

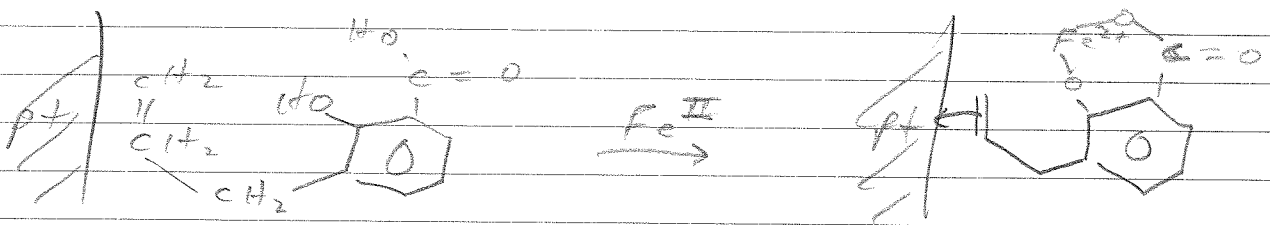
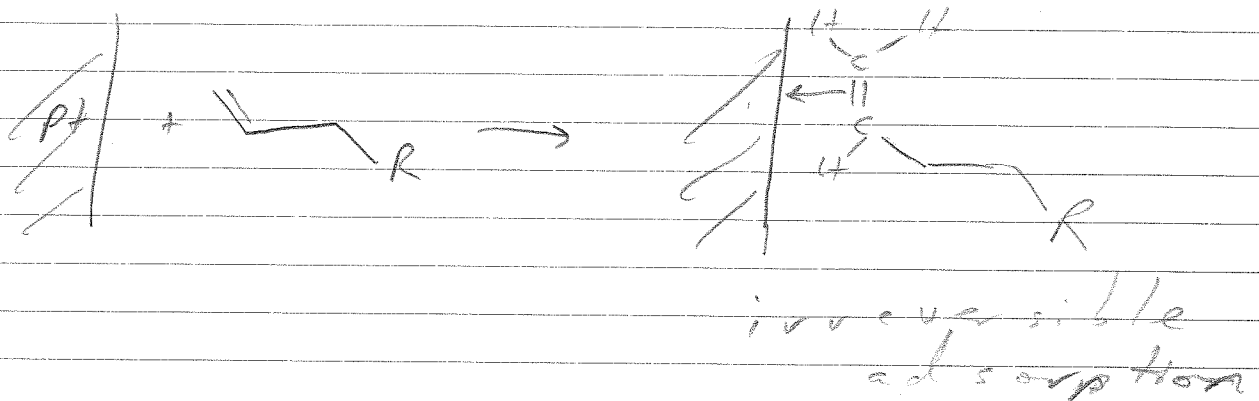
Modified Electrodes

1 of 1

WHY?

- Tailor Making of Surfaces
- Electrocatalysis
- Long-Distance E.T.
- Molecular Recognition

