Chapter II: Molecular catalysis for the hydrogen evolution reaction

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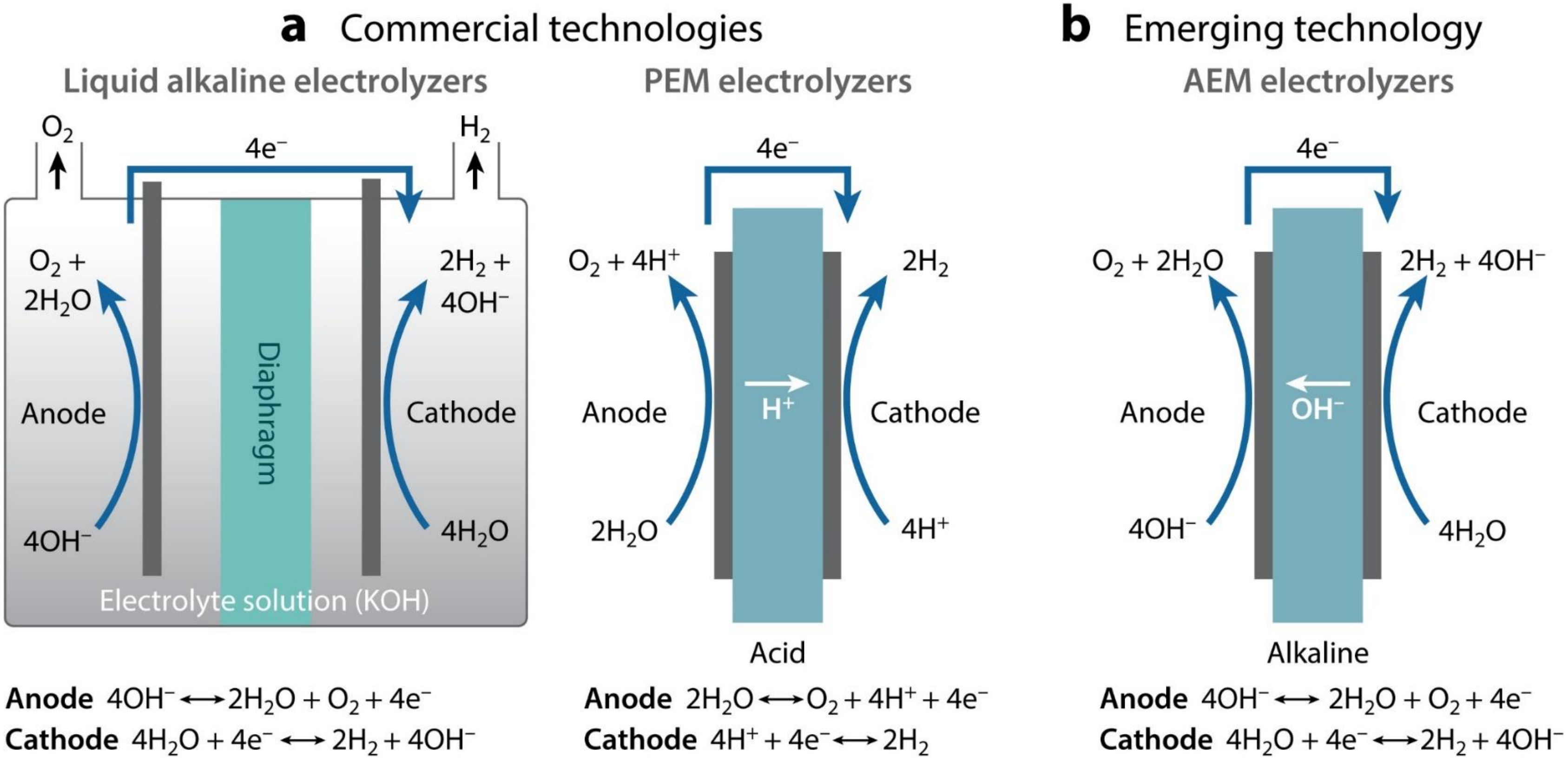
I. What is the hydrogen evolution reaction

The principle of electrolyzers is the same: water splitting reaction

$$2\,H_2O \xrightarrow{\text{Electricity}} 2\,H_2 + O_2$$



a Commercial technologies

Liquid alkaline electrolyzers

Anode $4OH^- \longleftrightarrow 2H_2O + O_2 + 4e^-$
Cathode $4H_2O + 4e^- \longleftrightarrow 2H_2 + 4OH^-$

PEM electrolyzers

Anode $2H_2O \longleftrightarrow O_2 + 4H^+ + 4e^-$
Cathode $4H^+ + 4e^- \longleftrightarrow 2H_2$

b Emerging technology

AEM electrolyzers

Anode $4OH^- \longleftrightarrow 2H_2O + O_2 + 4e^-$
Cathode $4H_2O + 4e^- \longleftrightarrow 2H_2 + 4OH^-$

Ayers K, et al. 2019.
Annu. Rev. Chem. Biomol. Eng. 10:219–39

Water Splitting is an Electrochemical Reaction

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

Overall reaction: $2\,H_2O \rightarrow O_2 + 2\,H_2$

At the cathode: $2H^+ + 2e^- \rightarrow H_2$ Hydrogen evolution reaction (HER)

At the anode: $2\,H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Oxygen evolution reaction (OER)

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

Catalysis for Hydrogen Evolution

$2H^+ + 2e^- \rightarrow H_2$	E° ~ 0 V vs. RHE	hydrogen evolution reaction
$H^+ + e^- \rightarrow H\bullet$	E° ~ - 2.3 V vs. RHE	overpotential of at least 2.3 V
$H^+ + 2e^- \rightarrow H^-$	E° ~ - 1.4 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• 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.

η = E(working) – E(reversible)

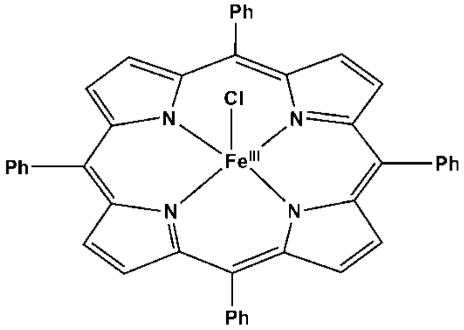
In some literature, η is taken as an absolute value.

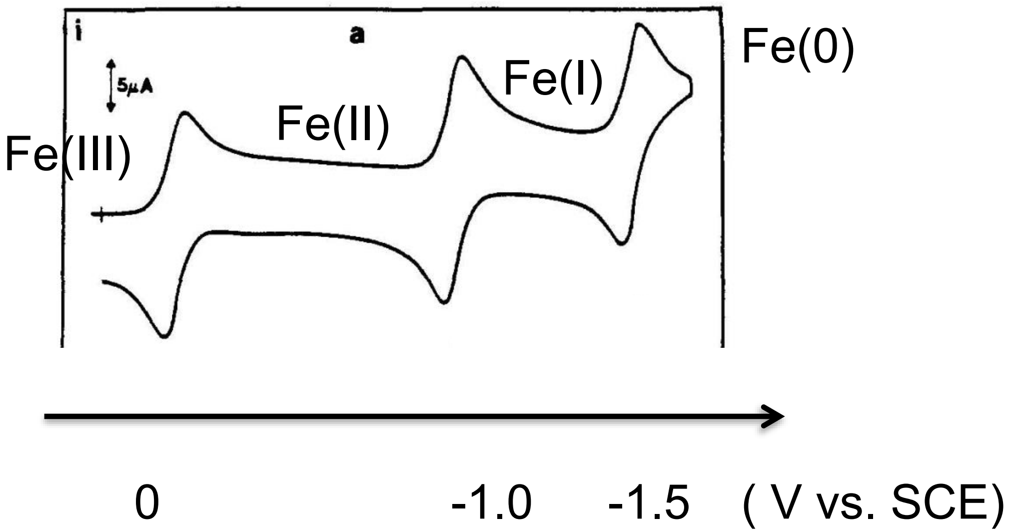
Overpotential can be considered as an «energy penalty» to make the reaction happen.

II. Mechanistic understanding examplified by case studies

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

Electrochemistry of a Fe Porphyrin Complexes





Cyclic votammetry in DMF

Three processes:

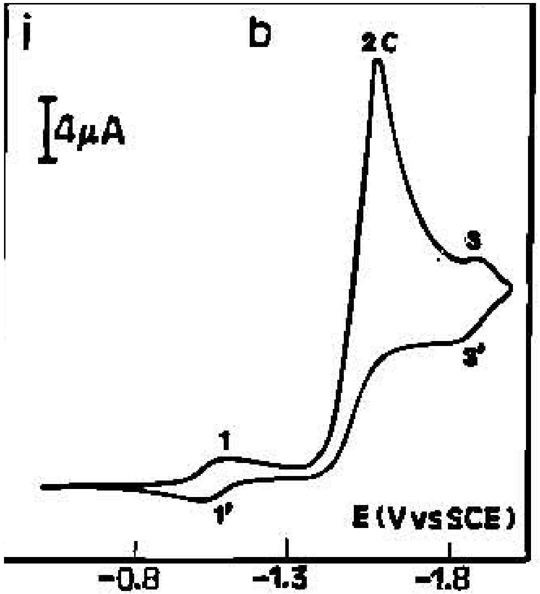
(1)Fe(III)-Cl $\rightleftarrows$ Fe(II) + Cl^-

(2) Fe(II) $\rightleftarrows$ Fe(I)

(3) Fe(I) $\rightleftarrows$ Fe(0)

Saveant *et al. J. Am. Chem. Soc.* **1996**, *118*, 3982-3983.

