

Chapter II: Molecular catalysis for the hydrogen evolution reaction

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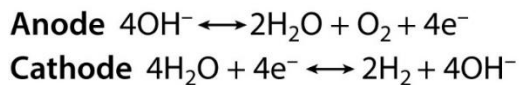
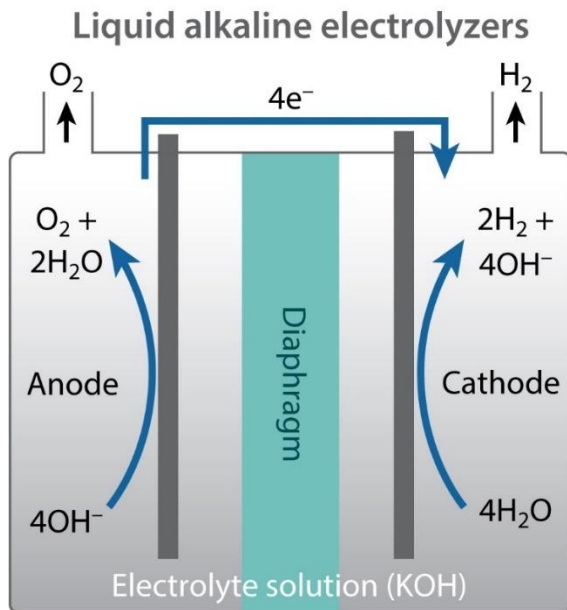
Case 3: A bio-inspired catalyst

I. What is the hydrogen evolution reaction

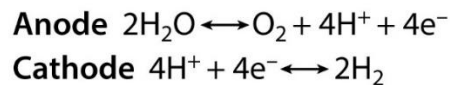
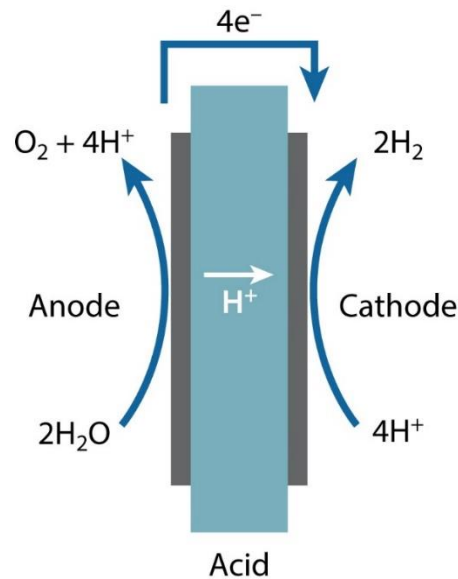
The principle of electrolyzers is the same: water splitting reaction



a Commercial technologies

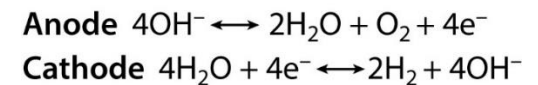
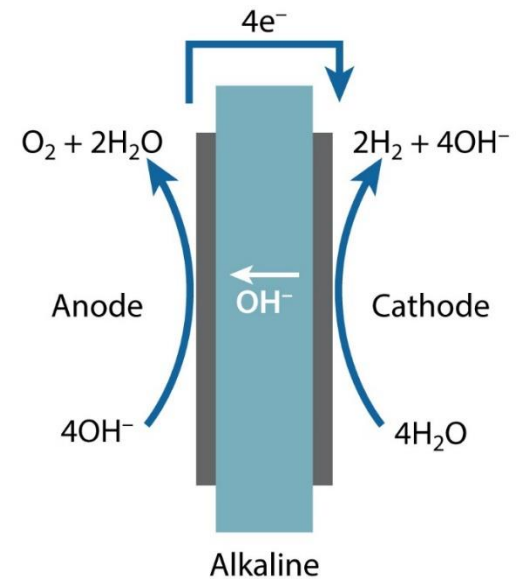


PEM electrolyzers



b Emerging technology

AEM electrolyzers



Water Splitting is an Electrochemical Reaction

In water splitting, two separate electrochemical half reactions are occurring.

Overall reaction: $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 2 \text{H}_2$

At the cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ Hydrogen evolution reaction (HER)

At the anode: $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ Oxygen evolution reaction (OER)

The two half reactions can be treated separated; they occur at different electrodes

Catalysis for Hydrogen Evolution



$$E^\circ \sim 0 \text{ V vs. RHE}$$

hydrogen evolution reaction



$$E^\circ \sim -2.3 \text{ V vs. RHE}$$

overpotential of at least 2.3 V



$$E^\circ \sim -1.4 \text{ V vs. RHE}$$

overpotential of at least 1.4 V

To make H_2 from H^+ , one needs to make H-H bond.
Going through intermediates such as H^- or H^\bullet will require a large overpotential.
To decrease the overpotential, a catalyst is needed.

Overpotential and energy efficiency

In electrochemistry, the potential is always measured against a reference electrode.

Overpotential is the potential difference between a given potential under discussion and the thermodynamic potential for a reversible reaction.

$$\eta = E(\text{working}) - E(\text{reversible})$$

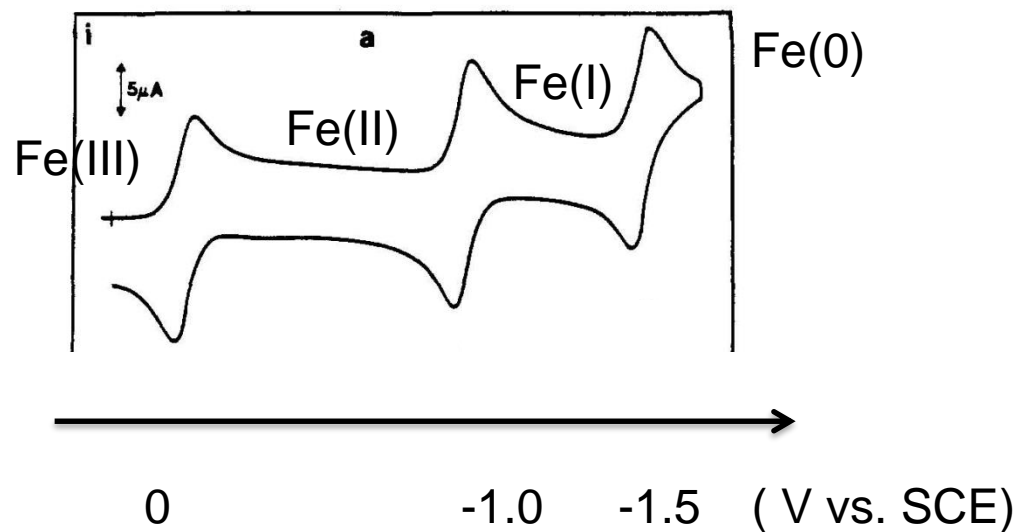
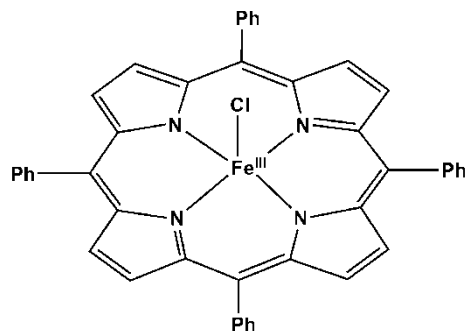
In some literature, η is taken as an absolute value.

Overpotential can be considered as an «energy penalty» to make the reaction happen.

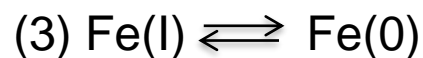
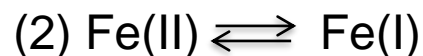
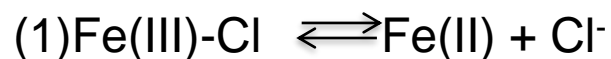
II. Mechanistic understanding exemplified by case studies

**Case 1: A classic catalyst:
a Fe-porphyrin complex
as HER catalyst**

Electrochemistry of a Fe Porphyrin Complexes

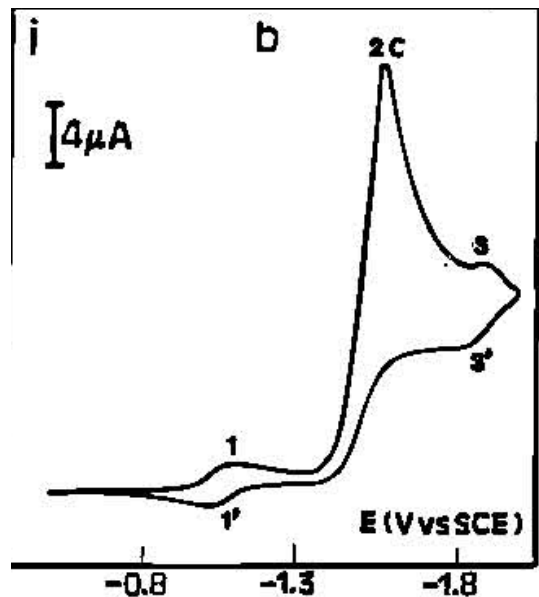


Three processes:



Cyclic votammetry in DMF

When 7 mM $[\text{Et}_3\text{NH}]\text{Cl}$ was added to a DMF solution containing 0.6 mM of the iron porphyrin complex, the cyclic voltammetry shows:

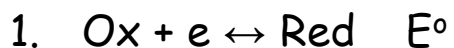


Peak 1 is the same feature as the redox peak for $\text{Fe(II)} \rightleftharpoons \text{Fe(I)}$ in the last slide

Peak 2 is at the same position as the redox peak for $\text{Fe(I)} \rightleftharpoons \text{Fe(0)}$ in the last slide, but the shape changed dramatically

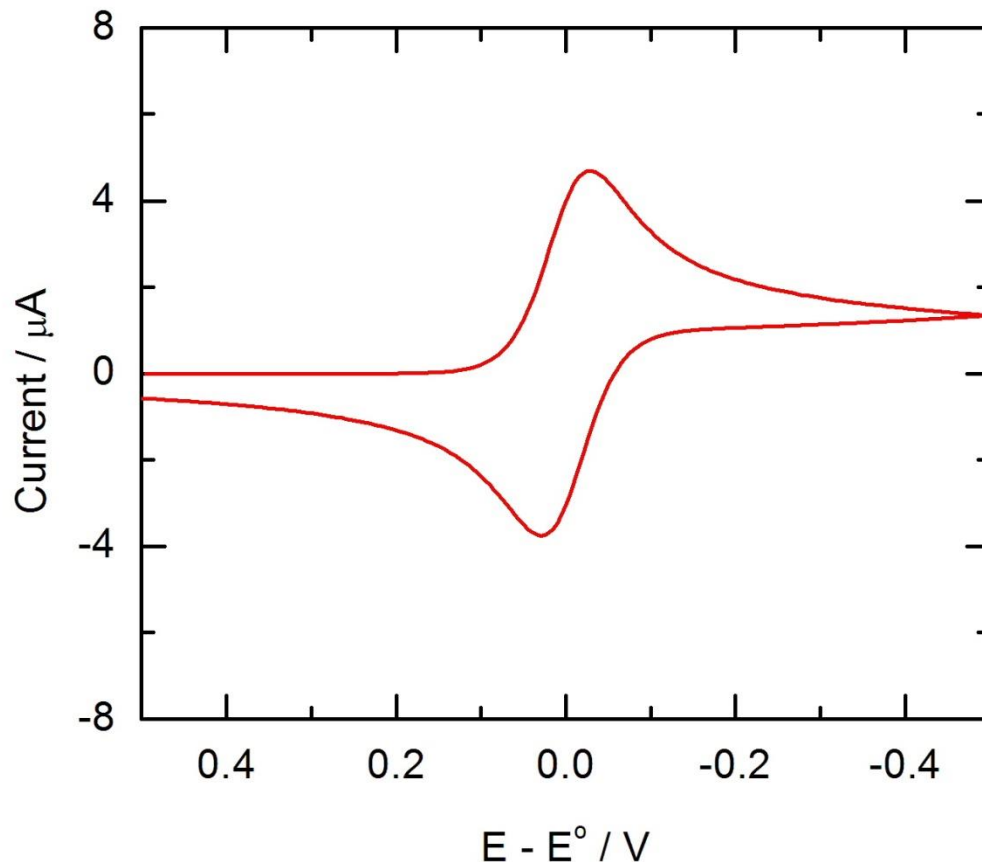
Peak 3 is a new peak

Electron Transfer:



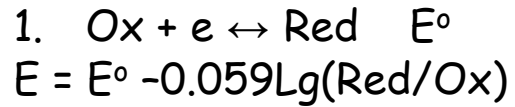
$$E = E^\circ - 0.059 \lg(\text{Red}/\text{Ox})$$

A molecule in solution undergoes a reversible electron transfer reaction. The cyclic voltammetric response is shown below. Nerst equation applies.