First Example of a modified electrode (chemisorption): Lene + Hubbard

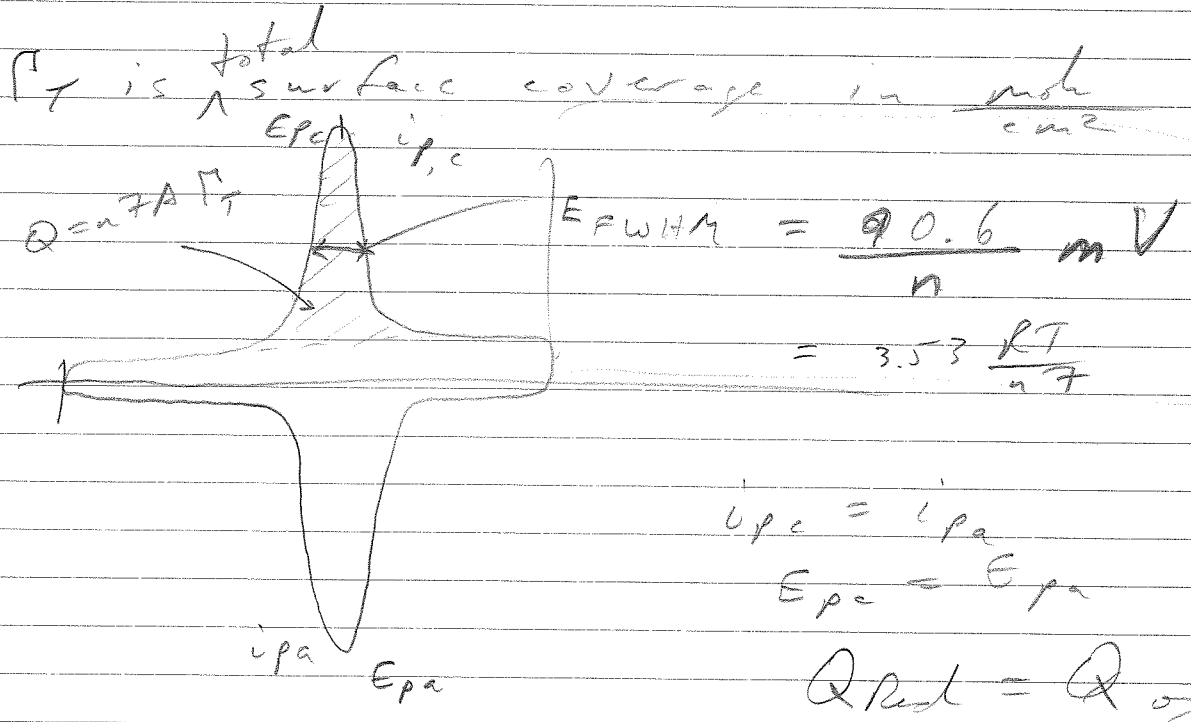


OK, What does voltammetry look like? (Chemically Rev.)

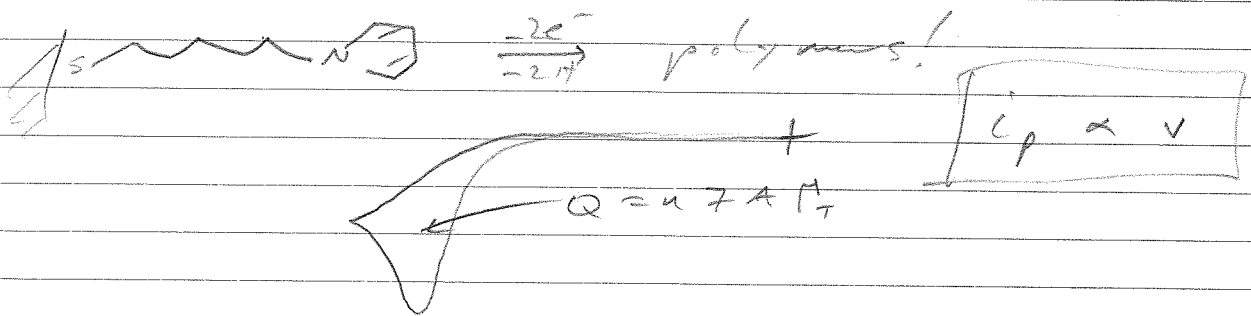
Well,

$$i = \frac{4i_p \exp\left[\frac{nF}{RT}(E - E_{s,p}^0)\right]}{\left\{1 + \exp\left[\frac{nF}{RT}(E - E_{s,p}^0)\right]\right\}^2}$$

When $i_p = \frac{n^2 F^2 A \Gamma_T v}{4RT}$

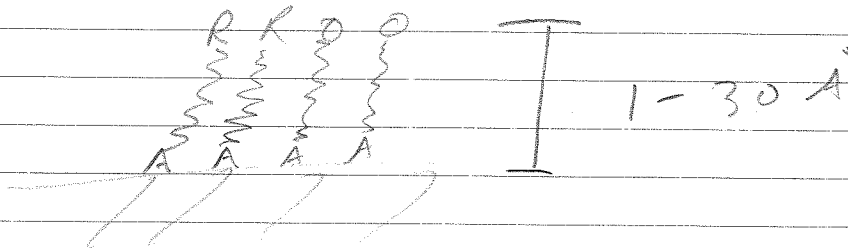


Although both EC Irrev. + Chem Irrev. systems exist, we will not explore them, except to say that an EC rxn. can be studied:

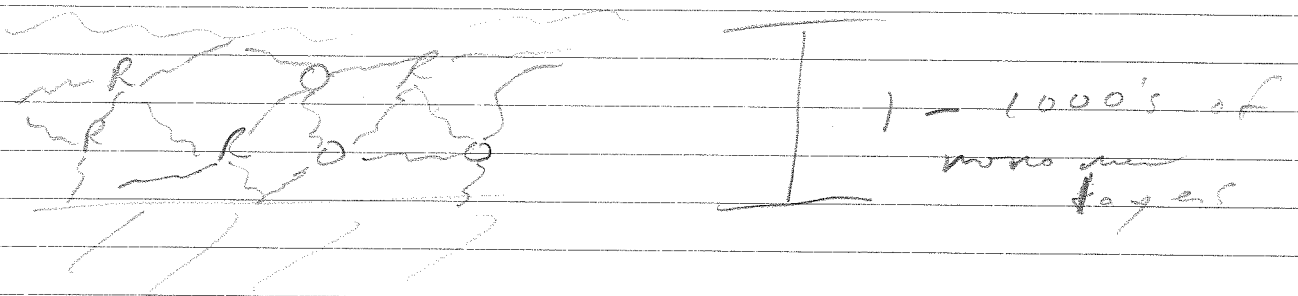


We can break up electrode modification ^{3 of} into two distinct areas:

① Mon. molecular Layers.

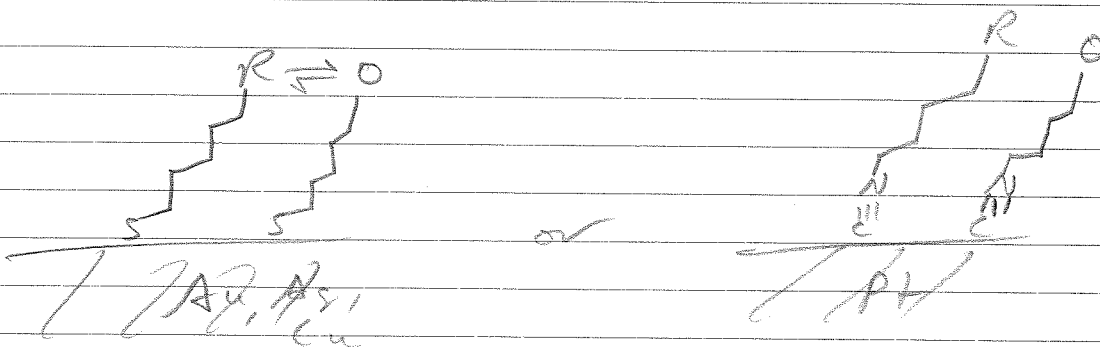
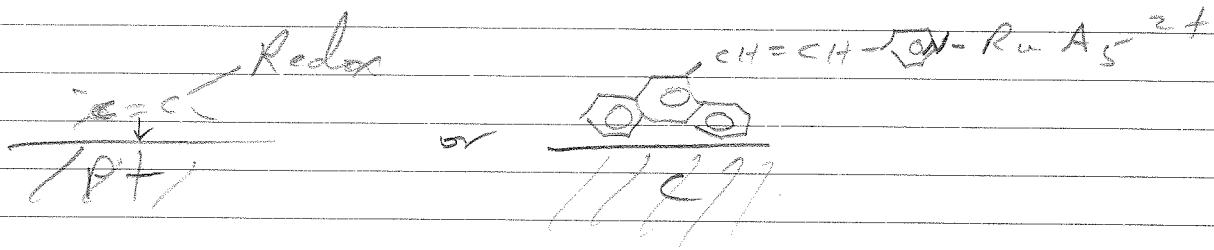


