

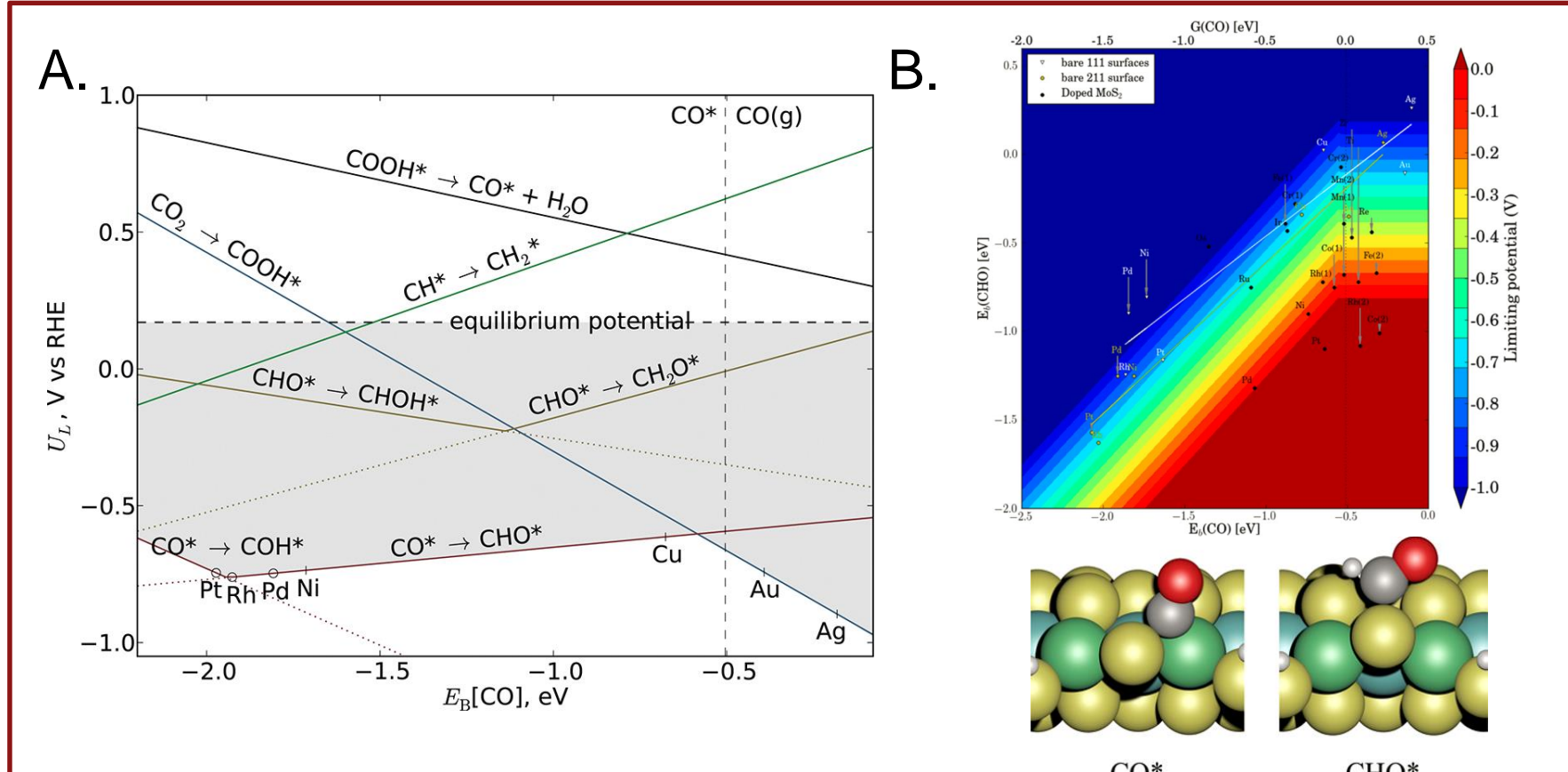
Understanding the Competition between Hydrogen Evolution and Carbon Dioxide Reduction on Transition Metal Phosphide and Sulfide Catalysts

