



Electrocatalysis with Discrete Transition Metal Complexes in Energy Conversion Systems



Chris Chidsey

Department of Chemistry, Stanford University

Other Team Members

Prof. Dan Stack

Prof. Bob Waymouth

Nick Conley

Charles McCrory

Ron Painter

Xavier Ottenwaelde

Anando Devadoss

David Pearson

Liezel Labios

GCEP Symposium, September 19, 2006

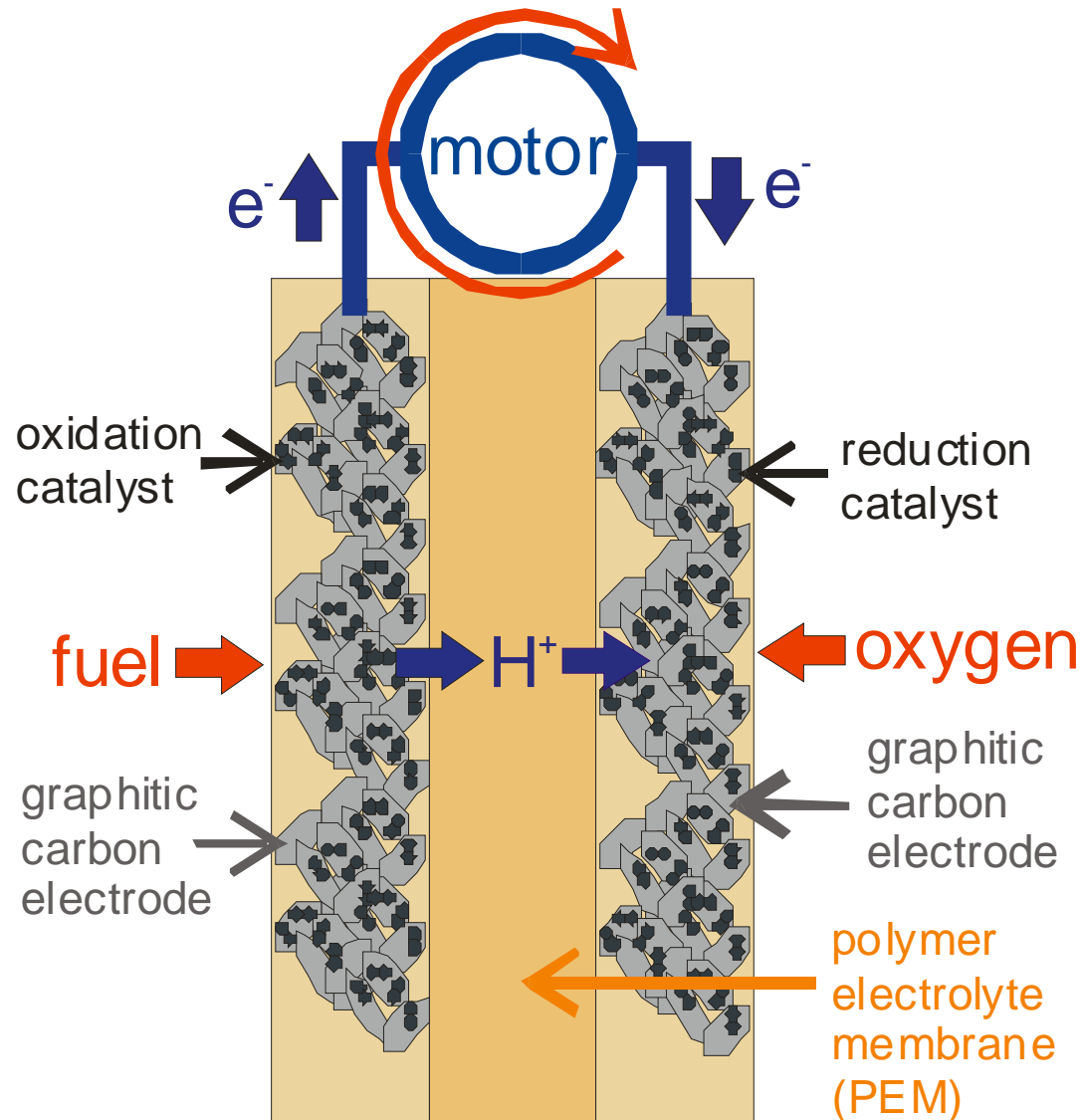


Outline



- Hydrocarbon Fuel Cells:
The Optimal Mobile Power Source?
- Electrocatalytic Reversibility:
From Efficient Power Delivery To Efficient Energy Storage
- Molecular Electrocatalysts on Carbon Electrodes
- The Ubiquitous Problem of O₂ Reduction
- The Many Challenges of Hydrocarbon Oxidation
C-H Activation, C-C Activation, CO Oxidation