② Polymeric Layers

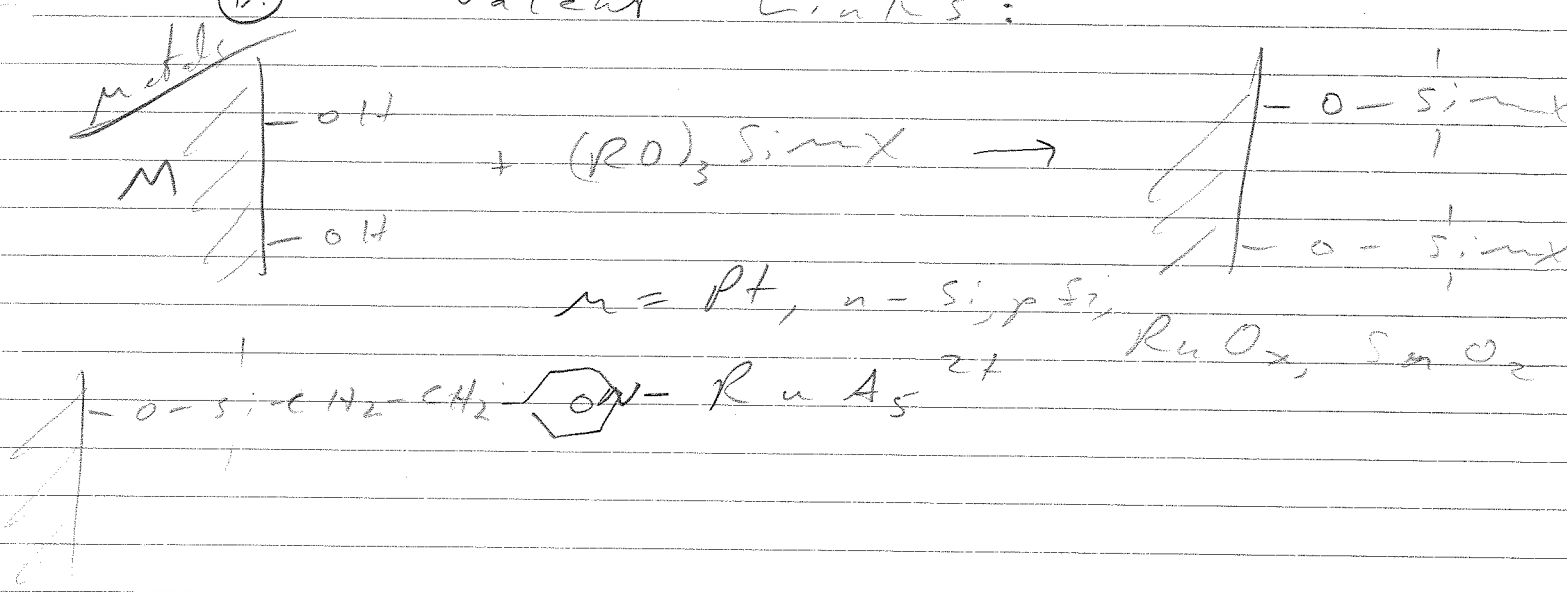


① Monolayers -

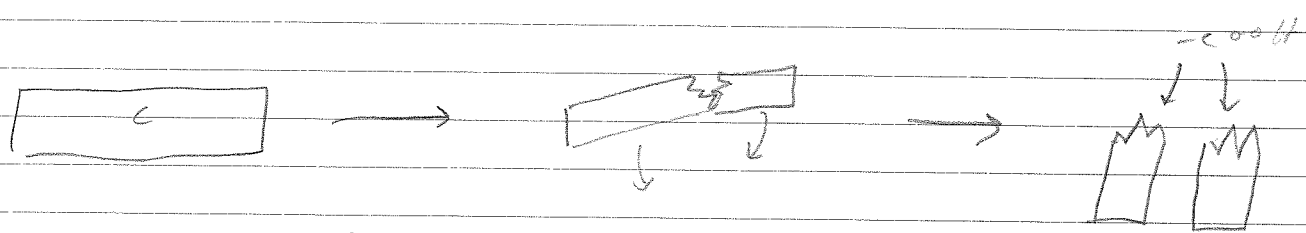
(A) Chemisorption.



(B) Covalent Links:

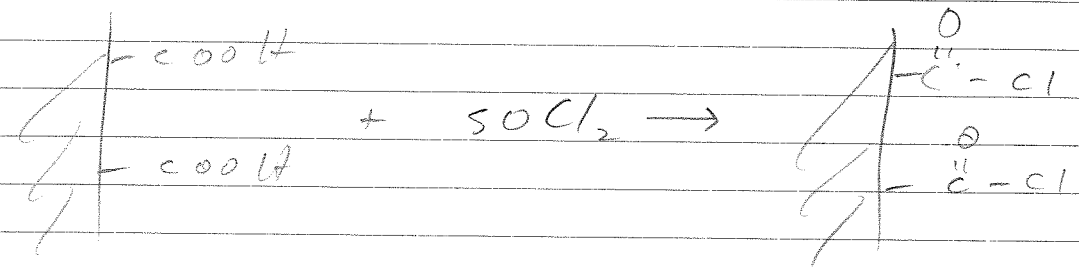
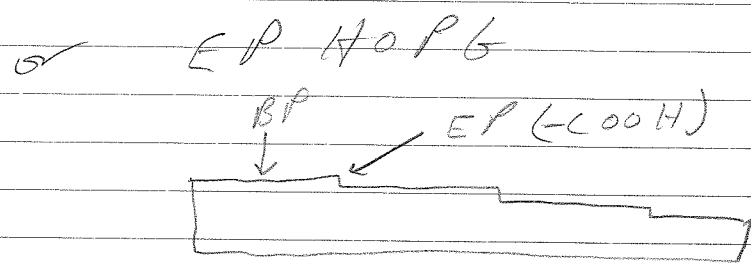
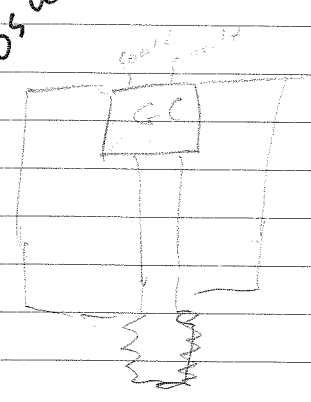