Alan T. Landers, Meredith Fields, Daniel A. Torelli, Jianping Xiao, Thomas R. Hellstern, Sonja A. Francis, Charlie Tsai, Jakob Kibsgaard, Nathan S. Lewis, Karen Chan, Christopher Hahn, Thomas F. Jaramillo

Summary

Using a combination of experiment and theory, we explored the competition between the hydrogen evolution reaction (HER) and CO₂ reduction (CO₂R) on transition metal phosphide and transition metal sulfide catalysts. Although multifunctional active sites in these materials could potentially improve their CO₂R activity relative to pure transition metal electrocatalysts, under aqueous testing conditions, these materials showed a high selectivity for the HER relative to CO₂R. Computational results supported these findings, indicating that CO₂R activity on these catalysts can be limited both thermodynamically and kinetically. We further explored the HER activity of these materials in different electrochemical environments to determine the cause of increased overpotential for the HER under CO₂R conditions. Lastly, we propose utilizing a nonaqueous electrolyte to limit hydrogen evolution during CO₂R. These theoretical and experimental results demonstrate that selective CO₂R requires electrocatalysts that possess both favorable thermodynamic pathways and surmountable kinetic barriers.

Introduction



(A) Scaling relations between adsorption energies of carbon dioxide reduction intermediates on elemental transition metal catalysts lead to large overpotentials.¹ (B) DFT calculations predict transition metal doped molybdenum sulfide catalysts adsorb CO on the metal sites and adsorb CHO on the sulfur sites, decoupling their binding energies and breaking the scaling between intermediates which limits the activity of transition metal catalysts.²

¹ Peterson, A.; Nørskov, J. J. *Phys. Chem. Lett.* **2012**, *3*, 251–258.
² Hong, X.; Chan, K.; Tsai, C.; Nørskov, J. *ACS Catal.* **2016**, *6*, 4428–4437.

Team

Experimental

Stanford: Alan T. Landers, Thomas R. Hellstern, Jakob Kibsgaard, Christopher Hahn, Thomas F. Jaramillo
Caltech: Daniel A. Torelli, Sonja A. Francis, Nathan S. Lewis

