Chemistry 117
Problem Set 4

Please note that for this problem set, you may NOT consult scientific literature. You may use your notes and Bard & Faulkner as usual, and the usual class collaboration policy holds.

This problem set is due to the box outside 210A Noyes no later than 2:30 p.m. on Mar 9, 2017.

1. Ferricyanide in solution has a redox potential of 0.2 V versus SCE, while the trinuclear [Fe(II)-Pt(IV)-Fe(II)] complex, shown below, exhibits a redox potential for the iron sites of 0.55 V versus SCE.
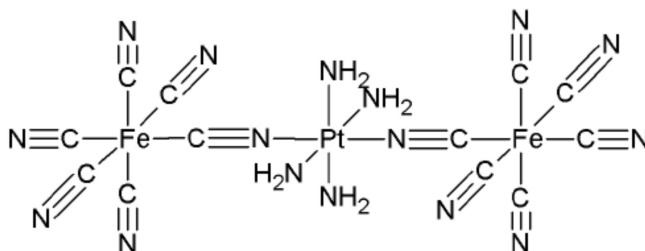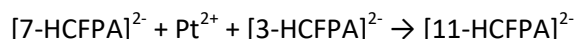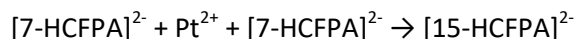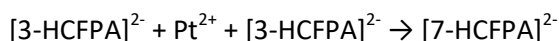

The molecule shown above can be polymerized by oxidizing the irons to the Fe(III) state in the presence of $[Pt(II)(NH_3)_4]^{2+}$ as shown in the scheme that follows, where n-HCFPA stands for hexacyanoferro-platinum amine complex containing n metal centers. Thus, the compound shown above is 3-HCFPA.

    Step 1: initiation

$$[3\text{-HCFPA}]^{4-} + ox \rightarrow [3\text{-HCFPA}]^{2-}$$

    Step 2: chain propagation

$$[3\text{-HCFPA}]^{2-} + Pt^{2+} + [3\text{-HCFPA}]^{2-} \rightarrow [7\text{-HCFPA}]^{2-}$$

$$[7\text{-HCFPA}]^{2-} + Pt^{2+} + [7\text{-HCFPA}]^{2-} \rightarrow [15\text{-HCFPA}]^{2-}$$

$$[7\text{-HCFPA}]^{2-} + Pt^{2+} + [3\text{-HCFPA}]^{2-} \rightarrow [11\text{-HCFPA}]^{2-}$$

$$\ldots$$

$$[n\text{-HCFPA}]^{2-} + Pt^{2+} + [m\text{-HCFPA}]^{2-} \rightarrow [(n+m+1)\text{-HCFPA}]^{2-}$$