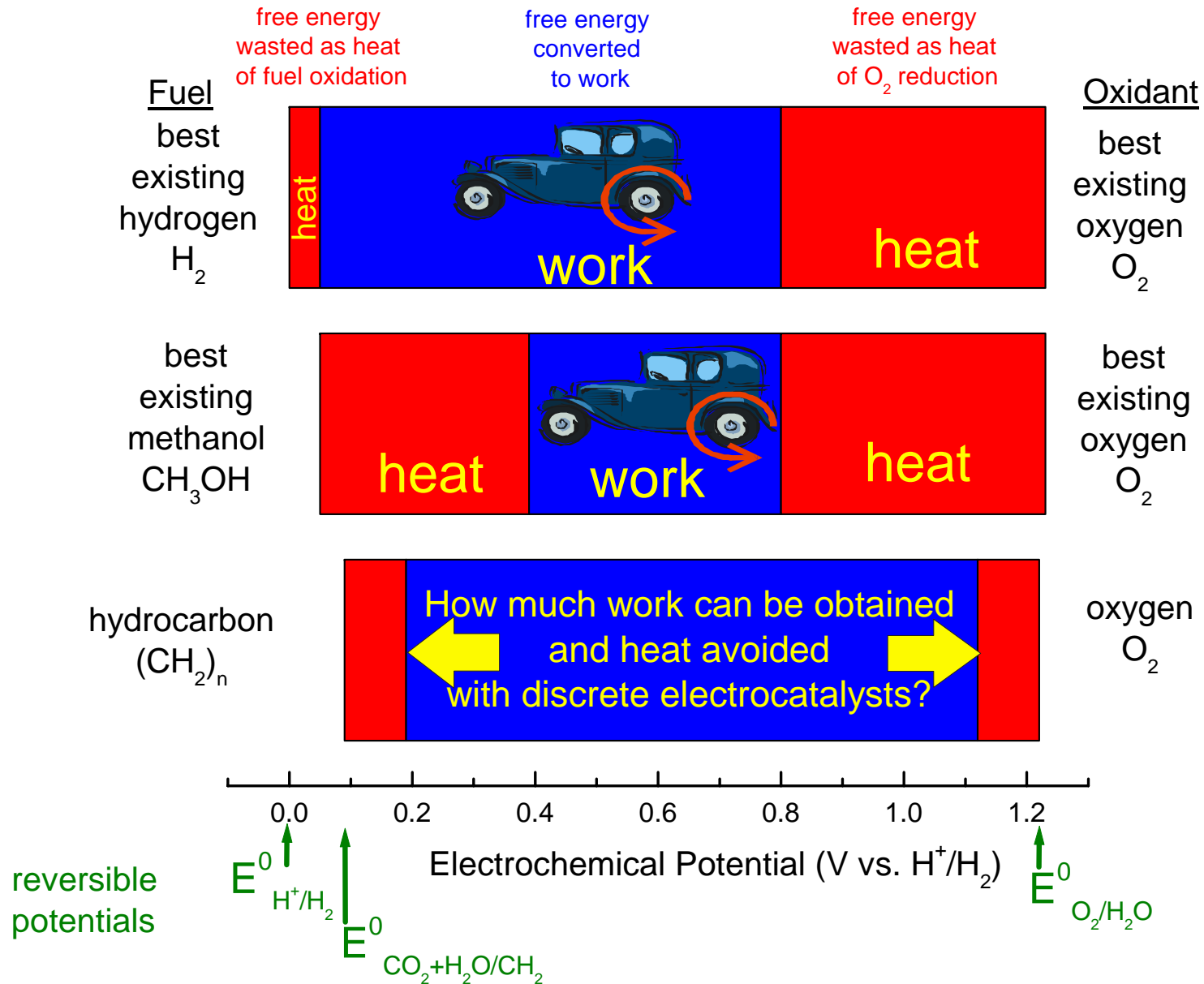
Polymer-Electrolyte-Membrane Fuel Cell



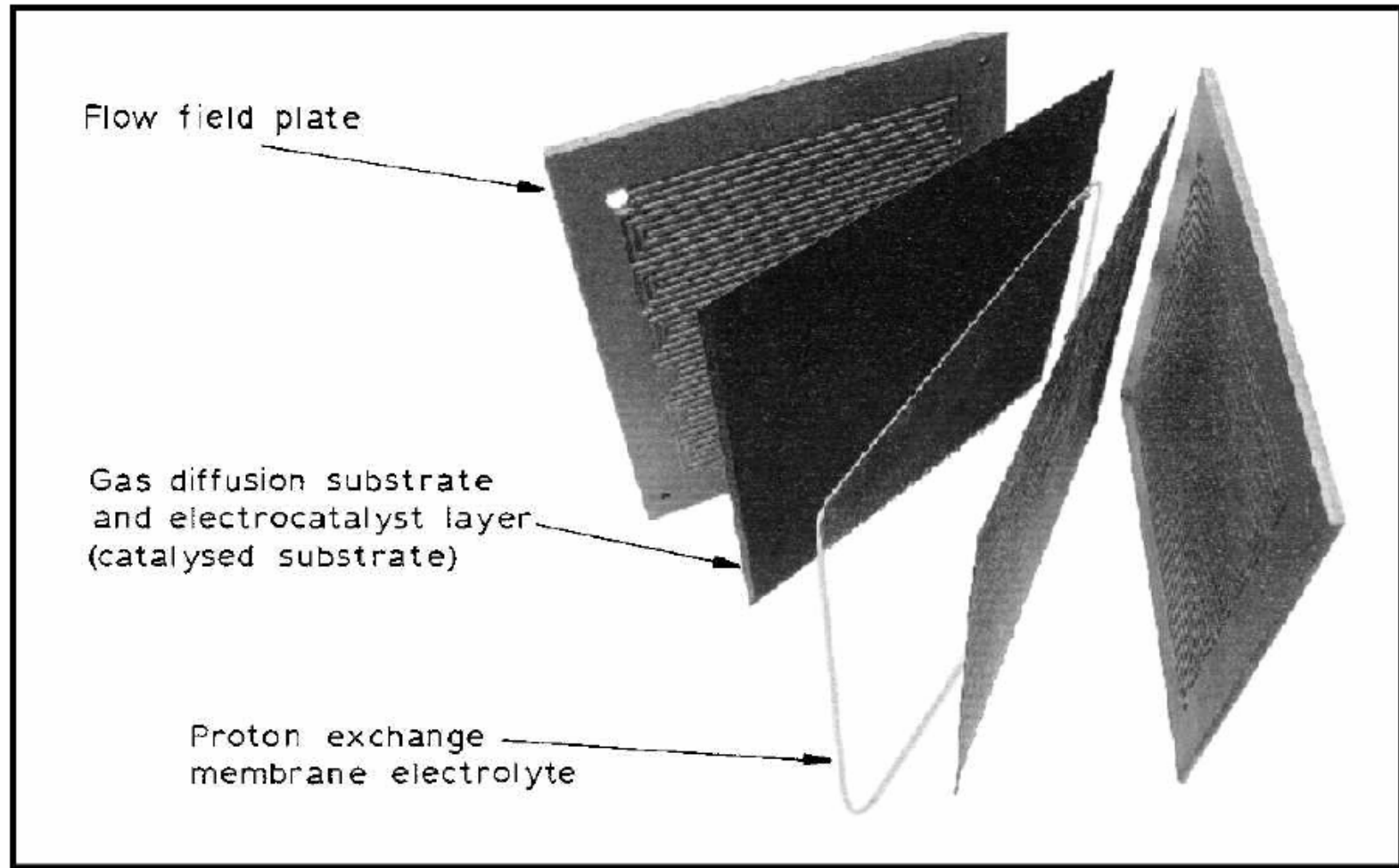
The Atkins Diet for Fuel Cells: Benefits of Long-Chain Hydrocarbons for Mobile Fuel Cells

- Twice the volumetric energy density of methanol
 - kerosene or diesel ~ 8 kWh/L
 - methanol ~ 4 kWh/L
- Twice the gravimetric energy density of methanol
 - kerosene or diesel ~ 10 kWh/kg
 - methanol ~ 5 kWh/kg
- Water insoluble, low flammability, low toxicity
- Existing production and delivery infrastructure
- Reduced leakage through polymer-electrolyte membrane

Electrocatalyst Efficiency



Can we find catalysts to insert into existing device?



*The basic unit cell of a proton exchange membrane fuel cell is assembled in the required numbers to deliver the necessary power output. The component layers of the membrane electrode assembly (two catalysed substrates and the PEM electrolyte) are laminated together and located between the flow field plates to form the unit cell (T. R. Ralph and M. P. Hogarth, *Platinum Metals Rev.*, 2002, **46**, (1), 3–14.)*

Leverage Ongoing Engineering of Polymer Electrolyte Membrane (PEM) Fuel Cells

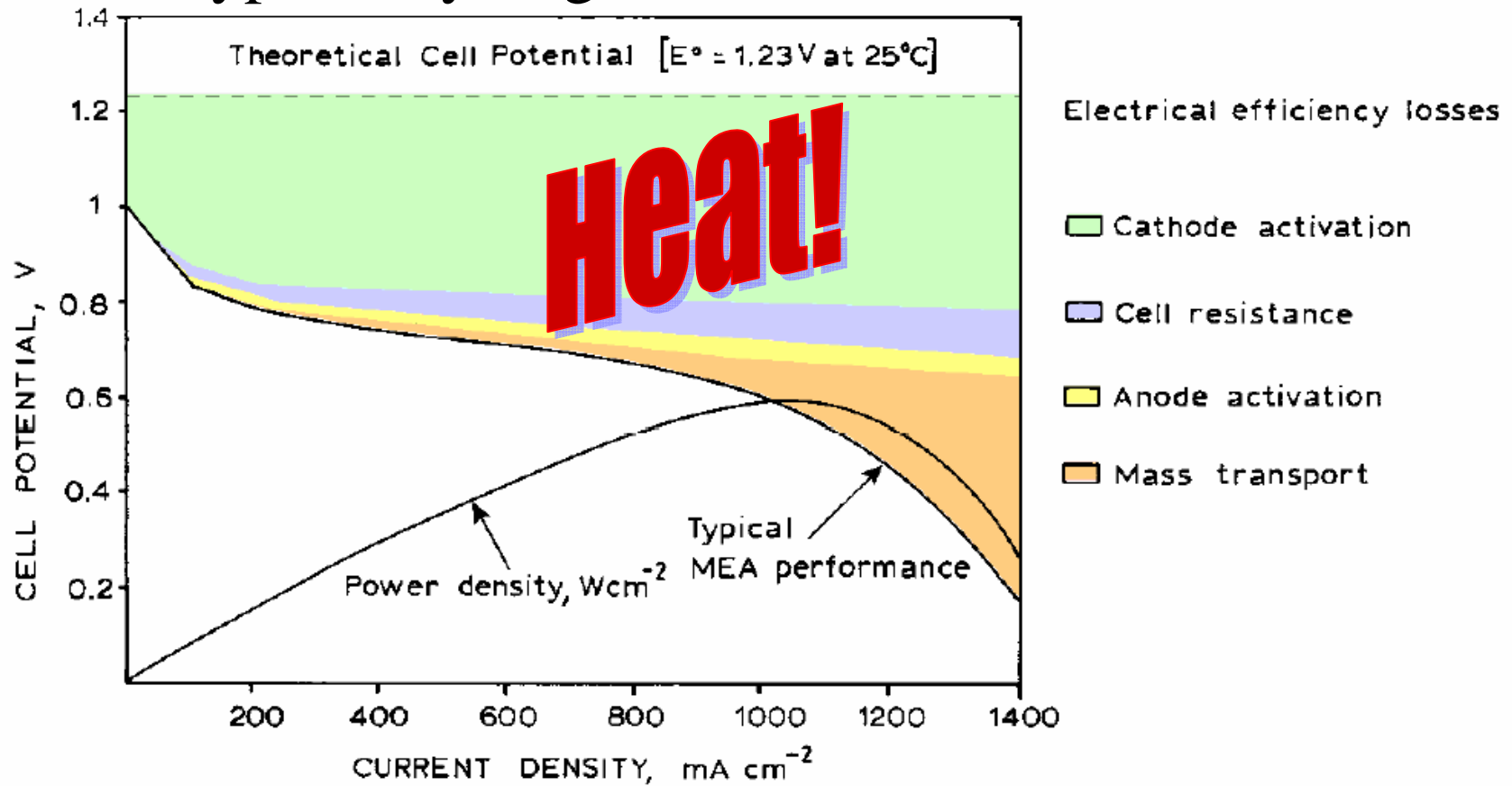
Benefits:

- Highly engineered mass and ion transport
- Robust, high-surface-area carbon-particle electrodes
- Highly developed electrical interconnects
(bipolar plates, corrosion resistance, etc.)
- Highly developed fuel and air systems
- Well developed thermal and water management

Challenge:

- Efficient and stable electrocatalysts in strong acid

Typical Hydrogen Fuel Cell Losses



*Schematic showing the typical cell potential versus current density output from an MEA operating on pure hydrogen and pure oxygen. The major factors that control the MEA performance in the various regions of the cell potential versus current density curve are identified along with their relative contribution to the electrical efficiency losses (T. R. Ralph and M. P. Hogarth, *Platinum Metals Rev.*, 2002, 46, (1), 3–14.)*

Toward Electrocatalytic Reversibility For Efficient Power Delivery

The Problem:

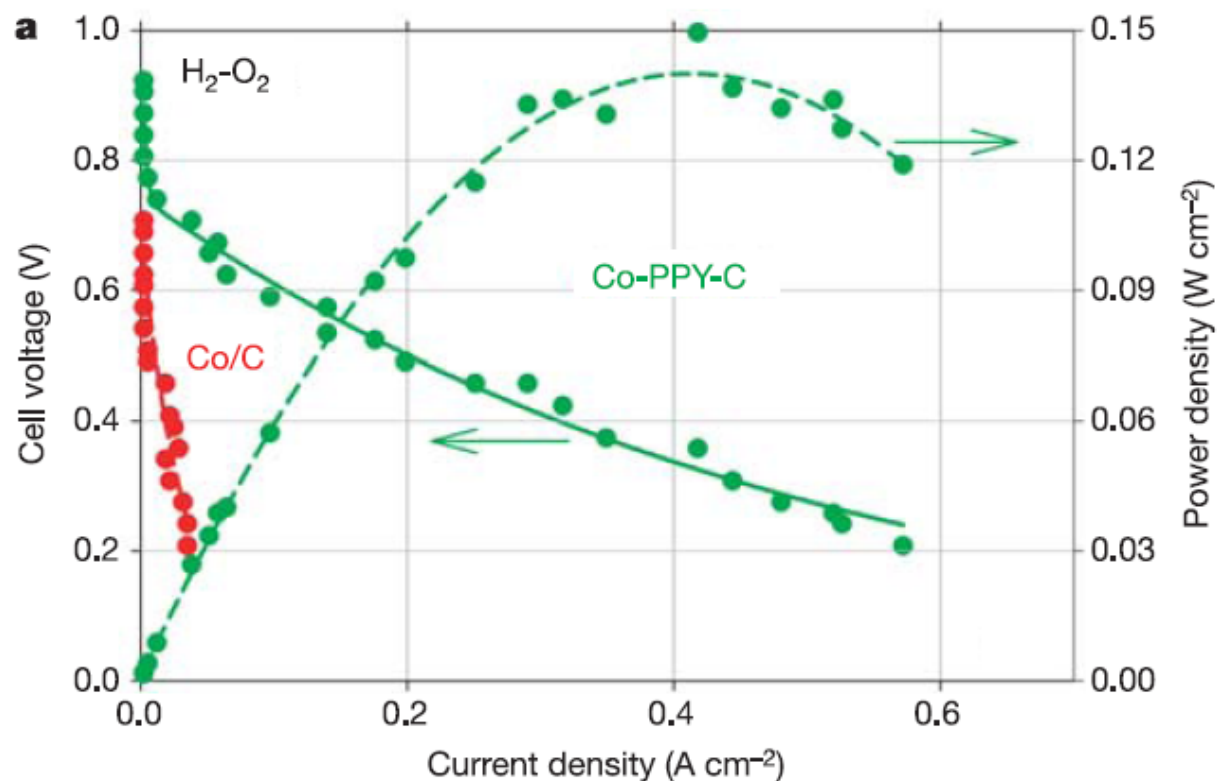
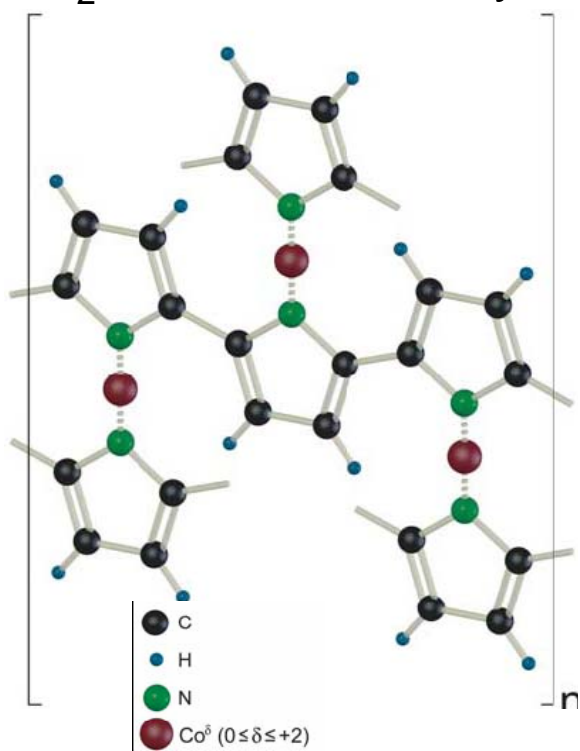
- Oxygen reduction (even in H₂ PEM cell) is highly inefficient – wastes ~30% of energy as heat.
- Methanol oxidation wastes at least 25% of energy
- Higher alcohol and hydrocarbon electrocatalysts are essentially non-existent

The Goal:

- Reduce the overpotentials needed to drive each step of O₂ reduction and each step of hydrocarbon oxidation.
- Requires faster rates at lower overpotentials

Recent Progress Using Non-Noble Ion Complexes with Polymers on Carbon

O₂-Reduction Catalyst



R. Bashyam, P. Zelenay, *Nature* 443, 63 (2006)

Electrocatalytic Reversibility II: Efficient Energy Storage

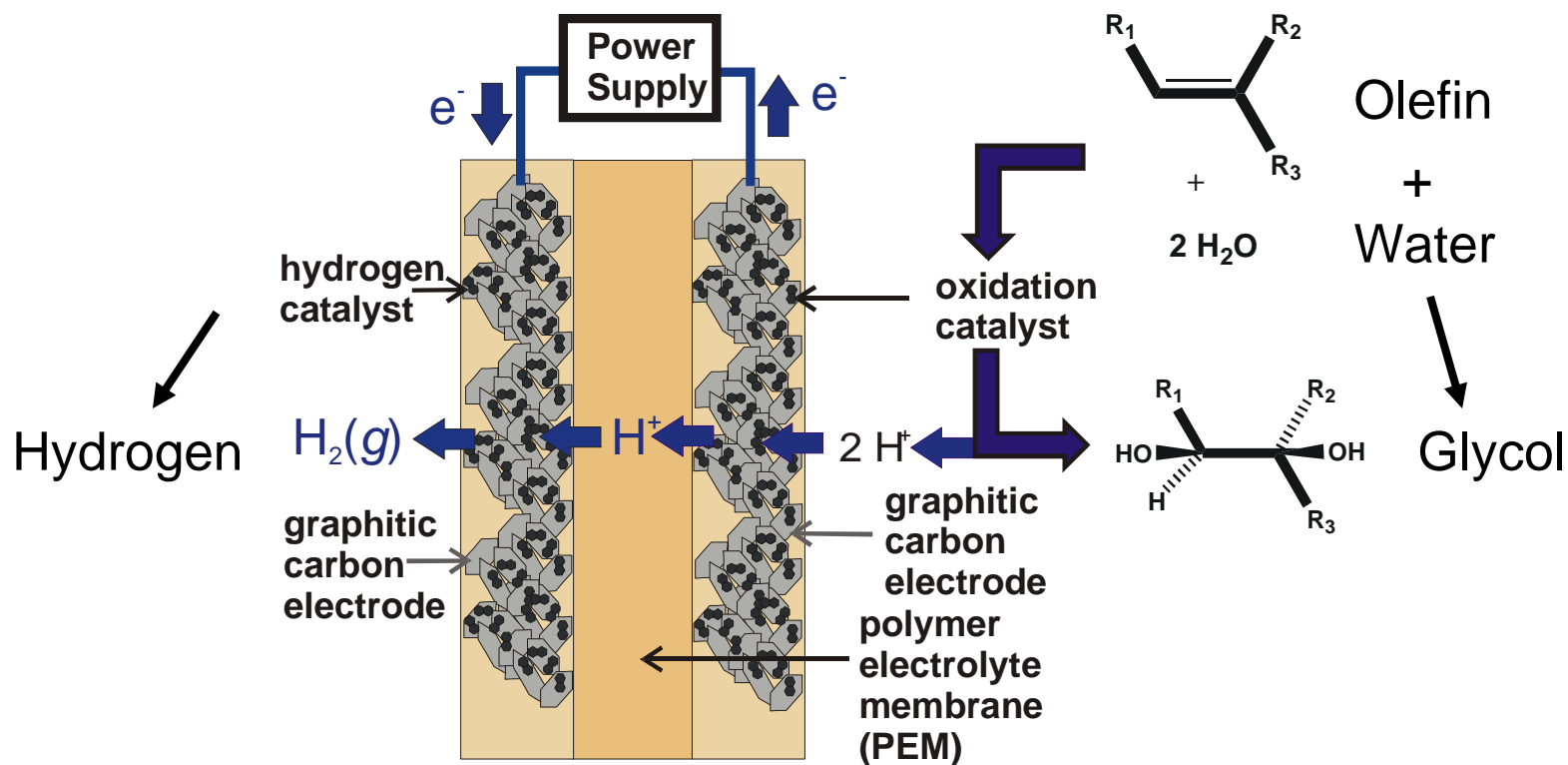
The Holy Grail:

- Truly reversible electrocatalysts could be used to reverse the fuel cell.
- Generate liquid fuel when electricity is plentiful for use when it is not.



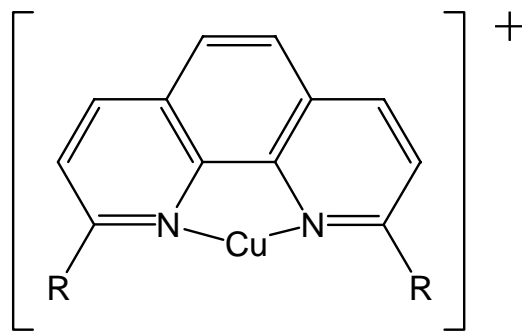
Electrocatalytic Reversibility III: Energy- and Atom-Economical Selective Chemical Transformations

Use every atom in reactants to make valuable products with minimal wasted energy.



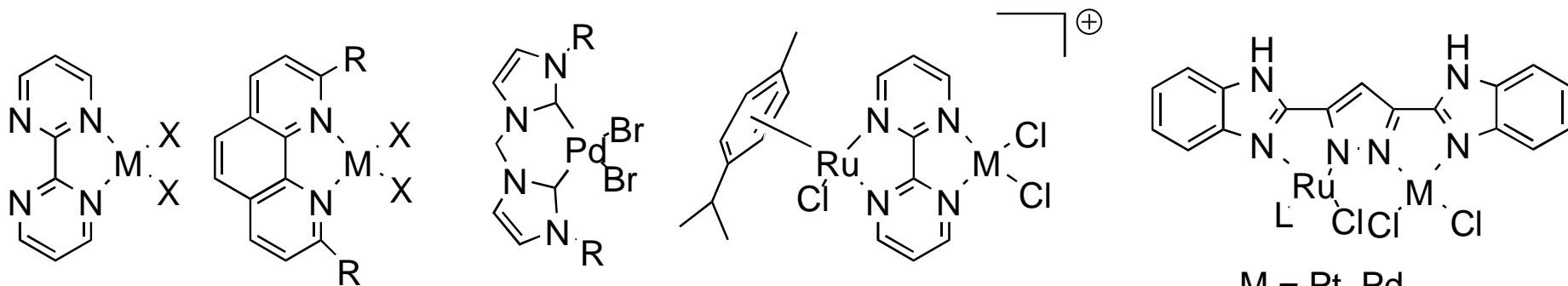
Molecular Electrocatalysts on Carbon Electrodes

- Current PEM-cell electrocatalysts are noble metal nanoparticles – limited ability to tailor reactivity
- Use coordination complexes of one or a few metal atoms strongly adsorbed to graphitic carbon
- For instance, copper complexes of phenanthroline adsorb strongly in water to graphite electrodes and electrocatalyze O₂ reduction.