Theoretical

Stanford: Meredith Fields, Jianping Xiao, Charlie Tsai, Karen Chan

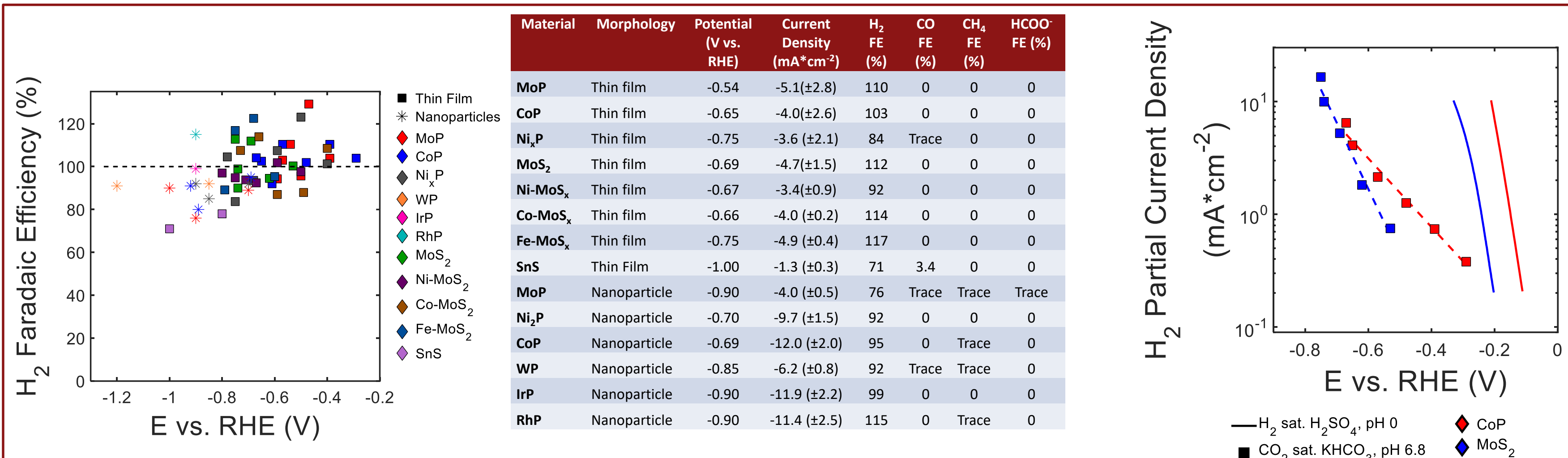
Outlook

- Identified several metal phosphide and sulfide catalysts as selective for the HER rather than CO₂R
- Studies in alternate electrochemical environments could suggest that the HER activity of CoP is poisoned under CO₂R conditions
- Demonstrated that both thermodynamic and kinetic analysis is required in prediction of active and selective CO₂R catalysts
- Nonaqueous CO₂R holds promise for reducing selectivity toward hydrogen and improving selectivity for C₂₊ products
- A methodology for testing catalysts in mixtures of aqueous and acetonitrile electrolytes will be developed

Acknowledgements

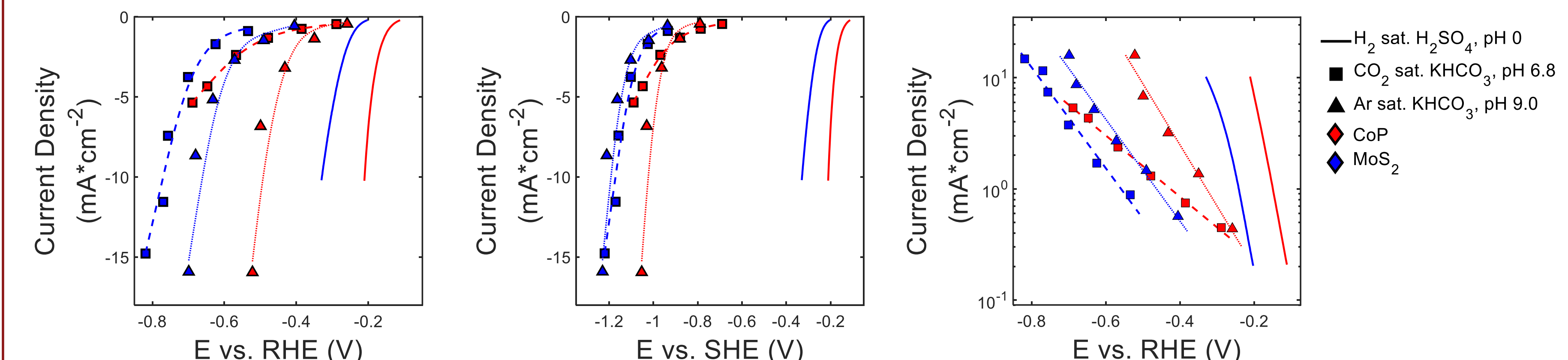
This material is based, in part, on work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy, under Award No. DE-SC0004993. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy (under Contract No. DE-AC02-05CH11231). Part of this work was performed at the Stanford Nano Shared Facilities (SNSF) and the Stanford Nanofabrication Facility (SNF), supported by the National Science Foundation under Award ECCS-1542152. We also acknowledge assistance from the Stanford NMR Facility. M.F. acknowledges a graduate fellowship through the National Science Foundation.