When 7 mM $[Et_3NH]Cl$ 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 Fe(II) $\rightleftarrows$ Fe(I) in the last slide

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

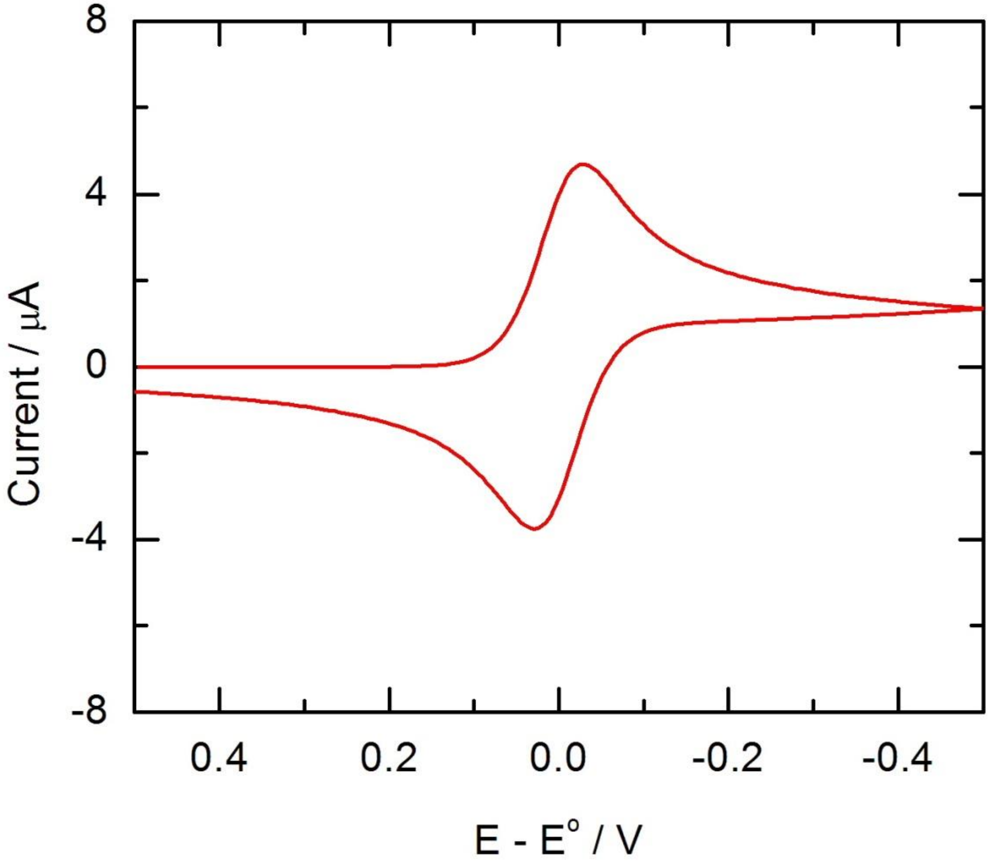
Peak 3 is a new peak

Electron Transfer:

1. $Ox + e \leftrightarrow Red \quad E^o$

$E = E^o - 0.059 Lg(Red/Ox)$

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:

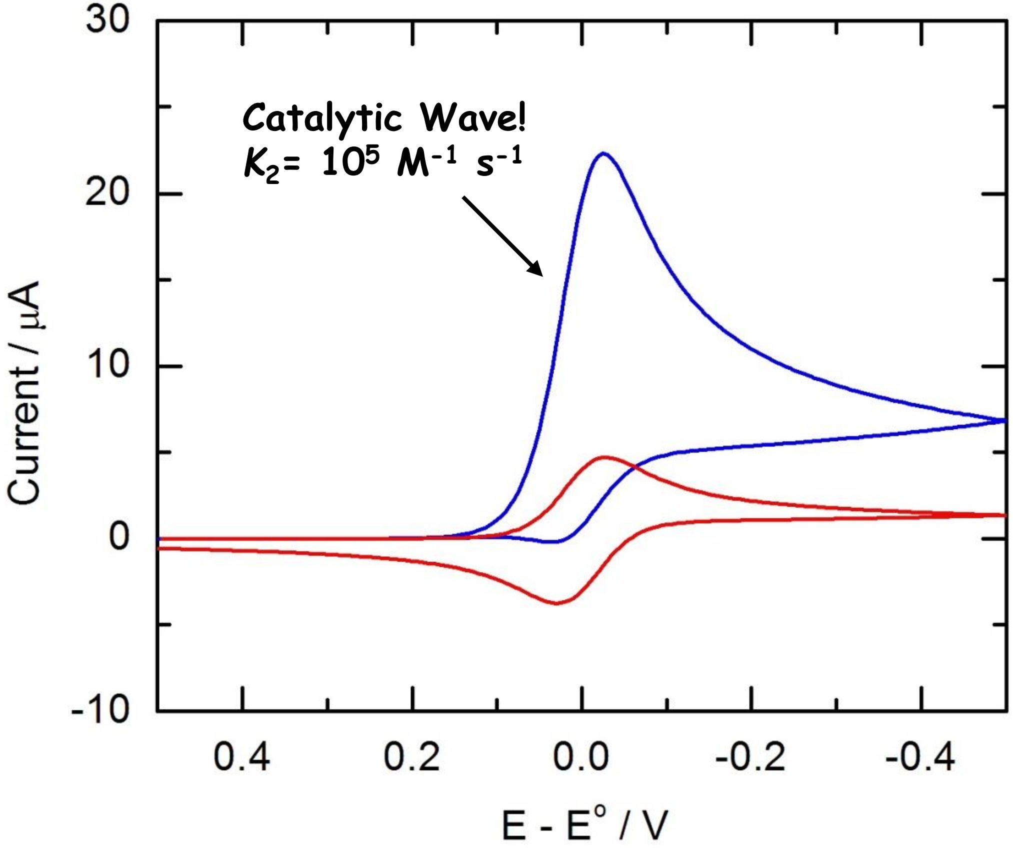
1. $Ox + e \leftrightarrow Red \quad E^o$

$E = E^o - 0.059 Lg(Red/Ox)$

Chemical Reaction:

2. $Red + A \rightarrow Ox + B \quad k_2$

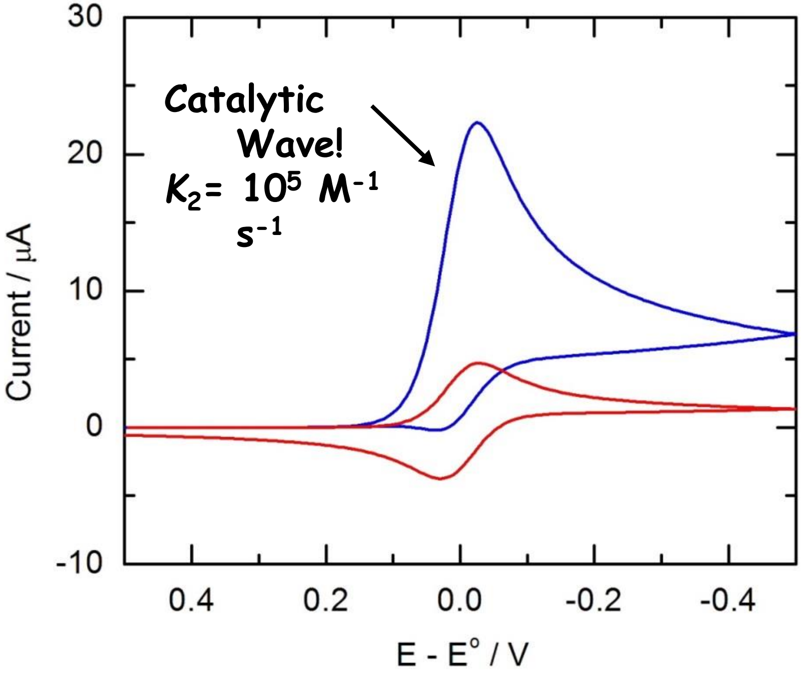
Electrocatalysis



Catalytic Wave!
$K_2 = 10^5$ M^{-1} s^{-1}

Cyclic Voltammogram for a Electrocatalytic reaction in solution.

Analysis of molecular electrocatalysis:

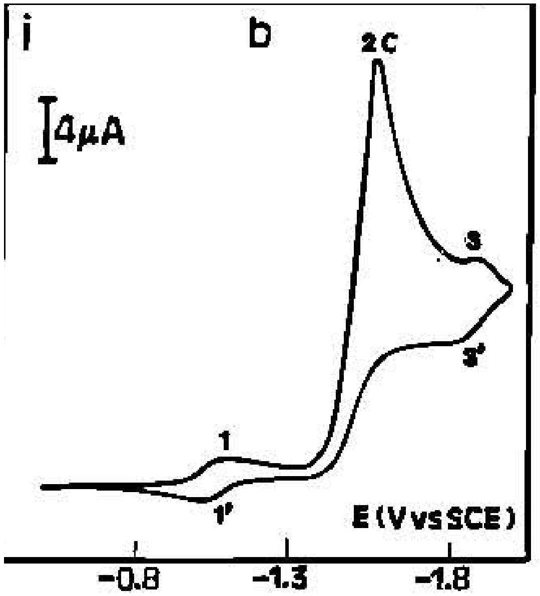


(1) Catalysis starts only near E = E°. Therefore, the minimum overpotential is dictated by the redox chemistry of the molecular catalyst. This means that the minimum overpotential can be changed by changing the catalyst.

(2) The current rises to a peak near E = E°; 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.

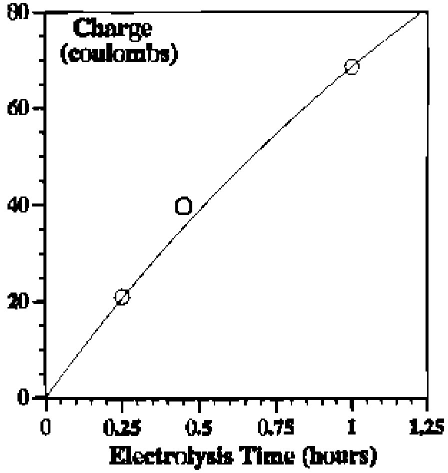
(3) Increasing overpotential beyond the peak current does not increase the current.

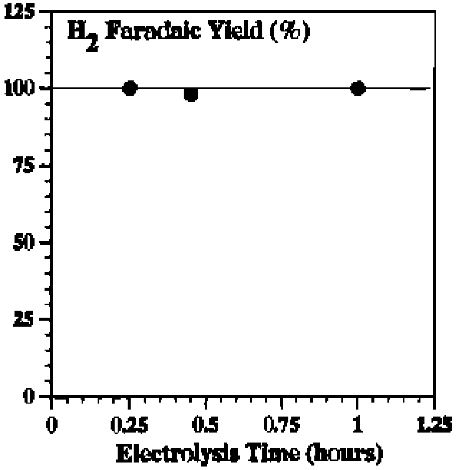
When 7 mM [Et$_3$NH]Cl was added to a DMF solution containing 0.6 mM of the iron porphyrin complex, the cyclic voltammetry shows:



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) H_2 was produced in a nearly 100% Faradaic yield.





