Theory-Guided Design and Optimization of Bio-Inspired Iron-Nickel Sulfide Electrocatalysts for Green Hydrogen Production

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Computer-Aided Design and Engineering

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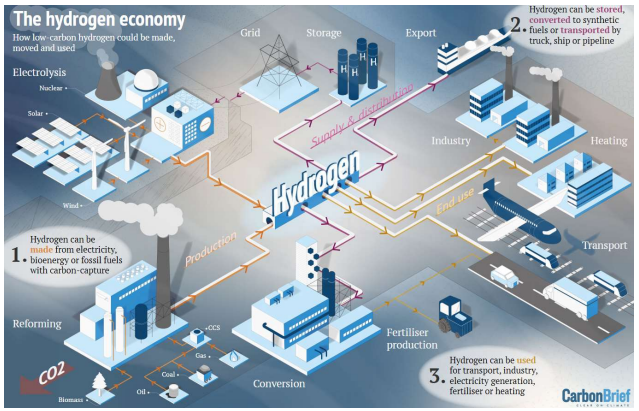
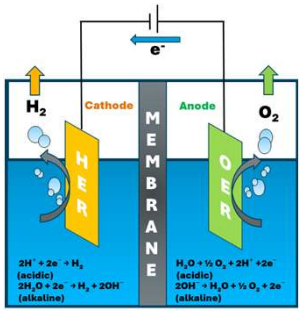
INTRODUCTION



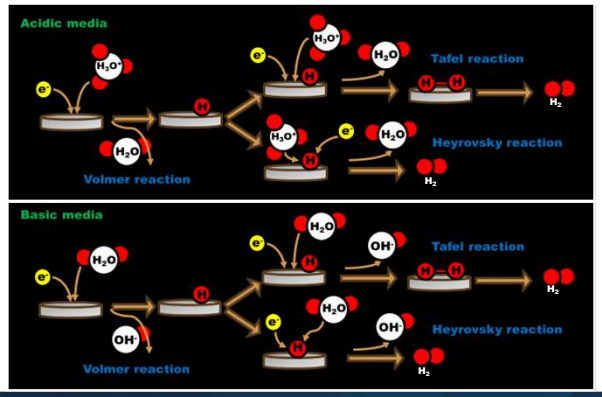
Hydrogen is a versatile energy carrier for tackling critical energy challenges and enabling deep decarbonization across various difficult-to-abate sectors, such as steel, chemicals, shipping, long-haul transport, and aviation.

Electrocatalytic water splitting

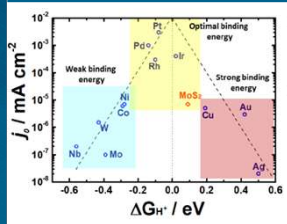


- Water electrolysis powered by renewable energy sources (e.g., solar and wind) produce "green" hydrogen with no greenhouse gas (GHG) emissions.
- Water electrolysis comprises two heterogeneous reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).
- The kinetically sluggish two-electron-transfer HER and four-proton-electron-coupled OER requires high overpotentials, which dramatically lower the performance of water electrolyzers, leading to increase electricity demands and costly hydrogen production.

Mechanism of Hydrogen Evolution Reaction



PROBLEM STATEMENT



HER requires High Overpotential (Energy Barrier)

- Noble & non-noble metal-based catalysts
- Platinum (Pt) is current state-of-the-art catalyst

Pt is Scarce & Expensive

- The kinetically efficient electrocatalysts composed of earth-abundant elements such as Fe, Ni, Co and S that possess active sites, high conductivity, stability, and cost-effective fabrication are necessary to produce hydrogen in the terawatt scale.

MATERIALS & METHODS

- Natural enzymes like [FeNi]- and [FeFe]-hydrogenase, with Ni- and Fe-sulfide active sites can catalyze the H^+/H_2 interconversion with remarkable efficiency.
- Hydrogenases offer fascinating blueprints for designing novel earth-abundant Fe-Ni sulfides-based electrocatalysts for green hydrogen.
- Fe-Ni sulfide minerals such as violarite ($FeNi_2S_4$) exhibit high electronic conductivities and feature structural Fe- and Ni-centers bridged by sulfur, resembling primary active sites of natural enzymes

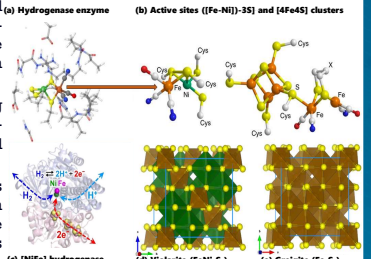
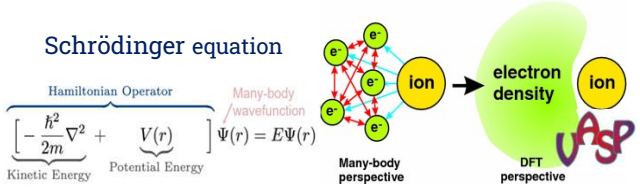