Results, Highlights, and Accomplishments

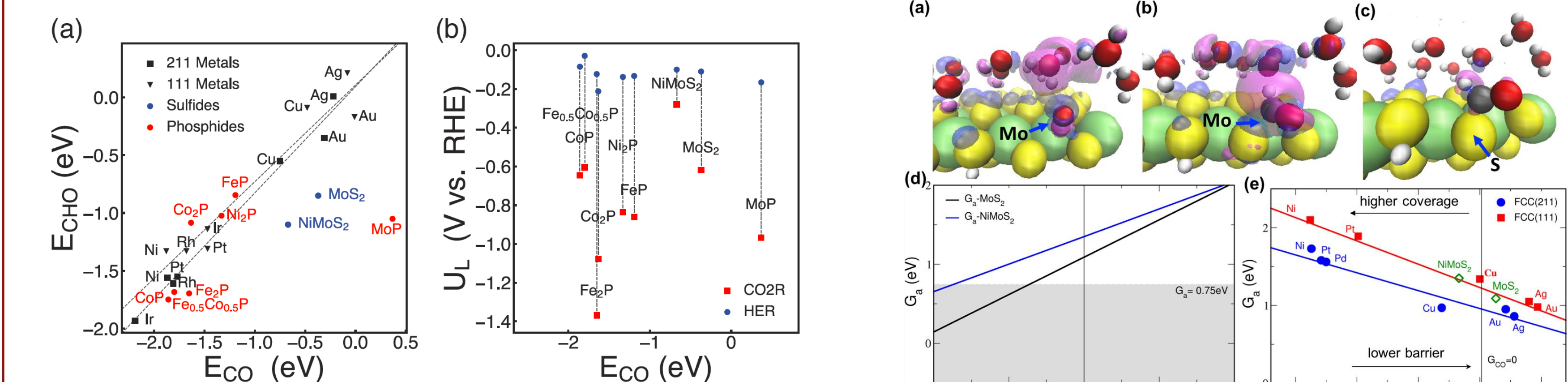


The tested transition metal phosphide and sulfide catalysts show a high Faradaic efficiency for H₂ production under CO₂R conditions. Less than 3.5 percent % of the current density went towards CO₂ reduction products on these materials.

These catalysts show a significant delay in current onset relative to HER testing conditions in H₂ purged, acidic media.



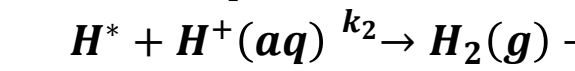
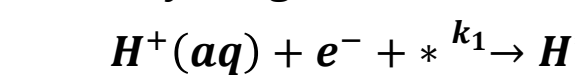
The activity of CoP for the hydrogen evolution reaction was evaluated in multiple electrolytes. At low overpotentials, CoP displays similar HER activity in Ar saturated and CO₂ saturated bicarbonate. At higher overpotentials, however, the activity of CoP in the CO₂ saturated electrolyte is suppressed relative to its activity in Ar saturated bicarbonate. This could suggest that CoP is poisoned by CO at more negative potentials.



Most of the metal phosphide and sulfide catalysts lie on the transition metal scaling lines for the binding energies of CO and CHO. Only Ni-MoS₂ shows a limiting potential for CO₂R within 0.5 V of its limiting potential for the HER.

The CO → CHO barrier is calculated to be too high for facile kinetics on Ni-MoS₂. These results suggest that the activation energy for this step relies on the binding energy of CO rather than CHO.

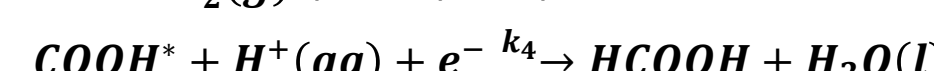
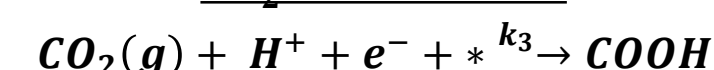
Hydrogen Evolution



$$rate_1 = k_1[H^+]\theta_*$$

$$rate_2 = k_2[H^+]\theta_H$$

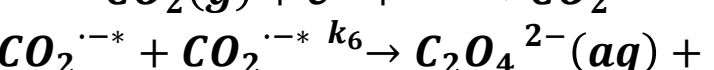
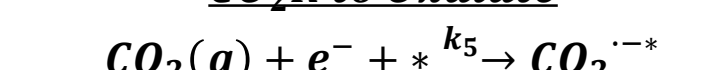
CO₂R to Formate



$$rate_3 = k_3[H^+]\theta_{CO_2}$$

$$rate_4 = k_4[H^+]\theta_{COOH}$$

CO₂R to Oxalate



$$rate_5 = k_5\theta_{CO_2}$$

$$rate_6 = k_6\theta_{CO_2}^2$$

Decreasing water concentration:

Decreases: [H⁺], θ_H

Increases: p_{CO₂}, θ_{COOH}, θ_{CO₂}

Advantages of CO₂R in Nonaqueous Solutions

- Control of proton concentration can influence selectivity
- CO₂ is more soluble in many nonaqueous solutions than in water
- Many nonaqueous solvents have a wider potential window than water
- Nonaqueous solvents allow for alternative electrolytes and proton donors