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

For HER,
$2H^+ + 2e^- \rightarrow H_2$
1 H_2 is made from 2 electrons if the Faradaic yield is 100%.

How about the mechanism of this catalysis?

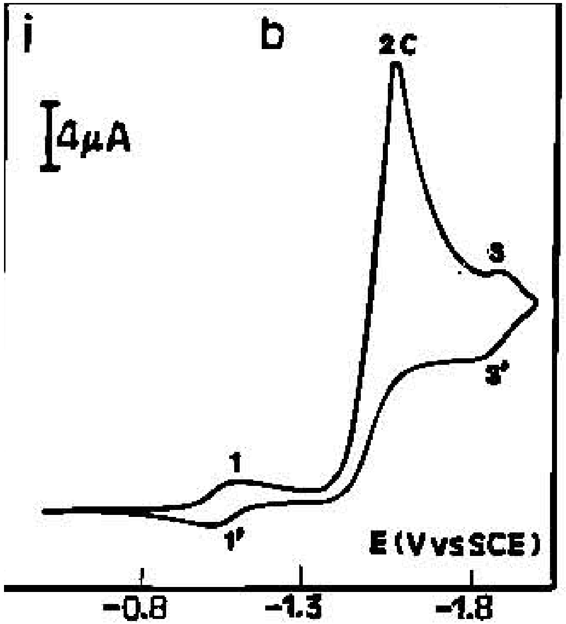
The following can be proposed based on electrochemical data:

$\mathrm{PFe(II)} + e \rightarrow \mathrm{PFe(I)^-}$ (E^0)-1.03 V vs SCE)
$\mathrm{PFe(I)^-} + e \rightarrow \mathrm{PFe(0)^{2-}}$ (E^0)-1.60 V vs SCE)
$\mathrm{PFe(0)^{2-}} + \mathrm{Et_3NH^+} \rightarrow \mathrm{PFe(II)H^-} + \mathrm{Et_3N}$ (k_1)
$\mathrm{PFe(II)H^-} + \mathrm{Et_3NH^+} \rightarrow \mathrm{H_2} + \mathrm{PFe(II)} + \mathrm{Et_3N}$ (k_2)

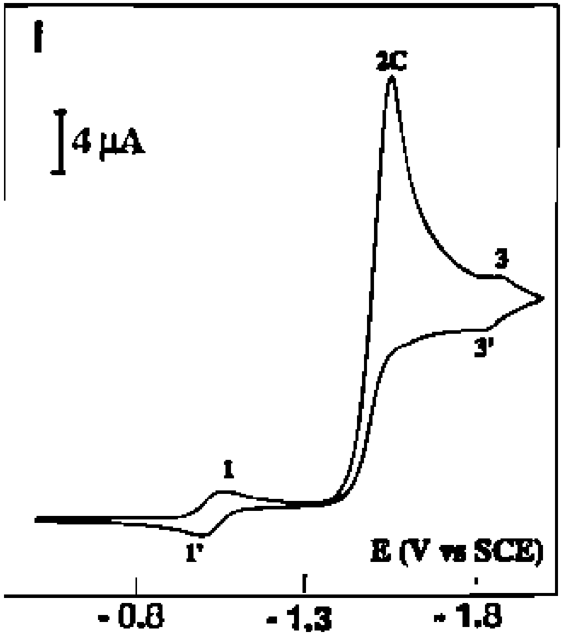
Other relevant reaction:
$\mathrm{PFe(II)H^-} + e \rightarrow \mathrm{PFe(I)H^{2-}}$ (E^0)-1.95 V vs SCE) peak 3
$\mathrm{PFe(II)} + \mathrm{PFe(0)^{2-}} \rightarrow 2\,\mathrm{PFe(I)^-}$ fast, diffusion limited $\Delta(G^0)$= -0.56 eV

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

Top: experimental data



Top: simulation data



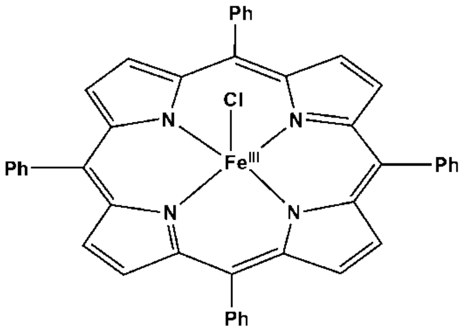
According to simulation,

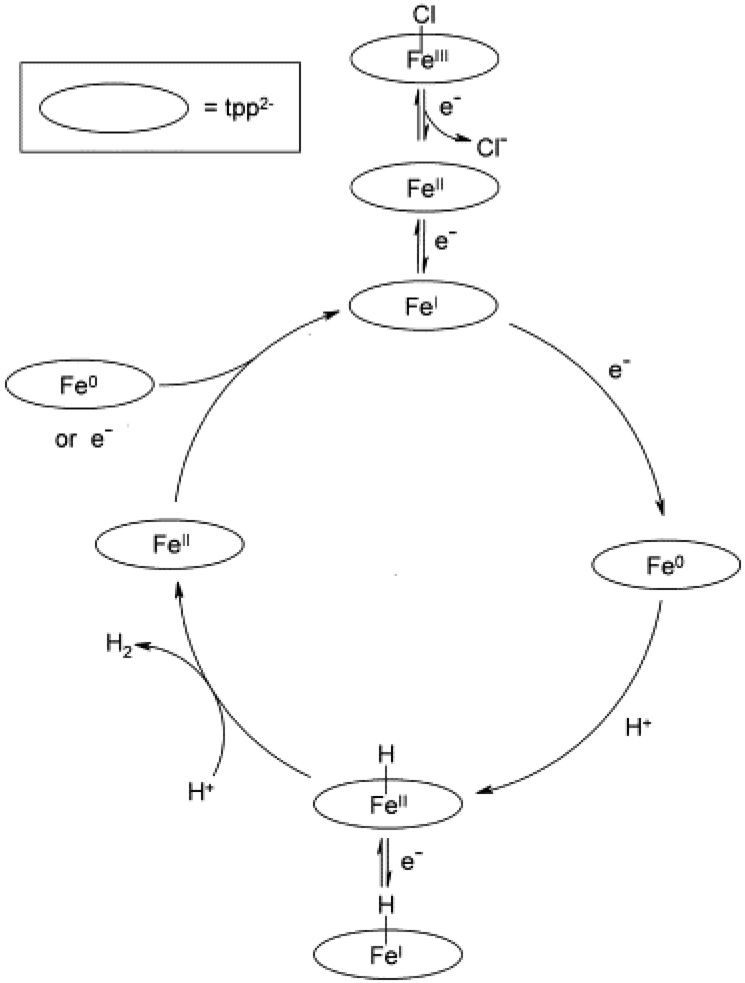
1. $PFe(0)^{2-} + Et_3NH^+$
$\rightarrow$ $PFe(II)H^- + Et_3N$ (k_1)
$k_1 = 2 \times 10^8\ M^{-1}\ S^{-1}$

2. $PFe(II)H^- + Et_3NH^+$
$\rightarrow$ $H_2 + PFe(II) + Et_3N$ (k_2)
$k_2 = 4 \times 10^5\ M^{-1}\ S^{-1}$

H_2 Evolution by Fe(0) Porphyrin Complexes

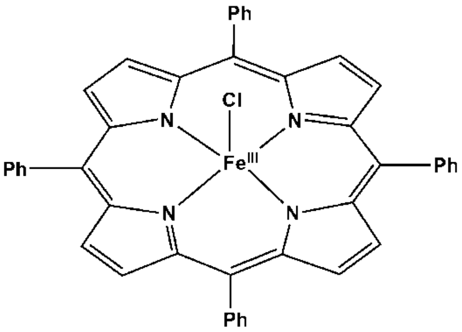
An overall mechanism can be established:





Saveant *et al. J. Am. Chem. Soc.* **1996**, *118*, 3982-3983.

Analysis of this catalytic system



What is the overpotential of this system?

Overpotential for HER in water

$H^+ + e^- \rightleftharpoons ½ H_2$ E(thermo)

$H^+ + e^- \rightleftharpoons ½ H_2$ E(working)

Overpotential = E(work) – E(thermo)

E(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(thermo) depends on the concentration of the reactive species. For HER:

In water, $E^{o'}$ (H^+/H_2)= E^o – (2.303RT/F)pH = E^o – 0.059pH
E^o 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(thermo) for HER in water; we just need to know the pH. The E(thermo) is identical to RHE.

Once E(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:

$$2\,HA\,(soln) + 2\,e^- \rightleftharpoons 2\,A^-\,(soln) + H_2 \qquad E^o_{HA} \qquad (1)$$

This reaction is made of 2 components:

(a): ionization of acid:

$$2\,HA\,(soln) \rightleftharpoons 2\,A^-\,(soln) + 2\,H^+\,(soln) \qquad K_{a,\,HA} \qquad (2)$$

(b): reduction of solvated proton:

$$2\,H^+\,(soln) + 2\,e^- \rightleftharpoons H_2 \qquad E^o_{H}{}^+ \qquad (3)$$

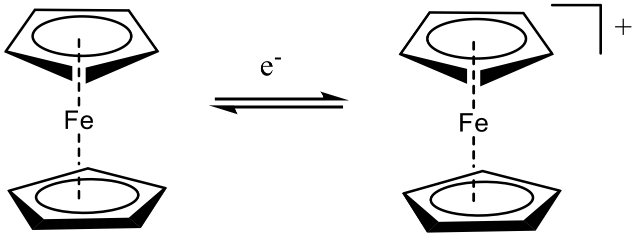
The thermodynamic potential of HER is then dependent on both the standard potential of proton reduction and the pKa of acid:

$$E^o_{HA} = E^o_{H+} - (2.303RT/F)pK_{a,HA} = E^o_{H+} -0.059pK_a \qquad (4)$$

The E^o_{H+} is a property of solvent, and it is different from NHE in water. For a given solvent, E^o_{H+} 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$^o_{H+}$ 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. pKa (Acid Dissociation Constants) and Thermodynamic Potentials for the HER for a Few Acids in Acetonitrile and *N*,*N*-Dimethylformamide

	acetonitrile		***N*,*N*-dimethylformamide**	
acid	pK_a	E_{HA}	pK_a	E_{HA}
perchloric acid	2.1	-0.26	dissociated	-0.77
trifluoromethanesulfonic acid	2.6	-0.29	dissociated	-0.77
p-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
p-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
p-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-*tert*-butylphenol	27.5	-1.77	unavailable	

Evans et al., *Inorg. Chem.,* **2006**, *45*, 9181 -9184.