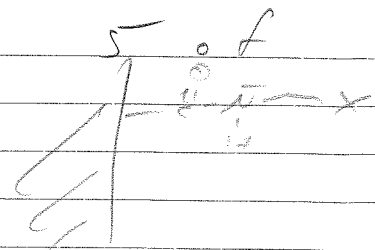
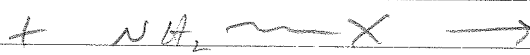
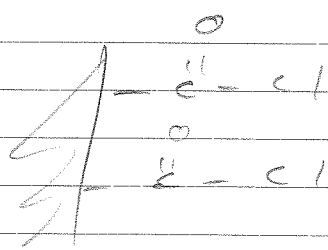
Carbon



Glassy Carbon → Vitreous Carbon

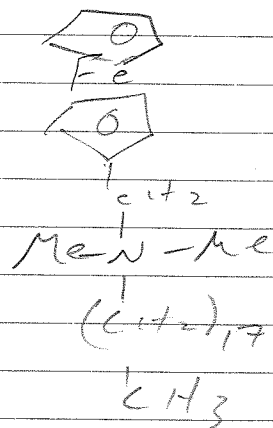
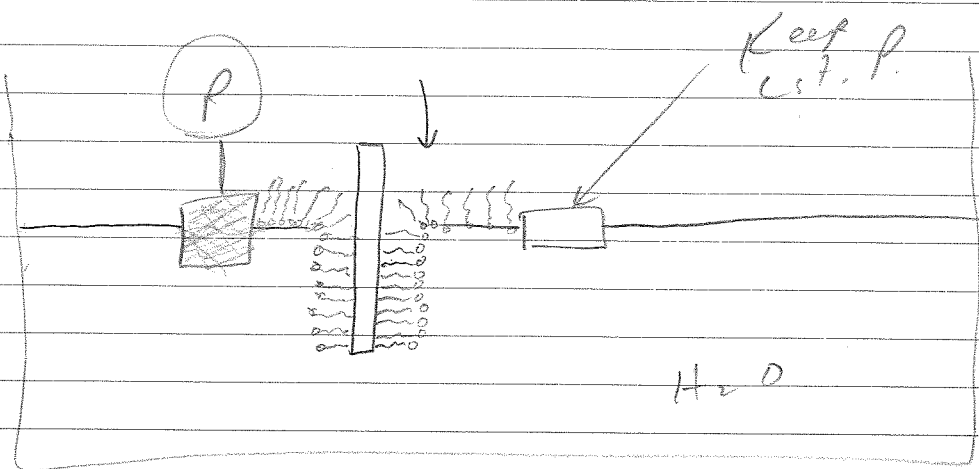
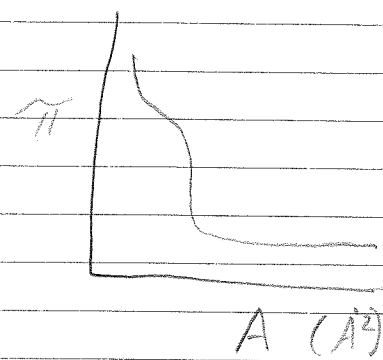
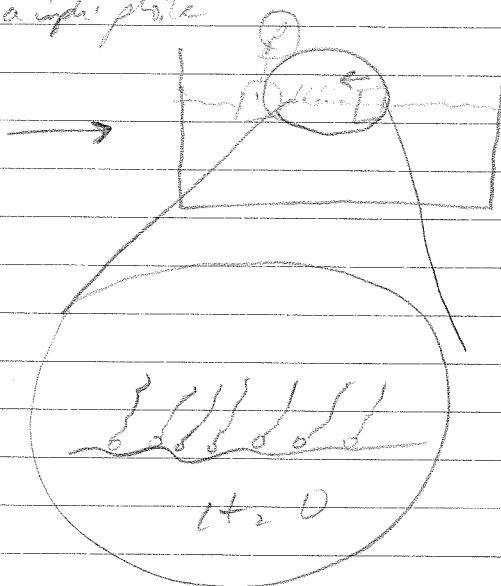
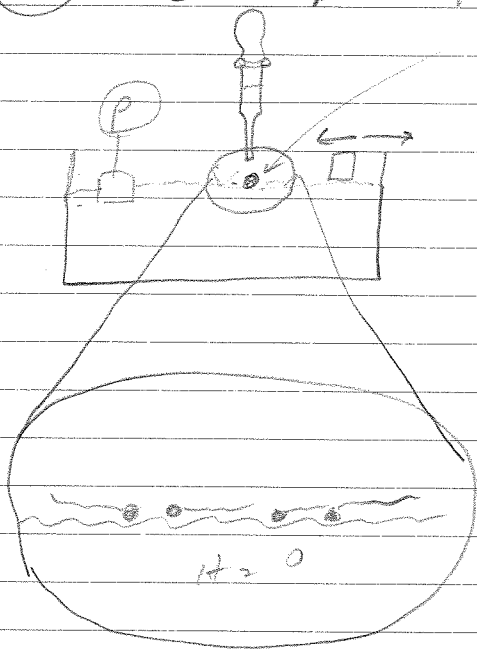
McCreech
McOSU





