

# **Chapter II: Molecular catalysis for the hydrogen evolution reaction**

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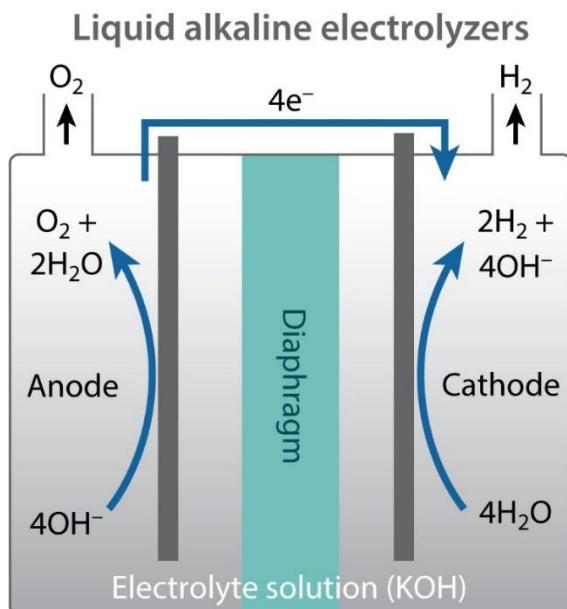
Case 3: A bio-inspired catalyst

# I. What is the hydrogen evolution reaction

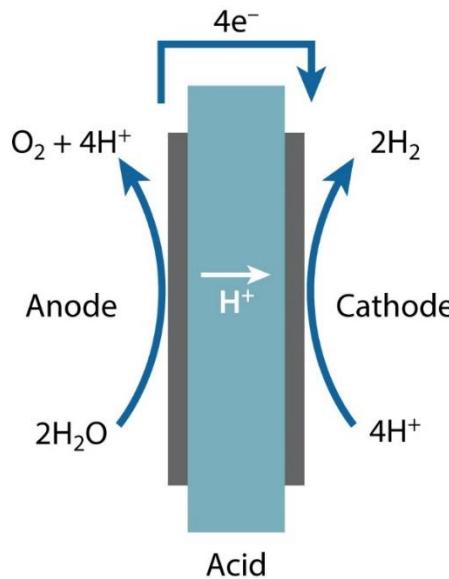
# The principle of electrolyzers is the same: water splitting reaction



## a Commercial technologies

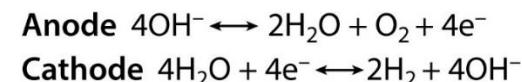
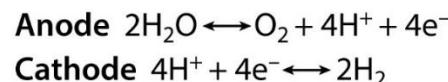
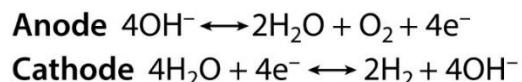
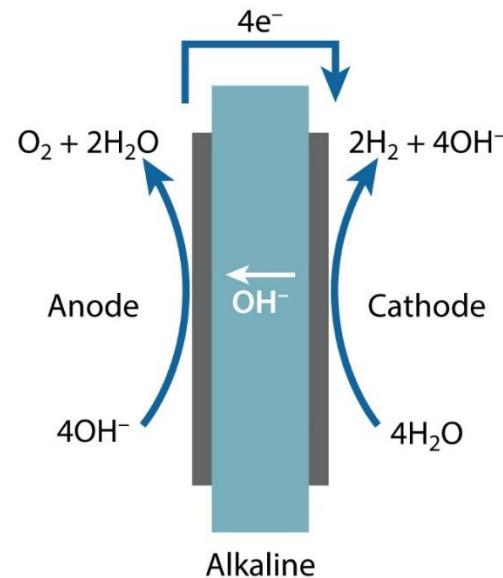


## PEM electrolyzers



## b Emerging technology

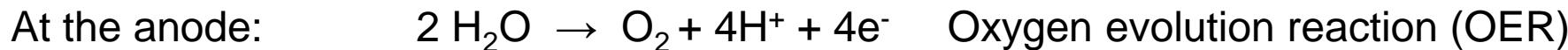
### AEM electrolyzers



## Water Splitting is an Electrochemical Reaction

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



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

# Catalysis for Hydrogen Evolution

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$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	$E^\circ \sim 0 \text{ V vs. RHE}$	hydrogen evolution reaction
$\text{H}^+ + \text{e}^- \rightarrow \text{H}\cdot$	$E^\circ \sim -2.3 \text{ V vs. RHE}$	overpotential of at least 2.3 V
$\text{H}^+ + 2\text{e}^- \rightarrow \text{H}^-$	$E^\circ \sim -1.4 \text{ V vs. RHE}$	overpotential of at least 1.4 V

To make  $\text{H}_2$  from  $\text{H}^+$ , one needs to make H-H bond.

Going through intermediates such as  $\text{H}^-$  or  $\text{H}\cdot$  will require a large overpotential.

To decrease the overpotential, a catalyst is needed.

## Overpotential and energy efficiency

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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.

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

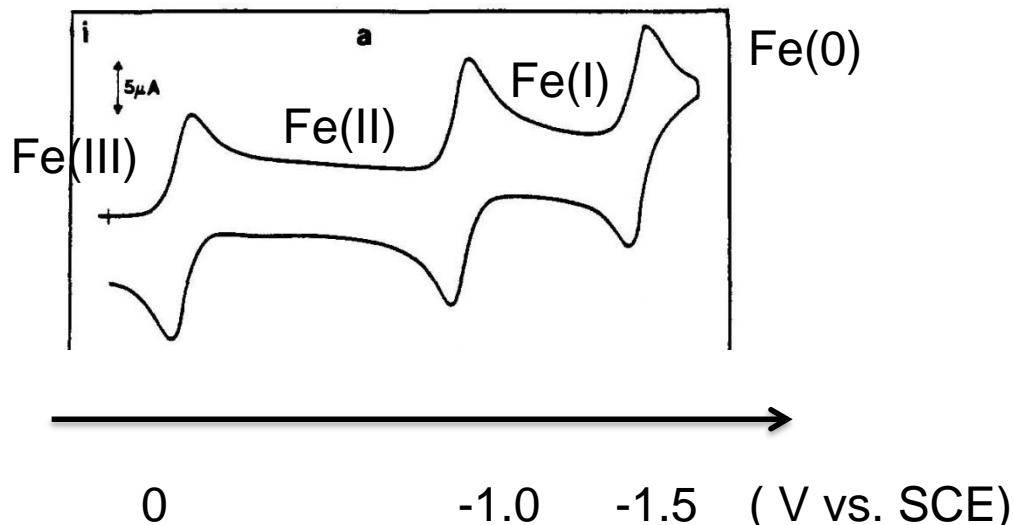
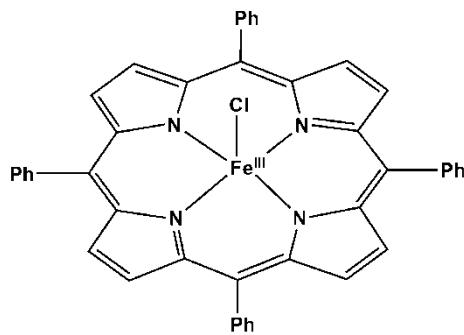
In some literature,  $\eta$  is taken as an absolute value.

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

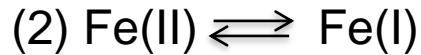
## II. Mechanistic understanding examplified by case studies

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

# Electrochemistry of a Fe Porphyrin Complexes

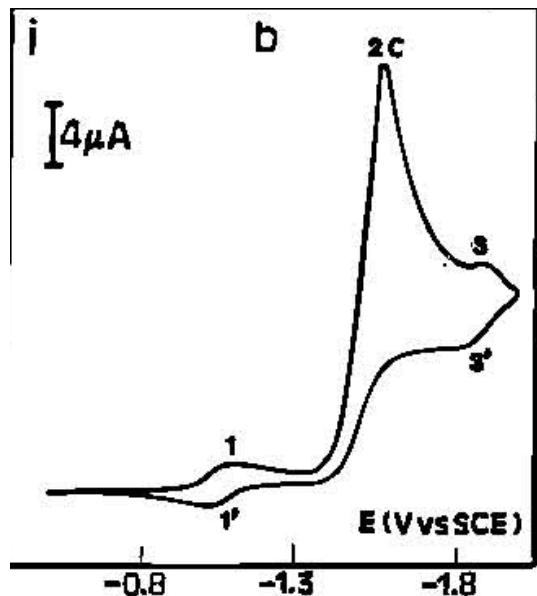


Three processes:



Cyclic voltammetry in DMF

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

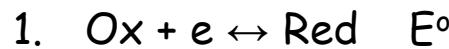


Peak 1 is the same feature as the redox peak for  $\text{Fe}(\text{II}) \rightleftharpoons \text{Fe}(\text{I})$  in the last slide

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

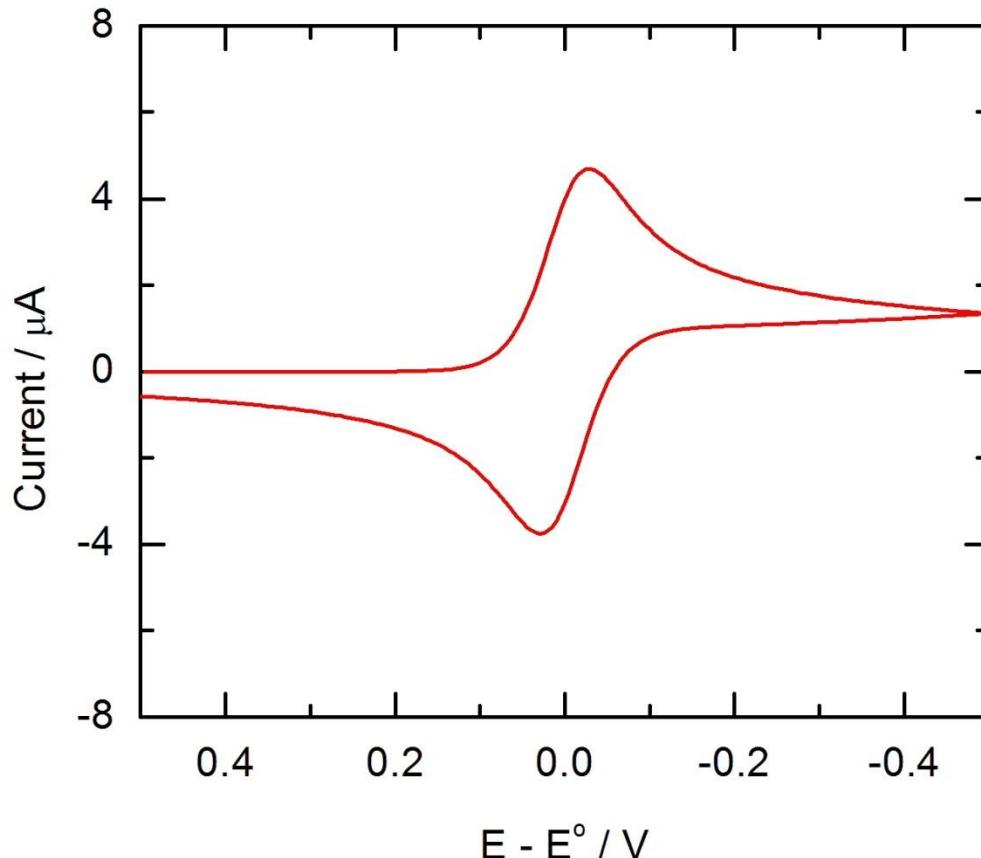
Peak 3 is a new peak

## Electron Transfer:



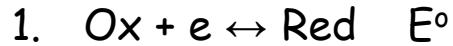
$$E = E^\circ - 0.059 \text{Lg}(\text{Red/Ox})$$

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



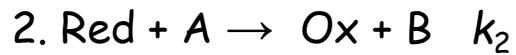
Cyclic Voltammogram for the reduction and re-oxidation of a redox species in solution.