Exercise: calculate the overpotential in the Fe-porphyrin system

Recall experimental conditions:

In DMF; $[Et_3NH]Cl$ as acid; Working potential at -1.6 V vs. SCE
As Fc/Fc^+ = 0.47 vs. SCE in DMF
E(working) = -1.6 vs. SCE = -2.07 V vs. Fc/Fc^+

Calculate the overpotential of the system

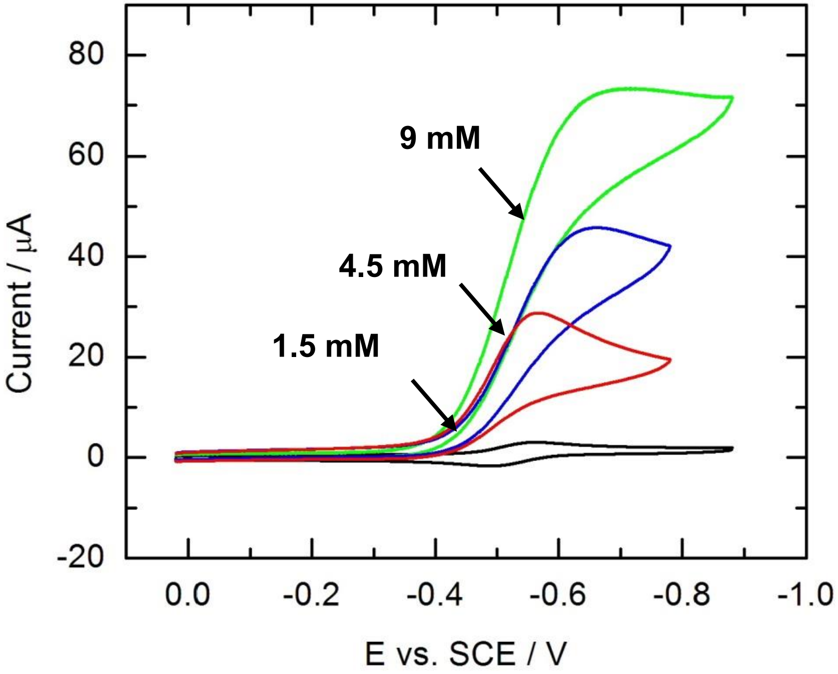
Exercise: Analysis of a catalyst (see separate file online posted after class)

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

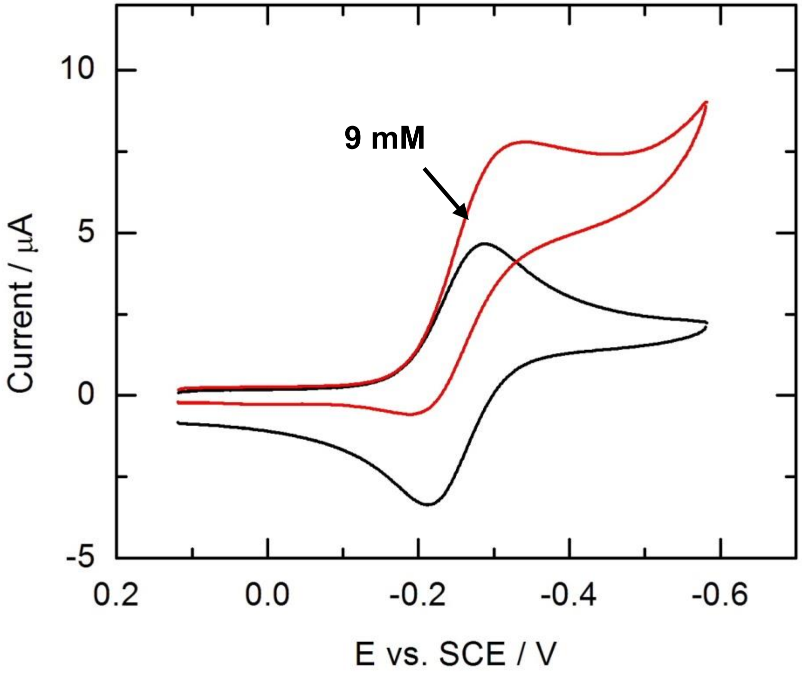
Two catalysts with similar structures

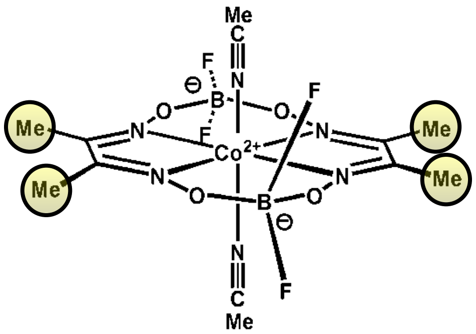
$TsOH\cdot H_2O$ in CH_3CN, $pK_a = 8$

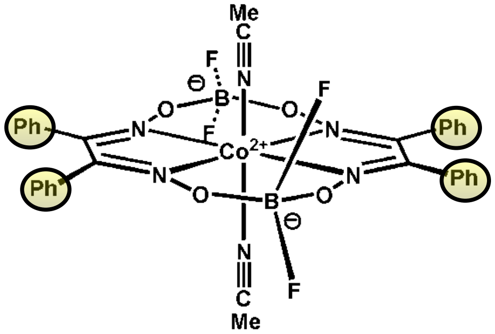
0.3 mM catalyst $Co(dmgBF_2)_2$



0.3 mM catalyst $Co(dpgBF_2)_2$

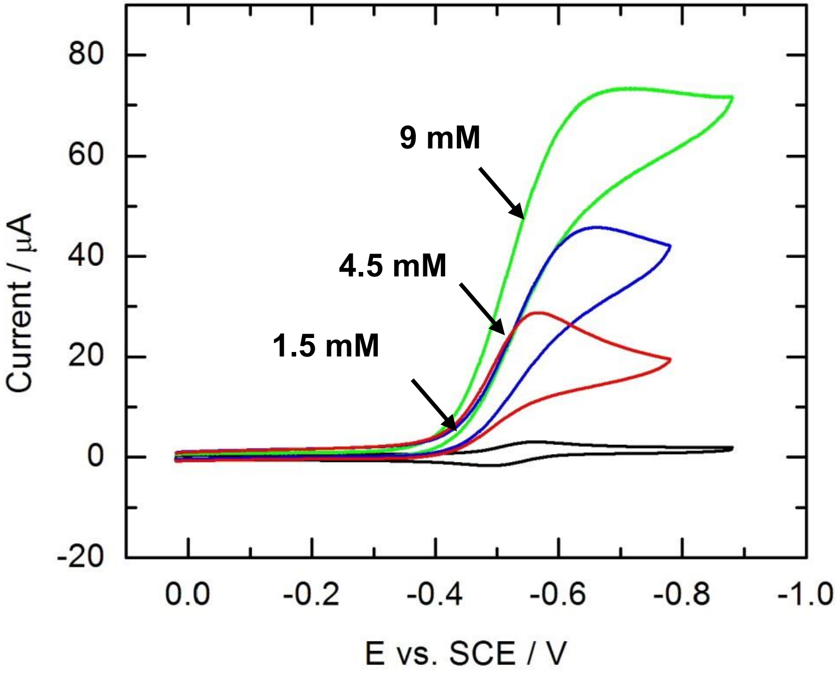




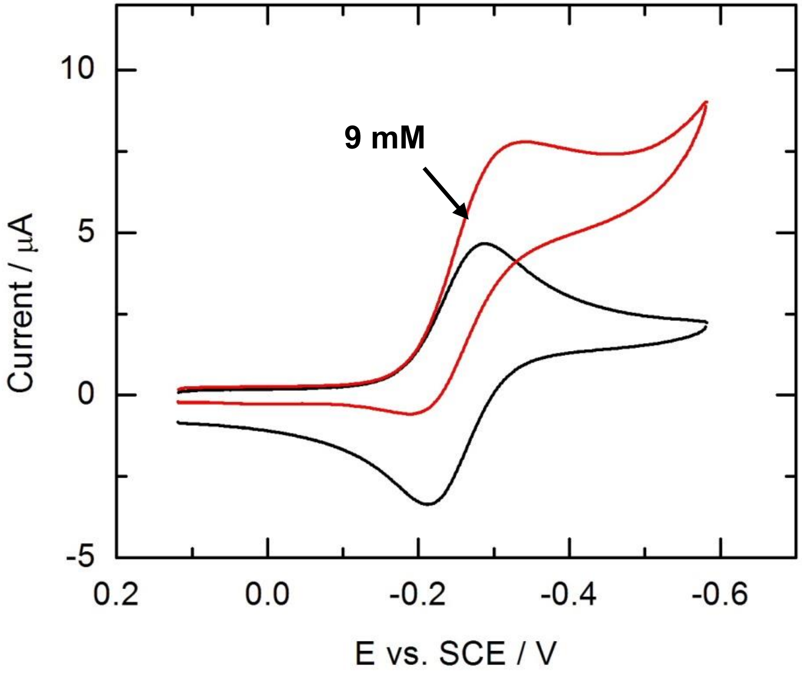


Comparison of catalysts

0.3 mM catalyst Co($dmgBF_2$)$_2$



0.3 mM catalyst Co($dpgBF_2$)$_2$



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.

Co($dpgBF_2$)$_2$ has a smaller overpotential for HER than Co($dmgBF_2$)$_2$.

The catalytic current by Co($dpgBF_2$)$_2$ is smaller than that by Co($dmgBF_2$)$_2$.