Make X electroactive.

(c) L-B Films
planar/polymer-aqueous phase

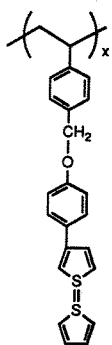
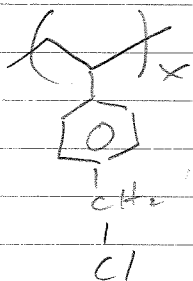


Allows packing density to be varied. SAMS cannot do this!

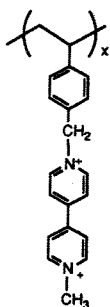
2) Polymeric Layers

A. Preformed Polys-

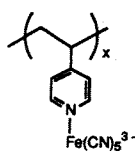
p. 24
January



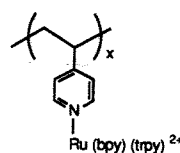
Ref. 89



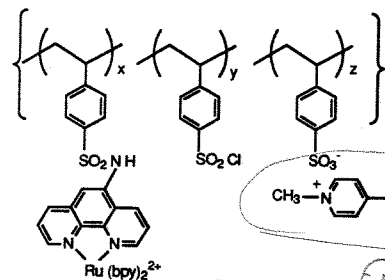
Ref. 214



Ref. 212

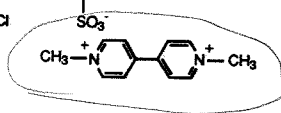


Ref. 213



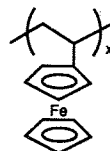
Ru(bpy)₂²⁺

Ref. 215, 216

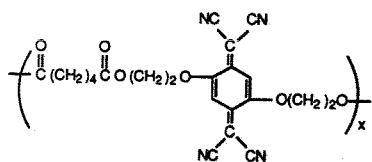


Ref. 215, 216

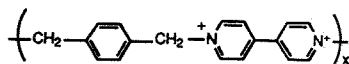
Free to Diffuse.