Lei & Anson, *Inorg. Chem.* 32, 1083-1089 (1995)

Some Other Possible Aromatic Complexes Of Late Transition Metals



M = Cu, Pd, Pt, Ru, etc.

M = Pt, Pd
L = terpy, cymene

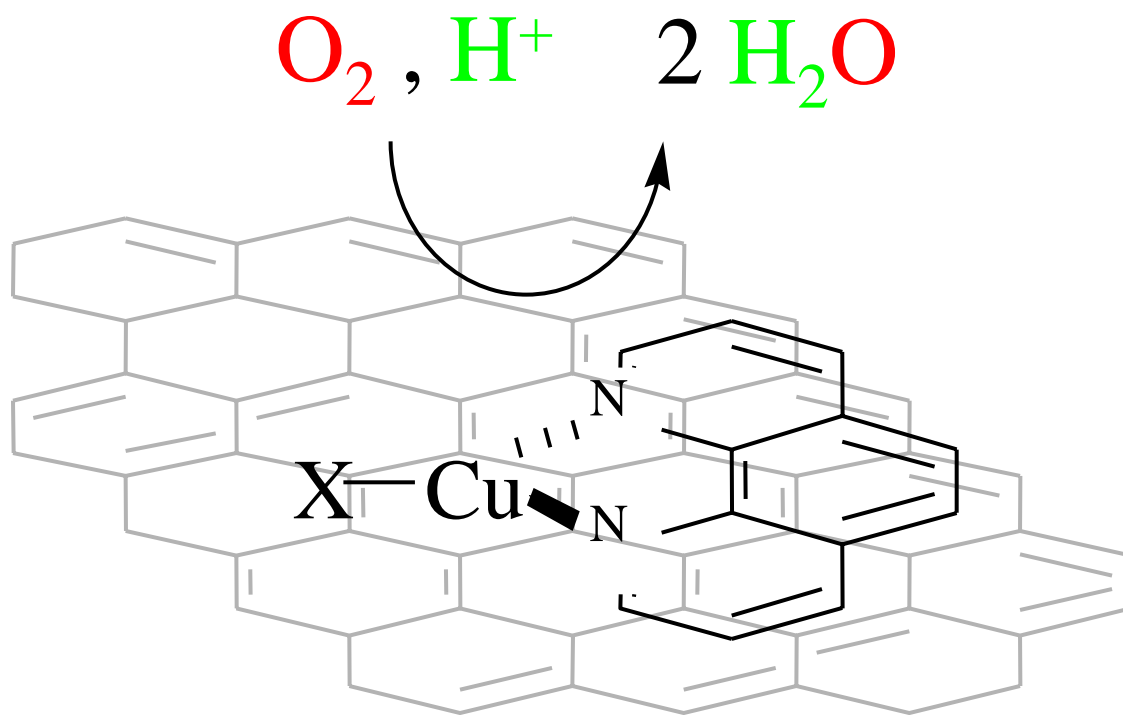
- All adsorb avidly to graphitic surfaces from water.
- Larger aromatic units can be appended to increase avidity
- Covalent bonding between aromatic and graphite can be used if needed (reduction of aryl diazonium ions etc.)

The Ubiquitous Problem of O₂ Reduction: The Prospect of Cu-Based Catalysts

- Trinuclear Cu(I) site in laccase enzymes can reduce O₂ at very positive potentials
- Laccase overpotential is only **-70 mV**
- Pt overpotential is **-370 mV**
 - Soukharev, Mano & Heller, *J. Am. Chem. Soc.* 126, 8368 (2004).

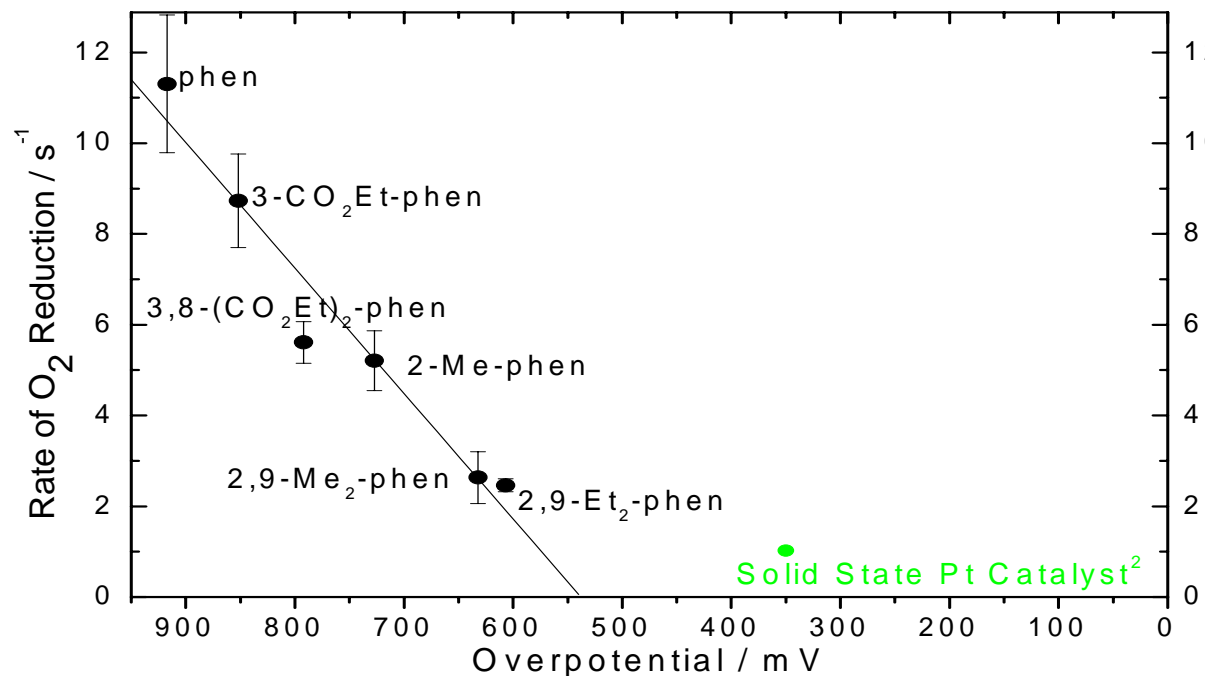
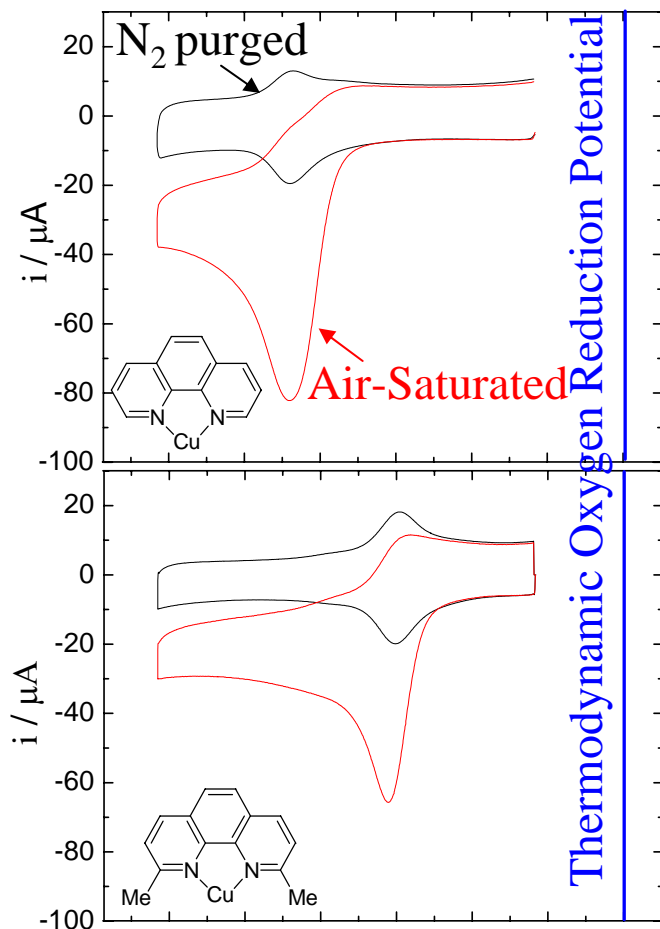
Initial Study: One Copper Ion

Proposed Mechanism: Transfer an electron from Cu(I) to the O_2 and then bind the resulting superoxide anion (O_2^-) to the Cu(II) to start reduction



$4e^-$ *Graphite*
Electrode

O₂ reduction as a function of substitution on phen ligand of Cu(I)