Fig. 1 |Schematic for bio-inspired novel earth-abundant Fe-Ni sulfides-based electrocatalysts

First-principles based density functional theory (DFT) methodology



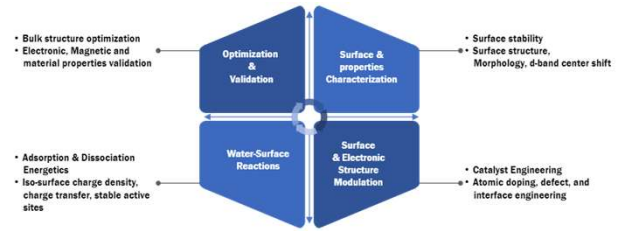
i. Atomic-level understanding of the effect of size and composition on the surface structures, stabilities, and crystal morphologies of the Fe-Ni-sulfide nanoparticles;

ii. Calculation of the redox properties of the Fe-Ni-sulfide surfaces, including the effect of surface enrichment by dopant metal impurities;

iii. Investigation of H_2O adsorption and dissociation at the different sites on the Fe-Ni-sulfide surfaces;

iv. Characterization of the electronic properties (density of states, d-band centers, charge transfers, etc.) to provide mechanistic insights into the reaction mechanisms from H_2O to H and OH intermediates and to H_2 product.

Research Streamline



RESULTS & CONCLUSIONS

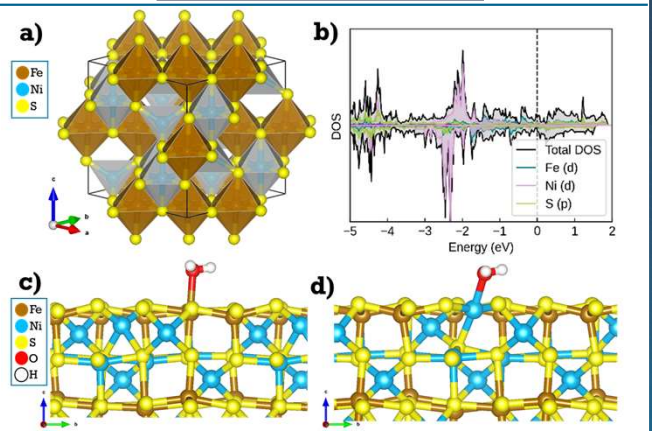


Fig. 2 |Preliminary results: (a) structure and (b) PDOS of bulk $FeNi_2S_4$. Optimized H_2O adsorption geometry on $FeNi_2S_4(001)$ at (c) Fe and (d) Ni-sites.

- Inverse-spinel violarite Bulk structure Fig.2(a) (Lattice parameter-a; DFT: a= 9.33 A°, Experimental: a= 9.46 A°)
- Surface Characterization: Three most stable are (001), (011), and (111) surfaces with surface energies of 0.84, 1.50, and 1.19 Jm^{-2}, respectively.
- Further investigations include the water dissociation, transition state structures, energy barriers, charge transfers, and vibrational frequencies.