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

$$HA + e^- \rightleftharpoons \tfrac{1}{2} H_2 + A^-$$

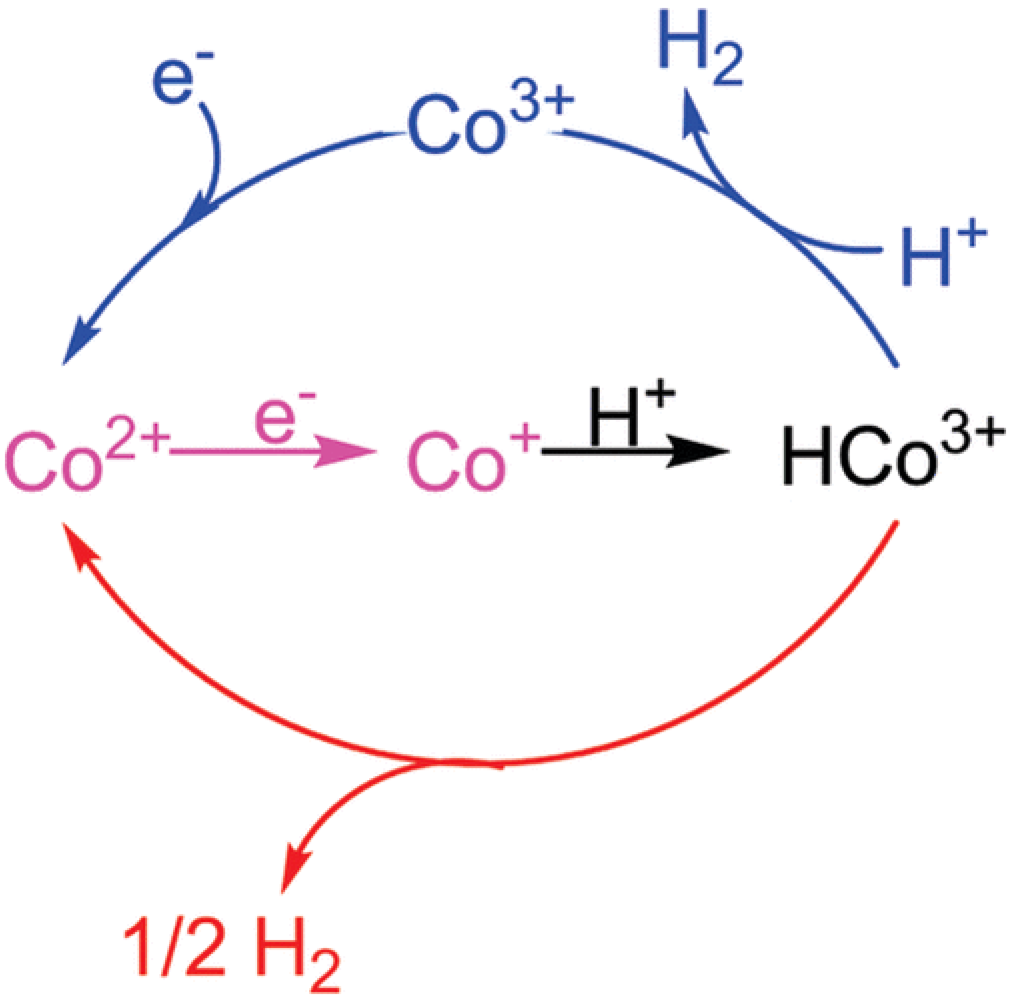
Proton Source	Thermodynamic potential for H_2/H^+ in CH_3CN (V vs. SCE)	Starting E for HER in CH_3CN (V vs. SCE)	Overpotential (mV)
CF_3COOH	**-0.51**	**-0.55** **(Co(dmgBF$_2$)$_2$)**	**40**
$TsOH{\cdot}H_2O$	**-0.23**	**-0.30 (Co(dpgBF$_2$)$_2$)**	**70**

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 Co(dmgBF$_2$)$_2$ with CF_3COOH.

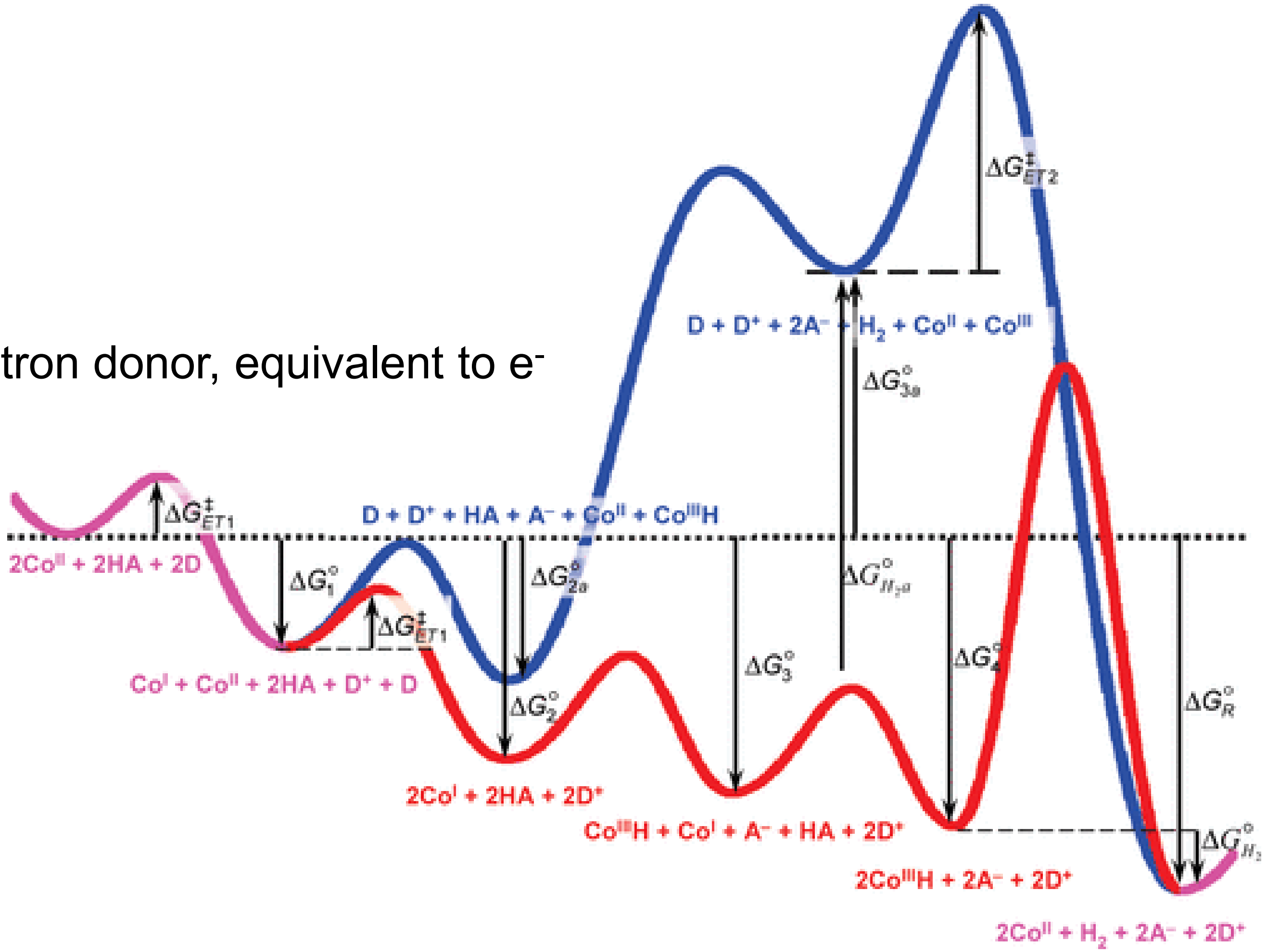
Hu X.L. et al. J. Am. Chem. Soc. 2007, 129, 8988-8998.

Two mechanistic possibilities



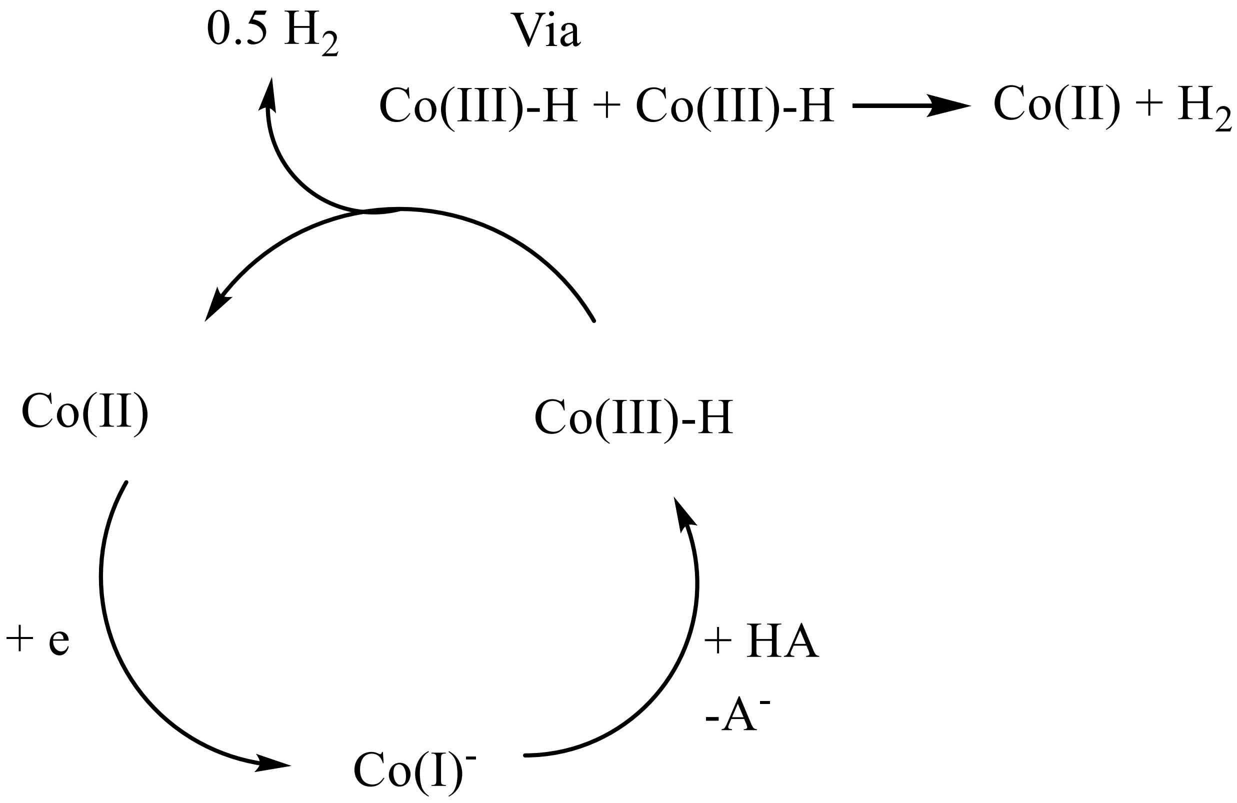
Thermodynamic analysis indicates that the bimetallic pathway is favored