**Electron Transfer:**

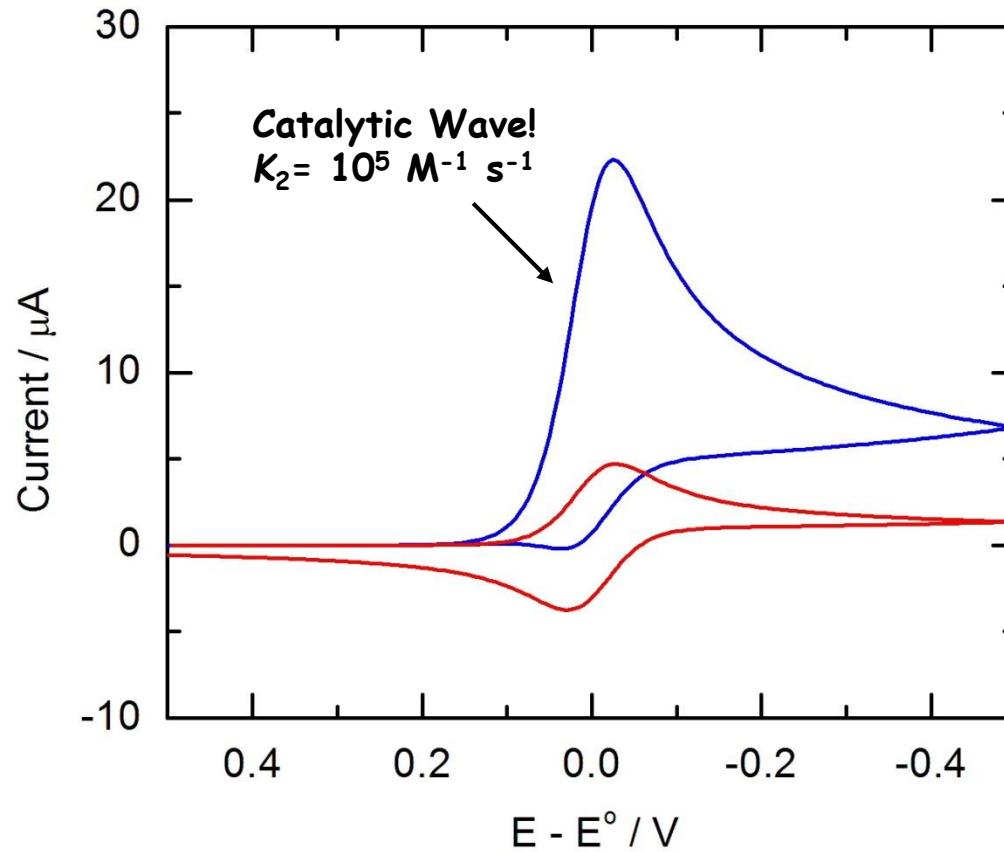


$$E = E^\circ - 0.059 \text{Lg}(Red/Ox)$$

**Chemical Reaction:**

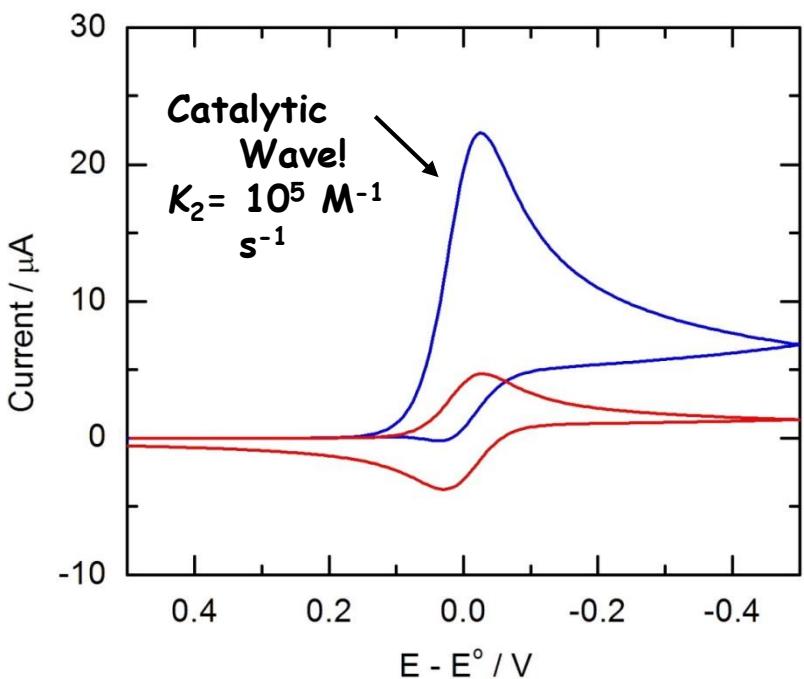


} **Electrocatalysis**



Cyclic Voltammogram for an electrocatalytic reaction in solution.

## Analysis of molecular electrocatalysis:

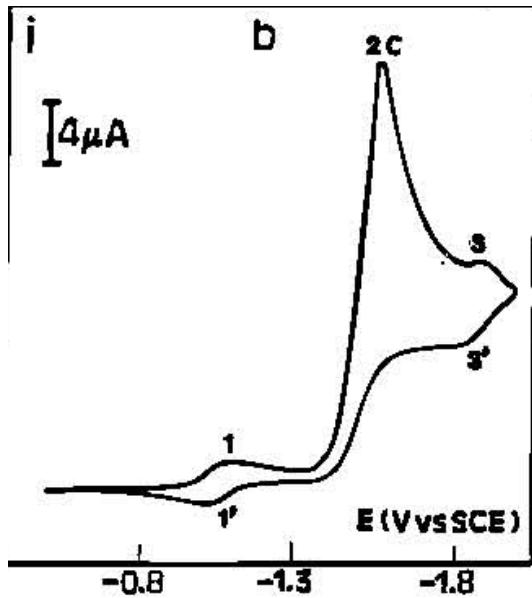


(1) Catalysis starts only near  $E = E^\circ$ . Therefore, the minimum overpotential is dictated by the redox chemistry of the molecular catalyst. This means that the minimum overpotential can be changed by changing the catalyst.

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



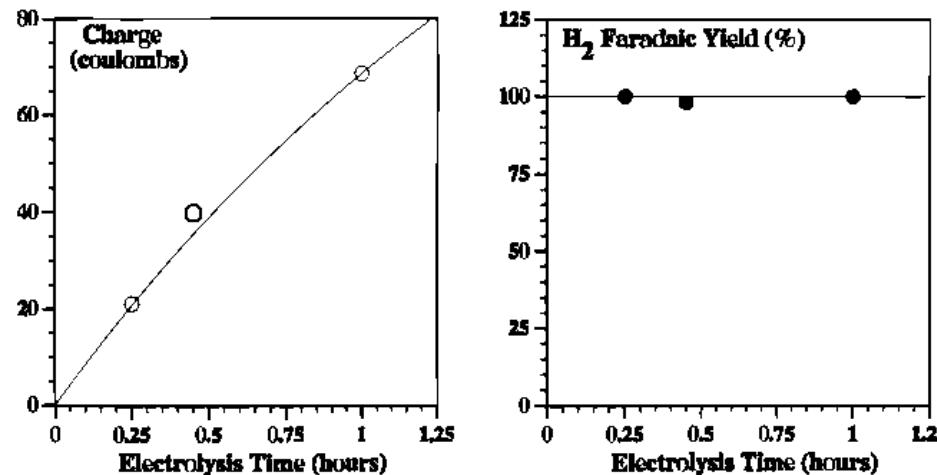
Peak 2c is a catalytic wave resulting from the formation of  $\text{Fe}(0)$ .

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)  $\text{H}_2$  was produced in a nearly 100% Faradaic yield.

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

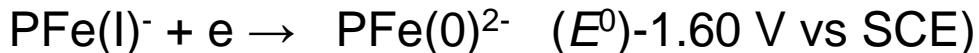
For HER,  
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

1  $\text{H}_2$  is made from 2 electrons if the Faradaic yield is 100%.

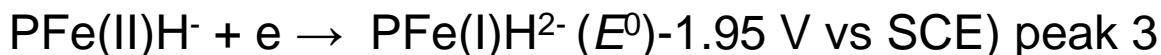


How about the mechanism of this catalysis?

The following can be proposed based on electrochemical data:

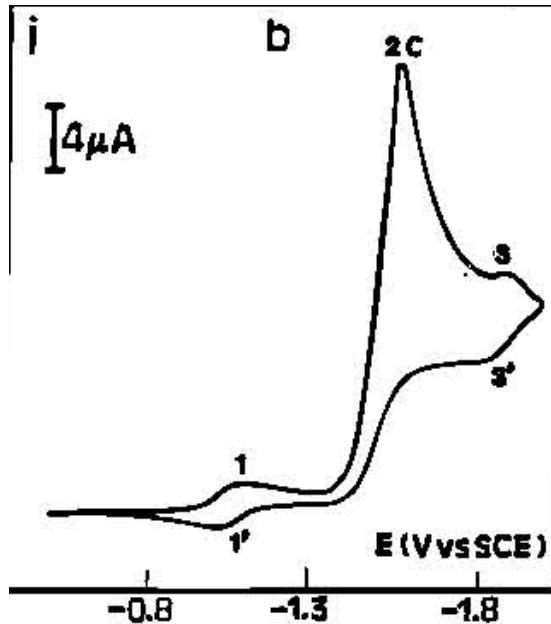


Other relevant reaction:



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

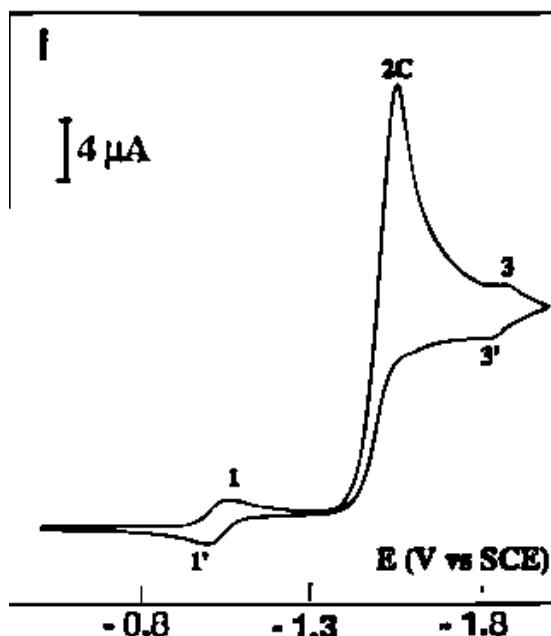
Top: experimental data



Top: simulation data

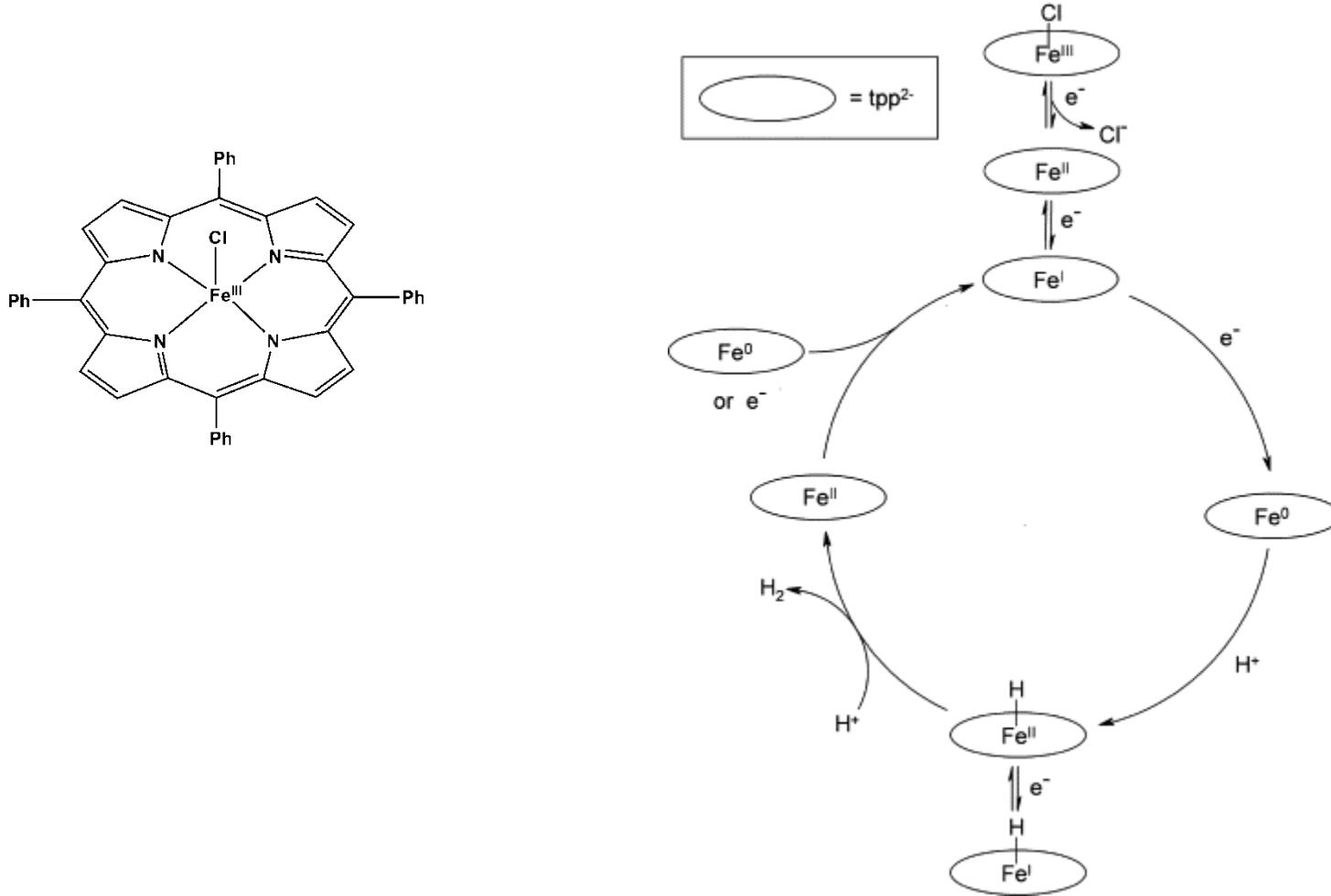
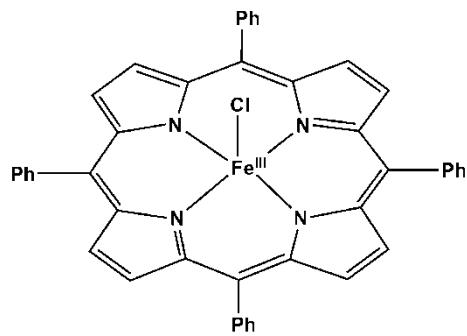
According to simulation,

1.  $\text{PFe}(0)^{2-} + \text{Et}_3\text{NH}^+ \rightarrow \text{PFe}(\text{II})\text{H}^- + \text{Et}_3\text{N}^- \quad (k_1)$   
 $k_1 = 2 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$
2.  $\text{PFe}(\text{II})\text{H}^- + \text{Et}_3\text{NH}^+ \rightarrow \text{H}_2 + \text{PFe}(\text{II}) + \text{Et}_3\text{N}^- \quad (k_2)$   
 $k_2 = 4 \times 10^5 \text{ M}^{-1} \text{ S}^{-1}$



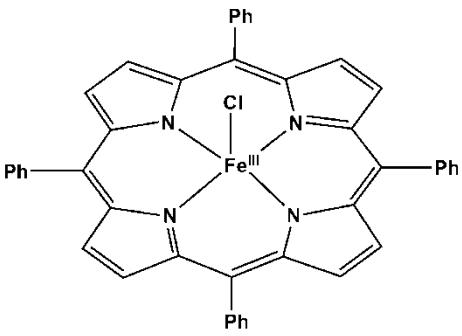
# $\text{H}_2$ Evolution by Fe(0) Porphyrin Complexes

An overall mechanism can be established:



## Analysis of this catalytic system

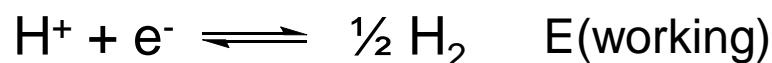
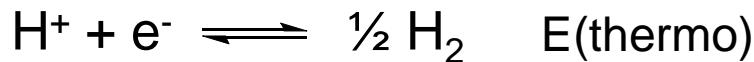
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What is the overpotential of this system?

## Overpotential for HER in water

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

$E(\text{thermo})$  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:

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

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

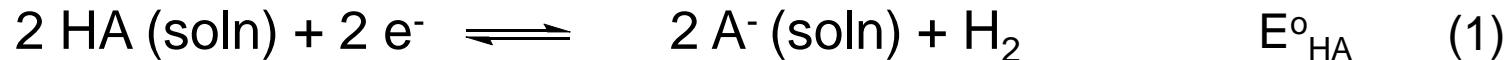
It is therefore easy to know the  $E(\text{thermo})$  for HER in water; we just need to know the pH. The  $E(\text{thermo})$  is identical to RHE.

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

## Overpotential in organic solvent

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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:

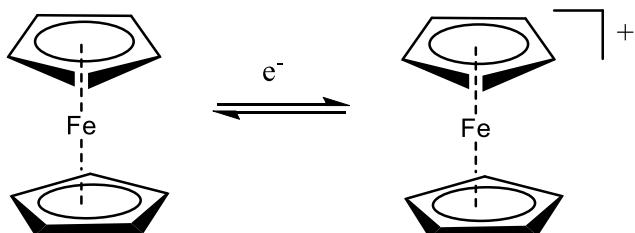
$$E_{\text{HA}}^{\circ} = E_{\text{H}^+}^{\circ} - (2.303RT/F)pK_{\text{a, HA}} = E_{\text{H}^+}^{\circ} - 0.059pK_{\text{a}} \quad (4)$$

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

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



$E^\circ_{\text{H}_+}$  has been determined in several solvents vs  $\text{Fc}/\text{Fc}^+$ :  
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

acid	acetonitrile		<i>N,N</i> -dimethylformamide	
	pK <sub>a</sub>	E <sub>HA</sub>	pK <sub>a</sub>	E <sub>HA</sub>
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

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Recall experimental conditions:

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

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

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

Calculate the overpotential of the system

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

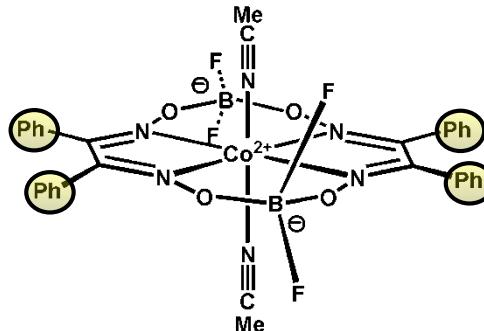
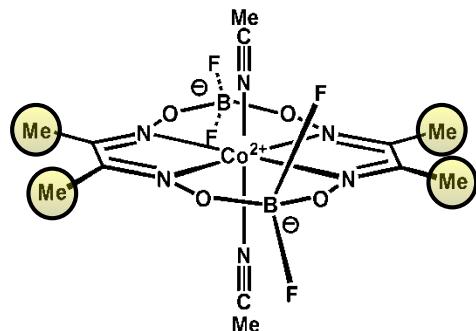
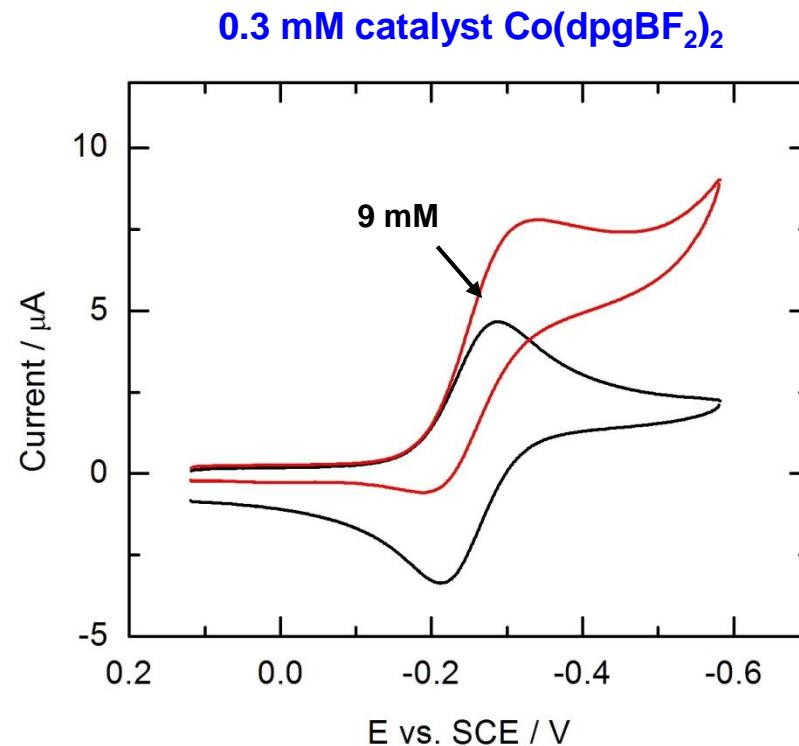
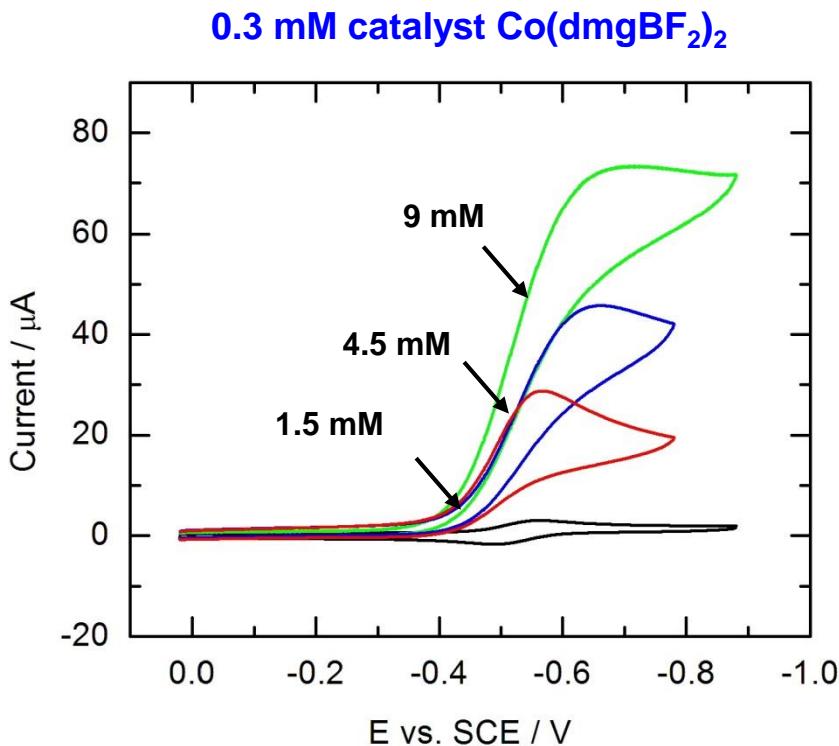
## **Case 2: A low-overpotential catalyst: Co complexes as HER catalysts**