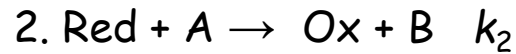


Cyclic Voltammogram for the reduction and re-oxidation of a redox species in solution.

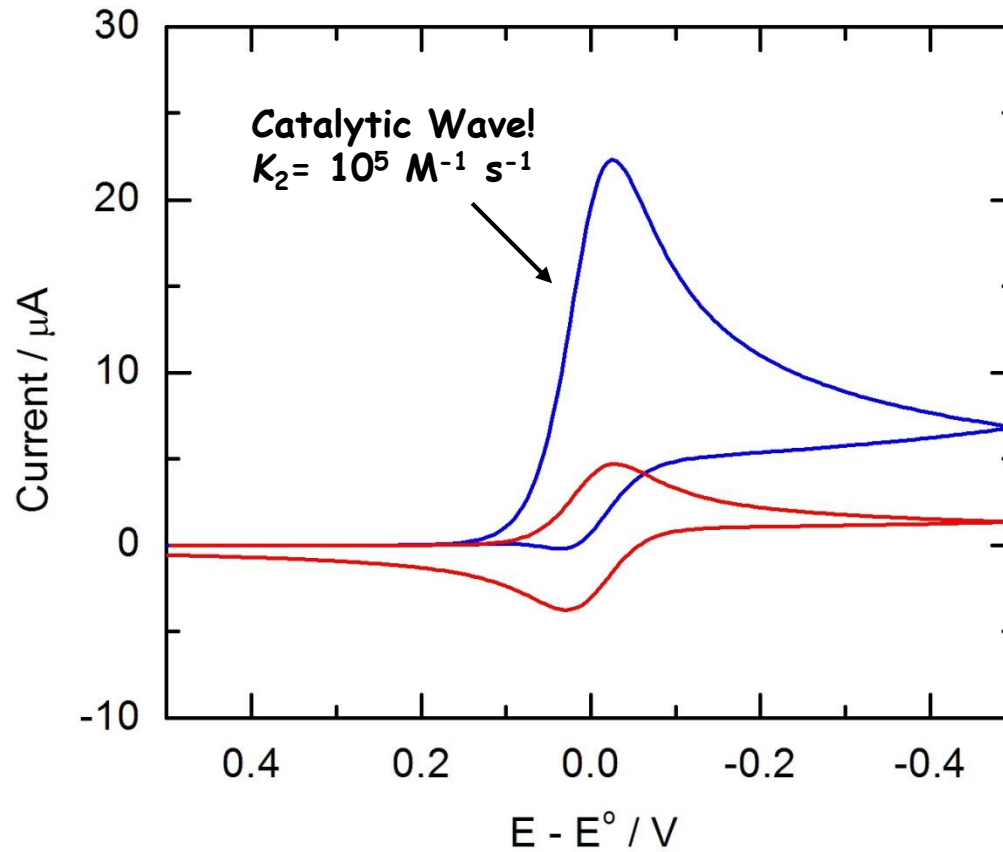
Electron Transfer:



Chemical Reaction:

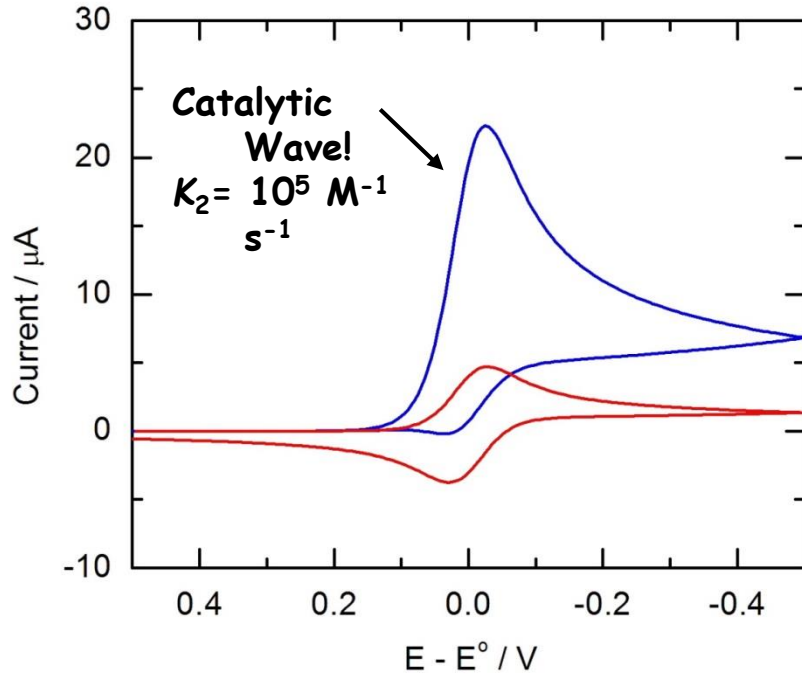


Electrocatalysis



Cyclic Voltammogram for a Electrocatalytic reaction in solution.

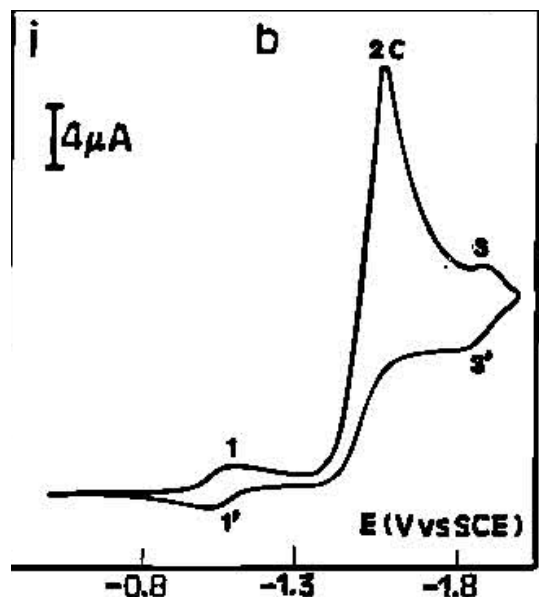
Analysis of molecular electrocatalysis:



- (1) Catalysis starts only near $E = E^\circ$.
Therefore, the minimum overpotential is dictated by the redox chemistry of the molecular catalyst. This means that the minimum overpotential can be changed by changing the catalyst.
- (2) The current rises to a peak near $E = E^\circ$; beyond that point, the current falls due to the limitation of diffusion of redox active species to the electrode. The peak current reflects the rate of catalysis, and is a property of the molecular catalyst.

(3) Increasing overpotential beyond the peak current does not increase the current.

When 7 mM [Et₃NH]Cl was added to a DMF solution containing 0.6 mM of the iron porphyrin complex, the cyclic voltammetry shows:

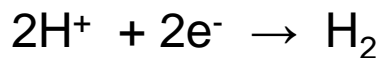


Peak 2c is a catalytic wave resulting from the formation of Fe(0).

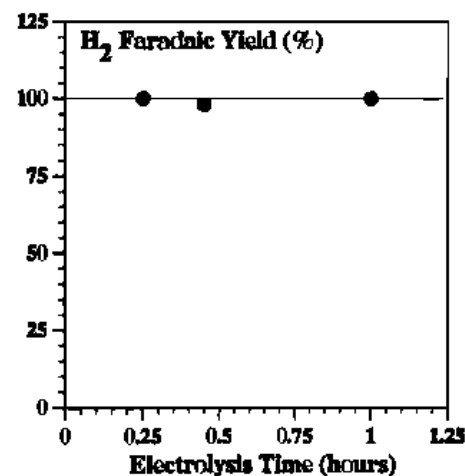
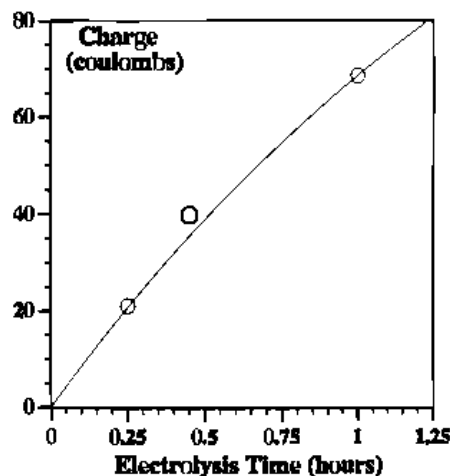
When the potential of the solution is fixed at -1.6 V for an hour (this is called electrolysis), the following took place: (1) A certain amount of charge was passed; (2) H₂ was produced in a nearly 100% Faradaic yield.

Faradaic yield:
The yield of product
versus the amount of
electric charge passed.

For HER,

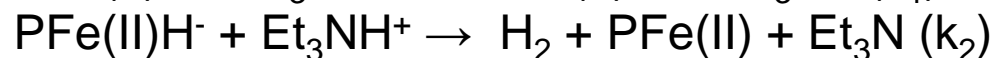
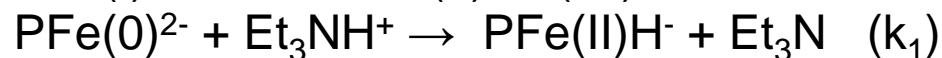
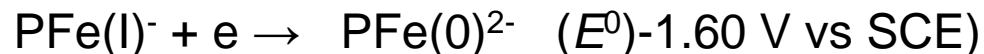
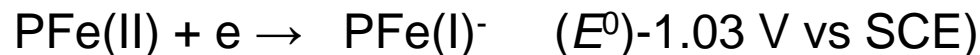


1 H₂ is made from 2 electrons if the Faradaic yield is 100%.

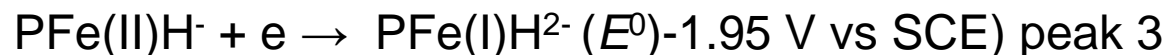


How about the mechanism of this catalysis?