   Step 3: termination

$$[n\text{-HCFPA}]^{2-} + red \rightarrow [n\text{-HCFPA}]^{4-}$$

Polymers, n-HCFPA, can be formed in a variety of geometries. If the reaction proceeds linearly (i.e. from terminal iron moieties only), then only irons with one or two bridging cyanides form (one for the end irons, two elsewhere). However, if branching occurs, then a given iron might have three or four bridging cyanides. A fairly linear relationship is experimentally observed between the Fe(II/III) redox potential and the number of bridging cyanides per iron as shown graphically on the next page.
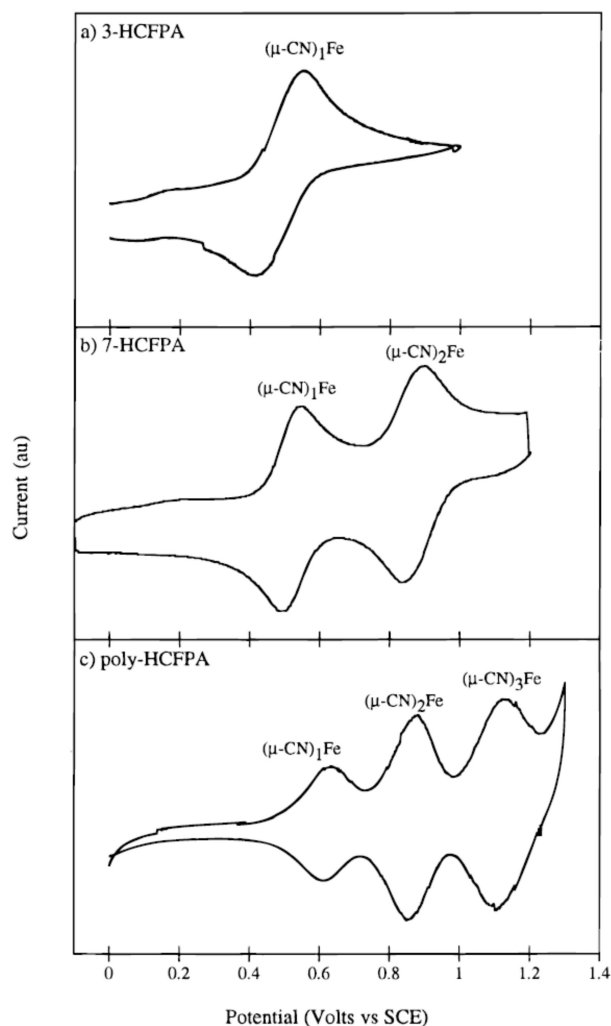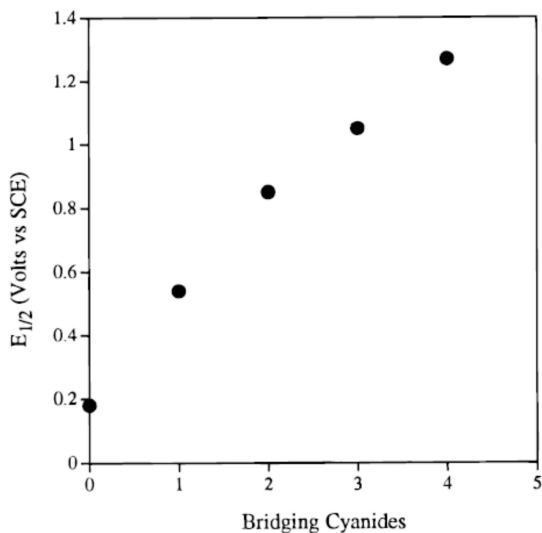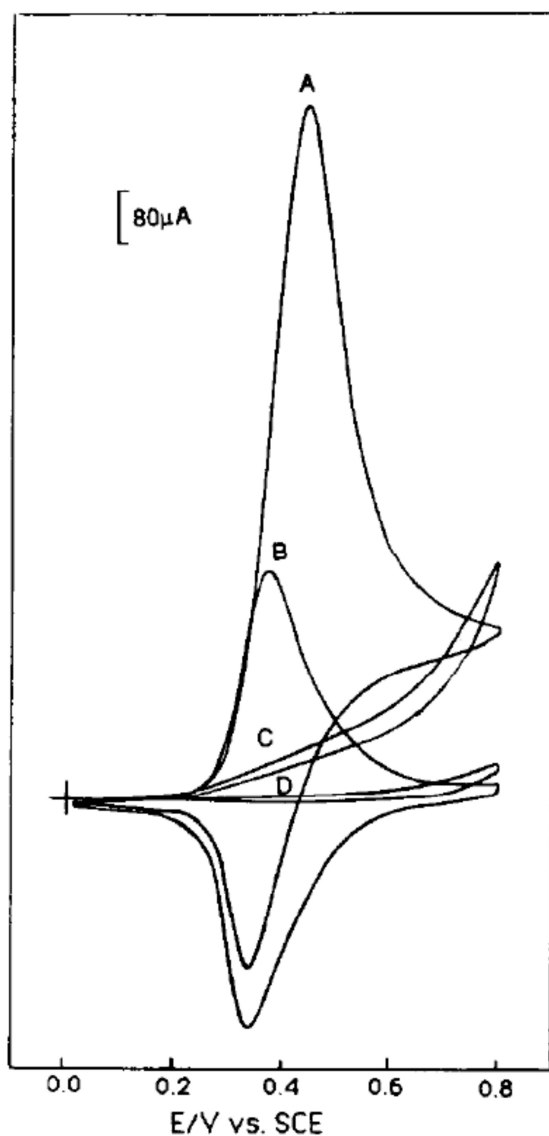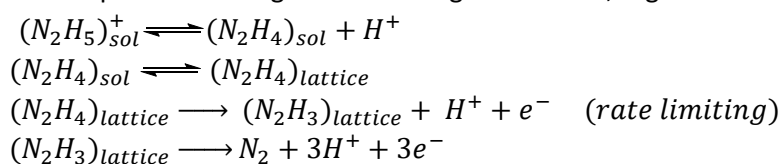
Cyclic voltammograms of a) 3-HCFPA showing a single wave at 0.54 V, b) 7-HCFPA with an additional wave at 0.85 V, and c) poly HCFPA.