***Well deserved nomination***

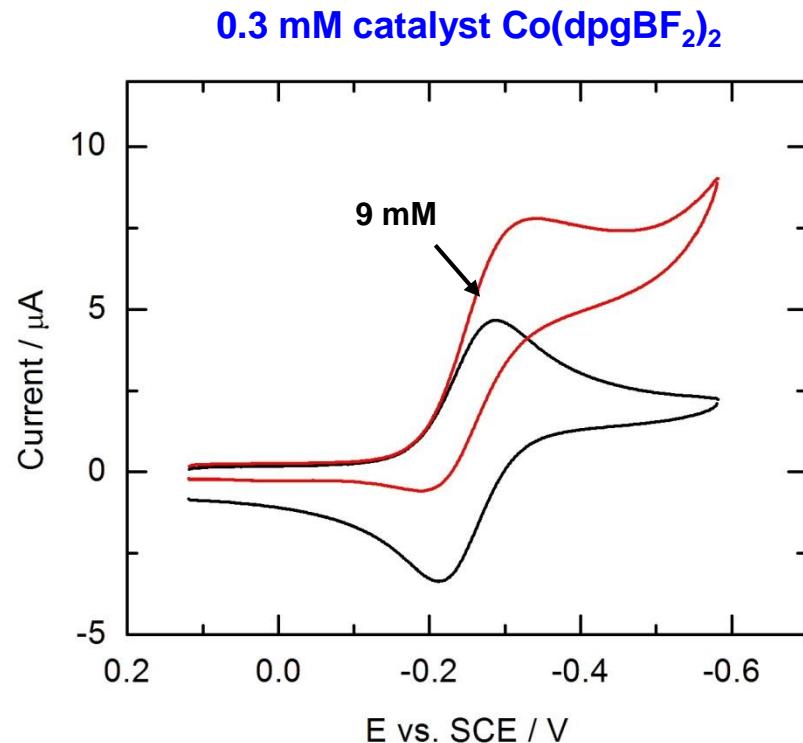
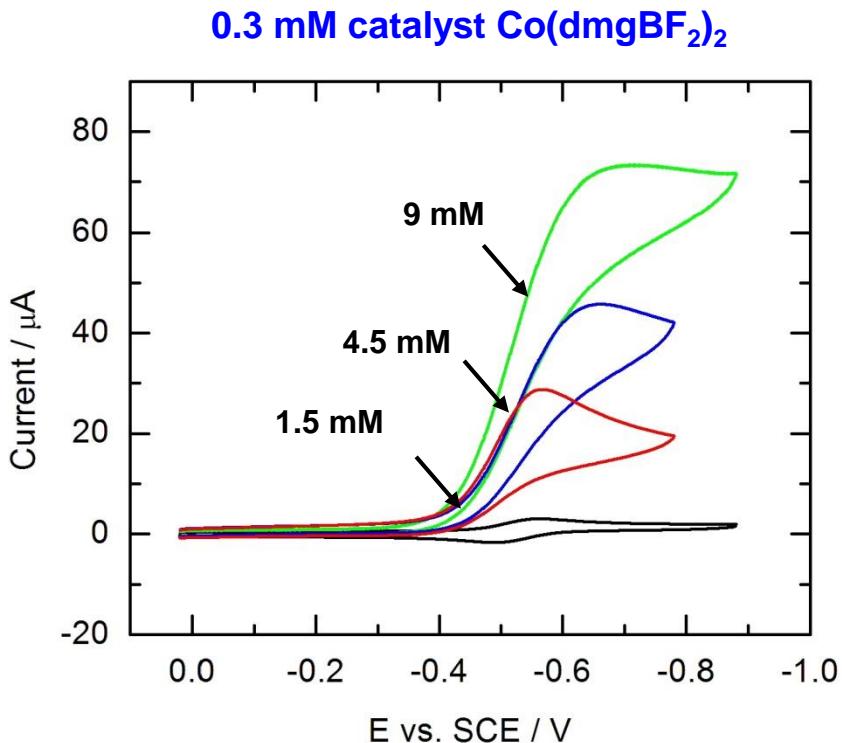


## Two catalysts with similar structures

TsOH·H<sub>2</sub>O in CH<sub>3</sub>CN, pK<sub>a</sub> = 8



## Comparison of catalysts



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.

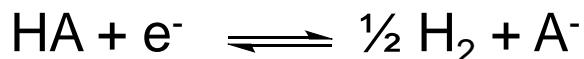
Overpotential at which catalysis occurs is different for different catalyst.

Co(dpgBF<sub>2</sub>)<sub>2</sub> has a smaller overpotential for HER than Co(dmgBF<sub>2</sub>)<sub>2</sub>.

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. 3

# Hydrogen Evolution at Low Overpotentials

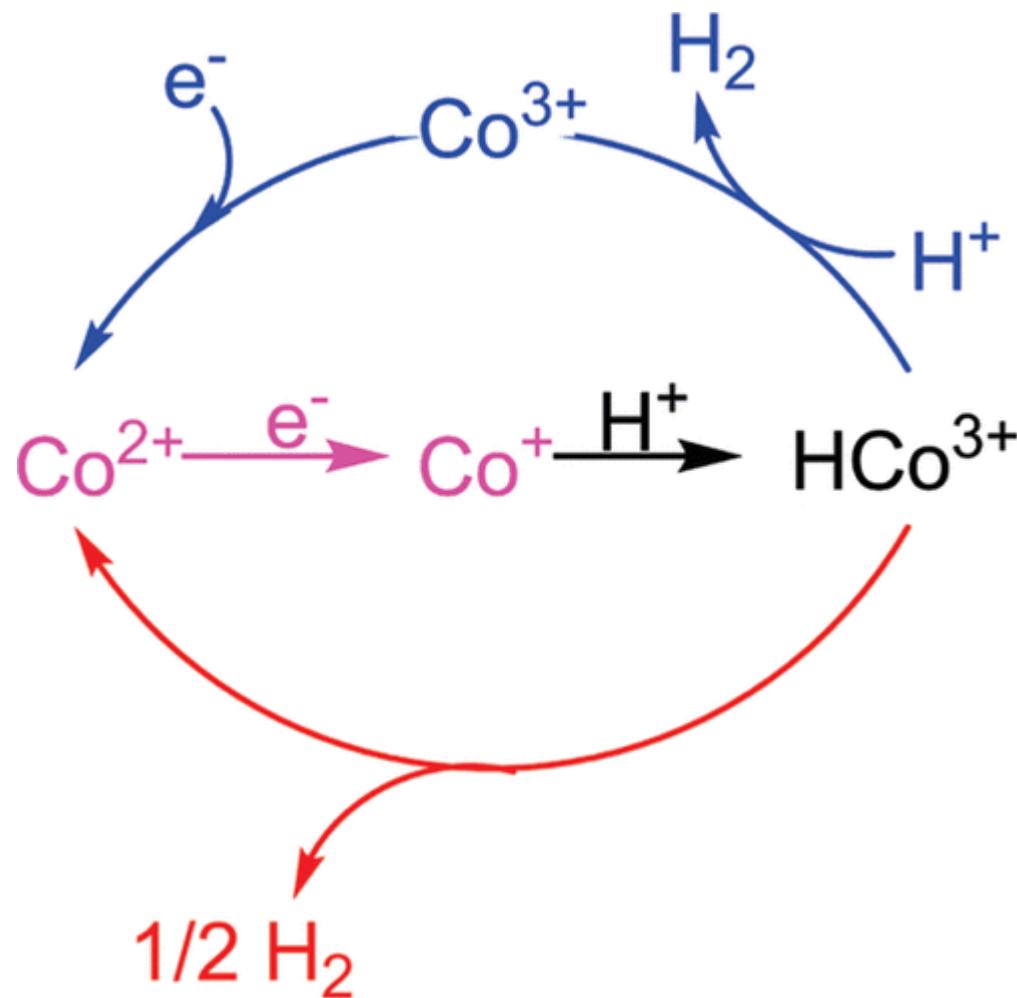


Proton Source	Thermodynamic potential for $\text{H}_2/\text{H}^+$ in $\text{CH}_3\text{CN}$ (V vs. SCE)	Starting E for HER in $\text{CH}_3\text{CN}$ (V vs. SCE)	Overpotential (mV)
$\text{CF}_3\text{COOH}$	-0.51	-0.55 ( $\text{Co}(\text{dmgBF}_2)_2$ )	40
$\text{TsOH}\cdot\text{H}_2\text{O}$	-0.23	-0.30 ( $\text{Co}(\text{dpgBF}_2)_2$ )	70