D is an electron donor, equivalent to e^-



Dempsey, et al. J. Am. Chem. Soc. 2010, 132, 3, 1060–1065

The favored mechanism



0.5 H_2

Via

$Co(III)\text{-}H + Co(III)\text{-}H \longrightarrow Co(II) + H_2$

Co(II)

Co(III)-H

+ e

+ HA

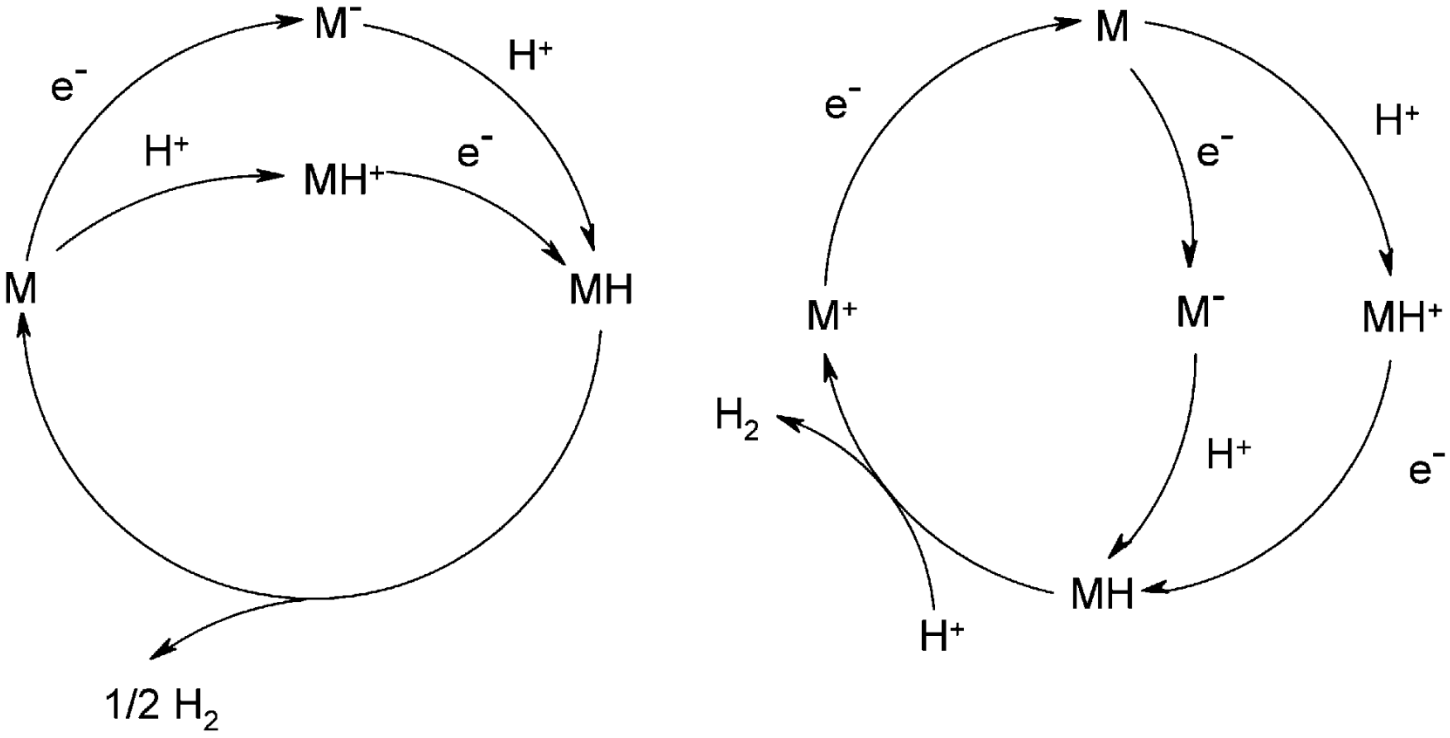
-A^-

$Co(I)^-$

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

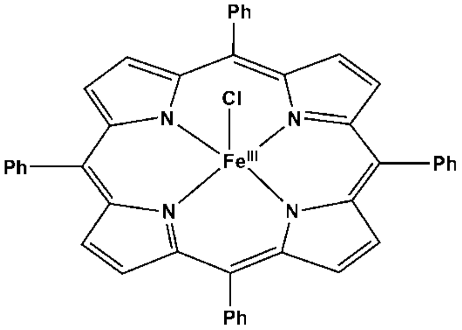
General mechanism for HER catalyzed by molecular complexes

M represents ML_n
Bimetallic H_2 formation: $MH + MH \rightarrow 2M + H_2$
Monometallic H_2 formation: $MH + H^+ \rightarrow M^+ + H_2$

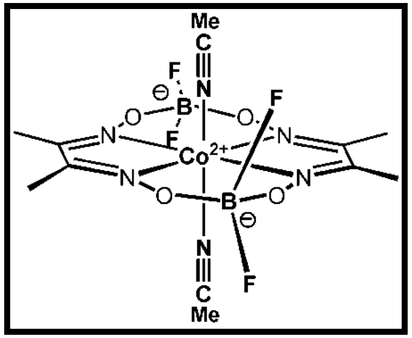


Case 3: A bio-inspired catalyst: nickel complexes for HER

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 x 10^5 M^{-1} S^{-1}
TOF = $k[H]^+$, TOF (max) = 4 x 10^5 s^{-1}

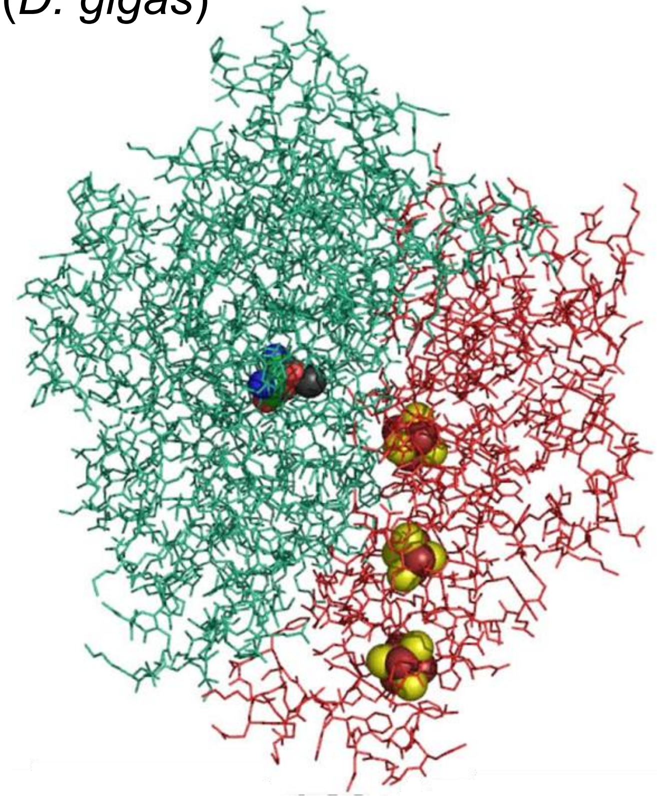


Overpotential = 0.04 V
TOF (max) = about 100 s^{-1}

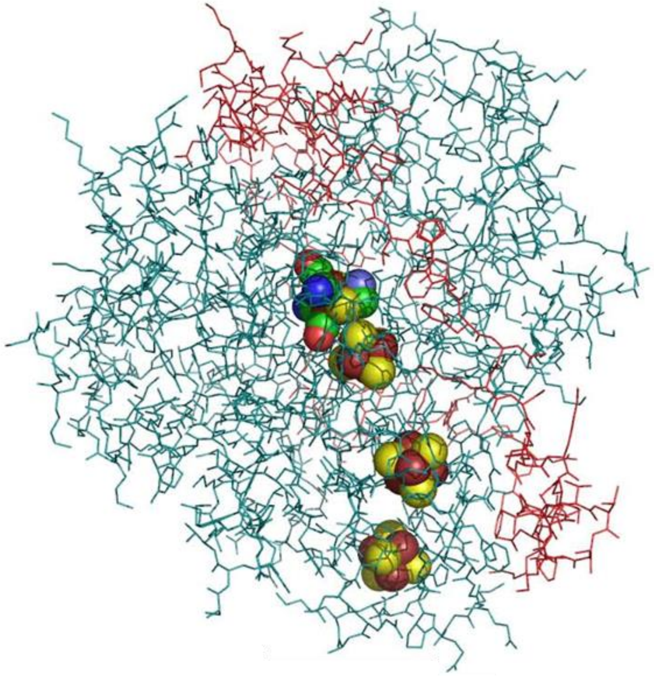
Try Biology!