The data summarized in the left panel was obtained from cyclic voltammograms similar to those shown in the right panel.

a) Use the cyclic voltammetric data provided to prove that the compound labelled as 7-HCFPA in b of the right panel is, in fact, 7-HCFPA.

b) What is a possible geometry (linear, branched, two-dimensional sheet, or three-dimensional network) of the polymer shown in c of the right panel?

c) If one wanted to form a sample that contained only linear polymer molecules with large values of n, how might this be achieved, starting from $[3\text{-HCFPA}]^{4-}$ and $[Pt(II)(NH_3)_4]^{2+}$?

2. This question pertains to a study of the oxidation of hydrazine (N_2H_4) to nitrogen (N_2) at a nickel ferrocyanide derivatized nickel electrode. Preliminary cyclic voltammetric data for this reaction, which was proposed to proceed through the following mechanism, is given below:

$$(N_2H_5)^+_{sol} \rightleftharpoons (N_2H_4)_{sol} + H^+$$
$$(N_2H_4)_{sol} \rightleftharpoons (N_2H_4)_{lattice}$$
$$(N_2H_4)_{lattice} \longrightarrow (N_2H_3)_{lattice} + H^+ + e^- \quad (rate\ limiting)$$
$$(N_2H_3)_{lattice} \longrightarrow N_2 + 3H^+ + 3e^-$$

Cyclic voltammograms for: A) oxidation of hydrazine at a derivatized Ni/[NiFe(CN)$_6$]$^{2-/1-}$ electrode; B) a derivatized nickel electrode in the absence of hydrazine; C) oxidation of hydrazine at a non-derivatized nickel electrode; and, D) a non-derivatized electrode in supporting electrolyte, only. Supporting electrolyte: 0.5 M NaNO$_3$ with 0.25 M phosphate buffer at pH 8.0. A potential scan rate of 100 mV/s was used.
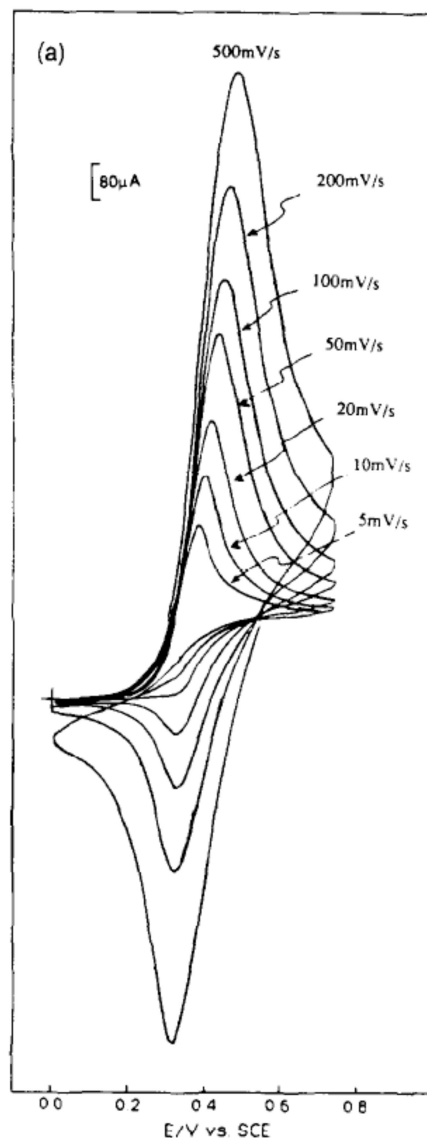
Cyclic voltammetric scan-rate dependence for a derivatized [NiFe(CN)$_6$]$^{2-/1-}$ electrode in an electrolyte composed of 5.0 mM hydrazine, 0.5 M NaNO$_3$, and 0.25 M phosphate buffer adjusted to pH 8.0. All scans start at 0 V and proceed to positive potentials.