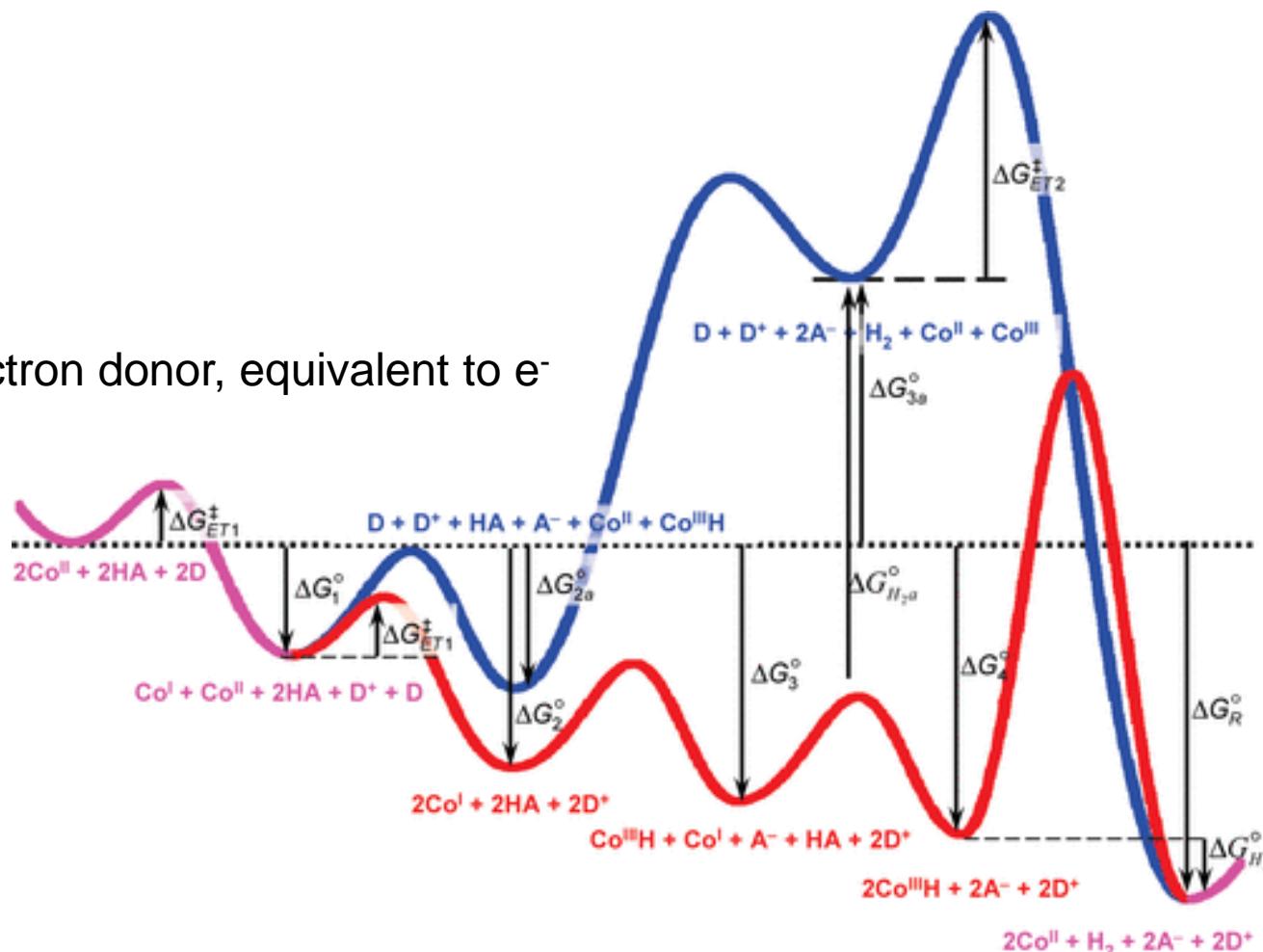
SCE is widely used in the literature as a reference potential. In  $\text{CH}_3\text{CN}$ ,  $\text{Fc}/\text{Fc}^+$  is 0.38 V vs. SCE.

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  $\text{CF}_3\text{COOH}$ .

## Two mechanistic possibilities

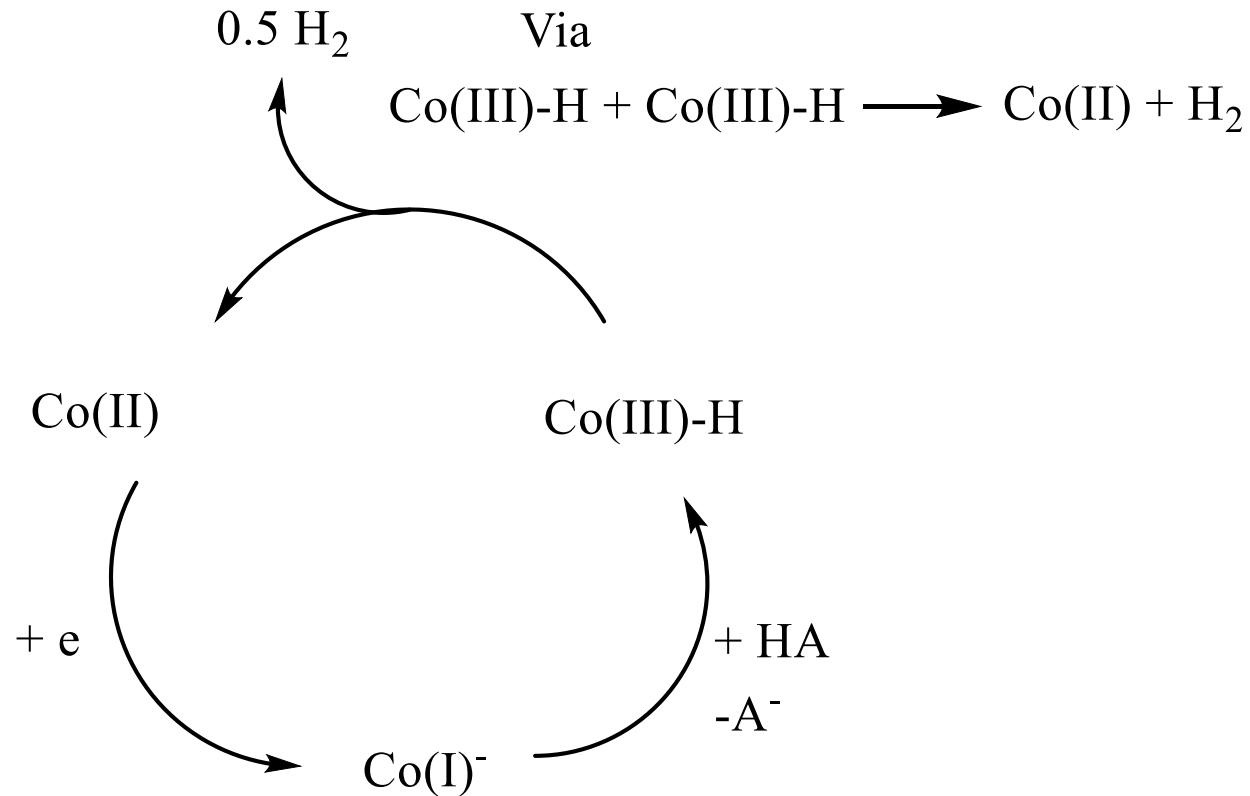


Thermodynamic analysis indicates that the bimetallic pathway is favored



D is an electron donor, equivalent to  $e^-$

## The favored mechanism



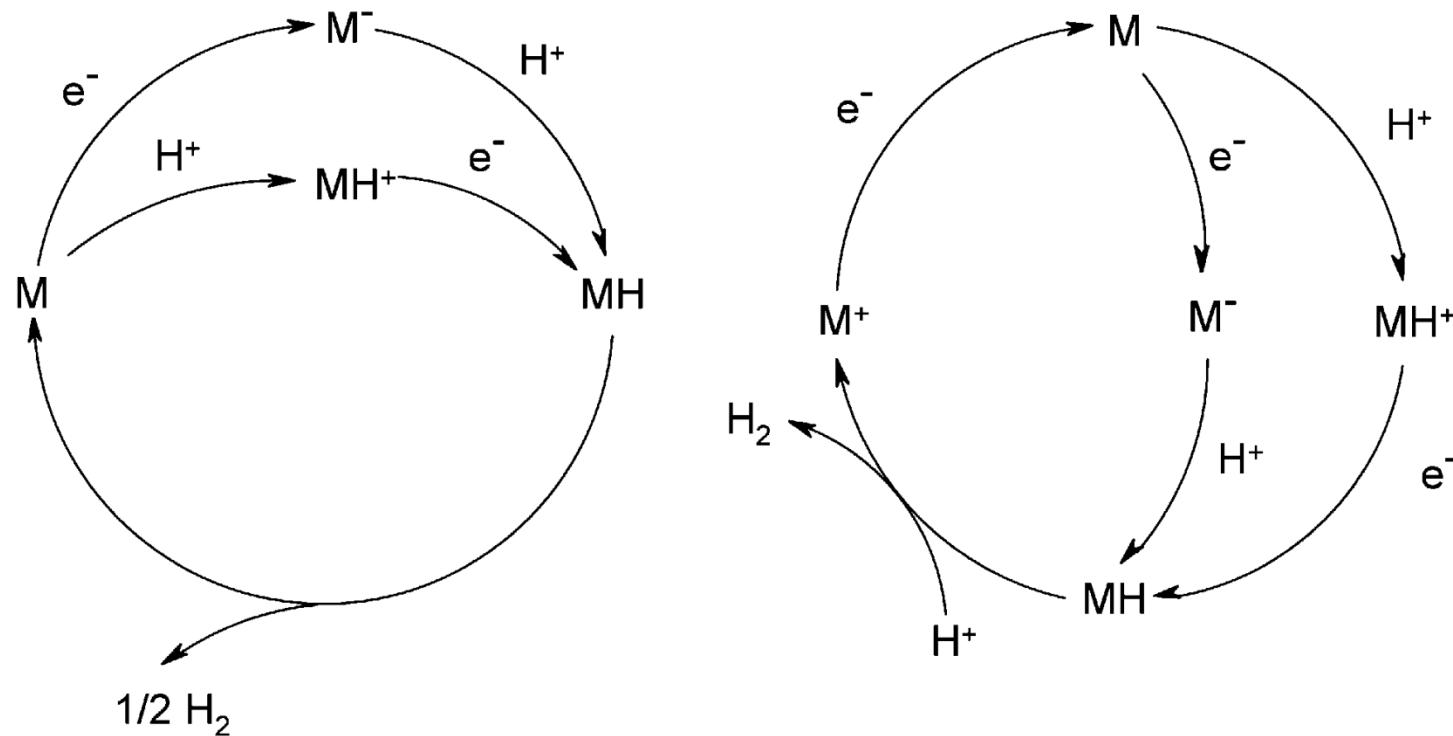
Exercise: Analysis of a catalyst (see separate file online posted after class)

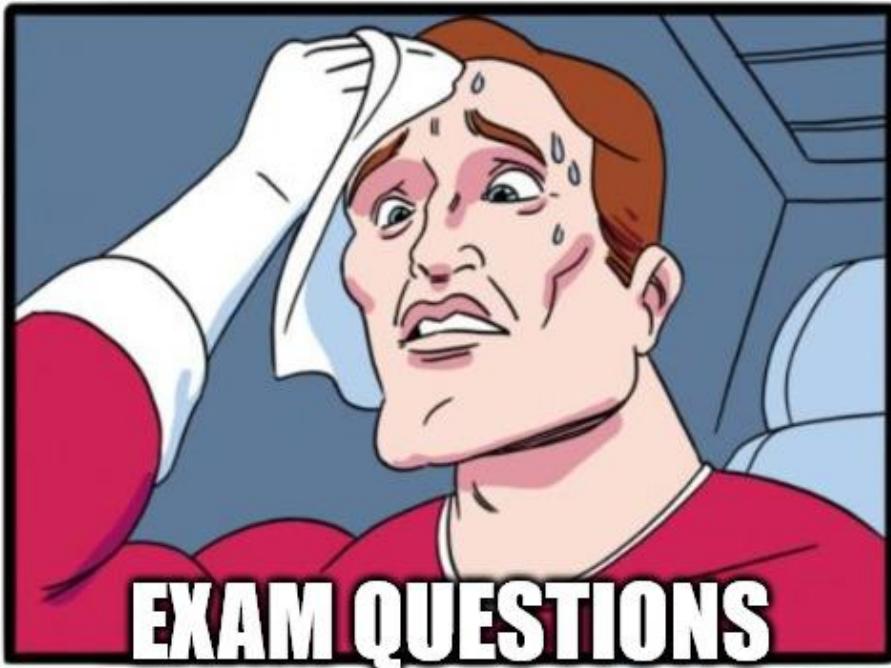
# General mechanism for HER catalyzed by molecular complexes

M represents  $ML_n$

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

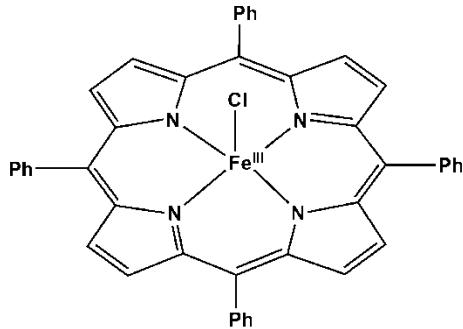
Monometallic  $H_2$  formation:  $MH + H^+ \rightarrow M^+ + H_2$





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

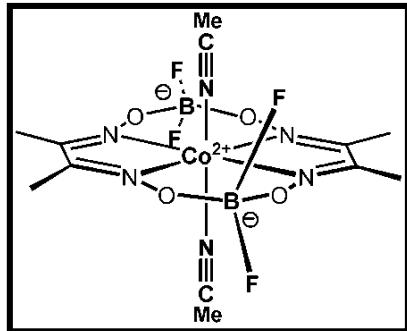
Typically lowering overpotentials of a system will lead to lower TOF.  
Can we lower overpotentials while keeping a high TOF?