The following can be proposed based on electrochemical data:

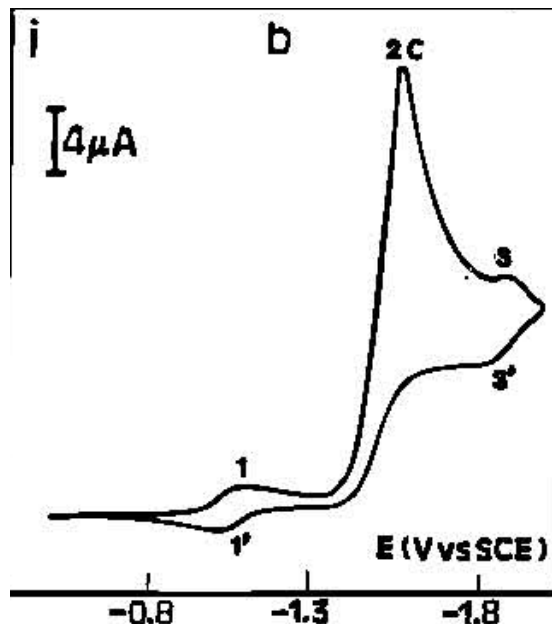


Other relevant reaction:



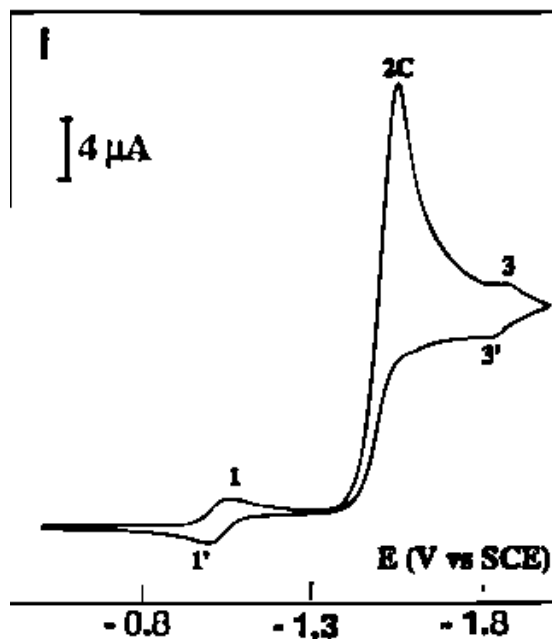
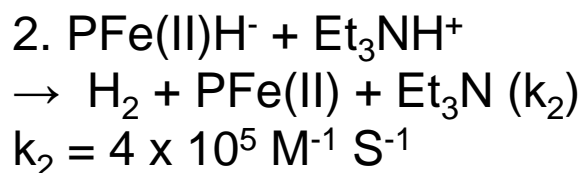
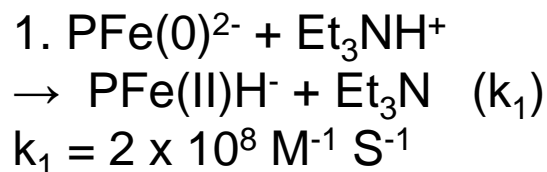
This proposed mechanism can be used to simulate the cyclic voltammety data.

Top: experimental data



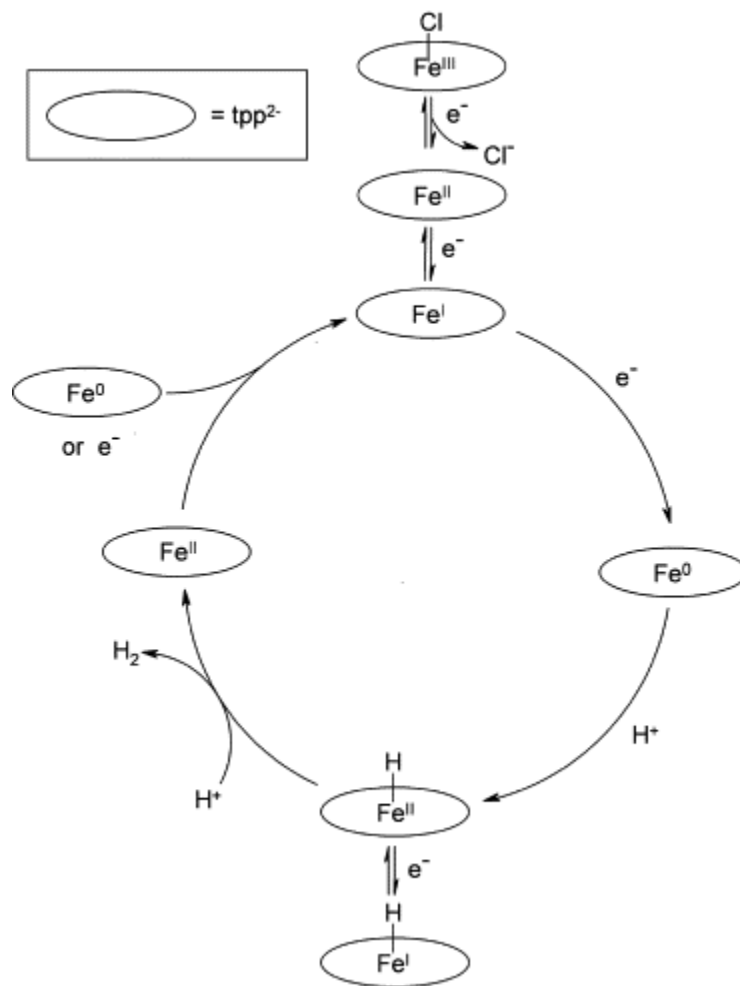
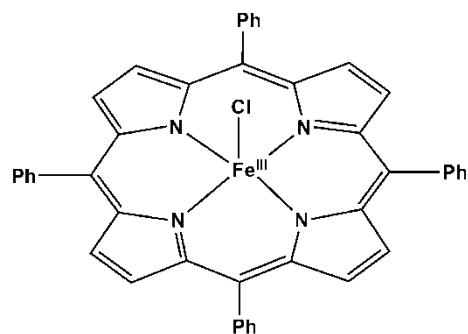
Top: simulation data

According to simulation,

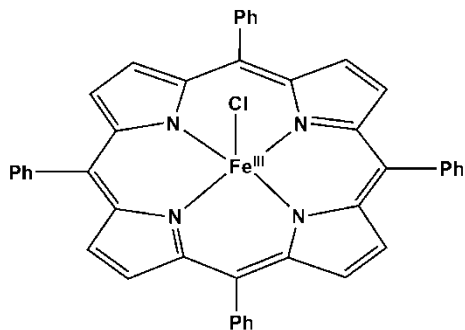


H₂ Evolution by Fe(0) Porphyrin Complexes

An overall mechanism can be established:

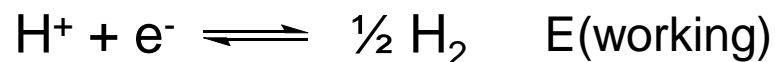
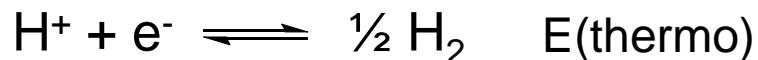


Analysis of this catalytic system



What is the overpotential of this system?

Overpotential for HER in water



$$\text{Overpotential} = E(\text{work}) - E(\text{thermo})$$

$E(\text{thermo})$ is also called the reversible potential for a given reaction. It is a thermodynamic quantity related to the equilibrium state; at this potential, the forward and backward reaction rates are equal.

$E(\text{thermo})$ depends on the concentration of the reactive species. For HER:

$$\text{In water, } E^{\circ'} (\text{H}^+/\text{H}_2) = E^{\circ} - (2.303RT/F)\text{pH} = E^{\circ} - 0.059\text{pH}$$

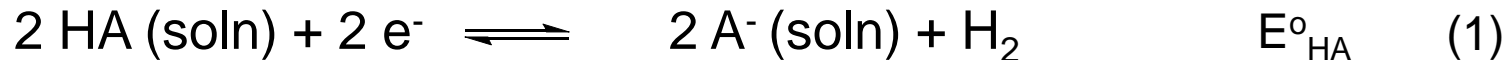
E° is a constant relative to a reference potential. For example, it is 0 V vs. Standard Hydrogen Potential (SHE), also called NHE.

It is therefore easy to know the $E(\text{thermo})$ for HER in water; we just need to know the pH. The $E(\text{thermo})$ is identical to RHE.

Once $E(\text{thermo})$ is known, it is also easy to calculate overpotential by applying the definition above.

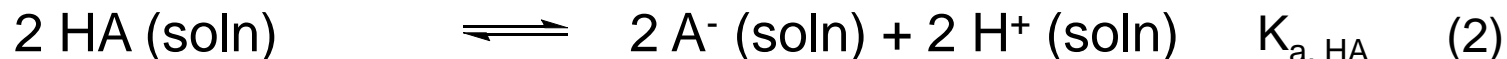
Overpotential in organic solvent

In non-aqueous solvent, for an acid HA, HER is:



This reaction is made of 2 components:

(a): ionization of acid:



(b): reduction of solvated proton:



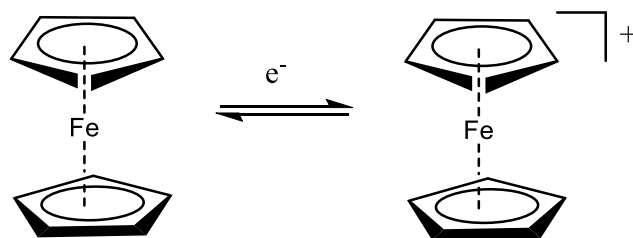
The thermodynamic potential of HER is then dependent on both the standard potential of proton reduction and the pKa of acid:

$$E_{\text{HA}}^{\circ} = E_{\text{H}^+}^{\circ} - (2.303RT/F)\text{pK}_{\text{a, HA}} = E_{\text{H}^+}^{\circ} - 0.059\text{pK}_{\text{a}} \quad (4)$$

The $E_{\text{H}^+}^{\circ}$ is a property of solvent, and it is different from NHE in water. For a given solvent, $E_{\text{H}^+}^{\circ}$ might be determined by some special experimental techniques.

Overpotential in organic solvent

In organic solvent, IUPAC (international union of pure and applied chemistry) recommends using ferrocene/ferrocenium (Fc/Fc^+) couple as the reference potential because it is constant in a given solvent.



$E^\circ_{\text{H}^+}$ has been determined in several solvents vs Fc/Fc^+ :
nitromethane (-0.080), acetonitrile (-0.260), dimethoxyethane (-0.400),
tetrahydrofuran (-0.440), *N,N*-dimethylformamide, DMF (-0.770), dimethyl
sulfoxide (-0.830), and pyridine (-1.020).

Read a paper about overpotentials in organic solvents for molecular catalysis

Table 1. pK_a (Acid Dissociation Constants) and Thermodynamic Potentials for the HER for a Few Acids in Acetonitrile and *N,N*-Dimethylformamide

acid	acetonitrile		<i>N,N</i> -dimethylformamide	
	pK _a	<i>E</i> _{HA}	pK _a	<i>E</i> _{HA}
perchloric acid	2.1	-0.26	dissociated	-0.77
trifluoromethanesulfonic acid	2.6	-0.29	dissociated	-0.77
<i>p</i> -toluenesulfonic acid	8.7	-0.65	2.6	-0.92
methanesulfonic acid	10.0	-0.73	3.0	-0.95
trichloroacetic acid	10.6	-0.77	3.5	-0.98
anilinium	10.7	-0.77	3.7	-0.99
pyridinium	12.3	-0.87	3.3	-0.96
dichloroacetic acid	13.2	-0.92	7.2	-1.20
chloroacetic acid	15.3	-1.05	10.0	-1.36
2,6-dinitrophenol	16.5	-1.12	6.1	-1.13
<i>p</i> -nitrobenzoic acid	18.5	-1.23	10.6	-1.40
triethylammonium	18.7	-1.25	9.2	-1.31
benzoic acid	20.7	-1.36	12.2	-1.49
<i>p</i> -nitrophenol	20.7	-1.36	12.2	-1.49
acetic acid	22.3	-1.46	13.2	-1.55
phenol	27.2	-1.75	>18	<-1.83
4- <i>tert</i> -butylphenol	27.5	-1.77	unavailable	

Exercise: calculate the overpotential in the Fe-porphyrin system

Recall experimental conditions:

In DMF; $[\text{Et}_3\text{NH}]\text{Cl}$ as acid; Working potential at -1.6 V vs. SCE