REFERENCES

1. Canaguier, S., Artero, V. & Fontecave, M. Modelling NiFe hydrogenases: Nickel-based electrocatalysts for hydrogen production. Dalton Transactions 315–325 (2008) doi: 10.1039/b713567j.
2. Vincent, K. A., Parkin, A. & Armstrong, F. A. Investigating and exploiting the electrocatalytic properties of hydrogenases. Chem Rev 107, 4366–4413 (2007).
3. Pershad, H. R. et al. Catalytic electron transport in Chromatium vinosum [NiFe]-hydrogenase: Application of voltammetry in detecting redox-active centers and establishing that hydrogen oxidation is very fast even at potentials close to the reversible H+/H2 value. Biochemistry 38, 8992–8999 (1999).
4. Amaro-Gahete, J. et al. Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production. Coordination Chemistry Reviews vol. 448 Preprint at https://doi.org/10.1016/j.ccr.2021.214172 (2021).
5. Stephenson, M. & Stickland, L. H. Hydrogenases: a bacterial enzyme activating molecular hydrogen. Biochemical Journal 25, 205–214 (1931).
6. Lebrun, F. Nearby Molecular Hydrogen. International Astronomical Union Colloquium 81, 276–279 (1984).
7. Ahmed, M. E. & Dey, A. Recent developments in bioinspired modelling of [NiFe]- and [FeFe]-hydrogenases. Current Opinion in Electrochemistry vol. 15 195–164 Preprint at https://doi.org/10.1016/j.coelec.2019.05.009 (2019).
8. Ibn Shamsah, S. M. Earth-abundant electrocatalysts for water splitting: Current and future directions. Catalysts vol. 11 Preprint at https://doi.org/10.3390/catal11040429 (2021).
9. Sun, L., Duboc, C. & Shen, K. Bioinspired Molecular Electrocatalysts for H2Production: Chemical Strategies. ACS Catal 12, 9158–9170 (2022). Zahran, Z. N., Mohamed, E. A. & Naruta, Y. Bio-inspired cofacial Fe porphyrin dimers for efficient electrocatalytic CO2 to CO conversion: Overpotential tuning by substituents at the porphyrin rings. Sci Rep 6, 1–12 (2016).
10. Parkin, A., Seravalli, J., Vincent, K. A., Ragsdale, S. W & Armstrong, F. A. Rapid and efficient electrocatalytic CO2/CO interconversions by Carboxydothermus hydrogenoformans CO dehydrogenase I on an electrode. J Am Chem Soc 129, 10328–10329 (2007).
11. Hansen, H. A., Varley, J. B., Peterson, A. A. & Nørskov, J. K. Understanding trends in the electrocatalytic activity of metals and enzymes for CO2 reduction to CO. Journal of Physical Chemistry Letters 4, 388–392 (2013).
12. Möller, F., Piontek, S., Miller, R. G. & Apfel, U. P. From Enzymes to Functional Materials—Towards Activation of Small Molecules. Chemistry - A European Journal 24, 1471–1493 (2018).
13. Arrigoni, F. et al. Catalytic H2evolution/oxidation in [FeFe]-hydrogenase biomimetics: Account from DFT on the interplay of related issues and proposed solutions. New Journal of Chemistry 44, 17895–17918 (2020).
14. Posada-Pérez, S. et al. CO2 interaction with violarite (FeNi2S4) surfaces: A dispersion-corrected DFT study. Physical Chemistry Chemical Physics 20, 20439–20446 (2018).
15. Qiu, S., Li, Q., Xu, Y., Shen, S. & Sun, C. Learning from nature: Understanding hydrogenase enzyme using computational approach. Wiley Interdisciplinary Reviews: Computational Molecular Science vol. 10 Preprint at https://doi.org/10.1002/wcms.1422 (2020).
16. Su, H. et al. Recent progress on design and applications of transition metal chalcogenide-associated electrocatalysts for the overall water splitting. Chinese Journal of Catalysis vol. 44 7–49 Preprint at https://doi.org/10.1016/S1872-2067(22)64149-4 (2023).
17. Wang, M., Zhang, L., He, Y. & Zhu, H. Recent advances in transition-metal-sulfide-based bifunctional electrocatalysts for overall water splitting. Journal of Materials Chemistry A vol. 9 8320–8363 Preprint at https://doi.org/10.1039/d0ta12125e (2021).
18. Miao, R. et al. Mesoporous iron sulfide for highly efficient electrocatalytic hydrogen evolution. J Am Chem Soc 139, 13604–13607 (2017).
19. Yang, Y. et al. Heterogeneous Ni3S2@FeNi2S4@NF nanosheet arrays directly used as high efficiency bifunctional electrocatalyst for water decomposition. J Colloid Interface Sci 589, 300–312 (2021).
20. Wu, Y. et al. Operando capturing of surface self-reconstruction of Ni3S2/FeNi2S4 hybrid nanosheet array for overall water splitting. Chemical Engineering Journal 427, (2022).
21. Maheskumar, V., Saravanakumar, K., Yea, Y., Yoon, Y. & Park, C. M. Construction of heterostructure interface with FeNi2S4 and CoFe nanowires as an efficient bifunctional electrocatalyst for overall water splitting and urea electrolysis. Int J Hydrogen Energy 46, 5080–5094 (2023).
22. Yamaguchi, A. et al. Electrochemical CO2 reduction by Ni-containing iron sulfides: How is CO2 electrochemically reduced at bisulfide-bearing deep-sea hydrothermal precipitates? Electrochim Acta 141, 311–318 (2014).
23. Piontek, S. et al. Bio-inspired design: Bulk iron-nickel sulfide allows for efficient solvent-dependent CO2 reduction. Chem Sci 10, 1075–1081 (2019).
24. Jiang, J. et al. Nanostructured metallic FeNi2S4 with reconstruction to generate FeNi-based oxide as a highly-efficient oxygen evolution electrocatalyst. Nano Energy 81, (2021).
25. Haidar, S., Roldan, A. & De Leeuw, N. H. Catalytic dissociation of water on the (001), (011), and (111) surfaces of violarite, FeNi2S4: A DFT-D2 study. Journal of Physical Chemistry C 118, 1958–1967 (2014).

ACKNOWLEDGMENT

- I express my heartfelt thanks to my research group and my advisor, Dr. Nelson Dzade for his continuous support and mentorship in conducting this research work.
- I also acknowledge the John and Willie Leone Family Department of Energy & Mineral Engineering for graduate assistantship, the Institute of Computational and Data Sciences for providing the computational resources; and to The Pennsylvania State University for providing me with the opportunity.

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