Hydrazine is sufficiently small that it can theoretically pass through the nickel ferricyanide lattice (much like a cation does). Thus the term $(N_2H_x)_{lattice}$ in the mechanism above refers to a species that is in the nickel ferricyanide lattice, while the subscript "sol" indicates a species in the aqueous electrolyte.

a) What process forms the peaks in scan (B) of the left-hand figure above? Rationalize your answer by considering the various cyclic voltammograms shown in that figure.

b) What is the coverage (moles/cm^2) of nickel ferricyanide based on the data in the left-hand figure, given that an electrode area of 0.01 cm^2 was employed? (Hint: see B&F section 14.3.2)

c) The peaks in scan (B) are quite symmetric, while the peaks in scan (A) are not. Why is this the case?

d) One can imagine three possible states of oxidation of hydrazine given the information provided:

   i. Directly at the nickel electrode surface (after passing through the nickel ferricyanide lattice).

   ii. At the outer surface of the nickel ferricyanide via a mediated charge-transfer mechanism.

   iii. In the nickel ferricyanide layer via a mediated charge-transfer mechanism.

   (Hint: From your answer to part a, you can already draw a conclusion about option i) The distinction between choices ii and iii is related to diffusion. Review Nicholson & Shain page 722, for the section on diagnostic criteria, particularly the part about how a plot like Figure 17 can distinguish between cases uncomplicated by kinetics (i.e., mainly dependent on diffusion) and the cases that are complicated by kinetics. Make a data table from the CVs and make a plot like Figure 17 ($i_p/v^{1/2}$ versus log v). Which case(s) in N&S does your plot most resemble, and what does that say about whether the mechanism is complicated by diffusion or not? For extra credit, extra education, and extra fun make a plot like Figure 18 to try to further narrow down the CV data we have for this problem to a particular N&S mechanism.

e) The data on the next page indicate the effect of alkali cations (Na$^+$, Rb$^+$, or Cs$^+$) on the nickel ferricyanide/hydrazine response. The driving force increases in the order Na$^+$<Rb$^+$<Cs$^+$. What kind of relationship between driving force and electron-transfer rate constant do the data appear to show, and how might you explain that relationship using a very naïve Marcus theory analysis? [Really, though, this effect probably has nothing whatsoever to do with Marcus theory, but is more likely related to the changes in lattice constant as discussed in the lecture!]

f) Rotating disk data for the hydrazine systems is shown below. In both cases shown, a Pt electrode is used, but the left-hand RDE results involve a nickel ferrocyanide modified Pt electrode, while the right-hand data is on a clean Pt surface. Use the bare Pt data to determine the diffusion coefficient for hydrazine in solution. Assume that the kinematic viscosity is 0.01 cm^2 s^{-1}.

g) Why is there a peak in the panel (a) data?

h) Assuming that the nickel ferricyanide coverage is the same as given in the first set of CVs shown (and calculated for question b), what is the charge-transfer (i.e. kinetic) current for the system in panel a?

i) Compare the kinetic currents obtained from plots of the RDE data for both the bare Pt and nickel ferricyanide derivatized electrode to draw a conclusion about whether nickel ferricyanide is a better or a poorer catalyst for hydrazine oxidation than a pure Pt surface?