As $\text{Fc}/\text{Fc}^+ = 0.47 \text{ vs. SCE}$ in DMF

$E(\text{working}) = -1.6 \text{ vs. SCE} = -2.07 \text{ V vs. Fc}/\text{Fc}^+$

Calculate the overpotential of the system

Exercise: Analysis of a catalyst (see separate file online posted after class)

Case 2: A low-overpotential catalyst: Co complexes as HER catalysts

Well deserved nomination



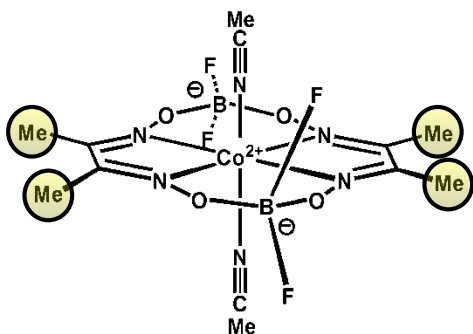
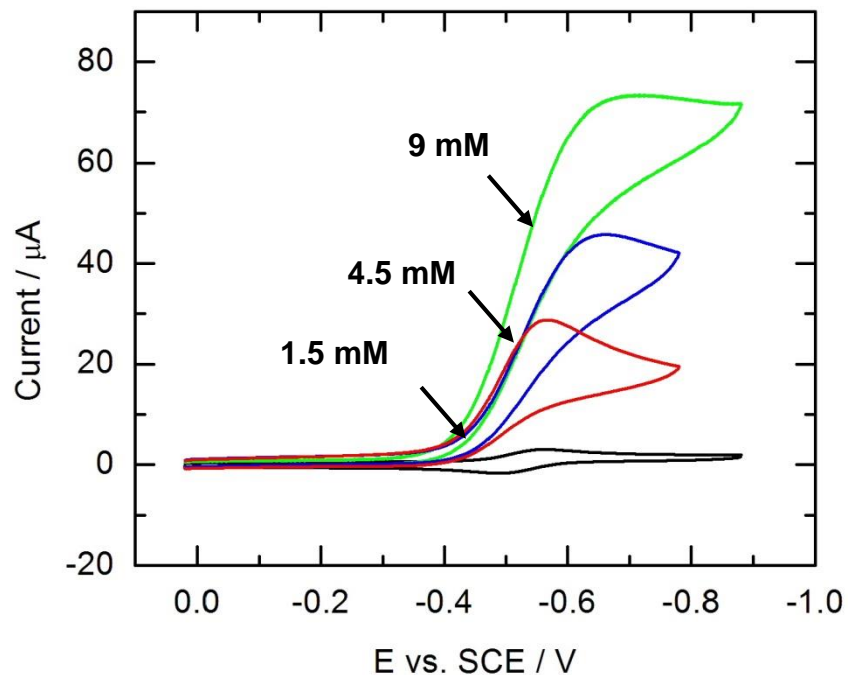
Prof. talking about

His own work

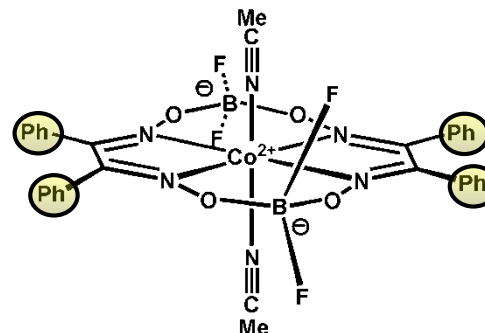
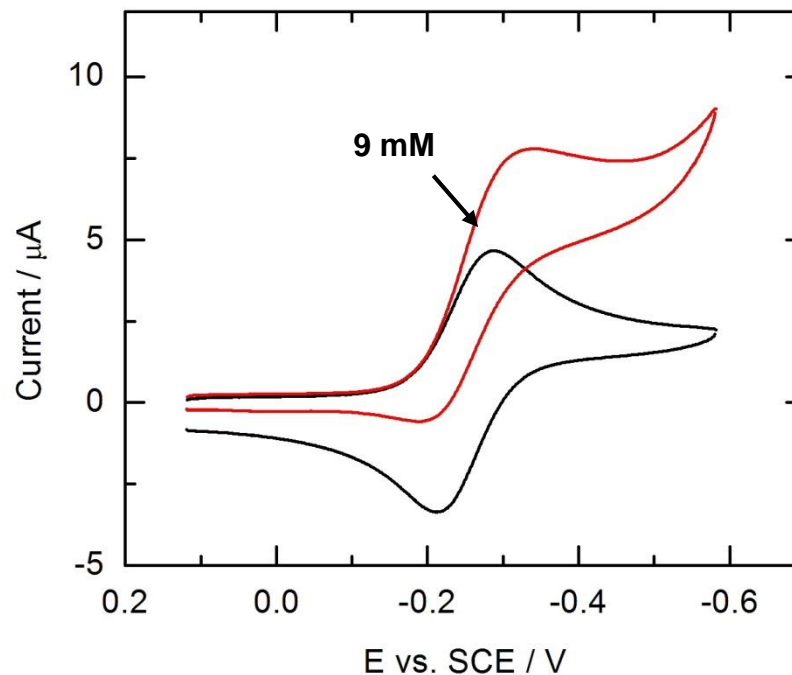
Two catalysts with similar structures

TsOH·H₂O in CH₃CN, pK_a = 8

0.3 mM catalyst Co(dmgbF₂)₂

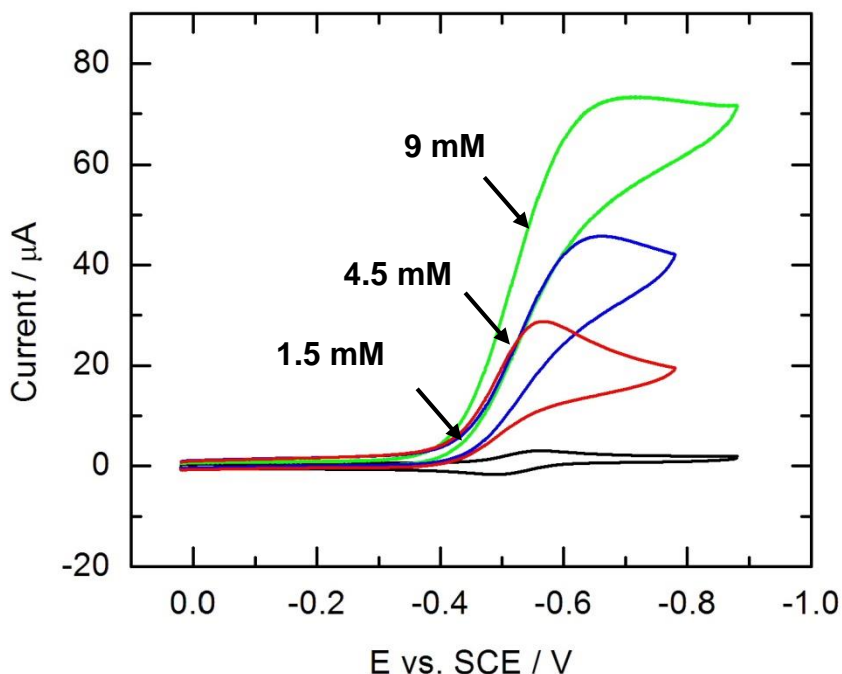


0.3 mM catalyst Co(dpgBF₂)₂

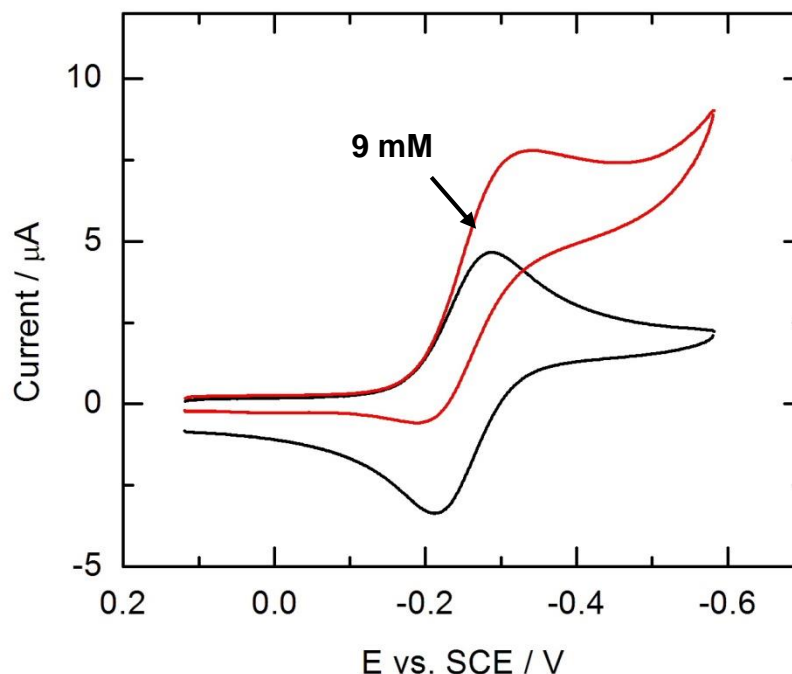


Comparison of catalysts

0.3 mM catalyst $\text{Co}(\text{dmgBF}_2)_2$



0.3 mM catalyst $\text{Co}(\text{dpgBF}_2)_2$



Under same conditions (same acid), a potential point in the left graph represents a same overpotential as its counter point in the right graph. That is, -0.4 V at left has the same overpotential as -0.4 V at right.

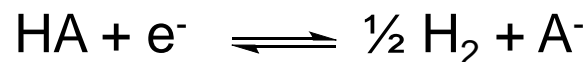
Overpotential at which catalysis occurs is different for different catalyst.

$\text{Co}(\text{dpgBF}_2)_2$ has a smaller overpotential for HER than $\text{Co}(\text{dmgBF}_2)_2$.

The catalytic current by $\text{Co}(\text{dpgBF}_2)_2$ is smaller than that by $\text{Co}(\text{dmgBF}_2)_2$.

We see a compromise of overpotential and reaction rate. When overpotential is smaller, the reaction is slower. This is typical for molecular catalysis.