Overpotential = 0.76 V

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

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



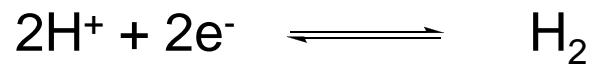
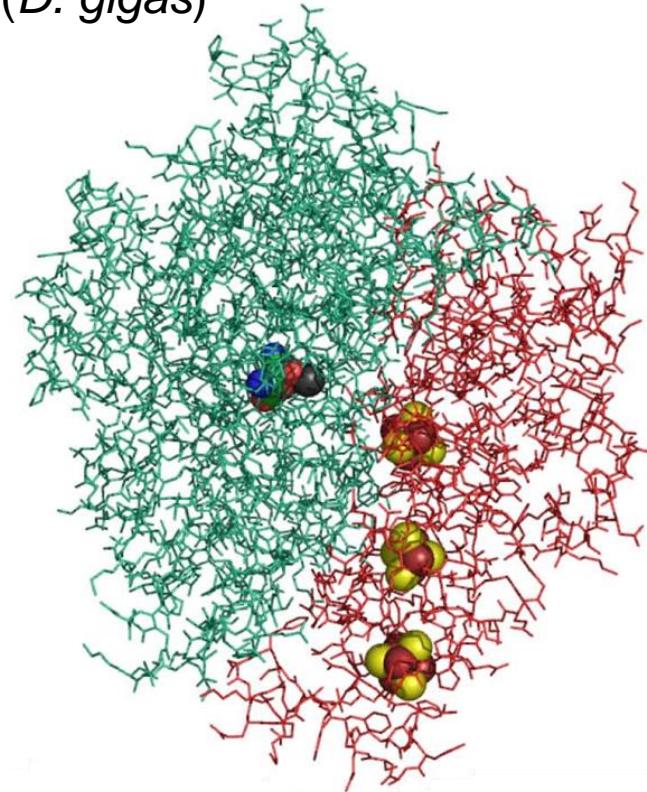
Overpotential = 0.04 V

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

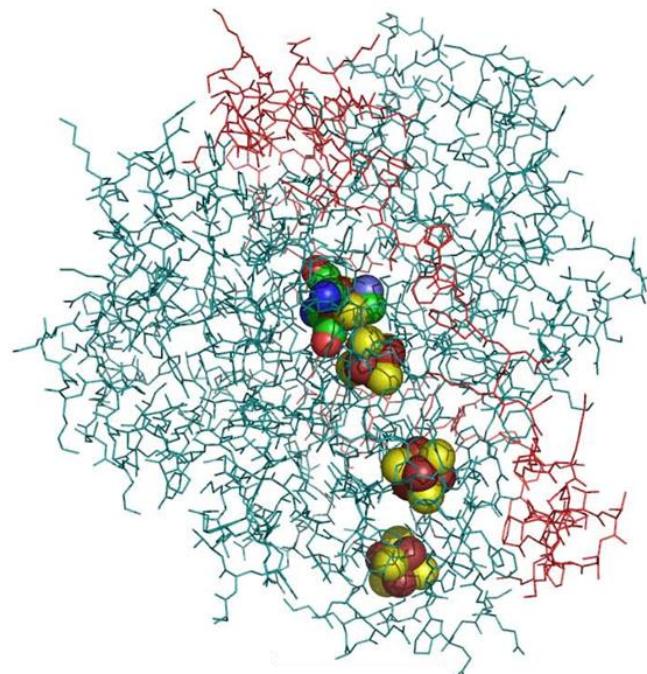
Try Biology!

# Hydrogenases Are Active H<sub>2</sub> Evolution Catalysts

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

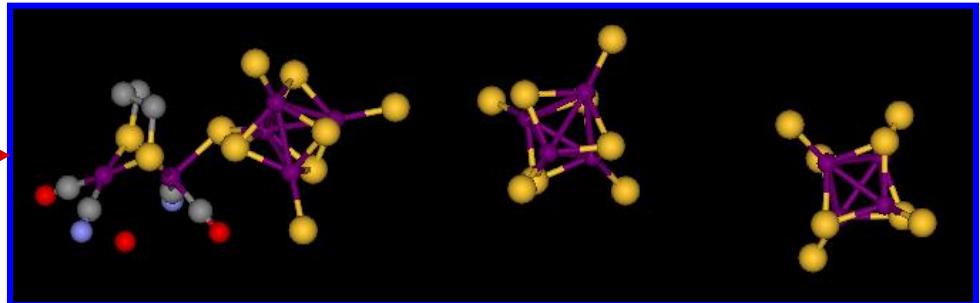
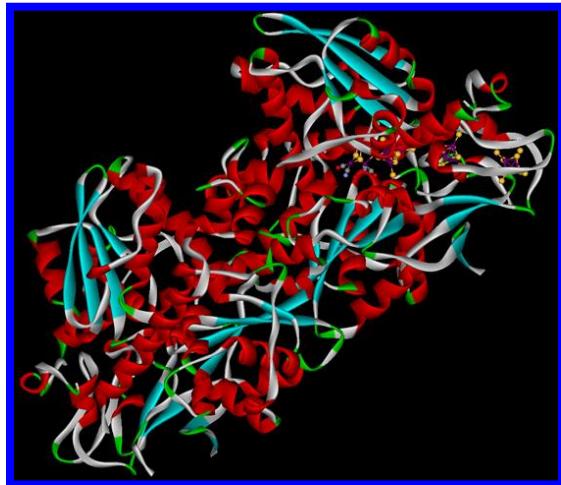


[FeFe]-hydrogenase  
(*D. desulfuricans*)

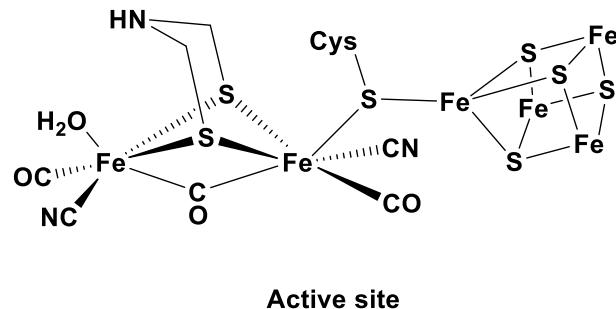


Activity: TOF= **700 - 9000 s<sup>-1</sup>** at  $\eta < 50$  mV  
Molecular weight: **50,000 - 90,000**

