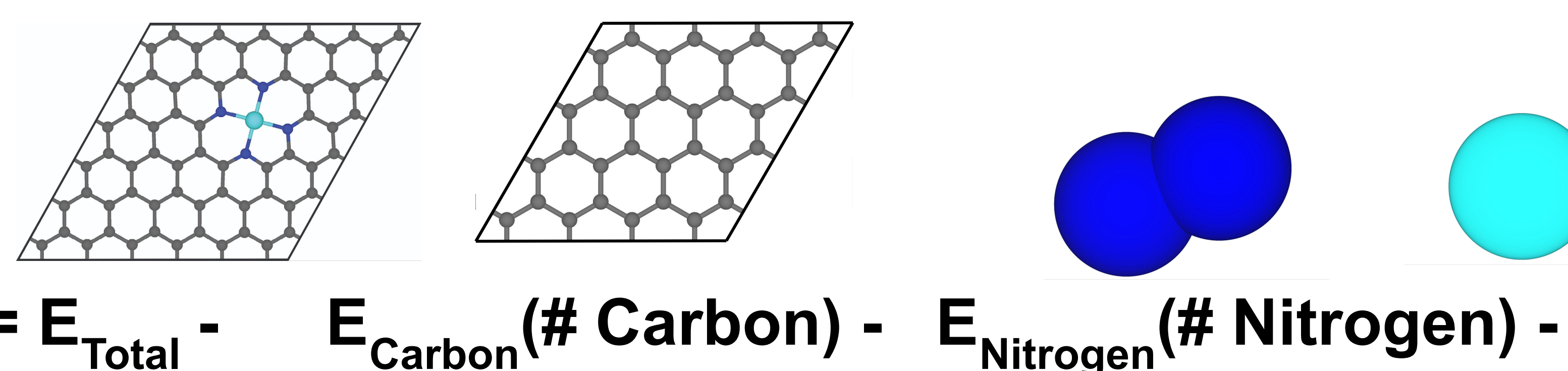
Computational Methods



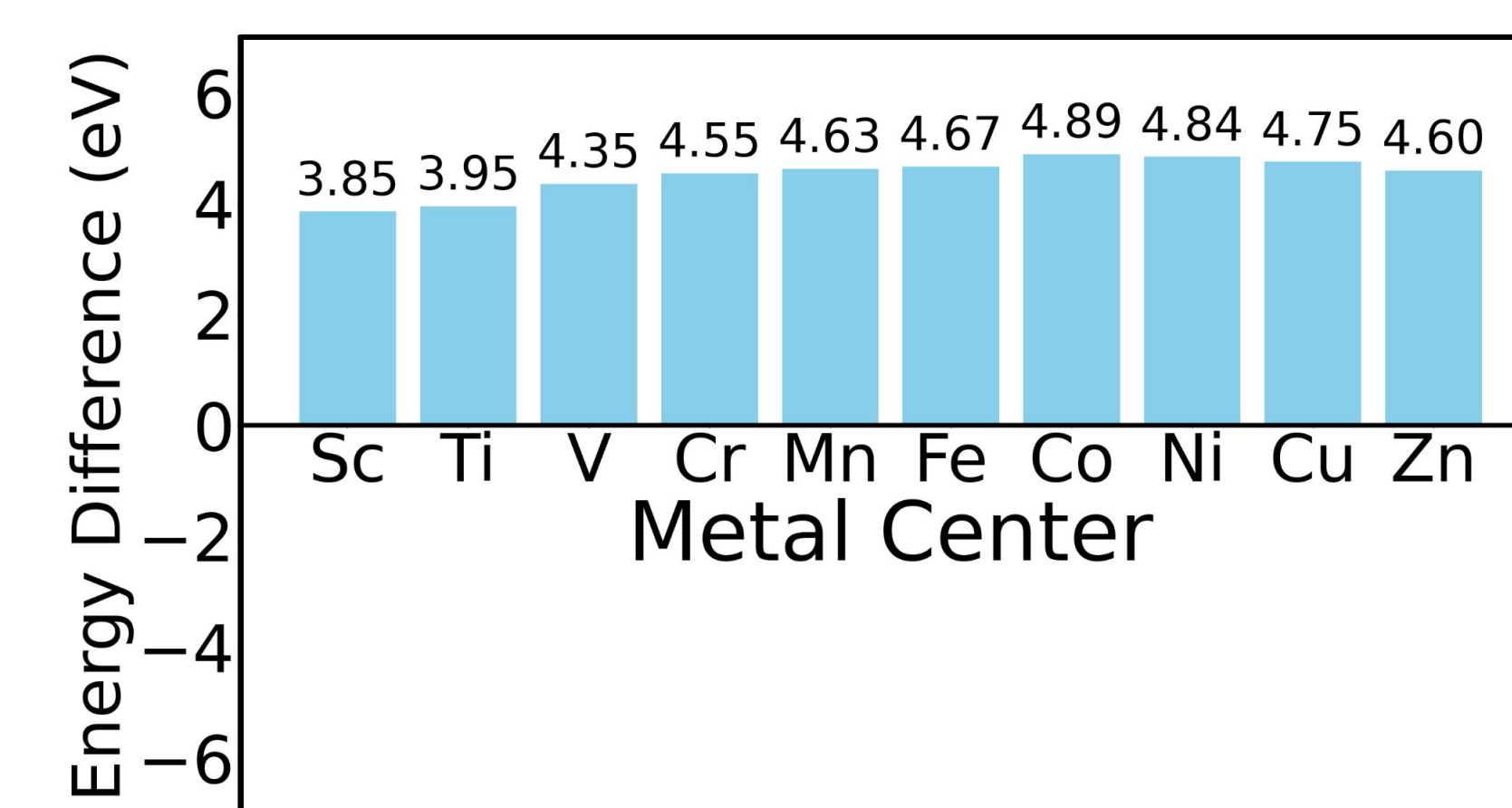
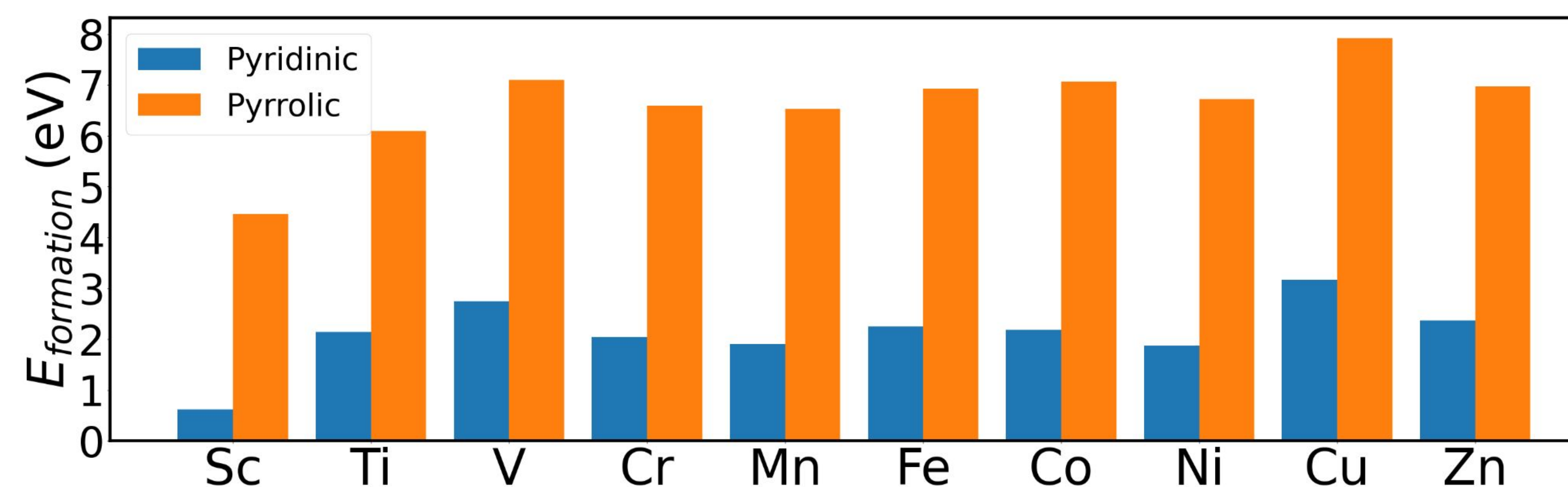
VASP (Vienna Ab initio Simulation Package): Force-based optimization that factors in electronic structure.