Hydrogen Evolution at Low Overpotentials

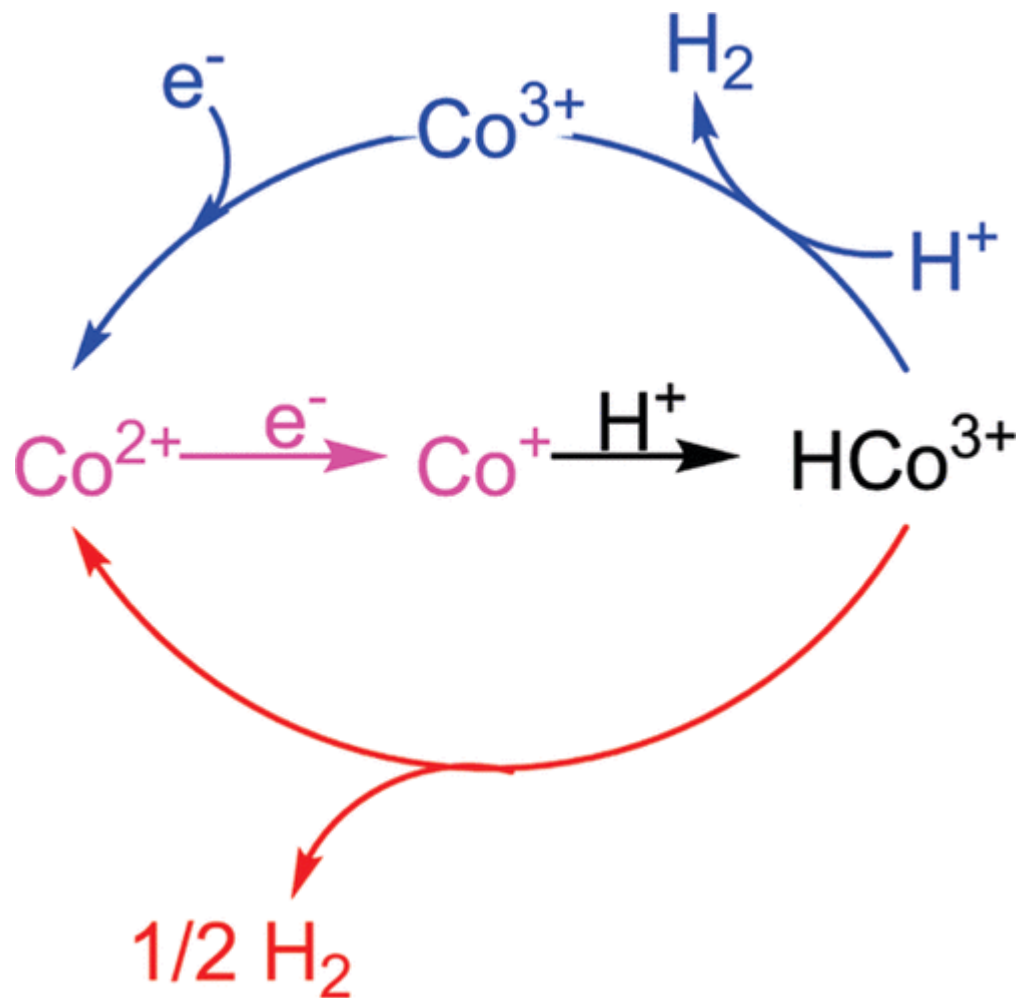


Proton Source	Thermodynamic potential for H_2/H^+ in CH_3CN (V vs. SCE)	Starting E for HER in CH_3CN (V vs. SCE)	Overpotential (mV)
CF_3COOH	-0.51	-0.55 (Co(dmgbF₂)₂)	40
$\text{TsOH} \cdot \text{H}_2\text{O}$	-0.23	-0.30 (Co(dpgBF₂)₂)	70

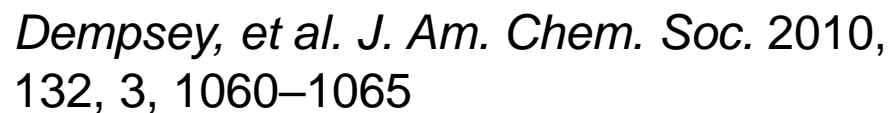
SCE is widely used in the literature as a reference potential. In CH_3CN , Fc/Fc^+ is 0.38 V vs. SCE.

It is demonstrated that a molecular catalyst for HER at a low overpotential is possible. The TOFs of these catalysts are not yet accurately determined. It is likely in the order of 10-100 for $\text{Co}(\text{dmgbF}_2)_2$ with CF_3COOH .

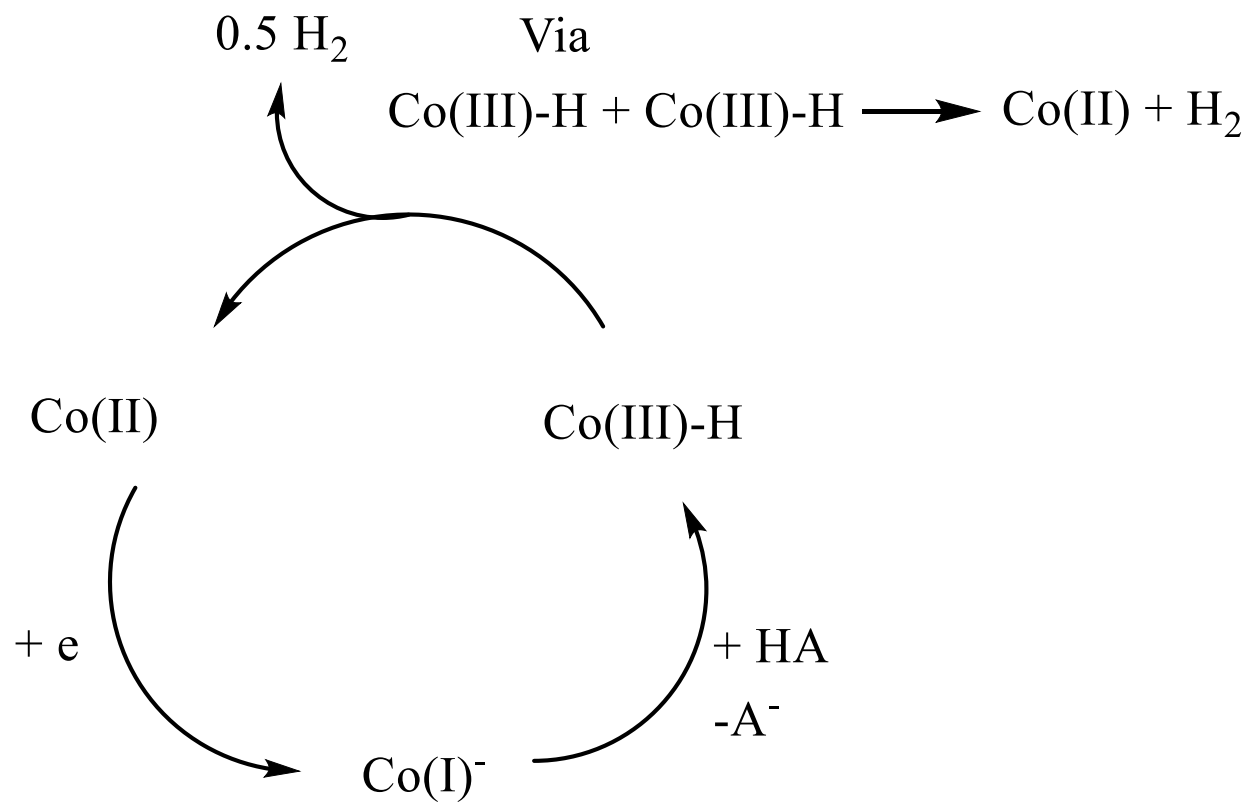
Two mechanistic possibilities



D is an electron donor, equivalent to e^-



The favored mechanism



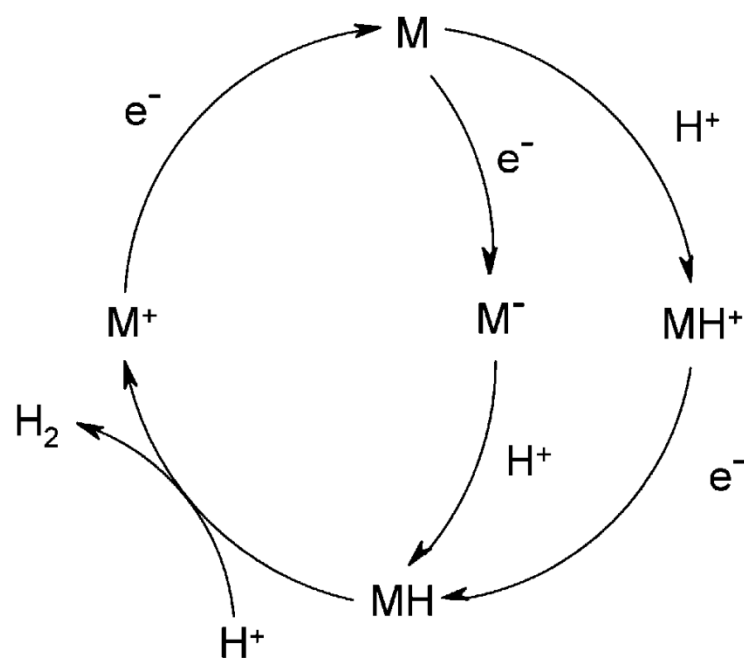
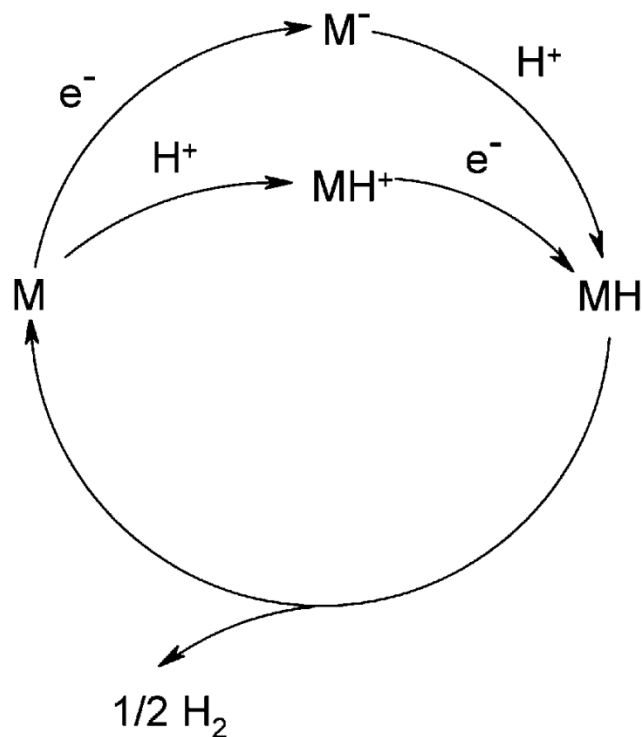
Exercise: Analysis of a catalyst (see separate file online posted after class)

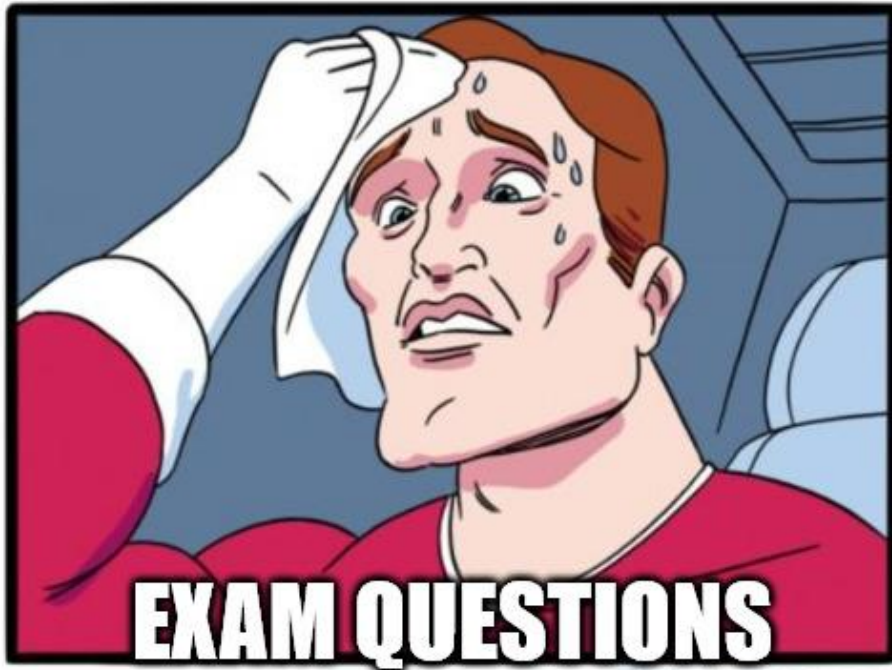
General mechanism for HER catalyzed by molecular complexes

M represents ML_n

Bimetallic H_2 formation: $MH + MH \rightarrow 2M + H_2$

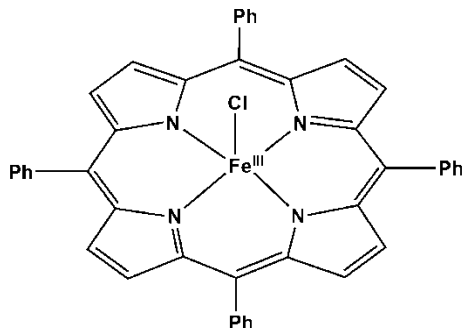
Monometallic H_2 formation: $MH + H^+ \rightarrow M^+ + H_2$





Case 3: A bio-inspired catalyst: nickel complexes for HER

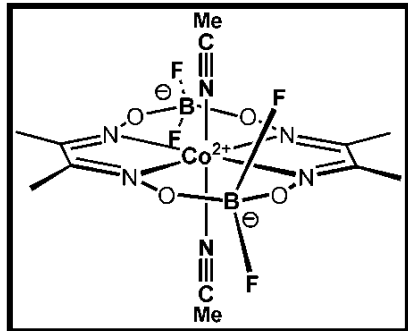
Typically lowering overpotentials of a system will lead to lower TOF.
Can we lower overpotentials while keeping a high TOF?