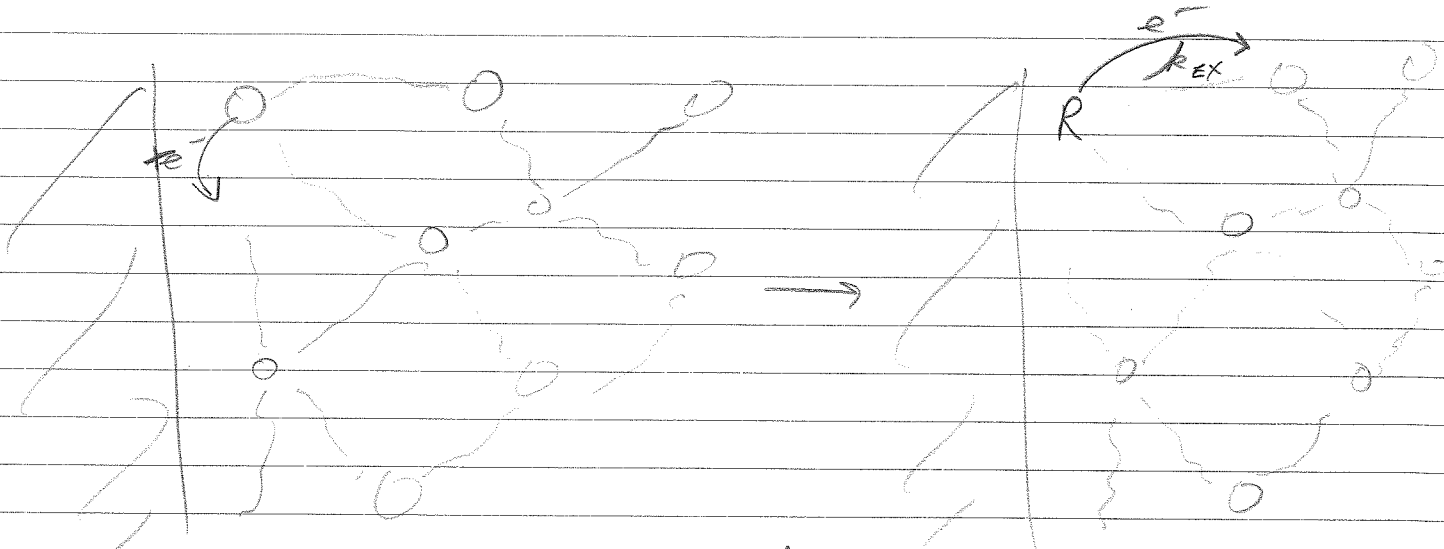
Ref. 41



Ref. 219

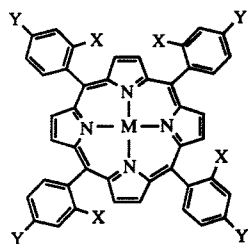
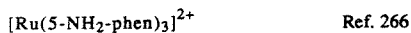
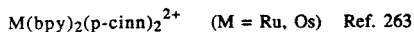
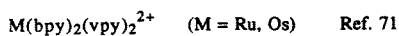
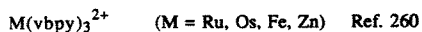
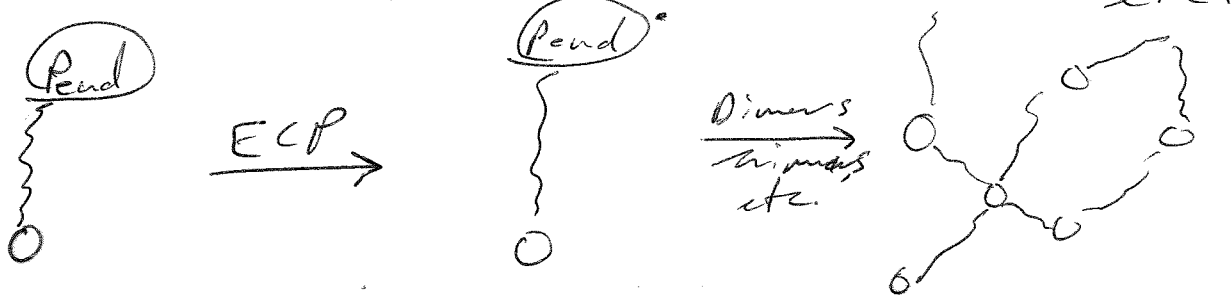


Ref. 217



Must have fast REX to see current!