(PBE-D3 XC functional, 400 eV ENCUT, 3x3x1 K-POINT).

After optimizing the structure, we combined computational data with thermodynamic equations to solve for the energy of formation.



Results



Metal Center	Pyridinic E _{formation}	Pyrrolic E _{formation}
Sc	4.469	0.6138
Ti	6.090	2.143
V	7.096	2.743
Cr	6.593	2.044
Mn	6.529	1.900
Fe	6.925	2.254
Co	7.070	2.181
Ni	6.721	1.876
Cu	7.922	3.169
Zn	6.966	2.366

Conclusion and Future Steps

Our results show that the pyridinic structures were definitively more stable than the pyrrolic structures. This conclusion was made because the pyridinic structures all had a lower energy of formation than their pyrrolic counterparts.

Future steps could include testing other pyrrolic moieties or testing the 4d and 5d metals with pyrrolic structures. Additionally, the efficiency of these catalysts could be tested to determine whether pyrrolic or pyridinic catalysts would be ideal.

References

- Kothakonda, M., LaCroix, S., Zhou, C., Su, J., & Zhao, Q. (n.d.). *Discovering Ni/Cu Single-Atom Alloy as a Highly Active and Selective Catalyst for Direct Methane Conversion to Ethylene: A First-Principles Kinetic Study*. ACS.
- Gallagher, C., Manish Kothakonda, M., & Zhao, Q. (2025, January 7). *Graphene-based single-atom catalysts for electrochemical CO₂ reduction: unraveling the roles of metals and dopants in tuning activity*. Physical Chemistry Chemical Physics.
- Nørskov, J., Abild-Pedersen, F., Studt, F., & Bligaard, T. (n.d.). *Density functional theory in surface chemistry and catalysis*. PNAS. <https://www.pnas.org/doi/10.1073/pnas.1006652108>
- Seh, Z. W., Kibsgaard, J., Dickens, C., Chorkendorff, I., Nørskov, J., & Jaramillo, T. (n.d.). *Combining theory and experiment in electrocatalysis: Insights Into Materials Design*. Science.

Acknowledgements

LAB

Dr. Qing Zhao, Assistant Professor
Colin Gallagher, PhD student
Center for STEM Education
Claire Duggan, Executive Director
Jennifer Love, Associate Director
D'mitra Mukasa, Victoria Berry, & Ahmed Othman,
YSP Coordinators
Nicolas Fuchs, Program Manager
Mary Howley, Administrative Officer