Overpotential = 0.76 V

$$k_2 = 4 \times 10^5 \text{ M}^{-1} \text{ S}^{-1}$$

$$\text{TOF} = k[\text{H}]^+, \text{ TOF (max)} = 4 \times 10^5 \text{ s}^{-1}$$



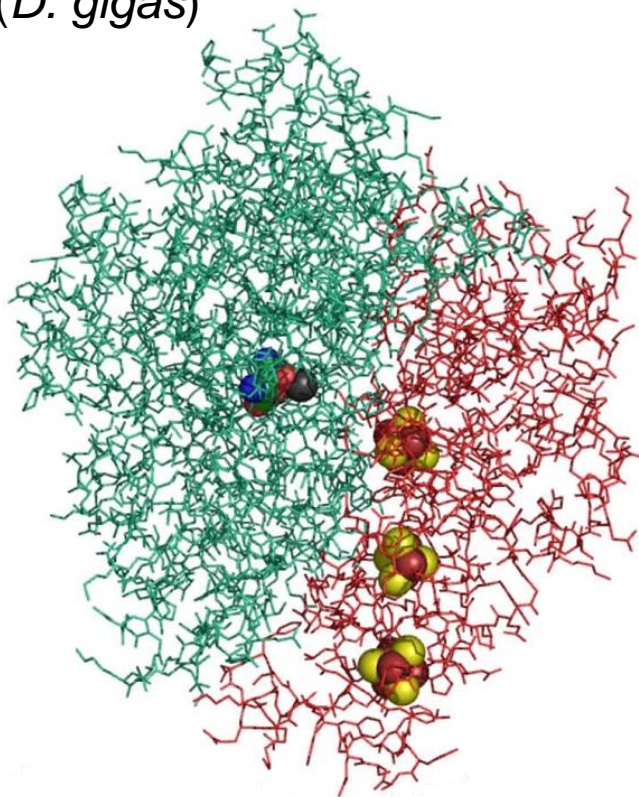
Overpotential = 0.04 V

$$\text{TOF (max)} = \text{about } 100 \text{ s}^{-1}$$

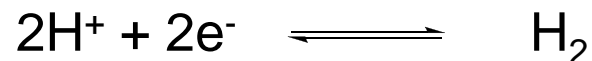
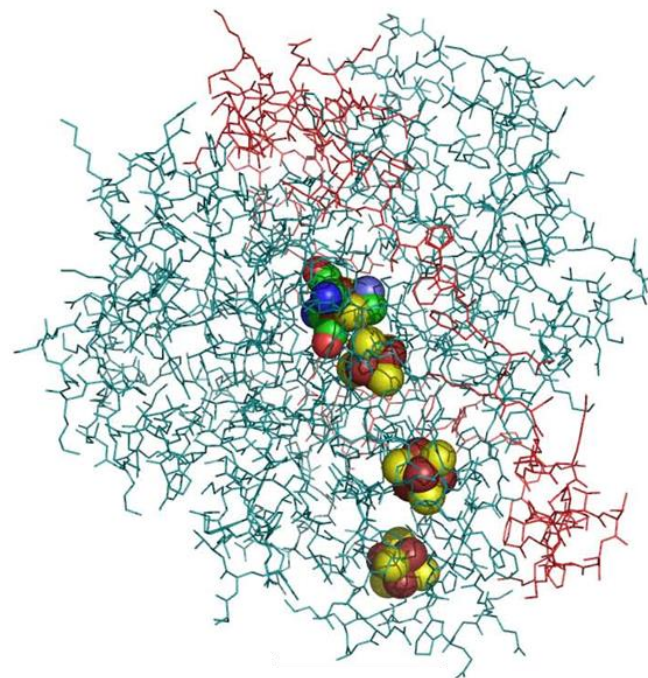
Try Biology!

Hydrogenases Are Active H₂ Evolution Catalysts

[NiFe]-hydrogenase
(*D. gigas*)



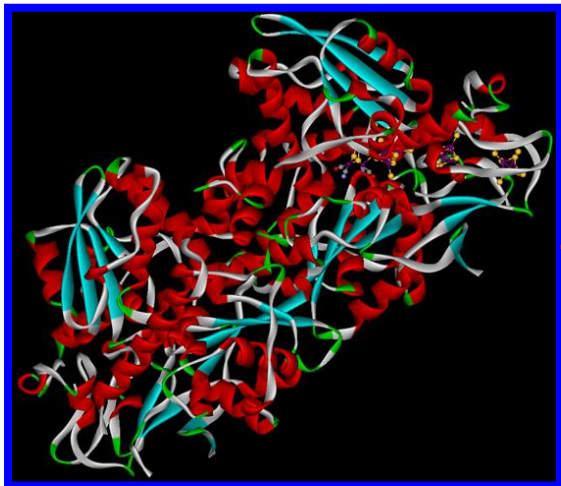
[FeFe]-hydrogenase
(*D. desulfuricans*)



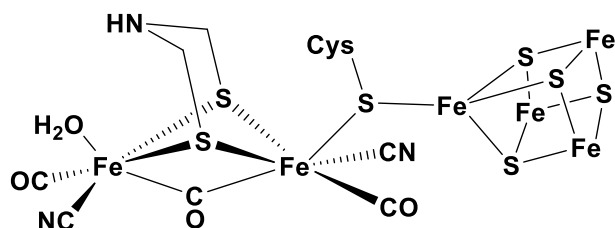
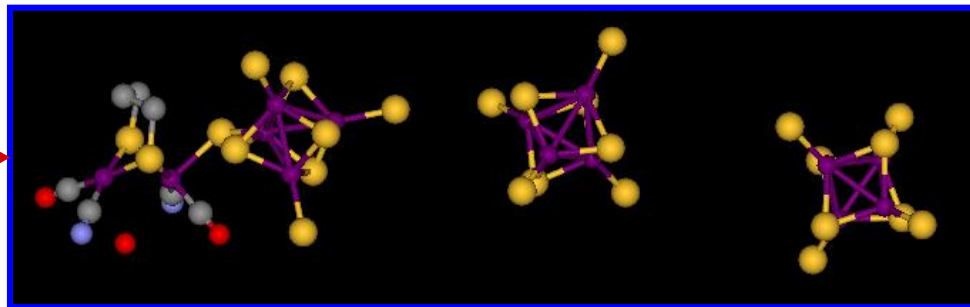
Activity: TOF= **700 - 9000** s⁻¹ at $\eta < 50$ mV

Molecular weight: **50,000 - 90,000**

The biomimetic approach



[FeFe]-hydrogenase

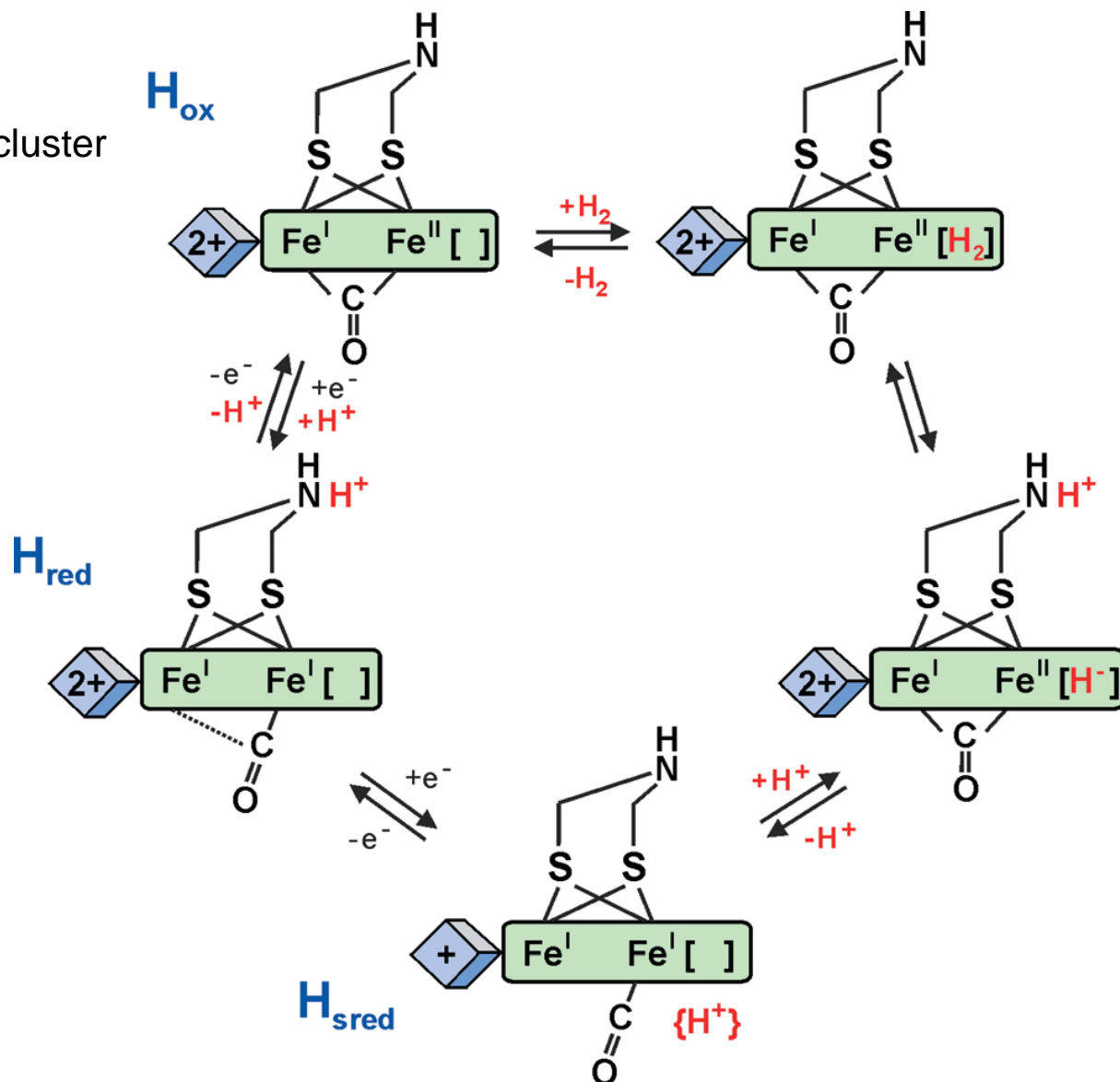


Active site

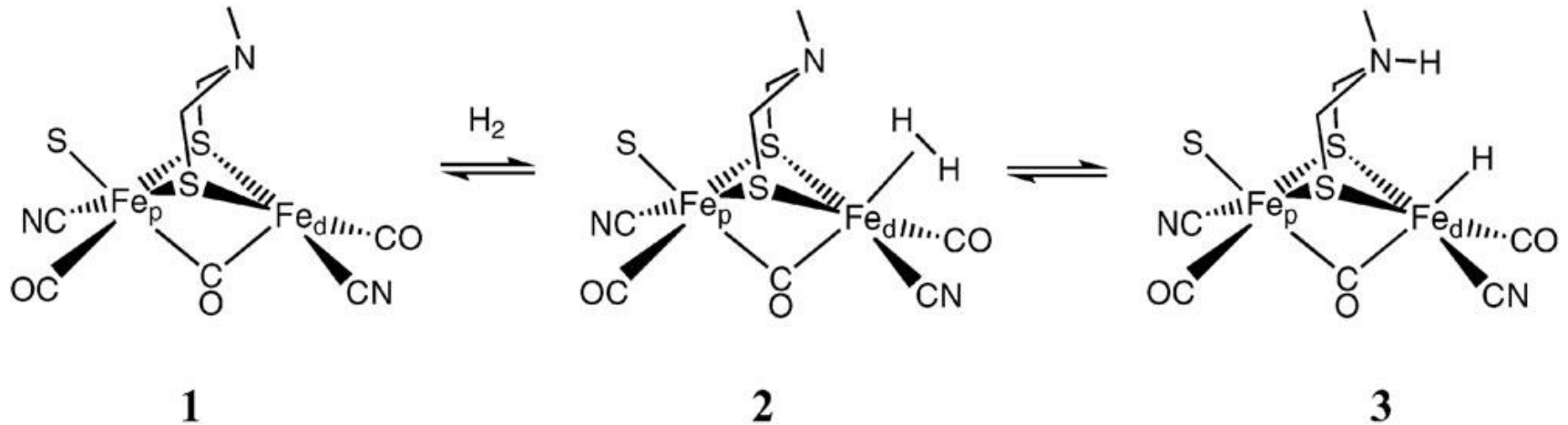
Over the years, many coordination complexes similar to the active site of hydrogenases have been prepared. These complexes are not as active as the enzymes, suggesting that the protein environment has an important role for catalysis.