Question e

Questions f-i
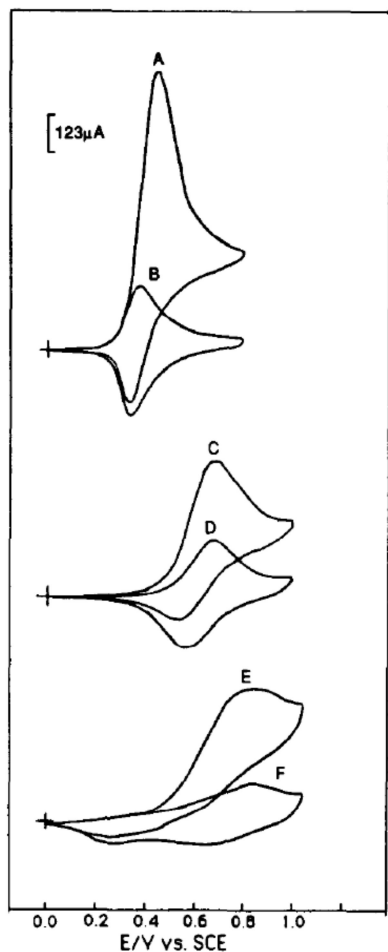
Cyclic voltammograms for oxidation of 5.0 mM hydrazine in various alkali metal cation containing supporting electrolytes at a derivatized Ni/[NiFe(CN)$_6$]$^{2-/1-}$ electrode. A pH = 8.0 phosphate buffer was employed. All scan rates are 100 mV/s. Solution composition: A) 0.5 M NaNO$_3$ + 5.0 mM N$_2$H$_4$; B) 0.5 M NaNO$_3$; C) 0.5 M RbNO$_3$ + 5.0 mM N$_2$H$_4$; D) 0.5 M RbNO$_3$; E) 0.5 M CsNO$_3$ + 5.0 mM N$_2$H$_4$; and, F) 0.5 M CsNO$_3$.
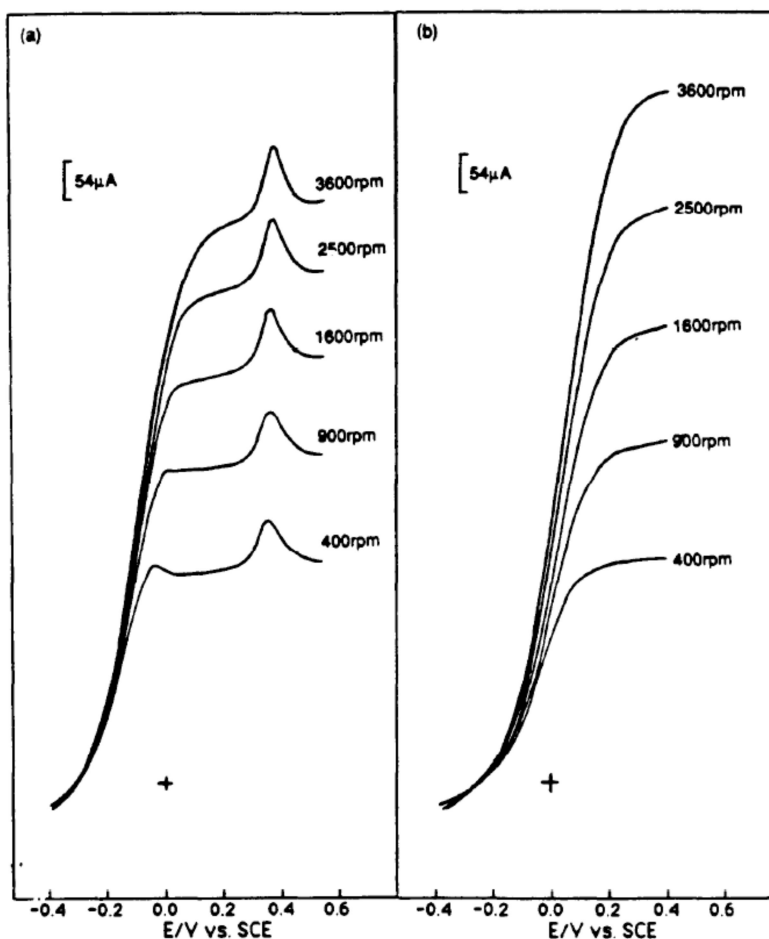
Typical rotating disk voltammogram as a function of rotation rate for the oxidation of 0.5 mM hydrazine at a) a derivatized Pt/[NiFe(CN)$_6$]$^{2-/1-}$ electrode, and b) a bare Pt electrode. Electrode potential was scanned at 10 mV/s. Electrode area is 0.15 cm^2.

3. Consider a large-step chronocoulometry experiment that is carried out on a reversible system that is surface confined. Assuming that the Cottrell equation holds, show that:

$$\left[\frac{Q(t)}{Q_T}\right]^2 = \left(\frac{4}{\pi}\right)\left(\frac{D_O}{d^2}\right)t$$

Where Q_T is the total amount of charge passed, D is the diffusion coefficient of the reactant, and d is the thickness of the surface confined layer. Hint: You will need to convert C* into Γ* to take into account the surface confined nature of the reactant. (Watch your units.)