(B) Electrochemically formed Polymers. 7 of



(M = Fe, Co, Mn, Zn, Cu, H₂, Ni, Ru)

(X or Y (not both) = -NH₂, -OH, -N)

Ref. 107, 271, 275

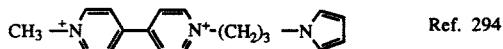
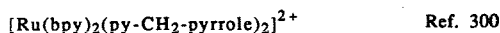
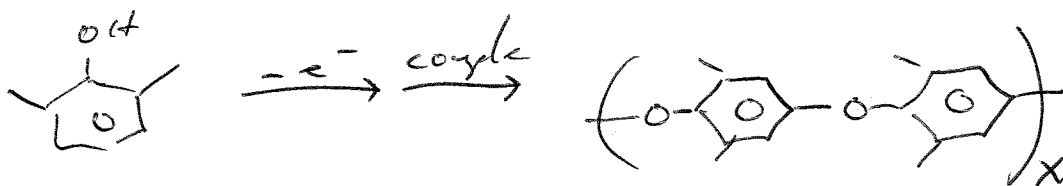


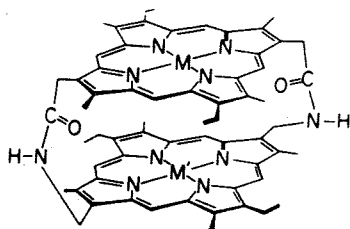
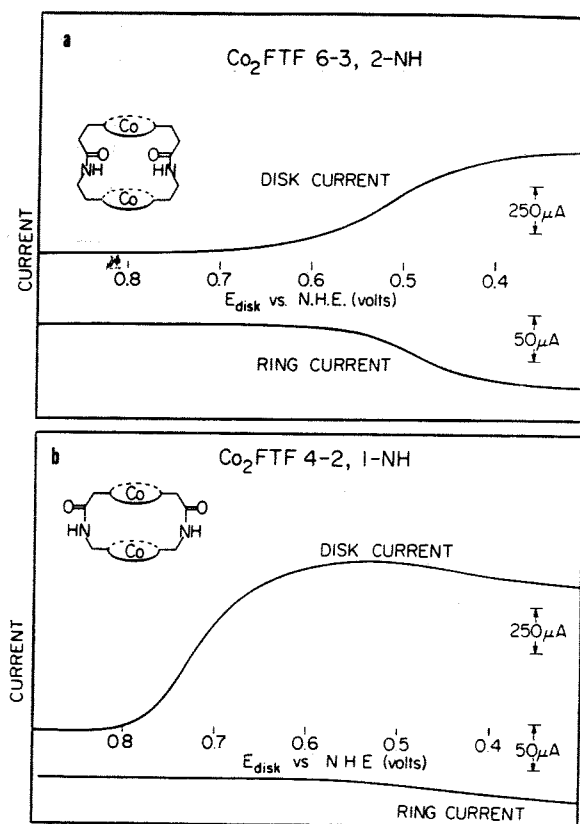
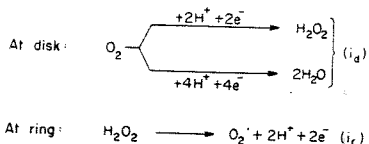
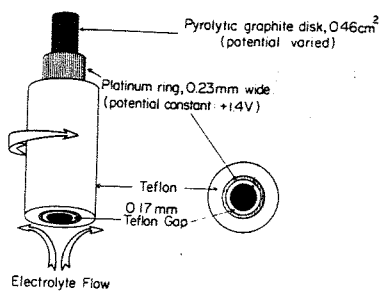
Figure 1.7. Example structures of electrochemically polymerizable redox monomers, where vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine, vpy = 4-vinylpyridine, p-cinn = N-(4-pyridyl)cinnamamide, 5-NH₂-phen = 5-amino-1,10-phenanthroline, py-CH₂-pyrrole = 3-(pyrrol-1-ylmethyl)pyridine.

Can also make insulating polymers.



- ① Used in corrosion protection.
- ② " " " diffusion studies.

RING-DISK ELECTRODE ASSEMBLY



M = M' = Co
 M = Pd, M' = Co

Figure 1.1. Electrocatalytic rotated disk electrode currents versus applied potential for Co₂FTF6 (upper) and Co₂FTF4 (lower) porphyrin (Por) dimers (six atom and four atom, β linked) coated on the rotated graphite disk, in O₂-saturated 0.5M CF₃CO₂H, and currents at rotated Pt ring showing that H₂O₂ is generated at the more positive potentials of the disk electrocatalysis in the case of Co₂FTF6 but not in the case of Co₂FTF4. [Reprinted with permission from J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, and F. C. Anson, *J. Am. Chem. Soc.*, 1980, 102, 6027. Copyright © (1980) American Chemical Society.]