Proposed catalytic cycle for HER by [FeFe]-hydrogenase

Blue box : Fe-S cluster

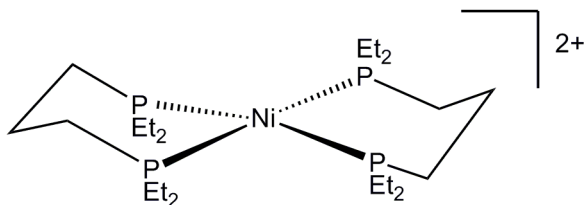


A special thing about the enzyme: The nitrogen atom is important to accept the proton

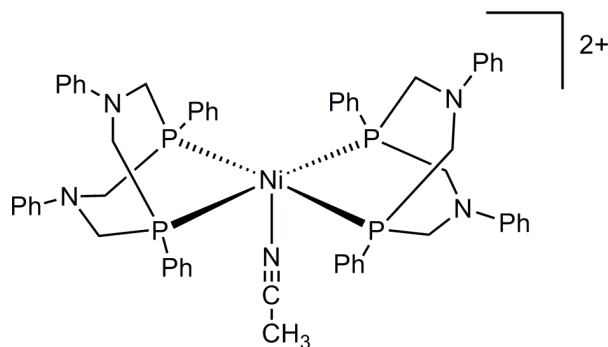


The intramolecular combination of proton and hydride might contribute to a superior catalytic activity, since intramolecular reactions often require less activation energy.

One might not use the same ligands and metals as Nature;
But one can use the same principle.



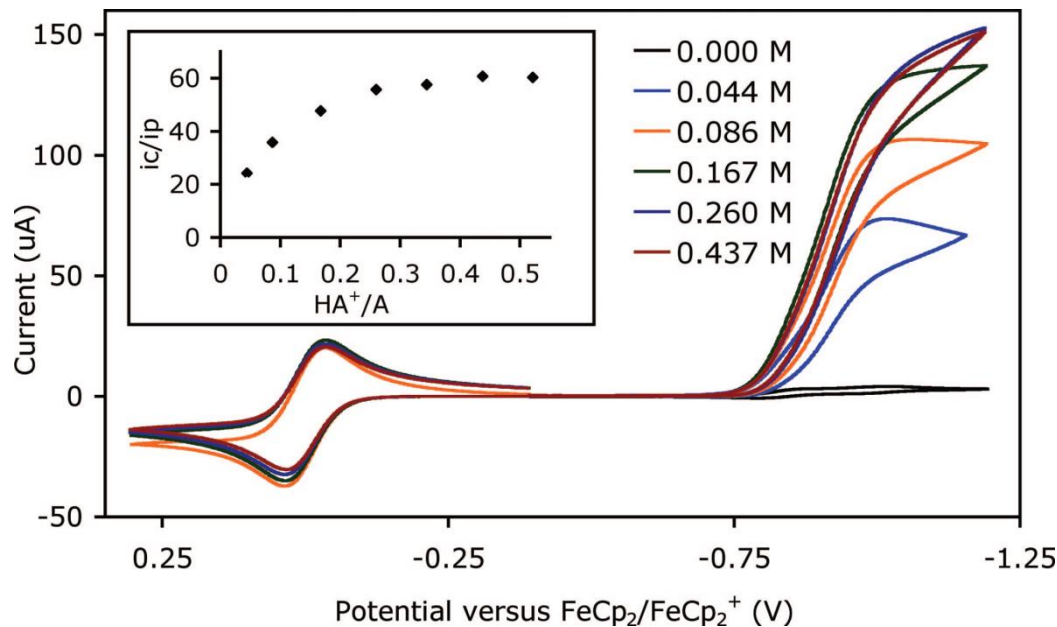
Not a catalyst



Catalyst

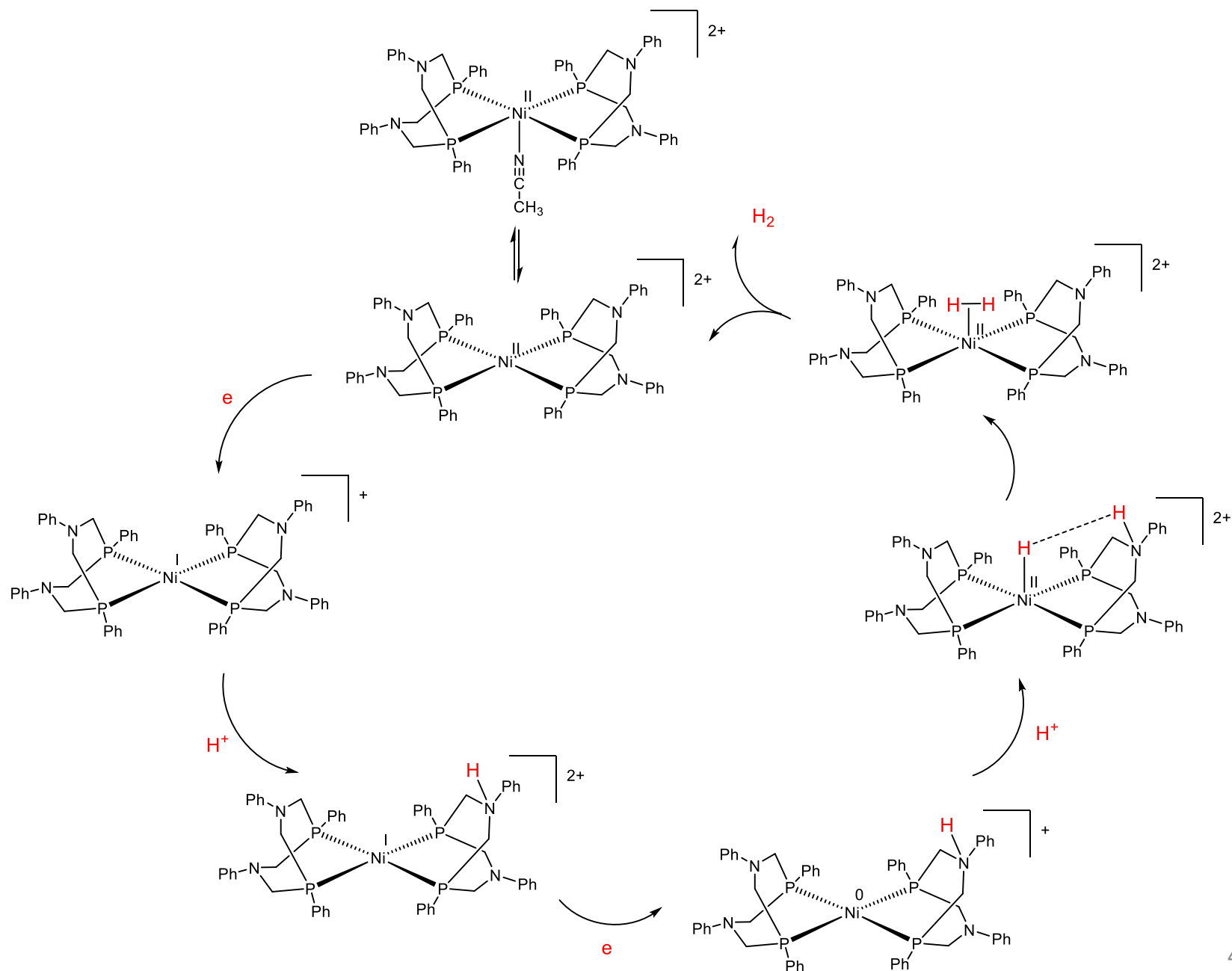


Catalyst (0.3 mM) in CH_3CN ;
Acid was protonated DMF (DMFH^+) (pka = 6.1).

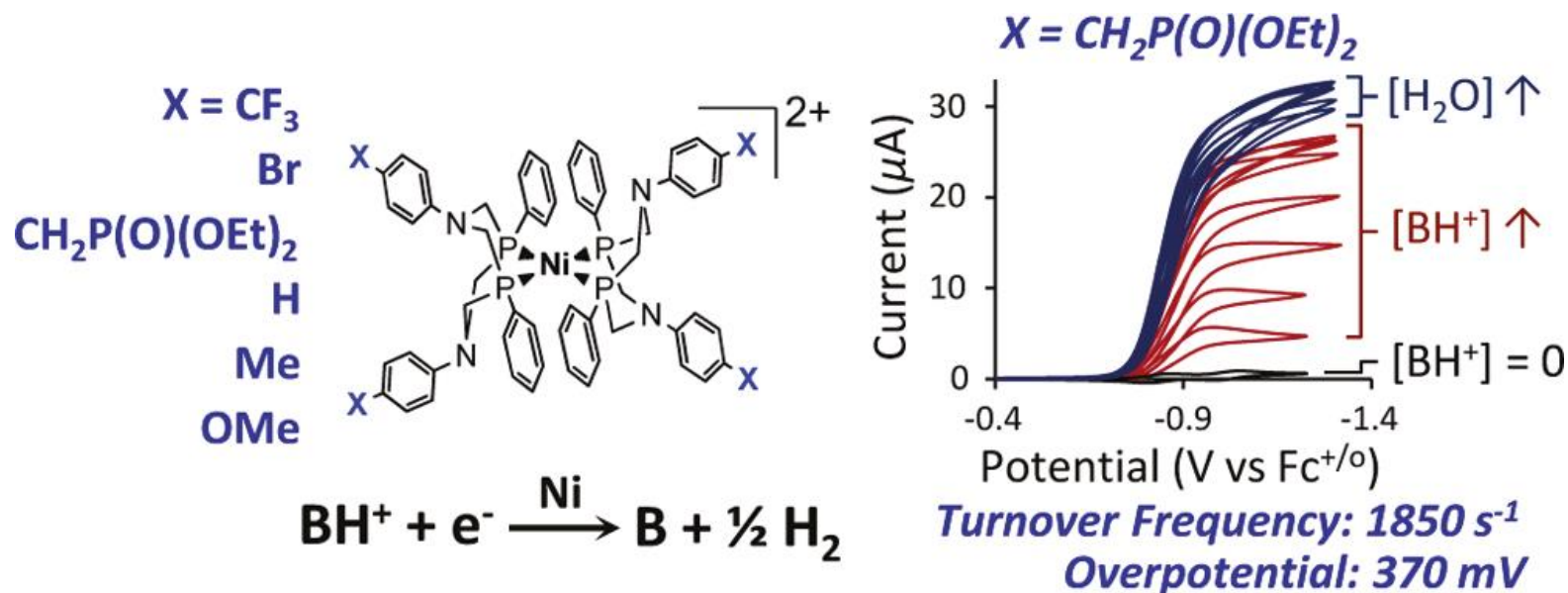


Catalytic wave observed at Ni(II)/Ni(I) couple; potential = -0.9 V vs. Fc/Fc^+ ; overpotential 280 mV; TOF = 350 s^{-1} . Current saturated at 0.3 M of acid.