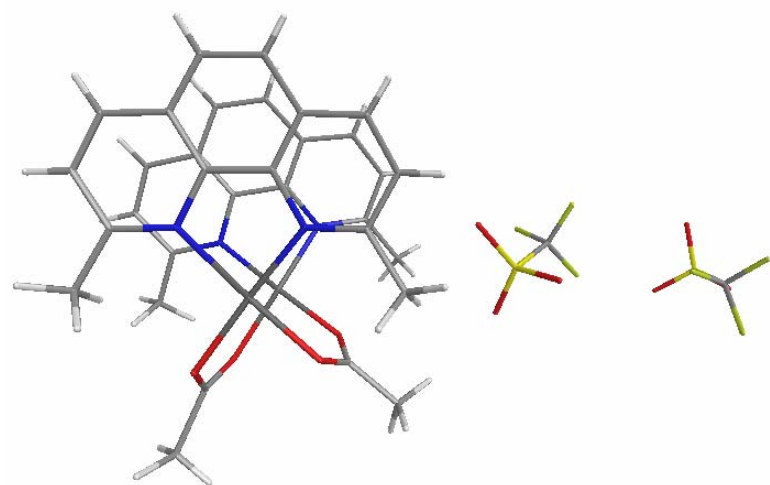


- Single Cu(I) site fails to bind O₂ at less than 550mV of overpotential

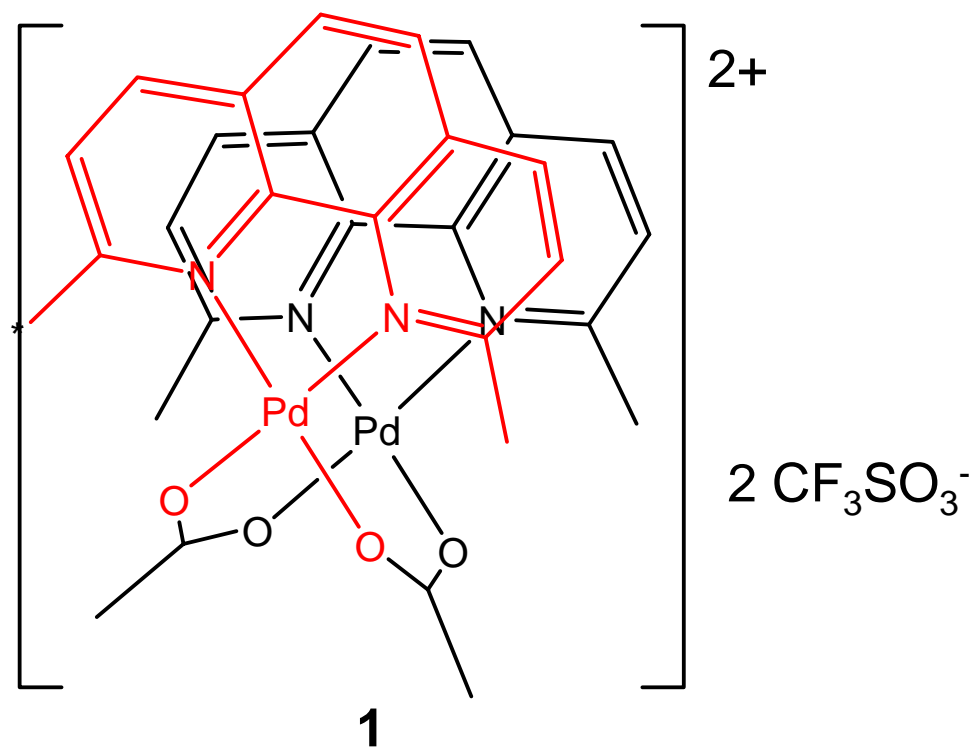
Conclusion from Cu(phen) Complexes on Graphite Electrodes

- The overpotential of O_2 reduction can be decreased by developing catalysts with electron-withdrawing substituents and with steric bulk near the Cu-center.
- As the overpotential of O_2 reduction is decreased by these ligand effects, there is a corresponding decreases in the rate of O_2 reduction.
- Acetic acid facilitates the O_2 reduction by phen-based catalysts. When no acetic acid is present, larger overpotentials are required for O_2 reduction.
- Future work will involve the development of multi-copper complexes that operate closer to the thermodynamic O_2 -reduction potential with similar O_2 -reduction rates.

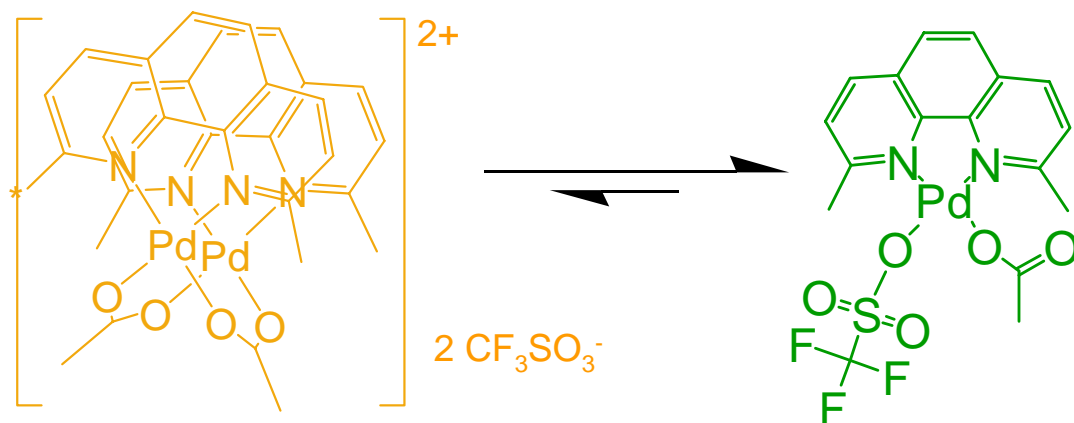
New Pd(II) Oxidation Catalyst



crystal structure



Dimer dissociates readily to active catalyst

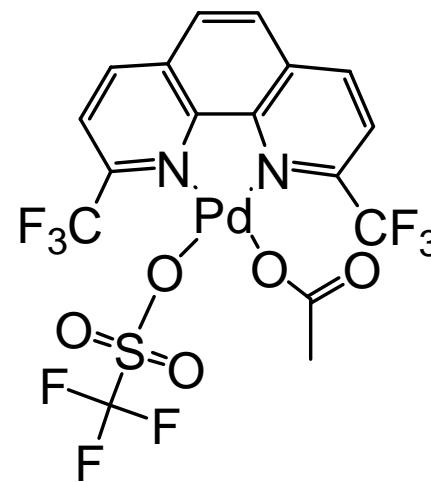


- Fast initial rates of oxidation of alcohols ($>0.05 \text{ s}^{-1}$) are observed at room temperature using air as the terminal oxidant.
- After ~15 minutes, the rate of oxidation of 2-heptanol decreases *linearly* with percent conversion. Inactivation of the catalyst occurs before the reaction is complete.
- One of the methyl groups is oxidized to a carboxylic acid.

Features of active Pd(II) oxidation catalysts

- Steric hindrance of dimerization
- At least one weak equatorial ligand
- Weak base to accept protons

candidate being synthesized



Methanol oxidation

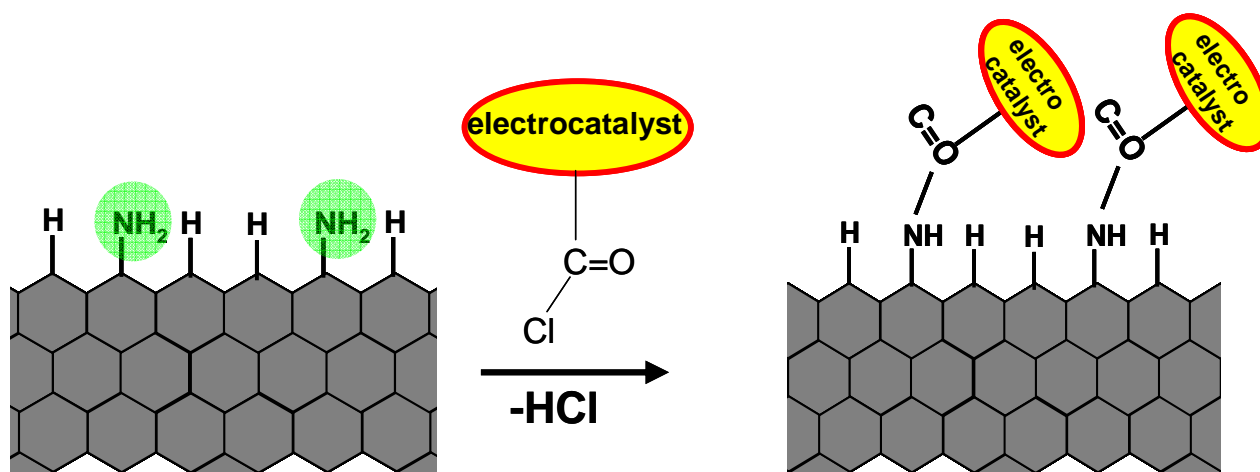
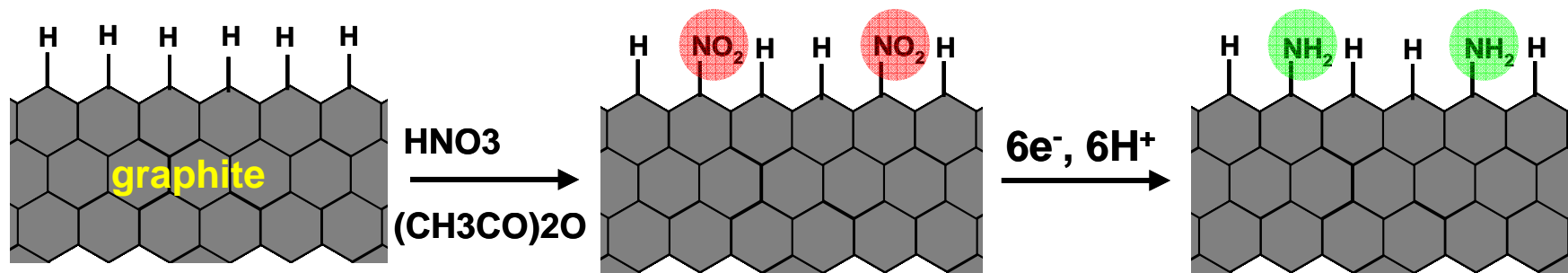
- The original catalyst is a competent catalyst for the oxidation of methanol and formaldehyde in the presence of benzoquinone in acetonitrile, implicating its potential as an anode catalyst in a methanol fuel cell.