Hydrogenases Are Active H_2 Evolution Catalysts

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



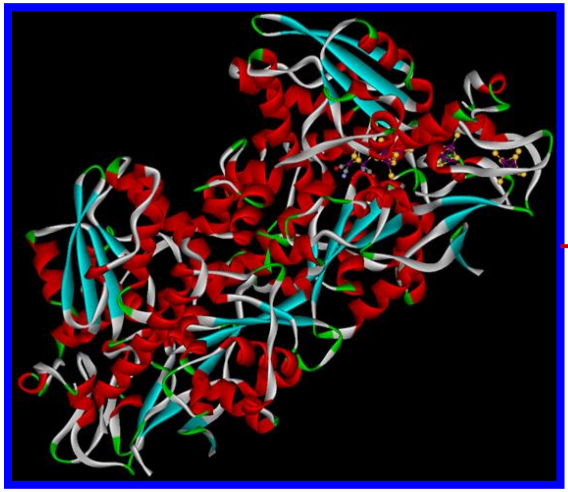
[FeFe]-hydrogenase
(*D. desulfuricans*)



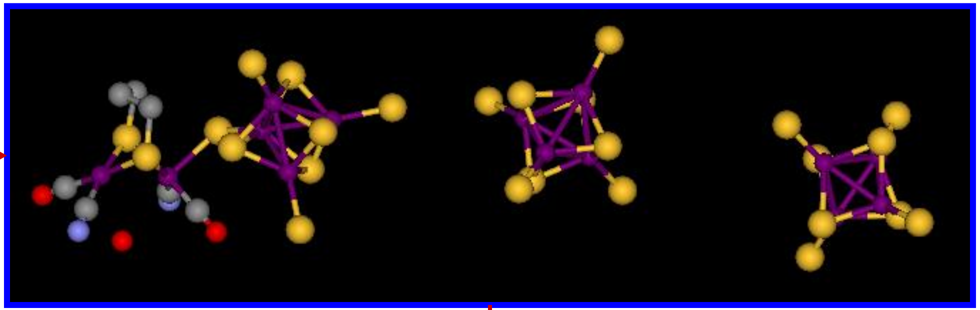
$$2H^+ + 2e^- \rightleftharpoons H_2$$

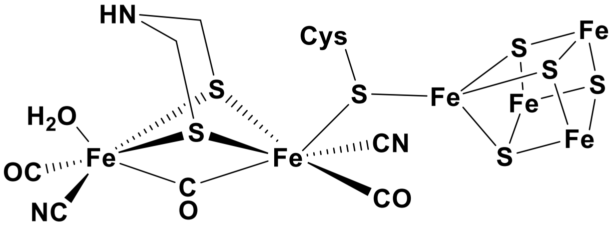
Activity: TOF= **700 - 9000** s^{-1} at $\eta < 50$ mV
Molecular weight: **50,000 - 90,000**

The biomimetic approach



[FeFe]-hydrogenase



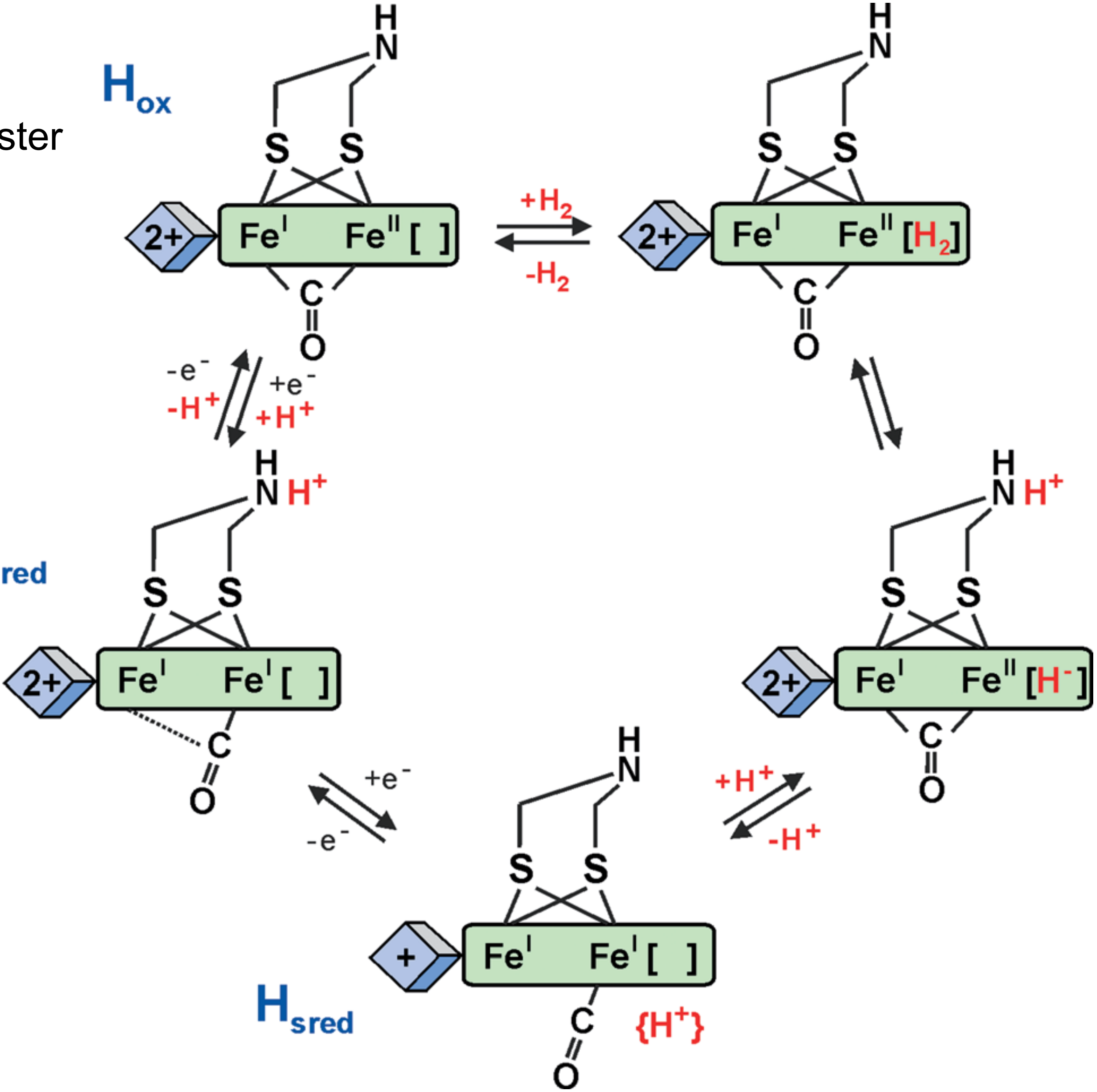


Active site

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.

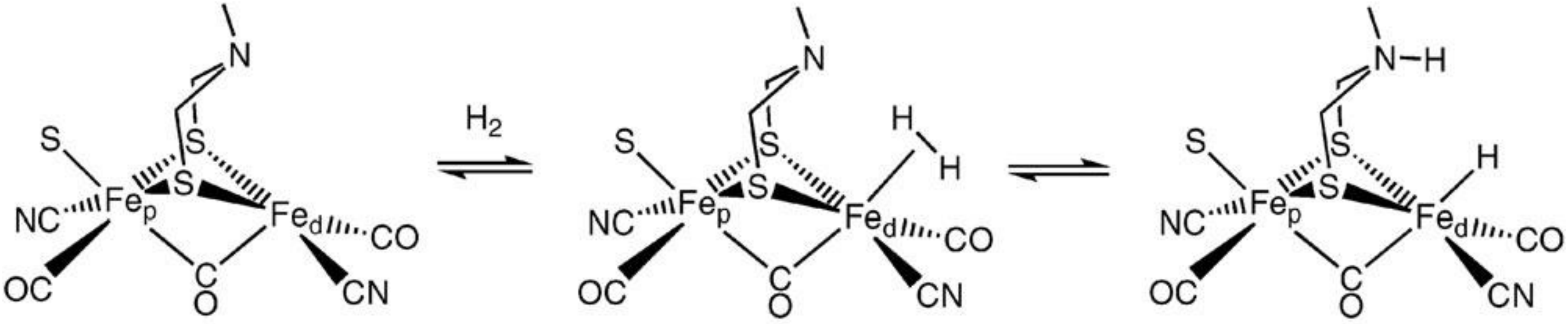
Proposed catalytic cycle for HER by [FeFe]-hydrogenase

Blue box : Fe-S cluster



Lubitz et al. Angew. Chem. Int. Ed. 2012, 51, 11458.

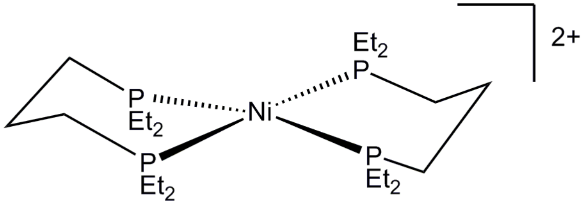
A special thing about the enzyme: The nitrogen atom is important to accept the proton



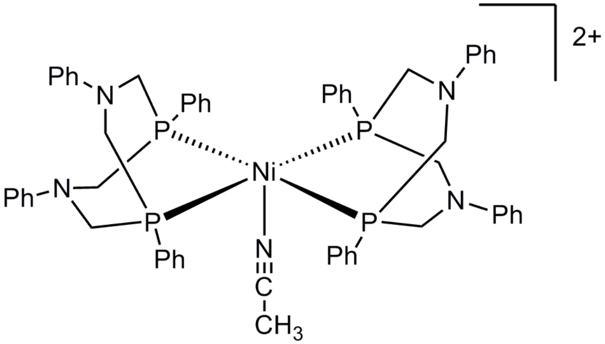
1 2 3

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.