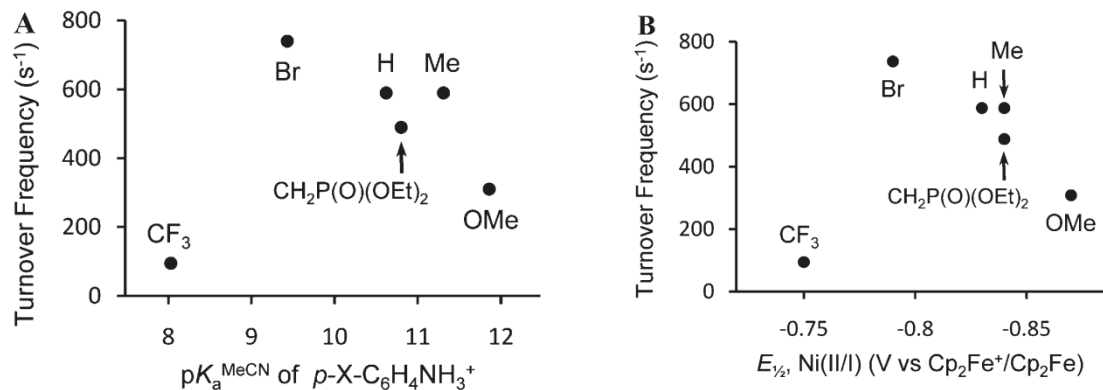
Mechanism of HER involving pendant amine as proton relay:



The substituents on phosphorus and nitrogen can be varied to turn the overpotential and turnover frequencies of the system.



For example, among these 6 catalysts, the following relations were determined:



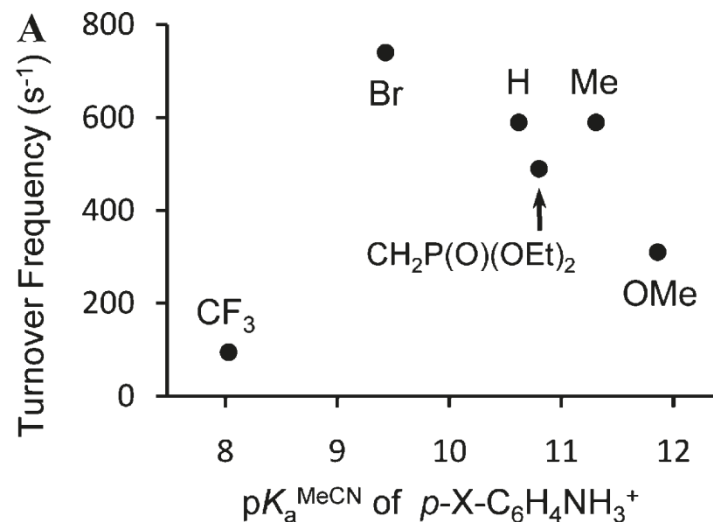


Figure 10 is a scatter plot showing the relationship between the turnover frequency (s⁻¹) on the y-axis and the half-wave potential ($E_{1/2}$, V vs $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$) on the x-axis. The y-axis ranges from 0 to 800 s⁻¹ with major ticks every 200 units. The x-axis ranges from -0.75 to -0.85 V with major ticks every 0.05 V. Data points are represented by black dots and labeled with their respective ligands: CF_3 , Br, $\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, H, Me, and OMe. Arrows indicate the transition from H to Me and from $\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$ to Me.

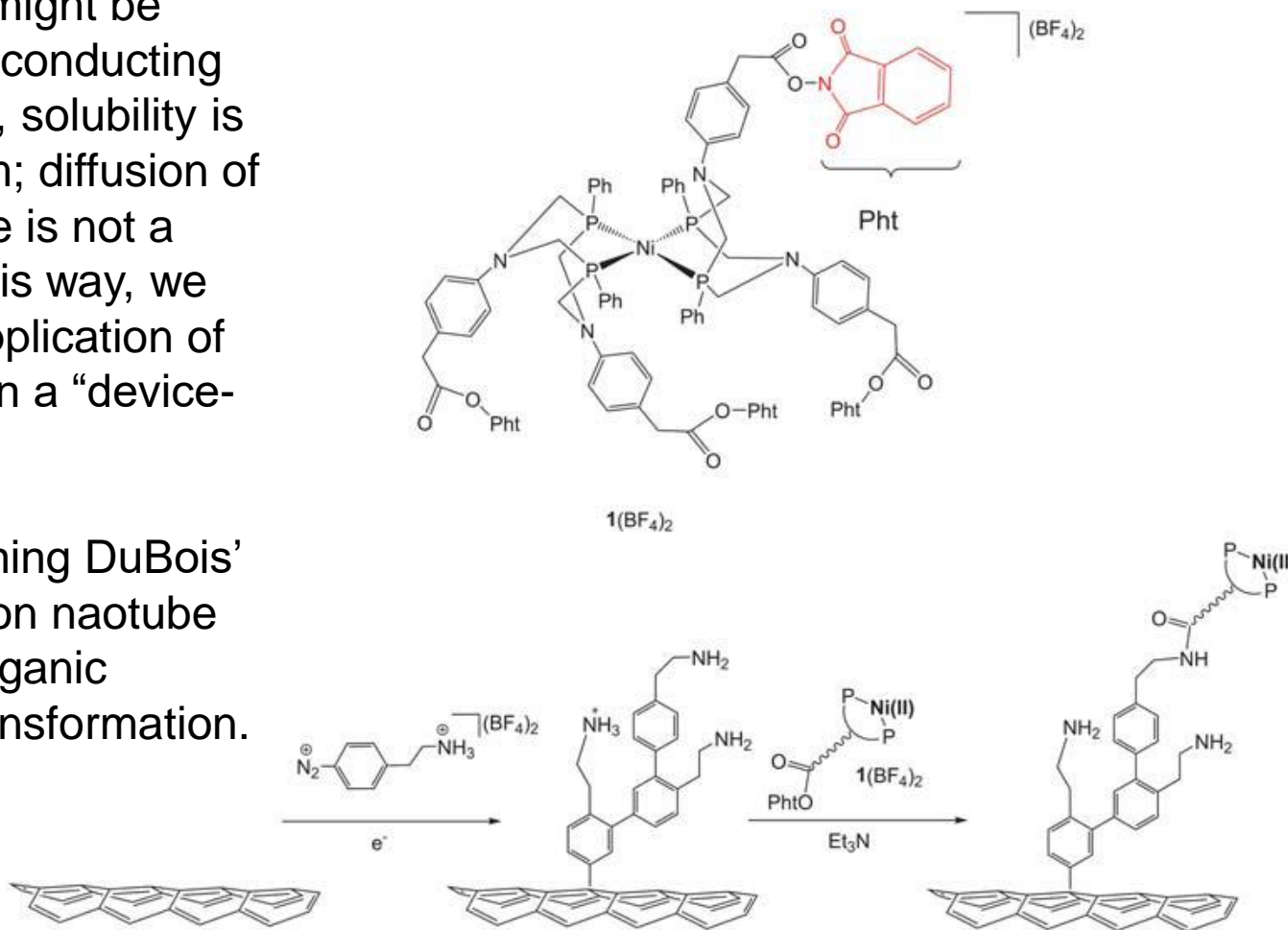
Ligand	$E_{1/2}$ (V vs $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$)	Turnover Frequency (s ⁻¹)
CF_3	-0.75	~100
Br	-0.81	~750
$\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$	-0.84	~300
H	-0.83	~600
Me	-0.83	~600
OMe	-0.86	~300

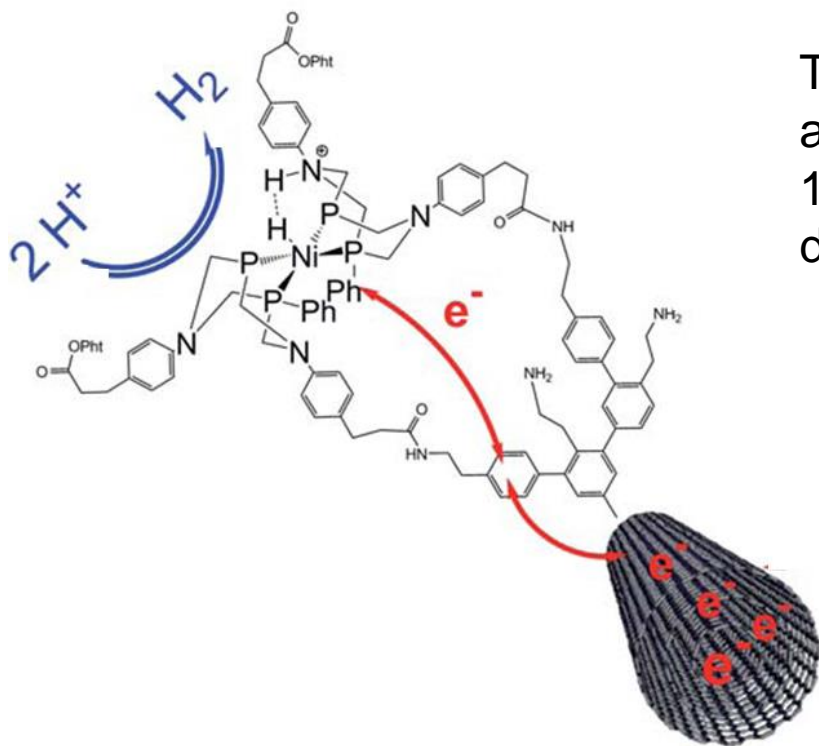
Structure-activity of this type will leads to an optimized catalyst, with high TOF and low overpotential.

Immobilization of molecular catalyst is a potential solution

Molecular catalyst might be immobilized onto a conducting substrate. This way, solubility is no longer a problem; diffusion of catalyst to electrode is not a problem neither. This way, we can evaluate the application of molecular catalyst in a “device-like” setting.

For example, attaching DuBois' catalysts onto carbon naotube was achieved by organic functional group transformation.





The system works in water; 4 mA/cm^2 at an overpotential of 300 mV; $\text{TOF} = 3 \text{ s}^{-1}$; 100000 turnovers in 10 hours without degradation.

This work points to a potential application of molecular catalyst in water splitting chemistry.

Artero, Palacin, et al. Science 2009, 326, 1384-1387.

Discussion and analysis: Strength and weakness of molecular HER catalysts

Conclusion

- Molecular complexes have been shown as HER catalysts, even at a low overpotential, and with a high turnover frequency.
- While several mechanisms exist, HER catalyzed by molecular complexes appear straightforward from a mechanistic point of view.
- The modularity of molecular chemistry is demonstrated. Catalysts can be turned and improved with the help of modern synthetic tools.
- Enzymes offer inspiration for the development of synthetic catalysts.
- Most molecular catalysts only work in organic solvents due to solubility and stability issues. The studies of these catalysts are fundamental in nature; the practical application of molecular catalysts in water splitting is yet to be demonstrated.