## The biomimetic approach



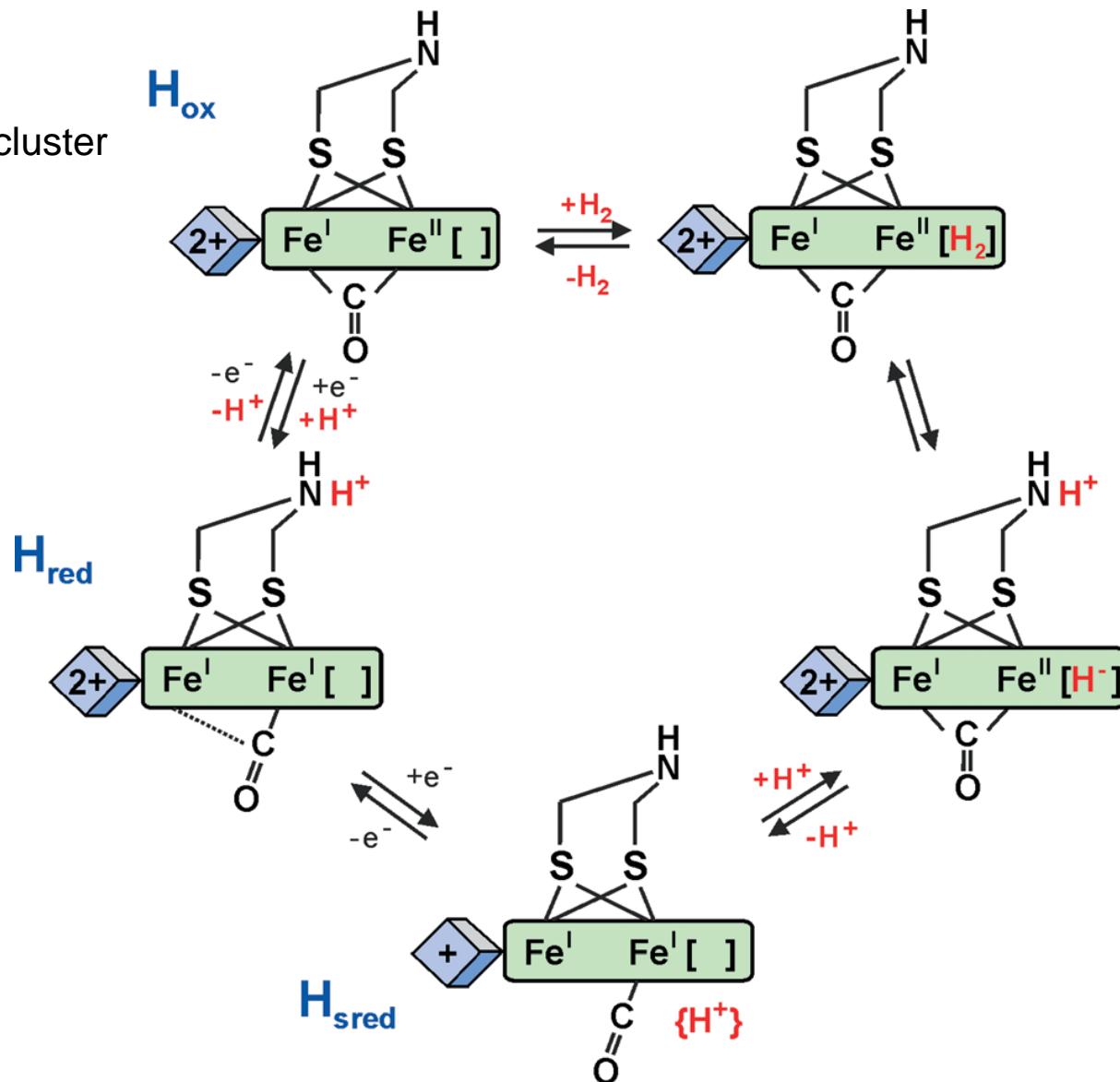
[FeFe]-hydrogenase



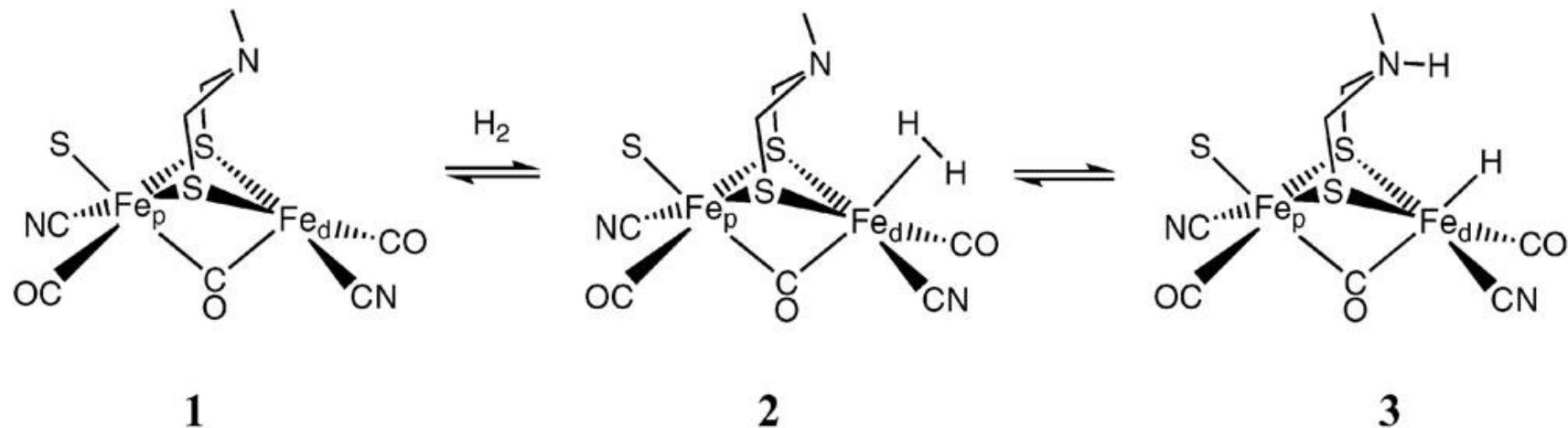
Over the years, many coordination complexes similar to the active site of hydrogenases have been prepared. These complexes are not as active as the enzymes, suggesting that the protein environment has an important role for catalysis.

# Proposed catalytic cycle for HER by [FeFe]-hydrogenase

Blue box : Fe-S cluster

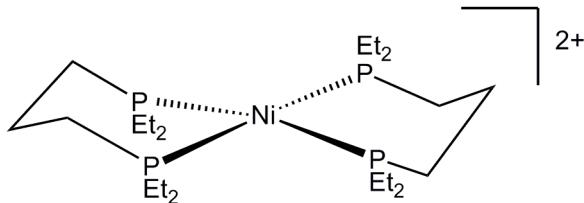


A special thing about the enzyme: The nitrogen atom is important to accept the proton

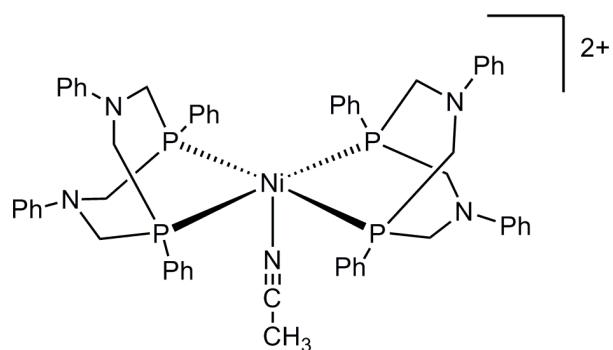


The intramolecular combination of proton and hydride might contribute to a superior catalytic activity, since intramolecular reactions often require less activation energy.

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



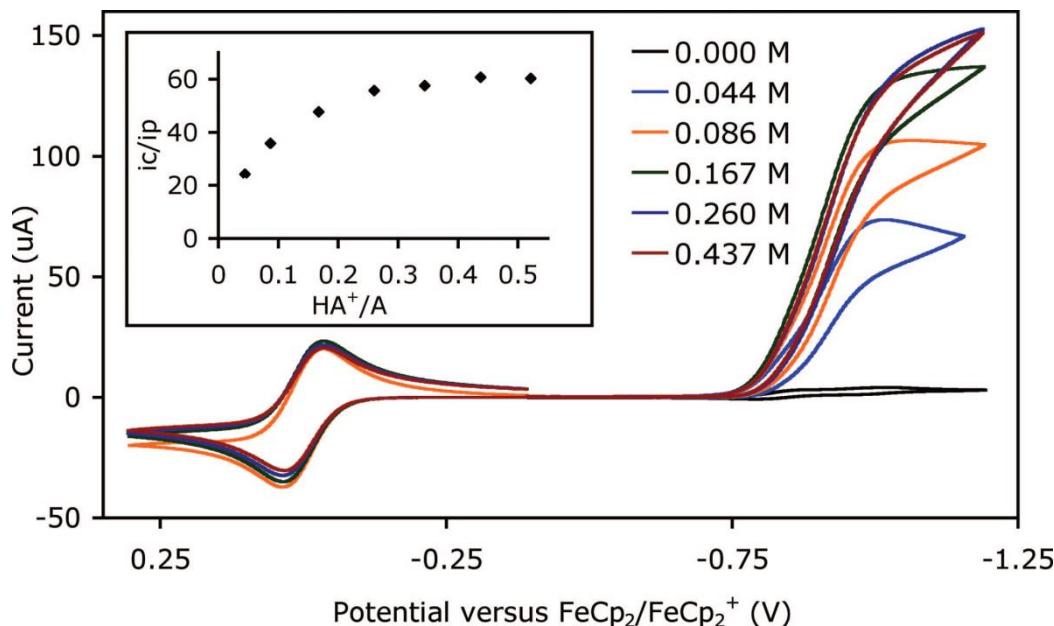
Not a catalyst



Catalyst

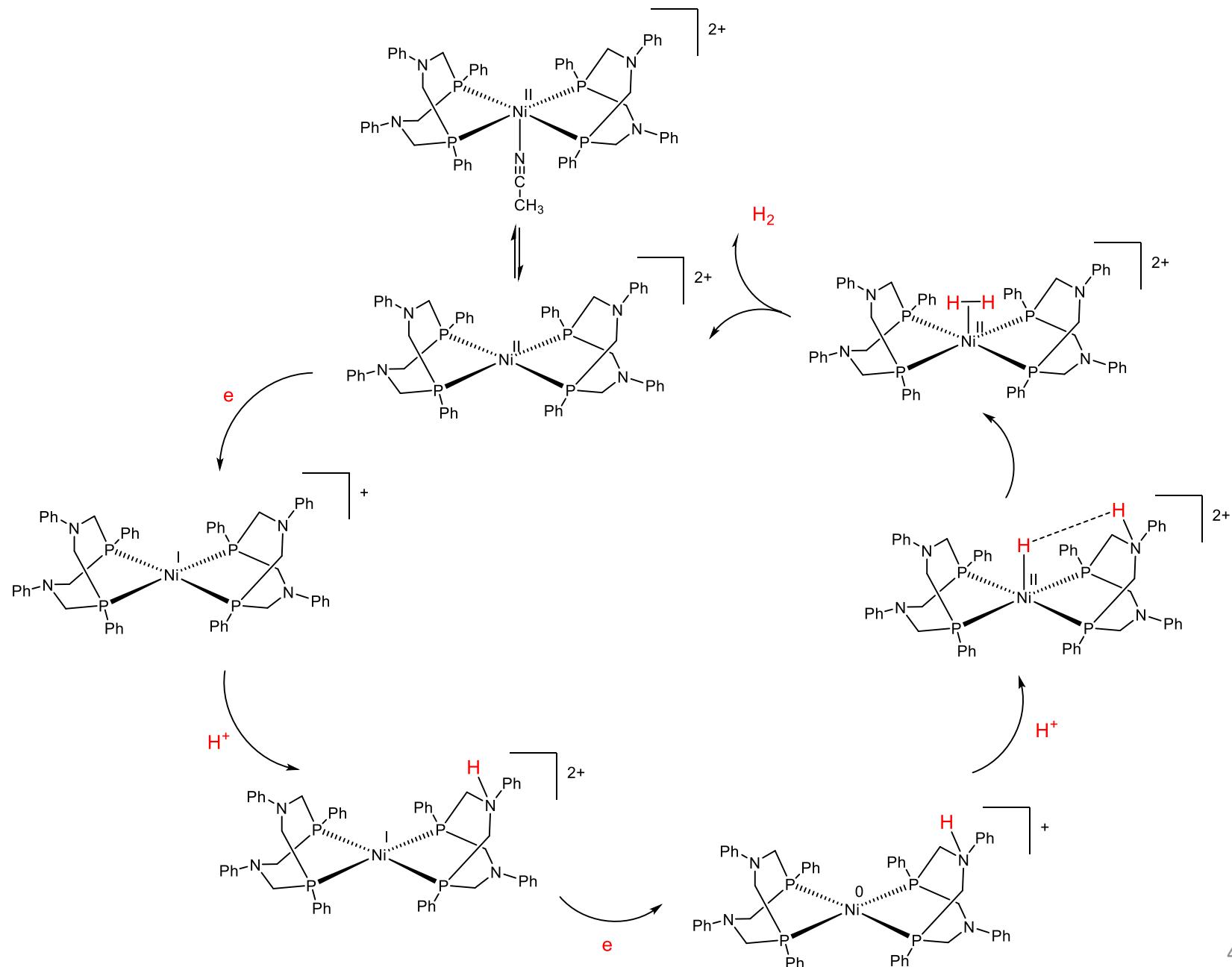


Catalyst (0.3 mM) in  $\text{CH}_3\text{CN}$ ;  
Acid was protonated DMF (DMFH)<sup>+</sup> ( $\text{pka} = 6.1$ ).

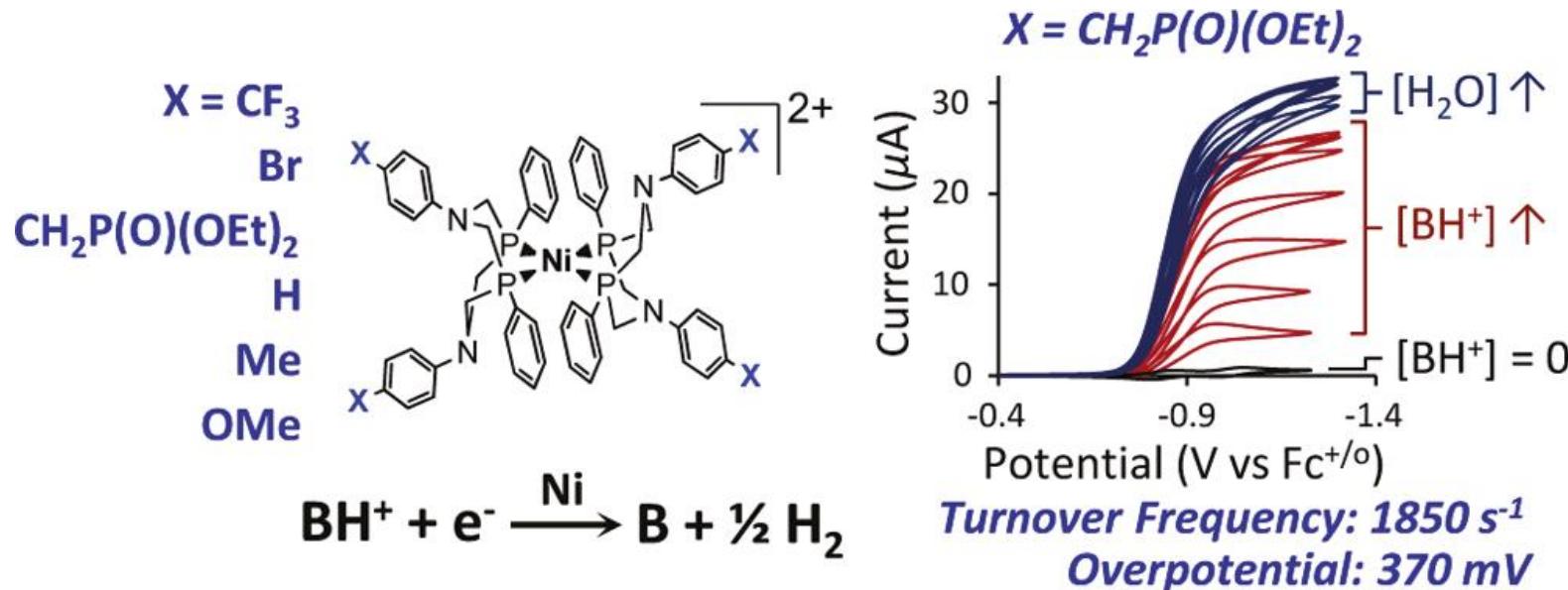


Catalytic wave observed at Ni(II)/Ni(I) couple; potential = -0.9 V vs.  $\text{Fc}/\text{Fc}^+$ ; overpotential 280 mV;  $\text{TOF} = 350 \text{ s}^{-1}$ . Current saturated at 0.3 M of acid.