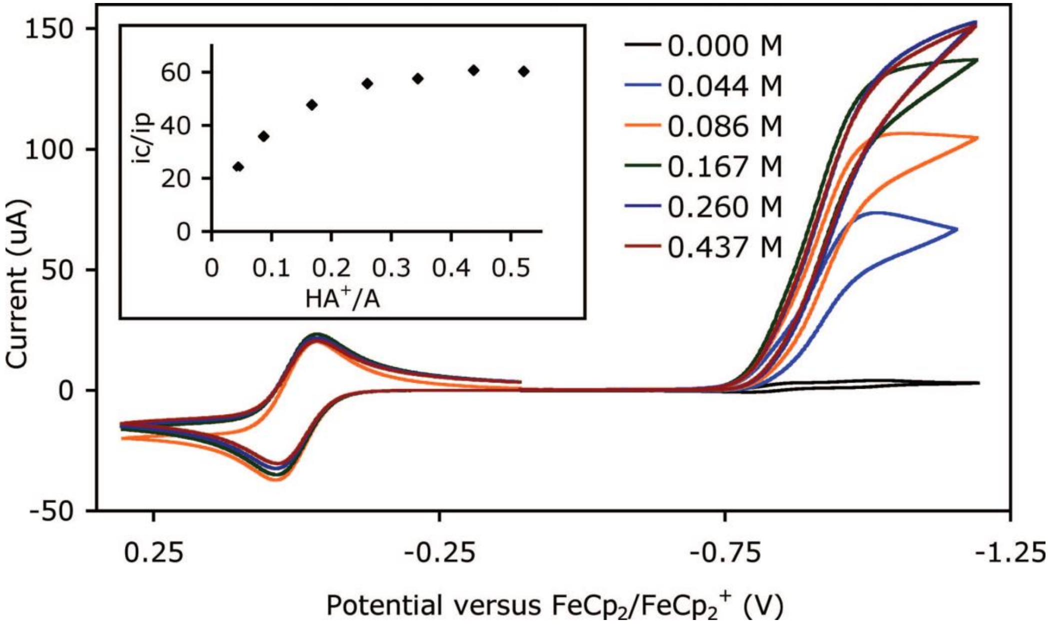
Not a catalyst



Catalyst

$2H^+ + 2e^- \rightarrow H_2$

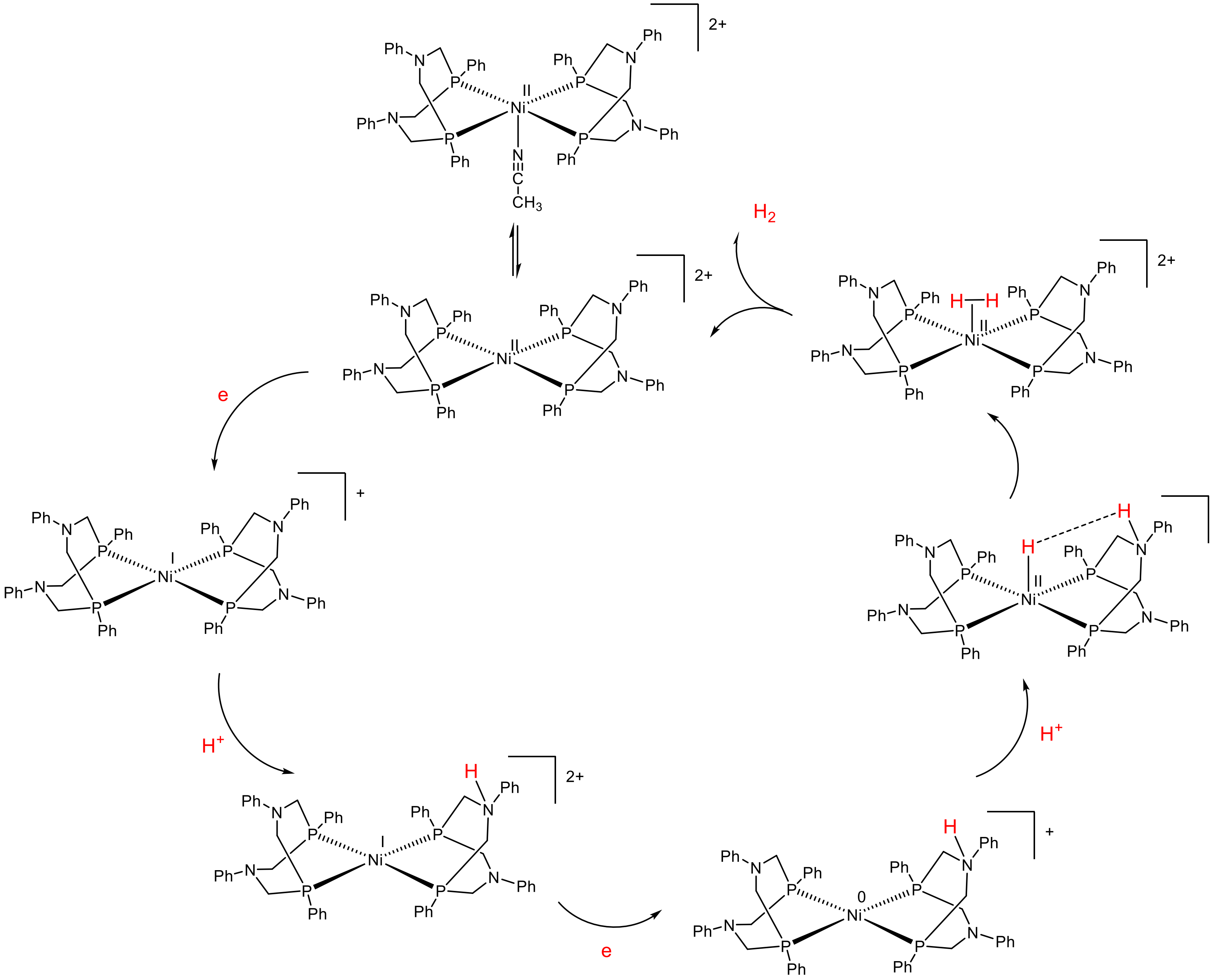
Catalyst (0.3 mM) in CH_3CN;
Acid was protonated DMF $(DMFH)^+$ (pka = 6.1).



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.

Dubois et al. P.N.A.S. 2007, 104, 6951.

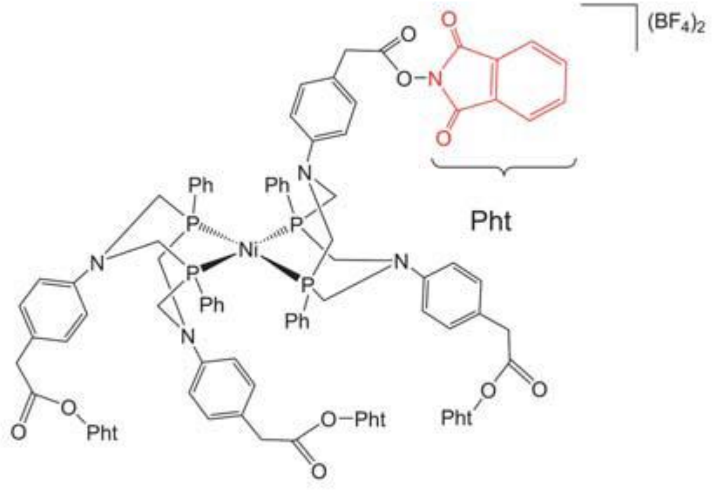
Mechanism of HER involving pendant amine as proton relay:



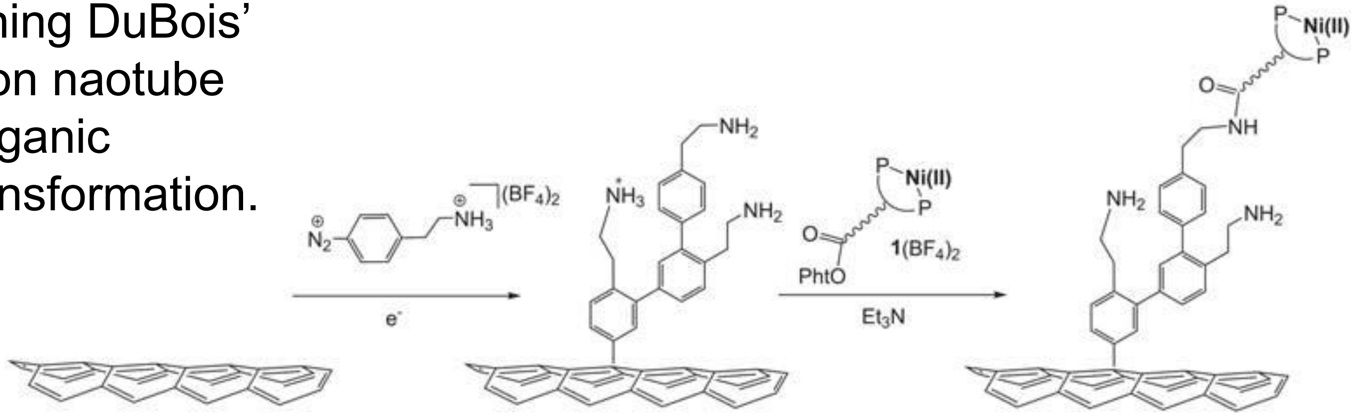
Immobilization of molecular catalyst is a potential solution

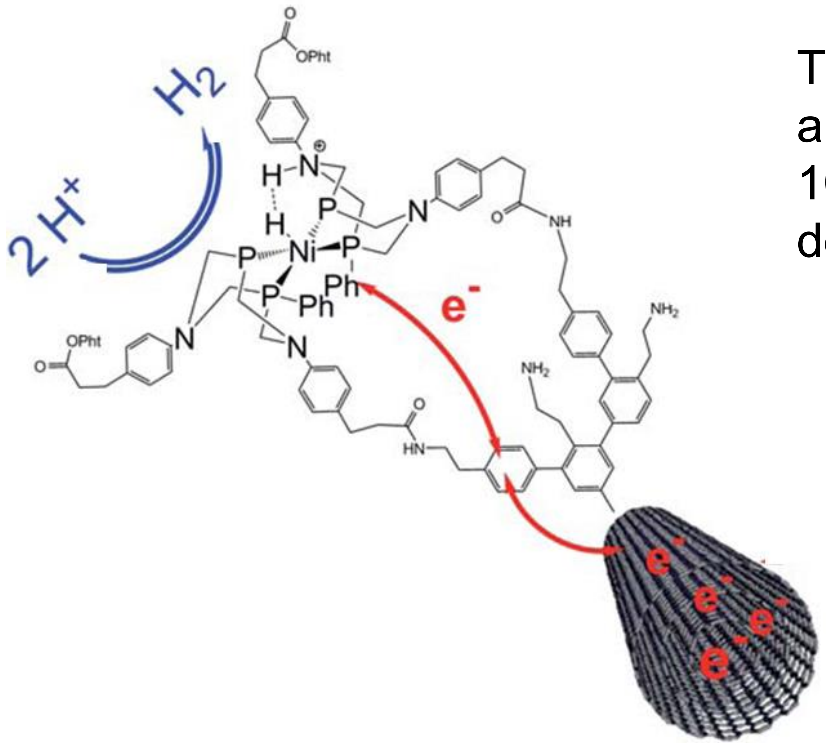
Molecular catalyst might be immobilized onto a conducting substrate. This way, solubility is no longer a problem; diffusion of catalyst to electrode is not a problem neither. This way, we can evaluate the application of molecular catalyst in a “device-like” setting.

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



$1(BF_4)_2$





The system works in water; 4 mA/cm^2 at an overpotential of 300 mV; TOF = 3 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.
- Enymes 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.