Future work

- Immobilize catalysts on an electrode surface for use as an oxidation electrocatalyst.
- Synthesize fluorinated complex and test it as a catalyst for alcohol oxidation.

Methods to covalently site-isolate molecular catalysts on graphitic carbon

nitro groups known to avoid each other

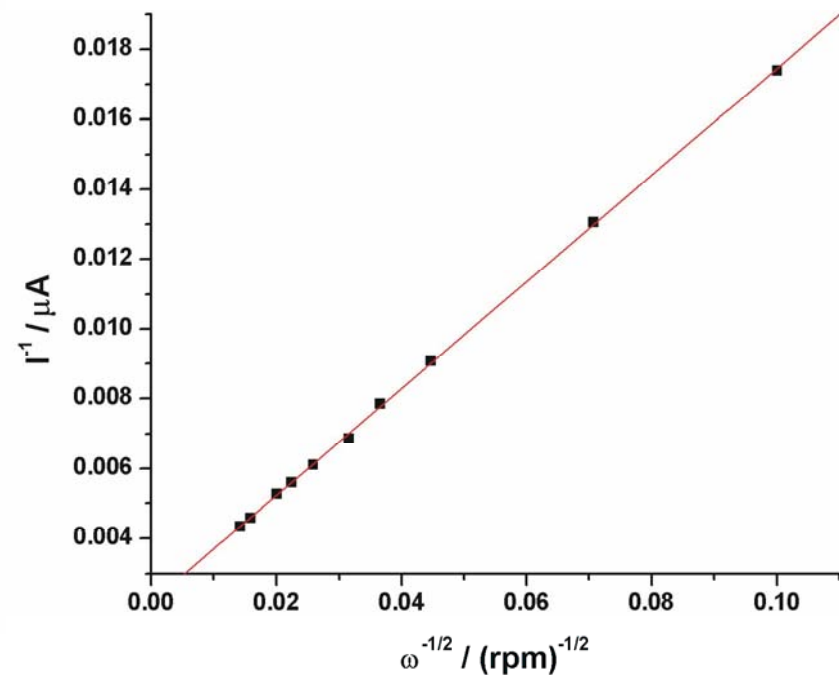
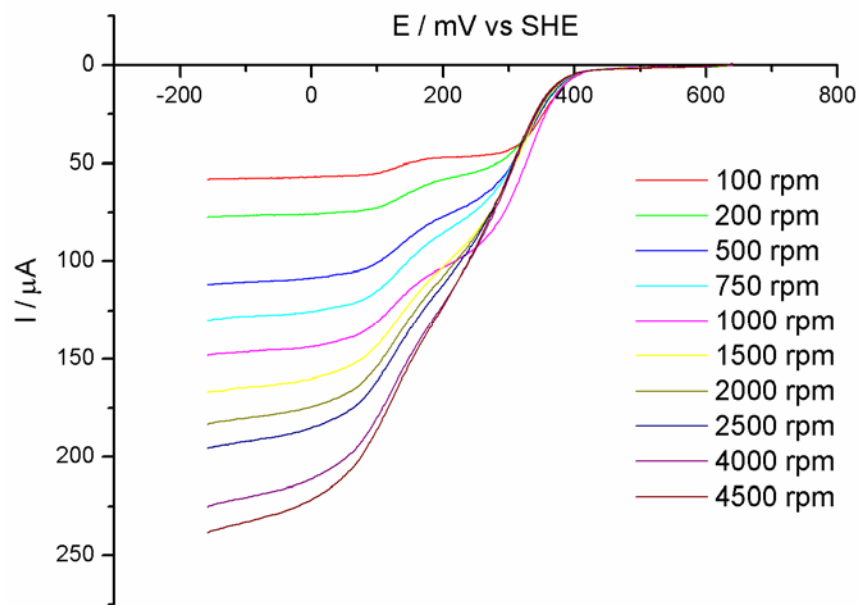


Prospects for Improved Electrocatalysts

- Need multiple metal ions in O₂-reduction catalysts
- Need appropriate proton donors and acceptors to promote rates of individual steps in catalytic cycle – this sets the optimal pH for each catalyst.
- Pd(II) with open equatorial sites attacks C-H bonds and thus requires careful ligand design.
- Need good ways to covalently site isolate molecular catalysts on graphitic carbon surfaces.

Initial work: Cu(Me₂phen)⁺ on Graphite Electrodes

Rotating disk voltammetry deconvolves mass transport

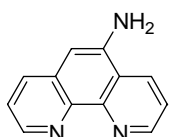


4 e⁻ reduction of O₂ to H₂O limited by O₂ binding rate ($\sim 1 \text{ s}^{-1}$)
- Repeats and confirms literature results

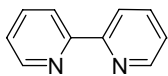
Cu(II) Reduction Potentials vs. O₂/H₂O

O₂ Reduction Peak Potential vs. O₂/H₂O

O₂ Reduction Rate

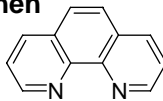


-925 mV
-935 mV



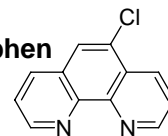
-925 mV
-925 mV

phen

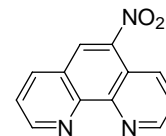


-915 mV
-930 mV
14.6 s⁻¹

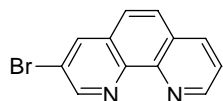
Cl-phen



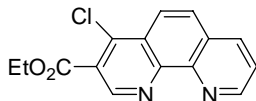
-885 mV
-895 mV
10.3 s⁻¹



-870 mV
-905 mV

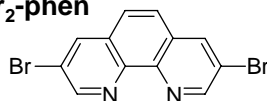


-850 mV
-865 mV

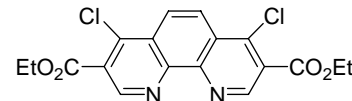


-850 mV
-865 mV

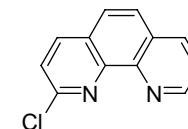
Br₂-phen



-805 mV
-825 mV
5.3 s⁻¹

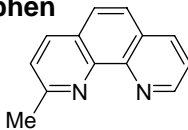


-790 mV
-810 mV

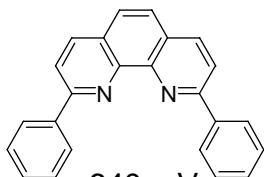


-790 mV
-825 mV

Me-phen

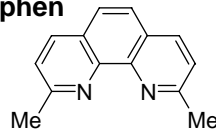


-725 mV
-745 mV
10.6 s⁻¹

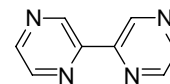


-640 mV
N/A

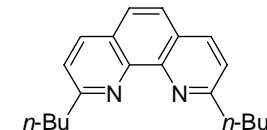
Me₂-phen



-630 mV
-650 mV
4.5 s⁻¹

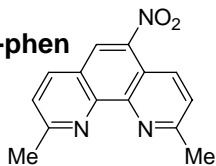


-600 mV
N/A

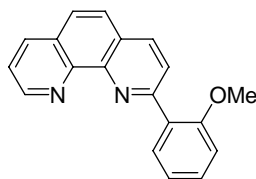


-580 mV
-880 mV

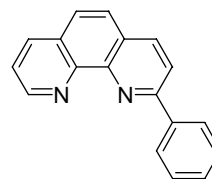
Me₂NO₂-phen



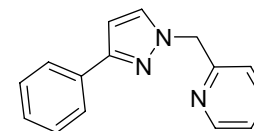
-545 mV
-865 mV



-520 mV
N/A



-505 mV
N/A



-475 mV
N/A

The First Challenge of Hydrocarbon Oxidation: C-H Activation

- Partial oxidation of methane and activation of other C-H bonds has been explored extensively
- Usually, complete oxidation is to be avoided.
- However, we WANT complete oxidation!
- Electrophilic, late transition-metal complexes are well known to insert into C-H bonds
- Perriana, Herrmann and others have shown insertion of acid-stable aromatic complexes of Pt(II) and Pd(II) into CH₄

C-C Bond Activation: Interesting Precedents

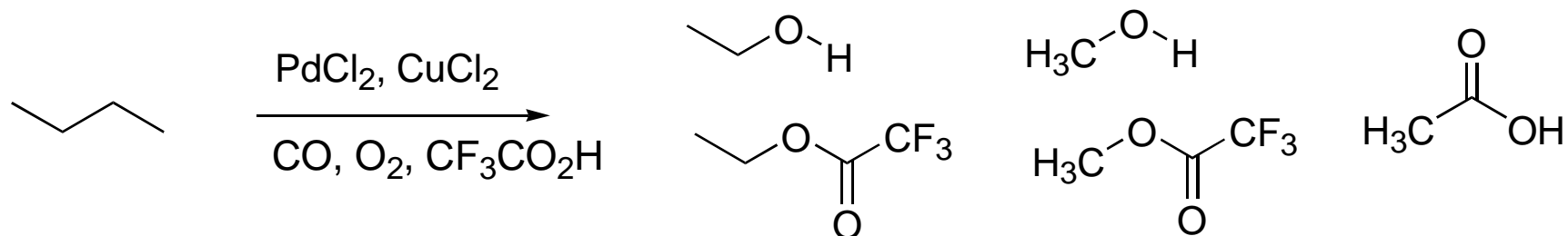


Figure 2. Sen's oxidative cleavage of butane.

