Understanding Designer Electrocatalysts for Energy Conversion Reactions: Adsorbed Molecules Can Behave Like Metals

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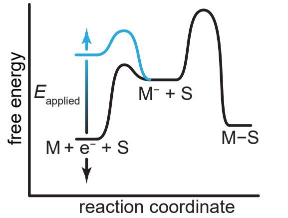
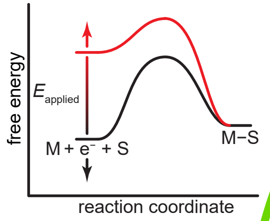
Introduction

A clean energy economy requires electrocatalysis to convert chemical & electrical energy.[1]

Molecular electrocatalysts:
+ Well-defined & tunable structure
− Discrete redox steps limit rates

Metallic electrocatalysts:
− Ill-defined & intractable structure
+ Concerted pathways allow high rates



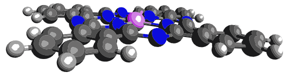


Molecules adsorbed to conductive surfaces have shown uniquely enhanced electrocatalytic rates & selectivities.[2]

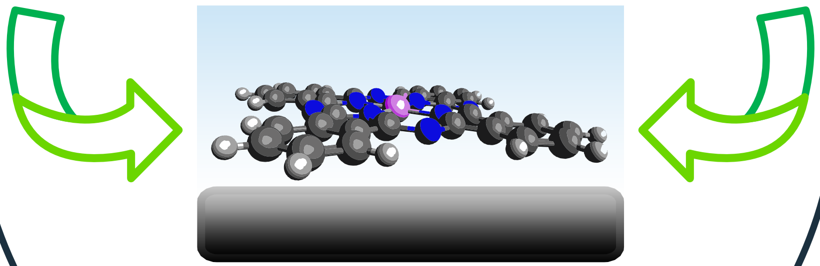
⟶ *What governs electrocatalysis by molecules on surfaces?*

Highlights

Molecules: Tunable Structure



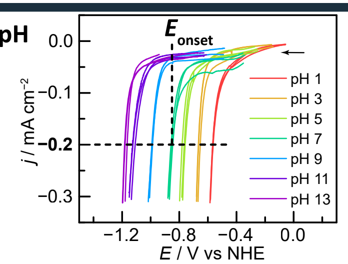
Metals: Robust Reactivity



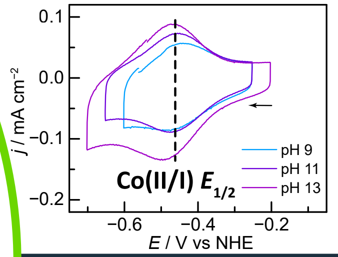
Molecules adsorbed on surfaces can access new reactivity pathways for electrocatalysis, enabling development of more efficient and selective energy conversion reactions.

Results

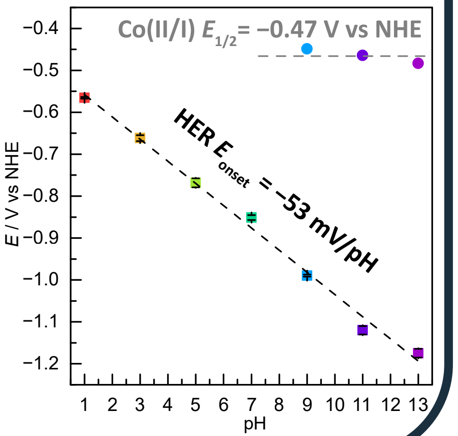
CoPc HER across pH



CoPc Redox Intermediate



CoPc Pourbaix Diagram

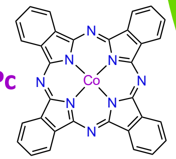


Materials & Methods

Systems under study: multi-component film electrodes

1. Molecular catalyst: cobalt(II) phthalocyanine
2. Conductive surface: carbon black powder
3. Polymeric binder: Nafion™
4. Bulk electrode: glassy carbon

CoPc

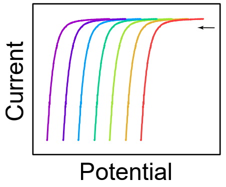


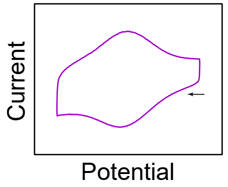
Mechanisms can be differentiated through electrokinetic studies.[3]

Hydrogen Evolution Reaction (HER) Catalysis: $2\ H^+ + 2\ e^- \rightleftharpoons H_2$

"Molecular" mechanism: ✗ ✗

"Metallic" mechanism: ✓ ✓





Uniform shift in HER with pH conditions? Redox intermediate still observed during HER?

Conclusions

Key takeaways from CoPc Pourbaix diagram:

1. Uniform shift in HER onset potentials with pH conditions, close to the theoretical Nernst shift of −59 mV/pH
2. Redox intermediate Co(II/I) signal is still observed at high pH conditions during HER catalysis

⟶ *Inconsistent with traditionally "molecular" mechanisms*

⟶ ***Molecules adsorbed on surfaces can access "metallic" mechanisms***

Continuing work includes further mechanistic studies, expansion to other molecular identities, and elucidation of new structure-function relationships & design principles for these designer electrocatalysts.

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(1) Stamenkovic, V. R. *et al*. Energy and Fuels from Electrochemical Interfaces. *Nat. Mater.* **2017**, *16*, 57. (2) Nam, D.-H. *et al*. Molecular Enhancement of Heterogeneous CO_2 Reduction. *Nat. Mater.* **2020**, *19*, 266. (3) Kaminsky, C. J. *et al*. Adsorbed Cobalt Porphyrins Act like Metal Surfaces in Electrocatalysis. *Nat. Catal.* **2022**, *5*, 430.