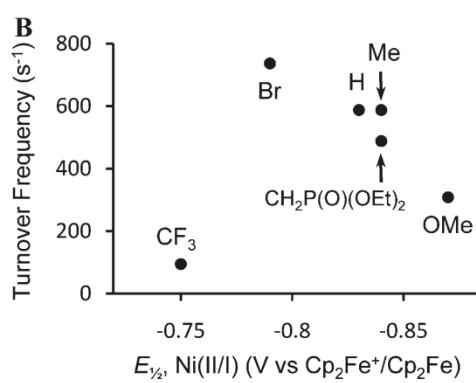
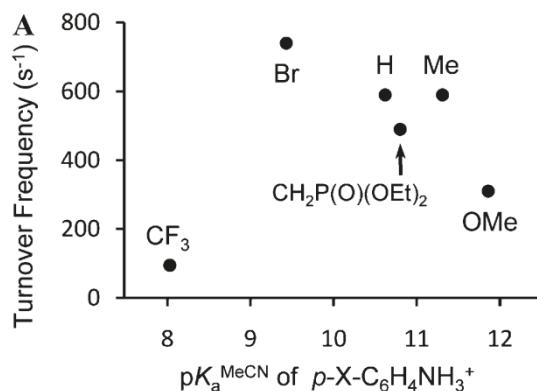
# Mechanism of HER involving pendant amine as proton relay:

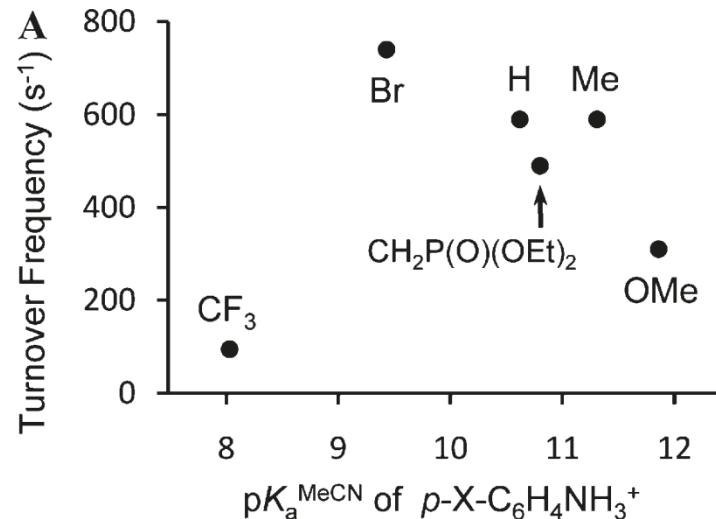
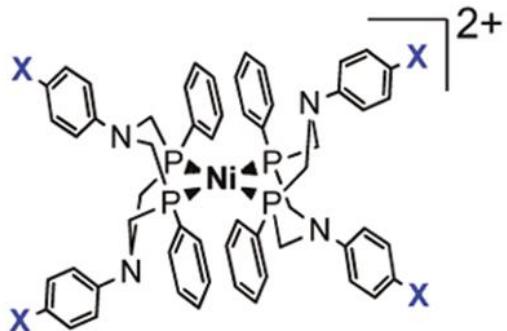


The substituents on phosphorus and nitrogen can be varied to turn the overpotential and turnover frequencies of the system.

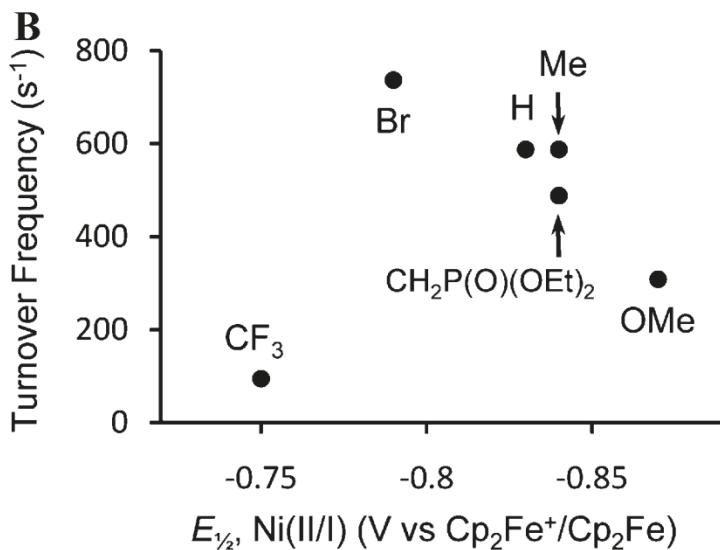


For example, among these 6 catalysts, the following relations were determined:





The TOF depends on pKa of pendant amine, but not linearly.



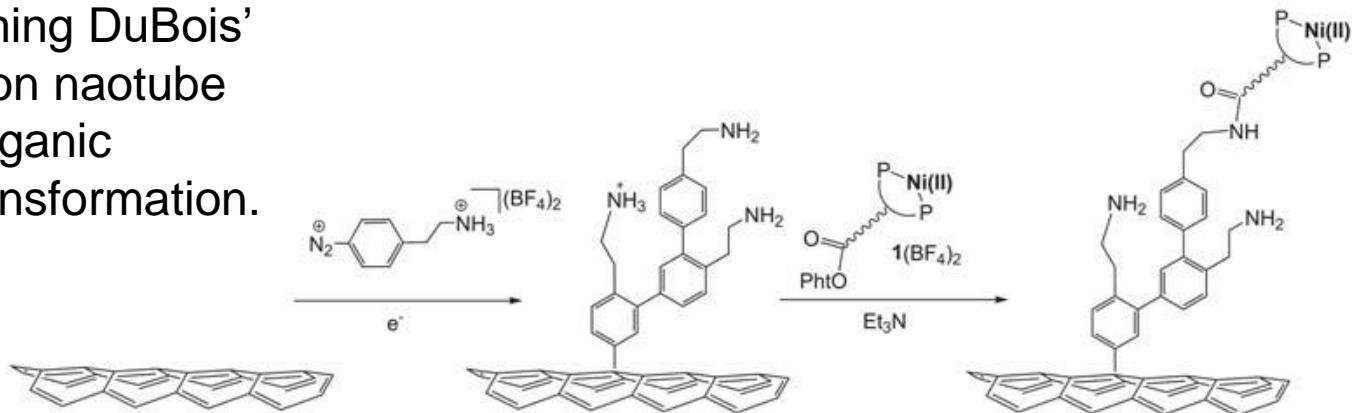
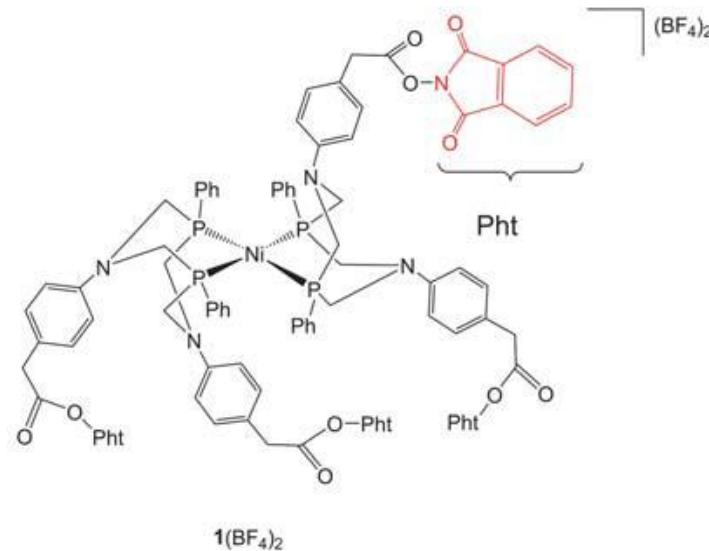
The TOF depends on overpotential, but again not linearly.

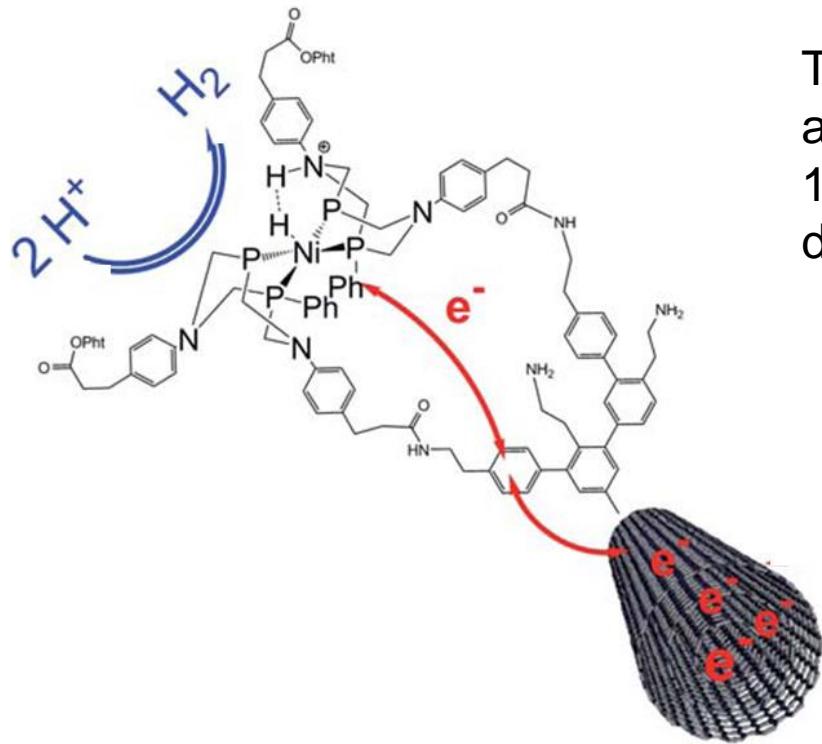
Structure-activity of this type will lead to an optimized catalyst, with high TOF and low overpotential.

# 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;  $4 \text{ mA/cm}^2$  at an overpotential of  $300 \text{ mV}$ ;  $\text{TOF} = 3 \text{ s}^{-1}$ ; 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.
- 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.