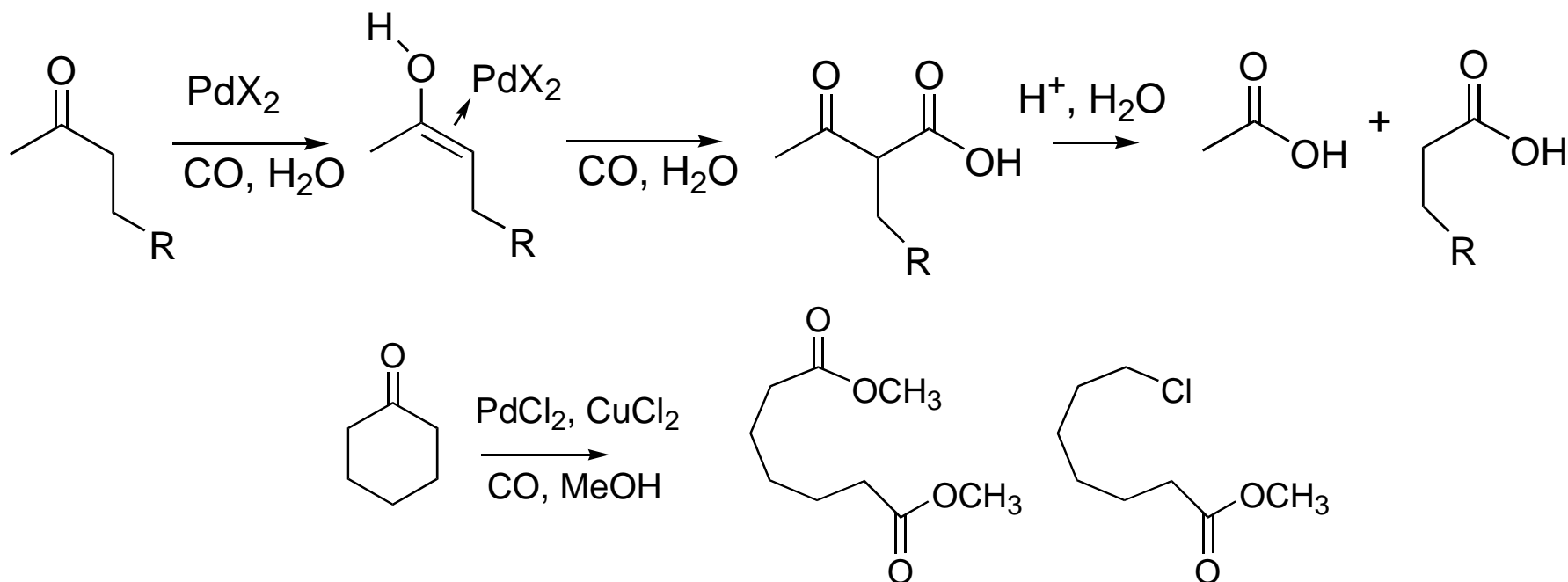


Figure 3. Henry's carbonylation of ketones followed by retro-Claisen condensation

Possible Strategies For C-C Bond Cleavage

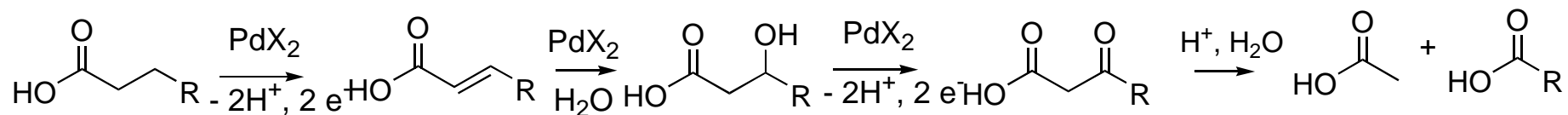


Figure 4. Proposed oxidative cleavage of long-chain carboxylic acids.

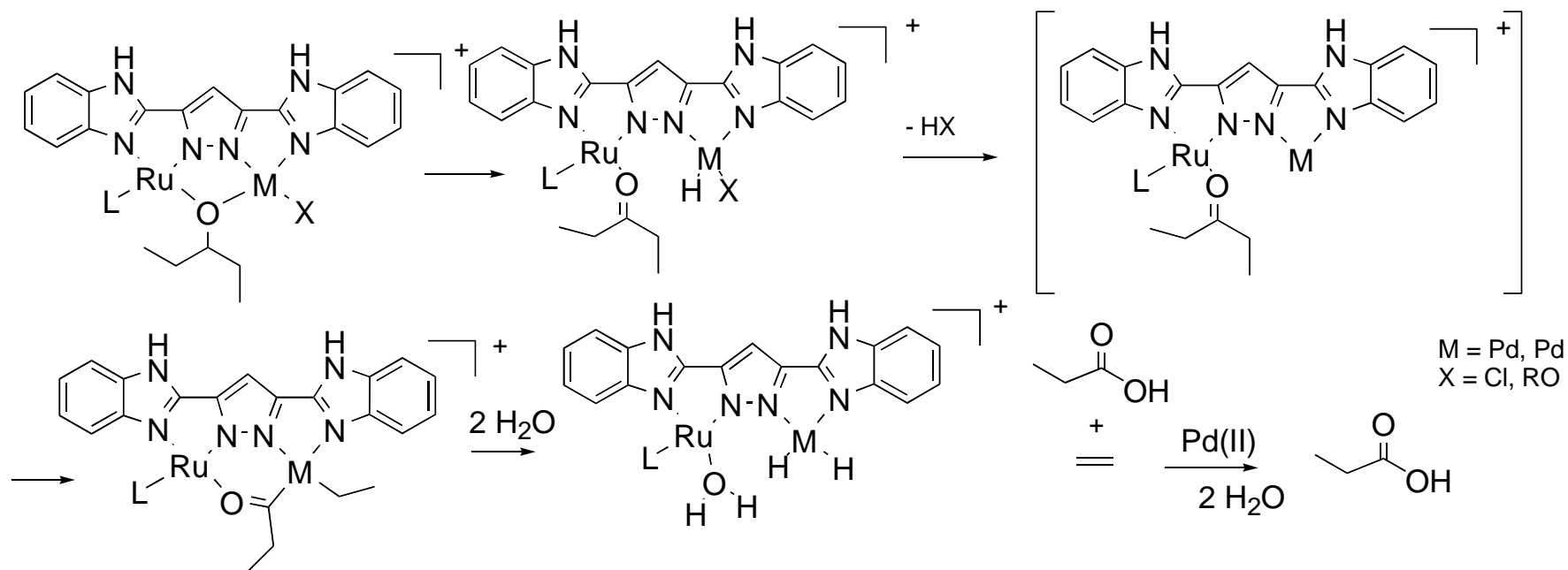
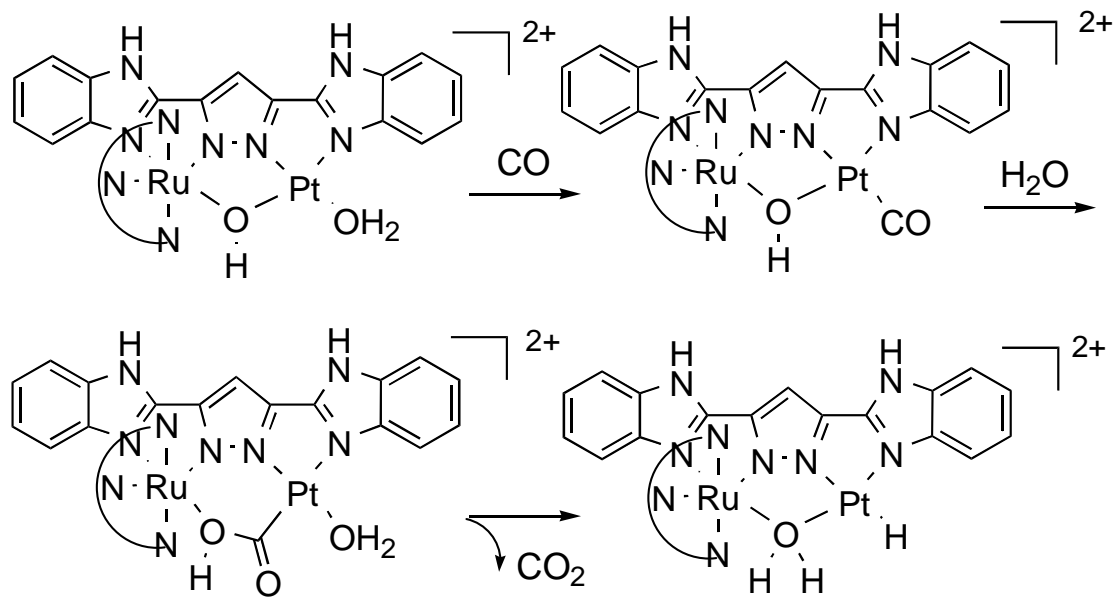


Figure 7. Bimetallic strategy for activating C-C bonds of ketones.

The CO Oxidation Challenge

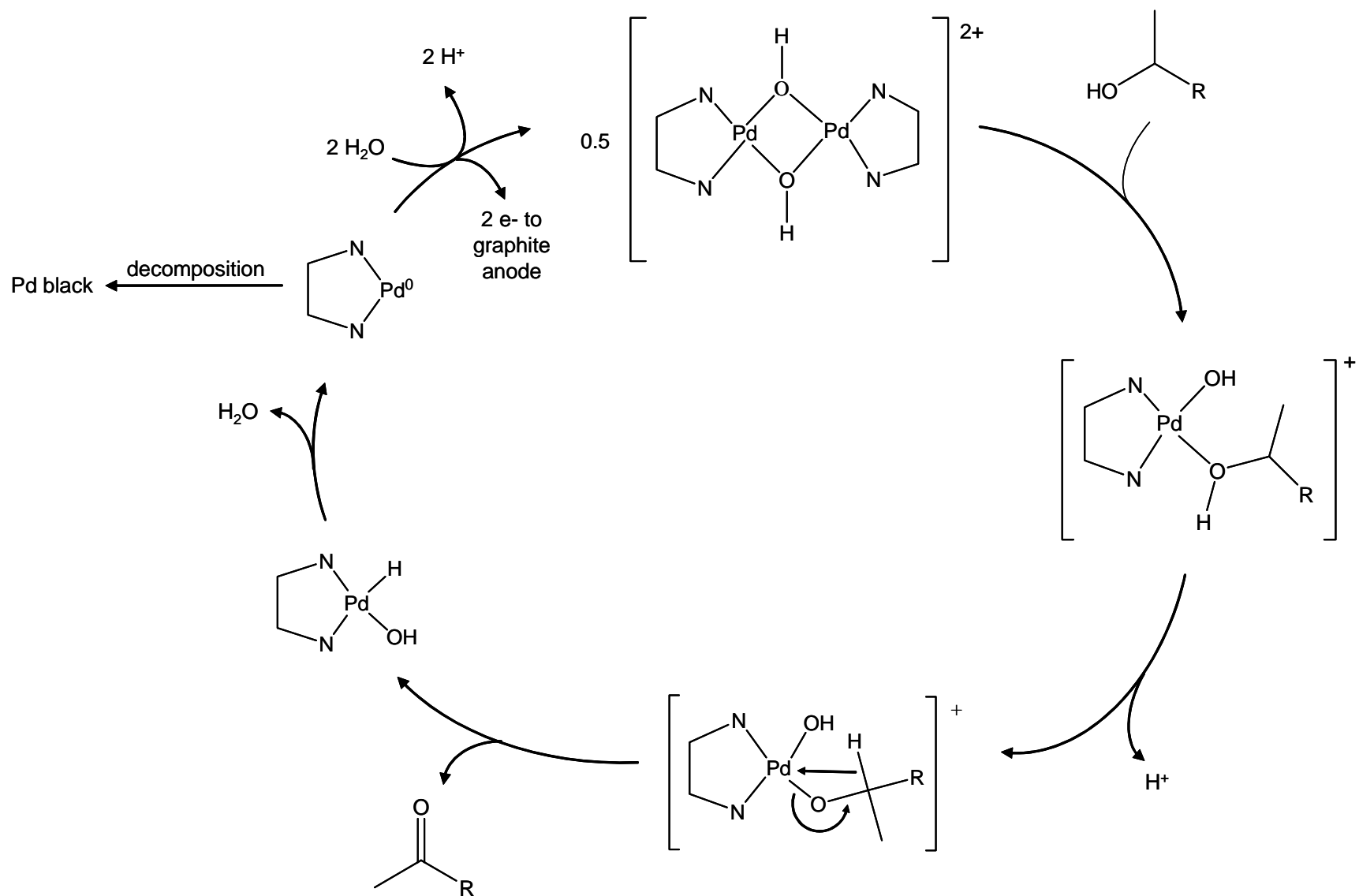
- CO poisoning of metallic Pt catalysts for H₂ oxidation is well known
- CO is expected to be a common intermediate in complete oxidation of all hydrocarbons
- We will explore mechanism of nucleophilic attack of H₂O on Pd(II)-CO and Pt(II)-CO complexes



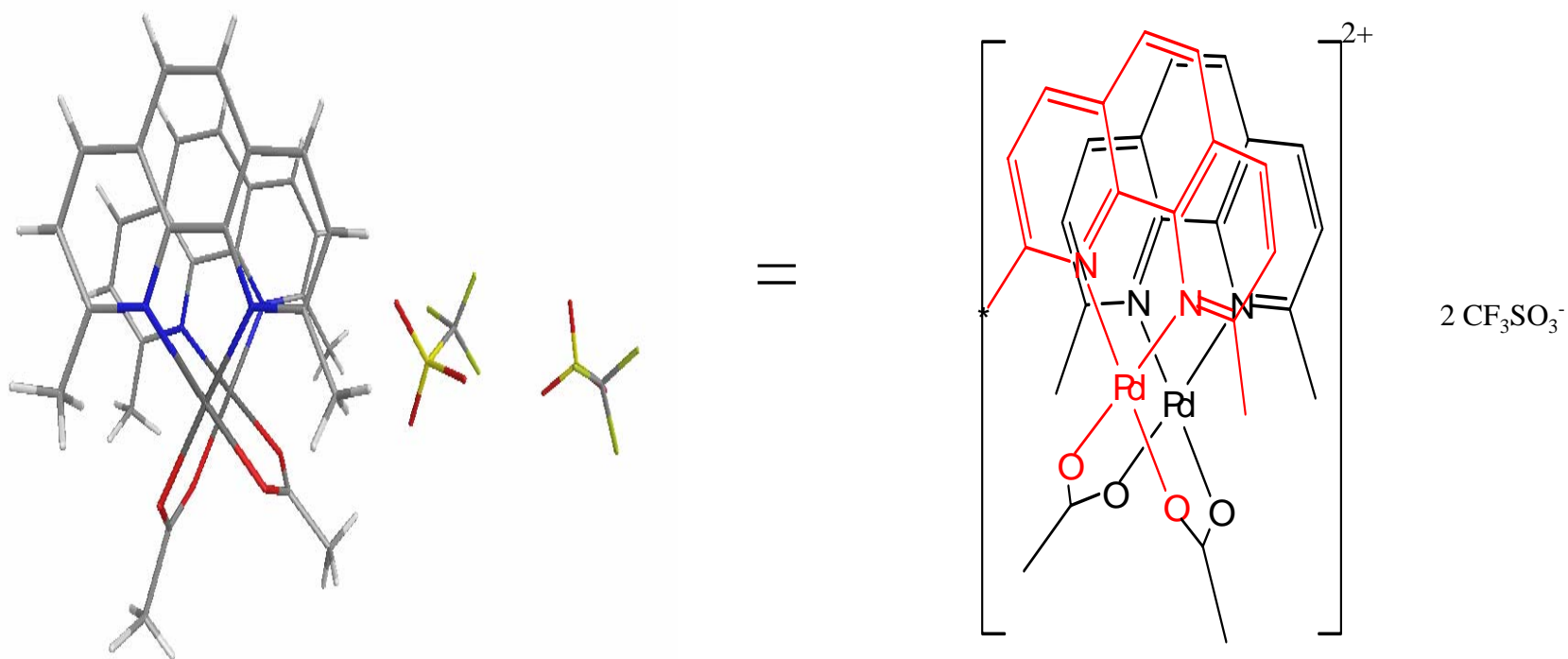
Planned Oxidation Studies

- Investigate monometallic Pd(phen) complexes for their ability:
 1. To catalyze an electrochemical version of water-gas shift reaction:
$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^-$$
 2. To electrocatalyze simple C-H activation such as alcohol oxidation.

Electrocatalysis of Alcohol Oxidation



Crystal Structure of New Alcohol Oxidation Catalyst



A Bimetallic Mechanism for C-C Activation

In the mechanism below, the alcohol will be oxidized to a ketone, resulting in an activated C-C bond that can insert into the proximal metal center. This will induce oxidative cleavage of the ketone and form a carboxylic acid as one of the products.



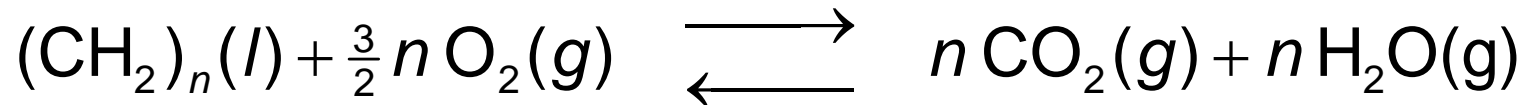
Rich Opportunity to Exploit Synergies Among Disciplines

Need to understand both engineering (PEM cells) and chemistry (homogeneous catalysis) to open up new opportunities:

1. Hydrocarbon fuel cell
2. Better O₂-electrodes and CO-resistant H₂-electrodes for hydrogen fuel cells.
3. Electrocatalysis for energy efficient chemical processes of commodity petrochemicals – particularly partial oxidations
4. Eventual electrosynthesis of hydrocarbon fuels by reverse reactions

Reversible Hydrocarbon Fuel Cell

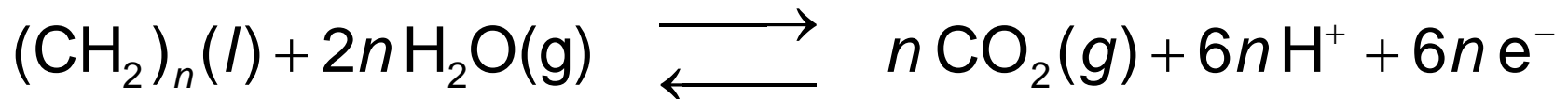
Approximate thermochemistry at 25°C and 1atm:



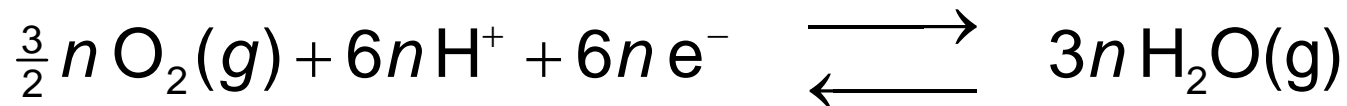
$$q_{rev \text{ rxn}} = T\Delta S_{rxn} = +n(17 \text{ kJ/mol})$$

$$\Delta G_{rxn} = -n(631 \text{ kJ/mol})$$

Approximate electrochemistry at 25°C, 1atm and pH 0:



$$E^0 = +0.09 \text{ V vs NHE}$$



$$E^0 = +1.18 \text{ V vs NHE}$$

Reversible cell potential = 1.09 V